SOURCE ZONE AND MODEL PARAMETER INFLUENCE ON NAPL PLUME DEVELOPMENT IN A HETEROGENEOUS AQUIFER

MICHAEL MARINOVICH
SUPERVISOR: DR. DAVID REYNOLDS
SCHOOL OF ENVIRONMENTAL SYSTEMS ENGINEERING
UNIVERSITY OF WESTERN AUSTRALIA
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Abstract

Non-aqueous phase liquid (NAPL) contaminations are a groundwater issue which has gained increasing worldwide attention since the 1980s. NAPLs able to dissolve into groundwater can cause severe environmental problems and health risks, as well as being notoriously difficult to remove. Numerical modelling of contaminations is an important method of understanding and predicting the extent of NAPL spills. This study builds on previous NAPL source and plume modelling work using MODFLOW and MT3DMS, and aims to investigate methods of improving modelled plumes’ replication of observations in the field. Field observations conducted by means of wells generally show high variability in dissolved plume concentrations with depth, a feature not displayed by the previous study’s results. The problem was approached from several angles. Firstly, a comparison of different advective transport solvers was performed. Results of using the Third-Order TVD (ULTIMATE) solution method instead of the Modified Method of Characteristics (MMOC) were compared. It was found that numerical dispersion was not to blame for the lack of variability in modelled plumes, and that using the higher-order solution scheme had negligible improvements on the situation. Dispersive mixing was explored as another influence on downstream characteristics. The results of this part of the investigation were inconclusive, as plumes displayed strong homogenisation with distance from the source zone as would be expected if dispersion was strong. However, varying aquifer dispersivity values had negligible effects. The final area of investigation was source zone strength (retention capacity) and distribution. This was found to be the single greatest influence on plume characteristics in the domain. The distribution of NAPL-contaminated nodes in the vertical and horizontal dictated plume shapes and concentrations in proximity to the source zone. In an effort to create conceptually sound source zones, a capillary pressure-based invasion percolation model was written. It successfully generated source zones which replicated natural NAPL behaviours such as pooling and residual fingering. Plumes from these zones, however, also suffered from the excessive dispersion of other cases. Variable plumes were only found in simulations where there was little NAPL mass involved and the majority of it was located at the downstream end of the source zone. Future work should investigate reasons for the unpredictable dispersion results. It is hypothesised that having a finer grid discretisation and thus modelling NAPL source zone processes at scales closer to the pore scale would result in simulated plumes which closer resemble field observations.
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<th>Term</th>
<th>Definition</th>
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<tbody>
<tr>
<td>[M], [L], [T]</td>
<td>Mass, length and time – units of measurement upon which all metric units are based</td>
</tr>
<tr>
<td>( \Delta x, \Delta y, \Delta z )</td>
<td>Symbol for a change of finite size in each of the three Cartesian directions</td>
</tr>
<tr>
<td>C or ( C^k )</td>
<td>Dissolved concentration of species ( k )</td>
</tr>
<tr>
<td>( C_L )</td>
<td>Correlation length</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetres</td>
</tr>
<tr>
<td>d</td>
<td>Days</td>
</tr>
<tr>
<td>D</td>
<td>Hydrodynamic dispersion coefficient ([L^2/T])</td>
</tr>
<tr>
<td>( D^* )</td>
<td>Molecular diffusion coefficient ([L^2/T])</td>
</tr>
<tr>
<td>dynes</td>
<td>Units of force, 1 dyne = ( 10^{-5} ) Newtons</td>
</tr>
<tr>
<td>g</td>
<td>Gravity, ( 9.81 ) m/s(^2)</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>( h_p )</td>
<td>Height of water providing pressure head above a point ([L])</td>
</tr>
<tr>
<td>i, j, k</td>
<td>Principal MODFLOW coordinate system directions</td>
</tr>
<tr>
<td>k</td>
<td>Intrinsic permeability ([L^2])</td>
</tr>
<tr>
<td>K</td>
<td>Hydraulic conductivity ([L/T])</td>
</tr>
<tr>
<td>L</td>
<td>Litres</td>
</tr>
<tr>
<td>m</td>
<td>Metres</td>
</tr>
<tr>
<td>MMOC</td>
<td>Modified Method of Characteristics</td>
</tr>
<tr>
<td>MODFLOW</td>
<td>The US Geological Survey’s Modular Groundwater Model</td>
</tr>
<tr>
<td>MT3DMS</td>
<td>Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems</td>
</tr>
<tr>
<td>NAPL</td>
<td>Non-aqueous phase liquid – may be referred to as dense non-aqueous phase liquid (DNAPL) or light non-aqueous phase liquid (LNAPL)</td>
</tr>
<tr>
<td>P</td>
<td>Pressure ([M/L/T^2])</td>
</tr>
<tr>
<td>( P_c )</td>
<td>Capillary pressure</td>
</tr>
<tr>
<td>( P_d )</td>
<td>Displacement (entry) pressure</td>
</tr>
<tr>
<td>q</td>
<td>Darcy flux ([L/T])</td>
</tr>
<tr>
<td>Q</td>
<td>Flow rate ([L^3/T])</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>r</td>
<td>Radius of curvature</td>
</tr>
<tr>
<td>$S_s$</td>
<td>Specific storage</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>ULTIMATE</td>
<td>Universal Limiter for Transient Interpolation Modelling of the Advective Transport Equations</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Velocity [L/T]</td>
</tr>
<tr>
<td>V</td>
<td>Volume of geologic material total [L$^3$]</td>
</tr>
<tr>
<td>$V_v$</td>
<td>Volume of void space [L$^3$]</td>
</tr>
<tr>
<td>$v_x$, $v_y$, and $v_z$</td>
<td>Velocities in the three principal Cartesian directions</td>
</tr>
<tr>
<td>z</td>
<td>Elevation head [L]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Compressibility of aquifer skeleton</td>
</tr>
<tr>
<td>$\alpha_L$, $\alpha_{TV}$, $\alpha_{TH}$</td>
<td>Dispersivity values – longitudinal, vertical and horizontal</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Compressibility of water</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Interfacial tension [dynes/cm] or [N/m]</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity</td>
</tr>
</tbody>
</table>
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First and foremost I would like to thank my supervisor for this study, Dr. David Reynolds, for his continuing advice, encouragement and assistance with the broader concepts of the project. Thank you for helping me find a project that I found interesting (even in the closing weeks!), and suggesting new directions.

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1 Introduction

Non-aqueous phase liquids (NAPLs) are a contaminant group whose serious subsurface contamination impacts have only been fully recognised since the early 1980s (Pankow et al. 1996). They can be grouped into those which are denser than water (Dense non-aqueous phase liquids or DNAPLs) and those which are less dense than water (Light non-aqueous phase liquids or LNAPLs). LNAPLs tend to float on the water table and are easier to detect than DNAPLs, which are able to penetrate below the water table and beyond. DNAPL contaminants include polychlorinated biphenyls (PCBs), chlorinated solvents, coal tar and creosote, whilst petroleum and fuel oils are the most common LNAPLs.

DNAPLs in particular have several key properties which give them unique groundwater contamination abilities, such as low interfacial tensions with water and low degradation by biological or chemical means. Relatively speaking, DNAPLs have solubilities high enough to cause groundwater contamination to levels much higher than human health tolerances (Feenstra et al. 1996). They differ from other contaminant types because their plumes can come from persistent sources below the water table which remain there and continue to contribute contaminants on a long term basis. For the past few decades, significant research has been conducted into understanding NAPL migration and plume development, in a bid to be able to better remediate spills and prevent further contamination of vital groundwater resources.

To be able to analyse how NAPLs have contaminated field sites, and predict contamination patterns, computer modelling can be employed. The migration of NAPLs in the subsurface is strongly influenced by aquifer properties and heterogeneity (Feenstra et al. 1996). Complete site characterisation of NAPL contaminants and aquifers is impossible with present technology due to costs and the microscopic nature of soil variations. Aquifer characteristics such as hydraulic conductivity can be replicated to a reasonable level of realism using statistical methods. These create aquifer domains with properties linked to probability distributions, which can be modelled to find their groundwater flow schemes.

Contaminant modelling has been done by adding a contaminant solving package to an aquifer’s numerical groundwater solution. The results of these simulations can vary greatly depending on
the computational packages used, the simulated aquifer properties and the simulated contaminant zone properties.

Several past modelling studies have investigated how NAPL source characteristics such as the distribution and mass can influence plume development. One such study by Jones et al. (2005) confirmed previous findings that aquifer heterogeneity and source zone properties had a significant influence on plume characteristics over a certain distance downstream. However, the domain modelled in the study showed a lack of variability in well concentrations, unlike field observations. This thesis was borne out of this study, and utilised the same aquifer domain for further investigation. It was hypothesised that varying the source zone’s mass and distributions, and investigating the conceptual basis behind it, could lead to an improvement in this situation. Investigation of the numerical solution techniques as well as other aquifer parameters used for the domain was also identified as an important area of research.

The main objectives for this thesis were thus:

1. To investigate the use of different contaminant transport solving techniques and assess their effects on plume results.
2. To test the sensitivity of the NAPL plume to dispersion, and assess whether dispersion parameters could be used to improve the plume’s variability near the source zone to better mimic field situations.
3. To further investigate NAPL source zone characteristics’ effects on plume development, and if possible construct source zones with a conceptual basis which improved the NAPL plume variability.

This dissertation describes the background behind the NAPL problem and groundwater contamination modelling techniques. It describes the methods of investigation used for the above three objectives in detail, followed by a presentation and discussion of all numerical modelling results.
2 Background & Past Work

The following section provides background information related to this thesis’ topic, and describes similar work undertaken in the past. It describes basic groundwater flow principles, and the groundwater flow equation as solved through modelling is explained. A general explanation of subsurface contaminant transport processes is presented, and the contaminant transport governing equations and the meanings of each term are explained. These two sections form the theoretical basis of the study.

The background information then explores the idea of non-aqueous phase liquid (NAPL) contamination of groundwater, this being the specific problem dealt with in this study. Some history and general characteristics of NAPLs are described. Following this a detailed description of the macro- and microscale dynamics of NAPL migration is given, along with an examination of information available on NAPL plume development and how it can be modelled.

The section finishes with a summary of previous work undertaken this area, including a description of the results of the specific paper which led to the inception of this study.

2.1 Groundwater flow fundamentals

On the broad scale, groundwater forms part of the Earth’s natural hydrologic cycle (Fetter 2001). Subsurface water is classified into different zones depending on the state of saturation, although hydrogeologists are usually most interested in the saturated zone (Bear 1979). Below the land surface, where there exists both air and water, is the unsaturated or ‘vadose’ zone. In this zone, water is at a lower pressure than atmospheric pressure. Travelling deeper into the subsurface, just before the water table, there exists a transitional area known as the capillary fringe. In this area, the pores between soil grains contain water approaching 100% saturation, however, capillary forces (which will be explained in greater detail at a later stage) hold the water in place. Below the capillary fringe, the pores are fully saturated with water, hence leading to this zone being named the saturated or ‘groundwater’ zone. The top of this zone which forms a groundwater
Background & Past Work

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The surface is known as the water table. Water below the water table is able to flow as groundwater, and in this area, the water pressure is higher than that of the atmosphere (Fetter 2001).

Groundwater flow is linked to energy conservation concepts. It has mechanical, thermal and chemical energy, although for the purposes of this study only the mechanical aspect is considered. In terms of mechanical forces acting upon groundwater, the first and most obvious is gravity which pulls water downward. The second force is external pressure, specifically atmospheric pressure and the pressure of overlying water in the saturated zone. The third force is molecular attraction, which causes water to stick to solid surfaces. Surface tension is caused by molecular attraction. The combination of adherence to solid surfaces and the existence of surface tension is responsible for capillarity (Fetter 2001), which is an important principle to this study in terms of both water and NAPL contamination.

2.1.1 Hydraulic head

Hydraulic head is a measure of the total energy of a fluid (Fetter 2001). Groundwater mechanical energy is made up of gravitational potential energy, kinetic energy, and fluid pressure energy. When these components are combined, the result is the familiar Bernoulli energy equation:

\[
\frac{v^2}{2g} + z + \frac{P}{\rho g} = \text{constant}
\]

Equation 2.1

where \(v\) is the velocity of the fluid [L/T], \(g\) is gravity [L/T^2], \(z\) is elevation above a reference elevation or datum [L], \(P\) is the pressure [M/L/T^2], and \(\rho\) is the fluid density [M/L^3]. Note that this equation measures all terms in units of energy per unit weight, or m (Fetter 2001).

If typical groundwater velocities are assumed to be small, the velocity component of Bernoulli’s equation, being small compared to the other two terms, vanishes, and the hydraulic head can be written as:

\[
h = z + \frac{P}{\rho g}
\]

Equation 2.2

For a fluid which is at rest, the pressure at a point is equal to the weight of overlying water per unit cross-sectional area (Fetter 2001):
\[ P = \rho g h_p \]

**Equation 2.3**

where \( h_p \) is the height of the water above the point providing a pressure head. This can be substituted into Equation 2.2 as follows;

\[ h = z + h_p \]

**Equation 2.4**

meaning that total hydraulic head is the sum of the elevation head and the pressure head, measured in units of \([L]\). The diagram below explains this. A well sunk into a subsurface groundwater zone under pressure is shown, and the components contributing to total hydraulic head are indicated.

![Diagram explaining elevation head and pressure head](image)

**Figure 2.1 Explanation of elevation head and pressure head contribution to total hydraulic head**

The elevation head at point P corresponds to the gravitational potential energy at that point due to the height above the datum (the bottom of the aquifer). The pressure head corresponds to the height of water above point P which is causing pressure downwards.

Where there is a difference in hydraulic head between two points, a hydraulic gradient is said to exist. Groundwater will flow in the opposite direction to this gradient, that is, from areas of higher to lower head. As groundwater flows from high to low head, it loses energy in the form of heat (Fetter 2001).

**2.1.2 Aquifer and soil characteristics**

Different subsurface areas can be classified into types depending on their groundwater transport abilities. An aquifer is defined as a geologic unit which can store and transport water at sufficient rates to supply reasonable amounts to wells (Fetter 2001). Sands and gravels, sandstones, etc.
limestones and dolomites are examples of aquifers. Aquifers may be unconfined or confined. A confined aquifer is bounded by impervious layers both above and below, while an unconfined aquifer has the water table serving as its upper boundary and can be recharged from the ground surface above (Bear 1979). Confining layers are further classified as aquitards, aquicludes and aquifuges (Fetter 2001). An aquitard is a layer of low permeability which can store groundwater and transport it slowly between aquifers, and can also be called a semipervious formation. An aquifuge is absolutely impermeable to water and does not contain nor transmit water. An aquiclude is placed conceptually between the previous two definitions, as while it may contain water, it does not transmit it in significant quantities (Fetter 2001; Bear 1979).

The following sections elaborate on aquifer characteristics, concentrating on measurable characteristics which are used as model parameters throughout this study.

**Porosity**

The porosity of a geologic material is the percentage of it which is void of solid material. Mathematically, porosity is found using the equation:

\[
\phi = \frac{100V_v}{V}
\]

**Equation 2.5**

where \( n \) is the porosity percentage, \( V_v \) is the volume of void space \([L^3]\), and \( V \) is the unit volume of geologic material, including voids and solids \([L^3]\) (Fetter 2001). Porosity will depend on the shape of porous medium grains and the distribution of grain sizes present. If grains were perfect spheres, they would pack tightly, lowering the porosity. A wide range of grain sizes means that smaller grains will fill the gaps between larger ones, also lowering porosity (Fetter 2001).
Specific storage

Specific storage is the amount of water per unit volume of a saturated porous medium that can be stored or expelled from storage due to compressibility of the medium’s solid structure and the pore water per unit change in head. It is a quantity applicable to both aquifers and confining layers. Specific storage is found by the following equation:

\[ S_s = \rho_w g (\alpha + \phi \beta) \]

Equation 2.6

where \( \rho_w \) is the density of water \([M/L^3]\), \( g \) is gravitational acceleration \([L/T^2]\), \( \alpha \) is the compressibility of the aquifer skeleton \([1/(M/LT^2)]\), \( \phi \) is porosity \([L^3/L^3]\), and \( \beta \) is the compressibility of the water \([1/(M/LT^2)]\) (Fetter 2001).

Hydraulic conductivity

Hydraulic conductivity \((K)\) is a measure of how easily a fluid may pass through a porous medium. It is a function of the permeability of the porous matrix, as well as fluid properties (Bear 1979; Fetter 2001).

Permeability, or intrinsic permeability, is solely dependent on the properties of the porous medium. It is a function of the size of the pore openings between which fluids move. It is given the symbol \( k \), and has the units \([L^2]\) (Fetter 2001).

The equation relating hydraulic conductivity \((K)\) to permeability is as follows:

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Equation 2.7

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

where \( K \) has the units [L/T], \( \rho \) is the fluid density [M/L\(^3\)], \( g \) is gravitational acceleration [L\(^2\)/T], and \( \mu \) [M/T/L] is the dynamic viscosity of the fluid, which is a measure of its resistance to shear forces causing fluid motion.

It follows that there is a wide range of possible permeability values for porous media containing different materials. Unconsolidated coarse sediments such as gravels and sands have higher permeabilities and allow water to pass more freely than clays, which have lower intrinsic permeabilities (Fetter 2001). The following table, modified from (Fetter 2001) displays typical order-of-magnitude permeabilities and hydraulic conductivities for known sediment types.

<table>
<thead>
<tr>
<th>Material</th>
<th>Intrinsic permeability [m(^2)]</th>
<th>Hydraulic conductivity [m/d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>(10^{-18} - 10^{-15})</td>
<td>(10^6 - 10^{15})</td>
</tr>
<tr>
<td>Silt, sandy silts, clayey silts, till</td>
<td>(10^{-12} - 10^{-13})</td>
<td>(10^3 - 10^4)</td>
</tr>
<tr>
<td>Silty sands, fine sands</td>
<td>(10^{-14} - 10^{-12})</td>
<td>(10^2 - 1)</td>
</tr>
<tr>
<td>Well-sorted sands, glacial outwash</td>
<td>(10^{-12} - 10^{-10})</td>
<td>(1 - 100)</td>
</tr>
<tr>
<td>Well-sorted gravel</td>
<td>(10^{-11} - 10^{-9})</td>
<td>(10 - 100)</td>
</tr>
</tbody>
</table>

Table 2.1 Typical intrinsic permeability and hydraulic conductivity values for sediments (modified from Fetter 2001)

These values show that with all other values held constant, water will flow through gravel at a much faster rate than through clay, for example. These values can also be used as a rough guide in modelling studies such as this one, to obtain a better concept of the type of material being represented.

**2.1.3 Groundwater flow equations**

In order to model groundwater flow, governing equations must be numerically solved. Groundwater flow theory begins with the most basic of equations, known as Darcy’s Law, in one dimension. For the purposes of modelling three dimensional flow and contaminant transport in an aquifer such as the one in this study, this must be expanded to include conservation of energy and mass, and the final result of this is the Laplace equation solved by MODFLOW.
**Darcy’s Law**

Darcy’s experiments of the mid-1800s investigated the migration of water through a porous medium. It was found that the rate of flow through a bed of a “given nature” is proportional to the difference in hydraulic head between two points, and inversely proportional to the length of the flow path (Fetter 2001). In addition, it was also found that the flow is proportional to a value related to the nature of the porous medium, namely hydraulic conductivity $K$:

$$Q = -KA \left( \frac{h_A - h_B}{L} \right)$$

**Equation 2.8**

$Q$ is the flow rate $[L^3/T]$, $h_A$ and $h_B$ represent the heads at points A and B between which the flow is being calculated $[L]$, and $L$ is the flow length $[L]$ (Fetter 2001). The negative sign is necessary in keeping with the mathematical convention relating to gradients, as it indicates that flow is the direction opposite to the hydraulic gradient. Equation 2.8 can be expressed more generally as:

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

**Equation 2.9**

where $dh/dl$ is the notation used for a head difference $dh$ over a small distance $dl$. A new factor, $q$, known as specific discharge or Darcy flux, is expressed by the following:

$$q = -K \left( \frac{dh}{dl} \right)$$

**Equation 2.10**

$q$ is not a true velocity, as it assumes flow through an open pipe and does not take into account the fact that water is only able to flow through the pores between solid grains. To find the actual groundwater velocity, the Darcy flux is divided by porosity:

$$v = \frac{q}{\phi}$$

**Equation 2.11**

Darcy’s law has been found to only be valid for conditions where resistance due to viscosity dominates. This means that groundwater must be slow-moving without turbulence for it to be applicable; under natural groundwater conditions turbulence does not occur (Fetter 2001)
Three-dimensional groundwater flow

Groundwater flow in three dimensions can be described by partial differential equations (PDEs) written in terms of the $x$, $y$ and $z$ directions and time $t$. They are written based on Darcy’s law and conservation principles. Firstly, conservation of mass assumes that there is no net change in mass of the fluid in the aquifer, and additionally, conservation of energy states that energy in a closed system can change from one form to another but cannot be created nor destroyed. Note that these equations apply to confined aquifers, as this study’s domain is a representation of one. Using a control volume approach and applying Darcy’s law to each dimension, the following three-dimensional groundwater flow equation can be derived:

$$\frac{\partial}{\partial x} \left( K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial h}{\partial z} \right) = S \frac{\partial h}{\partial t}$$

Equation 2.12

$K_x$, $K_y$ and $K_z$ are hydraulic conductivity tensors which state hydraulic conductivity for each Cartesian direction in terms of that direction as well as the other two directions (Fetter 2001). In three-dimensional flow each $K$ tensor will thus be a $3 \times 3$ matrix of scalar values. Equation 2.12 is the PDE solved by groundwater flow programs such as MODFLOW as in this study.

If it is assumed that there is no change in head over time, such as situations where the water table remains at a constant height, ‘steady state’ is assumed, with the result that the right hand side of Equation 2.12 becomes zero. We then have the three-dimensional partial differential equation known as the Laplace equation:

$$\frac{\partial}{\partial x} \left( K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial h}{\partial z} \right) = 0$$

Equation 2.13

These equations, being for a confined aquifer, assume that all flow in the aquifer is generated from water stored within the aquifer, with no leakage occurring from above (Fetter 2001)

2.2 Contaminant transport

This study models the behaviour of a dissolved plume originating from a NAPL source zone. Thus a description of solute transport theory in a porous medium is presented in this section as background information. The partial differential equation for contaminant transport is presented,
although not all of its terms were solved for in simulations. As with aquifer characteristics such as hydraulic conductivity, using mathematical equations to solve solute transport is limited by knowledge of site characteristics. Dissolution processes are understood fairly well presently, however solute transport processes are highly complex and solving the governing equation with limited field data can reduce the accuracy of results (Fetter 2001). The processes of advection, molecular diffusion and mechanical dispersion are explained by means of theory and past studies in the coming sections.

2.2.1 Three-dimensional contaminant transport equation

The partial differential equation which describes the fate and transport of a contaminant species $k$ in three dimensional transient groundwater flow systems is as follows:

$$\frac{\partial (\theta C^k)}{\partial t} = \frac{\partial}{\partial x_i} \left( \phi D_{ij} \frac{\partial C^k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i C^k) + q_s C_s^k + \sum R_i$$

Equation 2.14

where:

- $\phi$ = porosity of the medium [1]
- $C^k$ = dissolved concentration of the species $k$ [ML$^{-3}$]
- $t$ = time [T]
- $x_{i,j}$ = distance along the Cartesian coordinate axis in question [L]
- $D_{ij}$ = hydrodynamic dispersion coefficient tensor, [L$^2$T$^{-1}$]
- $v_i$ = seepage/linear pore water velocity [LT$^{-1}$]; related to the Darcy flux, specifically $v_i = q_i / \theta$
- $q_s$ = volumetric flow rate per unit volume of aquifer – represents fluid sources (positive) and sinks (negative).

This is the equation solved by MT3DMS, the Modular Three-Dimensional Multispecies transport model developed at the University of Alabama (Zheng & Wang 1999) and used in this study. The final two terms on the right hand side of Equation 2.14 refer to source/sink fluxes and chemical reaction fluxes.
2.2.2 Advection

Advection is the movement of contaminants due to the groundwater flow only, and at the same rate (Zheng & Wang 1999; Fetter 2001). The authors of the MT3DMS documentation state that advection dominates contaminant transport in many field-scale problems. Measuring the degree of advection domination can be done using the dimensionless Peclet number Pe:

$$Pe = \frac{|v|L}{D}$$

Equation 2.15

where $v$ is the absolute value of the seepage velocity vector $[LT^{-1}]$, $L$ is the characteristic length, usually taken as the grid cell width $[L]$, and $D$ is the dispersion coefficient $[L^2T^{-1}]$. When Pe is large, advection dominates, and for purely advective problems, Pe approaches infinity (Zheng & Wang 1999). Advection-dominated problems are sometimes prone to numerical problems (Zheng & Wang 1999). One of these, numerical dispersion, is a focus of this study, and will be discussed in greater depth in Section 2.6. Modelling work has shown that when the Peclet number decreases due to dispersion ($D$) at the pore scale increasing, there will be a ‘smoothing’ effect on contaminant concentration profiles, specifically the mean and standard deviation (Fiorotto & Caroni 2002).

2.2.3 Diffusion

Diffusion describes the movement of solutes from areas of high concentration to lower concentration. Diffusion of a solute through water can be described using Fick’s laws (Fetter 2001; Hemond & Fechner-Levy 2000).

$$F = \frac{D}{C}$$

where $F$ is the solute mass flux per unit area per unit time $[M/L^2T]$, $D$ is the molecular diffusion coefficient $[L^2T^{-1}]$, $C$ is the solute concentration $[M/L^3]$ and.

For cases where the concentration is changing with time, Fick’s second law is used, namely:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Equation 2.16

where $\partial C/\partial t$ is the rate of change of concentration with time $[M/L^3T]$, $\partial C/\partial x$ is the concentration gradient $[M/L^3/L]$ and $D$ is the molecular diffusion coefficient $[L^2/T]$. 

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Equation 2.16 is for one-dimensional situations, and for three-dimensional problems more general forms are needed (Fetter 2001). The equation above also uses a diffusion coefficient applicable to pure water. In porous media, diffusion is slower due to the dissolved species following longer pathways around mineral grains. To correct for this, an effective diffusion coefficient $D^*$ must be established:

$$D^* = wD$$

Equation 2.17

where $w$ is an empirical coefficient found through laboratory experiments, typically ranging between 0.5 to 0.01 for species which do not adsorb to the mineral surface (Freeze & Cherry 1979).

Diffusion controls the initial dissolution of a NAPL as well as influencing its further dilution downstream (Feenstra & Guiguer 1996). However, in areas of active groundwater flow the consensus is that diffusion effects are generally very small compared to those of the bulk water movement, and only increase in importance at very low flow velocities (Freeze & Cherry 1979; Zheng & Wang 1999).

2.2.4 Dispersion

Dispersion refers to the spreading of contaminants over a greater area than would occur from advection alone (Zheng & Wang 1999). It is made up of molecular diffusion (as discussed in the previous section) and mechanical dispersion. Molecular diffusion is based on solute movement due to concentration gradients, whilst mechanical dispersion occurs due to microscale deviations in flow from the mean groundwater velocity. These two processes are summed and together termed hydrodynamic dispersion or simply dispersion (Zheng & Wang 1999). For a ‘pulse’ source of contaminant, dispersion causes the concentration at the centre of mass to continually decrease, while for a ‘steady’ source such as the one in this study, concentrations at any point down-gradient will constantly increase (Reynolds 2005). Mixing which occurs along the streamline of fluid flow is termed longitudinal dispersion, while mixing occurring orthogonally to the flow direction is termed transverse dispersion (Fetter 2001).

Longitudinal dispersion occurs due to the following factors: (1) As fluid moves through a pore space, it will flow faster through the centre than along the edges; (2) Some of the fluid will have

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to travel longer pathways than other fluid; (3) Fluid travelling through larger pores will flow faster than fluid travelling through smaller pores. Figure 2.3 below illustrates these factors.

![Figure 2.3 Factors causing pore-scale longitudinal dispersion (Fetter 2001)](image)

Transverse dispersion is caused when a fluid flows through a porous medium but is diverted to the side. This occurs even in the laminar flow conditions found in most natural groundwater (Fetter 2001). The figure below visually demonstrates this phenomenon.

![Figure 2.4 Lateral dispersion of contaminant due to grain orientation (Fetter 2001)](image)

For dispersion in three dimensions, a hydrodynamic dispersion tensor needs to be defined. The method used for this study uses a horizontal transverse dispersivity, or $\alpha_{TH}$, and a vertical transverse dispersivity $\alpha_{TV}$ as proposed by Burnett and Frind (1987). Six dispersivity tensors consisting of three in the principal $x$, $y$ and $z$ directions and three cross terms are thus defined, although for brevity’s sake the equations for these are omitted here. Using these tensors, the dispersion term of the contaminant transport equation can be solved using modelling software such as MT3DMS.
2.3 Non-aqueous phase liquids (NAPLs)

Non-aqueous phase liquids, or NAPLs, the contaminant group of concern in this thesis, are a major source of groundwater contamination worldwide, but have only gained proper recognition in the last few decades (Pankow et al. 1996). NAPLs can be split into two subsections – those which are denser than water, or dense non-aqueous phase liquids (DNAPLs), and those which are less dense than water, or ‘light’ non-aqueous phase liquids (LNAPLs). Common DNAPL contaminants include polychlorinated biphenyls (PCBs), chlorinated solvents, coal tar and creosote, while petroleum and fuel oils are the best known LNAPLs. For the purpose of this thesis, where the modelled NAPL source zone is located below the water table, the focus of background information will be on DNAPLs, although some results from previous studies involving LNAPLs have proven useful. Additionally, though it is well known that vapour-phase NAPLs in the unsaturated zone also cause dissolved NAPL plumes to develop (Schwille 1988), information on the unsaturated zone is also kept to a minimum.

Background

Chlorinated solvents and other halogenated organics are by far the most commonly known DNAPL contaminants. While usage of chlorinated solvents began in Germany in the 19th century, widespread use only began during World War II, and increased during the next three decades (Pankow et al. 1996). Similarly to petroleum products, chlorinated solvents are generally produced and used in their organic, liquid form as ‘neat’ or ‘free-phase’ liquids. In their dissolved form in water supplies, they are found between the μg/L(ppb) and mg/L(ppm) concentrations. Chlorinated solvents differ from petroleum products in that they do not stop at the water table when released in substantial quantities. Once spilled, DNAPL sources are difficult to find, whereas petroleum products, being lighter than water (i.e. LNAPLs) float on the water table where they are easier to detect. Historically, DNAPLs were only found rarely in wells, so proper recognition of the groundwater problems caused by them only occurred with the development of analytical methods which determined dissolved organic contaminants at the μg/L and mg/L level (Pankow et al. 1996)
Impacts

Mackay & Cherry (1989) calculated that the dissolved solvents in a collection of plumes up to several kilometres in length contained the equivalent of 0.5-70 drums of neat solvent. An unpublished study of more than thirty other major chlorinated solvent sites shows that these results hold true. These amounts only represent small fractions of the presumably larger amounts of solvent that originally entered the ground. Thus, significant source zones probably exist and continue to feed plumes on a long-term basis (Pankow et al. 1996).

There are many more LNAPL groundwater spill sites than DNAPL contaminated sites. However large LNAPL plumes are rare compared to DNAPL plumes. This is due to their difficulties in penetrating far below the water table, and the fact that most mobile LNAPL components are susceptible to biodegradation (Pankow et al. 1996).

DNAPL spills are generally exceptionally difficult to remediate. Cases have occurred where plumes have reached drinking water wells at concentrations high above drinking guidelines. Steps must be taken in such cases, but it may often be more cost effective to contain further release of contaminant by controlling or isolating the source zone, rather than complete remediation. In cases where plumes reach hydrologic boundaries such as rivers or lakes, mass is transferred into these waters. However, surface water impact is usually negligible or nonexistent because of volatilisation and dilution. Surface water body remediation may not be justified in many cases as chlorinated solvents do not accumulate in food chains, unlike contaminants such as PCBs (Pankow et al. 1996).

Key properties

The following are key properties of DNAPLs as listed by Pankow (1996) which are responsible for their unique groundwater contamination ability, although they are found in some form in most DNAPL-related texts:

1. Highly volatile – traditional views were that depositing solvents to the unsaturated zone was acceptable, as they would easily volatilise upwards into the atmosphere. However, in reality, some is transported downwards into the subsurface through gaseous diffusion, some through infiltration of contaminated water, and some as a ‘free’ DNAPL phase. Volatility is also of little help in removing solvents once they reach the saturated zone, as transport across the capillary fringe can be very slow.
2. **High densities** – high densities relative to water mean that in sufficient quantities, DNAPLs can migrate below the water table. In the saturated zone, unstable solvent flow causes thin ‘fingering’ which can lead to accumulation of the liquid in ‘pools’ on top of low-permeability layers. Pools have a low cross section with respect to oncoming groundwater flow, and thus removal rates of dissolved solvent will generally be very low.

3. **Low viscosities** – this property allows rapid downward motion of chlorinated solvents in the subsurface. Basically, the higher the density/viscosity ratio in a NAPL, the more mobile it will be.

4. **Low interfacial tension** – between liquid DNAPL phase and water allows easier migration of the solvent into pores and fractures. This causes deep penetration. The same property also means that soils have low retention capacities for chlorinated solvents.

5. **Low absolute solubilities** – When sufficient solvent is spilled on the ground, pure DNAPL phase will be able to migrate through the ground more effectively, and may gather as a pool above a low permeability zone. Having a low solubility means that this pool could potentially feed plume development for decades or centuries.

6. **High relative solubilities** – A solvent spill can thus cause contamination to levels higher than human health tolerances.

7. **Low partitioning to soil materials** – Retardation of solvents due to sorption to soil particles plays a less significant role in their migration, and they can thus move at essentially the velocity of the groundwater.

8. **Low degradabilities** – (by biological or chemical means) - mean that their longevity in the subsurface can be high.

All of the above properties have direct implications on the fate of DNAPLs, and are important considerations when building conceptual models of DNAPL source zones such as the one in this study.

### 2.4 DNAPL migration

DNAPLs behave differently to other contaminants in the subsurface, as they are normally observed in more complex distributions which are strongly influenced by aquifer heterogeneity.
Factors affecting DNAPL subsurface behaviour can be described qualitatively, resulting in conceptual models for this behaviour and the ultimate fate of a DNAPL.

Prior to the proper recognition of the DNAPL problem there was no specific set of theories to deal with DNAPL behaviour. As a result DNAPLs were treated under the general paradigm applied for many decades to all types of contaminated groundwater sites, where the assumption was that contamination occurred due to aqueous wastes or leaching of contaminants above the water table (Feenstra et al. 1996). Under the DNAPL paradigm, however, it is acknowledged that contaminants in the groundwater can come from persistent DNAPL sources below the water table. Onsite, much of an infiltrated DNAPL contaminant is capable of remaining as a long term source of ‘residual’ and/or ‘free-phase’ DNAPL. Plumes developing from these source zones often travel large distances to eventually impact water supply wells or surface waters (Feenstra et al. 1996).

Figure 2.5 Typical DNAPL spill showing residual and pooled DNAPL, vapour and dissolved phases (Fetter 2001)
2.4.1 Capillary pressure

The primary control over DNAPL entry into porous or fractured media is capillary pressure (Feenstra et al. 1996; Reynolds 2005). Capillary pressure is the result of the fact that between two immiscible fluids such as water and DNAPL, there exists a tension at the interface known as the interfacial tension. While the shape of the macroscopic boundary between a DNAPL and water in the subsurface is controlled by gravity, interfacial tension controls fluid boundaries at the pore scale, and the orientation of these boundaries may be quite different (McWhorter & Kueper 1996). Another reason for capillary pressure being the main control over DNAPL migration is that the media which DNAPLs typically try to infiltrate have small pore or fracture openings (Feenstra et al. 1996).

Wettability and interfacial tension

Wettability is defined as a fluid’s affinity for a solid surface when in the presence of a second fluid (Reynolds 2005). Qualitatively, the fluid with the greater affinity for the solid is the ‘wetting’ fluid, while the fluid with a lesser affinity is the ‘nonwetting’ fluid. In laboratory and field experiments, typical DNAPLs are nonwetting on porous medium solids with respect to water, and wetting with respect to air (Feenstra et al. 1996). However, the wettability of a given system depends on the surface chemistry of the solid material, the groundwater composition and the DNAPL composition, all of which can vary considerably. Thus, at actual field sites, wettability relationships may be much more complex (Feenstra et al. 1996). For the capillary pressure relationships in this study, however, a simplified approach was taken where DNAPL was assumed to be the nonwetting fluid. In this situation, water coats the soil grains and occupies the smaller openings and pore throats, restricting the DNAPL to the larger ones. When the DNAPL is the nonwetting phase, its entry into wet geologic media is resisted by capillary forces (Feenstra et al. 1996).
When two immiscible fluids come into contact, the cohesive forces of each fluid (the tendency for like molecules to stay together) are unbalanced, creating an interfacial tension (McWhorter & Kueper 1996). The two fluids will form a curved interface whose area is as small as possible. Interfacial tension is expressed as a force per unit length, and is usually given the symbol $\sigma$, with the units of dynes/cm.

**Capillary pressure and displacement pressure**

To relate capillary pressure to interfacial tension and the pore size, a force balance at the curved surface, as performed in Corey (1994), results in:

$$\Delta P = \sigma \left[ \frac{1}{r_1} + \frac{1}{r_2} \right]$$

Equation 2.18

where $\Delta P$ is the pressure difference, $\sigma$ is the interfacial tension, and $r_1$ and $r_2$ are the principal radii of curvature of the interface. The fluid on the concave side of the interface, or the nonwetting fluid, has the higher pressure. If the interface is assumed to form part of a perfectly spherical shape, then $r_1 = r_2 = r$, and the capillary pressure equation

$$P_c = \frac{2\sigma}{r}$$

Equation 2.19

results (Corey 1994). For most water-DNAPL systems, interfacial tension ranges from 20 to 50 dynes/cm, although again this can be more complex in the field due to DNAPL mixtures or chemical degradation (McWhorter & Kueper 1996). The relative wettability of a DNAPL-water...
system to a solid is manifested through the contact angle which they make with the solid, and this can be added to Equation 2.19, however in many cases including this study, this is omitted and the DNAPL is presumed to be perfectly nonwetting. A simplified capillary pressure equation relating the wetting and nonwetting fluids is:

\[ P_c = \Delta P = P_{nw} - P_w \]

Equation 2.20

where \( P_{nw} \) is the pressure of the nonwetting fluid, and \( P_w \) is the pressure of the wetting fluid. In addition, when there are two immiscible fluids such as a DNAPL and water, the hydrostatic pressure equation can be used to calculate the capillary pressure at their interface, in this case, the bottom of a pool of DNAPL:

\[ P_c = \Delta \rho g z \]

Equation 2.21

where, when applied to this study, \( \Delta \rho \) is the density difference between fluids \([\text{M/L}^3]\), and \( z \) is the vertical depth below a datum, in this case the upper boundary of the model domain.

Although the geometry of a pore space is complex, it is possible to simplify this to the concept of a network of spaces connected by smaller pore throats. DNAPL has to overcome capillary tension in order to migrate further. To do this, it has to deform, and the pressure required to achieve this deformation is called the entry or displacement pressure of a given throat (Reynolds 2005; McWhorter & Kueper 1996). This value is proportional to the interfacial tension between the DNAPL and the water, and inversely proportional to the pore throat size. Once the displacement pressure is exceeded, DNAPL is able to form a connected pathway macroscopically and infiltrate as a ‘network’ into the medium. This means that a DNAPL trying to enter a medium with very fine grains requires high driving forces to overcome the high displacement pressures. In the field, low permeability zones can thus act as barriers to DNAPL migration (Reynolds 2005; Kueper & Frind 1988; McWhorter & Kueper 1996).

Leverett (1941) proposed the following scaling equation relating displacement pressure to porous media characteristics:

\[ P_d = \frac{P_{d0} \sigma}{\left(\frac{k}{\phi}\right)} \]

Equation 2.22
where \( P_d \) is the displacement pressure, \( P_d^0 \) is a scaling pressure, \( \sigma \) is the interfacial tension, \( k \) is the intrinsic permeability, \( \phi \) is the porosity and \( \lambda \) is an exponent related to the porous medium. Leverett’s equation used a \( \lambda \) of 0.50, while other capillary pressure laboratory experiments found results ranging between 0.40 and 0.50 (Kueper & Frind 1988). This particular ‘threshold’ capillary pressure is possibly the largest single control on the migration path in the subsurface (Reynolds 2005; McWhorter & Kueper 1996), and thus influences the final structure and fate of DNAPL sources there.

**Saturation**

There is a relationship between the relative amounts of water and DNAPL present and the resulting capillary pressure. Saturation describes the relative volumes of interstitial fluid occupied by each of the wetting and nonwetting fluids. The relevant equations are:

\[
S_w = \frac{V_w}{V_v} \quad (a)
\]

\[
S_{nw} = \frac{V_{nw}}{V_v} \quad (b)
\]

\[
S_w + S_{nw} = 1 \quad (c)
\]

**Equation 2.23**

where \( V_w \) and \( V_{nw} \) are the volumes of wetting and nonwetting fluids and \( S_w \) and \( S_{nw} \) are their corresponding volumes as a fraction of total pore space (McWhorter & Kueper 1996). There exists a relationship between saturation and capillary pressure, and this has to be measured for any given situation due to the complexity of pore space geometry (McWhorter & Kueper 1996). A capillary pressure curve shows the relationship between the two values for a given material and given fluids. The process of a DNAPL first invading a medium is called drainage. Imbibition is the process during which the ‘back end’ of a DNAPL body migrates away from the source and is replaced by water (McWhorter & Kueper 1996; Reynolds 2005). The relationship between capillary pressure and saturation is not the same for these two processes. Capillary pressure curves can also yield the displacement pressure for a given medium. Experiments such as Corey’s have shown that for most media, displacement pressure is achieved at water saturations of between 0.8 and 0.95 (Corey 1994).

### 2.4.2 DNAPL migration

As introduced in the previous section, the rate of migration of a DNAPL through a porous medium can be highly irregular (Kueper et al. 1993), and depends on: 1) the DNAPL density and
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viscosity; 2) the pressure driving the DNAPL; 3) the intrinsic permeability of the medium, and 4) the degree of DNAPL saturation (Feenstra et al. 1996). Higher density and lower viscosity DNAPLs infiltrate faster. More permeable media and higher DNAPL saturations will also cause faster infiltration. Once DNAPL release has ceased, the forces driving its movement begin to decrease, until eventually the DNAPL in the pore spaces becomes disconnected. These remnants are known as residual DNAPL, and once formed, they require very large hydraulic gradients to be mobilised (Feenstra et al. 1996; Reynolds 2005; McWhorter & Kueper 1996).

DNAPLs are able to partition themselves amongst other phases in the subsurface, including DNAPL, water, air and the subsurface solid (Feenstra et al. 1996). Contaminant molecules thus seek an equilibrium distribution amongst these phases, where a defined contaminant concentration exists in each phase. There are four partitioning processes which are of interest when addressing DNAPL behaviour in the subsurface: 1) dissolution of DNAPL into water; 2) volatilisation of dissolved chemicals from water into air; 3) vaporisation of DNAPL into air; and 4) sorption of dissolved chemicals from water to solids (Feenstra et al. 1996). This thesis’ model results deal only with the first of these processes. In the field, however, partitioning as a DNAPL moves downwards through the unsaturated zone is responsible for a significant loss of DNAPL mass, and will mean that the final depth of DNAPL migration will be reduced. As a result, the bulk volume of the medium containing DNAPL will decrease, or expressed differently, the retention capacity of the medium for the DNAPL will decrease (Feenstra et al. 1996). The retention capacity is simply defined as the volume of NAPL divided by the overall volume of the porous medium within which the NAPL migration occurred, including soil, gas and liquid (Kueper et al. 1997). Typical retention capacities for silts, sands and gravel deposits range between 0.25 and 3% by bulk volume. The lower end of this range applies to more heterogeneous deposits without laterally extensive capillary barriers (Kueper et al. 1997).

Residual and pooling

The diagram below from Feenstra et al. (1996) illustrates the unpredictability of DNAPL migration. Even though good geological information is often available on the macroscale in the field, microscale differences in aquifer characteristics can strongly influence DNAPL migration (Feenstra et al. 1996). In c), DNAPL has been deflected horizontally from where it was originally released. Because the free-phase DNAPLs in a) and b) only penetrate to a relatively shallow

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Depth, their plumes also do not extend over the entire depth of the aquifer. Although this is an oversimplified diagram, a study by (Rolle et al. 2005) stated that vertical dispersion of DNAPL plumes in the field is not strong, corroborating it.

![Figure 2.7 Conceptual models for DNAPL migration - a) partial penetration, b) partial penetration with offset, c) full penetration with offset, d) same as c), but at later stage, but after residual has dissolved (Feenstra et al. 1996)](image)

In d), DNAPL has infiltrated throughout the depth of the aquifer, due to having a higher initial mass released. Residual DNAPL thus exists at all depths and contributes to a plume spanning the entire depth. Pooling of DNAPL has occurred at the bottom of the aquifer, above an aquitard. Pools such as these are rarely found in the field because site investigation techniques are not suited to their detection, and prohibitively high numbers of samples would need to be taken to find small to medium sized pools.

Feenstra (1996) stated that existing data shows residual DNAPLs occupy 2-15% of pore spaces, while pooled DNAPL was said to be capable of occupying 40-70%. Kueper (1993) found residual saturations of between 1 and 15%, while Anderson (1988) gave values between 15% and 40% in a coarser ‘Ottawa’ sand experiment. Even higher residual saturations of up to 43% were found by Chatzis (1981). These variations in possible residual saturations aside, the implications on the resulting permeability of the medium are obvious; pooled DNAPL will considerably slow groundwater flow and thus be completely dissolved much slower than the same mass in residual

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form. For example, in an experiment by Schwille (1988), a pool of TCE 1.5m x 0.5m x 0.2m containing 50L of contaminant in a sandy aquifer with a linear groundwater velocity of 275m/yr was predicted to need at least 100 years to be dissolved completely.

Residual DNAPL forms a distributed source which is immobile and susceptible to dissolution by groundwater, forming a dissolved phase (McWhorter & Kueper 1996). There is a finite maximum saturation of water when imbibition takes place and the water attempts to re-invade pore spaces. Residual DNAPL is made up of ‘blobs’ and ‘fingers’ (ganglia) which have become separated from the main infiltrating body by water (McWhorter & Kueper 1996; Reynolds 2005). The amount of DNAPL which separates from the main body depends on local pore geometry, pore topology, fluid properties, the imposed pressure gradient, and the amount of DNAPL present before displacement by water (McWhorter & Kueper 1996). Additionally, the amount of residual DNAPL is a function of the initial saturation by that DNAPL. If a large number of pores and pore throats are initially invaded, then a higher number of pores will contain residual liquid (Kueper et al. 1993).

Pool formation occurs when a DNAPL encounters an aquitard or area of lower pore size (McWhorter & Kueper 1996). This is due to the driving force behind the DNAPL being unable to overcome the displacement pressure of the area (Kueper et al. 1993). Two things may happen in this situation; either the DNAPL release may stop and the system will remain static, or the DNAPL pool will continue to build in height and/or horizontal extent until the capillary pressure eventually surpasses a critical value, at which point it will penetrate the aquitard or spill over the edge of the low permeability zone (Kueper et al. 1993; McWhorter & Kueper 1996; Feenstra et al. 1996). Kueper’s 1989 experiment, using TCE infiltrated through sand lenses, showed that even after penetrating a lens of lower permeability, pooling and lateral movement of DNAPL would still occur above the lens. The two main conceptual outcomes of that study were that 1) in the field, there would be significant lateral flow of DNAPL where heterogeneities existed; and 2) that vertical migration of a DNAPL will always be accompanied by some degree of lateral spreading.
The study was limited in that it used very well defined sand lenses in the laboratory, with sharp changes in permeability unlike those seen in nature. However it did show qualitatively how pooling occurs, and related capillary pressure to pooling phenomena, which is important to the percolation approach taken later in this thesis.

Replicating DNAPL flow through the saturated zone has been investigated in several literary sources, in the forms of laboratory experiments and numerical modelling. The need for this type of research arises because the better understanding there is of the processes governing DNAPL migration in the subsurface, the more accurate numerical simulations will be in predicting the source zone extent and resulting plume characteristics. The next section reviews prior research in the plume area.
2.5 **DNAPL dissolution and plume development**

Plume shapes and concentration distributions are a function of DNAPL solubilities, groundwater velocities, the mass and distribution of the DNAPL material, the medium’s pore size distribution, and the aqueous-phase diffusion coefficient of the DNAPL (Feenstra & Guiguer 1996). Chemicals are initially dissolved and transferred into the flowing groundwater by means of molecular diffusion due to the concentration gradient at the DNAPL-water interface (Feenstra & Guiguer 1996). The local equilibrium assumption is often made when modelling dissolution. It assumes that mass transfer between phases occurs instantaneously compared to the bulk flow rates of the phases (Kueper & E.O. 1996), which implies that the mass fractions of components are uniformly distributed within all phases at all times. Laboratory and numerical modelling studies have shown that groundwater exiting residual DNAPL source zones does so saturated with dissolved DNAPL. Pools yield lower plume concentrations because of their reduced contact with flowing groundwater. In the field, saturated concentrations are rarely found in plumes, because of natural variabilities in the distributions of residual and pooled zones, dispersion processes and dilution in wells with tall screens (Feenstra et al. 1996).

Once dissolution has occurred, dispersion can influence DNAPL plumes. According to Feenstra (1996), several studies in the 1980s showed that dispersion was ‘almost without exception’ weak, particularly in the transverse direction. This disagreed with other studies, examples of which are given in the next section, such as a recent one by Ibaraki (2001). Clearly there was a need to assess dispersion’s effects on the specific model domain in this study. Feenstra (1996) was in agreement with Ibaraki (2001) and Jones et al. (2005) when it stated that source zone configurations, especially shape and size, are very influential on plume characteristics. Density of the DNAPL within the plume is not influential enough to cause plumes to sink as they flow away from the source zone (Feenstra et al. 1996)
The mass flux of contaminant is often more informative than the mass of the plume or its concentration profile (Feenstra et al. 1996). It is found by multiplying the plume concentrations by the groundwater fluxes through cross-sections orthogonal to the mean flow direction. This plume flux is equal to the mass dissolution rate of the DNAPL close to the source zone, but will change due to transformations as one moves down-gradient (Feenstra et al. 1996).

### 2.6 Modelling of groundwater contamination

Groundwater contaminations can be simulated over time using numerical methods to construct domains and to solve for groundwater flow and contaminant transport. This study uses these techniques to model a typical DNAPL contamination and its resulting dissolved plume. The following section provides a brief review of numerical methods and more detailed information on DNAPL and plume modelling studies.

Numerical models are used instead of analytical solutions when boundary conditions are complex or where parameter values vary within the model area (Fetter 2001). The governing equations...
need to be recast in algebraic form. These new equations are numerical approximations and thus their solutions are also numerical approximations (Fetter 2001).

Transforming a conceptual model into a mathematical model requires a database providing enough information to apply to the equations. All models begin with a groundwater flow model, which requires certain knowledge of the physical makeup of the aquifer, including its location, areal extent, aquifer and confining layer thicknesses, locations of surface water bodies and boundary conditions of all aquifers. Necessary hydraulic properties include the variation of transmissivity or permeability and storage coefficient of the aquifer, variations in permeability and specific storage of the confining layers, and hydraulic connections between surface water and aquifers. Hydraulic energy or hydraulic head, natural recharge and natural stream flows are also needed. Stresses on the system need to be modelled, including natural and artificial recharge, and changes in streams and surface water body levels (Fetter 2001).

Solute transport models require additional data to the flow model data. Effective porosity distribution, aquifer dispersivity values, density variations in the fluid, and natural solute concentration distributions in the aquifer are all required knowledge. Locations and strengths of contaminant sources must be known, as well as retardation factors for the solutes, rocks and soils in question. Once the flow model has run and produced a solution for fluid motion in the domain, the solute transport model is run and the solutions for retardation values and contaminant movement are added (Fetter 2001).

### 2.6.1 Modelling groundwater flow

The finite difference method is used for modelling groundwater flow by replacing a continuous conceptual model with a grid (finite difference grid). It is the most popular solution method for large aquifer systems, as it is conceptually and algebraically simple, with firm theory behind its implementation (Huyakorn & Pinder 1983). Equations are solved at each node point on the grid for unknowns such as hydraulic head. Known values such as hydraulic conductivity are also assigned to each node. There are types of finite difference grid – a block-centred grid with nodes at centre of each cell, and a mesh-centred grid, where nodes are placed at intersection of grid lines. Boundary conditions govern the choice between the two types – a block-centred grid is best when a flux is specified across a boundary, while a mesh-centred grid is better for models where
the head is fixed at the boundary (Fetter 2001). The basic grid is regular, with rows/columns perpendicular to each other and cells which are equilateral ($\Delta x = \Delta y$), although these sizes can be varied within the grid to model areas of interest in higher detail (Huyakorn & Pinder 1983). To solve the groundwater flow equation, boundary conditions need to be specified, in the case of this model, constant head boundaries.

2.6.2 Modelling of DNAPL migration

Modelling and laboratory investigation of DNAPL migration through the saturated zone is performed with the aim of being able to produce realistic source zones which behave as similarly to reality as possible. The following section describes concepts of DNAPL migration and source zones and highlights the need for a realistic source zone to be used in a study such as this one.

Initial downward migration of DNAPLs is mainly due to gravity, while lateral motion generally occurs when downward motion is prevented by low permeability lenses (Kueper et al. 1993; McWhorter & Kueper 1996; Feenstra et al. 1996; Ewing & Berkowitz 1998). Capillary “fingering” also occurs, with the resulting DNAPL distribution often found to be highly complex (Willson et al. 2006), and dependant on the displacement pressure distribution of the subsurface material (Kueper & Frind 1988).

It is possible to model capillary fingering using invasion percolation based models, using a decision-making process at the pore scale (Ewing & Berkowitz 1998). Ewing & Berkowitz (1998) developed an invasion percolation model where cells were assigned an ‘invadability number’ selected randomly or dependent on pore size. At each time step, the most invadable cell along the interface was invaded, and then added to the continually increasing list of invaded cells. Simulated behaviour at first resembled ‘lightning bolts’ through the medium, and failed to resemble field behaviour where several parallel fingers or more complex structures develop. Lateral movement as found in the field and supported in Kueper’s 1989 experiments was also not simulated. Adding randomness through stochastic selection of both the next independent finger to be invaded and the next invaded cell within this finger resulted in more realistic distributions. The work resulted in faster NAPL migration simulation, bearing in mind that the solution domain was only a 2.57m square. The limitation of this approach is that capillary fingering occurs at the pore scale, and pore size distributions can vary at the centimetre scale in natural systems (Kueper
Background & Past Work

& Frind 1988). Computational limitations mean that currently, as also stated nearly twenty years ago in Kueper & Frind (1988) it is not yet possible to model capillary fingering in a model domain of this study’s size at the true scale at which it occurs. A study by Gerhard (1993) used a heterogeneous, log-normally distributed sand aquifer, with 32 000 nodes, with a $\Delta x$ of 25cm and a $\Delta y$ of 12.5cm, and TCE was allowed to infiltrate from a point source. Figure 2.10 shows the results, with darker areas representing lower permeabilities. So while a source zone can be modelled at a discretisation scale which is reasonable small, to use this discretisation over a full model domain of the size of this study’s would be prohibitively demanding on computer hardware.

![Figure 2.10 TCE migration in heterogeneous aquifer from Gerhard (1993). Darker aquifer areas represent lower permeabilities.](image)

Another study by Anderson (1988) used a complex DNAPL source zone containing ‘fingers’ and pools in a 15m deep sandy aquifer and simulated its resulting plume. The figure below shows a projection of this source zone looking up-gradient, giving a good concept of what can be achieved in source zone modelling.
Residual DNAPL saturations, sizes and shapes are as yet unable to be linked through a model to porous media characteristics (Willson et al. 2006), so residual saturations are usually user-defined according to common known values. Porous media and fluid characteristics are used to govern the migration of DNAPL in this thesis, and the resulting source zone is then checked against known realistic values of DNAPL saturation.

### 2.6.3 Modelling of plume development

The contaminant transport equation can be solved for all its terms, however in this study, only the advection and dispersion terms were solved. There is still no single technique which produces completely satisfactory solutions under general hydrogeologic conditions (Zheng & Wang 1999).

Most methods can be classified as Eulerian, Lagrangian, and mixed Eulerian-Lagrangian. Eulerian methods use a fixed grid and solve using the finite difference methods, are mass conservative, and handle dispersion/reaction dominated problems well. However, for advection-dominated problems which exist often in the field, numerical dispersion and artificial oscillation can occur. Figure 2.12 shows examples of these two phenomena. Numerical dispersion acts to ‘smear’ concentration fronts artificially where they should be sharp, and similarly, artificial oscillation due to higher order methods can cause solutions to over- and undershoot their true values. To alleviate these problems, demandingly small grid sizes or time steps may be needed (Zheng & Wang 1999). Lagrangian approaches use particle tracking to solve both the advection and dispersion terms, in either a deforming grid or deforming co-ordinate in a fixed grid.
Advection-dominated problems can be solved with virtually no numerical dispersion, but without a fixed grid, numerical instabilities can occur when there are complex boundary conditions. Mass balance errors and the production of a ‘rough’ concentration solution which requires smoothing and interpretation after runs are other problems (Zheng & Wang 1999). Mixed Eulerian-Lagrangian approaches such as the Modified Method of Characteristics (MMOC) combine advantages of both methods, by using particle tracking for the advection term and a finite difference method for dispersion. Mass conservation cannot be guaranteed in some of these methods, and particle tracking can again lead to numerical errors. Computational efficiency can also be lower than the two separate methods. (Zheng & Wang 1999).

Figure 2.12 Diagrams showing the effects of numerical dispersion and artificial oscillation in contaminant transport modelling (Zheng & Wang 1999)

More recently, the total-variation-diminishing (TVD) set of techniques has been developed. TVD refers to the fact that over successive transport steps, the sum of the concentration differences between adjacent nodes diminishes to reduce unwanted oscillations. TVD methods are higher order finite difference methods and are mass conservative. While they reduce numerical dispersion, unwanted oscillations can develop, and flux limiters are usually used to nullify this.

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer
TVD schemes are generally much more accurate when solving advection-dominated problems, but have high computational demands. Compared to some Lagrangian and mixed Eulerian-Lagrangian methods such as the method of characteristics, TVD methods are not as effective in nullifying numerical dispersion while preserving concentration ‘peaks’, but their mass conservation, lower memory requirements, and some other advantages make them an excellent compromise between standard finite-difference and particle tracking based Lagrangian or mixed Eulerian-Lagrangian methods (Zheng & Wang 1999).

Mehl & Hill (2001) investigated several contaminant transport solution techniques including the modified method of characteristics (MMOC) and the TVD method, comparing them to laboratory results in contamination of a 2-D sand tank. Their results showed the MMOC to have shorter model execution times, but it suffered from substantial numerical dispersion. The TVD method had a modest execution time in their particular study, with very little numerical dispersion. There is clearly a need for investigation of the best solution technique for a given situation.

### 2.7 Stochastic methods

Modelling of groundwater flow can be limited by the high spatial variability of real aquifers in terms of parameters such as hydraulic conductivity and porosity. It is practically impossible to measure hydraulic conductivity, for example, at all locations. This creates uncertainty in groundwater flow modelling (van Leeuwen 2000). Hydraulic conductivity is probably the most important of these, as it is able to vary by orders of magnitude over only a few metres, while porosity in contrast is more homogeneous, with a maximum range of variation of only 15-35% (van Leeuwen 2000). Aquifer materials are the end product of geological processes with deterministic and stochastic components. Random field generators can be used to exploit the stochastic aspect and artificially generate aquifer property fields which are reasonable resemblances of reality (Robin et al. 1993).

#### 2.7.1 The natural-log normal distribution

A natural-log normal distribution is a probability distribution where the natural log of the random variable set is normally distributed. A distribution of this type can be defined by its mean $\mu$ and
its variance, $\sigma^2$. Previous studies of aquifer heterogeneity suggested that hydraulic conductivity values can be approximated by a natural-log normal distribution (Hoeksema & Kitanidis 1985; van Leeuwen 2000), in the following way:

$$Y = \ln X$$

**Equation 2.24**

where $X$ represents hydraulic conductivity, usually $K$. Deriving the natural-log normal distribution from the normal distribution results in:

$$f_X(x) = \frac{1}{x\sigma_Y\sqrt{2\pi}}\exp\left[-\frac{(\ln x - \mu_Y)^2}{2\sigma_Y^2}\right]$$

**Equation 2.25**

where $\mu_Y$ and $\sigma_Y$ are the mean and standard deviation of $Y$. As the variance is increased, the natural-log normal distribution becomes more skewed to the left. In order for permeability fields to be generated, $\mu_Y$ and $\sigma_Y$ must be specified in inputs to a random field generator.

The mean and variance of aquifer materials can be calculated from field measurements, and typical values for a host of aquifer materials is available in literature such as Gelhar (1993).

### 2.8 Past work

Many of the previous works already mentioned share elements with this study’s topics, however two in particular had very similar aims and used similar techniques to this one. Jones et al. (2005) in particular, being the paper which asked the questions leading to the formulation of this study, is described in this section, along with Ibaraki (2001). Both papers investigated NAPL source zones and plumes through modelling.

Ibaraki (2001) used a three-dimensional domain, infinite in the y- and z- directions, and semi-infinite in the x-direction, with a 25m x 5m source zone located at $x=0$. Jones et al. (2005) used a 300m x 45m x 15m domain with a 15m x 7.5m x 5m source zone.

Ibaraki investigated how contaminant plumes were influenced by the overall contaminant mass in the source zone, and found that as the source coverage ratio decreased, irregularities in concentration profiles near the source zone became more pronounced. This confirmed many field
studies which indicated that assuming complete coverage of the source zone by NAPL ‘hotspots’ was an overestimation of the problem (Ibaraki 2001).

Both Ibaraki and Jones et al. found that contaminant plumes eventually homogenised downstream from the source zones, becoming less variable in terms of concentration distribution. Near Jones et al.’s source zone, plume concentrations were variable, and attributed to the NAPL’s vertical distribution. They were lower than the solubility limit, in fact low enough to suggest that concentrations were being reduced due to dispersive mixing. Down-gradient, however, there was a point past which information on the source zone characteristics was not necessary to ascertain source strength. Ibaraki investigated changing NAPL source patch distributions, and found that many smaller patches would allow transverse dispersion to smear mass strongly, resulting in lower near-source concentrations.

A limitation which was pointed out in Jones et al. (2005) was that the concentration distributions near the source zone were not as variable as seen at many field sites, with very ‘smooth’ concentration fronts in contrast to highly variable preferential flow in the field, with a specific focus on the vertical concentration distribution. Figure 2.13 shows an increase in plume concentration with depth until a maximum concentration is reached, followed by a decrease of similar magnitude. This lacked the sudden changes in concentration found at field sites. Source zone characteristics were pointed out as a possible reason, as their distributions in the study were assigned to the highest hydraulic conductivity cells, in predefined source coverage percentages. This gave distributions where NAPL spread fairly uniformly over the entire zone in many small patches. Dispersion was also a possible reason, as in Ibaraki’s study as well as others such as (Rolle et al. 2005), increasing transverse dispersivity increased the efficiency of mixing and thus smeared the plume concentrations further.
Figure 2.13 Vertical contaminant distributions from Jones et al. (2005) showing smooth contamination fronts without significant concentration variability

Clearly there existed a need to further investigate certain model parameters’ influence on the NAPL plume in Jones et al. (2005). Numerical solution techniques for the contaminant transport equation could have caused the excessively smooth distributions. Dispersion needed to be varied to test for sensitivity, especially dispersion’s effects on this particular model, as there was conflict in literary sources as to the magnitude of influence of dispersion. In addition, an attempt was to be made to supply a more realistic conceptual model for the DNAPL source zone, following a similar concept to that used in Ewing & Berkowitz (1998).
3 Methodology

Following from the study by Jones et al. (2005), and the questions about modelled plume variability it raised, certain areas of investigation were devised as possible solutions to the problem. These were mentioned at the end of Chapter 2, but they are repeated here as being the specific aims of the study:

1. To compare solute transport solver techniques, specifically MMOC vs. Third Order TVD (ULTIMATE)
2. To investigate hydrodynamic dispersion’s influence on plume variability, by varying dispersivity parameters
3. To further investigate source zone distributions and masses’ effects on the resultant plume.

All simulations were run on an Intel Pentium 4 2GHz PC, with 1024MB of RAM, running Microsoft Windows XP Professional, using the US Department of Defence’s Groundwater Modelling System (GMS) Version 6.0.

3.1 Domain

The modelled domain used for this study was identical to that used in Jones et al. (2005). It was not intended to replicate any specific field site. Instead, it was a hypothetical area with characteristics typical of known contamination sites, with some assumptions made for the purposes of modelling.

The domain size was chosen to be 300m in the x-direction (\(\Delta x = 0.75m\), 400 nodes), 45m in the y-direction (\(\Delta y = 0.75m\), 60 nodes) and 15m in the z-direction (\(\Delta z = 0.25m\), 60 nodes). The total number of nodes was thus 1,440,000. The previous study by Jones et al. (2005) chose this level of grid discretisation as a balance between model accuracy and computational effort. Having a finer mesh would have increased model accuracy and allowed finer heterogeneities to be modelled in the aquifer, however the computational time required would have become prohibitive.
Methodology

Figure 3.1 Illustration of model domain and source zone

The designated source zone for free-phase NAPL contamination was 15m in the x-direction ($\Delta x = 0.75m$; 20 nodes), 7.5m in the y-direction ($\Delta y = 0.75m$; 10 nodes) and 5m in the z-direction ($\Delta z = 0.25m$; 20 nodes). It was located 15.75m downstream in the x-direction from the origin, and centrally located in the y- and z- directions. The down-gradient boundary of the zone was located at $x = 0m$ for the purpose of observation well readings.

Observation wells were placed in the domain along a centreline at 7.5m intervals, starting at $x = 0m$ (i.e. the down-gradient boundary of the source zone). Unlike the previous study by Jones et al. (2005), which used 2m screened wells for the entire 15m depth, this study used 1.5m screened wells in an effort to gain higher vertical resolution. This was due to the fact that the vertical concentration distributions were more important to this study. It should be noted that in field situations wells screens below 2m in size are very rare (Reynolds 2006).
Another method of recording results was measuring contaminant fluxes taken across the y-z plane of the model domain. These could be taken at any point from x = 0m to the domain’s downstream end. Contaminant plume mass fluxes were calculated using a program which output the flux at each cell in g/d for every timestep (every 10 days for 500-day stress period), at a specified x-location. The program multiplied plume concentrations by the groundwater flux through these cross-sections which were orthogonal to the plume migration direction. The data was then visualised as the flux planes shown in this study’s results by means of a MATLAB m-file which used a pseudocolour plot to show differences in mass flux. The total flux through the plane at each timestep was also calculated. Results were generated at 30m intervals downstream from the source zone, for the situation at the end of the 500-day stress period.

### 3.2 Permeability field generation

#### 3.2.1 Field generation (FGEN91)

Hydraulic conductivity forms what is categorised as a spatially continuous random field (Robin et al. 1993). It varies continuously in space and can be defined by a mean, variance and spatial persistence of the correlation between neighbouring values and the cross-correlation between jointly varying parameters of interest. FGEN91 is a random cross-correlated field generator (Robin et al. 1993) which is able to create random fields suitable for input into a finite difference...
Methodology

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer

grid such as MODFLOW’s, when supplied with input parameters which are the descriptive statistics of the field to be generated. In this study, FGEN91 was used to generate a single field representing intrinsic permeability ($k$) of the entire aquifer. The resulting field was then imported into MODFLOW and converted to hydraulic conductivity ($K$) using Equation 2.7.

The descriptive statistics used for the permeability field were the mean $\mu$, the variance $\sigma^2$ and the correlation length $C_L$. The correlation length refers to the maximum distance at which spatial values have influence on one another. In this case, correlation length can be used to estimate the maximum size of lenses of similar hydraulic conductivity. FGEN 91 operates on the direct Fourier transform method (Robin et al. 1993), and the permeability field generated was a truncated version of a larger field with dimensions corresponding to a power of two. FGEN91 transforms dimensions with a power of two using the fast Fourier transform method instead of the regular Fourier transform method, with lower roundoff error (Robin et al. 1993), so it is much more efficient to specify larger fields with dimensions in powers of two. As the intended field size was 400 x 60 x 60 nodes, the larger field size was thus set to 1024 x 128 x 128 nodes. The field is also truncated from a larger one in this way to manage circular periodicity, a symptom of the transform process. Once running, FGEN91 will continuously attempt to generate fields corresponding to the input statistics until a field is generated in which no values exceed a user-defined maximum $k$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean $\ln(k)$</td>
<td>-25.6</td>
</tr>
<tr>
<td>Variance $\ln(k)$</td>
<td>2.02</td>
</tr>
<tr>
<td>Correlation lengths</td>
<td>10 x 10 x 2</td>
</tr>
<tr>
<td>Maximum value of $k$ $[m^2]$</td>
<td>0.0000000025956129</td>
</tr>
</tbody>
</table>

This table shows the parameter values used in creating the permeability field. The correlation length of 10 x 10 x 2 was taken from the base case used in (Zhu & Sykes 1999). According to Jones et al. (2005) these values are relatively large compared to those used in previous studies (eg. Mayer & Miller 1996; Kueper & Gerhard 1995; Essaid & Hess 1993). As the domain was larger than those studies’ domains, using similar correlation lengths would have required a much smaller grid discretisation and thus made the simulations prohibitively demanding in terms of computation time. The $C_L$ values and domain discretisation ensured at
least 4 nodal points in each correlation length direction and 10 correlation lengths in the domain, accepted as reasonable for the grid resolution in heterogeneous systems (Zhu & Sykes 1999).

### 3.2.2 Limitations of permeability field

Natural heterogeneities form due to complex geological processes, and spatial stochastic methods such as this one, which uses a natural log-normal distribution, do not take these processes into account when generating \( k \) fields (Koltermann & Gorelick 1996). This can sometimes result in geologically unrealistic values being created, however, Koltermann & Gorelick (1996) stated that aquifer heterogeneity is imitated to a satisfactory level by statistical methods. Sudden transitions in soil properties such as faults along different rock types are not accounted for in a natural log-normal distribution, and complex variabilities such as buried channels may also not be represented in these stochastic fields. This should be taken into account when interpreting the results from studies such as this one.

### 3.3 Groundwater flow – MODFLOW

The following section describes the methods employed while using the US Geological Survey’s computer package MODFLOW to solve for groundwater flow in the domain. It is not intended to be an exhaustive description of MODFLOW’s structure and its use of finite difference methods to solve the groundwater flow equation. Instead, these are summarised with the focus on the use of the package in this study to achieve its specific aims.

A new MODFLOW solution was required for each model run, firstly due to the program’s requirements, but more importantly because source zone changes from one simulation to another affected the permeability in contaminated cells. This meant that the permeability field would also change, affecting the MODFLOW solution each time.

#### 3.3.1 MODFLOW structure and operation

MODFLOW (Harbaugh et al. 2000) is the US Geological Survey’s modular groundwater model. Its program structure can be split into packages, procedures, modules, and processes. Packages each incorporate a specific hydrologic modelling capability, such as leakage, recharge and
evapotranspiration. Finite difference methods for solving the simultaneous groundwater flow equation, such as the Preconditioned Conjugate Gradient method (used in this study) are also classed as packages. Overall program control is given by the Basic (BAS) package. Procedures are each small pieces, which when grouped together represent the program logic, and are useful from the programming perspective. Modules each contain the program code within a single procedure for a single package, so that when a certain package is needed, all of its modules can be collected together (Harbaugh et al. 2000).

**Global process**

The global process does not actually solve any equation. Instead, it functions as an overall control of programs and files (Harbaugh et al. 2000).

Spatial discretisation in MODFLOW’s finite difference grid is rectangular horizontally, but can be distorted vertically to improve model detail in areas of interest. A new aspect of MODFLOW-2000 is that grid cells need to have their geometry completely defined for subsequent use by other processes such as transport models. Grid cells are numbered in the following way, with x, y and z being this study’s 3D direction nomenclature and corresponding to MODFLOW’s i-, j- and k- directions respectively: Columns (x- or j-direction) are numbered starting from the left side of the grid. Rows (y- or i- direction) are numbered from the top edge of the grid when it is seen from a plan view. Layers are numbered starting from the top layer downwards (Harbaugh et al. 2000).

![Figure 3.3 MODFLOW's finite difference grid layout (Zheng & Wang 1999)](image)

*Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer*
In terms of time discretisation, this study only applies a steady-state groundwater solution to the contaminant transport solver, so only a single time step was used.

**Groundwater flow process**

MODFLOW solves a variation of the 3D groundwater flow equation (Equation 2.12):

\[
\frac{\partial}{\partial x} \left( K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_{zz} \frac{\partial h}{\partial z} \right) + W = S, \frac{\partial h}{\partial t}
\]

**Equation 3.1**

The hydraulic conductivity tensors are changed to \( K_{xx} \), \( K_{yy} \) and \( K_{zz} \), the components of the \( K \) tensor parallel to the major axes. Anisotropy parameters entered into MODFLOW by the user substitute the other components of the \( K \) tensor. \( W \, [T^{-1}] \) is a volumetric flux per unit volume for representing sources and sinks of water in and out of the system, such as the recharge occurring in this study. MODFLOW solves Equation 3.1 using the finite difference method at each cell (node) in the grid. The specific packages added to find the groundwater flow solution in this study are described below.

**Layer-Property Flow (LPF) package**

The LPF package is an internal flow package in which all of the hydraulic parameters input by the user are independent of cell dimensions. It uses Darcy’s Law, rewritten in terms of conductances in both horizontal directions. There are three different ways of determining horizontal conductance – in this study the harmonic mean method was used, which assumes that transmissivity (hydraulic conductivity multiplied by aquifer/cell thickness) is constant within a cell and changes at the boundary between cells (Harbaugh et al. 2000). The LPF package accepted the generated field from FGEN91 once it had been converted into hydraulic conductivity \( K \).

**Sources and sinks – Recharge package**

The recharge package simulates the input of water to the aquifer through rainfall and infiltration. Recharge quantities are normally specified for each stress period, in this case only a single one.
MODFLOW allows three options: recharge at the top layer, recharge at specified vertical cells, and recharge at the highest active cell. The third option was used in this study.

3.3.2 Aquifer properties

The simulation grid was set to imitate a confined aquifer by setting the top layer (Layer 1) to ‘Confined’ in MODFLOW’s LPF package. Anisotropy was assumed to be 1 (i.e. isotropic from the point of view of MODFLOW) in the vertical and horizontal, with only the variations in K from the stochastic field providing heterogeneity. A hydraulic gradient of 0.02 was constructed over the 300m length of the domain, by means of setting constant head boundaries at either end. The hydraulic heads at the upstream and downstream ends were set at 100m and 94m respectively.

Recharge was set to occur at the highest active cell (in this case, the top layer of the aquifer), and was set to a value of 0.001 m/d.

<table>
<thead>
<tr>
<th>Hydraulic/physical parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic gradient</td>
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</tr>
<tr>
<td>Porosity</td>
<td>0.30</td>
</tr>
<tr>
<td>Mean K (original statistical input to FGEN91)</td>
<td>6.46 m/d</td>
</tr>
<tr>
<td>Horizontal and Vertical Anisotropy</td>
<td>1</td>
</tr>
<tr>
<td>Recharge</td>
<td>0.001 m/d</td>
</tr>
</tbody>
</table>

Table 3.2 Summary of aquifer physical and hydraulic properties

3.3.3 Limitations

Some aquifer parameters were left at constant values for the sake of simplicity in both Jones et al. (2005) and this study. Porosity is one example, where a constant value of 0.3 was used throughout. In nature, porosity can be highly variable, with Fetter (2001) stating that some sedimentary rocks can range in porosity from 1 to 30%. This impacts on the eventual contaminant transport equation solution, as porosity influences both the advection and dispersion...
terms. Holding porosity at a constant value could thus reduce the variability of contaminant transport velocity and dispersion between cells in the domain.

MODFLOW only models saturated flow, so transport of vapour in the unsaturated zone was not a part of this study. This limits the ability of a study using this modelling package to represent all the processes occurring in the subsurface on release of a NAPL contaminant, as the unsaturated transport phase is removed. While literature does state that vapour-phase NAPL is also capable of dissolving below the water table as part of a contaminant plume, modelling this process fell out of the scope of this study.

### 3.4 Contaminant transport – MT3DMS

The US Army Corps of Engineers’ MT3DMS (Modular Three-Dimensional Multispecies Transport Model) (Zheng & Wang 1999) was used to simulate advective, diffusive and dispersive transport of the contaminant plume from $t_0$ to $t = 500$ days. The MT3DMS contaminant transport simulation setup made similar assumptions to Jones et al. (2005).

#### 3.4.1 MT3DMS numerical implementation

MT3DMS uses the same spatial discretisation style as MODFLOW, as described in Section 3.3.1. Like MODFLOW, MT3DMS uses a block-centred finite difference grid approach for model parameterisation. This means that a node is placed at the centre of each cell and concentrations calculated there, while parameters such as dispersivities are assumed constant over the extent of a cell. This approach again reflects the importance of grid discretisations, and how they can limit a model’s effectiveness in reproducing a given process. The topic of grid discretisation as a limiting factor is explained further in later sections.

This study applied MODFLOW’s steady state solution to a single 500-day stress period of contaminant transport in MT3DMS. The single 500-day stress period was further divided into 10-day timesteps. Timesteps are further divided by MT3DMS into smaller time periods called transport steps, where heads from the groundwater flow solution are considered constant during solving, to satisfy stability and accuracy requirements. In the case of this and the Jones et al. (2005) study, the transport step was left at an input value of 0.0, which indicated that MT3DMS would choose the transport step size.
It was observed by the authors of both studies that the step size chosen by MT3DMS was heavily dependant on the characteristics of the heterogeneous K field. This also impacted computation time. Due to the source zone setup procedure explained in Section 3.5, where K was halved in cells containing NAPL, the field changed in any simulation where the source zone was altered. Even though the source zone accounted for less than 0.3% of the total grid volume, changing the source zone coverage ratio from 30 to 5% coverage, for example, resulted in a difference in simulation time of the order of a few hours.

### 3.4.2 Contaminant transport solver comparison

The two solution methods were compared by means of running each to solve a two-dimensional cross section of the simulated domain in the x-z plane. The comparison was done in this way because of trial simulations using the ULTIMATE scheme being too time-consuming when run on the full-sized domain. The cross-section was taken along the centreline of the grid., with the new dimensions being 300m in the x-direction ($\Delta x = 0.75m$, 400 nodes), 0.75m in the y-direction ($\Delta y = 0.75m$, 1 node) and 15m in the z-direction ($\Delta z = 0.25m$, 60 nodes), for a total of 24 000 nodes. All hydraulic and physical parameters were kept identical to the Jones et al. (2005) base case, including the heterogeneity field and the source zone distribution.
**Modified Method of Characteristics (MMOC)**

The MMOC is a mixed Eulerian-Lagrangian backward particle tracking solution technique. It solves a Lagrangian version of the contaminant transport equation, using a Lagrangian method in a moving coordinate system to solve for advection, and either the explicit or implicit finite-difference method on a fixed Eulerian grid for the other terms.

Unlike the MOC method, which tracks numerous moving particles forward in time and keeps track of the concentration and position of each, the MMOC places a single fictitious particle at the nodal point \( m \) of the fixed grid at each new timestep \( (n+1) \). The particle is then tracked backward to find its position \( p \) at the old timestep \( (n) \). The concentration at the old position is interpolated from concentrations at neighbouring nodal points using a first-order polynomial interpolation, and this value is used to approximate the concentration at \( m \) due to the effect of advection alone (Zheng & Wang 1999).

![Figure 3.5 Illustration of particle locations at nodal point \( m \) and old time level point \( p \) (Zheng & Wang 1999)](image)

The MMOC is a relatively fast solution scheme as it only uses a single particle for each cell. It also requires less memory because it starts tracking particles at nodal locations, so there is no need to store the particle identities in memory. When combined with a lower-order interpolation scheme for concentrations, the MMOC is free of artificial oscillations. However, this can cause significant numerical dispersion, especially for sharp front problems (Zheng & Wang 1999). This fact was the reason for this study investigating the merit of using the MMOC in previous work, as
there was the possibility that Jones et al.’s simulated plumes were suffering from the numerical dispersion problem.

**Third Order TVD (ULTIMATE) method**

The ULTIMATE method uses a third-order polynomial interpolation scheme for nodal concentrations, and additionally contains a flux limiting procedure which minimises unphysical oscillations due to sharp fronts (Zheng & Wang 1999). The ULTIMATE scheme is mass conservative, free of excessive numerical dispersion, and essentially oscillation-free.

The diagram below illustrates the ULTIMATE interpolation scheme. A regularly spaced finite difference grid superimposed by a local coordinate system with the origin at nodal point \( j \) is shown. Velocity runs positive from left to right, and \( \Delta t \) is the time step size between the old time level \( n \) and the new time level \( n+1 \).

![ULTIMATE scheme in one dimension](image)

The particle originates a distance of \( v\Delta t \) upstream, and after a time step \( \Delta t \) it arrives at nodal point \( j \). The concentration carried by the particle is thus the concentration at \( j \). Because the concentration at the old time level \( n \) generally is not located at a nodal point, it has to be interpolated from the concentrations at the three nearby nodes as shown. A third-order polynomial formula is used for this, requiring four nodal points. As is shown in Figure 3.6, the ULTIMATE scheme is biased towards the upstream direction in its interpolation (Zheng & Wang 1999). ULTIMATE’s flux limiter acts to adjust concentrations at the cell interfaces after they have first been interpolated by the polynomial process. If the concentration at the interface \( j+1/2 \) lies between the two neighbouring nodal concentrations as in \( j \), the concentration profile is said to
be locally monotonic with no spurious oscillation. If this is not the case, the flux limiter is needed.

To assess monotonicity, all concentrations are normalised. If monotonicity is confirmed, the \( C_{j+1/2} \) is kept as is, however if monotonicity is not satisfied then \( C_{j+1/2} \) is set to the concentration at the closest upstream node \( C_j \).

The use of the Generalised Conjugate Gradient (GCG) solver package was examined for its effects on the computational time under ULTIMATE scheme. Under normal settings, the ULTIMATE scheme is always explicit and subject to stability constraints (Zheng & Wang 1999). When the GCG package is activated, however, the implicit finite-difference method is used to solve the advection term, without stability constraints. The dispersion, sink/source and reaction terms are also solved together implicitly in this case. In the Jones et al. (2005) study, the GCG solver package was activated. In this study, when using the ULTIMATE scheme on the full-sized domain in early trial simulations, the GCG package was switched off to assess its impact on simulation time, and was found to have no notable effect.

### 3.4.3 Hydrodynamic dispersion effects

Based on literature (and to some degree based on the level of contradiction in these sources), hydrodynamic dispersion’s effects on simulated plumes was investigated. This was done by running successive simulations where the dispersivity values in MT3DMS’ Dispersion package were reduced by a set proportion. MT3DMS’ input capabilities provide for longitudinal...
dispersion to be varied cell-by-cell, although longitudinal dispersivity was kept at a constant value of 3m throughout the simulated grid as per Jones et al. (2005). Transverse dispersivity is input in the form of the ratios of vertical ($\alpha_{TV}$) and horizontal ($\alpha_{TH}$) transverse dispersivities to the longitudinal value, and can only be varied from layer to layer.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>$\alpha_L$, $\alpha_{T}/\alpha_L$, $\alpha_{V}/\alpha_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>3m, 0.025, 0.01</td>
</tr>
<tr>
<td>Dispersion Case 1</td>
<td>3m, 0.0125, 0.005</td>
</tr>
<tr>
<td>Dispersion Case 2</td>
<td>3m, 0.00625, 0.0025</td>
</tr>
</tbody>
</table>

Table 3.3 Dispersivity values used in MT3DMS simulations

3.5 Source zone conceptual approaches

The NAPL source zone was investigated with the knowledge that literature (see Section 2.8) had found it to be a significant influence on near-source plume characteristics. The original base case from Jones et al. (2005) was compared to simulations containing an invasion percolation-based NAPL source, as well as some other simplified NAPL source configurations. Contaminant concentrations were kept the same as the previous study (1000mg/L, constant for the 500 day period).

3.5.1 Original random assignment of DNAPL

The method used in the previous study and in the base case for this study was to first specify a percentage of source zone nodes which would contain NAPL (for example 10, 20 or 30%). A NAPL saturation of 10% within each contaminated node was assumed, and this assumption continued for all source zones in this study. The retention capacity of the source zone was controlled by altering the coverage percentage. A program run in MATLAB was then used to generate the necessary input files for MODFLOW and MT3DMS, which contained the source zone location and concentration information. The location of contaminated nodes was correlated to those nodes with high $K$ values. The permeability of contaminated nodes was then halved to replicate the known effect of NAPLs reducing the pore space available for groundwater flow. The retention capacity of any given source zone could be found by multiplying the assumed 10%
saturation by the source coverage percentage; this number was used for analysis of the relative source zones’ strengths.

3.5.2 Percolation of NAPL

One of the aims of this study was to create a more realistic source zone which took into account subsurface morphology to a greater extent. This was done by means of a simple invasion percolation model. The model was based on capillary pressure being the driving force of subsurface NAPL flow. As described by (Ewing & Berkowitz 1998) the model involved a basic decision-making process at the nodal scale based upon the displacement pressure at each node.

![Flow chart illustrating basis of capillary invasion decisions at the nodal scale](image)

All programming work for the percolation model was done using The MathWorks Inc.’s MATLAB 7. Displacement pressure was calculated based on Leverett’s equation (Equation 2.22). Table 3.4 describes these parameters. The $P_d$ at the surface for the initial ‘scaling’ calculation was set at 2000 Pa, interfacial tension $\sigma$ was 0.02 N/m, the scaling factor $\lambda$ was set at...
0.65, and the density of NAPL set at 2650 kg/m$^3$. The calculation resulted in a scaling $P_d^{0}$ of $4.407595 \times 10^{-2}$. Leverett’s equation, containing this value, was then applied to every node in the source zone to calculate their individual $P_d$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_d^{0}$</td>
<td>$4.407595 \times 10^{-2}$</td>
</tr>
<tr>
<td>Gravity (g)</td>
<td>9.81 m/s$^2$</td>
</tr>
<tr>
<td>Interfacial tension ($\sigma$)</td>
<td>0.02 N/m</td>
</tr>
<tr>
<td>$\rho$(H$_2$O)</td>
<td>1 000 kg/m$^3$</td>
</tr>
<tr>
<td>$\rho$(NAPL)</td>
<td>2 650 kg/m$^3$</td>
</tr>
<tr>
<td>Permeability for scaling calculation (k)</td>
<td>$5 \times 10^{11}$ m$^2$</td>
</tr>
<tr>
<td>Porosity $\phi$</td>
<td>0.3</td>
</tr>
<tr>
<td>Scaling factor $\lambda$</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 3.4 Parameters used in Leverett displacement pressure scaling calculation and subsequent cell-by-cell $P_d$ calculations

Once the cell-by-cell $P_d$ throughout the source zone was calculated, the $P_c$ of all source zone cells was set at the mean of the $P_d$ values. An earlier percolation model used the static equation (Equation 2.21) to calculate $P_c$ based on the depth below the aquifer’s upper limit, however this was too time consuming and was abandoned. In order to generate varying contaminant fields with different degrees of invasion, the $P_c$ of the source zone then had the option of being multiplied by a constant (eg. 1, 0.8, etc). The emphasis of the model was not mathematical and physical accuracy, but more on generating contaminations which looked qualitatively correct, similar to the fields in Anderson (1988) for example (see Section .

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer
Figure 3.9 Example of NAPL percolation in the study model: In Step 1, NAPL percolates downwards, in Step 2, being unable to percolate downwards it migrates laterally. The red cells were impermeable.

The NAPL source zone cells were then each assigned a ‘1’ or a ‘0’ in an ‘entry’ array, which indicated whether or not they were invadable. After a single cell for initial invasion was input by the user, the model loop began. At each ‘timestep’, each address on the list of cells invaded at the previous timestep was examined. If downward percolation into the cell immediately below was possible, this newly invaded cell was recorded. However, if it was not, the 4 cells horizontal to the cell in question were examined. If invasion was possible at any of these, they were recorded. Once each cell in the ‘previously contaminated’ list was checked in this way, all newly invaded cells were recorded to an overall list, as well as being used to overwrite the ‘previously invaded’ list, ready to be used in the next timestep. The percolation process continued in this way until the first cell in the bottom source zone layer was contaminated. At this point the model loop was broken, and the complete list of contaminated cells stored in memory. The rest of the MATLAB m-file was devoted to using this information to prepare the GMS 6.0 input files, namely the permeability file for MODFLOW (k was once again halved for contaminated cells, as in the random NAPL assignment base case), the ICBUND file specifying contaminant locations for MT3DMS, and the concentration file which set these locations to 1000 mg/L.
**Limitations**

The percolation model applied the concept of basic pore-scale capillary invasion with pool thickness and $P_c$ thresholds for infiltration of a layer (in this case cell) at the nodal scale used in this study. Thus it applied the correct principles albeit on a scale a few orders of magnitude greater (cell-by-cell, with cell sizes of 0.75m x 0.75m x 0.25m) than the scale at which these processes operate in the field. This is the result of grid discretisation and the associated computational limitations.

Note that NAPL pool thickness was not a factor in the invasion decision process of this model. While NAPL in this model will spread laterally depending on $P_c$ similarly to how literature explains occurs in reality, the modelled invasion of a low permeability lens is more limited in its methods. In reality, as well as flowing laterally until it reaches the edge of a lens, NAPL can also build up behind the stationary front until it reaches a thickness sufficient to exceed the lens’ $P_d$. In the model environment, however, the only way to pass a low permeability lens was for NAPL to...
flow laterally until it reached the ‘edge’ of the lens and could again percolate downwards. This means that NAPL pool thicknesses in the final source zone output may have been less than what they could have been in a field situation.

3.5.3 Other low-mass conceptual models

Further modelling was conducted using several low-mass conceptual models in attempts to increase plume variability. Structures representing pools, along with simple ‘lines’ of NAPL at the downstream edge of the source zone were inserted into the source zone and modelled for the same 500-day period.

For two ‘pool cases’, two 4.5m square-shaped pools, each 0.75m thick in the vertical direction, represented a situation where only pooled NAPL remained at a site, the residual having been flushed by groundwater. For the first case they were placed at the downstream end of the source zone, with a vertical distance between them of 1.5m. For the second case, this vertical separation was maintained, however the top pool was moved to the upstream end of the source zone to simulate a situation where NAPL had been deflected in its migratory path. For a third case, NAPL was deposited in two lines running the entire width of the source zone in the y-direction (7.5m), with a width of a single cell in the x-direction (0.75m) and a height of 0.75m.

![Figure 3.11 Simplified source zone diagrams for three low-mass cases, with red colouring representing NAPL](image-url)

*Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer*
4 Results

Results of numerical simulations are presented below in terms of averaged vertical concentration distributions (averages taken over 1.5m screens). An example of the Jones et al. (2005) base case concentration distributions alone can be found in Section 2.8. Well results were found using the Python 2.4 software, which ran a separate code for each well screen (10 in all), to find the concentrations there for each of the 50 timesteps. These results were generated over a few minutes for each screen. Flux planes taken at 30m intervals downstream of the source zone are also used to visualise the contaminant plume. Note that when referring to depth, the downwards direction was treated as positive, so for example, ‘increasing depth’ means moving downwards in a well from the highest elevation of the domain, shown on the plots as $z = 15m$.

4.1 Numerical dispersion

The vertical concentration distribution results for the two-dimensional MMOC and ULTIMATE solution scheme comparison are shown in Figure 4.1. The retention capacity of the base case source zone used was 2.8%, which was at the upper range of field estimates according to literature. It was slightly smaller than the 3.0% retention capacity in the three-dimensional base case due to the particular ‘slice’ of the base case which was used having a slightly lower number of contaminated nodes than average. The maximum well concentrations of the two solution schemes decreased with distance from the NAPL source. The concentrations of the MMOC technique follow the ULTIMATE solution closely in wells at close proximity to the source zone. With increasing distance from the source zone, differences in concentrations between the two schemes increase. At these distances (eg. at $x = 45m$), the MMOC concentrations showed more moderate variation with depth, meaning that when the concentration peak occurred at approximately 11m elevation above the domain bottom, this peak was a lower value than the peak of the ULTIMATE scheme. Similarly, at the other extreme, when the concentration decreased to values below 100 mg/L near $z = 0m$, the ULTIMATE solution gave a lower concentration than the MMOC. The ULTIMATE solution clearly gave greater concentration extremes, with this effect increasing with downstream distance from the source zone. However, the shape of the ULTIMATE concentration distributions was still smooth and highly similar to
the MMOC base case, showing only one gradual increase to a peak concentration over a depth of about 4m at the well closest to the source zone.

![Comparison of averaged vertical concentrations: 2-D MMOC vs. ULTIMATE](image)

**Figure 4.1** Effects of using two different advection solution techniques (MMOC vs. ULTIMATE) on vertical plume concentration distributions

### 4.2 Dispersive influences

The results comparing the base case and the two reduced dispersivity cases show little variation between cases. The maximum concentrations in wells in the three cases are very similar (starting near the solubility limit of 1000 mg/L at x = 0m), and decrease with distance from the source zone, to a concentration of approximately 350 mg/L at 45m from the source zone. Throughout these decreases the concentration differences between the base case and the dispersion case are negligible, although they do increase slightly with distance from the source. Overall the concentration profiles of all three cases showed the same single, smooth increase in concentration at the depths corresponding to the vertical position of the NAPL source zone.

*Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer*
Contaminant fluxes close to the source zone were highest directly in line with the zone, with a maximum flux of 283 g/d. The contaminant flux distribution at x = 0m was already spread to a greater extent in the vertical than the source zone’s 5m height, as shown in the corresponding base case colour plot in Figure 4.3. The deep blue areas can be considered to be zero or negligible flux. Travelling downstream, the areal extent of highest flux area (>30 g/d), shown in deep red, decreased, while there was a clear spreading of the overall low to moderate flux area, mostly in the y-direction. This area of main mass flux, when viewed in these planes, was also deflected to the left as it moved downstream, so that by the x = 60m mark (the bottom plot of each case in Figure 4.3) it had been shifted by an order of 5-10m. Another observed feature was the existence of blue areas of negligible contamination interrupting the red moderate to high flux zones; these are most obvious in the 60m-distance plots.

Differences between the base and lowered dispersion cases were more noticeable in contaminant flux planes than they were in vertical concentration plots. With decreasing dispersion, close to the source, the maximum flux was reduced. This effect continued downstream, with noticeably lower fluxes at the centre of the main plume body at the 30m and 60m distances. The cross-sectional
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area of this main plume body also decreased at all distances from the source zone with
decreasing dispersion, and the effect became more pronounced with distance.

Figure 4.3 Contaminant mass fluxes for a) base case, b) transverse dispersion /2, c) transverse dispersion /4.
For each simulation fluxes are shown, from top to bottom, for x = 0, 30 and 60m.
**4.3 Source zone influences**

The differences between source zones used in this study become apparent when they are compared in three dimensions. The first base case source zone taken from Jones et al. (2005), with a source zone NAPL coverage ratio of 30% assigned to high-K cells, produced the distribution seen in Figure 4.4. This shows NAPL fairly evenly spread throughout the zone without ‘clustering’ as created in Ibaraki (2001), or complex residual and pooled structures. Furthermore, the projection of the source zone in the y-z plane shows that groundwater flowing through the zone encounters at least one contaminated node at every single y-z location, and will thus acquire a concentration of 1000 mg/L at each of these locations. The retention capacity of this base case zone was calculated to be 3%, which is at the upper limit of literature field estimates.

![Source zone at 30% nodal contamination](image1)

![Projection of contaminated cells in y-z plane](image2)

*Figure 4.4 Schematics of NAPL source zone in 3-D and y-z projection for high-K assigned NAPL base case*

The first percolation model result (Figure 4.5), where $P_c$ was set at the mean $P_d$ yielded a source zone with a much lower retention capacity of 0.9%, having contaminated 358 cells out of a possible 4 000 in the source zone. There was significant lateral movement of NAPL simulated by the model, as well as residual ‘fingering’ in certain areas, observed as isolated vertical migration paths. The projection of this source zone yielded a coverage in the y-z plane of 64% which was significantly less than the base case zone’s 100%.
An even lower-coverage source zone was percolated, with $P_c$ set to 0.65 multiplied by the mean $P_d$. It resulted in a zone with a retention capacity of 0.40% (158 nodes contaminated), and with a coverage in the y-z plane of 30.5%. There were two visible areas of pooling as shown in the 3-D plot in Figure 4.6, as well as several simulated NAPL fingers. These results bore a strong resemblance to the work of Gerhard (1993) and Anderson (1988), as complex and more conceptually valid NAPL distributions were visible.

The results after modelling of the two percolated cases are shown below and compared to the base case. On plots, the ‘low mass’ notation refers to the second percolated source zone which used a mean $P_d$ multiplier of 0.65 and thus had a lower mass of NAPL. The vertical concentration

*Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer*
distributions show very little change in overall shape from the source zone. Once again as one moves downwards through wells, there is a gradual increase to a maximum concentration which is encountered at a depth corresponding to that of the source zone, followed by a similar gradual decrease as the bottom of the domain is reached. There was no significant variability observed other than this. The maximum concentrations did, however change between the three cases. At the 0m well, the first percolation case had a 938 mg/L maximum, compared to the 996 mg/L base case maximum. The lower-mass percolation case had a maximum concentration which was still lower at 708 mg/L. Thus, with decreasing retention capacity and groundwater exposure to contamination in the y-z plane, plume concentrations also decreased. Moving downstream the same homogenisation of the plume as seen in previous simulations occurred. The two percolated cases’ concentrations rapidly converged, and remained lower than the base case concentrations even at the 60m well location.

Contaminant flux results agreed with the concentration distribution results; the plume flux near the source zone was lower than the source zone for the first percolated case and lower still for the second. This trend of lower flux for lower-retention capacity cases continued downstream.

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer
Similarly, the areal extent of the main flux zone decreased at all distances with decreasing retention capacity, although the shape of the zone did not change. It was difficult to visually assess the variability of fluxes from case to case.

The results of the pooled NAPL source zone cases showed vertical concentration variability corresponding to the locations of the pools in both the z- and x- directions. These pools yielded a retention capacity of 0.54%, putting them in the lowest area of literature estimates, and if projected in the y-z plane similarly to Figures Figure 4.4 through Figure 4.6 they would have shown a coverage of 18%. Firstly, it was observed that instead of the single peak in concentration in the 0m well, there were two concentration peaks, which in the first case with level pools represented concentrations almost as high as the base case peak at 925 mg/L and 951 mg/L. These peaks corresponded roughly to the depths at which the two pool sources were located. In the second pool simulation case, where the upper pool was located at the upstream end of the source zone (an offset of 9.5m in the x-direction), there were still two concentration peaks, however the peak corresponding to the upper pool was significantly lower than in the previous case at 325 mg/L. Moving downstream, the concentration profiles homogenised as per usual, with the two pool cases in particular showing very similar profiles which were lower in concentration than the base case (up to 150 mg/L compared to base case which was up to 350 mg/L). The evidence of two pools was already almost totally absent in the x = 15m well as the
Results

concentration profiles of both cases had been ‘smudged’ to only show a single gradual increase and decrease similar to the base and percolated cases.

Figure 4.9 Vertical NAPL concentration distributions at 15m intervals comparing base with pool cases: base case (retention capacity 3%), level pools case and offset pools case (retention capacities both 0.64%)

The biggest differences in contaminant flux between pooled NAPL cases and the base case were near the source. The main zone of flux with values higher than 20 g/d, seen in yellow, stretched over approximately 10m in the vertical in the base case, while in pooled cases this was reduced to 6m. There was also less mass flux occurring downstream in both cases. The influence of the offset upper pool in the second case was observed in its flux plane. In the level pools case, the main area of flux was fairly uniformly distributed, but in the offset case there was clearly a much higher flux occurring in the lower portion of this area, corresponding to the lower pool. Downstream, again, there was little difference in the fluxes between the two cases in terms of areal extent and magnitude, with the majority of the non-zero flux values being below 15 g/d.
Figure 4.10 Contaminant mass fluxes in g/d at 30m intervals for low-mass source zone configurations: two dual pool source simulations (retention capacity 0.54%) - a) two level pools and b) two offset pools; and third simulation with dual line source (retention capacity 0.05%).

The final simulation case, using two ‘line’-shaped NAPL sources with an overall source zone retention capacity of only 0.05% and a projected y-z coverage of 10% showed similar results to the pool cases in terms of concentrations and fluxes. It displayed an even more pronounced dual peak profile (Figure 4.11). The peak concentrations at x = 0m were lower than in the level pool case, at 644 and 520 mg/L. ‘Smearing’ of the plume concentrations occurred rapidly, with no evidence of the dual-source nature of the source zone at the next well 15m away. The contaminant flux from the two lines of NAPL (Figure 4.10) showed two very clear zones of increased flux at 0m from the source zone corresponding to the lines’ positions. As the plume
travelled downstream to a distance of 30m, however, these merged into a single area of increased flux which was both smaller in area and magnitude than the level-pool case. By the 60m mark, the increased flux zone had spread in similar fashion to all preceding cases, although it showed the lowest flux values at this point.

![Comparative vertical concentration distributions of 'line' sources with other sources at 0m from source zone](image1)

![Comparative vertical concentration distributions of 'line' sources with other sources at 15m from source zone](image2)

![Comparative vertical concentration distributions of 'line' sources with other sources at 30m from source zone](image3)

Figure 4.11 Vertical NAPL concentration distributions at 15m intervals comparing line source case (retention capacity 0.05%) with base case (retention capacity 3%) and level pools case (retention capacity 0.64%)

The modelled plumes’ variability in the vertical was compared over the entire length of the domain in the direction of groundwater flow (x-direction), by means of taking the standard deviation of the vertical concentrations every 7.5m. The results are displayed in Figure 4.12.

A way of statistically describing the variability of plume results was sought. Taking the standard deviation of concentrations at each well every 7.5m for each simulation produced inconclusive results (Figure 4.12). The highest standard deviation or spread of concentrations about the mean near the source zone belonged to simulations using the original high-K assigned source zone with the highest bulk retention capacity of 3%. Throughout the downstream distance, the two transverse dispersivity-reduced cases exhibited slightly higher standard deviations than the base case. The trend was for decreasing retention capacity in the source zone to cause a decrease in
Results

concentration variance. This meant that although on visual inspection of the ‘Line Case’ simulation’s well distributions in Figure 4.11, for example, concentration varied with depth more than any other case, the standard deviation of this case was consistently the lowest of all. The standard deviation displayed the same plume homogenisation between cases at a certain distance from the source zone as the Jones et al. (2005) study. The results began to converge to similar values between 50 and 100m from the source zone.

![Standard deviations of vertical concentration distributions for all 3-D simulations taken at 7.5m intervals](image)

Figure 4.12 Standard deviations of vertical concentrations taken at 7.5m intervals down-gradient of the source zone

Taking the variances of mass flux values over the entire x = 0m flux plane for each simulation gave similar results to the vertical concentration standard deviations (Figure 4.13). The base case, with the highest retention capacity of 3% gave the highest variance of 247 whilst the line source case with the lowest retention capacity of 0.05% had the lowest variance of 7. The flux variance decreased consistently with decreasing hydrodynamic dispersion in those cases. The lower-mass percolated case had a higher variance of 45 than the higher mass case variance, which was 37. Recalling that there was a very apparent flux difference at x = 0m between the level and offset pools cases (Figure 4.10), where the offset pools showed a much stronger flux adjacent to the closer lower pool, the offset pools’ flux variance was the higher of the two. At 21 and 35
respectively, both the level and offset pool cases showed significantly higher variances than the line case.

![Graph](image-url)

Figure 4.13 Variances of contaminant mass flux values in flux planes taken at x = 0m from the source zone.
5 Discussion

5.1 Numerical dispersion

The use of a pseudo two-dimensional domain instead of the full three-dimensional domain for the MMOC/ULTIMATE comparison was a simplification but was deemed necessary so that the question of numerical dispersion effects could be answered without taking up large amounts of computational effort.

The results did show some evidence of the ‘smearing’ effect which the MMOC can produce on contamination values. As stated in the results section, the ULTIMATE scheme tended to show higher concentration extremes, while the MMOC had a ‘moderating’ effect on the profile, tending to ‘underestimate’ the high extremes and ‘overestimate’ the low extremes. This effect was almost invisible at near-source distances but was accentuated with increasing distances, suggesting that hydrodynamic dispersion was acting over distance to influence this. The relative influences of advection and dispersion in the domain are further discussed in terms of Peclet number in Section 5.2.

It was concluded that using the ULTIMATE solution scheme on the model domain, along with requiring about seven times the computation time, would not significantly improve the variability of the NAPL concentration profile and was not responsible for the lack of resemblance to field data.

5.2 Dispersive influences

The results of decreased dispersivity simulations were unexpected. They yielded negligible differences in concentration profiles from the base case simulation. Whilst advection dominance was a possibility, dominance to such an extent was seen as completely nonsensical. Even the most unevenly distributed source zones in this study produced variable concentration profiles in near-source wells, but then had their plumes rapidly ‘smudged’, losing all trace of the source
zone heterogeneity (usually within 15m of travel). The conclusion from these results would naturally be that dispersion was strong in the aquifer, but varying the dispersivities in simulations by considerable proportions had little effect. Some analysis was conducted to try and find a reason behind these results.

The differences in plume characteristics from reducing dispersion, though unexpectedly small, were in line with expectation. The main zone of cross-sectional contaminant flux decreased in extent in the y- and z- directions with decreasing dispersion, as would be anticipated. The standard deviations of the decreased dispersion cases also showed that statistically, the concentration profiles in their wells were slightly more variable than in the base case. Another result of interest was the size of the concentration profile ‘bulge’ and the flux zone size at x = 0m. These two clearly showed that contaminant had spread vertically to a larger extent than only the 5m that the source zone occupied in the vertical. This can be attributed to both vertical transverse dispersion and the vertical component of groundwater flow (advection) acting to spread the contaminant over the 500-day stress period.

Dispersion can be credited to some extent with the 15 to 20m shift from the centre of the plume in the y-direction seen in all flux planes at 60m. The bulk shifting of a higher flux zone such as this is more likely to be due to rapid advection of contaminant through zones of higher permeability, where groundwater exploits pore scale heterogeneities and flows through a path of least resistance. The abrupt very dark blue low-flux zones interrupting the main contaminant plume can be attributed to low permeability lenses obstructing the flow of groundwater and dissolved contaminant.

The Peclet number was estimated for the base case using the velocity statistics in the x-, y-, and z- directions as calculated by MODFLOW. Dispersivity values for use in the Peclet number calculation were found using the equations from (Zheng & Wang 1999), however only the three principal direction values were calculated. The three cross terms of the tensor were neglected. The three equations were as follows:
\[ D_{xx} = \alpha_L \frac{v_x^2}{|v|} + \alpha_{TH} \frac{v_y^2}{|v|} + \alpha_{TV} \frac{v_z^2}{|v|} + D^* \]

\[ D_{yy} = \alpha_L \frac{v_y^2}{|v|} + \alpha_{TH} \frac{v_x^2}{|v|} + \alpha_{TV} \frac{v_z^2}{|v|} + D^* \]

\[ D_{zz} = \alpha_L \frac{v_z^2}{|v|} + \alpha_{TV} \frac{v_x^2}{|v|} + \alpha_{TV} \frac{v_y^2}{|v|} + D^* \]

Equation 5.1

Where \( v, v_x, v_y, \) and \( v_z \) were velocities in \([\text{m/d}]\), \( \alpha_L, \alpha_{TH} \) and \( \alpha_{TV} \) were the longitudinal and transverse dispersivities \([\text{m}]\), and \( D^* \) was the molecular diffusion coefficient \([\text{m}^2/\text{d}]\). Calculating the dispersion coefficients using the mean velocities in each direction gave \( D_{xx} = 1.8804 \text{m}^2/\text{d}, D_{yy} = 0.04706 \text{m}^2/\text{d}, \) and \( D_{zz} = 0.01881 \text{m}^2/\text{d} \). In the \( x \)-direction, the main direction of interest in terms of plume movement, with a characteristic length of \( \Delta_x = 0.75 \text{m} \), and a mean velocity of \( 0.6268 \text{m/d} \), the mean Peclet number was calculated to be 0.25. The Peclet number range in this direction was from a minimum of 0.00028 to a maximum of 9.5. The mean Pe’s in the \( y \)- and \( z \)-directions were 0.053 and 0.0081 respectively. These ranges are all low and indicate that the problem was not advection-dominated, which occurs when \( Pe \rightarrow \infty \). At smaller Peclet numbers such as this, pore scale dispersion effects are strong and tend to smooth concentration mean and variance (Fiorotto & Caroni 2002). These results should be interpreted with some care as they were only approximations.

Nonetheless, if assumed to be good approximations, the low Peclet numbers also have implications for the numerical dispersion aspect. They show that the problem is not advection dominated, and thus not a typical ‘sharp-front’ problem where numerical dispersion is a danger as explained by literature. The Pe values corroborate the 2-D MMOC and ULTIMATE comparison results which showed negligible differences in results when the latter more stable solution scheme was applied.

A way of testing if dispersion truly has a small influence on the plume would be to run MT3DMS on the domain without activating the dispersion package at all. If the results of these trials were very different to corresponding simulations where the dispersion package was activated, dispersion would be clearly proven to have an influence, and the values input by the user would have to be questioned.
5.3 Source zone influences

The influence of the source zone mass and distributions on plume characteristics were confirmed by the simulations in this study.

Experimentation with the percolation model showed that for a given heterogeneity field situation, there will be limits on the range of fields created, manifested in the $P_d$ multiplier used to calculate $P_c$ prior to running the model. These were found by trial and error – the lower limit was between 0.65 and 0.60, as at 0.60 the NAPL contaminated only two nodes before stopping. When the multiplier was increased above the higher mass case’s multiplier of 1, the NAPL began to exhibit ‘lightning-bolt’-like behaviour similar to early results of (Ewing & Berkowitz 1998), where NAPL capillary pressure was so high that it contaminated only a vertical line from the point of release to the bottom layer.

The percolation model had limits as a replication of natural behaviour. It could not be asked to replicate all capillary behaviours, and omitted some such as pooling at the bottom layer of the source zone. This was because the model was stopped at the moment that the first node in the bottom source zone layer was contaminated. The side boundaries of the designated source zone could also not be exceeded. This was an acceptable omission, however, especially as the source zone was merely suspended within the larger domain and was not designed to have different media characteristics to it, such as a bedrock layer directly below the bottom layer for example. Despite these limitations, the percolated source zones represented reality fairly well in terms of distribution and mass (or retention capacity), and were similar to zones used in past studies.

The percolated source zones appeared to have little effect on the variability of well concentrations, even though their masses were much less uniformly distributed in all directions than the base case. There was no information in the wells of the second ‘lower mass’ percolated zone of its two pooled structures, and fluxes also offered minimal visual evidence to this effect. The variance of the two percolated cases, however, did show that mass fluxes in the lower mass case were further statistically dispersed about the mean, and thus more variable. Again these results should be interpreted with caution as the flux variance is not a perfect descriptive statistic for assessing plume variability. The main factor which was proven by the percolated zones was
that a source zone containing less NAPL mass (i.e. lower retention capacity) will display lower concentrations and lower mass fluxes both near the source and downstream.

Jones et al. (2005) stated that the more variable near-source concentrations could be attributed to the vertical distribution of NAPL. This study confirmed this. In all cases it was observed that concentration and flux increases were aligned in depth with the location of contaminated source zone nodes, indicating that the plume was not dispersed greatly in the vertical initially. This changed downstream as the plume travelled through the heterogeneity field and became more dispersed.

In addition to confirming Jones et al.‘s findings on vertical distributions, this study found that the horizontal distribution of NAPL-contaminated nodes (in the x-direction) also had a considerable impact on the resulting plume emanating from any given source zone. This was because of the high factor of plume homogenisation over short distances. Although they were conceptually realistic, the percolated zones suffered from this phenomenon because of the position of the majority of their NAPL mass. The first percolated source zone had most of its contaminated nodes centred around the middle of the source zone which was 7.5m upstream of the first observation well. Within this travel distance the plume lost most information of the heterogeneity of its source. In the second case, the situation became worse, as even though NAPL distributions replicated pooling well, most NAPL mass was located either near the middle of the zone or towards the upstream end. Even though the contaminant flux variance increased, the well concentrations showed a lower standard deviation and little evidence of variability in their profiles. Conversely, variable plume concentrations were found in near-zone wells for cases such as the two pool and line cases, whose contaminated nodes were at the downstream end of the zone. The flux planes corresponding to these three cases, however, showed that their plumes had less mass travelling through the y-z plane, which showed that these measurements can be important in assessing a source’s strength due to its retention capacity.

Throughout the 500-day stress period, the NAPL concentration at the contaminated nodes was set at 1000 mg/L. This implies a persistent NAPL source at these points. This is not a strictly correct representation of the subsurface, because as literature has shown, groundwater flow acts to slowly ‘flush’ NAPL from its positions. Pooled NAPL generally has a lesser exposed area to groundwater flow and is more persistent. As this study showed, when two pools alone were
modelled, the degree of plume variability in the vertical direction was dependent on the vertical distribution of NAPL. Thus having persistent NAPL located throughout the entire vertical distance of the source zone, as even the more heterogeneous percolated source zones did, was responsible for the ‘smooth’ vertical concentration distribution. The main aim of this study was to understand why modelled vertical distributions in the previous study were unable to represent reality. Persistence is a possible reason. While it is reasonable to assume that within a 500 day timeframe residual NAPL has not yet been dissolved, many contaminated sites are only encountered years after the initial spill occurred. By this time NAPL may have been flushed so that only more resilient pools are contributing to plumes. This could be the reason for concentration fluctuations with depth in field wells. In future, modelling for longer stress periods (time permitting) with later periods having less NAPL residual present may be a more realistic approach which could yield more variable well profiles.

The pool and line case results showed how the source zone could be adapted to yield the sought-after variable well results. Placing several separate pools at various heights throughout the model, some of them offset in the x-direction, would undoubtedly result in near-source concentrations fluctuating with depth as occurs in the field. The question is, even though this may make this particular domain’s plume more realistic, how conceptually valid is it, and could the same principle of ‘source zone calibration’ be legitimately applied to modelled source zones in other domains? In situations such as Ibaraki’s, where dispersion’s influences were clear, adding conceptually sound source zone distributions coupled with varying dispersivities could result in the plume variability objective being realised. Unfortunately in this study, where dispersion behaviour is somewhat of an enigma, this approach was not as successful as hoped.

5.4 Limitations of results

There were limitations to the analysis of the results in this study. The well concentration profiles only took concentrations along a centreline away from the source zone. This technique has been used in other studies such as Ibaraki (2001). Changes in the plume either side of this centreline were not shown, and as was seen by the flux plane results, bulk plume movement can be significantly deflected away from the centreline due to dispersion and heterogeneity. Generating well results along several lines either side of this centreline would have yielded more complete plume results. An alternative in future may be to generate concentration ‘planes’ similar to the
fluctuations in plume development. Planar results are difficult to quantitatively interpret in terms of statistics, however. For the purposes of this study, simple vertical concentration profiles gave sufficient information on whether simulations were producing the desired variabilities seen in the field or not.

Well profile resolution was not an influential issue in this study. Because of the computational time involved in generating well results, 1.5m screens were used with the mean concentration over each screen (6 nodes in the z-direction) plotted as a data point on the graphs. This size was small, as in field porous media it is extremely rare to use screens smaller than 2m in length (Reynolds 2006). A trial profile of the base case using readings from all 60 vertical nodes was generated to check if the concentration averaging procedure was at all to blame for the ‘smeared’ results. The effect of this six-fold increase in resolution was extremely negligible upon inspection, and extracting results at this resolution would have been completely impractical.

Interpreting the statistical results of the concentration profiles and fluxes also had to be done with caution. The standard deviation and variance were exposed as unsatisfactory descriptive statistics for answering the variability questions asked of each simulation. For example, while dispersion cases behaved as expected when their standard deviations increased with decreasing dispersion, they gave lower flux variances. The most ‘successful’ simulations, where the pool and line cases yielded concentration profiles with higher variability and better resemblance to field situations, had the lowest concentration standard deviations and flux variances.
6 Conclusions

This particular modelled domain did not display expected plume behaviour in all areas of investigation, and not all causes of these discrepancies could be found. Out of the areas investigated, source zone distributions were found to be the greatest influence on near-source plume variability in the domain. The following are the study’s main findings and what they imply in the broader sense of NAPL contamination and modelling:

- **Numerical dispersion was not to blame for lack of plume variability**
  The two-dimensional comparison between the MMOC and the higher-order ULTIMATE advection solution schemes showed some evidence that the MMOC was causing ‘smoothing’ of concentration fronts. However this was only most evident as dispersion carried the plume further downstream, and the ULTIMATE scheme’s results did not show the variable profiles that were sought. The ULTIMATE scheme should only be used on domains where the need for accuracy and flux limiting justifies its computational demands.

- **Reducing transverse dispersivity had little effect on plume development**
  Although there was a high extent of plume homogenisation occurring over a short distance downstream from the source zone, which would usually be attributed to dispersion, varying domain dispersivities had a surprisingly negligible effect on the plume. This was despite calculated Peclet numbers indicating that dispersion would have important effects on contaminants in the domain. It is unclear what meaning, if any, these results carry; general literature theory on the subject conflicted as to the strength of dispersion in the subsurface, but similar studies to this one such as Ibaraki (2001) found dispersion to be a vital component of the contaminant transport equation with significant influence. It may be that these results are an idiosyncrasy of this particular domain and/or modelling scheme.

- **Source zone characteristics were proven to have clear influences on resultant plumes; however the ability to produce sought-after realistic plumes was hampered by rapid plume homogenisation with distance**
  The objective of investigating the source zone configuration and developing a realistic NAPL conceptual model was achieved. The simple capillary pressure invasion percolation model was
Conclusions

able to replicate NAPL migration to a good approximation of reality, and the resulting NAPL fields displayed characteristics similar to source zones created in other studies. The plumes resulting from these fields reinforced the results of the previous work which found that a higher source mass present (retention capacity) resulted in larger plumes with higher concentrations.

The plume shape and variability was also found to be dependent on the distribution of NAPL in the x- and z- directions. The x-direction dependence was largely due to the excessive ‘smearing’ of the plume, which meant that simulations where NAPL structures were placed at the downstream end of the source zone showed higher concentration variability near the source. This result was therefore a symptom of this model domain and set of parameters, and should be tested before it is assumed to hold true for others. The z-direction dependence made sense, as with groundwater flowing predominantly in the x-direction, wells would have concentrations changing with depth.

Useful tools for assisting with understanding groundwater contamination modelling results have been proven within this study. Along with the percolation model, the orthogonal projections of source zones showed that they can explain why concentration profiles look the way they do in a given situation. An example was the 100% distribution of the base case which was discovered using this method. The measurement of contaminant flux orthogonal to flow is also a much more informative way than centreline wells of visualising plume results and seeing changes between cases, although better methods needed to be found for statistical analysis.

An important limitation on any contaminant modelling work is computational effort, and this study was no different. While the percolation model was conceptually sound, as stated in its limitations description it was modelling pore-scale processes at a scale of tens of centimetres. Without being able to model pore-scale processes at a discretisation closer to the natural scale by using a much finer finite difference grid mesh, questions have to be asked of the model’s ultimate accuracy. Finer meshes would allow more detailed and heterogeneous source zone distributions, and as the results show, NAPL distributions in this domain, especially in the x- and z- directions, will be key to developing variable plumes near the source.
6.1 Recommendations

A model domain containing the abnormal results that this one does is limited in its future applications. Work will be restricted by the excessive dispersion of contaminant concentrations within metres of the source zone, whatever its real cause. In field situations, wells are costly and are only rarely located in proximity to the original NAPL source zone, and yet they still display concentration variability. This is not the case in this domain, and any future study would have to first focus on why this is so. Running the model with only an advective transport package and comparing the results would allow the user to ascertain dispersion’s importance to the situation, and whether dispersivity values need to be reviewed.

Future work could improve the temporal as well as spatial conceptualisation of simulated NAPL source zones. While the percolation model in this study developed reasonably realistic NAPL distributions, and the 500-day period is not usually sufficient for extensive residual dissolution to occur, future methods could improve on this simple model by taking into account the persistence of NAPL structures. This would be done by simulating the ‘flushing’ of residual NAPL nodes by reducing their concentrations over time, or even simply by setting their concentration to zero at a predetermined time, whilst allowing pooled structures to remain for longer periods.

In closing, this study, like most groundwater contamination modelling work, would benefit from operating on a spatial scale closer to that at which processes occur in nature. If revisited at a future time when it was computationally feasible to model NAPL migration and plume development at the centimetre scale with minimal numerical error, it is quite possible that the plume would show significantly more favourable results than it has done at this time.
7 References


References


Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer


Schwille, F. 1988, *Dense chlorinated solvents in porous and fractured media: model experiments (Engl. Transl.)*, Lewis Publishers, Ann Arbor, MI.


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*Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer*
Appendix A

**FGEN91 input file**

```
0.0000000025956129    Max k (m2)
1.0           Number of fields generated
20 1             ISEEDH, ISEEDG first seeds for H and G
1024 128 128      NFULL  nodal dimensions of full field
400 60 60         NTRUNC  nodal dimensions of truncated field
0.75 0.75 0.25     SSTEP  spatial step size (delta X, Y, Z)
-25.6  2.25       HMEAN,GMEAN  mean of H,G
2.02  0.05        HVAR,GVAR  variance of H,G
0.00  0.00        HNUG,GNUG  nugget of H,G
2             ITYPE   power spectrum type (1=gaussian, 2=exp. cov)
1             ICROSS  cross spectrum type (1=lin, 2=+ X-spec, -2=- X-spec, 3=user)
1.00          COHER   coherency sq (use COHER>0.0 for ICROSS=1)
10.00 10.00 2.00   HLAMDA  correlation lengths H
5.00 5.00 1.00     GLAMDA .................. G (ignored if ICROSS=1)
-0.1           ASLOPE  slope linear X-spectrum (ignored if ICROSS.NE.1)
0.0 0.0 0.0       DELAY  delay vector for G relative to H
1             IPSCRN = 1 -> progress output to screen
0             ICAUTO = 1 -> calculate and output autocovariances
0             IWBIN = 1 -> write fields in binary format
```
Appendices

Appendix B

7.1 Percolation model code

The following code was the percolation model procedure written as a MATLAB m-file. It includes the model code itself as well as the permeability data loading and input file creation procedures.

```matlab
%percolatesourcefast.m
% Michael Marinovich – last updated: 02/05/2006
clear;
format long e;
fid=fopen('NewPermp.dat','rt'); %loading permeability file with nodal %xyz coordinates
permmat=load('NewPermp.dat');
sigma=0.02;
phi=0.3;
alpha=0.65;
Pdinit=2000;
Pd0=4.407595e-02;
g=9.81;
rhowater=1000;
rhONAPL=2650;

Pd=(Pd0.*sigma)./(permmat(:,4)./phi).^alpha;
nodalPd=[permmat(:,1) permmat(:,2) permmat(:,3) Pd];

cellPd=zeros(400,60,60);
for ii=1:1440000 %creating Pd array for entire domain
    cellPd(nodalPd(ii,1),nodalPd(ii,2),nodalPd(ii,3))=nodalPd(ii,4);
end

layerPc=zeros(400,60,60);
for jj=1:60 %creating Pc array
    layerPc(:,:,jj)=(Pdinit+((rhowater-rhowater)*g*(60-jj)*0.25));
end

sourcePd=cellPd(22:41,26:35,21:40);
meansourcePd=mean(mean(mean(sourcePd)));
layerPc(22:41,26:35,21:40)=meansourcePd; %multiplier used here

entry=zeros(400,60,60);
for kk=1:400
    for ll=1:60
        for mm=1:60
            if layerPc(kk,ll,mm) > cellPd(kk,ll,mm)
                entry(kk,ll,mm)=1;
            else
                entry(kk,ll,mm)=0;
            end
        end
    end
end
```

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer
Appendices

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer

```matlab
%entry array of 1's and 0's for source zone area only
sourceentry = entry(22:41, 26:35, 21:40);

clear layerPc;
clear cellPd;

a = input('Input nodal x-value of initial contamination:');
b = input('Input nodal y-value of initial contamination:');
c = input('Input nodal z-value of initial contamination:');

contlistall = [a b c];
contlistlast = [a b c];
contlistcurr = [];
for cc = 1:50
    for aa = 1:size(contlistlast, 1)
        x = contlistlast(aa, 1);
        y = contlistlast(aa, 2);
        z = contlistlast(aa, 3);
        if z == 1
            break
        end
        nodestatenew = sourceentry(x, y, z - 1);
        if nodestatenew == 1
            contlistcurr(aa, :) = [x y z - 1];
        else
            hops = [x + 1 y z; x - 1 y z; x y + 1 z; x y - 1 z];
            for bb = 1:4
                if hops(bb, 1) == 0 | hops(bb, 2) == 0
                    elseif hops(bb, 1) > 20 | hops(bb, 2) > 10
                        else
                            nodestatenew = sourceentry(hops(bb, 1), hops(bb, 2), hops(bb, 3));
                            if nodestatenew == 1
                                contlistcurr = [contlistcurr; hops(bb, :)];
                            end
                        end
                    end
                end
            end
        end
    end
    contlistlast = unique(contlistcurr, 'rows');
    contlistall = [contlistall; contlistlast];
    contlistcurr = [];
end
contlistall = unique(contlistall, 'rows');
contx = contlistall(:, 1) + 21;
conty = contlistall(:, 2) + 25;
contz = contlistall(:, 3) + 20;
nxx = permmat(:, 1); nyy = permmat(:, 2); nzz = permmat(:, 3);
perms = permmat(:, 4);
Icbundperc = ones(size(perms));
Concentrationperc = zeros(size(perms));
NewPermperc = perms;
for ss = 1:size(contlistall, 1);
    for tt = 1:length(nxx);
        if nxx(tt) == contx(ss) & nyy(tt) == conty(ss) & nzz(tt) == contz(ss)
            countcont = countcont + 1;
            NewPermperc(tt) = perms(tt) / 2.0;
            Icbundperc(tt) = -1;
            Concentrationperc(tt) = 1000;
        end
        end
    end
    end
xx = ((nxx - 1) / 399). * 299.25;

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer
### 7.2 Highest-K source zone code

The following MATLAB code was the original code used in Jones et al. to generate source zones where NAPL was assigned to the highest-K cells.

```matlab
fp=fopen('fort.dat','rt');
Perm=load('fort.dat');
%Perm=A(:,1);                           % Assign First Column as Perm
%Icbund=A(:,1);                         % Also assign First Column as Icbund
Icbund=ones(size(Perm));
Concentration=zeros(size(Perm));

x = zeros(400*60*60,1);   % Size of the domain
y = zeros(400*60*60,1);
z = zeros(400*60*60,1);
count = 0;
for k = 14.75 : -0.25 : 0
    for j = 44.25 : -0.75 : 0
        for i=0 : 0.75 : 299.25
            count = count + 1;
x(count) = i;
y(count) = j;
z(count) = k;
        end
    end
end

a=input('Enter a value for the lower limit of x'); % Where you want the NAPL source zone to be located
b=input('Enter a value for the upper limit of x');
c=input('Enter a value for the lower limit of y');
d=input('Enter a value for the upper limit of y');
e=input('Enter a value for the lower limit of z');
f=input('Enter a value for the upper limit of z');
s=input('Enter a saturation percentage')/100.0;
rand('state',sum(100*clock));            % resets it to a different state each time
NewPerm = Perm;                           % Will produce different saturations
```

% Assign First Column as Perm
% Also assign First Column as Icbund
% Size of the domain
% These three lines assign x, y and z coordinates
% Where you want the NAPL source zone to be located
% The following halves the permeability in the nodes with NAPL
% resets it to a different state each time
% Will produce different saturations
for i = 1:length(x);
    Icbund(i) = 1;
    if (a<=x(i) & x(i)<=b);
        if (c<=y(i) & y(i)<=d);
            if (e<=z(i) & z(i)<=f);
                if (rand <= s);                   % rand must be between 0 and 1 hence at input divide by 100
                    NewPerm(i) = Perm(i)/2.0;  % The following halves the permeability in the nodes with NAPL
                    Icbund(i) = -1;               % A value of -1 means it is fixed
                    Concentration(i) = 1000;      % Assigns NAPL node a concentration value of 1000 mg/l
                end
            end
        end
    end
end

XYZP = [x y z NewPerm];
XYZI = [x y z Icbund];
XYZC = [x y z Concentration];
P = [NewPerm];
I = [Icbund];
C = [Concentration];

save NewPerm.dat XYZP -ascii                  % Output files with x y and z coordinates
save Icbund.dat XYZI -ascii                   % These three were created as a checking measure
save Concentration.dat XYWC -ascii

save NPerm.dat P -ascii                      % Output files listing only perm, concentrations or icb values
save Icb.dat I -ascii                        % These are the three you require in MODFLOW and MT3DMS
save conc.dat C -ascii

Source zone and model parameter influence on NAPL plume development in a heterogeneous aquifer