LIGHT NON-AQUEOUS PHASE LIQUID (LNAPL) VERTICAL AND LATERAL MIGRATION BEHAVIOUR DUE TO FLUCTUATING GROUNDWATER TABLE

LEE YIP YONG

SCHOOL OF CIVIL ENGINEERING
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by

LEE YIP YONG

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Name of Student: Lee Yip Yong

I hereby declare that all corrections and comments made by the supervisor(s)and examiner have been taken into consideration and rectified accordingly.

Signature:

____

Date : 30/7/2021

Endorsed by:

DR. MUHD HARRIS RAMLI
Pensyarah Kanan
Pusat Pengajian Kejuruteraan Awam
Universiti Sains Malaysia
Email: cemhr@usm.my

____
(Signature of Supervisor)

Name of Supervisor: Dr. Muhd Harris Ramli

Date: 4 August 2021

Approved by:

PROF DR FAUZIAH AHMAD
SCHOOL OF CIVIL ENGINEERING
UNIVERSITI SAINS MALAYSIA
14300 NIBONG TEBAL, PENANG

____
(Signature of Examiner)

Name of Examiner: PROF DR FAUZIAH AHMAD

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ABSTRAK

Tingkah laku migrasi *Light Non-Aqueous Phase Liquid* (LNAPL) adalah kompleks bergantung pada persekitaran bawah tanah yang berbeza. Untuk kerja pemulihan yang lebih baik, eksperimen tangki 2D dijalankan untuk mengkaji kesan turun-naik air tanah terhadap migrasi LNAPL secara lateral dan tegak. Media berpori yang digunakan adalah bergred buruk (SP) dan bersifat saliran yang baik. *Simplified Image Analysis Method* (SIAM) digunakan untuk mengakses pengedaran saturasi LNAPL dan air dalam domain tangki air 2D dengan dua jenis keadaan turun-naik dalam air tanah (senario musim lembab / kering) dan dua isipadu LNAPL yang dilepaskan. Paras air dinaikan dahulu kemudian diturunkan untuk senario musim lembab sementara urutan tersebut bertentangan dengan senario musim kering. Dalam scenario musim lembab dengan isipadu rendah, saturasi LNAPL pada paras air tertinggi meningkat kemudian turun menjadi 20 %. Tiada tanda-tanda LNAPL dijumpai pada air berparas awal kerana daya kapilari yang tinggi. Di 20 cm ke sebelah kanan sumber pelepasan, saturasi LNAPL meningkat menjadi 15% pada peringkat akhir menunjukkan ia mempunyai pergerakan lateral LNAPL. Dalam scenario musim kering, saturasi LNAPL pada paras air terendah kekal sifar. Saturasi LNAPL pada air berparas awal meningkat menjadi 16 % dan jatuh ke 11% setelah dipindahkan oleh daya kapilari atas sebab kenaikkan air, setelah itu terperangkap LNAPL di bawah zon saturasi. Terdapat permerhatian lonjakan saturasi LNAPL yang konsisten sehingga 13 % atas sebab pergerakan lateral. Sebagai perbandingan, LNAPL dalam musim kering mempunyai kedalaman penembusan serta anjakan radial yang lebih besar kerana kadar penyusupan dan penyebaran yang tinggi disebabkan oleh penurunan paras air. Gandaan isipadu LNAPL mengikut dua jenis urutan turun-naik air tanah juga menunjukkan tingkah laku migrasi lateral dan tegak yang serupa kecuali terdapat saturasi LNAPL yang lebih tinggi

yang terkumpul di setiap lokasi kajian, kedalaman penembusan dan anjakan radial yang lebih besar. Secara keseluruhan, SIAM menunjukkan keberkesanannya dalam penilaian taburan saturasi LNAPL dan air dalam skala dua-dimensi.

ABSTRACT

Migration behaviour of Light Non-Aqueous Phase Liquid (LNAPL) is complex depending on different subsurface environment. For better remediation efficiency, 2D tank experiments were conducted to study effect of the groundwater fluctuation on the lateral and vertical migration behaviour of LNAPL. The porous media used was poorly graded and has good drainage properties. Simplified Image Analysis Method (SIAM) was adopted to access saturation distribution of LNAPL and water in the domain of 2D water tank with two types of groundwater fluctuation (wet / dry season) and two volumes of LNAPL released. Water level first raise then drop for wet season scenario while opposite sequence for dry season scenario. In wet season scenario and low volume scenario, LNAPL saturation at the raised water level first increased then dropped to 20 %. No sign of LNAPL found at initial water level due to high capillary force. At 20 cm to the right of releasing source, final reaching LNAPL saturation increased to 15 % signified LNAPL lateral movement. In dry season scenario, LNAPL saturation at lowermost water level remained zero. LNAPL saturation at initial level increased to 16 % and fall to 11 % after displaced by capillary force due to raising water, thereafter entrapped immobile LNAPL below saturated zone. Consistent surge of LNAPL saturation to 13 % observed due to lateral movement. In comparison, LNAPL in dry season has greater penetration depth and radial displacement because of high infiltration and spreading rate induced by lowering of water tables. Double volume of LNAPL under these two groundwater fluctuations show similar vertical and lateral migration behaviour except that there would be higher LNAPL saturation deposited at each study location, greater penetration depth and radial displacement compared to the corresponding applied scenario. Overall, SIAM shows its effectiveness to evaluate saturation distribution of LNAPL and water in two-dimensional scale.

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LIST OF SYMBOLS

C_u	Coefficient of uniformity
C_c	Coefficient of curvature or gradation
C_7H_{16}	Heptane
$C_{16}H_{34}$	Hexadecane
D	Average optical density
d	Optical density
G_s	Specific gravity
Δh	Head difference or head loss
I	Intensity of reflected light
k	Coefficient of permeability
m	Mass
S_o	Degree of saturation of oil
S_w	Degree of saturation of water
v	Viscosity

LIST OF ABBREVIATIONS

AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials
BS	British Standard
COVID-19	Coronavirus Disease 2019
DCE,1,1	1,1-Dichloroethylene
DID	Department of Drainage and Irrigation
DNAPL	Dense Non-Aqueous Phase Liquid
DOE	Department of Environment
DSLR	Digital Single Lens Reflex
GWL	Groundwater Level
HSI	Hue-saturation-intensity
IAM	Image Analysis Method
ISCO	In-Situ Chemical Oxidation
LED	Light Emitting Diode
LIF	Laser-Induced Fluorescence
LNAPL	Light Non-Aqueous Phase Liquid
LRM	Light Reflection Method
LTM	Light Transmission Method
MATLAB	Matrix Laboratory
MCL	Maximum Contaminant Level
MIAM	Multispectral Image Analysis Method
NAPL	Non-Aqueous Phase Liquid
NEF	Nikon Electronic Format
OPEC	Organization of the Petroleum Exporting Countries
PCE	Tetrachloroethylene
PVC	Polyvinyl chloride
ROI	Region Of Interest
SIAM	Simplified Image Analysis Method
SVE	Soil Vapour Extraction
TCE	Trichloroethylene
THC	Total Hydrocarbon Content

TIFF	Tag Image File Format
U.S. EPA	United States Environmental Protection Agency
USCS	Unified Soil Classification System
WHO	World Health Organization
ZOI	Zone Of Influence

CHAPTER 1

INTRODUCTION

1.1 Background

Industrialization is taking place in most of the countries and brought the world into a modern era. Rapid industrialization increases the global economic growth eventually improves the standard living of mankind. In turn of these, industrial activities highly explore the fuel sources of the earth which crude oil remains the most important global commodity. Crude oil widely used in energy production, transportation and other manufacturing sectors. They are naturally occurring elements made up of hydrocarbons and need to be extracted from the Earth. Generally, their hydrocarbon molecular characteristic enables them to be refined into different products such as gasoline, diesel, lubricating oils and more specialized products like plastics. These hydrocarbons usually termed as non-aqueous phase liquids (NAPL) which exhibit immiscibility with water. Typically, there are two types of these materials depend on their density with water, in which known as light non-aqueous phase liquid (LNAPL) if it less dense than water and dense non-aqueous phase liquid (DNAPL) if denser than water.

The crude oil commonly processed and stored in closed refineries, pipelines or terminals. Increasing development of industries are demanding this resource hence expose more potential contamination of NAPL to subsurface and groundwater. Nigeria has recorded about 1020 oil spillage incidents at year 2000 (Nwachukwu and Osuagwu, 2014). Even at Port Dickson petroleum refinery, there was a case of kerosene leakage from distributing pipelines up to 20 years period and had caused a major LNAPL contamination in the subsurface environments (Nadzif, 2015). These similar incidents can happen worldwide by any mistakes from human, failure of facilities and equipment or due to disaster. LNAPL such as gasoline or diesel fuel that penetrated into the soil layer not only possibly pollute great amount of groundwater table and also may affected the soil degradation in term of the bearing capacity and shear strength parameter (Kererat, 2019). Therefore, removal or treatment process is desirable to remove as much as possible of its liquid phase from the ground.

However, it is challenging in detecting and estimating the migration and distribution of LNAPL. The migration behaviour of LNAPL depends on many factors such as subsurface geological condition, amount of release, groundwater flow and also the physical and chemical properties of compound (Trulli et al., 2016). Its fluid properties tend to move toward the groundwater table under gravitational force but its migration can be very unpredictable below surface due to complex nature of soil (Alazaiza et al., 2019). In porous media, LNAPL generally will flow through the unsaturated zone and travel laterally after reaching the capillary fringe (Newell et al., 1995). Thus, the parameter of groundwater flow shall include in this study to access its impact on NAPL migration.

Most of the time DNAPL are hydrocarbons that have low biodegradability, highly toxic and they tend to sink until the bed of groundwater table causing the contamination even troublesome (Hemond and Fechner, 2015). In this research, it only focuses on the migration behaviour of LNAPL in soil. The project aims to determine the vertical and lateral distribution of LNAPL during groundwater fluctuation. It also to determine the effect of volume of LNAPL on migration behaviour of LNAPL in soil. This research can simulate an event of LNAPL release to a ground surface in real life.

1.2 Problem Statement

LNAPL as a hydrocarbon commonly encountered at a contaminated site. Accidental spillage or improper disposal of products such as gasoline, diesel fuel, fuel oil can cause LNAPL to enter into the subsurface consequently pollute the groundwater table. As we know, the effect of groundwater contamination can be fatal once it is near to our potable water sources Presence of these flammable materials made the water easily ignites when expose to environment. Furthermore, LNAPL release on land surface would surely flow through vadose zone where large-scale of soil may get contaminated before contact with groundwater. Oil-polluted soil that has toxic and less permeable is harmful.

Despite that fact that most of the facilities were designed based on specifications or certain guidelines, leakage accidents still might occur during construction and operation process. The Pengerang Integrated Complex at Johor, a megaproject by Johor Petroleum Development Corporation Berhad (JPDC) expected to achieve crude oil storage capacity to 23.5 million barrels. (US Energy Information Administration, 2021). Similarly in Sabah, the state's first oil storage and refinery is under construction and would has its storage facility for 2 million cubic tons of petroleum products (Daily Express, 14 December 2019, p. 2). All of these upcoming projects just poses another high possibility of LNAPL release into subsurface. Remediation work is required to eliminate both contaminated soil and groundwater. It is challenging to detect and estimate the migration of LNAPL not mentioning the scale, cost, time and technologies. The migration of LNAPL at monitoring wells especially subjected to changing water table elevations is complex (Azimi et al., 2020). The restoration works therefore also more difficult hence there is a need to identify the relationship of the volume of LNAPL and groundwater fluctuation in soil with its two-dimensional distribution behaviour in porous sand media within subsurface.

1.3 Objectives

The objectives of this study are stated below:

1) To determine the effect of the groundwater fluctuation on the lateral and vertical migration behaviour of LNAPL
2) To determine the effect of the volume of the LNAPL on the lateral and vertical migration behaviour of LNAPL

1.4 Scope of Work

Collected soil samples need to put on several soil properties test to determine geotechnical properties of soil. Suitable parameters obtained shall establish selection of soil sample to be the porous media. Diesel will represent LNAPL as it is commercially available. A two-dimensional water tank with the selected porous media and different groundwater level acts as a subsurface environment along with the adoption of simplified image analysis method (SIAM) to access the migration behavior of LNAPL. Different volume of diesel added to simulate different intensity of release onto land surface. SIAM able to measure the saturation distributions of water and LNAPL in the setup.

1.5 Expected Outcome

The research shall find out the relationship between groundwater level and the lateral and vertical migration behavior of LNAPL in porous media. It also shall show the influence of the volume of LNAPL to its distribution within subsurface environment. The flow pattern of LNAPL based on different amount of release simulate the actual incident of LNAPL leakage on ground surface. From these research outcomes, it will contribute to soil remediation work in the future as the distribution of LNAPL can be easily determined. Thus, relevant remediation project could conduct with suitable coverage or scale by using limited time, workmanship and cost.

1.6 Dissertation Outline

This dissertation consists of total 5 chapters. Each chapter describe different component of the conducted research. Chapter 1 is about the introduction of this research project elaborated through its background, problem statements, objectives, scope of works as well as the expected outcome of the study. Chapter 2 is literature review that adapting theories, concept, studies, previous findings and justification related on to the research. Proper citations would be included in this section. While for Chapter 3 discusses on the research methodology, listed detailly every procedure and precautions along with proper tools to achieve research’s objectives. Chapter 4 is results and discussion. All obtained results would be tabulated and given detail explanations on behaviours of the study parameters. For discussion part, result would be justified to support the objectives of the study. Chapter 5 as the last chapter described the conclusion on the research project and made comprehensive recommendations according to the outcomes.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Non-Aqueous Phase Liquid (NAPL) is an organic compound defined for the contaminant which does not mix with water. Upon the exposure of these substances onto land surface, infiltration and distribution process would start and easily contaminate surrounding soil. It only exacerbated the contamination issue if they make their way to the groundwater level before restoration works carry out. Common NAPLs include gasoline, diesel and also heavy oil. These organic liquids that tend to sink in water defined as dense non-aqueous phase liquids (DNAPL) which potential to pollute region below water table. Contrary on that, they referred as light non-aqueous phase liquids (LNAPL) if float on water which may form a plume layer on top of water table. The contamination of petroleum-based liquid to subsurface usually associated with oil leakage or spillage incidents as a global problem (Delin et al., 1998). Its distribution in subsurface is possible to predict to certain extent particularly in permeable and porous soil as they percolate at ease to the saturated strata. Eventually the LNAPL reach saturated zone where it mainly flows horizontally according with the hydraulic gradient.

Variations of subsurface condition and different properties of fluid influence on migration behaviour of LNAPL. Soil's permeability, saturation, density, capillary pressure etc. affect the flow of LNAPL within the medium. On top of that, LNAPL characteristic such as its viscosity, wettability and surface tension also govern the distribution pattern of LNAPL. Accurate prediction of underground LNAPL distribution is important for proposing an effective LNAPL recovery strategy (Davis et al., 1993; Johnston et al., 2002; Rayner et al., 2007, cited in Lenhard et al., 2017).

2.2 Non-Aqueous Phase Liquid (NAPL)

Non-aqueous phase liquids (NAPL) are hydrocarbons that remains immiscible with water and involved formation of a separate interface preventing the mixing due to the differences in their physical and chemical properties. NAPL can be classify as either light non-aqueous phase liquids (LNAPL) if the density is lower than that of water, or dense non-aqueous phase liquids (DNAPL) if have greater density than water. Because of the poor water solubility of NAPLs, they are a probable long-term contamination source which can confined underground persistently and ultimately its concentration might develops to exceed maximum contaminant level (MCLs), a standard by United States Environmental Protection Agency (U.S. EPA) allow for permissible contaminant level in drinking water (Mateas et al., 2017). While migrating downward in subsoil, their residual liquids in vadose zone are among the future contamination sources to groundwater. Through experimental testing, higher density of NAPL and soil porosity as well as lower soil bulk density will increase the retention capacity (Zytner et al., 1993).

2.2.1 Light Non-Aqueous Phase Liquids (LNAPL)

LNAPL is an organic substance that immiscible with water and also having less density than water thus it tends to float as a layer on top of water table. It has a complex chemical composition consisting varies ratios of aliphatic and aromatic hydrocarbons (Tomlinson et al., 2014). LNAPL products typically made up of different elements that processes with different water solubility. Presence of additives such as alcohols improve its solubility component whereas the other components like benzene or toluene etc. contributes to its insolubility (Newell et al., 1995). They are among the very common material encountered at contaminated site, including fuels such as gasoline, diesel and kerosene.

2.2.2 Dense Non-Aqueous Phase Liquids (DNAPL)

DNAPL is heavier than water and also do not dissolve in water. Some common examples include trichloroethylene (TCE), tetrachloroethylene (PCE), 1,1-dichloroethylene (DCE,1,1), fluorene, phenanthrene, coal tar and creosote (Kamon et al., 2004). DNAPL in soil migrate downward through soil pores until saturated zone provided its amount exceed the capillary entry pressures, or they approaches an area with high vertical permeability or fracture (J.Brost et al., 2000). Upon penetration, DNAPL need to overcome different entry pressure of strata which are grain-size dependent, hence they tend to accumulate or flow laterally above a stratum before migrating further downward, and thus any slight change of grain-size may cause great deflection to their flow (Fountain, 1998). DNAPL usually hardly detected and believed as a major limiting factor in site remediation effort (Huling and Weaver, 1991). Remediation techniques shall be carefully considered to minimize risk of enhancing DNAPL mobility. Vacuum extraction, biodegradation, groundwater pumping and soil flushing are some primary technologies aimed to remediate the immobile and different phases of DNAPL components (Huling and Weaver, 1991).

2.3 LNAPL Contamination

LNAPL tend to pollute environment through accidental spills and leaks events, or perhaps intentionally release by industries or domestic users. (Ou et al.,2004, cited in Sakari et al., 2010). Uncontrolled release of LNAPL will infiltrate into the ground and potentially enter the aqueous system which is the groundwater table if large enough amounts are emitted. As a result, they remain at the top of water level as a separate phase (U.S.EPA, 2005). Depth always used as an indication to determine the seeping intensity of hydrocarbon into water samplings at polluted site.

In Malaysia, there is a plan to expand its oil storage capacity to counter the growth of crude oil trade in the region (US Energy Information Administration, 2021). Some of the future construction plans just enough to raise the concern of LNAPL contamination onto the nation land. As dedicated to ensure positive development of Sabah's oil and gas industry at the same time creating job opportunities, state-owned Sabah Oil and Gas Development Corp. Sdn. Bhd. (SOGDC) currently agreed to construct crude oil storage and refining plant in Sipitang Oil & Gas Industrial Park in Sabah. In addition, marine construction company Benalec started work on an oil storage terminal in Johor known as Tanjung Piai Integrated Petroleum & Petrochemical Hub (TPMIP). The project will build at a man-made island off the Straits of Malacca where 1.1 million m^3 crude storage capacity is expected ("Malaysia Benalec Fast-Tracks Tanjung Piai Maritime Project, Oil Storage," 2017). While on global scale, the OPEC oil cartel and countries that joined as its allies countries had decided to steadily increase oil production by 2 million barrels per day of from May 2021 to July 2021 as a global recovery from the COVID-19 pandemic (McHugh, 2021).

Indeed, the above scenarios reflected the high demand of crude oil in our world and the phenomena must keep on going. In another words, these also expose the risk of LNAPL contamination to soil or groundwater due to reasons of unpredictable mishap during extensive transportation, storage or production. Elevating possibilities of LNAPL pollution to the subsurface become a threat to our nature and standard living of humans.

2.3.1 Effects of LNAPL Contamination to Subsurface

LNAPL can influence the soil structure to various degree. Many researchers have discovered that soil contaminated with a certain degree of LNAPL will alter some of the geotechnical properties of the particular soils. Al Sanad (1995) and his colleagues investigated the influences of crude oil on the geotechnical properties of Kuwaiti sand

and found that addition of crude oil has increase the compressibility of sand (Rasheed et al., 2014). LNAPL also has the tendency to causing decrease in soil's bearing capacity as well as the friction angle. An experiment of lightweight penetration test shown that the ultimate bearing capacity of soil with two and four percent of gasoline decreased by 30 % and 52 % respectively as compared with dry soil condition. It can be explained by the presence of gasoline as a LNAPL in that soil lubricates the soil particles hence reduce its friction, eventually the overall bearing capacity and friction angle (Kererat, 2019). From another research paper, similar experiments conducted to study the effect of crude oil products on the soil's properties. Different tests such as the proctor compaction test, direct shear test and permeability test were performed by mixing the soil with different amount of kerosene and diesel in order to identify their corresponding effects. The results found that the increase of crude oil percentage also increase the apparent cohesion of soil however decrease the internal friction angle as well as the permeability of soil samples (Shaheen, 2011). Low density, higher viscosity and lower emulsifying properties of LNAPL make these substances easily absorbed into the ground thus negatively impact on the permeability and porosity of soil (Wang, 2009; He et al, 1999, cited in Wang et al., 2017). Soil particles that absorb low water-solubility of petroleum-based compound cannot readily infiltrated by water result in reducing the soil permeability (M. Hu, 2020).

LNAPL contaminants usually associate with oil products which generally abundant in carbon and nitrogen compounds, therefore has the potential to alter the composition of soil once it introduced to the underground environment (M. Hu, 2020). Pollution from the hydrocarbon pollution could hinder the growth of soil microbes, plants or crops. Other than causing effect to soil, their impacts on groundwater could not be neglected when they near to an aquifer. There is an investigation to analyse physical and chemical properties of water samples from boreholes where there has been a history of oil spillage. Result output showed that the Total Hydrocarbon Content (THC) for sample collected from oil polluted sites are higher along with low dissolved oxygen level and pH which exceed WHO Standard (Nwachukwu and Osuagwu, 2014).

2.3.2 Case Histories of LNAPL Contamination

LNAPL contamination is one of the undesirable events to be seen in our industrial era. It is still likelihood to happen in country that largely reliant on oil and also utilizing oil pipeline system. The situation similar to the deposition of waste products consequently leading a chain of effect to the nature. Few relevant cases would describe herein. On 14 August 2020, United States recorded the largest refined petroleum spill incident since 2000. It was announced the spill developed from 1.2 million gallons gasoline leaked from pipeline that was stretches from Texas to New Jersey (Brackett, 2021). Moreover, the particular pipeline company which had to take up responsibilities tested groundwater near the site and found that it consists of cancer-causing chemicals such as benzene, toluene, xylene and ethylbenzene. These chemicals belong to LNAPL.

Far in Kraut Point in Riverport on Nova Scotia's South Shore, an unknown source of LNAPL found to be seeped into the pavement. Fortunately there is no indication that the LNAPL enters the groundwater underneath as well as the ocean nearby according to the Department of Fisheries and Oceans Canada (DFO) and the department plans to clean up the site for 5 years long (Withers, 2021). Another case related to LNAPL contamination was at New Jersey. Gibbsboro, New Jersey had a former paint and varnish manufacturing factory contaminate floodplain soil at Sherwin-Williams / Hilliards Creek Site. The U.S. EPA proposes to clean up the soil contaminated with LNAPL paint solvent using excavation and bioremediation technology (Hrvacevic, 2021).

Landfill is also a common site to experience soil pollution. Taken the example of Truk-Away Landfill at Warwick, United Kingdom that operated from 1970 to 1978 and accepted dumping of different municipal and industrial wastes. According to report published by GZA GeoEnvironmental, LNAPL were found in groundwater monitoring wells at the site even though the environmental problem last over a decade ago (Carini, 2021). The news shown us that these organic pollutants able to stay underground and also in the water bodies for a long period.

In Malaysia, illegal dumping of chemicals into Kim Kim River at Pasir Gudang caused health threatening cases to residents nearby. Water samples taken by Department of Environment (DOE) and some common LNAPL found in the samples such as benzene, toluene, xylene and ethylbenzene ("Pasir Gudang: An emergency or not?," 2019). On top of that, Department of Drainage and Irrigation (DID) conducted cleaning process to remove 2.43 tonnes of chemicals and contaminated soil. On the other hand, there are a port and two oil refineries in Port Dickson where discovered a 20-year kerosene leak from distribution pipelines resulted in very serious LNAPL contamination to subsoil (Nadzif, 2015). The location also causing the hydrocarbon content in water to a range of 0.77-7.87 $\mu g \ell^{-1}$ (Law and Azahar, 1990, cited in Praveena et al., 2011).

2.4 LNAPL Movement in Porous Media

The movement of LNAPL in subsurface environment is still not accurately well-studied because of the subsurface heterogeneity. Most of the transport behaviour of LNAPL in soil were studied using oil products such as crude oil. When they spilled on the field particularly in porous media, most of them able to percolate into the unsaturated region and some left in the soil pores while staying stationary afterwards as residual saturation (Newell et al., 1995). Small volume of LNAPL released will potentially immobilised in partially saturated zone due to retentive capillary forces (Tomlinson et al., 2014). LNAPL also may accumulate on surface and flows as runoff as fine-grained soil has relatively lower infiltration capability. Along with LNAPL contaminant, other parts of toxic fluid might be evaporate or subject to biodegradation (Broje and Keller 2007; Revill et al. 2007, cited in Amro et al., 2013). If involve great amount of LNAPL in this case, the remainder would overcome soil retention capacity and move further into the water table where they share the pore spaces with water thereby polluting groundwater. LNAPL will start to displace groundwater once they developed enough head to penetrate into pore spaces filled with water and at the same time spreading laterally in a mostly radial direction (Los Angeles LNAPL Working Group, 2011). Because of the fluctuating groundwater table, LNAPL is usually smeared within the capillary fringe (U.S.EPA, 2005). The LNAPL laterally distribute along the top of saturated zone as a continuous layer under influence of gravity and capillary forces. Large mass of LNAPL also may compress the capillary fringe. Partial component of the LNAPLs which are soluble and dissolvable in groundwater may produce a plume of contamination. The extent of the LNAPL migration is based on the volume released, as LNAPL migrating deeper when released large volume (Alazaiza et al., 2019). The conceptual illustration for LNAPL release and migration is shown in Figure 2.1 below.

It should be realized that any spillage on ground is more manageable and controllable but quick infiltration process at sandy soil could make the problem fatal. In comparison with DNAPL, the spilling of LNAPL into underlying soil has higher risk as LNAPL tend to spread quickly especially in the sand media with high porosity (Kererat, 2019).

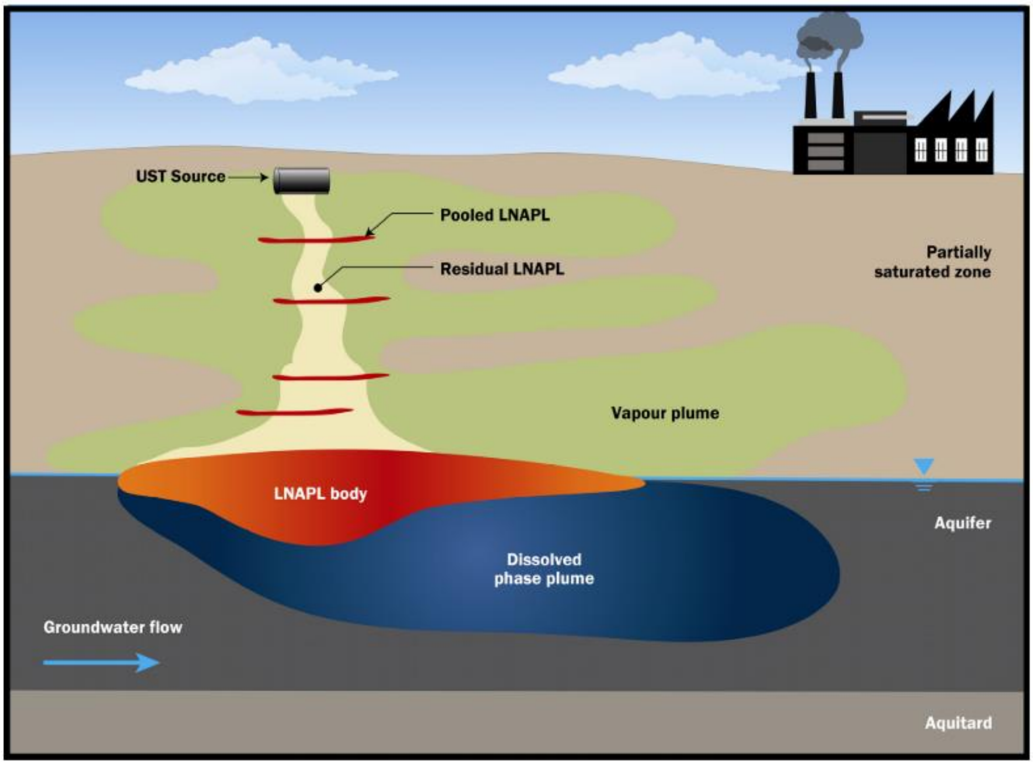

Figure 2.1 Simplified conceptual illustration for LNAPL release and migration (Tomlinson et al., 2014)

2.4.1 Fate of LNAPL in Subsurface

In subsurface, LNAPL may partition between phases either gaseous, solid, aqueous and NAPL. Their fate in the underground are depends on the processes including volatilization, dissolution, adsorption and biodegradation.

2.4.1(a) Volatilization

Volatilization of LNAPL occurred in the partially saturated zone, refers to the transformation of LNAPL that dissolved in water into the gaseous phase (Tomlinson et al., 2014). LNAPL contaminants at groundwater that volatilized are said to be partitioned into gaseous phase and would migrate within unsaturated zone through diffusion and advection (Kim and Corapcioglu, 2003). The volatilization can be defined using Henry's

Law with the ratio of concentrations or vapour pressures in the gaseous phase and aqueous phase (Tomlinson et al., 2014).

2.4.1(b) Dissolution

In term of dissolution process, LNAPL contaminants partition to gas phase and aqueous phase with the contact of groundwater. The dissolution process may contribute to long-term groundwater contamination (CL:AIRE, 2017). LNAPL will develop a dissolved-phase plume in groundwater or a vapour-phase plume above the groundwater table (Tomlinson et al., 2014). The extent of volatilization and dissolution of the contaminant is governed by vapour pressure and solubility respectively (Kim and Corapcioglu, 2003). Furthermore, their solubility can be controlled by some parameters such as temperature, pH, cosolvents, dissolved organic matter, and salinity (Newell et al., 1995).

2.4.1(c) Adsorption

Sorption is the partitioning of the dissolved LNAPL in groundwater into the solid phase. They partition onto soil materials typically fracture walls, the soil grains surfaces or the surfaces of the solid portion of the rock matrix. Generally, the adsorped LNAPL present in a small amount in the soil mass, but it removes plume mass and can restrict plume migration hence known as a relatively important natural attenuation process (Tomlinson et al., 2014).

2.4.1(d) Biodegradation

Compound in aqueous phase like LNAPL able to be degraded biologically by microorganisms living in the underground. Crude oil product can be consumed by microorganisms as nutrients for growth and proliferation while the material being oxidized into organic or inorganic compounds such as methane, carbon dioxide and water (M. Hu, 2020). Generally, most of the microorganisms were discovered near to the oil body as well as the upper half of the plume layer (Delin et al., 1998). The LNAPL in contaminant which trapped in unsaturated zone tend to subject to degradation and transformation. However, studies on pipeline spillage of NAPL have shown that significant amount of oil was recovered even after 25 years from the spillage incident hence implying the slow naturally attenuation process (Wang et al., 1998 cited in Totsche et al., 2003).

2.4.2 Factors Govern Distribution of LNAPL

It is perplexing to determine the exact migration behaviour of LNAPL under the soil. The behaviours can be affected by various of factors and conditions. In most of the spillage incidents, the saturation of LNAPL govern its distribution in subsurface environment and the saturation vary substantially throughout the soil media make it almost unpredictable. Through researches, LNAPL distribution, migration behaviour or flow patterns can be studied which useful to make approximation during actual cases. In terms of governing the distribution of LNAPL in soil, it is believed to be involve with properties of the soil or rock and also the fluid properties of LNAPL itself. Regarding the soil or rock properties, variation in permeability and porosity of different soil control the flow of fluid within the medium whilst affecting the infiltration capacity as well. Besides, other parameters and properties also can influence on LNAPL migration such as release volume, viscosity, density, adsorption, infiltration and wettability.

2.4.2(a) Soil or Rock Properties

Respect to liquid movement within soil, it often refers to concept of permeability, and porosity. Term “permeability” defines the ability of soil to transmit water. Several factors that affecting permeability and porosity including particle size distribution, shape of soil particles and texture, voids ratio, degree of saturation, fluid type and temperature. Small soil particles have little voids between them so decrease the permeability. For the effect of particle shape and texture, rounded and smooth particles give less resistance to flow of liquid. Porosity, on the other hand, described as the ratio of total volume of pore spaces including that occupied with molecules to the total volume of that particular material. Clays typically have higher total porosity (40 % to 70 %) than that of coarse-grained soil (25 % to 50 %) (Kremesec and Padlo, 2005).

2.4.2(b) Density

Density is the ratio of mass per volume. Density reflects multiple relation to the condition of soil especially the compaction applied. Regarding to soil and mineralogy, density usually expressed in term of specific gravity. Specific gravity defines the density of a liquid compared to the density of same volume of water at 4 ^oC which water assume to has its maximum density. Specific gravity is an essential soil parameter even helps in calculation of void ratio, porosity, degree of saturation, bulk density etc. In soil mechanic, high bulk density of soil media generally being compacted indicating less voids that resists movement of liquid through it. Density difference also tells the movement of contaminants as in the case where LNAPL with specific gravity less than 1.0 floats on water table unlike DNAPL. Changes in temperature affects inversely to the density of liquid and there are recovery measures that used heat produced to transform DNAPL to LNAPL hence restrict its mobility (Newell et al., 1995). Moreover, hydraulic conductivity of liquid decreases with depth as bulk density increases (Newell et al., 1995).

2.4.2(c) Viscosity

Viscosity defines as resistance to flow. Hydraulic conductivity relates to the ease of fluid moves through soil media and significantly affected by viscosity. Viscosity of a fluid can be altered by temperature. The phenomena easily visualized when oil become thinner with increasing temperature and thickens with drop of temperature. Viscosity of fluid mostly decreases at higher temperature as great thermal energy overcome the binding forces between particles result in higher mobility of fluid to flow within porous medium. Hence, hydraulic conductivity rises with the decrease in viscosity. LNAPL with lower viscosity such as petrol typically stabilize after weeks or months while higher viscosity LNAPL like crude oil steadily move within soil and take months to years to eventually stabilize (Tomlinson et al., 2014). Low viscosity NAPL also tend to flow faster than that of higher viscosity. There was model study proved that light heating oil with v = 4 mm^2s^{-1} travel four times slower than water whereas trichloroethylene with v = 0.4 mm^2s^{-l} moves 2.5 times quicker than water (Schwille, 1984).

2.4.2(d) Adsorption

Adsorption is a process defining the adhesion of liquid molecules or ions to a surface. In soil medium, introduction of liquid often results in formation of a thin liquid films around the soil particles and the process not only affected by the particular liquid but also the soil structure. There are physical and chemical adsorption. Physical adsorption bonded with weak Van der Waals forces onto the surface while chemical adsorption typically has stronger bond. LNAPL molecules tend to adhere to soil particles upon deposition on soil's top layer whereby the adsorped LNAPL molecules on soil particles likely to cause even more adsorption of molecules (M. Hu, 2020). In this way, soils adsorbed with oil molecules are said to be contaminated. The adsorption of LNAPL on soil mostly caused by physical adsorption because fine, viscous and hydrophobic properties of its particles prone to bond to solid surfaces by intermolecular force and electrostatic attraction (M. Hu, 2020).

2.4.2(e) Interfacial and Surface Tension

When there is a contact between two substances, tension exist in between. The surface tension refers to property of a liquid surface in which relevant to cohesive interactions. Interfacial tension, on the other hand, defines the adhesion forces at the interfaces of two different liquids. In soil environment, the release of LNAPL along with the presence of groundwater exhibit tension force against each immiscible fluid. The interaction could be happened between air and water, LNAPL and water or LNAPL and air. Comparison between water-air and water-LNAPL system, water would rise higher in the former instead of the latter as the LNAPL is denser than air and has lower interfacial tension as well (Kremesec and Padlo, 2005). Furthermore, LNAPL can rise higher when interface with air rather than water but would not rise as high as the water in the water-air system because the surface tension is less than that of water-air (Kremesec and Padlo, 2005). Surface tension increases with the increase of molecular size, for instance heptane (C_7H_{16}) possess higher surface tension relative to hexadecane ($C_{16}H_{34}$) with 20.5 mN/m and 28.1 mN/m respectively (Tomlinson et al., 2014). Generally, higher interfacial tension between liquids allow their interface to be more stable (Newell et al., 1995).

2.4.2(f) Wettability

Wettability is the tendency of liquid to spread over a solid surface and it determines the intermolecular interactions between solid which is the soil or rocks and the liquid such as LNAPL in this context. In reservoirs, porous media can be classified as water-wet or oil-wet. The wetting ability is measured by the contact angle. Different range indicating a different wettability as such that the smaller the contact angle value, the greater the wettability, meaning the tendency of liquid to spread and adhere to the solid surface. Contrary, higher angle is due to the surface repels that fluid away from it. For instance, part of the negatively-charged crude oil preferably adheres to limestone with net positive charge thereby carbonate reservoirs known as oil-wet (Amro et al., 2013). In unsaturated zone, preferentially water will wet solid surfaces but if only LNAPL and air present in the particular zone, LNAPL became the fluid that coat the soil grains. In saturated zone, groundwater overcome LNAPL to wet soil grains where generally LNAPL floats on the water level as non-wetting fluid to soil (Newell et al., 1995).

2.4.2(g) Infiltration and Soil Moisture

The factor of soil moisture can be associated with weathering conditions due to natural phenomena. The time when LNAPL contact with soil surface can either be dry or wet as such in warm weather or rainfall season. The pore spaces within soil medium are occupied by air, water and solid depending on its saturation. Moreover, the moisture condition of soil affects the penetration rate of the fluid to seep through (Seredin et al., 2017). According to research by Amro et al. (2013), penetration depth of crude oil in both dry and wet system (rainfall season) were studied through a setup of two separated columns with dry and wet soil respectively. Result shown that crude oil in wet system has higher initial penetration depth but it overtaken significantly by that of dry system at final stage of experiment. Hence, the migration of LNAPL in moist soil would develop quickly during early stage which preferably to have immediate remediation works. While for dry soil, the LNAPL tend to travel deeply if left untreated for a long period of time. In term of infiltration effect, an experimental study by Kamaruddin (2012) established to study the effect of rainfall on the migration of LNAPL in silica sand. It shown that the LNAPL migrated downward easily with the rainfall recharge eventually reduced the residual saturation of LNAPL at top portion of capillary surface (S. A. bt. Kamaruddin, 2012).

2.4.2(h) Saturation and Residual Saturation

Saturation is the ratio of volume of a fluid such as LNAPL to the total pore spaces volume in porous medium. Residual saturation refers to the saturation which immobilized between pore spaces due to capillary pressure. The residual saturation of LNAPL is essential parameter in determining LNAPL movement, recovery range and remedial endpoints (Johnston and Adamski, 2005). The degree of residual saturation is affected by pore size distribution, wettability of fluids and soil, interfacial tension, hydraulic gradients, ratios of fluid viscosities and densities, gravitational force, buoyancy force and flow rates (Mercer and Cohen, 1990; Demond and Roberts, 1991, cited in Newell et al., 1995). Movement of LNAPL in the soil under fluctuating water table would leave certain amount of residual LNAPL in both saturated or unsaturated zone (Atteia et al., 2019). Groundwater fluctuation prevent further migration of LNAPL as they may entrapped as residual once water level rises (Kremesec and Padlo, 2005). Water table fluctuations vital for LNAPL redistribution, its mobility and the partitioning into other phases (Gatsios et al., 2018). In normal spill scenario, fine textured media have low

LNAPL saturations thus a low residual saturation of LNAPL (Johnston and Adamski, 2005).

2.4.2(i) Capillary Pressure

Capillary pressure is the difference in pressure between the non-wetting phase and the wetting phase. In porous media, fluid like LNAPL can be held within the soil pores by capillary forces as residuals. A minimum capillary pressure in the pore space known as entry pressure must be overcome by the non-wetting fluid before migrate into the medium. Generally, capillary pressure is greater with smaller pore size, drops of initial moisture content and higher interfacial tension (Newell et al., 1995). Substantial amount of pressure required to get the water out from the small pores therefore coarse-grained soils have a relatively small capillary fringe whereas fine-grained soils like clays would exhibit a larger capillary fringe which keep the soil mostly at moist condition (Kremesec and Padlo, 2005).

2.4.2(j) Relative Permeability

Permeability of fluid has close relation to its saturation and capillary pressure. The main factor affecting the migration of LNAPLs in porous media is the relationship between relative permeability, saturation and capillary pressure (L. M. Hu et al., 2009). The ratio of effective permeability of a fluid at a certain saturation to its absolute permeability at full saturation is referred as relative permeability. Therefore, the measure is saturation dependent either that particular fluid's saturation or the saturation of another fluid within the medium. Relative permeability is ranges from 0 to 1 (Kremesec and Padlo, 2005). Relative permeability curves in Figure 2.2 helps to define various forms of multiphase flow regimes at any location. LNAPL will not migrate if is below its residual saturation. When the saturation of LNAPL increases, relative permeability of porous media with respect to that fluid also increases nonlinearly (Tomlinson et al., 2014). In another words, higher water saturation causes lower LNAPL conductivity and vice versa (Tomlinson et al., 2014).

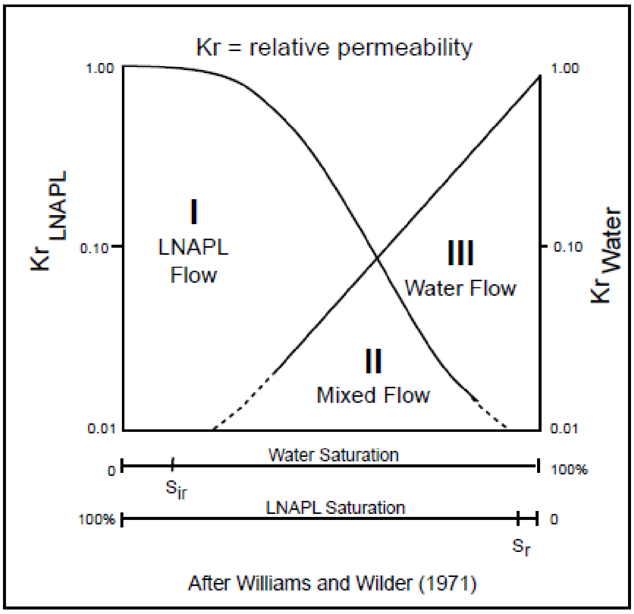

Figure 2.2 Conceptual relative permeability curves of the water and LNAPL phases in a porous media as a function of their saturation (Newell et al., 1995)

2.4.2(k) Preferential Flow

Preferential flow is a critical mechanism of NAPL movement in the unsaturated region as the flow according to the path with minimal resistance. Preferential flow may be caused by different situation such as flow along macropores or flow along structures with higher permeability (Totsche et al., 2003). LNAPL migrates preferentially through coarse-grained materials rather than fine-grained materials. LNAPL also may flow through some constructed preferential pathways like poorly grouted monitoring wells or trenches with pipelines. While in rock or impermeable clay media, the preferential paths for migration of LNAPL often relies on the fractures and its density, orientation and aperture distribution (Newell et al., 1995). Large volume of NAPL migrate along macropores as well as sedimentation discontinuities are the major preferential pathways that result in vast spreading laterally. Abrupt textural changes and capillary rise area often found to accumulate great amount LNAPLs (Totsche et al., 2003).

2.5 Simplified Image Analysis Method (SIAM)

There are multiple techniques to study the migration behaviour of NAPL through experiments such as Laser-Induced Fluorescence (LIF) logging or electrical resistivity tomography (García-Rincón et al., 2020; Alesse et al., 2019). Techniques also can be non-destructive and non-intrusive as such in photographic techniques including Light Reflection Method (LRM), Light Transmission Method (LTM) and Multispectral Image Analysis Method (MIAM) (S. A. Kamaruddin et al., 2011). On the other hand, image analysis method (IAM) is a method in which digital images that taken at designated time intervals could be analyzed to monitor changes in intensity. LRM and IAM is interdependent as LRM used during the image acquisition whereby IAM be an alternative for image processing and analysis (S. A. Kamaruddin et al., 2011). The basic concept of image analysis refers to features identification within a digital image where brightness would appear similar at same features (McNeil et al., 2006). This technique will not affect plume dynamics while enables observation concentration distributions in the entire flow domain of glass or acrylic tank experiments along with the use of tracer (McNeil et al., 2006) Tracers or dyes used is to allow visual qualitative or quantitative research on LNAPL plume evolution. Processing and analysis of images from IAM usually involve program and function in MATLAB application. It is reliable tool to monitor LNAPL migration (Alazaiza, Maskari, et al., 2021). In the research of Sa'ari et al. (2015), IAM used to study the migration of LNAPL in double-porosity soil. The two-dimensional LNAPL migration behaviour in the experiments were able to visualize based on the