Experimental and Modelling Studies on the Spreading of Non-Aqueous Phase Liquids in Heterogeneous Media

FRITJOF FAGERLUND
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Abstract

Non-Aqueous Phase Liquids (NAPLs) include commonly occurring organic contaminants such as gasoline, diesel fuel and chlorinated solvents. When released to subsurface environments their spreading is a complex process of multi-component, multi-phase flow. This work has strived to develop new models and methods to describe the spreading of NAPLs in heterogeneous geological media.

For two-phase systems, infiltration and immobilisation of NAPL in stochastically heterogeneous, water-saturated media were investigated. First, a methodology to continuously measure NAPL saturations in space and time in a two-dimensional experiment setup, using multiple-energy x-ray-attenuation techniques, was developed. Second, a set of experiments on NAPL infiltration in carefully designed structures of well-known stochastic heterogeneity were conducted. Three detailed data-sets were generated and the importance of heterogeneity for both flow and the immobilised NAPL architecture was demonstrated. Third, the laboratory experiments were modelled with a continuum- and Darcy’s-law-based multi-phase flow model. Different models for the capillary pressure ($P^c$) – fluid saturation ($S$) – relative permeability ($k_r$) constitutive relations were compared and tested against experimental observations. A method to account for NAPL immobility in dead-end pore-spaces during drainage was introduced and the importance of accounting for hysteresis and NAPL entrapment in the constitutive relations was demonstrated.

NAPL migration in three-phase, water-NAPL-air systems was also studied. Different constitutive relations used in modelling of three-phase flow were analysed and compared to existing laboratory data. To improve model performance, a new formulation for the saturation dependence of tortuosity was introduced and different scaling options for the $P^c$-$S$ relations were investigated. Finally, a method to model the spreading of multi-constituent contaminants using a single-component multi-phase model was developed. With the method, the migration behaviour of individual constituents in a mixture, e.g. benzene in gasoline, could be studied, which was demonstrated in a modelling study of a gasoline spill in connection with a transport accident.

Keywords: NAPL, Multi-phase flow, Modelling, Experiment design, Heterogeneity, Constitutive relations, Multi-constituent contaminants, Capillary pressure, Relative permeability, Hysteresis

Fritjof Fagerlund, Department of Earth Sciences, Villav. 16, Uppsala University, SE-75236 Uppsala, Sweden

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List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:


In all the above listed papers, the author of this thesis was responsible for development and enhancement of conceptual and numerical models, experimental design and building of experimental equipment, running and monitoring of experiments, output data analysis, numerical modelling, interpretation and analysis of results and writing the papers. For paper II, M. Odén
conducted a preliminary modelling study. Other co-authors have contributed with advice and feedback on all aspects of the work undertaken.

In addition, the following papers, related to this thesis but not appended to it, have been published in conference proceedings:


The first one of these is a preliminary study of the topics dealt with in paper I, and the two latter ones present preliminary modelling results of the experiments presented in papers III and IV.
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Abbreviations

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<td>BC</td>
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</tr>
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<td>BCB</td>
<td>Brooks-Corey-Burdine relative-permeability model</td>
</tr>
<tr>
<td>BCM</td>
<td>Brooks-Corey-Mualem relative-permeability model</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, Toluene, Ethylbenzenes and Xylenes</td>
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<td>DBP</td>
<td>Dibuthylphtalate</td>
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<td>DNAPL</td>
<td>Dense non-aqueous phase liquid</td>
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<td>DWL</td>
<td>Drinking-water limit</td>
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<tr>
<td>EC</td>
<td>Equivalent carbon (number)</td>
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<td>GPR</td>
<td>Ganglia-to-pool ratio</td>
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<td>HBCB</td>
<td>Hysteretic BCB</td>
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<tr>
<td>HVGBCB</td>
<td>Hysteretic VG in combination with hysteretic BCB</td>
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<td>HVGM</td>
<td>Hysteretic VGM</td>
</tr>
<tr>
<td>iTOUGH2</td>
<td>Inverse TOUGH2</td>
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<td>LNAPL</td>
<td>Light non-aqueous phase liquid</td>
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<td>LUFT</td>
<td>Leaking Underground Fuel Tank</td>
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<td>NAPL</td>
<td>Non-aqueous phase liquid</td>
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<tr>
<td>NWP</td>
<td>Non-wetting phase</td>
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<td>PCE</td>
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<td>TOUGH2</td>
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<tr>
<td>TPHCWG</td>
<td>Total Petroleum Hydrocarbon Criteria Working Group</td>
</tr>
<tr>
<td>VG</td>
<td>van Genuchten capillary-pressure model</td>
</tr>
<tr>
<td>VGB</td>
<td>van Genuchten-Burdine relative-permeability model</td>
</tr>
<tr>
<td>VGM</td>
<td>van Genuchten-Mualem relative-permeability model</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>WP</td>
<td>Wetting phase</td>
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Introduction

Non-aqueous phase liquids

Chemicals which are harmful to humans and other living organisms are constantly utilised, stored and transported in large amounts throughout our environment. Our understanding of the spreading behaviour of such chemicals once they are released to the environment, by malpractice or by accident, is essential for (i) assessment of risks, (ii) formulation of strategies to prevent contamination and (iii) design of adequate remediation schemes. A large proportion of these chemicals are organic liquids commonly known as non-aqueous phase liquids (NAPLs), contaminants that are scarcely soluble and essentially immiscible with water.

In the subsurface, a NAPL is separate from the aqueous and gas phases. Hence, where it is present three mobile fluid phases can coexist and simultaneous flow of water, NAPL and air may take place. The chemicals forming the NAPL may also be present as volatilised components in the gas phase (soil air), as dissolved in the aqueous phase and as absorbed onto the solid medium. Thereby a volatile organic compound (VOC) may be transported with each mobile fluid phase (water, NAPL and air) and its migration in soil and groundwater systems is a complex process of multi-component, multi-phase flow.

Light non-aqueous phase liquids (LNAPLs) include gasoline, diesel fuel and most non-halogenated petroleum-derived liquids. They have lower densities than water and therefore float on the water table of an aquifer. Dense non-aqueous phase liquids (DNAPLs) include industrially used chlorinated solvents such as trichloroethylene (TCE), perchloroethylene (PCE) and carbon tetrachloride (TCA). They are denser than water and can penetrate the water table, thus reaching deep into an aquifer. A schematic picture of typical spreading behaviour is shown in Figure 1.

Many NAPLs have low solubility in water while at the same time, the resulting dissolved concentrations by far exceed drinking water limits (DWLs) and other environmental standards regulating them. Hence subsurface occurrences of NAPLs dissolve slowly and may constitute long-term sources of serious groundwater contamination.
Multi-constituent contaminants

Gasoline is together with diesel fuel the most common chemical in spills in connection with accidents in Sweden (Björklund et al. 2001). Both are mixtures of hundreds of chemical constituents, some of which, such as the BTEX fraction (Benzene, Toluene, Ethylbenzenes and Xylenes), are harmful even at low concentrations. The many constituents complicate the migration and fate of such multi-constituent contaminants. Because of differences in solubility and volatility, the various constituents partition differently between the phases and consequently also the composition and properties of the NAPL change with time. Furthermore, the constituents have different adsorption and biodegradation properties and competitive effects between them exist. Phase partitioning during the spreading of a hydrocarbon mixture is illustrated in Figure 1 (red rectangle labelled 1).

To understand and describe the subsurface behaviour of chemicals present in multi-constituent NAPLs, it is necessary to take the multi-constituent nature of the governing processes into account. Numerical models that have been developed for this purpose are referred to as multi-constituent (or compositional) multi-phase models and include e.g. Baehr and Corapcioglu...
(1987), Sleep and Sykes (1993a and b), Unger et al. (1995), Pope et al. (1999), Adenekan et al. (1993) and Pruess and Battistelli (2002). However, such models remain relatively few and are often complicated to use.

While several studies have investigated the migration and fate of multiple organic components in the aqueous phase using single-phase models: e.g. Frind et al. (1999), Schirmer et al. (2000), Huntley and Beckett (2002), Molson et al. (2002) very few studies have investigated multi-constituent behaviour in relation to a mobile organic (non-aqueous) phase. In such modelling there is also a need to define strategies to model compounds that consists of hundreds of different constituents (such as gasoline and diesel fuel) because the inclusion of every constituent in the model may not be computationally feasible.

**Constitutive relations**

As result of capillarity, when multiple fluids coexist in a permeable medium, a pressure difference, referred to as capillary pressure, $P_c$ [ML$^{-1}$T$^{-2}$], exists between the phases. For a given medium, the capillary pressure can be related to fluid saturations, $S$ [-], i.e. the proportions of the pore space occupied by different fluids. The two most commonly used $P_c$–$S$ functions for multi-phase flow are those by Brooks and Corey (1964) (BC function) and van Genuchten (1980) (VG function). These functions have been developed for two-phase flow, but can, according to theory developed by Parker et al. (1987) be scaled and used for three-phase flow calculations.

Another important property of multi-phase systems is that the different fluids obstruct the movement of each other in the permeable medium. The permeability of the medium to each fluid is therefore reduced in comparison to single-phase conditions. The relative permeability, $k_r$ [-], is the reduced effective permeability divided by the saturated (absolute) permeability, $k$ [L$^2$], and quantifies this reduction. Relative permeability can also be related to fluid saturations. Because the $P_c$–$S$ function contains information about the pore sizes that the fluids occupy, relative permeability as a function of saturation is commonly approximated from $P_c$–$S$ functions. The methods of Burdine (1953) and Mualem (1976) have been widely used to obtain a closed-form expression for the $k_r$–$S$ relation. Usually the Burdine method has been used in conjunction with the BC model, producing the BCB $k_r$–$S$ function, and the Mualem method in conjunction with the VG model, obtaining the VGM $k_r$–$S$ function.

Capillary pressure and relative permeability strongly influence fluid migration in multi-phase systems and are essential components in continuum-type models of multi-phase flow (see e.g. Charbeneau, 2000; Helmig, 1997; Mercer and Cohen 1990; Parker 1989). Therefore their relation to fluid satu-
ration, i.e. the $P_c$–$S$ and $k_r$–$S$ relations are referred to as constitutive relations of multi-phase flow.

The dependence of the constitutive relations on saturation history is referred to as hysteresis. An effect of hysteresis is that the $P_c$–$S$ and $k_r$–$S$ relations are different if the fluid that preferentially wets the solid grains (wetting fluid) is imbibing, displacing the non-wetting fluid, or if it is draining out from the permeable medium. The constitutive relations are also affected by entrapment and immobilisation of fluids during the multi-phase flow process. Models that incorporate hysteresis and non-wetting-fluid entrapment include the models by Parker and Lenhard (1987) and Lenhard and Parker (1987), Gerhard and Kueper (2003a, b), Van Geel and Roy (2002), Lenhard et al. (2004) and Niemi and Bodvarsson (1991) in combination with Finsterle et al. (1998).

There is no general agreement about which $P_c$–$S$ and $k_r$–$S$ functions are the most accurate and appropriate to use in models of multi-phase flow. However, comparative studies of the performance of different constitutive models remain few and testing of these models against experimental data is largely lacking. The special characteristics of both two-phase (air-water and NAPL-water) and three-phase (air-NAPL-water) systems need to be considered. Studies of three-phase systems have been conducted by e.g. Oliveira and Demond (2003), Oostrom and Lenhard (1998) and Schroth et al. (1998). Studies of two-phase systems include e.g. Demond et al. (1996), Dury et al. (1999), Gerhard and Kueper (2003c) and Rathfelder and Abriola (1998), Stonestrom and Rubin (1989).

**Geological heterogeneity**

In natural systems the migration, immobilisation and final distribution of NAPLs is largely controlled by geological heterogeneity at various scales. Larger scale features such as lenses and interfaces between different subsurface deposits may direct the general movement of mobile NAPL and give rise to pools, perched on top of low-permeable units. On smaller scales, heterogeneity may allow the formation of preferential flow channels and control small-scale entrapment of NAPL. Capillary forces vary with the heterogeneity of the medium and capillarity can therefore have a large influence on migration and entrapment in multi-fluid systems.

As shown by many researchers including Parker and Park (2004), Phelan et al. (2004), Soga et al. (2004), Bradford et al. (2003), Saenton et al. (2002), Dekker and Abriola (2000), Oostrom et al. (1999), Powers et al. (1998) Mayer and Miller (1996) and Powers et al. (1994) the characteristics of the source zone of contamination are highly important for NAPL dissolution and the delivery of contaminant mass to groundwater. E.g. the location of a DNAPL in the groundwater flow field and the interfacial area between the
DNAPL and the aqueous phase influence and may limit the rate of mass transfer. Geological heterogeneity has a major influence on the subsurface architecture of the NAPL and the source zone.

Geological heterogeneity is often of stochastic character and can then be described by its geostatistical characteristics. However, our present-day understanding of NAPL spreading and immobilisation in such systems is limited. Field studies on NAPL infiltration have not provided sufficient characterisation of the porous medium to allow direct comparison with numerical models e.g. Kueper et al. (1993) and Poulsen and Kueper (1992). Most controlled laboratory experiments, on the other hand, have so far concentrated on fundamental but simplified cases of geological heterogeneity e.g. Kueper et al. (1989), Illangasekare et al. (1995), Hofstee et al. (1998) and Oostrom et al. (1999). In these studies immobile NAPL saturations have been measured at the end of the experiments, but the dynamic behaviour of the NAPL has only been monitored photographically and by visual identification of the NAPL front.

Aims and objectives

The overall aim of this thesis was to develop new methods and models to describe the migration of multi-phase pollutants in subsurface systems and improve current understanding of the governing processes. This was addressed by means of theoretical modelling analyses, model developments as well as experimental studies, with special emphasis on geologically heterogeneous systems. Experimental methods can be used for a direct study of multi-phase flow and migration processes. They are also needed for the development and validation of different conceptual and numerical models. Modelling, in turn, can be used to simulate the migration processes for different scenarios, thereby extending the study of the governing processes. A large number of scenarios can be studied and the effects of various parameters can be investigated once the model has been tested and validated against well-controlled data. The combination of experimental and modelling methods has the potential to fuse the directness and reliability of experimental work with the vast applicability and predictive capability of numerical simulations.

The specific objectives of this study were:

i. To develop a numerical method for modelling the migration of commonly occurring NAPL mixtures such as gasoline, taking their multi-constituent character into account (paper I).

ii. To analyse and compare the performance of different constitutive relations for three-phase flow and based on the outcome further develop the existing models (paper II).
iii. To develop experimental methods and generate detailed data on NAPL infiltration and immobilisation in heterogeneous saturated systems (papers III, IV), including:
  - development of a methodology for continuous measurement of NAPL saturations in both space and time in laboratory experiments using multiple-energy x-ray-attenuation techniques (paper III).
  - studies of NAPL infiltration, entrapment and the formation of source-zone architecture in complex heterogeneous systems, including layered systems (Paper III) and systems with stochastic heterogeneity (Paper IV).

iv. To model this experimental data, testing the capability of continuum-based models and the associated constitutive relations to capture NAPL infiltration and immobilisation in saturated systems of complex geological heterogeneity (paper V).

In the following text the basic theory of multi-phase flow will first be presented followed by the methods, model developments, results and conclusions of this thesis.
Multi-phase flow theory

Interfacial tension and wettability

When two or more immiscible fluids coexist in a porous medium their distribution and transport properties depend on their mutual interactions as well as interactions with the solid medium. Across the interface of a liquid in contact with another substance (such as a gas, solid or immiscible liquid) an interfacial tension, \( \sigma \) [\( \text{MT}^{-2} \)], exists. This results from an imbalance in the attractive forces between the molecules at the interface. For example at an air-water interface the water molecules are more strongly attracted inward to the bulk of the water than outward to the air molecules. Interfacial tension can be defined as the work necessary to enlarge the interfacial area by one unit of area (Tindall and Kunkel 1999).

In the subsurface different fluid phases compete for contact with the solid medium. Adhesive forces between the fluids and the solid determine which fluid preferentially coats the grain surfaces. This fluid is called the wetting fluid, whereas the fluid phase that has the weakest adhesive attraction to the solid is called the non-wetting fluid (e.g. Fetter 1999). The wettability of a fluid with respect to a solid can be determined by measuring the contact angle, \( \theta \) [-]. A drop of the fluid is applied to a flat surface of the solid and immersed in a background reference fluid. The contact angle is defined as the angle between the fluid-fluid interface and the solid surface at the point where the three phases meet, measured inside the test fluid. If \( \theta \) is less than 90°, the test fluid is wetting (Figure 2 a and b), if \( \theta > 90° \) it is non-wetting (Figure 2 c).

![Figure 2. Contact angles for three fluid pairs. Water and NAPLs are usually wetting with respect to air, and thus \( \theta < 90° \) (a and b). NAPLs are normally non-wetting (\( \theta > 90° \)) with respect to water (c). After Domenico and Schwartz (1998).](image-url)
In the unsaturated zone the order of wettability is normally water – NAPL – air and the NAPL can be referred to as the intermediate wetting fluid. In such system the water (which is the wetting fluid) coats the solid grains and fully occupies the smallest pore-spaces. The NAPL, in turn, coats the water surfaces and is restricted to somewhat larger pore-spaces, whereas the air is found in the middle of larger pores (see Figure 3). NAPL-wet systems may develop if a NAPL is spilled on soils with a very high content of organic material such as peat or humus (Fetter 1999), and also systems of spatially varying wettability exist.

![Figure 3](image)

**Figure 3.** Intersection of a pore containing water, NAPL and air. Water is the wetting fluid, air is non-wetting and the NAPL is the intermediate wetting phase. $r_{an}$ [L] denotes radius of curvature of the air-NAPL interface.

**Capillarity**

The greater affinity of the wetting phase for the solid medium produces suction on this phase into smaller pore spaces and capillary tubes. E.g. in the presence of air, water can rise in a capillary tube until there is an equilibrium of forces between the upward capillary suction and downward gravity. Where an interface between a non-wetting and wetting phase exists, the pressure therefore has to be higher in non-wetting phase. Otherwise the non-wetting phase would be expelled from the capillary/pore. Capillary pressure, $P_c [ML^{-1}T^{-2}]$, is defined as the difference in pressure over the interface:

$$P_c = P_{nwet} - P_{wet}$$  \hspace{1cm} (1)

Here $P_{nwet} [ML^{-1}T^{-2}]$ is the pressure in the non-wetting phase and $P_{wet} [ML^{-1}T^{-2}]$ is the pressure in the wetting phase (e.g. Parker, 1989).
The narrower the pore, the higher is the capillary suction on the wetting phase and the higher is the capillary pressure over a fluid-fluid interface. Under static conditions the capillary pressure is inversely proportional to the mean radius of curvature of the fluid-fluid interface, \( r_c \) [L]. For a circular tube, the tube radius \( r \) [L] can be related to \( r_c \) and \( \theta \): \( r = r_c \cos(\theta) \). \( P_c \) is also directly proportional to the interfacial tension and can be computed from the relation (Parker, 1989):

\[
P_c = \frac{2\sigma}{r_c}
\]

(2)

Starting from a non-wetting-phase saturated system, the smallest pores are filled with wetting phase first due to the stronger suction. The capillary pressure between the two fluids can therefore be related to the saturation of each fluid, and for a given medium (and fluid pair) a relationship between \( P_c \) and \( S \) can be established.

In heterogeneous media spatial variations in the capillary properties of the medium can have large effects on the migration behaviour of fluids. Areas of larger pores can act as capillary barriers for the wetting phase, which preferentially resides in the smallest available pores. Areas of smaller pores can act as capillary barriers to the non-wetting phase, which needs to be at higher pressure to enter smaller pores.

### Parametric models

General parametric models of the \( P_c-S \) relation include the models by Brooks and Corey (1964) (BC model) and van Genuchten (1980) (VG model). Regarding immobile (irreducible) wetting-phase bound in the smallest pores as essentially part of the solid medium, effective scaled saturations are first defined. The effective wetting and non-wetting saturations \( S_{\text{wet}} \) and \( S_{\text{nwet}} \) are given by:

\[
\bar{S}_{\text{wet}} = \frac{S_{\text{wet}} - S_{\text{wet,r}}}{1 - S_{\text{wet,r}}}
\]

(3)

\[
\bar{S}_{\text{nwet}} = \frac{S_{\text{nwet}}}{1 - S_{\text{wet,r}}}
\]

(4)

where \( S_{\text{wet}} \) [-] is the wetting phase saturation, \( S_{\text{wet,r}} \) [-] is the irreducible or residual wetting-phase saturation and \( S_{\text{nwet}} \) [-] is the non-wetting-phase saturation. According to the VG model the \( P_c-S \) relation is parameterised as follows:
Here $\alpha$, $n$ and $m$ are the VG-model curve-fitting parameters. $\alpha$ has units $1/\text{Pa} \cdot \text{M}^{-1} \cdot \text{T}^{-2}$ while $n$ and $m$ are dimensionless. According to the BC model:

$$
\bar{S}_{\text{rel}} = \left[ 1 + \left( \frac{\alpha P_c}{P_d} \right)^n \right]^m
$$

(5)

where $P_d$ [ML$^{-1}$T$^{-2}$] is the displacement pressure and $\alpha$ [-] is a curve-fitting parameter related to the pore-size distribution.

Normally the $P_c-S$ relation is measured for a fluid pair of air and water. However, according to theory by Parker et al. (1987), the relation can be scaled to apply also for other fluid pairs. Equation (2) states that $P_c$ is proportional to $\sigma$. The idea is therefore that equations (5) and (6) can be scaled using the ratio of the interfacial tensions between two fluid pairs. In the equations, $P_c$ is exchanged for $P_c^{\text{ref}}$ where $P_c^{\text{ref}}$ [ML$^{-1}$T$^{-2}$] is the capillary pressure for the reference fluid pair and $\beta = \sigma^{\text{ref}}/\sigma$ [-] is the scaling factor. $\sigma^{\text{ref}}$ [MT$^{-2}$] is the interfacial tension between the fluids in the reference system and $\sigma$ is the interfacial tension between the fluids of interest.

In three-phase systems, Equations (5) and (6) can be employed (usually scaled) in a pair-wise manner provided that a strict order of wettability can be assumed. The reader is referred to paper (II) for a more thorough description of $P_c-S$ relations in three-phase systems.

**Hysteresis and entrapment**

$P_c-S$ relations depend on the saturation history and whether the wetting fluid is drained from the medium by an increase in $P_c$ (drainage) or is entering the medium, expelling the non-wetting fluid (imbibition). Figure 4 shows the $P_c-S$ relation for water and Soltrol 220 (NAPL) in a typical laboratory sand (sand # 30) parameterised using the VG model. $P_{\text{cap}}$ [ML$^{-1}$T$^{-2}$] denotes capillary pressure between NAPL and water. A first-order imbibition scanning curve for reversal at water saturation $S_w = 0.4$ has been plotted using a modified version of scanning-curve theory by Mualem (1984). $P_c-S$ hysteresis has four primary causes: (i) geometric or ink-bottle effects, (ii) differences in contact angles during drainage and imbibition, (iii) non-wetting-phase entrapment and (iv), shrinking and swelling of the porous medium (Tindall and Kunkel, 1999).
As can be seen in Figure 4 the water (wetting-phase) saturation, $S_w$, does not reach zero but approaches a finite residual value for high $P_{cnw}$. Furthermore, along the imbibition branches $S_w$ does not reach one at $P_{cnw} = 0$, because some NAPL has been trapped and remains in the medium occluded by water. The amount of entrapped non-wetting phase, $S_{n\text{wet},t}$, depends on the maximum non-wetting-phase saturation previously reached. Therefore $S_{n\text{wet},t}$ is higher for the main imbibition curve than for the 1st order scanning curve with reversal at $S_w = 0.4$. In Figure 4 the (final) trapped NAPL saturation has been predicted using a model by Land (1968), which for a NAPL-water system states that:

$$S_{n\text{f}} = \frac{S_{n\text{a}}}{1 + RS_{n\text{a}}^\text{max}}$$

(7)

Here $S_{n\text{f}}$ [-] is effective final entrapped NAPL saturation, $S_{n\text{a}}^{\text{max}}$ [-] is the effective maximum NAPL saturation previously reached (e.g. $1 - 0.4 = 0.6$ for the scanning curve shown in Figure 4).

$$R = \frac{1}{S_{n\text{a}}} - 1$$

(8)
where $S_{nt}^{\text{max}}$ [-] is the maximum possible effective final entrapped NAPL saturation, corresponding to the endpoint of the main imbibition curve. Following Lenhard et al. (2004), immobilised wetting phase is here referred to as residual, and immobilised (water-occluded) non-wetting phase as entrapped. In a NAPL-water system, as the non-wetting phase with respect to water, NAPL is immobilised as water imbibles entrapping blobs and ganglia of NAPL. In a three-phase system, as the wetting phase with respect to air, NAPL is mainly immobilised in thin films and in small pore spaces in contact with the air phase.

Relative permeability

Idealising fluid flow through a permeable medium as flow through non-circular tubes of various sizes and shapes enables expression of permeability as the product of three terms Bear (1972):

$$k = \phi BT$$

(9)

Here $k$ [L$^2$] is the intrinsic permeability tensor. $\phi$ [-], the porosity accounts for the total cross-sectional area available for fluid flow. $B$ [L$^2$] is the conductance tensor and is function of sizes and shapes of flow channel cross-sections. $T$ [-], the tortuosity tensor, accounts for the crookedness of the fluid flow paths (Bear, 1972):

$$T = (L/L_e)^2$$

(10)

where $L$ [L] is the straight distance over an element of permeable medium and $L_e$ [L] is the average effective length of the flow path.

When two or more separate fluid phases coexist in the subsurface, each fluid is restricted to a subset of the pore space and the permeability of the medium to each phase is reduced in comparison to the saturated permeability. Using the conceptual model of Equation (9), the reduction in permeability results from reduced conductance and increased crookedness of the flow paths. Relative permeability $k_{rc} [-]$ to phase $\kappa$ is defined as the ratio of the reduced permeability $k_{rc} [L^2]$ to the intrinsic, saturated permeability:

$$k_{rc} = k_{rc}/k$$

(11)

Like capillary pressure, relative permeability is a function of fluid saturations. However, compared to the $P_c-S$ relation, $k_{rc}-S$ relations are difficult and tedious to measure experimentally. Therefore $k_{rc}-S$ relations are often calculated from known parameterised $P_c-S$ functions. This is done under the
assumption that the $P_c-S$ function contains information about the pore radii of the pore space that each fluid phase occupies. The $P_c-S$ function can thereby be used to predict the relative reduction in conductance (which depends on pore radii) compared to the saturated (1-phase) case. Reduction in permeability due to increased crookedness of the flow paths is more difficult to predict and has usually been assumed be a power function of the phase saturation. The two most commonly used methods to calculate $k_r(S)$ from $P_c(S)$ data are the Burdine (1953) and Mualem (1976) models. According to the Burdine model the wetting- and non-wetting-phase permeabilities, $k_{r,wet}$ [-] and $k_{r,nwet}$ [-], respectively, in a two-phase system are given by:

$$k_{r,wet} = X_{r,wet} \left\{ \int_0^{S_{wet}} \frac{dS_{wet}}{P_c^2(S_{wet})} \right\}^{1/2} \int_0^{S_{wet}} \frac{dS_{wet}}{P_c^2(S_{wet})}$$

$$k_{r,nwet} = X_{r,nwet} \left\{ \int_0^{S_{nwet}} \frac{dS_{wet}}{P_c^2(S_{wet})} \right\}^{1/2} \int_0^{S_{wet}} \frac{dS_{wet}}{P_c^2(S_{wet})}$$

Here $X_{r,wet} = L_e/L_{e,wet}$ [-] is the wetting-phase effective tortuosity factor, where $L_{e,wet}$ [L] is the average effective length of the flow path for the wetting phase over and element of permeable medium. $X_{r,nwet} = L_e/L_{e,nwet}$ [-] is the non-wetting-phase effective tortuosity factor, where $L_{e,nwet}$ [L] is the average effective length of the flow path for the non-wetting phase. $P_c(S_{wet})$ is found by inverting Equation (5) or (6) producing two possible $k_r-S$ functions: van Genuchten–Burdine (VGB) and Brooks–Corey–Burdine (BCB). Burdine (1953) furthermore assumes that $X_{r,wet} = S_{wet}$ and $X_{r,nwet} = S_{nwet}$.

Mualem (1976) assumes that the larger length scale of larger pores makes them more likely to be connected and therefore arrives at a somewhat different expression for the relative permeability:

$$k_{r,wet} = \left[ X'_{r,wet} \right]^{0.5} \left\{ \int_0^{S_{wet}} \frac{dS_{wet}}{P_c(S_{wet})} \right\}^{1/2} \int_0^{S_{wet}} \frac{dS_{wet}}{P_c(S_{wet})}$$

$$k_{r,nwet} = \left[ X'_{r,nwet} \right]^{0.5} \left\{ \int_0^{S_{nwet}} \frac{dS_{wet}}{P_c(S_{wet})} \right\}^{1/2} \int_0^{S_{wet}} \frac{dS_{wet}}{P_c(S_{wet})}$$

Here $\left[ X'_{r,k} \right]^{0.5} (k = \text{wet for wetting phase, } \kappa = \text{nwet non-wetting})$ is a correction factor which accounts for tortuosity. $X'_{r,k}$ is not necessarily the same as $X_k$ in the Burdine model. Mualem (1976), however, following the assumption of Burdine (1953) that $X_k = S_k$, assumes that $X'_{r,k} = S_k$. Under this
assumption Mualem obtained the best fit to empirical data using a value of 0.5 for the exponent. Combining Mualem’s model with Equations (5) and (6), respectively, results in the \( k_r-S \) functions: van Genuchten–Mualem (VGM) and Brooks–Corey–Mualem (BCM). The VGB, BCB, VGM and BCM models are described in more detail and for three-phase systems in paper (II).
Modelling

The numerical models of multi-phase flow and transport used in this work are, in essence, mathematical descriptions of the processes that govern system behaviour implemented in an executable code where the governing equations are solved simultaneously. Simulations have been performed using the numerical codes T2VOC (Falta et al., 1995), TMVOC (Pruess and Battistelli, 2002) and iTOUGH2 (Finsterle, 2000). All three codes belong to the TOUGH (Transport Of Unsaturated Groundwater and Heat) family of codes and are extensions and further developments of the TOUGH2 model (Pruess, 1991; Pruess et al., 1999).

TOUGH2 and its above-mentioned extension modules are multidimensional numerical models for simulating the coupled transport of air, water, VOCs and heat in permeable media. The flow of fluid phases occurs under pressure, gravitational, and viscous forces and three flowing fluids (i.e. gas, water and NAPL) can be modelled simultaneously. In T2VOC one organic chemical (VOC) can be modelled at a time whereas in TMVOC several chemical constituents can be modelled simultaneously. iTOUGH2 is an inverse modelling software for TOUGH2 modules (Pruess et al., 1999) including T2VOC.

In the following sections a short description of the main assumptions and governing equations of these numerical models is given. Then the main applications of the models to this thesis as well as further model developments are described. The description given here is based on T2VOC (Falta et al., 1995), which is the most employed model in this research, but is generally accurate also for TMVOC. For a more thorough description of the models, the reader is referred to Falta et al. (1995), Pruess et al. (1999) and Pruess and Battistelli (2002).

Assumptions

Fluid fluxes are described by a multi-phase extension of Darcy’s law and in the gas phase mass transport also occurs by molecular diffusion. The three phases are assumed to be in local thermal and chemical equilibrium. No other chemical reactions than (i) inter-phase mass transfer, (ii) adsorption of VOC on the solid phase, and (iii) decay of VOC by biodegradation are assumed to take place. Inter-phase mass transfer processes include evapora-
tion, boiling and condensation of the NAPL and water components, dissolution of NAPL into the aqueous phase, equilibrium phase partitioning of the organic chemical between the gas, aqueous and solid phases as well as equilibrium phase partitioning of air between the gas, aqueous and NAPL phases.

Heat transport is mediated by conduction, convection and gaseous diffusion. Heat transfer due to phase transitions are accounted for considering both latent and sensible heat. Thermophysical properties (such as density, specific enthalpy, viscosity etc.) of the different phases are normally calculated as functions of temperature and pressure.

Governing equations

To describe component transport in a non-isothermal multi-phase system, a mass balance equation for each component as well as an energy balance equation is needed. For an arbitrary flow region \( V_n \) \([L^3]\) with surface area \( \Gamma_n \) \([L^2]\) the balance equations in integral form for the components \( \zeta (\zeta = w, a, c) \) are given by (Falta et al. 1995):

\[
\frac{d}{dt} \int_{V_n} M^\zeta \, dV_n = \int_{\Gamma_n} F^\zeta \cdot \mathbf{n} \, d\Gamma_n + \int_{V_n} q^\zeta \, dV_n
\]

where \( M^\zeta [ML^{-3}] \) is the mass of component \( \zeta (\zeta = w, a, c) \) per unit volume of the porous medium, \( F^\zeta [ML^{-2}T^{-1}] \) represents the mass flux of component \( \zeta \) into \( V_n \), \( \mathbf{n} \) is the inward unit normal vector, and \( q^\zeta [ML^{-3}T^{-1}] \) is the rate of mass generation of component \( \zeta \) per unit volume.

The first term in Equation (16) represents mass (or heat) accumulation, the second term fluxes and the third term sources and sinks. The sink/source term can be used to implement biodegradation of organic chemicals, production and injection wells as well as boundary conditions. The mass accumulation terms for water and air (\( \zeta = w, a \)) contain a summation of component mass over the three fluid phases \( \zeta (\zeta = g – gas, w – aqueous, n – NAPL) \), and hence:

\[
M^\zeta = \Phi \sum_\kappa S_\kappa \rho_\kappa x_{\kappa}^\zeta
\]

where \( \Phi [-] \) is the porosity, \( S_\kappa [-] \) is the phase saturation, \( \rho_\kappa [ML^{-3}] \) is the density of phase \( \kappa \), and \( x_{\kappa}^\zeta [-] \) is the mass fraction of component \( \zeta \) in phase \( \kappa \). For the organic chemical component (\( \zeta = c \)) mass accumulation in the solid phase by adsorption is included. In the standard formulation of the code adsorption is linear and regarded as directly proportional to the fraction of organic carbon \( f_{oc} [-] \) in the soil. Consequently the linear distribution coeffi-
cient $K_D$ [M$^{-1}$L$^3$] equals $K_{oc} f_{oc}$ where $K_{oc}$ [M$^{-1}$L$^3$] is the organic carbon partition coefficient. Heat ($\xi = h$) is accumulated in both the solid and fluid phases.

Normally the aqueous and NAPL phases consist almost entirely of water and organic chemical respectively, with only small fractions of other mass components present. The fluxes of water, air and chemical components include contributions from the three fluid phases. For the aqueous and NAPL phases ($\kappa = w, n$), the phase fluxes, $F_\kappa$ [ML$^{-2}$T$^{-1}$], are given by a multiphase extension of Darcy’s law:

$$F_\kappa = -k \frac{k_R P_\kappa}{\mu_\kappa} (\nabla P_\kappa - \rho_\kappa g) \quad (18)$$

Here $k$ [L$^2$] is the intrinsic permeability, $k_{R \kappa}$ [-] is the relative permeability of phase $\kappa$ and, $\mu_\kappa$ [ML$^{-1}$T$^{-1}$] is the $\kappa$-phase dynamic viscosity, $P_\kappa$ [ML$^{-1}$T$^{-2}$] is the fluid pressure in phase $\kappa$, and $g$ [LT$^{-2}$] is the gravitational acceleration vector. In the gas phase, mass transport of each component occurs both due to advection and molecular diffusion.

**Model for multi-constituent multi-phase flow**

In paper I a new modelling methodology was developed that accounts for the multi-constituent character of NAPLs in the framework of their multi-phase transport. The approach was implemented by using a single-constituent three-phase simulator (T2VOC), and was applied to a modelling study on the spreading of gasoline, which consists of hundreds of organic constituents. It is not computationally feasible or necessary for practical purposes to keep track of all the chemical constituents present in many petroleum-derived fuels such as gasoline. Therefore a method to group constituents with similar properties into a limited number of “fractions” was first chosen. The approach was similar to that of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) (Gustafson et al. 1997) and was based on the equivalent carbon (EC) number. A distinction was, however, made between aromatic and aliphatic hydrocarbons, because of their somewhat different phase-partitioning properties. All known gasoline constituents were classified as belonging to one of eight fractions. The relative amount of each fraction in standard gasoline was then calculated based on data by LUFT (1988). To keep track of especially toxic constituents, benzene and toluene were treated individually in fractions 5 and 6, respectively. The resulting gasoline fractions are shown in Table 1.
Table 1. Representation of gasoline as eight fractions. (paper I)

<table>
<thead>
<tr>
<th>EC Interval</th>
<th>Mean weight-%</th>
<th>Average EC number</th>
<th>Fraction number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-6</td>
<td>35.9</td>
<td>5.04</td>
<td>1</td>
</tr>
<tr>
<td>&gt;6-8</td>
<td>23.6</td>
<td>7.17</td>
<td>2</td>
</tr>
<tr>
<td>&gt;8-10</td>
<td>5.8</td>
<td>8.12</td>
<td>3</td>
</tr>
<tr>
<td>&gt;10-12</td>
<td>0.2</td>
<td>11.3</td>
<td>4</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene (5-7)</td>
<td>1.9</td>
<td>6.5</td>
<td>5</td>
</tr>
<tr>
<td>Toluene (&gt;7-8)</td>
<td>12.6</td>
<td>7.58</td>
<td>6</td>
</tr>
<tr>
<td>&gt;8-10</td>
<td>14.2</td>
<td>9.13</td>
<td>7</td>
</tr>
<tr>
<td>&gt;10-12</td>
<td>5.8</td>
<td>10.8</td>
<td>8</td>
</tr>
</tbody>
</table>

Mass transfer from the non-aqueous phase to the aqueous and gas phases is according to Raoult’s law (see e.g. Falta, 2002) proportional to the mole fraction of the constituent in the free-phase gasoline. By simulating the eight fractions individually using T2VOC, but updating the gasoline composition after predetermined time intervals a partial coupling between the fractions was achieved. Thereby dissolution and volatilisation rates were changed accordingly when the gasoline composition was updated. This method was named the partially coupled fraction-by-fraction (PCFF) approach and is described in more detail in paper I. The PCFF approach was applied to a gasoline-spreading scenario based on a real accident, where a gasoline-transporting lorry is damaged and leaks. For this scenario the PCFF approach was validated by simulating the spreading also with the fully coupled TMVOC model and comparing the results.

Comparison and development of three-phase constitutive models

In paper II different existing formulations of the $k_r$-$S$ relation for three-phase flow were compared and tested against experimental data presented by Illangasekare et al. (1995). The $k_r$-$S$ models analysed were the BCB, VGB, BCM and VGM models, and based on the results these models were further developed. The $k_r$-$S$ relations were implemented in the T2VOC numerical simulator and simulations reproducing the conditions of the experiments were conducted.

$P_s$-$S$ data is often available only for a reference fluid pair (usually air and water), which in the case of three-phase systems, requires the use of scaled $P_s$-$S$ functions. In the modelling of a three-phase water-NAPL-air system,
where water is the primary wetting fluid, it is a requirement that the capillary pressure between water and air \( (P_{cgw}) \) equals the sum of capillary pressures between water and NAPL \( (P_{cnw}) \) and between NAPL and air \( (P_{cgn}) \) so that: 
\[
P_{cgw} = P_{cnw} + P_{cgn}
\]
The scaling factors, \( \beta \), therefore need to be formulated so that this requirement is fulfilled. Three methods modifying the standard way of scaling (by Parker et al., 1987) and ensuring that the above requirement is met, were therefore tested in the modelling.

It was observed that all the constitutive models experienced some similar problems in the match to experimental data. The mismatch was deemed to be related to the saturation dependence of the tortuosity factor in the \( k_r-S \) function. Therefore an addition to the \( k_r-S \) function was made allowing the NAPL tortuosity factor, \( X_m [-] \), to vary non-linearly with saturation:

\[
X_m(\bar{S}_n) = \left( \frac{Z(\bar{S}_n)}{\bar{S}_n} \right)^\gamma \bar{S}_n
\]  

(19)

where \( \bar{S}_n [-] \) is the effective NAPL saturation and \( Z [-] \) is a function of \( \bar{S}_n \) given by:

\[
Z(\bar{S}_n) = \frac{\arcsin(2\bar{S}_n - 1)}{\pi} + \frac{1}{2}
\]  

(20)

The strength of the desired non-linear behaviour is controlled by the value of the exponent \( \gamma \). For \( \gamma = 0 \), \( X_m \) varies linearly with \( \bar{S}_n \) as was originally suggested by Burdine (1953). For positive values of \( \gamma \), \( X_m \) varies nonlinearly, as shown in Figure 5. Compared to the linear case \( (\gamma = 0) \) a positive \( \gamma \) results in lower \( X_m \) at high NAPL saturations meaning that the effective path length for NAPL flow, \( L_{e,n} [L] \), first increases fast when \( S_n \) starts to decrease from its maximum value. At low \( S_n \), \( X_m \) is higher compared to the linear case. Here, when \( S_n \to S_n^r \) (the residual NAPL saturation value) \( X_m \) exhibits a sudden drop to zero meaning that \( L_{e,n} \) does not increase smoothly to infinity forcing \( X_m \) to zero. Instead there is a finite maximum value for \( L_{e,n} \) which is reached at the point when the NAPL permeability (and \( X_m \)) becomes zero (i.e. \( S_n = S_n^r \)). In the modelling study of paper II this type of nonlinear saturation dependence of \( X_m \) was investigated and the optimal value for \( \gamma \) was sought.
NAPL infiltration and immobilisation in saturated media

In papers III and IV, described more thoroughly below, detailed data-sets on NAPL infiltration and immobilisation in water-saturated heterogeneous media were generated. Paper V investigated the capability of different constitutive models to capture the NAPL migration processes observed in these two previous papers. Especially effects of hysteresis and fluid immobility in the constitutive relations were investigated.

In the studied NAPL-water system, the NAPL acted as a true non-wetting phase (NWP) as it displaced water (the wetting phase - WP) during drainage and interacted with imbibing water during subsequent imbibition. Conceptually, the flow and entrapment process was therefore different compared to the three-phase system described in paper II, where NAPL, as the intermediate wetting-fluid, mainly interacted with the non-wetting air phase.

Following Niemi and Bodvarsson (1988 and 1991) and Finsterle et al. (1998), two-phase hysteretic versions of the VG and BC $P_c$-$S$ functions as well as the VGM and BCB $k_r$-$S$ functions were implemented in T2VOC/iTOUGH2 (Falta et al., 1995; Finsterle, 2000). The scanning curves were based on the modified dependent-domain theory by Mualem (1984),
adding NWP entrapment according to Land (1968), Lenhard and Parker (1987) and Parker and Lenhard (1987) (see Figure 4).

In addition to entrapped water-occluded NAPL, a new function that accounts for temporary immobility of NWP in dead-end pore spaces during drainage was introduced. The reasoning is that before connected flow channels of NWP are established over an element of porous medium, the NWP saturation has to reach a threshold value: the $k_{r,nwet}$-emergence NWP saturation. Thereafter, as long as the WP saturation exceeds its residual (irreducible) value some pore-throats will be occupied and clogged for NWP flow by WP. This creates dead-end pore-spaces in which residing NWP will be immobile until the NWP pressure is high enough to displace the WP in the pore throat. At full NWP saturation, no pore throats associated with the saturated permeability will be clogged by WP and the NWP is fully mobile. Therefore, the proposed function for immobile NWP during drainage is initialised at a maximum value when NWP permeability emerges, the emergence saturation. Then the immobile NWP saturation decreases as the total NWP saturation increases and reaches zero when the medium is fully NWP saturated.

The function can be used with both hysteretic and non-hysteretic $k_{r,S}$ functions. In the latter case it describes both NWP immobility during drainage and NWP entrapment during imbibition. For the hysteretic case a different function is used during imbibition, based on the final entrapped NWP saturation according Land (1968). After reversal from drainage to an imbibition scanning curve the dead-end-immobile NWP is partially remobilised and partially entrapped by water occlusion.

In all, five different constitutive models were analyzed:
i. The non-hysteretic BC $P_{r,S}$ function together with the non-hysteretic BCB $k_{r,S}$ function, referred to simply as BCB.
ii. Non-hysteretic VG $P_{r,S}$ and VGM $k_{r,S}$ functions, referred to as VGM.
iii. Hysteretic BC $P_{r,S}$ and BCB $k_{r,S}$ functions: HBCB.
iv. Hysteretic VG $P_{r,S}$ and VGM $k_{r,S}$ functions: HVGM.
v. The hysteretic VG $P_{r,S}$ function together with the hysteretic BCB $k_{r,S}$ function, referred to as HVGBCB.
Experimental methods

Experiment design

Presently very few well-controlled experimental data exist that would allow the analysis of NAPL-plume evolution in heterogeneous systems. Yet, such data are in great need for an improved understanding of the relevant processes as well as for the validation of any predictive model.

In the present work, experimental methods were developed and used to investigate NAPL infiltration and immobilisation in heterogeneous water-saturated media (papers III and IV). In the conceptual model that was analysed a DNAPL migrates downwards until it encounters a finer formation where pooling occurs. The finer formation is mildly dipping which allows the pool to move in the down-dip direction by gravitational forces. The objective was to investigate the effects of heterogeneity in both the coarser formation where most of the vertical migration occurs and in the finer formation, into which the NAPL may penetrate. Heterogeneity can be expected to affect the vertical migration and entrapment along the migration path, the shape and thickness of the pool and the chances for NAPL penetration into the finer formation. The properties of resulting subsurface NAPL architecture are essential for NAPL-water interactions and the dissolution of contaminants to the groundwater. The conceptual model is illustrated in Figure 6.

The DNAPLs of interest for this study (TCE, PCE, TCA etc.) are highly toxic and volatile. They constitute a health risk in the laboratory and generate large amounts of toxic wastes when used in experiments with flowing water. In comparison, the use of a non-toxic chemical would be safer, faster, cheaper and environmentally sounder. Therefore an alternative approach using a much less toxic and less volatile LNAPL - Soltrol 220 was taken. In water-saturated media the vertical driving force on a NAPL is the sum of the buoyancy and gravitational forces. For DNAPLs the net force is directed downwards while for LNAPLs it is directed upwards. In both cases the magnitude of the force is directly proportional to the density difference between the NAPL and water. As shown in paper III, an LNAPL moving upwards can mimic DNAPL downward migration in an equivalent up-side-down system. To create the “equivalent up-side-down system” the system of interest was simply turned up-side-down. In contrast to the original conceptual model shown in Figure 6 the lower zone is coarser and the upper zone finer.
LNAPL was injected in the lower zone and migrated upward towards the interface to the finer zone.

Figure 6. Conceptual model of DNAPL infiltration and immobilisation in saturated porous media.

Figure 7. Sand tank used in the experiments. LNAPL is injected in the lower coarser zone and migrates up towards the interface to the zone of finer sand.
The flume (Figure 7) had inner dimensions of approximately 71 x 53 x 4.7 cm, excluding the constant-head wells on the sides. The tank walls were made of Plexiglas reinforced with a metal frame and lined with glass. An LNAPL injection system delivering LNAPL along a line across the thickness of the tank at a constant rate was constructed. The injection thereby constituted a point source in two dimensions. A finite volume of NAPL was injected at a constant rate during the first 2-4 hours of the experiment, after which injection was stopped and only redistribution of NAPL took place. At each end of the flume a constant-head boundary was constructed. By maintaining a small head difference between the two constant-head reservoirs a slow water flow was induced through the flume.

To investigate effects of heterogeneity in each zone, a series of three experiments were conducted in this experimental setup. In experiment 1 both sand zones were homogeneous. In experiment 2 the lower coarser zone was heterogeneous while the upper finer zone was homogeneous. In experiment 3 the lower coarser zone was homogeneous while the upper finer zone was heterogeneous. In experiments 2 and 3 the heterogeneous zones were designed by generating a number of spatially correlated random permeability fields, having predetermined average permeability, variance and spatial correlation lengths. For each experiment one such field was chosen, based on its suitability for the physical experiment, and was carefully packed in the flume using 5 discrete sands. The discrete blocks of sand used in the packing had dimensions of 3 cm in the horizontal and 1 cm in vertical directions. In experiment 2, 744 blocks were used while in experiment 3, 624 blocks were used.

The flume was packed wet and the discrete blocks were packed allowing some smoothing of block edges so that sharp edges and straight rectangular shapes were avoided. The smoothing eliminated preferential flow along the block edges. In all experiments the interface between the two distinct sand zones was dipping at an angle of 3.25°. In Figure 7 the packing used in experiment 2 can be seen as captured by the digital camera. However, some of the discrete sands look alike. For more details about the packing and the different sand configurations the reader is referred to papers III and IV.

X-ray measurement methods

To study the dynamic behaviour of the NAPL and the immobilisation process a methodology to continuously measure NAPL saturations in space and time was developed. Point measurements of fluid saturations were taken using a multiple-energy x-ray-attenuation technique. The x-ray tube and detector were mounted on a moving frame and were moved using high-precision motors to take measurements at pre-programmed locations in the flume. By successively increasing the number of spatial measurement points
and returning to take measurements at the same points after successively longer time intervals, the evolution of the NAPL distribution with time was successfully monitored. At selected times the x-ray-measurement system was moved to the side and digital images of the flume and the coloured NAPL were taken. The measurement system is shown in Figure 8.

\begin{center}
\includegraphics[width=\textwidth]{figure8.png}
\end{center}

\textit{Figure 8. X-ray attenuation measurement system and experiment setup.}

The x-ray attenuation system measures material path lengths $l_\kappa [L]$ ($\kappa = w$ – water, $n$ – NAPL, $s$ – solid silica sand) that the x-ray beam passes through. At the detector, photons of different energies are counted. Comparing the photon count as a function of photon energy before NAPL injection (system at reference state) and after that NAPL has appeared, the amount of water that has been replaced by NAPL can be calculated. The NAPL length $l_n$ that corresponds to the reduction in photon count is calculated using a maximum-likelihood-estimator methodology (developed and described in more detail by Hill et. al. (2002), based on Lambert-Beer’s law:

$$E[Y_e] = E[X_e] \sum_{\varepsilon, \rho_e, \rho_{ee}}^{N_e} \rho_{ee}$$

Here $Y_e [\cdot]$ is the number of photons of energy $\varepsilon [ML^2T^{-2}]$ observed at the detector for the reference state of the system, $X_e [\cdot]$ is the number of photons
of energy $\epsilon$ observed with changes in material lengths $\Delta l_\kappa [L]$ that the photon beam passes through. $\rho_\kappa [ML^{-3}]$ is the density of material $\kappa$ and $\mu_\kappa [L^2M^{-1}]$ is the attenuation coefficient of material $\kappa$ at energy $\epsilon$. The material length $l_\kappa$ is negative if a material is removed and positive if it is added, compared to the reference state. Further description of the x-ray system and the methodology for material-path-length calculation is given by Ferré et al. (2005), Hill III et al. (2002), Hill III (2001).

Similarly as for the NAPL length, the material lengths of water and sand can be used to calculate the spatial distribution of porosity and length of voids $l_v$ between the sand grains. Fluid saturations are calculated as the measured fluid path length divided by the void length: $S_\kappa = l_\kappa/l_v$. In order to apply Equation (19) the attenuation coefficients as functions of energy for all materials of interest (water, NAPL and sand) need to be determined. This was done by measuring attenuation for successively increased known material lengths for one material at a time and solving Equation (19) for $\mu_\kappa$. Water and the test LNAPL, Soltrol 220, have relatively similar attenuation properties. Therefore, to improve accuracy in the path length calculation, the attenuation properties of NAPL were separated from that of water by spiking the Soltrol adding 10% by weight iodoheptane, which increases the attenuation of the NAPL. The NAPL was also coloured red using the dye Sudan IV. The properties of the test NAPL are given in paper III.
Results and discussion

Modelling of multi-constituent multi-phase flow

In the scenario modelled in paper I, gasoline was spilled from a lorry along a ditch parallel to a road. The question of interest was how the gasoline and its constituents would spread towards a small river, which was located 110 m away and also parallel to the road. The spill along the ditch was viewed as a line source in a two-dimensional cross-section towards the river. As the free-phase gasoline formed a pool and spread on the water table, its different constituents were volatilised and dissolved at different rates which also depended on the gasoline composition. With the PCFF approach especially toxic and therefore interesting constituents in gasoline could be studied individually. This is demonstrated in Figure 9 which shows benzene concentrations in the aqueous phase at different times after the spill. As can be seen in Figure 9, according to this simulation, dissolved benzene concentrations of more than 1000 \( \mu \text{g/l} \) reached the river 30 days after the spill. Comparing to Swedish maximum permissible values for benzene in groundwater (10 \( \mu \text{g/l} \)) and in surface water (300 \( \mu \text{g/l} \)) (Swedish Environmental Protection Agency, 2002), this would be of environmental concern and highlights the importance of immediate remedial actions for these types of spill scenarios.

To assess the performance of the PCFF approach it was compared to simulations using the fully coupled TMVOC model. In general the PCFF approach matched the results using TMVOC well. This is illustrated in Figure 10 which shows the predicted total mass in the aqueous phase of the different aromatic constituents using the two models. PCFF overestimated the volatilisation of fraction 1 (C4-C6 aliphatics), which was volatilised at a high rate (see paper I). Thereby the gasoline composition changed with time so that the mole fractions of the other fractions were slightly overestimated, which resulted in slightly overestimated mass-transfer rates. The effect was small but can be seen in Figure 10 where PCFF generally predicted slightly higher total mass in the aqueous phase compared to TMVOC. Generally the output from the PCFF approach, about e.g. concentrations of aromatic constituents in the aqueous phase, was deemed useful.
Figure 9. Aqueous concentration of fraction 5 (benzene) as predicted using the PCFF approach at (a) 7, (b) 14, (c) 30 and (d) 60 days after the spill, respectively. (paper I)

Figure 10. Total mass of the aromatic gasoline fractions (5-8) in the aqueous phase, as predicted with the PCFF and TMVOC models. (paper I)
Comparison and development of three-phase constitutive models

In paper II the performances of existing $k_r$-$S$ relations for three-phase flow were compared and evaluated against experiments by Illangasekare et al. (1995) where dibuthylphtalate (DBP) was injected in a two-dimensional sand tank. The tank was unsaturated with water content at capillary equilibrium. Three cases were tested: (1) homogeneous sand, (2) homogeneous sand with a coarse lens embedded, (3) homogeneous sand with a fine lens embedded. The size of the domain for each experiment case was roughly 0.5 x 0.9 m and the thickness of the sand tank was 0.05m. As the NAPL migrated downwards in this three-phase system the position of the NAPL front was monitored over time by taking digital images. Simulations of cases (1) and (2), using one of the four tested constitutive models – the BCB model, are shown in Figure 11. Column 1 (a and d) shows the base-case simulations, column 2 (b and e) shows simulations using improved scaling of the $P_c$-$S$ functions and column 3 (c and f) shows the effect of the nonlinear tortuosity factor for the optimum value of $\gamma = 2$.

Comparing with the experiments (see paper II or Illangasekare et al., 1995) it was found that all four constitutive models (BCB, VGB, BCM, VGM) had some common problems in the match to experimental data. The two main concerns were:

(i) The model results showed too much horizontal spreading in general and a too strong capillary barrier effect causing excessive spreading on top of the coarse lens. This problem was addressed by changing the scaling method for the $P_c$-$S$ function. Compared to the base case, the improved scaling resulted in lower capillary pressure between the NAPL and the gas phase. This meant that there was less capillary suction on the NAPL to move into small air-filled pore spaces, the spreading became more dominated by the gravitational force and there was less horizontal spreading. At the interface to the coarse lens the capillary barrier effect was also reduced. The scaling-induced changes can be seen comparing Figure 11 a and b as well as d and e.

(ii) The spreading occurred too fast during the beginning of the migration period (i.e. looking at the 15-, 23- and 24-minute contours in Figure 11) and was too slow during the end of the migration period (80-, 82- and 185-minute contours in Figure 11). This was addressed by incorporating a nonlinear saturation dependence of the tortuosity factor and fitting the nonlinearity exponent $\gamma$. The best fit was found for $\gamma = 2$. The effect of letting $\gamma = 2$ for the BCB model can be seen in Figure 11 c and f.
Figure 11. Simulations of NAPL spreading using the BCB model showing the NAPL front after start of injection at times given in minutes. a, b, c homogeneous case. d, e, f embedded coarse lens. Scales on axes are in metres. (paper II)

Figure 12 shows the vertical distance from the NAPL front to the injection point as observed in the experiments and as predicted by the four different models. The improved models using scaling method 3 and $\gamma = 2$ are shown as solid lines whereas the results of the base-case simulations with existing parametric models are shown as dotted lines. With scaling method 3 and $\gamma = 2$ all four constitutive models generally performed somewhat better. Although none of the constitutive models was distinctly better than the other three, qualitatively, including observed behaviour at coarse- and fine-lens interfaces, the improved BCB and VGM models seemed to perform the best.
Figure 12. Vertical distances from the NAPL front to the injection point as a function of time for simulations using a nonlinear tortuosity factor with $\gamma=2$, scaling method 3. Observed values (triangles) and base-case simulations (dotted lines) are given for comparison. (a) homogeneous sand, (b) coarse lens embedded. (paper II)
Experiments on NAPL infiltration and immobilisation

In the following sections the main results of the experimental investigation on NAPL infiltration and immobilisation in saturated formations are presented. The base case (paper III) presenting the experimental method along with the experimental results for a system with two homogeneous layers is followed by studies of the effects of heterogeneity in each of the two layers (paper IV).

Base case

In the base case (experiment 1, paper I), both the upper zone consisting of fine (# 50) sand and the lower zone consisting of medium-grain (# 30) sand were packed homogeneously. Repeated measurements of NAPL saturation ($S_n$) at a large number of points in space were taken to produce data on NAPL saturation as a function of time at these points. Such data for three different points in the flume are shown in Figure 13. During the first 3.6 hours of the experiment 500 cm$^3$ of NAPL was injected at a constant rate. After that the injection was stopped and the NAPL was allowed to redistribute and move through the flume.

![Figure 13. NAPL saturation as a function of time at 3 different locations between the point of injection and the interface to the finer zone; closest to the injection point: circles, in between: squares, at the interface: crosses.](image)

At all three points shown in Figure 13 a maximum NAPL saturation ($S_n^{\text{max}}$) was reached at some point in time, after which $S_n$ started to decline. Generally the rate of decline depended on the distance to the interface to the finer zone. Close to the point of injection (circles) the decline was the fastest, whereas closer to the interface (squares) it became slower and just below the interface it was very slow (crosses). When the NAPL became immobile $S_n$...
stabilised at a constant value. Within 2 cm of the interface (crosses) there was still a very slowly moving pool at 530 hours after start of injection, which is the reason why $S_n$ was higher here than elsewhere in the tank.

At the different spatial points $S_n$ data was collected at slightly different times as the x-ray measurement system scanned the flume taking point measurements. However, because the time behaviour of $S_n$ was well captured, $S_n$ could be determined at any given time at all spatial points by interpolating data of the type shown in Figure 13. Thereby the spatial distribution of NAPL saturation could be determined at any time. As an example the spatial distribution of $S_n$ plotted as contours on top of a digital image taken 505.6 hours after the start of injection is shown in Figure 14.

When the spatial distribution of NAPL had been determined the total NAPL volume, $V_n$ [m$^3$] in the flume could be calculated. The total volume was calculated from the spatial distribution of NAPL path lengths, $l_n$ [m], which is generally very similar to that of $S_n$. However, because $l_n$ is independent of porosity it contains less measurement uncertainty than $S_n$. Approximately 22 hours after the start of injection the NAPL had spread along the interface all the way to the left constant-head well and slowly started to exit the measurement domain. Before the NAPL started to exit, $V_n$ must equal the known injected NAPL volume. This information can be used to further calibrate the measurements of $l_n$ and $S_n$. A slight offset that may occur in the fine-tuning
of the measurement system can be eliminated by applying a linear correction factor which obtains a correct total volume estimate. In this case the correction factor was 0.97. Estimates of $V_n$ as a function of time, before and after calibration, are shown in Figure 15. As the NAPL exited the domain of measurements the estimate of $V_n$ decreased accordingly.

![Figure 15. Estimates of the total NAPL volume ($V_n$) remaining in the flume, before calibration (triangles) and after calibration (circles). (paper III)](image)

Heterogeneous coarse zone

In experiments 2 and 3 (paper IV), effects of stochastic geological heterogeneity were investigated. Experiment 2 considered heterogeneity in the coarser zone where the NAPL was injected. Influenced by the heterogeneity, the NAPL moved upwards toward the interface to the finer zone where it may pool and spread, or potentially penetrate into the finer material. The average permeability of this heterogeneous zone was the same as the corresponding homogeneous zone of the base case. During the first 2.63 hours 600 cm$^3$ of NAPL was injected at a constant rate, after which injection was stopped. The evolution of the spatial NAPL distribution with time is shown in Figure 16 using first a digital image and at later times contour plots of $S_n$ based on x-ray-attenuation measurements.
Figure 16. Spatial distribution of NAPL in experiment 2; (a) at the end of injection (2.63h), (b) at 34h after injection and (c) when all NAPL had become immobile (474h). (paper IV)
The general movement of mobile NAPL was upwards towards the interface, where it spread and after approximately 33 hours started to move out through the right constant-head well. The path of the NAPL as it migrated up towards the interface was largely controlled by small-scale heterogeneity. At 474 hours (≈ 20 days), shown in Figure 16c, the NAPL had become immobile everywhere in the tank. High NAPL saturations were still found in the two coarsest sands. To exit these sands the NAPL generally had to move through medium-grain (# 30) sand. At such material interfaces a capillary barrier preventing NAPL to flow at low saturations existed. In the # 30 sand, which was the most abundant of the 5 sands of the heterogeneous zone, NAPL saturations stabilised at values around 0.15 everywhere except in a thin pool at the interface where higher saturations were found.

It can be concluded that the NAPL was immobilised through two forms of entrapment. In the medium-grain # 30 sand the NAPL could generally migrate upwards without being stopped by capillary barriers to finer sands. Without the presence of capillary barriers, NAPL was immobilised when small blobs and ganglia were snapped off and left behind in a discontinuous state as water imbibed and the NAPL saturation decreased. This type of immobilised NAPL can be referred to as discontinuous entrapped NAPL or ganglia. The second form of entrapment was seen in the two coarsest sands (# 8 and 16) as well as in the medium-grain (# 30) sand at the interface to the finer zone. Here NAPL was entrapped because its movement was restricted by the presence of capillary barriers. Because entrapment occurred without snap-off into discontinuous pieces, this type of immobilised NAPL can be referred to as continuous entrapped NAPL or pools.

Heterogeneous fine zone

In experiment 3, effects of heterogeneity in the upper finer zone were investigated. As in the base case, the lower zone consisted of homogeneous medium-grain (# 30) sand. 500 cm$^3$ of NAPL was injected during 4.35 hours. At the end of injection Figure 17a, the NAPL had reached the interface. Here heterogeneity in the, on average, finer sand above the interface provided points of entry for the NAPL to penetrate upwards into this zone. Once the NAPL had entered the upper zone the pressure in the NAPL could build up as the buoyancy column increased. This enabled the NAPL to penetrate further through areas of finer sand. As can be seen in Figure 17 more mass successively moved into the upper zone. At about 48 hours the NAPL had found its way to the left constant-head well through a small flow channel and started to exit the experiment domain.
Figure 17. Spatial distribution of NAPL in experiment 3; (a) at the end of injection (4.33h), (b) at 25h after injection and (c) when all NAPL had become immobile (385h). (paper IV)
At 385 hours, Figure 17c, the NAPL had become immobile everywhere in the tank and the thin flow channel to the left well was no longer active. The NAPL saturation in the #30 sand below the interface stabilised at a value in the order of 0.15 everywhere, which was consistent with the two previous experiments. In the upper heterogeneous zone higher NAPL saturations existed especially in areas of coarser sand. Snap-off at larger scale, which was also seen in experiment 2 (Figure 17c), can be observed on the right side of the NAPL body where the pool just below the interface had retracted leaving 2 small blobs behind. Also a relatively large NAPL occurrence that contained high saturations, located approximately at \((x, z) = (52, 30)\), had been disconnected from the main NAPL body.

**Entrapment**

The detailed measurements of NAPL saturations in space and time allowed study of the immobilisation process. By plotting NAPL volume (or mass) as a function of NAPL saturation, the saturation characteristics of a NAPL occurrence could be analysed. This has been done for the final stage of the 3 experiments in Figure 18 which shows the fraction of the total NAPL volume occurring at different saturations. In the heterogeneous zones NAPL saturations measured in the different discrete sands have been separated. The distribution of NAPL volume over different saturations is of interest because the saturation affects the flow of water through a NAPL occurrence and the contact area between NAPL and water.

In experiment 1, at 520 hours after start of injection (Figure 18a) there was still a thin pool of mobile NAPL directly adjacent to the interface to the finer sand zone (see also Figure 14 for comparison). In Figure 18a this pool can be seen in the saturation range from approximately 0.2 to 0.4. Elsewhere in the tank, however, the NAPL occurred at lower saturations in the form of immobilised, discontinuous blobs and ganglia. A peak in the distribution over saturation can be seen at \(S_n = 0.15\), indicating that most NAPL is immobilised at saturations around this value.

In experiment 2, at 474 hours (Figure 18b) all NAPL was immobile in the flume. Compared to experiment 1, a much larger proportion of the NAPL was entrapped at higher saturations. At material interfaces inside the heterogeneous zone capillary barriers existed. Here the NAPL was immobilised at a continuous state because the flow was restricted by the NAPL pressure, which needs to be large enough to drive NAPL flow into finer material. At saturations above 0.5 NAPL occurred mainly in the two coarsest sands (#8 and 16). This is expected because higher (equilibrium) saturations can exist in these materials at a given capillary pressure compared to the finer sands. As in experiment 1, in the medium-grain #30 sand, a peak in the distribution occurred at approximately \(S_n = 0.15\). Also here this indicates that as NAPL was immobilised the proportion of NAPL within this \(S_n\) range increased.
Also at the end of experiment 3, at 385 hours (Figure 18c) the NAPL was immobile everywhere. In the lower homogeneous zone all the NAPL occurred at saturations below 0.22. Similarly to the other 2 experiments, there was a distinct peak in the distribution around $S_n = 0.16$ arising from immobilised NAPL in the medium-grain # 30 sand. In the upper heterogeneous zone NAPL was immobilised at higher saturations. Because high pressures built up in this zone before NAPL could move through fine materials. Somewhat higher saturations occurred in the medium (# 30) and coarse (# 16) sands, compared to experiment 2.

Figure 18. NAPL distribution as a function of saturation at the end of the three experiments. NAPL in different sands type indicated by colour; from coarsest to finest: dark red (sand # 8), red orange (# 16), yellow (# 30), cyan (# 3050), blue (# 70).
In homogeneous media where the NAPL was immobilised in the absence of capillary barriers a relationship between the maximum NAPL saturation previously reached, $S_{n}^{\text{max}}$, and the final entrapped saturation, $S_{nt}$, could be established. Using data on $S_{n}(t)$ of type shown in Figure 13 characteristics of this relation could be analysed for the parts of the experimental domains which were not affected by entrapment at capillary barriers. Such data, from the lower homogeneous sand zone of experiment 3, are shown in Figure 19 along with fitted entrapment models: i.e. the Land (1968) model (Equations 7 and 8) and a constant-value entrapment model.

The ganglia-to-pool ratio (GPR) (Lemke et al., 2004) is the mass ratio of NAPL occurring as discontinuous blobs and ganglia and NAPL residing in pools, i.e. NAPL at continuous state. In practice the easiest way to define a GPR is by assigning a cut-off value for $S_{n}$ below which NAPL is regarded as ganglia and above which NAPL is regarded as pools. Here (following Lemke et al., 2004), GPR was calculated choosing the cut-off value to be the maximum (discontinuous) entrapped saturation of the Land (1968) model, $S_{nt}^{\text{max}} = 0.17$ (see Equations 7 and 8). The resulting evolution of GPR with time for experiment 2 is shown in Figure 20 (circles). The sensitivity of the GPR to the cut-off value is illustrated by plotting the GPR also for cut-off values of 0.15 (squares) and 0.19 (triangles).
Figure 20. Ganglia-to-pool ratio for a cut-off value 0.17 (circles). GPR for cut-off values of 0.15 (squares) and 0.19 (triangles) shown to visualise sensitivity to the cut-off value. (paper IV)

As can be seen the GPR increased with time. The reason is that as the NAPL moved through the flume, at the receding edge of the mobile NAPL body, some NAPL was continuously snapped off and left behind as immobile ganglia. When all NAPL had become immobile, the GPR stabilised. For experiment 2, the final GPR values were approximately 0.38, which indicates that pools (NAPL at continuous state) clearly dominate the distribution of NAPL over saturation. For experiment 1, the GPR at 520 hours was 3.1 indicating clear domination ganglia. For experiment 3, GPR at 385 hours was 0.78 showing that more NAPL exists as pools although the relative amounts are fairly even. The relation of the final GPR values to the distribution of NAPL over different saturations can be seen by comparing to Figure 18. Here it can also be seen if the GPR will be sensitive to small changes in the cut-off value. If a large portion of the NAPL is found at saturations close to the cut-off value (a peak in the distribution in Fig. 18), then the sensitivity will be high. This was the case especially for experiment 1, Fig. 18a.

Modelling of NAPL infiltration and immobilisation

In paper V different constitutive relations for two-phase NAPL-water systems were analysed and compared by modelling experiments 1 and 2 presented in papers III and IV, respectively. The five tested constitutive models are described briefly in the Modelling chapter above and in more detail in paper V.
Figure 21. Observed and simulated spatial distribution of NAPL saturation at 23.9 hours after the start of injection. (paper V)

During the NAPL-injection periods in the beginning of the two analyzed experiments (the first 3.6 and 2.6 hours, respectively), the entire system was
at drainage. When the injection stopped and the NAPL started to redistribute in the flume, reversal to imbibition started to occur in parts of the NAPL-invaded volume. Figure 21 shows the observed and simulated distribution of NAPL saturation ($S_n$) for experiment 1, 23.9 hours after the start of injection. Here the results for the non-hysteretic BCB and hysteretic HBCB models are shown.

Compared to the experimental results (Figure 21a), the BCB model (Figure 21b) overestimated the speed of migration predicting a too fast NAPL movement up towards the interface leaving behind only $S_n$ below the $k_{r,nwet}$-extinction saturation. The result was similar for the other tested non-hysteretic model (VGM). These models also predicted the pooled NAPL at the interface to move along the interface in a slug-like way which was not observed in the experiment.

The HBCB model (Figure 21c) as well as the other hysteretic models produced better matching results with slower upward movement and a more realistic pool. The reason is that in elements where reversal to imbibition has occurred, $P_c$ decreases fast along the imbibition scanning curve (see e.g. Figure 4). Thereby the pressure gradient for NAPL flow into areas where drainage still occurs decreases and the flow slows down. It can be concluded that hysteretic $P_c-S$ functions influence the predicted speed of NWP (NAPL) flow and improves the match to observations.

In experiment 2 NAPL was immobilised both behind capillary barriers at material interfaces and as snapped-off discontinuous blobs and ganglia. After 474 hours (Figure 16), all NAPL in the flume was considered immobile. Figure 22 shows the simulated spatial distributions of $S_n$ at this time. Here the results for the VGM, HVGM and HVGBCB models are shown. However, with respect to the models not shown, the results for the BCB model were similar to those of the VGM model and the results for the HBCB model were similar to those of the HVGBCB model.

To predict the observed distribution of entrapped $S_n$, the models need to capture both types of entrapment. In # 30 sand all models, including the non-hysteretic ones, captured the first type of entrapment relatively well. Because the relation between historic maximum $S_n$ ($S_n^{\text{max}}$) and final entrapped saturation ($S_n^{\text{f}}$) is relatively flat for all $S_n^{\text{max}}$ greater than roughly 0.3 (Figure 19), approximating $S_n^{\text{f}}$ as a constant (non-hysteretic models) works reasonably well.

Compared to the experiment (Figure 16), the VGM model (Figure 22a) predicted too much entrapment in the coarsest (# 8 and 16) sands. The reason is that the strengths of the capillary barriers between these two sands and the third-coarsest # 30 sand were overestimated by this model. This, in turn, occurred because only drainage $P_c-S$ properties were used in the non-hysteretic models (VGM and BCB), while during imbibition the barriers are generally weaker. E.g. comparing sands # 30 and # 16, the difference in (scaled) displacement pressures during drainage: $P_{ad}(\#30) - P_{ad}(\#16)$ equals
340 Pa, whereas during (main) imbibition: \( P_{\text{a}}(\#30) - P_{\text{a}}(\#16) = 190 \) Pa (see also Table 1 in paper V).

The HVGM and HVGBCB models (Figure 22b, c) predicted less entrapment in the coarsest sands because the hysteretic models (obviously) are more capable of capturing the \( P_c-S \) relation during imbibition. However, the HVGM model predicted slightly too little entrapment behind capillary barriers.

Generally in the modelling of both experiments, the results that matched the experiment best were those by the HBCB and HVGBCB models. It was concluded that the HBC and HVG \( P_c-S \) functions performed equally well. The, in comparison, poorer accuracy of the HVGM-model predictions was attributed to the use of the closed-form VGM \( k_r-S \) function (obtained from Equation (15) by van Genuchten, 1980), where the VG parameters have to be fitted under the constraint \( m=1-1/n \). Parameters fitted under this constraint were only used in the \( k_r-S \) function while the VG (and HVG) \( P_c-S \) function employed in the simulations were fitted with no constraint on \( m \) and \( n \). Under the constraint on \( m \) it may not be possible to represent the well-sorted pore-size distributions of the industrially produced sands used in this and many other laboratory experiments with sufficient accuracy. For such sands \( P_c \) increases abruptly when NWP saturation emerges (\( S_w \) starts to decrease from 1). Especially, for two-phase flow, when NAPL infiltrates and is immobilised in water-saturated media it is deemed important to accurately represent these characteristics. See Figure 4 for an example of VG \( P_c-S \) curves fitted with no constraint on \( m \). It is emphasised that the less accurate fit is attributed to the fitting procedure where the constraint on \( m \) is applied and not to the VG model itself.
Figure 22. Simulated spatial distribution of NAPL using the VGM, HVGM and HVGBCB models at 474 hours after start of injection (paper V). (Observed result shown above in Figure 16c)
Summary and conclusions

The subsurface spreading of organic contaminants that may exist in a non-aqueous liquid phase is a complex process of multi-phase flow and transport. The spreading is complicated by many factors. This work has dealt with (i) multi-constituent NAPLs, (ii) constitutive relations of capillary pressure and relative permeability as functions of fluid saturations, (iii) geological heterogeneity and (iv) NAPL immobilisation and entrapment. The focus has been to develop new models and methods to improve current understanding of the governing processes. The work has included conceptual model developments, numerical modelling analyses, laboratory experiments and development of experimental methodology.

In paper I, a partially coupled fraction-by-fraction (PCFF) methodology to model the subsurface spreading of gasoline, taking its multi-constituent nature into account, was proposed. The methodology allows the different gasoline fractions, such as benzene and toluene, to be studied individually as the gasoline mixture migrates through the ground and its different constituents dissolve, volatilise, and spread in the aqueous and gaseous phases at different rates. This individual study of gasoline constituents is necessary in order to assess risks and quantify environmental impacts, and makes it possible to compare predicted concentrations to maximum permissible values and environmental standards.

In a comparative modelling study of a gasoline spill in connection with an accident, the PCFF approach, used with the T2VOC simulator, was evaluated against the fully coupled multi-constituent TMVOC code. Here the PCFF method in general produced good predictions of spatial distributions of gasoline constituents, such as BTEX concentrations in the aqueous phase. The results are preliminary and are intended to demonstrate the performance of the PCFF model, as further validation against field and/or laboratory data are needed. Compared to modelling multi-phase transport of gasoline as a single-constituent compound using average properties, the PCFF approach has the potential to greatly improve predictions the fate of gasoline constituents in the subsurface.

In paper II, NAPL infiltration to unsaturated media with embedded lenses of different materials was modelled, using four different three-phase $k_r$-$S$ functions. The performance of the different models was compared to experimental data for three different scenarios; homogeneous medium sand, medium sand with an embedded lens of coarser sand and medium sand with
an embedded lens of finer sand. In its original form, no model produced predictions that matched the experimental data to a satisfactory degree, and some problems common to all four models could be identified. To accommodate these, some further developments to the existing constitutive models were proposed.

When modelling a three-phase system, scaling of the $P_c-S$ functions has to be done in such way that the capillary pressures add up. While different scaling options exist, it was found in the present work that the best predictions of NAPL migration were obtained when focusing on achieving a correct description of the NAPL-gas phase capillary pressure. Such scaling avoided excessive capillary drive on the NAPL to move into air-filled pore spaces and diminished the overestimation of horizontal spreading.

The fit to the observed speed of the NAPL-front propagation was improved by modifying the saturation dependence of the tortuosity factor in the $k_r-S$ function. Traditionally (e.g. Burdine, 1953) it has been assumed that the effective flow paths of the fluids in a multiphase system increase linearly as the saturations decrease. Here a nonlinear relationship was introduced for the $k_r$ function. It was assumed that the length of the effective flow path ($L_{e,n}$) increases fast when the fluid saturation decreases from unity (i.e. in the highest saturation range). Then, as saturation decreases towards its residual value, $L_{e,n}$ does not go smoothly to infinity (as implied in the traditional approach) but rather goes towards a finite maximum value which is reached at the point when $k_r$ becomes zero. This is physically sounder than the traditional approach since $L_{e,n}$ indeed should have a finite value at the point of NAPL-permeability extinction. With the improved formulation of tortuosity all the tested $k_r-S$ models performed better than the base-case formulations. With both improved scaling and tortuosity especially the BCB and VGM constitutive models produced good predictions of the observed experimental results.

In papers III and IV NAPL infiltration and immobilisation in a saturated heterogeneous media was studied experimentally. Such data is deemed especially valuable as presently very few well-controlled experimental data on the spreading of NAPLs in heterogeneous media exist. Yet, such data are greatly needed both for an improved understanding of system behaviour as well as for validation of any predictive models.

In the first of the two companion papers (paper III), a methodology to continuously measure NAPL saturations in space and time was presented. In a two-dimensional sand tank precise measurements of fluid saturations and porosity were obtained using a multiple-energy x-ray-attenuation technique. The methodology allowed the monitoring of dynamic migration behaviour of NAPLs. It was tested and developed for a base-case system consisting of two distinct sand zones separated by a mildly dipping interface. In paper IV, the measurement methodology was used to study the effects of small-scale, sto-
chastic heterogeneity in each of the two sand zones on the migration and entrapment of NAPL.

The observations and conclusions made in the two companion papers can shortly be summarised as follows:

(i) Heterogeneity produced variations in capillary resistance to NAPL flow which largely governed the NAPL flow path as the NAPL preferentially moved into the coarser pores where capillary pressures were lower.

(ii) NAPL immobilisation in heterogeneous media occurred as a result of two main types of entrapment. When NAPL was able to move through the ground without being forced to flow through a capillary barrier, the NAPL was predominantly entrapped by snap-off and was left behind as discontinuous blobs and ganglia. Here the trend in the relationship between $S_a$ and $S_{a,max}$ was well predicted by the Land (1968) model. When the NAPL had to flow through an interface to finer material where a capillary barrier existed, it was normally at least partly, trapped in a continuous state behind the barrier.

(iii) In the heterogeneous zones the NAPL was entrapped over a wider range of saturations compared to the homogeneous zones. In the latter, a major part of the entrapped NAPL was found within a relatively low and narrow saturation range because entrapment predominantly occurred by snap-off. Also where both types of entrapment occurred, a peak in the entrapped saturation distribution was seen within such range. The upper limit of the peak range constituted a reasonable cut-off value for the ganglia-to-pool ratio.

(iv) Local heterogeneity may allow NAPL to enter a formation which on average is so fine that the NAPL would not enter if it was homogeneous. Once the NAPL has entered, pressures may build up in the flow channels enabling further advancement and penetration into fine-grain areas. Because of the domination of finer materials, the NAPL entrapped inside such a formation may be accessible only to very slow aqueous-phase flow, which means that dissolution will be slow. Therefore heterogeneity which allows NAPL to enter into, on average, fine formations limits the rate of dissolution, and increases the longevity of contamination from the entrapped sources.

(v) A detailed data set on the infiltration, redistribution and immobilisation of NAPL in saturated heterogeneous media was presented. The careful packing of the flume in combination with precise measurements at a large number of well-known locations allowed a unique and exact monitoring of dynamic NAPL behaviour in formations where complex, small-scale heterogeneity was present. The dataset can be used to validate conceptual and numerical models for further study of flow and entrapment of NAPLs in complex heterogeneous systems.

In paper V, simulations using different constitutive models were analysed and compared to experiments 1 and 2 presented in papers III and IV, respectively. Both non-hysteretic and hysteretic models including NAPL entrap-
ment were tested and a new relation for temporary NWP immobility during drainage was incorporated.

The results showed that hysteresis needs to be accounted for in constitutive models to correctly predict observed NAPL infiltration and redistribution in saturated media because of the two following main reasons:

(i) When NAPL is delivered from areas undergoing imbibition (declining $S_n$) to areas where drainage still occurs (increasing $S_n$), the pressure gradient for NAPL flow decreases because $P_c$ decreases fast along the imbibition scanning curve. Therefore, accounting for $P_c-S$ hysteresis, the speed of NAPL (NWP) migration becomes slower in both homogeneous and heterogeneous media compared to if the system is assumed to be non-hysteretic.

(ii) When the NWP flows over an interface to a finer material the barrier effect induced by capillary resistance is stronger during drainage than during imbibition. Therefore, predicting NWP flow solely using drainage $P_c-S$ characteristics will overestimate the strengths of (breached) capillary barriers and the amount of NWP entrapped behind them.

In general the two models that matched experimental observations best were (1) the hysteretic van Genuchten (VG) $P_c-S$ relation in combination with the hysteretic Brooks-Corey-Burdine (BCB) $k_r-S$ relation, denoted HVGBCB, and (2) the hysteretic Brooks-Corey (BC) $P_c-S$ relation in combination with the hysteretic BCB $k_r-S$ relation, denoted HBCB. These models also produced very similar results. The conclusion was that the hysteretic VG $P_c-S$ relation, with parameters fitted with no constraint on $m$, performed equally well as the hysteretic BC $P_c-S$ model. The reason why the hysteretic van Genuchten-Mualem (HVGM) model predictions differed more from the observations is found in the closed-form (H)VG $k_r-S$ function. To produce the closed-form equation, a set of VG parameters, requiring $m=1-1/n$ needed to be used. This parameter set was different than in the otherwise employed VG $P_c-S$ relation. Under the constraint $m=1-1/n$, the best fits of $m$ do not seem to represent the pore-size distributions of the test sands well enough to predict a $k_{rn}(S_n)$ that reproduces the observed NAPL migration.

It was concluded that the continuum-based models, with underlying assumptions of Darcian flow, used in the simulations can reproduce the observed stable NWP-infiltration and immobilisation behaviour, even in complex heterogeneous media, provided that accurate constitutive relations are used.
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Spridning av flerfasföroreningar i heterogen mark – studier med experiment och modellering

Flerfasföroreningar är miljöskadliga ämnen som kan förkomma i en egen vätskefas skild från vatten och som dessutom delvis löser sig i vatten och förångas till luft. Exempel på sådana ämnen är vanligt förekommande organiska vätskor som bensin och dieselolja samt industriellt använda klorerade lösnings- och avfettningsmedel (TCE, PCE, TCA m.fl.). Flerfasföroreningar kan spridas samtidigt i de mobila faser (vatten, markluft, organisk vätska) som samexisterar i marken och kan fastläggas på markpartiklar. Spridningen är därför komplicerad och styrs av det samtidiga flödet av de mobila faserna samt utbytet av komponenter (föroreningar) mellan de olika faserna.

Detta arbete syftar till att utöka kunskapen om spridningen av flerfasföroreningar i mark och att utveckla experimentella och numeriska metoder och modeller för att studera spridningsbeteendet. Ökad kunskap kan underlätta (i) bedömningen av risker vid utsläpp och läckage, (ii) val av förebyggande åtgärder för skydd mot föroreningar, (iii) utformning av saneringsstrategier för förorenade områden.

Avhandlingen har inriktats på tre särskilt viktiga faktorer.
(1) Föroreningar som i sin organiska fas är blandningar av ett flertal olika kemiska komponenter. Här innefattas bl.a. bensin och diesel som är mycket vanligt förekommande både i förorene områden och vid plötsliga utsläpp i samband med olyckor under t.ex. transporter. Spridningen av dessa föroreningar kompliceras av att de olika komponenterna har olika spridningsbeteenden med avseende på bl.a. lösning, förångning, adsorption och nedbrytning.

(2) Kapillära krafter och reducerad permeabilitet vid flerfasflöde. När separata vätske- och gasfaser samexisterar i marken påverkas deras flöde och retention av kapillära krafter. Tryckskillnaden mellan faserna, kapillärtrycket ($P_c$), kan relateras till mättnadsgraden ($S$), d.v.s. andelen av porutrymmet som upptas av de olika faserna. Permeabiliteten för var och en av de faser som konkurrerar om porutrymmet minskar och denna minskning, som kvantifieras av den relativa permeabiliteten ($k_r$), kan också relateras till mättnads-
graden. Dessa relationer kan benämnas grundläggande relationer för flerfaser-
flöde och är avgörande för hur en organisk vätska rör sig i mark.
(3) Markens geologiska heterogenitet. Variationer i markens kapillära egen-
skaper och permeabilitet har stor inverkan på spridning och kvarhållning av
organisk fas. Hur den organiska fasen kvarhålls i marken, samt dess läge och
struktur då den blivit orörlig, är av särskilt intresse eftersom detta påverkar
lösningsprocessen och föroreningen av grundvattnet under lång tid.

I artikel I utvecklades en modelleringsteknik för att studera spridningen
av flerkomponentsföroreningar (benämnd PCFF-metoden). Metoden tillämp-
pades på bensin som är en blandning av hundratals organiska komponenter.
Komponenterna delades in i åtta representativa grupper. Med en befintlig
enkomponentsmetod studerades varje föroreningssyndrom för sig och efter
givna tidsintervall lades resultaten ihop och bensinens sammansättning upp-
daterades. Metodiken gör det möjligt att studera spridningen i mark och
grundvatten av enskilda komponenter som harror från ett bensinutsläpp.
Däremed kan beteendet hos särskilt miljöskadliga komponenter som t.ex.
BTEX isoleras, vilket är nödvändigt för riskbedömning och jämförelser av
föroreningssyndromer med gränsvärden. I en jämförande modelleringstudie av
e en tankbilsolycka utvärderades PCFF-metoden mot en mer avancerad fler-
komponentsmetod (TMVOC). Resultaten för bl.a. BTEX-halter i grundvat-
tnet överensstämde väl och visade att PCFF-metoden är användbar för denna
typ av scenarier.

I artikel II simulerades spridningen av en organisk vätska i omättad sand
för tre olika fall av heterogenitet: (1) homogen medelgrov sand, (2) homogen
medelgrov sand med en lins av grov sand, samt (3) med en lins av fin sand. I
simuleringarna användes olika formuleringar av de grundläggande $P_c$–$S$
- och $k_c$–$S$-relationerna. Resultaten jämfördes med tidigare presenterade exper-
imentella data. I sin standardform kunde ingen av de fyra modellformulering-
ar som testades återskapa resultaten från experimenten särskilt väl. Problem
som var gemensamma för samtliga modeller identifierades i skalningen av
$P_c$–$S$-relationen och i formuleringen av slingighet (eng. tortuosity) i $k_c$–$S$
-relationen.

I ett trefassystem av vatten, organisk vätska (olja) och luft förkommer ka-
pillärtryck parvis mellan faserna. I numerisk modellering beskriver dessa
vanligen med s.k. skalade $P_c$–$S$-relationer. När man summerar kapillärtryck-
en vatten – olja och olja – luft måste summan bli samma som kapillärtrycket
vatten – luft. Det finns dock olika möjligheter att göra skalningen så att detta
kriterium uppfylls. Resultaten visade att för utbredningen av den organiska
vätskan är kapillärtrycket mellan denna och luftfasen mest avgörande. Där-
för bör man tillämpa en skalningsmetod som garanterar korrekt beskrivning
av just denna kapillärtrycksrelation. Genom att modifiera skalningsmetoden
kunde tidigare överskattningar av kapillärt sug på den organiska fasen och
påföljande överskattning av horisontellt utbredning minskas väsentligt.
För att kunna simulera den observerade utbredningshastigheten hos den organiska vätskan gjordes en omformulering av slingrighetens beroende av vätskans mättnadsgrad. I befintliga $k_r-S$-modeller antas slingrighetsfaktorn, kvoten mellan vätskans effekativa flödesväg för ett mättat medium ($L_{e, sat}$) och flödesvägen vid lägre mättnadsgrader $L_e(S)$, minska linjärt en minskning av vätskans mättnadsgrad. Ju längre $L_e(S)$ desto lägre är alltså slingrighetsfaktorn. Denna modellformulering innebär indirekt $L_e(S)$ skulle gå mot oändligheten när mättnadsgraden går mot sitt minsta möjliga värde (residualvärde). Här antogs istället ett olinjärt samband mellan slingrighetsfaktorn och $S$, där $L_e$ ökar snabbt då $S$ minskar från sitt maximala värde men sedan går mot ett ändligt maximum då $S$ går mot residualvärdet. Den nya formuleringen av slingrigheten gav goda prediktioner av spridningshastigheten med alla fyra testade modeller.

I artikel III och IV undersöktes infiltration och kvarhållning av en organisk vätska i vattenmättade heterogena medier. I artikel III utvecklades en metodik för att kontinuerligt mäta andelen organisk vätska i porutrymmet i rum och tid. I en tvådimensionell mätuppställning gjordes noggranna mätningar av mättnadsgrad och porositet med hjälp av röntgenmätteknik och utbredningen av den organiska vätskan kunde studeras dynamiskt. Mätmetoden utvecklades för ett grundscenario bestående av två distinkta sandzoner skilda av en svagt lutande gränsyta. I artikel IV studerades effekten av småskalig, rumsligt korrelerad stokastisk heterogenitet i vardera zonen på utbredning och kvarhållning av organisk vätska i dylika tvåzonssystem.

Nedan följer en kort sammanfattning av resultaten från de två artiklarna:

(i) Geologisk heterogenitet påverkar den organiska vätskans flödesväg genom marken. I den mättade zonen håller sig den organiska fasen företrädesvis till grövre porer där kapillärtrycket för en given mättnadsgrad är lägre än i finare porer.


(iii) I de heterogena zonerna kvarhölls organisk vätska inom ett bredare spektrum av mättnadsgrader än i de homogena zonerna. I de senare återfanns merparten kvarhållen organisk vätska inom ett smalt spektrum av låga mättnadsgrader, vilket beror på att kvarhållningen huvudsakligen skedde genom
avknoppning. Mättnadsgraden av organisk vätska påverkar permeabiliteten för vattenflödet och vid höga mättnadsgrader blir det sannolikt att vattenflödet kringgår områden där organisk vätska förekommer.

(iv) Lokal heterogenitet kan göra det möjligt för den organiska vätskan att tränga in i geologiska formationer som i genomsnitt har låg permeabilitet. I de flödeskanaler som då uppkommer kan trycket öka i den organiska vätskan vilket kan göra det möjligt för vätskan att tränga lägre in i den låg­genomsläppliga formationen. Organisk vätska som kvarhålls i en sådan formation är endast i kontakt med mycket långsamma vattenflöden, vilket gör att lösningen av organiska komponenter till vattnet blir långsam. Därigenom blir grundvattnets föroreningskälla långvarig.

(v) En detaljerad dataserie över infiltration, spridning och kvarhållning av en organisk vätska i vattenmättade medier har presenterats. Den noggranna packningen av sanden i experimentuppställningen i kombination med precisa mätningar på välbestämda punkter gjorde det möjligt att studera det dynamiska beteendet hos den organiska vätskan i formationer där komplex små­skalig heterogenitet förekom. Denna dataserie kan användas till att utveckla och validera konceptuella och numeriska modeller för vidare studier av spridning och kvarhållning av organiska vätskor i komplicerade geologiska miljöer.

I artikel V modellerades spridningsförloppen i experiment 1 och 2 från artikel III respektive IV. Simulerade resultat med olika modellformuleringar analyserades och jämfördes med experimenten. Hysteresis i \(P_c-S\)- och \(k_r-S\)-relationerna samt kvarhållning genom avknoppning av den organiska vätskan infördes i modellen. Vidare utvecklades en enkel relation för att beskriva partiell orörlighet hos den organiska vätskan i porer vars halsar tillfälligt blockeras av vatten då mediet avvattnas. Fem olika modeller, varav tre innefattade hysteresis, testades.

Resultaten visade att man behövde ta hänsyn till hysteresis i \(P_c-S\)- och \(k_r-S\)-relationerna för att prediktera observerad infiltration av organisk vätska i det vattenmättade mediet. De två huvudorsakerna var:

(i) När andelen organisk vätska börjar minska övergår flödesregimen till vätning och p.g.a. hysteresis minskar då trycket i den organiska vätskan snabbare än vid avvattnning. Därigenom minskar även tryckgradienten för flöde av organisk vätska från ett område där vätning pågår till ett angrän­sandt område och flödet blir långsammare.

(ii) När organisk vätska flödar genom en gränsytta vid ett finare material är den kapillära barriären vid gränsytan starkare vid avvattnning än vid vätning. För att inte överskatta andelen organisk vätska som fängas bakom sådana barriärer måste hänsyn tas till skillnader i mediets kapillära egenskaper vid avvattnning respektive vätning.

Liknande simuleringresultat erhölls med Brooks-Corey (BC) och van Genuchten (VG) \(P_c-S\)-relationerna, som båda presterade väl när hysteresis innefattades. VG \(P_c-S\)-relationen fungerade bra så länge parameter-
anpassningen gjordes med oberoende parametrar \( m \) och \( n \) och inte under det vanligt förkommande antagandet \( m=1-1/n \). Troligtvis kan porstorleksfördelningen hos de välsorterade sandmaterial som användes inte representeras tillräckligt bra under villkoret \( m=1-1/n \).

Sammantaget konstaterades att de kontinuumbaserade modeller för flersfasflöde som testades kunde återskapa det observerade flödet av organisk vätska, även i det mycket komplexa heterogena mediet, under förutsättning att korrekta grundläggande flödesrelationer användes.
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