AIR AND LNAPL ENTRAPMENT IN THE PARTIALLY SATURATED FRINGE: 
LABORATORY AND NUMERICAL INVESTIGATIONS

A Dissertation

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Andrea M. Dunn, B.S.E., B.S., M.S.Env.E.

Stephen E. Silliman, Director

Graduate Program in Civil Engineering and Geological Sciences 
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Laboratory experiments and numerical simulations were used to investigate air and LNAPL entrapment in the Partially Saturated Fringe (PSF) at the local scale of a heterogeneous groundwater system. Investigations led to the determination of several system properties that have a significant influence on entrapment in this region. Laboratory investigations were conducted to gather information and used in the verification of the numerical model TOUGH2/T2VOC in reference to air/LNAPL entrapment. This model was then used in conjunction with laboratory experiments to further investigations. Laboratory and numerical investigations focused on imbibition within simple heterogeneous systems. It was determined that several factors influence the degree of entrapment in the PSF. The rate of rise of the water table in the system has a significant influence on the amount of LNAPL entrapped in heterogeneities. Specifically, as the rate of water table rise increased, the amount of entrapment in heterogeneities decreased. It was also determined that connectivity of heterogeneities has a significant influence on the degree of air/LNAPL entrapment in the PSF. As the connectivity of coarse sand inclusions increased, the amount of air/LNAPL entrapped in these regions,
and within the entire system, decreased. Specific sediment properties were also
determined to have a significant influence on the degree of entrapment in the system. It
was determined that in a system with coarse inclusions surrounded by finer sediment, as
the sediment characteristics of the lens became more similar to those of the surrounding
media, less air/LNAPL became entrapped. Specifically, the air entry pressure and degree
of sorting of the lens were investigated. As the air entry pressure of the lens increased
and/or the degree of sorting of the lens decreased, less air/LNAPL became entrapped in
the system. To our knowledge, this is the first demonstration of entrapment of air or
LNAPL in the PSF through active processes, and thus provides a solid foundation for
future investigations into the PSF and possible application of remediation technology in
this region.
CONTENTS

FIGURES........................................................................................................................................ iv
TABLES........................................................................................................................................... vii
ACKNOWLEDGMENTS ........................................................................................................................... viii
CHAPTER 1  INTRODUCTION........................................................................................................ 1
  1.1 Motivation for Study ............................................................................................................ 1
  1.2 Definition of the Region Surrounding the Water Table.................................................... 3
  1.3 Terms Used.......................................................................................................................... 5
  1.4 Previous Studies in the PSF .............................................................................................. 7
    1.4.1 Previous air/water investigations in the CF ............................................................. 7
    1.4.2 Previous LNAPL Investigations in the PSF............................................................ 8
  1.5 Investigations in the PSF by the Author ....................................................................... 10
    1.5.1 Initial Investigations of AEBs............................................................................... 11
    1.5.2 Experimental Demonstration of Entrapment of Air............................................. 14
    1.5.3 Conclusions from Our Recent Studies................................................................. 16
  1.6 Investigations and Dissertation Outline.................................................................... 16
CHAPTER 2  NUMERICAL MODEL AND MODEL VERIFICATION................................. 19
  2.1 Model Specifics.................................................................................................................... 20
    2.1.1 Governing Equations .......................................................................................... 20
    2.1.2 Capillary Pressure and Relative Permeability Functions.................................... 25
  2.2 Model Verification ............................................................................................................ 26
  2.3 Extension of Model .......................................................................................................... 35
CHAPTER 3  INFLUENCE OF SEDIMENT CHARACTERISTICS ON AIR
             ENTRAPMENT .................................................................................................................. 36
  3.1 Conceptual Description of Experiments.................................................................... 36
  3.2 Questions Addressed in these Numerical Experiments.......................................... 37
  3.3 The Simulations and Parameter Sets.......................................................................... 38
  3.4 Results.............................................................................................................................. 41
  3.5 Observations..................................................................................................................... 44
FIGURES

Figure 1.1 – Forces affecting the rise of water in a capillary tube............................... 6
Figure 1.2 - Schematic of Laboratory Tank................................................................. 12
Figure 1.3 – Drainage of Zones B and C ................................................................. 13
Figure 1.4 – Moisture content versus water table height for Zones C and B .......... 15
Figure 2.1-(a) schematic of flow cell with dimensions (b) experimental flow cell (c) numerical simulation grid of flow cell................................................................. 28
Figure 2.2 - Results of imbibition simulation with Schroth parameters ................. 32
Figure 2.3 - Experimental vs. Simulated Results for Zone C during drainage......... 33
Figure 2.4 - Experimental vs. Simulated Results for Zone B during drainage
demonstrating water entrapment in enclosed coarse zone................................. 34
Figure 2.5 - Experimental vs. Simulated results for Probes 5, 6, and 7 demonstrating air entrapment during imbibition.................................................. 35
Figure 3.1 -TOUGH2 simulation grid for modeling varying van Genuchten parameters 39
Figure 3.2 - Soil water retention curves for varying Po values. ............................... 40
Figure 3.3 - Soil water retention curves for varying Lambda values..................... 41
Figure 3.4 - Percent Water Saturation vs. Water Table Height for the effect of varying air entry pressure values (Po) for the coarse sand lens on air entrapment in the lens.... 42
Figure 3.5 - Percent Saturation vs. Water Table Height for the effect of the degree of sorting (varying λ) in the coarse sand lens on air entrapment in this lens. 43
Figure 4.1 - LNAPL entrapment at different rates of imbibition. Rates of imbibition are:
(a) 0.4 cm/hr (b) 4 cm/hr (c) 40 cm/hr............................................................... 52
Figure 4.2 – Simulation grid (left) and laboratory tank (right) for LNAPL/water drainage and imbibition experiments. Numbers represent TDR probe locations throughout
tank. Circled zone is used for data reported in Section 4.4. Dimensions of the flow
cell are illustrate in the schematic (bottom). ............................................... 55
Figure 5.4 - Simulated entrapment at end of imbibition for medium connectivity. Left is distribution of sand, showing pockets of coarse sand. Right shows LNAPL entrapment within coarse sand............................ 81

Figure 5.5- Covariance structures for all 30 medium connectivity permeability fields. Simulations 15 and 18 have tails outside of the desired range. ................................. 83

Figure 5.6 - End of imbibition simulation of high connectivity matrix. Left is distribution of sand. Right shows LNAPL entrapped in coarse regions. ................................. 84

Figure 5.7 - Covariance structures for all 30 high connectivity permeability fields. Tails of fields 2, 4, 8, 12, 14, 26, and 27 lie outside of the desired +/- 10%. ...................... 86

Figure 5.8 - Simulation grid for investigating the effects of sediment characteristics on LNAPL entrapment................................................................. 90

Figure 5.9 - Effect of Po on LNAPL entrapment. Lambda is constant at 0.864........... 91

Figure 5.10 - Effect of lambda on LNAPL entrapment. Po is constant at 256 N/m². ...... 92
TABLES

TABLE 2.1 - PHASE COMBINATIONS AND PRIMARY VARIABLES ........... 24

TABLE 2.2 - RELATIVE PERMEABILITY AND CAPILLARY PRESSURE
FUNCTION PARAMETERS ................................................................. 31

TABLE 4.1 – TERMS INCLUDED FOR MASS BALANCE OF EACH PHASE .... 48

TABLE 4.2 - RELATIVE PERMEABILITY AND CAPILLARY PRESSURE
FUNCTION PARAMETERS ................................................................. 50

TABLE 5.1 – LOW CONNECTIVITY SIMULATION RESULTS FOR ENTRAPPED
LNAPL .............................................................................................. 79

TABLE 5.2 – MEDIUM CONNECTIVITY SIMULATION RESULTS FOR
ENTRAPPED LNAPL ........................................................................ 82

TABLE 5.3 – HIGH CONNECTIVITY SIMULATION RESULTS FOR ENTRAPPED
LNAPL .............................................................................................. 85

TABLE 5.4 – COMPARISON OF ENTRAPPED LNAPL WITH DIFFERENT
CONNECTIVITIES OF SEDIMENT DISTRIBUTION ......................... 87
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1.1 Motivation for Study

Studies of the flow and transport surrounding the water table have shown this region to be very complex in terms of hydraulics, geochemistry, and biology (Dunn et al., 2005; Dunn and Silliman, 2003; Dunn, 2003; Silliman et al., 2002; Zhang et al., 1999; Rosenberry and Winter, 1997; Boufadel et al., 1999; Jawitz et al., 1998; Lahvis et al., 1999). Despite the relatively extensive literature suggesting the impact of the capillary fringe (CF) on various hydrologic processes, little work has appeared in the literature providing controlled experiments on the hydraulic conditions that exist in the region bounding the water table. Focused studies of flow and transport phenomena shown to be important in the capillary fringe region have been extended to investigation of both sides of the water table. For example, Ronen et al. (1989) reported reduced hydraulic conductivity in the regions immediately below the water table and suggested that this reduction in permeability is related to the presence of small gas bubbles below the water table. Ronen et al. (1997, 2000) developed theoretical and field-based arguments demonstrating both compactness of the capillary fringe (in the presence of relatively uniform sand) and the presence of a significant air phase below the water table. Based on field cores, Ronen et al. (2000) showed that the moisture content above the water table went from near saturation to near residual saturation over very short vertical distances. It
was also demonstrated that sands at depths greater than one meter below the water table were at moisture contents below full saturation, indicating that gas may be trapped at depth below the water table.

Silliman et al. (2002) also investigated this complex zone bounding the water table and demonstrated qualitatively that the region immediately above the water table can be quite active in flow and chemical transport processes previously thought to occur predominantly below the water table. In particular, it was demonstrated that the presence of coarse sand lenses and layers above the water table can, during drainage, lead to substantial vertical exchange of water and chemicals between the regions above and below the water table. It was observed in this study that sediments can exist at high moisture content well above the water table due to heterogeneities in the system and low air-permeability in the overlying fine sediments. These authors introduced the term Air Entry Barrier (AEB) to describe the physical conditions under which high moisture content can exist in coarse sands above the water table. This research was further extended by Dunn and Silliman (2003) quantitatively to include behavior of AEBs below the water table. It was demonstrated that heterogeneity at the local scale, both within the CF and in the region immediately below the water table, can result in extremely complex distributions of soil moisture both above and below the water table, including regions of entrapped air below the water table which can be maintained and exist at pressures greater than atmospheric pressure. The recent observations of AEBs and the complex distribution of saturations both above and below the water table has indicated that this is a diverse region requiring more study to obtain a better understanding of the hydraulic
behavior around the water table and has also lead to some difficulties when using classical terminology to describe this region.

1.2 Definition of the Region Surrounding the Water Table

A number of definitions of the CF exist within the literature. All of these definitions accept the water table \((p = \text{gauge pressure} = 0)\) as the lower limit of the CF. Differences among the definitions are generally related to the definition of the upper limit of the CF. While these definitions are generally precise and often physically relevant, they are subject to difficulties at the local scale related to the heterogeneity, and thus spatial variation in the relative degree of saturation within the CF. The demonstration by Dunn and Silliman (2003) of the presence of entrapped air in the region bounding the water table has brought question to these classic definitions. Hence, a definition of the CF that is applicable at the local scale and based on a measure of the height to residual moisture content becomes somewhat problematic from the standpoints of both measurement and description of important flow and transport processes.

A more adequate definition of the region bounding the water table at the local scale can be developed in terms of the relative connectivity of the liquid and gas phases both above and below the water table. For example, the region below the water table for which the liquid phase is well connected horizontally while the air phase is discontinuous (or non existent) will likely demonstrate both horizontal and vertical pore water velocities associated with the regional gradient and local heterogeneity. In contrast, the region above the water table for which the liquid phase is poorly connected horizontally while the air phase is well connected to the air phase in the overlying vadose zone will exhibit behavior more classically associated with the vadose zone. There is a transition zone
between these two regions that has recently been referred to as the “partially-saturated” fringe bounding the water table (or PSF in contrast to the CF) (Berkowitz et al., 2004). The PSF is bounded from above by the lower portion of the unsaturated zone, where fluid movement is dominated by gravity driven flow and fingering, and from below within the upper portion of the groundwater zone, characterized by fully three-dimensional flow and minimal entrapped air. It should be noted that the lower boundary of the PSF is not considered to be the water table, as partially saturated regions can exist below what has classically been defined as the water table (gauge pressure equal to zero). Thus, the definitions of the upper and lower boundaries of the PSF are in some sense arbitrary, making the definition of PSF subjective and based on the particular application under consideration. It is suggested, therefore, that there does not currently exist an adequate definition describing the behavior of the CF at the local scale. Rather, definition of the PSF at the local scale effectively accounts for the connectivity of the liquid and air phases (and, potentially, additional phases such as a light non-aqueous phase liquid (LNAPL) or dense vapor-phase contaminant) within the porous medium.

The local-scale behavior of the CF, or more appropriately the PSF, plays a major role in defining the geochemistry and microbiology near the water table as it represents a zone of active mixing among waters, chemicals, and microorganisms derived from recharge, influx boundaries, hydraulic exchange with groundwater, diffusion, and gas exchange with both the vadose and saturated zones. Thus, the PSF may have far greater impact than previously perceived on the microbiology, geochemistry, and hydraulics of the groundwater system. Since this zone can have a significant influence on the behavior
of the groundwater system, it is important to obtain a firm understanding of the mechanisms involved in the region.

### 1.3 Terms Used

Included in the definition of the PSF is the existence of regions of variable saturation, on both sides of the water table. Regions of either high moisture content above the water table or entrapped gas below the water table are related to the interplay of capillarity and relative permeability. During drainage of a porous medium, the medium will remain saturated above the water table (the level at which water pressure is equal to atmospheric pressure) due to capillary rise. Capillary pressure is defined as the difference between pressure in the air phase and pressure in the fluid phase. A medium will remain saturated until the capillary pressure exceeds the so-called “air entry pressure”, or the pressure required for air to displace fluid in a pore space. Due to smaller pore sizes in fine-grained media, the air entry pressure for a fine-grained medium is significantly higher than the air entry pressure for a coarse-grained medium. This observation is consistent with the observation that the height of capillary rise is greater in the fine grained medium.

There are a couple of key concepts which are important to understand in the description of the following work.

*Air Entry Barrier (AEB):* Defined and studied in detail in Silliman et al. (2002), Dunn and Silliman (2003), and Dunn (2003), AEBs can exist in the presence of coarse sand lenses and layers above the water table. During drainage, coarse sediments with high moisture content can exist well above the water table due to heterogeneities in the system
and low air-permeability in the overlying fine sediments. During imbibition, heterogeneity in the Partially Saturated Fringe (PSF) can result in extremely complex distributions of soil moisture both above and below the water table, including regions of entrapped air below the water table which can be maintained and exist at pressures much greater than atmospheric pressure.

**Capillary Pressure:** In a two phase, air-water, system (Figure 1.1), if we assume the air phase to be at atmospheric pressure, then the water phase just below the meniscus in the tube is at a pressure less than atmospheric.

![Figure 1.1 – Forces affecting the rise of water in a capillary tube.](image)

At equilibrium (Equation 1.1), the difference in the air pressure, $p_{\text{air}}$, and water pressure, $p_{\text{w}}$, at this interface is termed the capillary pressure, $p_c$.

$$p_c = p_{\text{air}} - p_{\text{w}}$$

**Equation 1.1 - Definition of capillary pressure**
1.4 Previous Studies in the PSF

1.4.1 Previous air/water investigations in the CF

Several authors have noted the importance of the CF in the characterization of the properties of a groundwater system. Previous studies have investigated the CF as a unique region of the subsurface which impacts groundwater hydraulics surrounding a fluctuating water table (Abdul and Gillham, 1984; Gillham, 1984; Mixon, 1988; Li et al. 1997). It was observed by Nwankwor et al. (1992) that excess storage of water can occur above the water table and by Akindunni and Gillham (1992) that the drainage of this water has a significant effect on hydraulics, specifically the response of unconfined aquifers to pumping. Zhang et al. (1999) noted that the capillarity of a system significantly influences the relationship between the pumping frequency, i.e., continuous or pulsed, and the fluid response.

Another aspect of the hydraulics of the CF that has been investigated by a number of authors is the formation and function of seepage faces. Wise et al. (1994) showed that the location of the water table and the height of the seepage face are functions of the capillary forces exerted in the vadose zone. The significance of capillary flow on modeling of the seepage face and flow patterns has also been recently investigated (Shamsai and Narasimhan, 1991; Romano et al., 1999; Boufadel et al., 1999).

The CF has also been shown to impact groundwater response to other transients influencing the groundwater system. Examples include the impact of the CF on the specific yield of an aquifer (Nachabe, 2002), water table dynamics, particularly in response to infiltration events (e.g., Rosenberry and Winter, 1997; Neilsen and Perrochet, 2000), solute transport (Kinouchi, 1991), hillslope hydrologic processes (Iverson et al.,
1997; Torres et al., 1998), response to precipitation (Jayatilaka et al., 1996; Jayatilaka and Gillham, 1996), storm hydrographs in streams (e.g., Williams et al., 2002; Jayatilaka et al., 1996), the response to wave run-up (Li et al., 1997) and groundwater response to tidal fluctuations (Ataie-Ashtiana et al., 2001).

These studies indicate that there are many factors involved with the CF, or upper portion of the PSF, that can significantly affect the hydraulic behavior of a groundwater system. Although these studies are a noteworthy start to the investigation of the PSF, they do not discuss impact of heterogeneity below the water table. Hence, it is anticipated that there are additional hydraulic behaviors of the PSF that require further study.

1.4.2 Previous LNAPL Investigations in the PSF

Light Non-Aqueous Phase Liquids (LNAPLs) represent an important class of contaminants in groundwater systems that have recently begun to be studied more in depth as to their behavior and influence on groundwater systems and with the PSF. They are substances that are immiscible with, and less dense than, water. LNAPLs represent some of the most ubiquitous environmental contaminants, with oil-based products such as petrol, diesel, and kerosene being the most widespread LNAPLs in the environment (GeoDelft, 2003).

When an LNAPL is released into the subsurface, it will commonly migrate downwards towards the water table or low-permeability zones. We often conceptualize the behavior of LNAPLs in the vicinity of the water table as one of spreading laterally across the surface of the water table, thus forming a layer of free product on the top of the water table.
Studies of LNAPLs have shown that LNAPLs will be distributed vertically in the vicinity of a fluctuating water table, including becoming entrapped as a distinct phase both above and below the water table. Several different mechanisms of entrapment have been investigated. These methods include infiltration of the LNAPL (Schroth et al., 1995; Kechavarzi et al., 2000), fingering (Illangasekare et al., 1995a), entrapment of small bubbles of LNAPL in homogeneous media (Reddi et al., 1998), LNAPL entrapment in layered media (Illangasekare et al., 1995a; Illangasekare et al., 1995b; Schroth et al., 1998; Walser et al., 1999), and entrapment within heterogeneous inclusions (Illangasekare et al., 1995b; Van Dijke and Van Der Zee, 1997). Further, it has been shown that NAPLs entrapped in subsurface formations can act as long-term sources of contamination in a groundwater system (Saba et al., 2001). It has also been argued that during displacement of resident groundwater, i.e. flooding or pumping, buoyancy forces can act to effectively entrap LNAPLs in the CF contributing to the inefficient removal of the contaminant from the aquifer (Jawitz et al., 1998).

Illangasekare et al. (1995a) conducted experiments involving layering in the saturated zone beneath the water table. It was demonstrated that the presence of these layers can create fingering of the contaminant among the layers. Illangasekare et al. (1995b) investigated NAPL flow and entrapment through the saturated and unsaturated regions of both homogeneous and heterogeneous media. Layered heterogeneities in the system were found to modify the migration pattern and velocity of the contaminant plume. Fine sand lenses acted as barriers to the transport of LNAPLs. Lenses of coarse sand which were positioned across the path of the contaminant plume in the flow field were observed to produce a trap for the LNAPL.
Other studies have also been conducted on the impact of heterogeneity on distribution of LNAPLs. Results from these studies have demonstrated that both small- and large-scale heterogeneities in a system can lead to significant variations in the saturation of NAPL (Kueper et al., 1989; Illangasekare et al., 1995b). It has been stated that capillary phenomena result in the preferential infiltration of NAPL into regions comprised with larger pore spaces. However, the initial entry of the NAPL into finer grained media requires a substantial NAPL pressure to overcome the displacement pressures associated with the media (Powers et al., 1998). During drainage, capillary forces across the oil-water interface lead to the trapping of NAPL at high saturations in areas with larger pores and pooling of NAPL above lenses of finer-grained media (Nambi and Powers, 2000). NAPL can also be entrapped as discrete blobs during NAPL displacement when the pore body-pore throat contracts and causes snap-off to occur (Wilson et al., 1990).

1.5 Investigations in the PSF by the Author

Expanding on the recent qualitative work of Silliman et al. (2002) on the investigation of AEBs, Dunn and Silliman (2003) and Dunn (2003) provided initial quantitative studies on the existence and formation of AEBs in a simple heterogeneous laboratory system. This work will be discussed briefly here in order to provide the necessary background information for the expansion of this preliminary work into the detailed investigations of entrapment in the PSF presented in this dissertation.
1.5.1 Initial Investigations of AEBs

Investigations were conducted in a laboratory flow cell (0.51 m length x 0.16 m width x 0.39 m height), illustrated in Figure 1.2, which contained coarse sediment inclusions of varying degrees (A, B, and C in Figure 1.2) within a matrix of finer sediment. The sands comprising the porous medium used in these experiments are commercially available pre-sieved silica sands identical to those used by Silliman et al. (2002). Two grain sizes of sand were used in these experiments, herein termed “fine” and “coarse”. The "fine" sand was a 40/50-mesh sand (0.30 - 0.425 mm grain size), with capillary rise of approximately 20 cm. The "coarse" sand was a 12/20- mesh sand (0.85 – 1.55 mm) with an air-entry pressure of approximately 6 cm. Volumetric soil moisture content was measured non-invasively over time at various locations within the tank using time domain reflectometry (TDR) based on a Campbell Scientific TDR-100. Fifteen 3-rod TDR probes were constructed with rod spacing set at 1 cm. These were calibrated in the laboratory. Details for these instruments are found in Dunn (2003). Locations of TDR probes in the experimental set up are labeled with numbers in Figure 1.2. Finally, a 5-psig pressure transducer was installed to allow measurement of water and air pressure in the lower-most coarse sand region (D in Figure 1.2).

Three degrees of vertical connectivity were investigated, including isolated regions (2 cm thickness) of coarse sand at vertical intervals (A in Figure 1.2), a single region of coarse sand (15 cm thickness) overlain by fine sand (B in Figure 1.2), and a single region of coarse sand connected to the surface of the porous medium (C in Figure 1.2). An additional region of coarse sand (approximately 15 cm vertical dimension, D in Figure 1.2) was constructed in a lower region of the experiment to allow for direct
measurement of water and air pressure during drainage and imbibition, respectively. The effects of capillarity and relative permeability on moisture content behavior were investigated in each of these regions during drainage and imbibition of the system.

Figure 1.2 - Schematic of Laboratory Tank. Location of TDR probes are numbered

Drainage experiments were initiated by packing the sands under saturated conditions to the upper edge of the flow tank. The water table was then lowered in 2 cm increments until it was at the base of the tank. At each 2 cm increment, moisture content was monitored using the TDR probes and pressure was measured at the transducer.

In order to illustrate the effects of AEBs on saturation of the system during drainage, Zones B and C, as labeled in Figure 1.2, will be discussed. Zone B is a lens of coarse sand surrounded by a matrix of fine sand and illustrates the effects of having an
enclosed lens of a specific grain size overlain by a sediment of different (finer) grain size. Zone C is a column of coarse sediment connected to the atmosphere and is used to illustrate behavior of coarse sand that is not overlain by fine sand.

Figure 1.3 illustrates moisture content data taken during drainage of the experimental set up shown in Figure 1.2 for Zone C (1.3a) and Zone B (1.3b).

Figure 1.3 –

a) Drainage of the continuous coarse zone connected to the atmosphere (Zone C in Figure 1.2). As the water table was lowered, there was a sequential drop in moisture content at each of the TDR probes.

b) Drainage of the 15 cm coarse lens overlain by fine sediment (Zone B in Figure 1.2). Moisture content remained high for all TDR probes until the top of the CF of the overlying fine sand was approximately at the upper boundary of the coarse lens, at which point all TDR probes indicated drainage without a change in water table height.

Figure 1.3 illustrates that the difference between a coarse lens with no fine-sand cover (Zone C) and a fine-sand cover (Zone B). For a continuous (vertical) lens of coarse sediments not overlain by fine sediments (Zone C and Figure 1.3a), air will enter the coarse sand (upon decline of the water table) at the air entry pressure of the coarse sand.
In contrast, if the coarse sediments are overlain by fine sand (Zone B and Figure 1.3b), water cannot drain from the coarse grained sediments (during drainage) until the air entry pressure of the overlying fine sand has been surpassed (thus allowing passage of air into the upper surface of the coarse sand). As the air-entry pressure of the fine sand is higher than that of the coarse sand, the coarse sand overlain by the fine sand remains saturated with water to significantly lower water table levels than is observed for the coarse sand that is not overlain by fine sand.

1.5.2 Experimental Demonstration of Entrapment of Air

Demonstration of the impact of heterogeneity during drainage led to the further investigations of the effects of AEBs during imbibition of the system. Although the earlier work of Ronen et al. (1989, 1997, 2000) suggests entrapment of air below the water table, there has been no direct evidence provided that heterogeneity can cause air to be entrapped below the water table during imbibition. Dunn (2003) and Dunn and Silliman (2003) address this issue by demonstrating that reversing the motion of the water table in the AEB experiments presented in the previous section leads to entrapment of air below a rising water table. In this case, capillary rise through the fine sediments lead to saturation (with water) of the fine-grained sand overlying the coarse sand before the air in the upper region of the coarse sand was released to the vadose zone. As the relative permeability to the air phase rapidly approached zero in the fine-grained medium, the air in the coarse sand became trapped.

This effect is illustrated through comparison of the results shown in Figure 1.4a-b. Figure 1.4a provides the moisture response at the four TDR probes in Zone C during imbibition (the tank had been fully drained and then the water table was allowed to rise in
While hysteresis is apparent (none of the probes returns to 100% saturation), it is observed that each probe wets sequentially as the water table rises. For Zone B (Figure 1.4b), the lowermost TDR probes once again show increase in moisture content as the height of the water table is increased. However, TDR probes 5 and 6 show only modest increases in moisture content (with TDR 5 showing essentially zero change) despite the water table being raised to an elevation above both probes. That is, probes 5 and 6 indicated that this portion of the Zone B remained partially saturated with the air phase. This result was consistent with visual observation of the tank indicating that the upper portion of this coarse sand zone remained effectively saturated with the air phase and therefore that entrapment of air occurred below the water table due to heterogeneity in grain size.

Figure 1.4 –

a) Moisture content versus water table height for zone C during imbibition.

b) Moisture content versus water table height for zone B during imbibition. Probes 9, 8, and 7, located in the lower portion of the coarse lens, resaturated sequentially, while Probe 6 only partially resaturated, and Probe 5 remained approximately at residual moisture, despite an increase in the water table height to levels above the top of the coarse zone.
1.5.3 Conclusions from Our Recent Studies

As noted in section 1.4, previous studies of the CF and PSF have demonstrated that this region of the subsurface exhibits complicated behaviors, including transport in coarse sand zones above the water table (Silliman et al., 2002) and less than full water saturation and reduced permeability below the water table (e.g., Ronen et al., 1989; Ronen et al., 1997; Ronen et al., 2000). However, previous to the work presented in our studies discussed above (Dunn, 2003; Dunn and Silliman, 2003), there was little direct evidence of entrapped air phases in the PSF or information on the mechanisms leading to this entrapment. Hence, our prior work based on laboratory experiments provides the foundation for the continuing studies of air/water behavior within the PSF and sets the stage for study of the hydraulic behavior of LNAPLs under conditions of drainage and imbibition.

1.6 Investigations and Dissertation Outline

This dissertation extends previous work on the impact of macroscale heterogeneities in the PSF through new studies of air and LNAPL behavior within the PSF. Previous to the work presented here, only a limited amount of research had been published in the study of entrapment of air or LNAPL below the water table. The work included in this dissertation provides the first studies with which we are familiar demonstrating that both air and LNAPLs can be entrapped below the water table through imbibition in the presence of hydraulic heterogeneities. Also, this work provides initial insight into the characteristics of the heterogeneities and properties of the LNAPLs which will influence the degree of entrapment. The findings in this dissertation provide a substantial foundation for the understanding of entrapment behavior in the PSF and the
effects of this entrapment on hydraulic behavior in the system. This work lays the groundwork for further study of both natural processes in the PSF and possible technologies for enhanced remediation within the PSF.

The main objective of the research presented herein is to further the understanding of the potential for and stability of entrapment (both air and LNAPL) within the PSF in heterogeneous groundwater systems. In order to advance this objective, specific investigations into the following topics were conducted:

- the potential for LNAPL entrapment below the water table due to the impact of heterogeneity on the imbibition process
- the influence of the degree of heterogeneity (connectivity of coarse regions in a fine sand matrix) on air and LNAPL entrapment
- the influence of the rate of imbibition (rate of water table rise) on LNAPL entrapment
- the influence of sediment properties on air and LNAPL entrapment. Specifically:
  o the influence on air entry pressure on entrapment
  o the influence of degree of sorting of sediment on entrapment

The investigation of these topics will be conducted both experimentally and numerically. Experiments were utilized to investigate simple heterogeneous groundwater systems and the entrapment behavior of a very simple LNAPL (zero dissolution and zero volatility) in these systems. Both air/water and LNAPL/water systems were investigated numerically with the utilization of a verified numerical model. The overall contributions of this research include the demonstration of the presence of air and LNAPL phases below the water table, discussions of the mechanisms leading to this entrapment, the demonstration of formation of these entrapped phases due to natural processes, and the
discussion of the characteristics of the sediments and the hydraulic properties of the LNAPL which will influence the degree of this entrapment.

The second chapter of this dissertation examines and demonstrates verification of the numerical model (TOUGH2/T2VOC) used in the numerical investigations. Chapter 3 expands on the numerical investigation of the influence of sediment properties on air entrapment in an air/water system. Chapter 4 provides the results of experimental and numerical investigation of the entrapment of LNAPL during imbibition of a heterogeneous LNAPL/water system. In Chapter 5, expansions of this work are presented which include numerical studies on the influence of connectivity of heterogeneities and sediment properties on LNAPL entrapment. Chapter 6 ties together the presented research and elaborates on future efforts that are necessary to continue to expand upon the knowledge of behavior within the PSF.
CHAPTER 2

NUMERICAL MODEL AND MODEL VERIFICATION

The experimental work on two-phase, air/water, heterogeneous systems conducted for this dissertation was used to calibrate and verify a numerical model for multiphase flow in heterogeneous media. This model was applied first to the study of air and water entrapment in the Partially Saturated Fringe (PSF) and then to the study of Light Non-Aqueous Phase Liquid (LNAPL) entrapment in the PSF. The use of calibrated and verified numerical modeling in the study of the PSF can be highly beneficial in allowing for accurate and less time consuming investigations to occur than would be permitted by laboratory experimentation. This chapter describes the numerical code, its applications to the current project, parameter estimation and calibration/verification of the model.

The computer model utilized in this study is TOUGH2 - Transport Of Unsaturated Groundwater and Heat, version II and it’s extension T2VOC, developed at Lawrence Berkeley National Laboratory (Pruess et al., 1999). TOUGH2 is a multi-dimensional numerical model for simulating the coupled transport of water, vapor, non-condensable gas, and heat in porous and fractured media. This model uses an integral finite difference method for spatial discretization, and first-order, fully implicit time differencing. TOUGH2 has been used for many different applications, of which a few are the modeling of various aspects of the Yucca Mountain nuclear waste repository site in Nevada.
(Bodvarsson et al., 2003; Zhang et al., 2003; Huang et al., 1999; Ahlers et al., 1999; Ritcey and Wu, 1999; Wittwer et al., 1994), gas production and migration in landfills (Nastev et al, 2001), simulating non-Newtonian fluid flow and displacement in porous media (Wu and Pruess, 1998), and the study of geothermal brines and non-condensable gas (Battistelli et al, 1997; Oldenburg and Pruess, 1995).

T2VOC is a numerical simulator for three-phase non-isothermal flow of water, soil gas, and volatile organic chemicals (VOCs) in multi-dimensional heterogeneous porous media (Falta et al., 1995). T2VOC has the ability to simulate migration of total mass, as well as constituent migration and reactions, in all combinations of the three phases – water, VOC, and gas. As with TOUGH2, T2VOC has been applied to a number of simulation scenarios, including the remediation of NAPL below the water table by steam-induced heat conduction (Gudbjerg et al., 2004), air sparging for remediation of NAPL contamination (Mortensen et al., 2000; Hein et al., 1997; McCray and Falta, 1997), and thermally enhanced soil vapor extraction of trichloroethylene (Kling et al., 2004), among others.

2.1 Model Specifics

2.1.1 Governing Equations

The flow of phases through the groundwater system has been investigated by numerous scientists and described in various ways. Different forms of flow equations have been used and developed in the description of the transport of water and other phases through the sediment of a groundwater system. Darcy’s law (Equation 2.1) has
been used throughout the study of groundwater to describe flow through a saturated groundwater system.

\[ Q = -KA \cdot (dh/dl) \]

- \( Q \) – discharge \([L^3/T]\)
- \( K \) – hydraulic conductivity \([L/T]\)
- \( A \) – cross-sectional area \([L^2]\)
- \( dh/dl \) – hydraulic gradient

**Equation 2.1 - Darcy's Law**

The following general overview of the workings of the T2VOC model is based on Chapter 4 and Appendix A of the T2VOC User’s Guide (Falta et al., 1995). T2VOC is a multiphase simulator that treats gas, water, and VOC as separate phases. Each phase will have a primary component (gas, water, or VOC) within which there can exist components of the other two phases. In the non-isothermal calculations, heat is considered a fourth component. Due to the fact that all simulations used in this dissertation are completed for isothermal conditions, equations presented are for these conditions.

In order to develop the flow equations used in the T2VOC simulations, a mass balance equation is used for each of the three components (Equation 2.2):
Equation 2.2 – Mass balance equation for each of the three components in T2VOC model

The q term can represent various forms of sinks and sources such as fluid injection or withdrawal or reactions. The mass term, M, is calculated as the sum of the contributions from the separate phases (Equation 2.3):

\[
\frac{d}{dt} \int_{V_n} M^\kappa dV_n = \int_{A_n} F^\kappa \cdot ndA_n + \int_{V_n} q^\kappa dV_n
\]

\[
M = \text{mass of } \kappa \text{ per } V_n
\]

\[
\kappa = \text{component (air, water, chemical)}
\]

\[
V_n = \text{unit porous medium volume}
\]

\[
F^\kappa = \text{mass flux of } \kappa \text{ across } A_n \text{ of } V_n
\]

\[
A_n = \text{surface area of unit volume}
\]

\[
q^\kappa = \text{mass generation per unit volume}
\]

\[
n = \text{unit}
\]

**Equation 2.2 – Mass balance equation for each of the three components in T2VOC model**

The flux term is calculated as the sum of the advection term and the diffusion term. Advection is calculated with a multiphase extension of Darcy’s Law as follows (Equation 2.4):

\[
\int_{V_n} M^\kappa dV_n = \phi \sum_{\beta} S_{\beta} \rho_{\beta} X_{\beta}^\kappa
\]

\[
\phi = \text{porosity}
\]

\[
\beta = \text{phase (air, water, chemical)}
\]

\[
S_\beta = \text{saturation}
\]

\[
\rho = \text{density of phase } [M/L^3]
\]

\[
X_{\beta}^\kappa = \text{mass fraction of component } \kappa \text{ in phase } \beta
\]

**Equation 2.3 - Mass term. Sum of the contributions from the separate phases**
Fick's Law is used to calculate the mass flux of component $\kappa$ by diffusion of the gas and water phases as shown in Equation 2.5:

$$F^\kappa = \sum_\beta - X_\kappa \beta k^\kappa \beta P^\beta \left( \nabla P^\beta - \rho^\beta g \right)$$

$k = \text{intrinsic permeability} [L^2]$
$X = \text{mass fraction as defined in Eqn 2.3}$
$k_{\kappa \beta} = \text{relative permeability to phase } \beta$
$\rho = \text{density} [M/L^3]$
$\mu = \text{viscosity} [F*L^2]$  
$P = \text{pressure} [M/LT^2]$  
$g = \text{gravitational acceleration vector} [L/T^2]$  

**Equation 2.4 - Multiphase extension of Darcy's Law used for advection term**

Fick’s Law is used to calculate the mass flux of component $\kappa$ by diffusion of the gas and water phases as shown in Equation 2.5:

$$F^\kappa_{\text{diffusion}} = \sum_\beta - \phi S^\kappa \beta D^\kappa \beta \rho^\beta \nabla X^\kappa \beta$$

$D^\kappa_\beta = \text{molecular diffusion coefficient of } \kappa \text{ in the } \beta \text{ phase}$

**Equation 2.5- Fick's Law used for diffusion in the gas and water**

In T2VOC, the developed set of equations (Equation 2.2 for each component) is discretized in space and time using the integral finite difference technique and first-order backward finite differences, respectively. The non-linear algebraic equations describing flow with multiple phases present are solved by Newton-Raphson iteration. The linear equations which arise from this are solved by iterative preconditioned conjugate gradient techniques. The balance equations are solved for independent primary variables (pressure, saturation, mass fraction of phases, and mole fraction of phases). Since all
three phases may not be present in all gridblocks at all times, it is necessary to switch between different sets of primary variables for each phase combination. The model assumes that the water phase is always present and thus, there are four possible phase combinations, as listed in Table 2.1.

### Table 2.1

**Phase Combinations and Primary Variables**

<table>
<thead>
<tr>
<th>Phases</th>
<th>Primary Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$P_{\text{water}}$, $X_{\text{air-water}}$, $\chi_{\text{NAPL-water}}$, $T$</td>
</tr>
<tr>
<td>Water, NAPL</td>
<td>$P_{\text{NAPL}}$, $S_{\text{water}}$, $X_{\text{air-water}}$, $T$</td>
</tr>
<tr>
<td>Water, gas</td>
<td>$P_{\text{gas}}$, $S_{\text{water}}$, $\chi_{\text{NAPL-gas}}$, $T$</td>
</tr>
<tr>
<td>Water, NAPL, gas</td>
<td>$P_{\text{gas}}$, $S_{\text{water}}$, $S_{\text{gas}}$, $T$</td>
</tr>
</tbody>
</table>

**Note:**
- $X_{\text{air-water}}$ is mass fraction of air in the water phase.
- $\chi_{\text{NAPL-gas}}$ is mole fraction of chemical in the gas phase.
- $\chi_{\text{NAPL-water}}$ is mole fraction of chemical in the water phase.
- $T$ is temperature.

In each iteration, the concentration of each component is checked to determine whether the phase is present in a gridblock, and a switch of primary variables is made corresponding to the new phase combination. In systems with multiple phases present, specific conditions must exist for this phase switch to take place. The capillary pressure which exists for the phase initially present must be overcome by the secondary phase pressure in order for the secondary phase to move into the position of dominant phase, forcing the initial phase out. The pressure at which this critical point is exceeded is referred to as the air entry pressure.

The air entry pressure becomes especially significant when investigating the change in phases in the presence of heterogeneities, such as in the situation presented in
Chapter 1 when discussing AEBs. The equations used for modeling purposes must be able to describe behavior seen with AEBs in that the differential pressure between the two phases can be affected by the pore size of the overlying fine sand. The variable air entry pressure in these situations is taken into account in the equations used in T2VOC.

For each of the four primary variables in these equations, a set of secondary variables (i.e. density, viscosity, enthalpy, etc.) can be calculated that fully describe the thermodynamic properties of the system. The relative permeability and capillary pressure-saturation relationships are included in this set of secondary variables. These relationships are soil specific and fundamental in multiphase flow and are discussed further below.

2.1.2 Capillary Pressure and Relative Permeability Functions

Multiphase capillary pressure and relative permeability functions are among the most important secondary variables affecting the multiphase flow of the system. However, these functions are very difficult to predict in a general fashion due to the variability of the pore space geometry in the media and the complexity of the interactions with multiple fluids. It is also very difficult to experimentally determine capillary pressure and relative permeabilities in three phase systems (Falta et al., 1995). Since these two functions are difficult to determine, it is common to develop three-phase capillary pressure and relative permeability functions from two-phase relationships (Leverett, 1941; Leverett and Lewis, 1941; Stone, 1970; Aziz and Settari, 1979; Parker et al., 1987). In T2VOC, there are several three-phase relative permeability and capillary pressure models available. These are provided in Appendices C and D of the T2VOC User’s Guide (Falta et al., 1995). Specific capillary pressure and relative permeability
functions that were used for simulations presented in this dissertation (capillary pressure function of vanGenuchten model and relative permeability function of vanGenuchten-Maulem model) are discussed further below.

2.2 Model Verification

The AEB experiments described above (Dunn 2003; Dunn and Silliman, 2003) were used to verify the numerical model through comparison of experimental results with those predicted via the model using previously characterized media properties. Specifically, these data were used to verify the TOUGH2 model for entrapment behavior observed in the laboratory experiments for air/water systems. A general overview of the validation process is as follows.

Parameters previously determined for each sediment used in experimentation by Schroth et al. (1996) were utilized for initial drainage and imbibition simulations of the air/water heterogeneous system investigated in the laboratory (Dunn and Silliman, 2003). The results of these simulations demonstrated the ability of the numerical model to simulate the general entrapment behavior observed in the laboratory. There were slight differences between the numerical and experimental results in the degree of entrapment. It was noted that there were differences in the experimental procedures between Schroth et al. (1996) and Dunn and Silliman (2003). In order for the numerical model to more closely represent the conditions present in our laboratory during experimentation, it was determined that parameters which we were able to measure directly in our laboratory should be used in lieu of those previously published in Schroth et al. (1996). Specifically, we were able to measure residual air and water saturations and therefore used these measured values as the input parameters in the numerical model (replacing the equivalent
parameters as estimated in the work of Schroth et al. (1996)). All other parameter values were based on values published by Schroth et al. (1996). The results of the numerical model using the measured residuals were in close agreement with laboratory results. It is important to note that the results of the numerical model were obtained without the fitting of any parameters. Only published and measured values were used as parameters.

In order to demonstrate the validation of the TOUGH2 model in reference to the ability to simulate entrapment in heterogeneous air/water systems, a comparison was made between prediction by the numerical model and observations (as discussed in Chapter 1) from our earlier laboratory work. The experimental flow cell with the heterogeneous distribution of fine and coarse sands utilized for model calibration and validation is shown schematically in Figure 2.1a, with a photograph of the flow cell in Figure 2.1b.
Figure 2.1-(a) schematic of flow cell with dimensions (b) experimental flow cell - numbers are TDR probe locations. Zones A, B, C, and D consist of coarse sediments in various vertical connectivity distributions. (c) numerical simulation grid of flow cell. Coarse zones and TDR probes are in the same locations in the simulation grid as in the laboratory flow cell.

Figure 2.1c shows the numerical simulation grid used to simulate the laboratory experiment in TOUGH2. The media was broken up in to a grid of rectangular elements, which were 1 cm in length and 0.5 cm in height. There were 51 elements in the length of the media and 78 elements in height, giving the media a dimension of 51 cm wide by 39
cm high, matching the dimensions of the experimental flow cell. The sediment types assumed in the numerical model were the fine and coarse sediments used in the laboratory experimentation as characterized by Schroth et al. (1996). The coarse sand had a density of 2665 kg/m$^3$, a porosity of 0.348, and x, y, and z permeabilities of 6e-10 m$^2$. The fine sand had a density of 2663 kg/m$^3$, porosity of 0.348, and x, y, and z permeabilities of 9.6e-11 m$^2$.

Schroth et al. (1996) utilized the van Genuchten-Mualem relative permeability model and the van Genuchten capillary pressure function in order to describe the properties of these sediments. In the TOUGH2 numerical model, the hydraulic conductivity of the sediment was therefore characterized using the van Genuchten-Mualem numerical model, shown as Equation 2.6.

\[
K_{rel}(h) = \left[ \frac{1 - (\alpha h)^{n-1} \left[ 1 + (\alpha h)^{n} \right]^{m}}{1 + (\alpha h)^{n}} \right]^{2}
\]

With \( m = 1 - 1/n \), water retention parameters \( \alpha \) and \( n \) (Schroth et al., 1996), and \( h \) is the capillary pressure head.

**Equation 2.6- van Genuchten-Mualem model (van Genuchten 1980)**

The TOUGH2 numerical model allows for the use of the van Genuchten permeability relationship to simulate relative permeability and the van Genuchten-Mualem capillary model for the capillary pressure function, as shown in Equations 2.7 and 2.8, respectively (Mualem 1976; van Genuchten 1980).
\[
\begin{align*}
\lambda &= \frac{1}{m} - 1/1^* \\
S_{\text{cap}} &= \frac{S_l - S_{\text{lr}}}{S_{\text{ls}} - S_{\text{lr}}}, \quad S = \frac{S_l - S_{\text{lr}}}{1 - S_{\text{lr}} - S_{\text{gr}}}, \\
S_l &\text{ is water saturation, } S_{\text{lr}} \text{ is irreducible water saturation, } S_{\text{ls}} \text{ is satiated water saturation, } S_{\text{gr}} \text{ is irreducible gas saturation, } k_{rl} \text{ is the liquid phase relative permeability, } k_{rg} \text{ is the gas phase relative permeability.}
\end{align*}
\]

**Equation 2.7- Relative permeability function used in TOUGH2 – van Genuchten-Mualem model (Mualem 1976; van Genuchten 1980)**

\[
k_{rl} = \begin{cases} 
\sqrt{S^*} \left( 1 - \left( 1 - S^* \right)^{1/\lambda} \right)^2 & \text{if } S_l < S_{\text{ls}} \\
1 & \text{if } S_l \geq S_{\text{ls}} 
\end{cases}
\]

\[
k_{rg} = \frac{1 - k_{rl}}{\left( 1 - \tilde{S} \right) \left( 1 - \tilde{S}^2 \right)} \quad \text{if } S_{gr} = 0
\]

**Equation 2.8- Capillary pressure function used in TOUGH2 - van Genuchten function (van Genuchten 1980)**

\[
P_{\text{cap}} = -P_0 \left( S^* \right)^{1/\lambda} - 1 \quad \text{with restriction } -P_{\text{max}} \leq P_{\text{cap}} \leq 0
\]

With \( S^* = (S_l - S_{\text{lr}})/(S_{\text{ls}} - S_{\text{lr}}), P_0 = \rho_w g/\alpha, \alpha \) is fitting parameter.

All of the TOUGH2 parameters used for model simulations for both the coarse and fine sands, based on values reported by Schroth et al. (1996), are reported in Table 2.2.

30
### TABLE 2.2
RELATIVE PERMEABILITY AND CAPILLARY PRESSURE FUNCTION
PARAMETERS USED IN TOUGH2 SIMULATION

<table>
<thead>
<tr>
<th>Parameter in TOUGH2</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Permeability Function - van Genuchten-Mualem model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse Sand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP (1)</td>
<td>$\lambda$</td>
<td>0.864</td>
</tr>
<tr>
<td>RP (2)</td>
<td>$s_{r}$</td>
<td>0.20</td>
</tr>
<tr>
<td>RP (3)</td>
<td>$s_{l}$</td>
<td>1</td>
</tr>
<tr>
<td>RP (4)</td>
<td>$s_{gr}$</td>
<td>0.06</td>
</tr>
<tr>
<td>Fine Sand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP (1)</td>
<td>$\lambda$</td>
<td>0.918</td>
</tr>
<tr>
<td>RP (2)</td>
<td>$s_{r}$</td>
<td>0.25</td>
</tr>
<tr>
<td>RP (3)</td>
<td>$s_{l}$</td>
<td>1</td>
</tr>
<tr>
<td>RP (4)</td>
<td>$s_{gr}$</td>
<td>0.06</td>
</tr>
<tr>
<td>Capillary Pressure Function - van Genuchten model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse Sand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP (1)</td>
<td>$\lambda$</td>
<td>0.864</td>
</tr>
<tr>
<td>CP (2)</td>
<td>$s_{r}$</td>
<td>0.01</td>
</tr>
<tr>
<td>CP (3)</td>
<td>$1/o_{P_{o}}$ drainage</td>
<td>1.54E-03</td>
</tr>
<tr>
<td>CP (4)</td>
<td>$P_{max}$</td>
<td>1800</td>
</tr>
<tr>
<td>CP (5)</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Fine Sand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP (1)</td>
<td>$\lambda$</td>
<td>0.918</td>
</tr>
<tr>
<td>CP (2)</td>
<td>$s_{r}$</td>
<td>0.01</td>
</tr>
<tr>
<td>CP (3)</td>
<td>$1/o_{P_{o}}$ drainage</td>
<td>4.62E-04</td>
</tr>
<tr>
<td>CP (4)</td>
<td>$P_{max}$</td>
<td>4000</td>
</tr>
<tr>
<td>CP (5)</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

NOTE: Symbols are as defined in T2VOC User Manual (Falta et al., 1995)

When these values were used, the numerical model was able to produce the general entrapment behavior observed in the laboratory. Figure 2.2 illustrates the observed and predicted moisture contents during imbibition for five of the TDR probes shown in Figure 2.1a. As implied by both the experimental and numerical results in this figure, air was entrapped in the upper portions of the larger isolated coarse regions in the system (demonstrated by the partial resaturation of Probe 5) and throughout the small coarse regions (as demonstrated by Probe 2 remaining at residual saturation). These results validated the model in reference to the ability of the model to reproduce the observed behavior of water entrapment during drainage and air entrapment during imbibition with
parameters reported for these sands as produced in another laboratory. These initial simulations produced general validation of the model in reference to simulation of the mechanisms that can lead to AEBs.

Figure 2.2 - Results of imbibition simulation with Schroth parameters. Air entrapment is observed in the coarse regions demonstrated by the low saturation of Probe 2 at all water table heights and the partial resaturation of Probe 5.

In reviewing the parameters reported by Schroth et al. (1996), it was observed that the data observed in our laboratory for the residual saturations of water and air differed from those of the values given by Schroth et al. (1996). Therefore, the validation simulation was repeated using the residual saturations measured by TDR probes during our experiments rather than those determined by Schroth et al. (1996). These residuals are:

Residual Water Saturation: Coarse Sand – Schroth = 0.034, Experimental = 0.20
Fine Sand – Schroth = 0.057, Experimental = 0.25

Residual Air Saturation: Coarse Sand – Schroth = 0.151, Experimental = 0.06
Fine Sand – Schroth = 0.151, Experimental = 0.06
Figure 2.3 shows the results for Zone C (the zone not covered by fine sand - Figure 2.1b) of simulations using these measured residual saturations (all other parameters as in the previous simulation). It is apparent that the model reproduces extremely well the observed behavior during drainage for this coarse sand that is not covered by fine sand. More importantly, Figure 2.4 shows results for Zone B (coarse sand covered by fine sand – Figure 2.1b) and demonstrates that the model replicates the entrapment of water in Zone B followed by the rapid desaturation of this zone as air first invades the upper portion of the coarse sand through the overlying fine sand. Reproduction of this entrapment behavior, using measured rather than calibrated parameters, provided significant confidence in the numerical model.

![Drainage of Zone C Experimental vs. Simulated Results](image)

Figure 2.3 - Experimental vs. Simulated Results for Zone C during drainage. This zone demonstrates expected drainage behavior without the effect of AEBs.
Results for Zones B and C are also accurately reproduced for the imbibition experiments. Figure 2.5 shows the observed and predicted results for probes 7-9 in Zone B. As with the drainage experiments, there is close agreement between the observed variation in moisture content and the moisture contents predicted with the numerical model, thus further increasing our confidence in the utility of this model to predict behavior in heterogeneous media. It is noted that all parameters are the same for the drainage and imbibition experiments.
2.3 Extension of Model

With the validation of the model in simulating air entrapment as discussed in this chapter, it was determined that further studies of the influences of sediment properties on air entrapment could be conducted numerically. Chapter 3 discusses how varying specific sediment properties affect the formation of AEBs and the degree of air entrapment in these regions. Extensions of the numerical model to investigations of LNAPL entrapment behavior in water/LNAPL systems are presented in Chapters 4 and 5.
CHAPTER 3

INFLUENCE OF SEDIMENT CHARACTERISTICS ON AIR ENTRAPMENT

The validation of the numerical model TOUGH2 as used for the study of air/water systems provides for the opportunity for advanced numerical investigations of air/water behavior observed in the Partially Saturated Fringe (PSF). As observed previously, heterogeneity at the local scale in the PSF can result in extremely complex distributions of soil moisture both above and below the water table. One of the key components involved in the further study of air/water systems is the investigation of various properties of the heterogeneities of the system that affect the formation and degree of air entrapment in the PSF.

In order to properly understand the distribution of soil moisture in the PSF, it is essential to understand how various properties of the medium affect the degree to which air is entrapped in a system. As an extension of the laboratory studies reported in Dunn (2003) and reviewed previously, two specific soil characteristic parameters (degree of sorting and air entry pressure) were investigated numerically to determine their impact on air entrapment in a heterogeneous system.

3.1 Conceptual Description of Experiments

Two properties of unsaturated porous media that affect distribution of soil moisture and water/air fluxes are the air entry pressure and degree of sorting of sediments. The investigations presented in this chapter focus on the impact of variation in
these properties on air entrapment within a heterogeneous medium. As discussed in Chapter 2, the TOUGH2 model has been validated against our laboratory experiments using the same sands as discussed in Schroth et al. (1996). We therefore used the published properties for these sands as the starting point for analysis of the impact of variation in air-entry pressure and sorting on air entrapment. Hence, we use TOUGH2 along with the van-Genuchten (capillary pressure function) and van Genuchten-Mualem (relative permeability) models with initial parameters (using measured laboratory values for residual saturations) as presented in Chapter 2.

While we are directly interested in air entry pressure and degree of sorting, these parameters are not directly included in the van-Genuchten capillary pressure function (Equation 2.8): $P_{cap} = -P_0 \left( \left[ \frac{S^*}{S^*_{sat}} \right]^{1/\lambda} - 1 \right)^{-\lambda}$

Rather, the two parameters in the pressure-saturation expressions which are investigated here are $P_0$ and $\lambda$. In a physical system the degree of sorting will directly impact the value of $\lambda$. A greater degree of sorting, or high degree of sediment uniformity, in the physical system will be represented by a high $\lambda$ value in the numerical simulations. Hence, variation in degree of sorting is herein modeled via variation in $\lambda$. Similarly, air entry pressure is directly related to $P_0$. A media with a high air entry pressure can be represented in the numerical model with a high $P_0$ value. Hence, variation in the air-entry pressure is herein modeled via variation in $P_0$.

3.2 Questions Addressed in these Numerical Experiments

For the work presented here, imbibition was modeled through a heterogeneous medium consisting of a coarse sand lens embedded in a fine sand matrix (based on the description of the sediments used in the laboratory work presented in Chapter 2).
Multiple runs were simulated, using variation in the values for either $P_0$ and $\lambda$ in each run, thus allowing simulation of the impact of changes in air-entry pressure and degree of sorting. The two main questions addressed were as follows:

- Will an increase in the air entry pressure of the coarse sediment (approaching the air entry pressure of the fine sediment) result in decreased entrapment of air below the water table during imbibition?

- Will an increase in the degree of sorting, or uniformity, of the coarse sediment result in increased entrapment of air below the water table during imbibition?

### 3.3 The Simulations and Parameter Sets

In order to address these questions, a simulation grid was created in TOUGH2 that contained two zones of coarse sediment surrounded by fine sediment. The two-dimensional simulation grid was set to have a length of 2 m and a height of 1.5 m. The sizes of the zones of coarse sediments (shown in lighter gray in Figure 3.1) were 0.6 m wide by 0.42 m high and 0.6 m wide by 0.15 m high. Figure 3.1 is an illustration of the grid used in the following simulations.
Figure 3.1 - TOUGH2 simulation grid for modeling varying van Genuchten parameters. Black surrounding area are modeled as reservoirs, light gray inclusions are coarse sand in which parameters are varied, surrounding matrix of uniform finer sand. Black dots indicate locations where moisture content was recorded. Circled black dot is the location reported in results.

For each simulation, the system began fully saturated with water. Drainage was simulated until the system reached steady state with the water table at the bottom of the grid. The imbibition phase of the simulation was then initiated. The water table was increased in increments, allowing the system to come to equilibrium between each change in water table height. The increments used in each simulation were at water table heights 0 m, 0.24 m, 0.48 m, 0.75 m, 0.87 m, 0.99 m, 1.11 m, 1.25 m, and 1.50 m. Predicted moisture content versus height of the water table was recorded at each of the locations represented by black dots in Figure 3.1.
Multiple simulations were conducted using varying values for $\lambda$ and $P_0$. In order to address the first question, a constant degree of sorting, represented by $\lambda = 0.864$, was simulated for three values of $P_0$: 1445 N/m², 649 N/m², 400 N/m². Figure 3.2 illustrates the soil water retention curves for the coarse sand using a constant $\lambda = 0.864$ and the varying $P_0$ values. The combination of parameters $P_0 = 649$ N/m², $\lambda = 0.864$ matches the combination of parameters fit to the coarse sand in the laboratory experiments described in Chapter 2.

![Soil Water Retention Curves for Varying Po (Lambda = 0.864)](image)

*Figure 3.2 - Soil water retention curves for varying Po values.*

In order to address the second question, various values of $\lambda$ (0.7, 0.5, and 0.3) were used in combination with a constant value for $P_0$ (= 649 N/m²). The higher $\lambda$ values
represent more sorting. Figure 3.3 illustrates the effects of varying the $\lambda$ value on the capillary pressure curves.

![Soil Water Retention Curves for Varying Lambda (P_o=649 N/m$^2$)](image)

**Figure 3.3 - Soil water retention curves for varying Lambda values.**

### 3.4 Results

Although results for each simulation were obtained for each location marked in Figure 3.1, only results for the circled location in Figure 3.3, located in one of the coarse lenses, are reported here as the results were quite consistent across all points monitored. Further, TOUGH2 provides predicted moisture contents rather than predicted percentage of air present within a grid element. Hence, the moisture content is reported as an inverse
indication of the amount of air entrapped in this coarse lens (e.g., the higher the moisture content, the lower the air saturation).

The results addressing the first question, the impact of air entry pressure on entrapment during imbibition, are shown in Figure 3.4. This graph indicates that the highest air entry pressure, represented by a $P_0$ value of 1445 N/m², resulted in a maximum water saturation of 0.94 in the upper portion of the coarse sand. In comparison, the maximum saturation obtained with the middle air entry pressure value, $P_0 = 649$ N/m², is 0.70, while $P_0 = 400$ N/m² resulted in a maximum water saturation of 0.64. Hence, the maximum water saturation increased with an increase in $P_0$ such that the amount of air entrapped in the coarse sand decreased with increasing in $P_0$.

![Effect of Air Entry Pressure of Sand Lens on Air Entrapment](image)

**Figure 3.4 - Percent Water Saturation vs. Water Table Height for the effect of varying air entry pressure values ($P_0$) for the coarse sand lens on air entrapment in the lens.**
The results relative to the second question are shown in Figure 3.5. The lowest value for maximum moisture content observed at the measurement point was equal to a saturation of 0.73 (at a water table height of 150 cm) and was observed for $\lambda = 0.7$ which is representative of a high degree of sorting in the coarse sand. With a $\lambda$ of 0.5, the maximum moisture content at the measurement point was 0.788. With a low degree of sorting, $\lambda = 0.3$, the maximum saturation at this point increased to 0.858. As saturation is inversely related to air saturation, the volume of air entrapped increased with increasing $\lambda$ or, in other words, increased with increased degree of sorting.

Figure 3.5 - Percent Saturation vs. Water Table Height for the effect of the degree of sorting (varying $\lambda$) in the coarse sand lens on air entrapment in this lens.
3.5 Observations

The results shown in Figures 3.4 and 3.5 illustrate that varying the air entry pressure and degree of sorting of sediment can have an influence on the amount of air entrapped during imbibition in a heterogeneous system. It was found that an increase in the air entry pressure of the coarse sediment led to a lower degree of entrapment and less air in the coarse sediments. It was also observed that an increase in the degree of sorting or uniformity of grain size of the coarse sediment results in entrapment of more air in the coarse sand. These results both imply that the degree of heterogeneity in a porous medium will have significant impact on the potential for entrapment of air below the water table and also that the variation in entrapment of air with changes in the degree and types of heterogeneity may be estimated through knowledge of the variation in critical sediment properties such as capillary rise, the variation in air entry pressure among the various sediments present and the degree of sorting within the coarser sediments.
CHAPTER 4

LNAPL ENTRAPMENT

The results presented previously in this dissertation demonstrate that heterogeneity at the local scale within the PSF can result in extremely complex distributions of soil moisture both above and below the water table. The main objective of the research presented in the next two chapters is to extend this investigation to the effects of heterogeneities on the hydraulic entrapment of LNAPLs in a two-phase water/LNAPL system using both laboratory and numerical investigations.

4.1 Hypotheses

The research presented in the following two chapters focuses on three hypotheses that have been chosen as interesting concepts when considering the hydraulics of LNAPL entrapment in a two phase (LNAPL/water) heterogeneous system. This research focused on the conditions of a rising water table in a heterogeneous groundwater system.

The following hypotheses concerning heterogeneity and hydraulic entrapment of LNAPL within the PSF are investigated:

- In a two-phase (LNAPL/water) heterogeneous system, LNAPL will become entrapped, during imbibition, in coarse sediments.
In a two-phase (LNAPL/water) heterogeneous system, the rate of water table fluctuation will influence the amount of entrapped LNAPL. Specifically, as the rate of rise in the water table increases, the total volume of LNAPL which is hydraulically entrapped in the PSF will decrease.

The connectivity and sediment properties of coarse lenses within a fine sand matrix will influence the amount of LNAPL entrapped. Specifically, as the connectivity of the coarse regions increases, the total volume of LNAPL hydraulically entrapped will decrease. Also, as the sediment properties of the enclosed coarse sand lens become more similar to the surrounding sand, less LNAPL entrapment is likely to occur.

These hypotheses were investigated using both laboratory experiments and numerical modeling. Investigation of the first two hypotheses involved laboratory experiments which were used for the verification of the numerical model simulations. Once the model was verified, numerical simulations were used to expand this investigation. The third hypothesis was investigated with the use of numerical modeling and is in the focus of Chapter 5.

4.2 Use of Model for Initial Investigations and Experimental Design

Preliminary investigations with LNAPL/water systems were conducted with the use of the numerical model T2VOC, as the model has been verified using previously published data with air/water experimentation (as discussed in Chapter 3). Schroth et al. (1996) also characterized these same sands in association with the LNAPL Soltrol 220®.
As the proposed experiments were designed to focus solely on the hydraulics of LNAPL entrapment near the water table, an LNAPL was chosen for the numerical and experimental studies that minimized potential impacts from dissolution, volatilization, chemical reaction, toxicity, or biological degradation. Based on prior studies by other authors (Illangasekare et al., 1995a and 1995b; Walser et al., 1999), these constraints led to the selection of Soltrol 220® (Phillips Chemical Co. – henceforth referred to as Soltrol), an LNAPL with low toxicity, solubility, susceptibility to biological degradation, and volatility. More reactive or soluble LNAPLs would be required in order to extend these studies to LNAPLs of current interest to remediation studies. Oil Red O dye (Fisher Scientific), a commercially available, non-toxic dye that does not alter the properties of the Soltrol was utilized to color the oil so behavior could be monitored visually.

Soltrol has a density of approximately 790 kg/m³. Parameters for the hydraulic behavior of Soltrol, as presented by Schroth et al. (1996), were used in numerical simulations to guide the design of our laboratory experiments. Based on Schroth et al. (1996), it was assumed that the coarse sand has a particle density of 2665 kg/m³, porosity of 0.348, and an isotropic absolute permeability of 3e-9 m². Similarly, the fine sand is assumed to have a particle density of 2663 kg/m³, porosity of 0.348, and isotropic absolute permeability of 4.8e-10 m².

When solving the simulations, for each phase present in a system, there will be a set of mass balance equations developed for each of the three components in that phase. Table 4.1 presents a summary of each of the terms involved in the mass balance of each phase present in the system.
TABLE 4.1

TERMS INCLUDED FOR MASS BALANCE OF EACH PHASE

<table>
<thead>
<tr>
<th>For each phase:</th>
<th>Mass $M^\kappa$</th>
<th>Flux $F^\kappa_{\text{advective}}$</th>
<th>Flux $F^\kappa_{\text{diffusive}}$</th>
<th>Generation $q^\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (g)</td>
<td>$M^g$ $M^l$ $M^o$</td>
<td>$F^g_{\text{ad}}$ $F^l_{\text{ad}}$ $F^o_{\text{ad}}$</td>
<td>$F^g_{\text{dif}}$ $F^l_{\text{dif}}$ $F^o_{\text{dif}}$</td>
<td>$q^g$ $q^l$ $q^o$</td>
</tr>
<tr>
<td>Liquid (l)</td>
<td>$M^g$ $M^l$ $M^o$</td>
<td>$F^g_{\text{ad}}$ $F^l_{\text{ad}}$ $F^o_{\text{ad}}$</td>
<td>$F^g_{\text{dif}}$ $F^l_{\text{dif}}$ $F^o_{\text{dif}}$</td>
<td>$q^g$ $q^l$ $q^o$</td>
</tr>
<tr>
<td>Oil (o)</td>
<td>$M^g$ $M^l$ $M^o$</td>
<td>$F^g_{\text{ad}}$ $F^l_{\text{ad}}$ $F^o_{\text{ad}}$</td>
<td>$F^g_{\text{dif}}$ $F^l_{\text{dif}}$ $F^o_{\text{dif}}$</td>
<td>$q^g$ $q^l$ $q^o$</td>
</tr>
</tbody>
</table>

NOTE: $\kappa$ is component present in each phase

While Table 4.1 is somewhat simplistic (e.g., all terms appear in each phase), it is useful in illustrating the terms that are included in a particular system under investigation. For example, when investigating a system containing only the LNAPL and water phases, all of the terms in the first line (Gas) of Table 4.1 can be eliminated from the equations, as well as any term involving the gas phase ($M^g$ and $F^g_{\text{ad}}$ for both liquid and oil phases). Further, there will be no generation terms present, and, as Soltrol was chosen as the LNAPL, diffusive flux terms will be considered negligible. This will eliminate all of the terms presented on the right half of Table 4.1, leaving only 8 terms ($M^l$ and $M^o$ for both LNAPL and liquid phases and advective flux terms $F^l$ and $F^o$ for both LNAPL and liquid phases) to be included when solving the equations for an LNAPL/water system using Soltrol as the LNAPL. As more complexity is added to a system, the number of terms involved in the solution is increased.

The modified version of Stone’s 3-phase relative permeability function was utilized for both the fine and coarse sands (Equation 4.1).
\[
k_{rg} = \left[ \frac{S_g - S_{rg}}{1 - S_{wr}} \right]^n
\]

\[
k_{rw} = \left[ \frac{S_w - S_{wr}}{1 - S_{wr}} \right]^n
\]

\[
k_{rn} = \left[ \frac{1 - S_g - S_w - S_{nr}}{1 - S_g - S_{wr} - S_{nr}} \right] \left[ \frac{1 - S_{wr} - S_{nr}}{1 - S_w - S_{nr}} \right] \left[ \frac{(1 - S_g - S_{wr} - S_{nr})(1 - S_w)}{(1 - S_{wr})} \right]^n
\]

When \( S_n = 1 - S_g - S_w \) is near irreducible Soltrol saturation, \( S_{nr} \leq S_n \leq S_{nr} + 0.005 \), Soltrol relative permeability is taken to be:

\[
k'_{rn} = k_{rn} \cdot \frac{S_g - S_{nr}}{0.005}
\]

\( S_i \) – Saturation of phase \( i \)
\( S_{ri} \) – Residual saturation of phase \( i \)
\( k_{ri} \) – Relative permeability of phase \( i \)
\( n \) - constant

**Equation 4.1 - Modified version of Stone's first three phase method for relative permeability function (Stone, 1970)**

The van Genucthen Capillary Pressure Function was utilized for both sands (Equation 3.3). Although this was originally a two-phase function, it has been modified to accommodate three phases (Falta et al., 1995). This is done by assuming that the gas-NAPL capillary pressure will be equal to zero. This is a reasonable assumption as the wettability order of the phases is aqueous phase, NAPL phase, and gas phase. In accordance with this, the gas-water capillary pressure is usually much stronger (more negative) than the gas-NAPL capillary pressure. To simplify the three phase equations, the gas-water capillary pressure is assumed to be a significant degree greater than the gas-
NAPL capillary pressure and as such, the gas-NAPL capillary pressure is negligible in the calculations. The capillary pressure between the NAPL and aqueous phases, $P_{cnw}$, is given by: $P_{cnw} = P_{cgw} - P_{cgn}$ (the capillary pressure between the gas and water phases minus the capillary pressure between the gas and NAPL phases). For the purposes of this research, using the modified three phase capillary pressure functions, and assuming the gas-NAPL capillary pressure is zero, then $P_{cnw} = P_{cgw}$. Values for the parameters used in the T2VOC model were taken from Schroth et al. (1996) and are presented in Table 4.2 for both the fine and coarse sands.

### TABLE 4.2

**RELATIVE PERMEABILITY AND CAPILLARY PRESSURE PARAMETERS USED IN T2VOC MODEL FOR FINE AND COARSE SANDS**

<table>
<thead>
<tr>
<th>Relative Permeability Function - Stone’s 3-Phase (Modified)</th>
<th>Coarse Sand</th>
<th>Value Assigned</th>
<th>Coarse Sand</th>
<th>Value Assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2VOC Parameter Parameter in Eqn 4.1</td>
<td>Value Assigned</td>
<td>T2VOC Parameter Parameter in Eqn 4.1</td>
<td>Value Assigned</td>
<td></td>
</tr>
<tr>
<td>RP (1) $S_{wr}$</td>
<td>0.16</td>
<td>CP (1) $\lambda$</td>
<td>0.864</td>
<td></td>
</tr>
<tr>
<td>RP (2) $S_{nr}$</td>
<td>0.16</td>
<td>CP (2) $S_{lr}$</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>RP (3) $S_{gr}$</td>
<td>0</td>
<td>CP (3) $P_{0}^{-1}$ [1/N/m²] drainage = 2.71E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP (4) $n$</td>
<td>3</td>
<td>CP (4) $P_{max}$ [N/m²]</td>
<td>1100</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fine Sand</th>
<th>Value Assigned</th>
<th>Fine Sand</th>
<th>Value Assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP (1) $S_{wr}$</td>
<td>0.12</td>
<td>CP (1) $\lambda$</td>
<td>0.918</td>
</tr>
<tr>
<td>RP (2) $S_{nr}$</td>
<td>0.12</td>
<td>CP (2) $S_{lr}$</td>
<td>0.01</td>
</tr>
<tr>
<td>RP (3) $S_{gr}$</td>
<td>0</td>
<td>CP (3) $P_{0}^{-1}$ [1/N/m²] drainage = 7.49E-04</td>
<td></td>
</tr>
<tr>
<td>RP (4) $n$</td>
<td>3</td>
<td>CP (4) $P_{max}$ [N/m²]</td>
<td>1.37E-03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Capillary Pressure Function - van Genuchten model</th>
<th>Coarse Sand</th>
<th>Value Assigned</th>
<th>Coarse Sand</th>
<th>Value Assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2VOC Parameter Parameter in Eqn 4.1</td>
<td>Value Assigned</td>
<td>T2VOC Parameter Parameter in Eqn 4.1</td>
<td>Value Assigned</td>
<td></td>
</tr>
<tr>
<td>CP (1)</td>
<td>$\lambda$</td>
<td>0.864</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP (2)</td>
<td>$S_{lr}$</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP (3)</td>
<td>$P_{max}$ [N/m²]</td>
<td>1100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP (5)</td>
<td>$S_{ls}$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fine Sand</th>
<th>Value Assigned</th>
<th>Fine Sand</th>
<th>Value Assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP (1)</td>
<td>$\lambda$</td>
<td>0.918</td>
<td></td>
</tr>
<tr>
<td>CP (2)</td>
<td>$S_{lr}$</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>CP (3)</td>
<td>$P_{max}$ [N/m²]</td>
<td>1.37E-03</td>
<td></td>
</tr>
<tr>
<td>CP (5)</td>
<td>$S_{ls}$</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:** Drainage and Imbibition have different values for CP(3) as the air entry pressure ($P_{0}$) is different for drainage and imbibition due to hysteresis.
Using the specified characteristics, a series of simulations was conducted in order to investigate the first stated hypothesis and determine if LNAPL could entrap in coarser sand regions surrounded by a finer sand matrix. Grids containing a simple configuration of coarse sand lenses in a fine sand matrix were used for drainage and imbibition simulations. For each of these simulations, the grid was initially set to be fully saturated with the water phase. LNAPL was then introduced across the entire upper surface (all top grid elements) and water was withdrawn from the bottom layer of grid elements to simulate drainage of the system. In order to maintain a constant flux through the system, LNAPL was introduced at the top and water was withdrawn from the bottom of the tank at the same volumetric rate. Once the system was drained to a water table at the base of the grid, imbibition was simulated. For imbibition, water was introduced through all bottom grid elements at a specified rate, and all top grid elements were allowed to have free flow, simulating an overflow region. This simulation was continued until free phase water was present in the top reservoir. A number of simulations were conducted using different flow rates.

These simulations predicted that LNAPL would become entrapped in the coarse sand regions during imbibition of the system. One of the key observations made due to these simulations was that the entrapment of the LNAPL in the system is highly dependent on the rate of rise of the water table during imbibition. If the height of the water table is increased too quickly, the entire system is flushed of LNAPL, eliminating entrapment and leaving the system fully saturated with water (except for expected residual LNAPL). Figure 4.1 illustrates the difference in amount of LNAPL entrapment in the simulated system at three different rates of imbibition.
Figure 4.1 - LNAPL entrapment at different rates of imbibition. Rates of imbibition are: (a) 0.4 cm/hr (b) 4 cm/hr (c) 40 cm/hr. Saturation of LNAPL (SO) is reported.

It is noted that there is effectively no entrapment of LNAPL at the higher rate of rise of the water table, while substantial LNAPL is entrapped at the lower rate. This difference results from the fact that the fine sand above the coarse sand remains at relatively high LNAPL saturation during the higher rate of water table rise (c), thus providing an exit pathway for the LNAPL in the coarse sand. When the water table is raised more slowly (a), the LNAPL in the fine sand has time to migrate away from the region above the coarse sand, thus reducing the LNAPL in the fine sand to residual saturation before the LNAPL in the coarse sand is under a positive gradient for vertical migration. Because of the reduced LNAPL saturation, the fine sand has minimal permeability to the LNAPL phase, thus entrapping the LNAPL in the coarse sand.

These simulations aided greatly in the design of three aspects of the experimental set up. First, the overall size of the laboratory tank was determined after observing the simulated behavior of LNAPL entrapment. It was observed in simulations that the coarse inclusions had an impact on the hydraulic behavior in the surrounding fine sand (near the
edges of these inclusions). It was observed that these flow anomalies occurred on both sides of the coarse sand lenses and influenced approximately 4 cm of flow on each side of the lens. This was taken into consideration in the design of the width of the laboratory tank. It was determined that five coarse regions, each 4 cm in width, of varying height would be included in the laboratory set up. It was also determined using the numerical simulations that each of these coarse lenses needed to be spaced at least 8 cm apart, in order to avoid influence of the flow anomalies on the hydraulic behavior of the neighboring coarse region. These considerations led to an overall width of the laboratory tank of 56 cm.

The second design aspect aided by the initial numerical studies was the determination of the height of the tank and the desired height of coarse regions in the system. Initial simulations were studied in order to determine the amount of LNAPL that would become entrapped in heterogeneities. The laboratory tank was made tall enough to include coarse sand regions that were predicted to entrap LNAPL in the top portion of the zone and resaturate with water in the bottom portion of the zone. A range of heights (from 5 cm to 40 cm) for each coarse sand zone was included to ensure partial entrapment in these regions. The laboratory tank height was determined to be 53 cm of sediment.

The third aspect that was aided by the initial numerical simulations was the determination of the rate of rise of the water table. Based on the initial simulations, it was determined that it was important to use a flow rate in the laboratory that would allow entrapment of LNAPL below the water table as well as be a realistic flow rate to conduct laboratory experiments. An ideal flow rate was determined to be approximately 0.14
m³/day. This flow rate is equivalent to an approximate (short term) rate of rise in the water table of 1.6 m/day, a rate that might be observed during a significant infiltration event or during reaction to a change in rate of production at a local groundwater well. This flow rate was determined to be the optimal flow rate for investigation, and flow rates both faster and slower than this rate were used for determination of flow rate effect on the system.

4.3 Laboratory Experiments – Materials and Methods

Laboratory experiments were performed in the tank shown in Figure 4.2. The dimensions were 56 cm (length), 53 cm (height), and 16 cm (width). This tank was constructed out of Plexiglas and held together with bolts and silicon glue. Reservoirs were located on the top and bottom of the tank, each approximately 3 cm high. Ports were located along the length of each of the reservoirs in order to allow injection or withdrawal of either LNAPL or water throughout the experiments. These ports allowed introduction of LNAPL at the upper boundary of the sand during drainage experiments (along with removal of water at the base of the sand) and introduction of water at the base of the sand (with outflow of LNAPL from the upper reservoir) during imbibition experiments. Ports were also located on either side of the reservoirs and a manometer tube with shut off valves at the top and bottom was used as an external connection between the top and bottom reservoir in order to determine water table height during each experiment.
Figure 4.2 – Simulation grid (left) and laboratory tank (right) for LNAPL/water drainage and imbibition experiments. Numbers represent TDR probe locations throughout tank. Circled zone is used for data reported in Section 4.4. Dimensions of the flow cell are illustrate in the schematic (bottom).

4.3.1 Time Domain Reflectometry

One of the developments for the study of the PSF was the use of a Time Domain Reflectometry (TDR) system for laboratory measurement of moisture content. The TDR system is based on a Campbell Scientific TDR-100 and three-rod TDR probes developed
in our laboratory. This system allows for multiple probes to be installed in the flow cell with the ability to measure moisture content and electrical conductivity at each probe with a frequency of approximately one measurement per 10 seconds. The probes were constructed (based on an adaptation of Evett and Ruthardt, 2001) in order to minimize the size of the probes, and thus minimize the disturbance to the system and the volume averaged for the signal. Details of probe construction methods can be found in the Master’s thesis of the author, Dunn (2003). The developed TDR probes were previously calibrated for air/water systems in our laboratory.

These TDR probes have been tested in our laboratory on several LNAPL/water mixtures (in open vessels without porous media present) in order to determine their ability to differentiate between two phases - water and LNAPL (work conducted by undergraduate research assistant in our laboratory – Brian Zambpell). It has been determined the TDR system can be used to determine the dominant phase present. The results, seen in Figure 4.3, are consistent whether the LNAPL and water are in distinct phases or the LNAPL and water are vigorously shaken into an emulsion. This development in TDR technology allows for the use of this technology in providing a reliable measurement instrument in the study of water/LNAPL systems utilized in this work. Moisture content, in reference to LNAPL/water systems will herein be used to refer to the percent water present in the system as reported by the TDR probes and software. It is noted that this reading cannot, at present, be related to actual moisture content present within the porous medium. Rather, the readings are used solely as an indicator of high versus low moisture content.
Figure 4.3 - TDR response in water/LNAPL system showing approximately linear relationship between % LNAPL and probe reading. The LNAPL fraction is established in the laboratory. The moisture content is reading from the TDR software.

4.3.2 The Sediments

The same two grain sizes of pre-sieved, silica sand that were used in the air-water experiments described in previous chapters were used in all water-LNAPL experiments.

4.4 LNAPL Experiments

4.4.1 Laboratory Procedure

A simple heterogeneous distribution of sediments was used for numerical and laboratory experimentation during the verification stage of the model. As the exact capillary rise of the water above the water table in the two-phase LNAPL/water system was not specifically known, multiple enclosed coarse zones of varying heights were included in the experimental layout in order to maximize the probability of observing entrapment of LNAPL. The zone seen on the far left of the tank (with TDR probes 18-20)
was included as a control to verify expected behavior in a region where vertical flow was not influenced by overlaying fine sand.

The laboratory tank was filled under saturated conditions (with water), packing the sand in small lifts, using dividers to separate grain sizes. When the tank was fully packed, the upper surface was fitted with a small reservoir extending over the horizontal upper surface of the sand (approximately 3 cm in height), and the entire tank was sealed with a Plexiglas lid. The sealed tank allowed for control over the pressure and phases present within the system.

Once the tank was sealed, the drainage experiment was initiated. LNAPL was introduced into the system from the upper reservoir and water was withdrawn from the lower reservoir. The water table was lowered at a constant flow rate, as controlled by a peristaltic pump with two pump heads, thus injecting (LNAPL) and withdrawing (water) from the system at the same rate. LNAPL was continually introduced into the system through the upper reservoir in order to fully occupy the second phase of the system, such that no air was present in the media. Injection and withdrawal from the system was continued until free phase LNAPL was present in the bottom reservoir of the tank. Throughout the experiments, data were taken from the TDR probes located in various positions in the tank to determine the dominant phase present at these points, and photographs were taken to visually record LNAPL behavior in the system.

Once LNAPL had reached the bottom reservoir and final TDR data were recorded for drainage, the imbibition experiment was initiated. Water was injected through the bottom reservoir and LNAPL was withdrawn from the top reservoir at a specified flow rate. Three flow rates were used for experimentation in order to determine the effects of
flow rate on LNAPL entrapment. For the high and medium flow experiments (described below), the flow through the system remained constant through the entire experiment, as the peristaltic pumps were able to simulate flow rates at these velocities. The low flow imbibition experimental procedure differed from the medium and high flow ones, as the peristaltic pump was not able to obtain a low enough flow rate for continual flow through the system to take place. In order to achieve a very low flow rate, flow was initiated through the tank at an extremely low rate for a period of 15 minutes, then shut off for the next 24 hour period, allowing the system to equilibrate. This step procedure was continued for 31 days.

TDR data were recorded and photographs were taken throughout the imbibition experiments. When the water level reached the upper reservoir, flow was terminated. The system was then allowed to come to equilibrium and the process of drainage and imbibition experiments was repeated with a different flow rate. Flow rates used were low (0.018 m³/day), medium (0.14 m³/day), and high (0.71 m³/day). These flow rates were equivalent to approximate rates of imbibition of 2.8 cm/hr, 22 cm/hr, and 110 cm/hr.

4.4.2 Results

Laboratory results for the three different flow rates were recorded both qualitatively (visual record with photographs) and quantitatively (TDR measurements of moisture content and electrical conductivity).
**Low Flow Rate (0.018 m$^3$/day)**

**Laboratory:** Throughout each laboratory experiment, digital images were taken of the experimental apparatus as the water table was raised in the system. Water table height was monitored and recorded each day, and moisture content and electrical conductivity measurements were taken. Figure 4.4 illustrates the LNAPL behavior as observed visually at various water table heights (0 cm, 27 cm, and 53 cm) during the low flow rate experiment.

![Image of experimental apparatus](image_url)

**Figure 4.4 - Low flow rate (0.018 m$^3$/day) imbibition results. Soltrol 220 is dyed red for visualization. (a) Water table height is 0 cm. (b) Water table height is 27 cm. (c) Water table height is 53 cm. Water table heights are marked with blue lines.**

This experiment was conducted over a period of 31 days. Visual observations of this experiment demonstrate that the LNAPL was displaced vertically with the raising of the water table. The contact between water and LNAPL remained approximately at the height above the water table predicted from the capillary rise of each sand. At the end of this experiment, only residual concentrations of LNAPL were present throughout the system. There were no significant portions of LNAPL entrapped in the system. Figure 4.5 illustrates the moisture content readings taken by TDR Probes 14-17 at the beginning and end of the low flow rate experiment. These probes, circled in Figure 4.2, are part of one
of the enclosed coarse zones and represent the behavior seen in each of the enclosed coarse zones.

Figure 4.5 – Moisture content of enclosed coarse zone at flow rate of 0.018 m$^3$/day, with the water table at the base of the tank (0 cm) and at the upper reservoir (53 cm). Locations of probes can be seen in Figure 4.2. Probe 14 is the highest probe in the zone and Probe 17 is the lowest.

The coarse zone containing Probes 14-17 resaturated with the water phase to a saturation of ~25% water, approximately full resaturation with hysteresis taken into account. For the coarse zone with access to the upper reservoir, LNAPL also flowed freely out of the coarse region and into the upper reservoir, leaving the system nearly fully saturated with water (except for residual LNAPL saturation).

**Numerical:** Figure 4.6 illustrates the numerical result predicted by the model for imbibition at the slow flow rate. Figures are shown for the same water table heights displayed in laboratory experiments in Figure 4.4. The model indicates trapping of the
LNAPL (Figure 4.6), despite the observation that all LNAPL was displaced in the laboratory experiment (Figure 4.4). This discrepancy between model and experiment is discussed below.

**Figure 4.6 - Simulation results for low flow rate imbibition test entrapping LNAPL.** (a) Water table height is 0 cm. (b) Water table height is 27 cm. (c) Water table height is 53 cm. Water table heights are marked with blue lines.

*Medium Flow Rate (0.14 m$^3$/day)*

*Laboratory:* Figure 4.7 shows the results of the imbibition experiment with the flow through the tank at a rate of 0.14 m$^3$/day. The flow was continuous until the water table reached the upper reservoir.

**Figure 4.7 - Medium flow rate (0.14 m$^3$/day) imbibition results. Soltrol 220 is dyed red for visualization.** (a) Water table height is 0 cm. (b) Water table height is 27 cm. (c) Water table height is 53 cm. Blue lines indicate location of water table.
As the water table was raised, the LNAPL migrated in accordance to the height of the capillary rise in each sand. However, as the water table continued to be raised, a high concentration of LNAPL remained in the upper portions of all four coarse zones not connected to the top reservoir of the tank, including when the water table reached the upper reservoir (53 cm). Figure 4.8 illustrates the moisture content readings for Probes 14-17, locations shown in Figure 4.2, at the beginning (water table at 0 cm) of the experiment as well as immediately after the water table reached the upper reservoir (53 cm).

![Imbibition at Medium Flow Rate (0.14 m\(^3/\)day)](image)

Figure 4.8 - Moisture content of enclosed coarse zone at flow rate of 0.14 m\(^3/\)day, with the water table at the base of the tank (0 cm) and at the upper reservoir (53 cm). Locations of probes can be seen in Figure 4.2. Probe 14 is the highest probe in the zone and Probe 17 is the lowest.

As is illustrated in Figure 4.8, the area of the coarse zone surrounding Probe 14 remained saturated with the LNAPL phase (very low measured water saturation). The
area around Probe 15 became partially saturated with the water phase (higher measured water saturation). Both Probes 16 and 17, at the bottom of this coarse zone, showed a strong degree of resaturation with the water phase (high measured water saturation). It appeared that approximately 7 cm of LNAPL was entrapped in the upper portion of all enclosed coarse zones.

The experiments were allowed to continue after the water table reached the upper reservoir. Flow was stopped, and the system was allowed to come to equilibrium. This was done to investigate the stability of the entrapped LNAPL in the system. Interestingly, a result different from what was observed with entrapped air, the entrapped LNAPL continued to migrate slowly through the fine sand over time. After 24 hours of having the water table at the upper reservoir, only residual LNAPL remained in the coarse sands. This experiment therefore demonstrated behaviors consistent both with entrapment of LNAPL and long-term equilibration of the two phases (LNAPL and water).

*Numerical:* The short-term results of the numerical simulation of the experiment with the medium flow rate were in close agreement with the laboratory experimental results. Figure 4.9 illustrates the results of the numerical simulation for the medium flow rate.
As can be seen in Figure 4.9, approximately 7 cm of LNAPL was entrapped at a high LNAPL concentration in the upper portion of each enclosed coarse zone. The simulation was able to demonstrate the same behavior as observed in the laboratory. However, the numerical results deviated from the observations in that the numerical results predicted that the entrapment of the LNAPL was permanent (within the time scale of the simulation) without the longer-term migration of the LNAPL out of the coarse sand.

In order to determine if a change in parameters could lead to significant changes in predicted behavior of the system, a second set of numerical simulations was performed. Figure 4.10 illustrates the imbibition simulation at the medium flow rate with an LNAPL present that has a higher residual saturation (50% in fine sand, 26% in coarse sand).
Figure 4.10 - Imbibition simulation with high residual LNAPL saturation in sediments at medium flow rate. Left is the beginning of the simulation (water table at base of grid) and right is the end of the simulation (water table at top of grid). Blue lines show approximate water table height.

As seen in Figure 4.10, the majority of the LNAPL migrates out of the system when the residual saturation of the LNAPL in the sediment above each coarse zone is high enough to allow continual flux from these regions. This simulation indicates that a slightly higher permeability (due to increased residual saturation) in the fine sands will lead to rapid loss of LNAPL from the coarse sand zones. The implications of this observation are discussed in detail later in the dissertation.

High Flow Rate (0.71 m³/day)

Laboratory: For the high flow rate experiment, a flow rate of 0.71 m³/day was used. Figure 4.11 shows the results of the fast imbibition experiment at water table heights 0 cm, 27 cm, and 53 cm.
Three features were noted during imbibition. First, a significant portion of the LNAPL was displaced during imbibition. This included LNAPL in each region of the experimental medium. Second, a significant amount of LNAPL (e.g., well above residual) remained in each of the coarse zones not connected to the top reservoir of the tank. Finally, the LNAPL concentration in these coarse zones appeared to increase with height in the coarse zone, with the highest concentrations apparent just below the contact with the overlying fine sand. The zone connected to the top reservoir behaved as in the prior experiments.

Figure 4.12 illustrates the moisture content readings for Probes 14-17, locations indicated in Figure 4.2, at the beginning of the experiment and immediately after the water table reached the upper reservoir (53 cm).
Imbibition at High Flow Rate (0.71 m³/day)

![Graph showing moisture content vs. water table height for probes 14, 15, 16, and 17.]

Figure 4.12 - Moisture content of enclosed coarse zone at flow rate of 0.71 m³/day, with the water table at the base of the tank (0 cm) and at the upper reservoir (53 cm). Locations of probes can be seen in Figure 4.1. Probe 14 is the highest probe in the zone and Probe 17 is the lowest.

The area surrounding Probe 14 was dominated by the LNAPL phase (low measured moisture content). The area around Probe 15 became partially saturated with the water phase (medium measured moisture content). Both Probes 16 and 17, at the bottom of this coarse zone, were dominated by the water phase (high measured moisture content). As with the previous experiment, when the system was allowed to remain undisturbed for a period of 24 hours after the water table had been raised to the upper reservoir, the LNAPL concentration declined to residual saturation through slow migration of the entrapped LNAPL to the upper reservoir.

**Numerical:** The results of the numerical simulation of the experiment with the high flow rate (Figure 4.13) were in general agreement with the laboratory experimental results through the period of active rise in the water table. As can be seen in the figure,
approximately 4 cm of LNAPL was predicted to be entrapped at a high LNAPL concentration in the upper portion of each enclosed coarse zone. Two significant differences were observed between the experimental and the simulated results. First, the numerical model did not demonstrate the smearing of the LNAPL throughout the coarse sands (as was observed in the laboratory). Second, the numerical model did not predict the long-term migration of the LNAPL to the upper reservoir.

![Simulation results for high flow rate imbibition experiment entrapping LNAPL. (a) Water table height is 0 cm. (b) Water table height is 27 cm. (c) Water table height is 53 cm. Water table position is indicated by blue lines on the figures.](image)

**Figure 4.13** - Simulation results for high flow rate imbibition experiment entrapping LNAPL. (a) Water table height is 0 cm. (b) Water table height is 27 cm. (c) Water table height is 53 cm. Water table position is indicated by blue lines on the figures.

### 4.4.3 Observations

Investigations reported here demonstrate that entrapment of LNAPL in significant quantities can occur (at least temporarily) below the water table due to heterogeneities in the system. Further, the volume of LNAPL entrapped is highly dependent on the rate of imbibition of the system. Numerical simulations and experimental results reported in this chapter demonstrate results in agreement with the first 2 proposed hypotheses for this investigation: (1) LNAPL can become entrapped during imbibition, and (2) As the rate of
flow of the rising water table increases, the total volume of LNAPL entrapped in the PSF region will decrease.

In reference to the first hypothesis, it was demonstrated that LNAPL could become entrapped in the coarser regions of a heterogeneous system during imbibition. Laboratory data demonstrated this entrapment over the short term. However, entrapment was not permanent, as residual saturation within the overlying fine sand remained high enough to allow for flow of the LNAPL out of the coarser regions over time. Numerical simulations indicate that LNAPL can become entrapped in the coarser regions of the system. However, it is possible that the model concluded that the system had reached steady state when in reality there were extremely small changes in the system which would eventually lead to the slow leakage of the LNAPL out of the coarse regions.

Laboratory experiments and numerical simulations verify the second hypothesis in demonstrating that the total volume of LNAPL entrapped in the PSF is dependent on the rate of imbibition. In numerical simulations, it was predicted that approximately 21 cm of LNAPL would be entrapped in the coarse sand under the slow flow rate. The medium flow rate simulation predicted approximately 7 cm of LNAPL in the coarse regions, and the fast flow rate simulation predicted approximately 4 cm of LNAPL in the coarse regions. Laboratory data for the medium and fast flow rate experiments demonstrate similar behavior on a short term basis, as approximately 7 cm of LNAPL was entrapped in the coarse zones during the medium flow rate experiment and approximately 4 cm of LNAPL was entrapped during the fast flow experiment. The laboratory data for the slow flow rate experiment were inconsistent with this hypothesis.
The observed inconsistency among the long-term numerical and experimental results, as well as the inconsistency between the laboratory results for the low velocity imbibition and our second hypothesis led to consideration of the hydraulic mechanisms impacting entrapment and stability of entrapped LNAPL. This analysis led to identification of a possible, complex interplay among three rates impacting LNAPL entrapment. These three rates are:

1) rate of rise of the water table
2) rate of capillary rise within each of the sediments
3) rate of leakage of LNAPL through the fine sand at (or near) residual saturation

The rate of rise of the water table impacts the rate at which water is introduced into the pores of the sediment. Similarly, the rate at which water comes to equilibrium with the height of capillary rise within the sediments affects the height and degree of saturation at which water exists above the water table. Finally, the rate of leakage of LNAPL out of the coarse sand zones is limited by the rate at which LNAPL is able to migrate through the overlying fine sands at, or close to, residual saturation.

When the rate of rise in the water table (rate of imbibition) is high relative to the rates of rise of water in the capillary fringe and migration of LNAPL through the fine sand at residual saturation, water above the water table in both sediments will not have time to come to equilibrium relative to the equilibrium height of the capillary rise. This will result in reducing the height of the capillary fringe (and difference between the relative height) in the two sands. Similarly, the rate of leakage of LNAPL out of the coarse sands will become negligible, thus preventing migration of the LNAPL prior to entrapment by the rise in the water table.
In contrast, when the rate of water table rise is slow relative to the time to
equilibrium in the capillary fringe, but still high relative to the rate of migration through
the fine sands, conditions are optimized for entrapment. In this situation, the capillary rise
(and difference in relative capillary rise in the two sands) is maximized, thus providing
opportunity for the fine sand above the coarse sand to come to residual saturation well
ahead of the arrival of the water table. Further, the high rate of rise of the water table
relative to the rate of migration through the fine sand leads to substantial entrapped
LNAPL remaining in the coarse sand as the water table rises above the upper limit of the
course sand.

Finally, if the rate of migration of LNAPL through the fine sand (at, or close to,
residual saturation) is high relative to the rate of rise in the water table, the opportunity
for entrapment of LNAPL is minimized. Under these conditions, any LNAPL that exists
in the coarse sand below fine sand has the time to migrate through the overlying fine sand
prior to the time at which the water table arrives at the upper limit of the coarse sands.
Hence, the opportunity for entrapment of LNAPL below the rising water table is
substantially reduced.

Consideration of these relative rates under the three conditions discussed in the
previous paragraphs is consistent with observations from our laboratory experiments.
Although beyond the scope of this dissertation, further study of the relative impact of
these rates (and additional rates related to dissolution, volatilization, or degradation for
non-conservative LNAPLs) appears warranted.
CHAPTER 5

NUMERICAL INVESTIGATIONS OF LNAPL ENTRAPMENT BEHAVIOR

LNAPL entrapment in the PSF has been shown to be dependent on the rate of imbibition of the groundwater system. It is recognized that other properties of the system may also influence this entrapment. In particular, the physical (hydrodynamic) characteristics and distribution of sediments are expected to have substantial impact on LNAPL entrapment in heterogeneous media and are therefore the focus of this chapter. Specifically, the effects of connectivity of coarse sediments in a fine sand matrix on LNAPL entrapment are discussed, as are the impacts of degree of sorting and air entry pressure. These effects are studied using two computer programs. A random field generator was used to produce heterogeneous distributions with prescribed statistical similarities (Silliman and Wright, 1991). T2VOC was then used to conduct the associated simulations.

5.1 Discrete Analysis

Random heterogeneous fields consisting of two sediments – ‘coarse’ and ‘fine’- were generated using a discrete random field generator (Silliman and Wright, 1991; Silliman and Caswell, 1998; Silliman et al., 1998). This field generator is able to produce second-order stationary random fields with specified constant mean and autocorrelation structure (henceforth called simply correlation structure). The discrete analysis field
generator is able to produce a discretely varying random field in which regions of random size are assigned constant parameter values.

This generator was used to simulate a series of bimodal, correlated random permeability fields. These fields consisted of random distributions of the two sediments. The generator was used to develop various levels of correlation in the permeability fields. Three different levels of correlation were investigated (low, medium, and high) in this work. Examples of the fields produced by this generator are shown in Figure 5.1.

![Image](image1.png)

**Figure 5.1 - Discrete analysis random permeability field generator; examples of low, medium, and high levels of correlation. Within these images, the lighter material represents the fine sand whereas the coarse sand is represented by the darker material.**

Each random permeability field generated was used as the distribution of sediments in T2VOC to simulate multiphase flow (LNAPL/water). For each field generated the following parameters were used:

- Size of simulation grid: (56, 53). There were 56 elements in the horizontal direction and 53 elements in the vertical direction. Each element was of size 1 cm x 1 cm. These values were based on the size of the laboratory tank used for experimentation - 56 cm in the horizontal direction, 53 cm in the vertical direction.

- Probability of coarse sand occurring: 0.25

- Anisotropy: ½ (length of simulated zone in x/ length of simulated zone in y)
- Maximum horizontal radius of individual permeability zone:
  - 2 elements (results in low level of correlation – Figure 5.1 left)
  - 4 elements (results in medium level of correlation – Figure 5.1 middle)
  - 6 elements (results in high level of correlation – Figure 5.1 right)

Thirty realizations were simulated for each of these levels of correlation. Each was investigated to determine if it was statistically similar, in terms of both percent coarse sand and correlation structure, to the desired theoretical field. Those fields which were considered similar were used in the overall analysis of that connectivity. Specifically, if the percent coarse sand was within +/- 8% of the desired 25%, the field was deemed acceptable for further analysis. This range was developed from observation of the fields generated with the high correlation. It was observed that, within these fields, the percentage coarse sand either fell below 33% or above 40%. It was observed that the fields containing over 40% contained one or more exceptionally large regions of coarse sand. As these features dominated the behavior of the porous medium, these realizations were considered extreme and were therefore identified as inappropriate for further analysis. In an effort to eliminate realizations which were dominated by large individual regions of fine sand (difficult to identify from inspection of the fields), it is assumed that a symmetric cutoff below 25% would be used as the lower percent cut-off. Hence, the final range was 17% - 33% (25% +/- 8%).

In terms of correlation structure, the theoretical correlation structure approaches zero at the large separation distances. Hence, realizations for which the calculated correlation structure at large separation distances differs substantially from zero are considered to deviate from the desired field structure. Hence, each realization was
selected for further analysis only if the tail of the correlation structure was within the range +/- 0.1.

5.2 Methods for Numerical Simulations

For each simulation, the initial hydraulic condition was represented by the medium being fully saturated with water. Drainage of the system was modeled by altering the boundary conditions of the grid, simulating the invasion of LNAPL following the decline of the water table. LNAPL entered through the upper boundary at a rate of $10^{-4}$ kg/sec and mass was withdrawn at the bottom boundary at the same rate. This produced an approximate flux rate through the simulation region of 0.9 m$^3$/day/m width (rate of drainage/imbibition of 22 cm/hr) which was determined in the previous chapter as an acceptable flow rate for numerical simulations and laboratory experiments. Once the boundary conditions resulted in the condition of free phase LNAPL at the base of the simulation grid, the boundary conditions were adjusted to simulate imbibition. For these simulations, water was injected through the lower surface reservoir at a rate of $10^{-4}$ kg/sec, and the upper reservoir was allowed to have free overflow of mass. Imbibition was continued until a free water phase existed at the upper surface of the grid.

Once drainage and imbibition simulations were complete, the total LNAPL entrapment was determined. In order to compare the amount of LNAPL entrapped in each simulation and determine how the connectivity influences the amount of LNAPL entrapment, the percent LNAPL present as averaged over the entire system and as a percent of the amount of coarse sand present was determined at the end of imbibition. In the numerical simulations, the percent LNAPL present at the end of the simulation was determined by calculating the sum of each phase in each element. In order to determine
the percent of the coarse sediment that contains LNAPL at the end of the simulations, the number of coarse elements with an LNAPL saturation of 50% or higher was divided by the number of elements that contained coarse sand. The value of 50% saturation was determined suitable for use as the cut off point between saturated and unsaturated with LNAPL since, based on the results seen for each simulation the saturation tended to be very high (above 75%) or very low (below 25%) such that 50% is a good dividing point between saturated with water and saturated with LNAPL.

5.3 The Effects of Connectivity on LNAPL Entrapment

In accordance to the overall goal to investigate the influence of various sediment properties and distributions on the influence of entrapment in the PSF, it is hypothesized that the connectivity of coarse sediment in a finer sand matrix will have a significant impact on the amount of LNAPL entrapped in the heterogeneous system. Specifically:

In a two-phase (LNAPL/water) heterogeneous system, the total volume of LNAPL entrapped below the water table will decrease as the mean connectivity (mean level of correlation) of coarse sediment inclusions increases.

In order to investigate this hypothesis, drainage and imbibition simulations were conducted for the three different levels of correlation outlined above.
5.3.1 Results of Simulations

Low Connectivity

The low connectivity simulations resulted in LNAPL entrapment in many of the coarse regions. Figure 5.2 shows a typical result at the end of imbibition. The left figure is the sediment distribution and the right figure shows the distribution of LNAPL.

![Simulated entrapment at end of imbibition for low connectivity. Left is distribution of sand, showing small inclusions of coarse sand. Right shows LNAPL distribution.](image)

Table 5.1 shows the results of the LNAPL entrapment for the 30 simulations using low connectivity. The volume of LNAPL at the end of the simulation is presented here in terms of the average LNAPL saturation in the entire system at the end of imbibition and the percent LNAPL as compared to the percent coarse sand present in the system.
As can be seen in Table 5.1, the average LNAPL concentration at the end of the low connectivity simulations is 20%. The average LNAPL concentration present in the coarse sand is 81%. When the percent coarse sediment for each of the random fields was investigated, it was determined that each field had a total percent coarse sediment between 17-33%, the range deemed acceptable for further analysis of these fields.
Figure 5.3 shows the covariance structure of each of the random fields used for analysis. As seen in Figure 5.3 the tails of the covariance structures for the low connectivity distributions all fall within +/- 0.1, suggesting that all 30 simulations reasonably reproduce the desired spatial statistics. The results from all 30 realizations were used in estimating mean LNAPL saturation for this level of correlation.

![Low Connectivity Covariance Structures](image)

**Figure 5.3 - Covariance structures for all 30 low connectivity permeability fields.**

*Medium Connectivity*

The medium connectivity simulations showed LNAPL entrapment in various portions of the coarse regions present in the system. Figure 5.4 shows a typical simulation at the end of imbibition. It was noted in several of the simulations that the lower portions of many of the larger coarse sand inclusions became saturated with water following
imbibition, while the top portion of these regions remained saturated with LNAPL. Table 5.2 shows the results of the LNAPL entrapment for all 30 simulations of the medium connectivity distribution of sediment.

Figure 5.4 - Simulated entrapment at end of imbibition for medium connectivity. Left is distribution of sand, showing pockets of coarse sand. Right shows LNAPL entrapment within coarse sand.
Prior to calculation of final average concentrations, simulations for which the
mean percentage coarse sand was outside the acceptable range (17% - 33%) or for which
the resulting correlation structure differed substantially from the desired structure were
removed. The percent coarse sediment in each simulation was examined, and it was
determined that two of the simulations were outside of the coarse sediment range of 17-
33%.
As shown in Figure 5.5, the correlation structure of the generated random field was also assessed for each realization to determine whether select simulations achieved the desired level of correlation.

As can be seen in Figure 5.5, there were two simulations which have the tail of their covariance structure lying outside of +/- 0.1%. These two simulations are 15 and 18. In accordance to the constraints outlined above, simulations 15, 17, 18, and 27 were not included in further statistical analysis. When these simulations were removed from analysis, the average entrapped LNAPL in the system was 14% and the average entrapped LNAPL in the coarse regions was 58%.

Figure 5.5- Covariance structures for all 30 medium connectivity permeability fields. Simulations 15 and 18 have tails outside of the desired range.
High Connectivity

The high connectivity simulations showed LNAPL entrapment in portions of the larger coarse regions. Figure 5.6 shows a typical simulation at the end of imbibition. The left figure is the sediment distribution and the right figure is the entrapped LNAPL.

![Image of sediment distribution and entrapped LNAPL](image.png)

**Figure 5.6 - End of imbibition simulation of high connectivity matrix. Left is distribution of sand. Right shows LNAPL entrapped in coarse regions.**

In Figure 5.6, it can be seen that the LNAPL is not entrapped in the entire portion of each of the larger coarse regions. Rather, the bottom of these regions can fill with water such that LNAPL is entrapped only in the upper part of these coarse regions, and then only if the upper portion is isolated from the upper source of pure LNAPL (or top of grid in this case). It is also interesting to note that complex geometries, such as observed in the coarse inclusion in the upper-right portion of this figure, can lead to local entrapment of LNAPL despite connection of a part of the coarse zone to the source of LNAPL.
Table 5.3 shows the results of the LNAPL entrapment for all 30 of the simulations of the high connectivity distribution of sediment (without regard to acceptability of the individual simulations).

### TABLE 5.3
HIGH CONNECTIVITY SIMULATION RESULTS FOR ENTRAPPED LNAPL

<table>
<thead>
<tr>
<th>Simulation #</th>
<th>LNAPL % saturation</th>
<th>% coarse sand</th>
<th>LNAPL/%coarse</th>
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<td>0.10</td>
<td>0.21</td>
<td>0.46</td>
</tr>
<tr>
<td>2</td>
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</tr>
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<td>0.25</td>
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</tr>
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<td>0.33</td>
<td>0.36</td>
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<tr>
<td>22</td>
<td>0.06</td>
<td>0.42</td>
<td>0.15</td>
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<tr>
<td>23</td>
<td>0.12</td>
<td>0.26</td>
<td>0.44</td>
</tr>
<tr>
<td>24</td>
<td>0.14</td>
<td>0.44</td>
<td>0.32</td>
</tr>
<tr>
<td>25</td>
<td>0.13</td>
<td>0.33</td>
<td>0.40</td>
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<tr>
<td>26</td>
<td>0.09</td>
<td>0.30</td>
<td>0.31</td>
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<tr>
<td>27</td>
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<td>0.27</td>
<td>0.47</td>
</tr>
<tr>
<td>28</td>
<td>0.15</td>
<td>0.26</td>
<td>0.58</td>
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<tr>
<td>29</td>
<td>0.16</td>
<td>0.31</td>
<td>0.51</td>
</tr>
<tr>
<td>30</td>
<td>0.15</td>
<td>0.24</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Avg LNAPL Conc: 0.11    Avg LNAPL/coarse: 0.46

As with the results for the medium connectivity, the large regions simulated in this relatively small grid area lead to spatial statistics which do not necessarily converge to the desired statistics. Hence, once again, simulations for which the mean percentage
coarse sand was outside the acceptable range (17% - 33%) or for which the resulting tail of the correlation structure differed substantially from zero were removed prior to estimation of the final LNAPL saturation statistics. When the percent coarse sediment was investigated, it was found that nine of the fields were outside of the desired range. As can be seen in Figure 5.7, there is a range over which the covariance structures are distributed, however, in general most have similar shape and tend to zero. There are seven additional realizations which lie outside of the desired tail range of +/- 0.1. When all fields which do not comply with the constraints are eliminated, fourteen simulations remain. The average entrapped LNAPL across these simulations is 13% and the average LNAPL entrapped in the coarse sand is 50%.

Figure 5.7 - Covariance structures for all 30 high connectivity permeability fields. Tails of fields 2, 4, 8, 12, 14, 26, and 27 lie outside of the desired +/- 10%.
5.3.2 Discussion of Effect of Connectivity on LNAPL Entrapment

When investigating the effects of connectivity on LNAPL entrapment and distribution in these heterogeneous systems, it is interesting to compare the total percent of entrapped LNAPL in the system and the amount of entrapped LNAPL in the coarse regions of the system. The numerical modeling presented thus far in this chapter, as summarized in Table 5.4, demonstrates that the total percentage LNAPL saturation and the percentage LNAPL present in coarse sediment decreases with increasing connectivity. As can be seen from Table 5.4, as the connectivity between the coarse sediment regions increases, both the overall total percent entrapped LNAPL and the percent LNAPL entrapped in the coarse sediment decrease.

<table>
<thead>
<tr>
<th></th>
<th>LNAPL % Saturation</th>
<th>%LNAPL/%coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>0.20</td>
<td>0.81</td>
</tr>
<tr>
<td>Medium</td>
<td>0.14</td>
<td>0.58</td>
</tr>
<tr>
<td>High</td>
<td>0.13</td>
<td>0.50</td>
</tr>
</tbody>
</table>

In systems with low connectivity of coarse sediment, the coarse material is distributed as a large number of small, disconnected coarse sand lenses. Hence, imbibition results in essentially complete LNAPL saturation of each of the coarse sand
inclusions. The resulting percentage of LNAPL entrapped in the coarse sediment was therefore high (81%) with LNAPL saturating a similar percentage of the medium as was occupied by coarse sand (20% LNAPL versus 25% coarse sand).

As the connectivity of the coarse sediments increased, the coarse regions present in the fine sand matrix increased in size and decreased in number (as the total percent coarse sand present in the system remained the same). When these lenses encompassed a vertical dimension greater than the difference in capillary heights for the coarse versus fine sands, the lower portion of these coarse sand inclusions became saturated with the water (versus LNAPL) phase. Further, there was a higher probability that an individual coarse sand inclusion made direct contact with the upper reservoir (source of pure LNAPL), thus allowing outflow of the LNAPL. Both of these effects led to a decrease in LNAPL saturation within the porous medium, as observed by the decrease in mean LNAPL percentage from 20% (low connectivity), to 14% for the medium connectivity, to 13% for the highly connected coarse sand regions. Similarly, the saturation within the coarse sediments varied from 81% to 58% to 50%, respectively.

Thus, it is concluded that connectivity of coarse sediments has a significant impact on the amount of LNAPL that will become entrapped in the system. The major characteristics impacting this entrapment are the vertical correlation structure of the coarse regions, the difference in CF heights of the two sediments, and the probability that the coarse sediments will make direct contact with the source of pure LNAPL.
5.4 The Influence of Sediment Characteristics on LNAPL Entrapment

5.4.1 Description of Simulations

As demonstrated previously in this chapter, and paralleling the discussion of air/water systems, connectivity of heterogeneities has an effect on LNAPL entrapment in LNAPL/water systems. It was noted in Chapter 3 of this dissertation that air/water systems were also highly dependent on the sediment characteristics. Hence, continuing the parallel with our work in air/water systems, it is hypothesized here that sediment characteristics will have similar effects on LNAPL entrapment. Two specific soil characteristic parameters were investigated to determine their impact on LNAPL entrapment in a simple heterogeneous system.

The two sediment properties investigated here, which were discussed and investigated in reference to air/water systems in Chapter 3, are the entry pressure and the degree of sorting of the coarse sediment. These two properties are incorporated via $P_0$ (air entry pressure) and $\lambda$ (degree of sorting) in the pressure-saturation expressions discussed in Chapter 3 (Equations 3.2 and 3.3).

It is here hypothesized that, in a system containing coarse sand lenses in a finer sand matrix:

1) *As the air entry pressure, as represented by $P_0$ in the numerical simulations, of the enclosed coarse sediments increases relative to the air entry pressure of the fine sediment, the coarse sediments will entrap less LNAPL.*

2) *An increase in the degree of sorting of the coarse sediments, represented by $\lambda$ in the numerical simulations, will result in an increase in entrapped LNAPL.*
In order to test these hypotheses, a simple heterogeneous system was simulated using T2VOC to model imbibition of the system with varying sediment characteristics. Figure 5.8 shows the numerical simulation grid used for these simulations.

![Simulation grid](image)

Figure 5.8 - Simulation grid for investigating the effects of sediment characteristics on LNAPL entrapment. Lighter gray areas are coarse sand lenses in fine sand matrix. TDR indicates locations for which data were recorded.

A heterogeneous field consisting of varying heights of coarse sand lenses in a matrix of fine sand was used for all simulations. Sediment properties of the coarse sand were varied in order to test the stated hypotheses. The first hypothesis, how air entry pressure effects LNAPL entrapment, was tested by holding the $\lambda$ value of the coarse sediment constant (at 0.864) while varying the $P_0$ of the coarse sediment. Three $P_0$ values were tested: 100, 256, and 500 N/m$^2$. The $P_0$ of the surrounding fine sand was 730 N/m$^2$. The second hypothesis, how the degree of sorting, $\lambda$, of the coarse sediment effects LNAPL entrapment was tested by holding the $P_0$ value of the coarse sediment constant
(at 256 N/m²) while varying the $\lambda$ values (0.3, 0.5, and 0.7). $\lambda$ of the surrounding fine sand was 0.918.

5.4.2 Results and Discussion of Simulations

Effects of Air Entry Pressure

Figure 5.9 shows the final predicted distribution of LNAPL saturation at the end of each imbibition simulation.

As illustrated in Figure 5.9, as the $P_0$ of the coarse sand increases, the amount of LNAPL entrapped in the coarse sand decreases.

Effects of Degree of Sorting

Figure 5.10 shows the final predicted distribution of LNAPL saturation at the end of each imbibition simulation.
As illustrated in Figure 5.10, as the $\lambda$ of the coarse sediment increases, the amount of LNAPL present in the coarse sand increases.

**Discussion**

The results of these numerical simulations indicate that sediment properties have a significant impact on the degree of LNAPL entrapment in these systems. The hypotheses are supported by these investigations.

**5.5 Major Findings**

Several aspects of LNAPL entrapment in a heterogeneous LNAPL/water system were discussed in this chapter. It is recognized here that the entrapment observed in these numerical simulations may be temporary entrapment in a physical system, as observed in Chapter 4. The major findings with regard to LNAPL entrapment include:

- The **total** volume of LNAPL entrapped below the water table decreases as the mean connectivity (mean level of correlation) of coarse sediment increases

- The volume of LNAPL entrapped below the water table *in the coarse sediment* of a heterogeneous system decreases as the mean connectivity of the coarse sediment increases
Sediment properties have a significant influence on the entrapment of LNAPL in coarse regions below the water table.

- As the degree of sorting of the coarse sediment increases, more LNAPL is entrapped in the system.
- As the air entry pressure of the coarse sediment increases, less LNAPL is entrapped in the system.
CHAPTER 6

IMPLICATIONS OF WORK

6.1 Major Findings

This dissertation consists of a number of investigations of hydraulic behavior in the Partially Saturated Fringe (PSF) of a groundwater system. This research provides direct evidence of the hydraulic entrapment of air and Light Non-Aqueous Phase Liquids (LNAPL) in the PSF due to natural processes and discusses several factors influencing this entrapment. Previous to the work presented here, only a limited amount of research had been published in the study of entrapment of air or LNAPL below the water table.

In previous work with air/water systems, Silliman et al. (2002) studied the movement of the water phase in coarse sand zones above the water table. Although this work introduced the investigation of Air Entry Barriers, or AEBs, these authors did not discuss entrapment of an air phase below the water table. Other authors who have contributed to previous work with air/water systems, such as Ronen and co-authors (e.g., Ronen et al., 1989; Ronen et al., 1997; Ronen et al., 2000), suggested that a reduction in permeability in the first couple of meters below the water table was related to the presence of residual air saturation in the form of air bubbles below the water table. Although these authors investigated the existence of a possible entrapped air phase below the water table, they did not provide either direct evidence of the presence of these bubbles or suggest that heterogeneity might lead to entrapment of larger zones of air
below the water table. Prior to the efforts presented in this dissertation and the associated Masters Thesis (Dunn, 2003), there was little direct evidence of the presence of an entrapped air phase below the water table or discussion of the mechanisms that might lead to this entrapment.

In reference to the investigation of LNAPLs within the PSF, there is a wider body of literature published which discusses the entrapment of LNAPLs below the water table. Several authors (e.g., Illangasekare et al., 1995a; Illangasekare et al., 1995b; Nambi and Powers, 2000) have performed laboratory studies to investigate both the existence of entrapped LNAPL below the water table and the impact of such entrapped LNAPL on the hydraulic behavior in the vicinity of the water table. These previous studies have demonstrated the ability of entrapped LNAPL to exist below the water table and the stability of this entrapped LNAPL. However, there has been no prior research reported which has addressed the mechanisms by which entrapment could occur or conditions under which entrapment is more or less likely to be stable. At present, there have been no previous studies with which we are familiar, either laboratory or field, which have demonstrated formation of entrapped LNAPLs in the vicinity of the water table based on natural processes.

The work presented here therefore provides the first studies with which we are familiar demonstrating that both air and LNAPLs can be hydraulically entrapped below the water table during imbibition in the presence of hydraulic heterogeneities. Further, this work provides initial insight into the physical characteristics which will influence the degree of entrapment. Within this dissertation, it has been shown that air and LNAPL entrapment is significantly influenced by the degree of connectivity of heterogeneities,
the rate of imbibition, and the capillary rise, permeability, and air entry characteristics of the sediments. This work represents a fundamental advancement in our understanding of the PSF, by enhancing the understanding of the hydraulic behavior in this region, and may be used as a first step towards possible enhancement of remediation strategies based on entrapment of air and/or LNAPLs.

6.2 Limitations

Although this work has been significant in demonstrating both entrapment of air and LNAPL below the water table and the major hydraulic factors that influence this entrapment, there are limitations to conclusions drawn from this work. First, the laboratory experiments and the majority of the numerical simulations were conducted on simple geometric arrangements of two sediments using sands which had been extensively characterized by other authors. While the numerical investigations of the influence of varying sediment properties extended this work to include sediment properties different than the Accumin sands used in our experiments, even these experiments involved simple geometries and only two sediments. While these simple geometries allowed study of the hypotheses set forth in this dissertation, extension of this work, through laboratory, numerical and field efforts, into more complex media is necessary to determine the degree to which entrapment is likely to occur in realistic media under realistic rates of drainage and imbibition.

Second, the laboratory conditions were based on a ‘clean’ environment in which no microorganisms that would be naturally present under field conditions were added to the experiments (although it is noted that there was no effort made to sterilize the media or water used in these experiments). Bacteria may affect entrapment or the behavior of
entrapped air or LNAPL following entrapment and should be studied as a part of continuing research on entrapment.

Third, the laboratory and numerical investigations presented here were based solely on the properties of the LNAPL, Soltrol 220. Soltrol 220 was selected as it is a very easy LNAPL to use in laboratory studies due to its low volatility and flammability. However, dissolution and interaction with biological populations are both critical aspects of LNAPL behavior in the PSF. Hence, the current studies represent only select hydraulic aspects of LNAPL behavior in the PSF such that more complex LNAPLs are required for future studies and for consideration of applications to remediation.

Fourth, the studies included only vertical movement of the water, air, and LNAPL phases. Real systems will involve both vertical and horizontal gradients in the PSF. The interaction of entrapped fluids (air or LNAPL) with horizontal gradients in the fluid phase may add new complexities to the entrapment and stability of air or LNAPLs, and therefore should be considered in future research efforts.

Finally, this work did not include consideration of possible applications for the purpose of advancing remediation technologies (see section 6.3, below). It is encouraged that future research focus both on fundamental mechanisms and applications to possible remediation scenarios (both enhanced remediation and challenges posed to existing strategies).

6.3 Future Work

The work presented here lays the hydraulic foundation for the basic understanding of the factors affecting air and LNAPL entrapment within the PSF. While the work presented is preliminary in the investigations of air and LNAPL entrapment in the PSF, it
lays a solid foundation that can be built upon in order to advance investigations further for possible future applications in physical systems. The knowledge gained through this work provides for the opportunity for further study of the behavior of more complex LNAPLS in the PSF as well as the possible future study of natural biogeochemical conditions in the PSF.

The simulations and experimentation presented in this work are a good starting point to advance the study of LNAPL entrapment in the PSF. A solid foundation in understanding LNAPL behavior can be gained by investigations into several aspects of heterogeneous systems. An important step in gaining a further understanding of LNAPL entrapment behavior is the investigation of various types of LNAPL, including more volatile LNAPLs than that used in the presented studies. Increasing the volatility of the LNAPL may lead to noticeable changes in entrapment behavior in the heterogeneous systems. These investigations can take place both numerically and experimentally, as T2VOC has the capability of adjusting specific LNAPL parameters in order to change the properties of the LNAPL simulated. Simulations of more volatile LNAPLs will be useful in the determination of future LNAPLs to be used in experimentation. Advancing the investigations of the behavior of various LNAPLs in these systems will bring this work one step closer to becoming more applicable in field investigations.

Another important aspect of LNAPLs that can be investigated in order to advance this work towards a complete understanding of hydraulic behavior in the PSF is the investigation of the dissolution and degradation of the LNAPL in the system. T2VOC has the capability to include these properties of LNAPLs for the further advancement of the numerical investigations of these systems.
When further investigations into two-phase LNAPL/water systems have been conducted and a more solid understanding of the hydraulic behavior of these systems is gained, the next major step will be the investigation of three-phase systems (air, water, and LNAPL). These investigations can take place numerically and experimentally. Including three phases in these investigations will allow for a more complete application of this knowledge to field investigations.

With a solid understanding of the hydraulics of entrapment and LNAPL behavior in a three phase system in the PSF in place, the next step of this process would be to expand the investigations to include the biogeochemical interactions in this system. These future investigations should include the study of how microorganisms affect the entrapment and degradation of air and LNAPLs in these systems, including the investigation of microorganism behavior in three phase systems to determine how the mixture of phases is affected by (or affects) microorganism behavior. The initial step of these investigations can be conducted numerically, as T2VOC has the capability of modeling biological behaviors in the system. Laboratory experiments can also be utilized in these investigations to calibrate the modeling process.

The work presented here provides a basic understanding of air and LNAPL entrapment in the PSF and allows for future application of this knowledge to the further study of more complex systems in the PSF. With extension of this work through the investigations of volatility, dissolution, and degradation of the LNAPL and expansion to three-phase systems including biological behavior, further understanding of LNAPL behavior in the PSF can lead to future application of remediation technologies within the PSF.
REFERENCES


