THE BEHAVIOUR OF LNAPL IN SAND DUE TO FLUCTUATING GROUNDWATER

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SCHOOL OF CIVIL ENGINEERING
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THE BEHAVIOUR OF LNAPL IN SAND DUE TO FLUCTUATING GROUNDWATER

By

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ABSTRAK

Tumpahan minyak banyak berlaku di seluruh dunia. Kejadian tumpahan minyak boleh berlaku semasa minyak pengangkutan, pengeluaran dan pemprosesan, dan juga disebabkan oleh kebocoran produk petroleum daripada kapal tangki minyak. Walaupun berlakunya kejadian tumpahan minyak yang minimum, sifat-sifat tanah akan diubah atau mendatang kesan buruk tertentu kepada persekitaran. Minyak yang lebih ringan daripada air dalam kepadatan, cenderung untuk terapung di atas air bawah tanah ketika minyak menyusup masuk ke dalam tanah. Oleh itu, kerja-kerja pemulihan perlu dilakukan untuk membersihkan tanah yang tercemar oleh minyak untuk mengelakkan kesan buruk jangka panjang kepada alam sekitar mahupun manusia sebab kegunaannya. Oleh sebab mahal dan kesulitan aktiviti mengesan tumpahan minyak di kawasan tanah yang besar, pembelajaran asas penghijrahan minyak akan memudahkan mengesan dan mengatasinya tanah yang tercemar secara berkesan. Pembelajaran tingkah laku penghijrahan minyak atau NAPL bawah tanah dalam perubahan aras air tanah akan membolehkan kita untuk mengkaji bagaimana NAPL berhijrah di dalam tanah dan mengedarkan dalam air bawah tanah. Oleh itu, satu dimensi ujian kolum telah dijalankan untuk mengkaji tingkah laku migrasi NAPL dalam pasir yang kian perubahan air tanah. Keturunan dan kenaikan air bawah tanah akan menyebabkan NAPL untuk mengagihkan semula dan berkumpul di dalam kawasan surut. Walaupun sifat-sifat NAPL yang membolehkan ia terapung atau berhijrah bersama-sama dengan air tanah, sesetengah NAPL akan terkumpul di kawasan surut. Ini dapat diperhatikan melalui profil tepu NAPL dan air dalam sampel pasir.

ABSTRACT

Oil spill has been happening worldwide. The incidents of oil spillage can be happened during oil transportation, production and processing, as well as due to leakage of petroleum products from oil tankers. Even a minimal oil spill incidents happened, the soil properties will be altered or environment will be impacted with certain adverse effect. Oil which is lighter than water in density, tends to float on groundwater while they infiltrate into the ground. Thus, remediation work must be done to clean the contaminated soil by oil to prevent long term adverse effect on the environment or even humans upon consumption. Due to the difficulty and expensive tracing activity of oil spill in such huge area of soil, learning the fundamental of oil migration will facilitate the tracing and remediate contaminated soil effectively. Learning the behaviour of the oil or non-aqueous phase liquid (NAPL) migration in the soil due to its groundwater will allow us to study how the NAPL migrates in soil and distributes in groundwater. Hence, one-dimensional column test was carried out to study the behaviour of the NAPL migration in sand due to fluctuating groundwater. Fluctuating of groundwater will cause NAPL to redistribute and accumulate in the receded area. Despite the properties of NAPL which allow it floats or migrate along with groundwater table, certain amount of NAPL will be accumulated in area of groundwater receded. These can be observed through the saturation profile of NAPL and water in a sand sample.

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LIST OF ABBREVIATIONS

AASHTO	**A**merican **A**ssociation of **S**tate **H**ighway and **T**ransportation **O**fficials
DNAPL	**D**ense **N**on-**A**queous **P**hase **L**iquid
LNAPL	**L**ight **N**on-**A**queous **P**hase **L**iquid
NAPL	**N**on-**A**queous **P**hase **L**iquid
OPEC	**O**rganization of the **P**etroleum **E**xporting **C**ountries
USCS	**U**nified **S**oil **C**lassification **S**ystem

NOMENCLATURES

D_{30}	Average Particle Size
C_c	Coefficient of Gradation
V	Bulk Volume
Q	Discharge Volume,
D_{10}	Effective Particle Size of 10 Percent Fines
D_{60}	Effective Particle Size of 60 Percent Fines
Vv	Effective Volume of Pores
C	Grain Shape Constant
h	Head difference
k	Hydraulic Conductivity
Φ	Krumbein Phi Scale
$H_{c,\max}$	Maximum Capillary Height
φ	Porosity
S	Saturation
Gs	Specific gravity
C_u	Uniformity Coefficient
γ_d	Unit Weight of Dry Soil
γ_w	Unit Weight of Water
e	Void Ratio
w	Water Content

CHAPTER 1

INTRODUCTION

1.1 Background

Non-aqueous phase liquids (NAPLs) are organic compounds immiscible with water, like oil and petroleum products. NAPLs that are denser than water, like chlorinated solvents, such as trichloroethylene, are often labelled as dense non-aqueous phase liquids (DNAPLs). Conversely, non-aqueous phase liquids are called as light non-aqueous phase liquids (LNAPLs) when they are lighter than water, such as oil, gasoline, benzene and petroleum products.

Non-aqueous phase liquids (NAPLs) causes contamination of soils, aquifers and groundwater constitute a major environmental issue of concern, worldwide (Zoller and Reznik, 2006). Occurrence of subsurface contamination of soil, aquifers and groundwater with NAPLs are mainly sourced from waste disposal sites, industrial spills, gasoline stations, etc. The penetration of NPALs into soils and groundwater is due to result of accident, improper codes of chemical or fuel handling and disposal.

Figure 1.1 : An aerial view of an oil spill near the town of Usinsk, Russia (Deseret News, 2011).

Oil spills are serious environmental issues, often leading to long term impacts on the environment, ecology and socioeconomic activities of the area. Potential sources of groundwater contaminations by oil can be during oil transportation, production and processing, leakage of petroleum products from oil tankers, etc. Contamination of soil by oil spills is causing pollution of groundwater (Yoon et al., 2013). This is causing groundwater to become unsafe and unfit for human use as well as other living organisms. To the certain extent, soil contamination by NAPLs will alter the geotechnical properties of soil in term of CBR value and atterberg limit, which eventually lead to a concern on constructing structures on contaminated lands (Solly et al., 2014).

Soil contamination causing by NAPLs has been a serious issue worldwide. From 1978 to 1995, world-wide were reported more than 4100 major oil spills of 10,000 gallons or more (Pourvakhshouri et al., 1998). According to Global Soil Forum, a total of 33.7% of soil contamination is accounted for polycyclic aromatic hydrocarbon (PAH) and mineral oil in Europe (Pascucci, 2011). In São Paulo State, Brazil, Environmental Company provided statistics about 76.8% that the state was verified with contamination area (Barbosa et al., 2014). Scoping down to Malaysia, port of Tanjung Pelepas, is struck with an oil spill accident occurred on August 24 at Malaysia (Agility, 2016). With all serious cases and news, remediation strategies should be implemented by either governments or private authorities to recover contaminated soil.

Several treatment technologies have been proposed for treating petroleum hydrocarbon contaminated sites. These treatment methods are in-situ and ex-situ treatment using cleaning technologies such as thermal treatment, biological treatment, chemical extraction, soil washing and aerated accumulation techniques.

By in situ treatment method, oil contaminated soil treatment is carried out either by bioremediation, or chemical physical processes such as incineration, air sparging, etc. However, in situ techniques are more effective on sandy soils than in clayey soil. Degradation of oil in the in-situ process requires adequate amount of oxygen to be occurring depending on the penetration depth of hydrocarbon in soil and the properties of soils. A sandy soil will have more voids for aeration than clayey soil.

Thus, study of distribution, configuration and migration of NAPLs in subsurface environments are of great importance for environmental and earth research applications (Al-Raoush, 2014). From method of assessing to implementing efficient remediation strategies, distribution, morphology and mass transfer characteristics of NAPLs are of great influences to high efficient remediation strategies. A thorough study of transport and mass transfer properties are necessary for solving soil and groundwater contamination.

NAPLs frequently migrate through subsurface into unsaturated zone by gravity and capillary forces. DNAPs will eventually rest on the bottom of the water table due to its density while LNAPs tend to spread laterally along the water table (Paria, 2008; Comegna et al., 2013). NAPLs will form a complex two-phase or three-phase flow with water and air in the ground (Nakamura and Kikumoto, 2014). Along the transportation, NPALs tend to contaminate soil and groundwater occupying part of void space in soil. Through mechanisms, oil is carried by water often interact with each other and with the soil. Mechanisms such as adsorption, ion exchange, chemical reactions, etc, are continuously affecting the concentration of chemical constituents present in the percolating water.

To study the movement of diesel migration, several methods such as simplified image analysis method can be done to improve the study which directly ease the work of tracing the oil distribution in soil and groundwater.

1.2 Problem Statement

Oil spill has been a major issue to be concerned in the era when industry of fossil fuel is growing wide. Transportation, leakage and any type of accidents on oil spill are contributing to the cause of oil contaminated soil. Spilt oil infiltrates into soil through pore space of soil eventually to the groundwater. Shortage of water are forcing us to acquire new water source such as groundwater. Polluted groundwater should be treated as it causes an extent of danger and hazard to human health upon consumption.

Although there are a few methods to treat contaminated soil, tracing the area of contaminated soil have been difficult. Due to its nature of liquid state and added complexity of soil and oil, distribution of the oil on a large scale of the soil increases the difficulty of the tracing work as well as the remediation work on treating the contaminated soil.

Infiltration process of oil is complicated by the seasonal fluctuation of water table due to changes of rainfall. Fluctuation of groundwater level can cause vertical displacement and redistribution of LNPAL within the saturated and unsaturated zone. As the water table falls, LNPAL which floating on top of the water table will be drained downwards as the fall of water table. However, a portion of LNAP will retain within the soil pores due to interfacial forces and capillary forces. The entrapped LNAPL residual is difficult to be displaced by water when water table is rise again. Therefore, the movement of the groundwater table together with the LNAPL can be properly studied by the simplified image analysis method.

1.3 Objectives

The objectives of the study are

a) To determine the capillary height of groundwater in sand.

b) To analyse the saturation changes of diesel over time in sand due to fluctuating groundwater.

c) To assess the behaviour of diesel in sand due to fluctuating groundwater.

1.4 Scope of Work

Porous media (sand) had been characterized based on its particle size, specific gravity, void ratio by using laboratory investigations. After setting up the medium, model of a NAPL contaminant (diesel) migrating through 1-D column test was done. Fluctuation of groundwater was simulated and behaviour of the dispersion and intensity of NAPL in fluctuating groundwater was studied. Simple image analysis was carried out to compare different results from the physical modelling.

1.5 Expected Outcome

Modelling of the behaviour of NAPL contaminant in groundwater able to improve precision of detection work in real case as well as remediation work in treating NAPL-contaminated soil and groundwater. Improving efficiency in detecting behaviour of NAPL contaminant in groundwater is expected from this study. This study does more than just investigating intensity of NAPL contaminant in groundwater, but also key solution for remediation work efficiency.

1.6 Dissertation Outline

1.6.1 Chapter 1

Introduction describes background of the study, problem statements, objectives to achieve, scope of works and expected outcome of this study.

1.6.2 Chapter 2

Literature review discusses related studies and researches done from others. Information are collected to support this study with approved references.

1.6.3 Chapter 3

Methodology presents procedures to achieve the objectives of this study. It covers the flow chart for this study from soil properties experiment to simulation of physical model using 1-D column test.

1.6.4 Chapter 4

This chapter is about analysing and discussing results. After obtaining data and results from tests, the results are analyse and explained thoroughly achieving the objectives of this research.

1.6.5 Chapter 5

Chapter 5 is conclusion of this research. This chapter draws conclusion that summarize the important content throughout the research.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

Non-aqueous phase liquid, NAPL comprised light non-aqueous phase liquid, LNAPL and dense non-aqueous phase liquid, DNAPL. Physical properties like density, give rise the difference between LNAPL and DNAPL. Oil is classified into LNAPL and DNAPL depending on its constituent components after fractional distillation. Throughout decades, human activity on oil extraction has increased across the world. It is undoubtedly oil spill or minor leakage will happen. Either oil spill into the soil or into the sea, contamination occurs onto the environment which eventually imposing health issue to human upon as well as flora and fauna upon consumption of contaminated groundwater or sea. Oil spill happens due to leakage of oil storage tank, during transportation, processing and packaging, etc. Evaluating LNAPL movement in soil due to fluctuating groundwater is important to improve the effectiveness of remediation work. When the groundwater fluctuates, the capillary fringe changes as this will cause the LNAPL to redistribute and accumulated in fluctuated area due to its physical properties of LNAPL.

2.2 Non-Aqueous Phase Liquid

Non-aqueous phase liquid (NAPL) is liquid contaminants that does not dissolve in water such as oil, gasoline and petroleum products. NAPL comprises two types that are light non-aqueous phase liquid (LNAPL) and dense non-aqueous phase liquid (DNAPL). Density simply categorizes NAPL into LNAPL and DNAPL. For LNAPL, it has relatively lower density to water while DNAPL has a higher density than water.

As a result, LNAPL tends to float on top of the groundwater while DNAPL sinks below the groundwater until an impermeable bedrock is reached (Yoon et al., 2013). Health hazard is upon consumption of groundwater due to its pollution on groundwater.

2.2.1 Dense Non-Aqueous Phase Liquid

Dense non-aqueous phase liquid or DNAPL is a liquid that denser than water and immiscible with water. When DNAPL is discharged into subsurface of soil, it tends to sink below water table and stop after reaching impermeable bedrock. Examples of materials that are DNAPLs when spilled include: chlorinated solvents such as trichloroethylene, coal tar, mercury, etc. DNAPLs are present at numerous hazardous waste sites and are suspected to exist at many more. Due to the many variables influencing DNAPL transport and fate in the subsurface, and consequently, the ensuing complexity, DNAPLs are largely undetected and yet are likely to be a significant limiting factor in site remediation.

2.2.2 Light Non-Aqueous Phase Liquid

Light Non-Aqueous Phase Liquid usually abbreviated to LNAPL, is a liquid contaminant that is less dense than water and does not mix easily with water. Differences in the physical and chemical properties of water and LNAPL result in the formation of a physical interface between the liquids which prevents the two fluids from mixing. Therefore, they co-exist with water in pore space of aquifer.

LNAPL affects ground-water quality at many sites across the country. Releasing of petroleum products is the most common LNAPL related ground-water contamination problems. These products are typically multicomponent organic mixtures composed of chemicals with varying degrees of water solubility. Many components (e.g., n-dodecane and n-heptane) have relatively low water solubility under ideal conditions. Other components (e.g., benzene, toluene, ethylbenzene, and xylenes) are slightly soluble. Some additives (e.g., methyl tertiary-butyl ether and alcohols) are highly soluble. Physical and chemical properties which affect transport and fate of selected LNAPL compounds and refined petroleum products are presented in Table 2.1. In general, LNAPLs pose potential long-term sources for continued ground-water contamination at many sites (Mclean and Bledsoe, 1992). Therefore, further study of its behaviour in groundwater is important for remediation work and detection work.

Table 2.1 : Representative properties of selected LNAPL chemicals commonly found at Superfund sites (Mclean & Bledsoe 1992), water, and selected petroleum products (Lyman et al. 1990)

Chemical	*Density†* (g/cm^3)	*Dynamic† Viscosity (cp)*	*Water† Solubility (mg/l)*	*Vapor† Pressure (mm Hg)*	*Henry's Law† Constant* $(atm\text{-}m^3/mol)$
Methyl Ethyl Ketone	0.805	0.40	2.68 E+05	71.2	2.74 E-05 [2]
4-Methyl-2-Pentanone	0.8017	0.5848	1.9 E+04	16	1.55 E-04 [2]
Tetrahydrofuran	0.8892	0.55	3 E+05 [1]	45.6 [2]	1.1 E-04 [2]
Benzene	0.8765	0.6468	1.78 E+03	76	5.43 E-03 [1]
Ethyl Benzene	0.867	0.678	1.52 E+02	7	7.9 E-03 [1]
Styrene	0.9060	0.751	3 E+02	5	2.28 E-03
Toluene	0.8669	0.58	5.15 E+02	22	6.61 E-03 [1]
m-Xylene	0.8642 [1]	0.608	2 E+02	9	6.91 E-03 [1]
o-Xylene	0.880 [1]	0.802	1.7 E+02	7	4.94 E-03 [1]
p-Xylene	0.8610 [1]	0.635	1.98 E+02 [1]	9	7.01 E-03 [1]
Water	0.998 [6]	1.14 [6]	----	----	----
Common Petroleum Products					
Automotive gasoline	0.72-0.76 [3]	0.36-0.49 [3]	----	----	----
#2 Fuel Oil	0.87-0.95	1.15-1.97 [5]	----	----	----
#6 Fuel Oil	0.87-0.95	14.5-493.5 [4]	----	----	----
Jet Fuel (JP-4)	~0.75	~0.83 [5]	----	----	----
Mineral Base Crankcase Oil	0.84-0.96 [6]	~275 [4]	----	----	----

† Values are given at 20°C unless noted.
[1] Value is at 25°C.
[2] Value is at unknown temperature but is assumed to be 20°- 30°C.
[3] Value is at 15.6°C.
[4] Value is at 38°C.
[5] Value is at 21°C.
[6] Value is at 15°C.

2.3 Soil Contamination due to Oil Spill

Oil or fossil fuel has been a major concern to the world as it has been a primary source of energy to daily basis such as vehicle fuel. Even though with implementing of advanced technology of renewable energy resources, oil energy is still widely used across the world. In the third quarter of 2016, world oil demand and OPEC oil supply from International Energy Agency register its high with approximately 97.05mb/d and 33.6mb/d respectively (International Energy Agency, 2017).

By the law of supply and demand, a high demand for oil comes with high supply. A high supply of oil increases rate of oil extraction from the soil. However, the oil industry faces inevitably risks accidental discharges into soils, surface water or groundwater during transportation, whether by land or by sea, or during the oil drilling process, or due to leakages from storage tanks, etc (Wang and Shao, 2009).

Oil possess toxicity and carcinogenetic properties which are causing negative impacts to human and environment. According to research from Claxton (2014), fossil fuels many times dispose toxic substances into the environment. These unwanted toxicants are associated with fuel spills, the refining of fuels, and the combustion of fuels. Bejarano and Michel (2016) have studied the impacts of oil spills on sand beach ecosystem. According to Mulligan et al. (2001), oil spill ultimately becomes a continuous source of the soil and groundwater contamination.

There are a few of major oil spill happening worldwide. One of the biggest oil spill (520 million gallons) was in Kuwait in 1991 as known as Gulf War oil spill (Bush, 1992). Also, the Mingbulak oil spill also known as the Fergana Valley oil spill was the worst terrestrial oil spill in the history of Asia (Chennai Online, 2015). The total loss was reported around 88 million gallons. The 1992 disaster was considered as a largest inter terrestrial oil spill recorded.

In Malaysia, Tanjung Piai National Park here will be closed after an oil spill washed up onto a 600m coastal stretch located in the park and nearby Pulau Kukup (Wild Singapore News, 2012). Some minor cases can be seen on daily basis, such as leakage of oil storage underneath the surface, etc. Although the amount of pollution is insignificant to cause an serious impact on environment, studies and remediation works should be carried out to prevent any cases further deteriorating.

2.3.1 Remediation Work

Exploration and extraction of petroleum cause potential negative impact to environment in different degree. Accidental oil spill, leakage and other form of accidents are sources of soil and groundwater contamination. From the research of Zarlenga et al. (2016), continuous contaminant release in the subsurface environment on adverse human health effects. Therefore, removal of NAPL from contaminated soil and water aquifer has become a vital step to mitigate the negative impacts.

Different methods are applied to treat NAPL contaminants in soil depending the soil condition and NAPL condition. The efficiency of the remediation methods based on several factors such as amount of spilled oil, penetration depth of oil into soil, type of oil and polluted soil, and the age and degree of contamination. Each treatment method has their limitations. Therefore, every different case will be applied with different technique and approach to improve its efficiency.

Remediation technologies comprised ex-situ and in-situ methods as shown in Table 2.2. Ex-situ methods involve excavation of contaminated soil and subsequent treatment at the surface as well as contaminated groundwater. Example of ex-situ methods are thermal remediation, soil scrubbing, land farming, biopiling, bioreactors, “pump and treat”, etc. In-situ methods treat the contamination without removing the soils or groundwater. For example, in-situ approaches include thermal remediation, chemical oxidation, soil vapor extraction, bioventing, biosparging, bioslurping, etc.

Table 2.2 : Compound removal and soil constraints for various remediation techniques (Williams, 2002).

Remediation Technique	Effectively Removed Compounds	Soil Constraints
Ex Situ Techniques		
Thermal Remediation	TPH, PAH, BTEX, PCB, PCP, PCDD, PCDF	No specific constraints
Soil Scrubbing	TPH, BTEX, PAH, PCB, heavy metals, dioxins	Must be made homogeneous to treat
Landfarming	PAH, PCP	No specific constraints
Biopiling	BTEX, PAH, TNT, RDX	Must be made homogeneous to treat
Bioreactors	PAH, PCB	Must be separated by particle size in order to treat
In Situ Techniques		
Thermal Remediation	BTEX	Must be homogeneous, have high permeability and low organic content
Chemical Oxidation	PAH, TCE	Must be permeable
Soil Vapor Extraction	BTEX	Must have low percent fines and correct moisture content
Bioventing	PAH, nonchlorinated solvents	Must be homogenous, may be unsaturated
Biosparging	PAH, nonchlorinated solvents	Must be homogenous and saturated
Bioslurping	Free Product (Petroleum)	Must be homogenous and saturated
Phytoremediation	TPH, BTEX, PAH, TNT, RDX	Must have contamination in shallow soil

2.3.2 The Behaviour of LNAPL in Subsurface

According to the study from Kim and Corapcioglu (2003), when the LNAPL is released onto the subsurface, which is soil, the LNAPL migrates downwards through vadose zone. Vadose zone is an either unsaturated or partially saturated subsurface media above groundwater table. The vadose zone consists of both solid material and voids. These voids are pore spaces that primarily filled with air and water. LNAPL will be retained along its flow path by adsorptive and capillary forces at the residual saturation. NAPL spill of a relatively small finite quantity will become immobile and occupied within vadose zone.

Capillary fringe is located at bottom part of vadose zone which is partially saturated with water pulled upwards by capillary forces from underlying saturated zone. If greater volume of LNAPL is spilt into soil, LNAPL will migrate completely through unsaturated zone and accumulate on groundwater. When LNAPL reaches the capillary fringe, it tends to displace water in pore spaces resulting dispersion of LNAPL in soil. The behavior of NAPL migration can be seen in Figure 2.1.

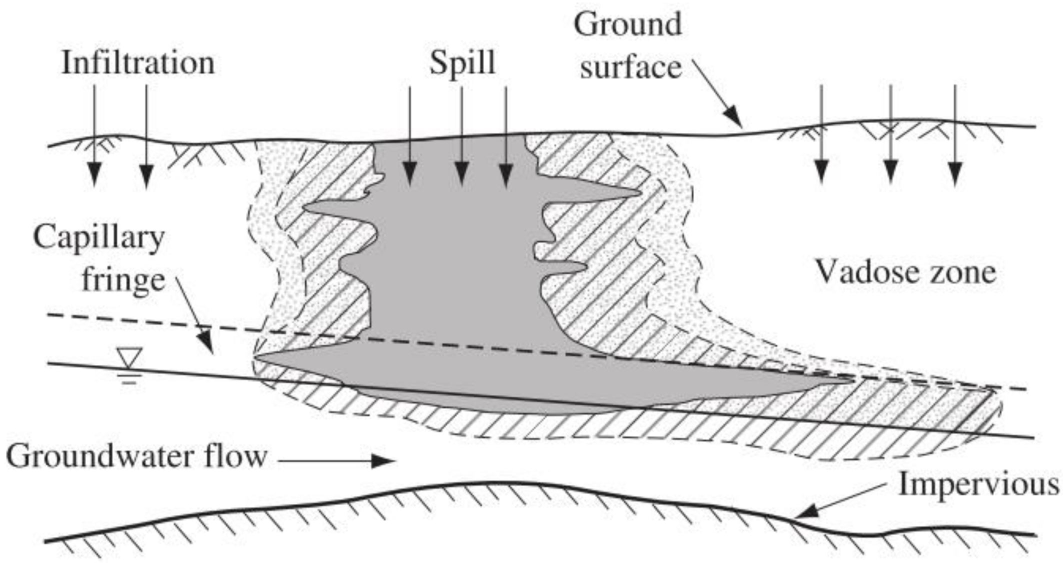

Figure 2.1 : Large oil spill in soil (Bear & Cheng 2009)

2.4 Properties of Porous Media (Sand)

2.4.1 Soil Colour

Soil color is used in soil classification and the Munsell Color Chart is the standard method of colour determination (Thompson et al., 2013). Soil has a wide range of colour like yellow, red, black, etc. Soil colour usually comes from organic matter and iron. Soil color analysis is a fast and inexpensive analysis for soil properties such as soil organic carbon (SOC) content and iron oxides (Baumann et al., 2016).

2.4.2 Soil Texture

Soil is made up of different-sized particles. Soil particle size can be colloidal particles, particles in ecology, particles present in granular material and particles that form a granular material. Soil texture are classified based on proportion of soil content such as sand, silt and clay particles.

Soil particle size distribution is widely used in soil classification and in estimating soil hydraulic properties such as soil water retention curve, soil hydraulic conductivity and soil bulk density (Zhao et al., 2016). To measure particle size and its distribution, it can be done by chemical, mechanical, ultrasonic or sieving and sedimentation and others (Gee and Or, 2002).

Sand is a natural granular material composed of finely divided rock and mineral particles. Sand particles range in diameter from 0.0625 mm to 2 mm. It is finer than gravel and coarser than silt. Sand can also refer to a textural class of soil or soil type from Figure 2.2.

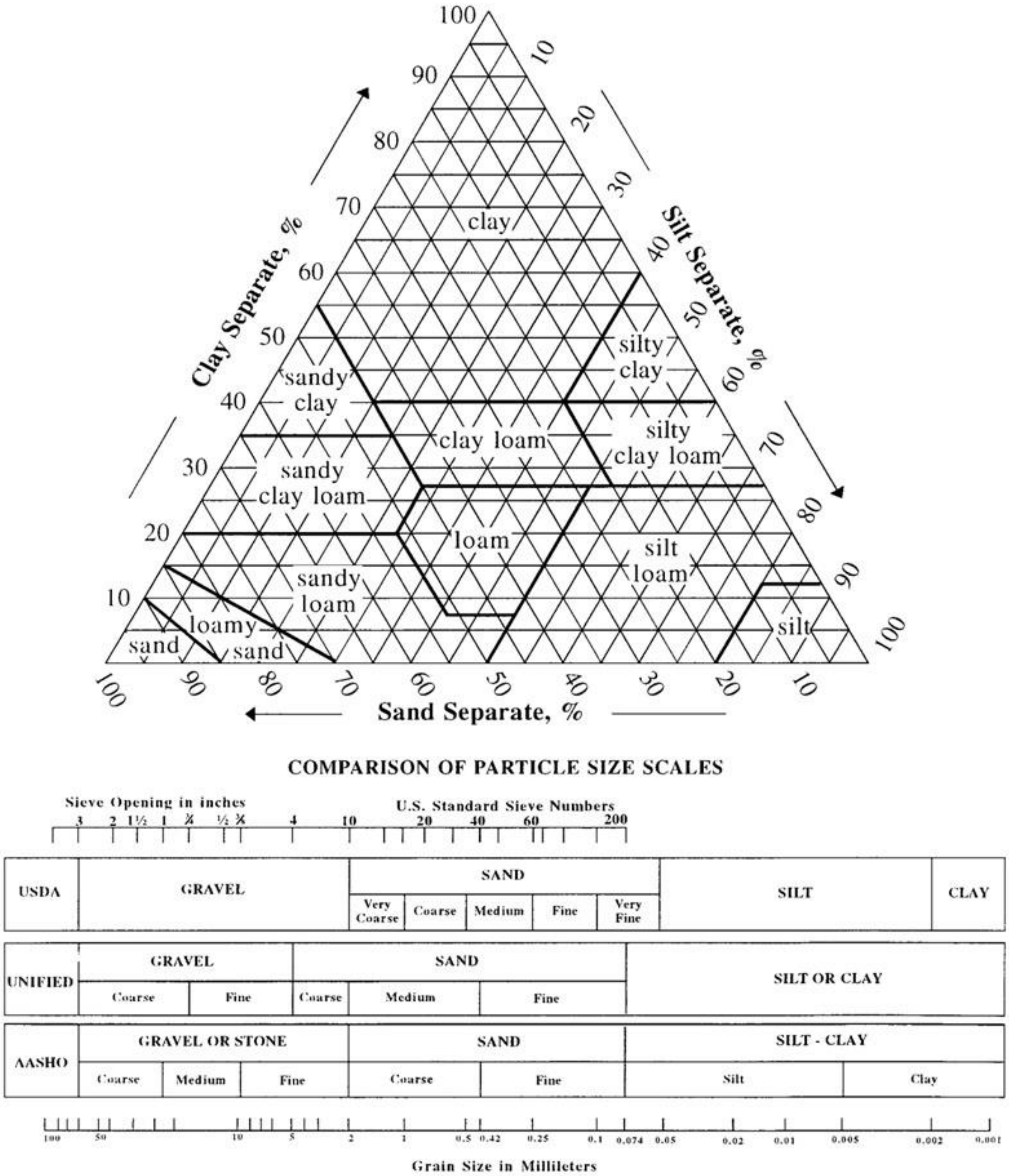

Figure 2.2 : Soil classification by its texture (United States Department of Agriculture, n.d.).

2.4.3 Porosity, Void Ratio and Degree of Saturation

Soil porosity refers to open spaces in soil between mineral particles or organic matter as shown in Figure 2.3. Pore space of soil is usually occupied by water or air. Porosity influences the movement of air and water. Porosity of soil decreases as particle size increases.

$$\varphi = \frac{Vv}{V} \tag{2.1}$$

Where φ is porosity; V_v is effective volume of pores; V is bulk volume of sample.

Porosity φ is the fraction of the total soil volume that taken up by the pore space. Thus, it is a quantification of the amount of space available to fluid within a specific body of soil. Being simply a fraction of total volume, φ can range between 0 and 1, typically falling between 0.3 and 0.7 for soils (Nimmo, 2004).

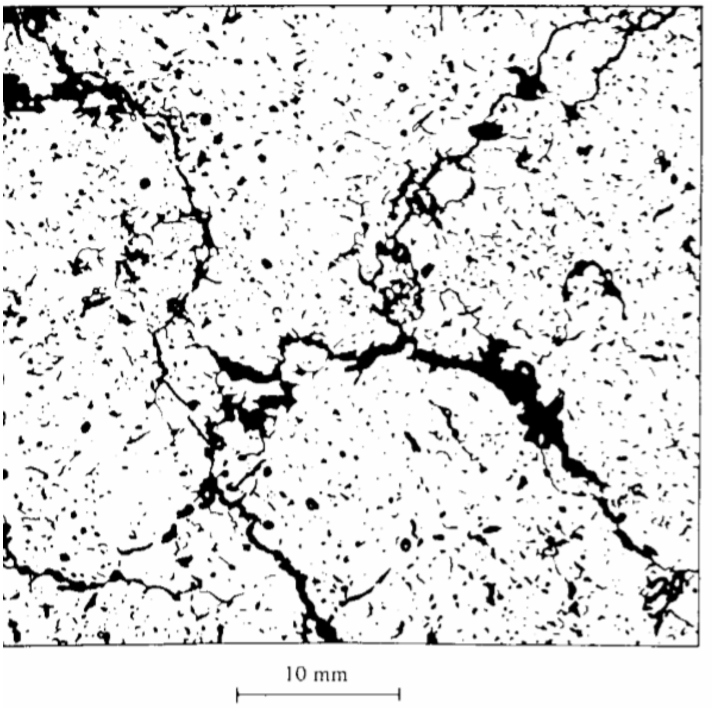

Figure 2.3 : Cross section of a typical soil with pore space in black. (Nimmo, 2004)

Void ratio depends on the consistency and packing of soil particles. It is affected by compaction and different type of soil depicts different void ratio. In short, void ratio is a quantity related to porosity and defined as the ratio:

$$\boldsymbol{e} = \frac{\boldsymbol{V_V}}{\boldsymbol{V_S}} = \frac{\boldsymbol{V_V}}{\boldsymbol{V_T - V_V}} = \frac{\boldsymbol{\varphi}}{\boldsymbol{1-\varphi}} \tag{2.2}$$

Where e is void ratio; V_V is effective volume of pores; V_T is total volume of sample; φ is porosity.

Water content is the quantity of water contained in a soil, which can be referred to degree of saturation. In mathematical terms, degree of saturation is the ratio of volume of water to the volume of voids:

$$\boldsymbol{S} = \frac{\boldsymbol{V_W}}{\boldsymbol{V_V}} \tag{2.3}$$

Where S is degree of saturation; Vw is volume of water in pores; Vv is effective volume of pores.

The relationships between void ratio, porosity and degree of saturation can be simply explained in Figure 2.4.

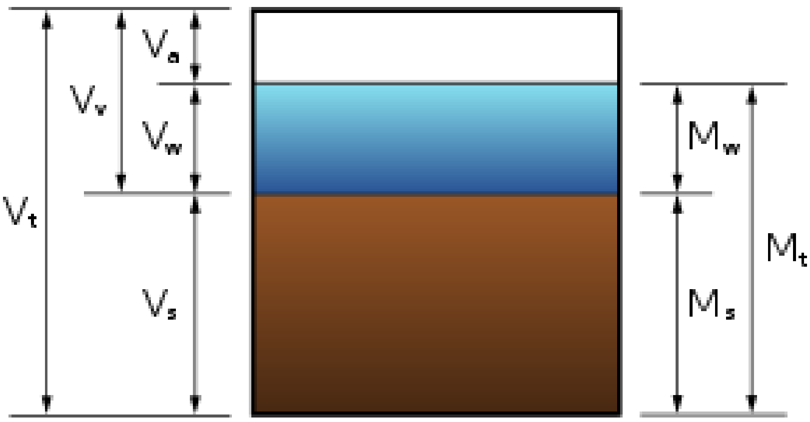

Figure 2.4 : Soil composition by volume and mass, by phase of water, air, void, soil and total.

2.4.4 Composition

According to ISO 14688-1, sand is graded as fine, medium and coarse with ranges 0.063 mm to 0.2 mm to 0.63 mm to 2.0 mm. Sand sizes are based on the Krumbein phi scale, where size in $\Phi = -\log_2 D$; D being the particle size in mm. On this scale, for sand the value of Φ varies from −1 to +4, with the divisions between sub-categories at whole numbers.

Soil has more than 85 % sand-sized particles by mass (Of & In 1976). The most common constituent of sand is silica (silicon dioxide, or SiO_2), usually in the form of quartz due to its chemical inertness and hardness, which is the most common mineral resistant to weathering. The composition of mineral sand is highly variable, depending on the local rock sources and conditions. The Table 2.3 shows different sand types and its general identifications. (Pettijohn et al., 1987).

Table 2.3 : Sand types and its constituent element (“Sand Types - Sandatlas,”, n.d.)

Images	Type of sand	Constituent elements
	Coral sand	Calcareous fragments of biogenic origin
	Volcanic ash	Fine mixture of minerals and rock fragments from volcanic eruption such as plagioclase, quartz, amphiboles, and pyroxenes.
	Glass sand	Mineral grains that come from disintegrated rocks such as Plagioclase, quartz, K-feldspar, and biotite together become an igneous rock granodiorite.
	Immature sand	Composed of mineral grains that come from disintegrated rocks. Constituents of this sand are plagioclase, quartz, K-feldspar, and biotite which gives an igneous rock granodiorite.

	Gypsum sand	Composed of tabular gypsum grains
	Continental sand	Mostly composed of quartz but may also contain other minerals like feldspar, mica, and biogenic grains.
	Silica sand	The particular sand deposit contains quartz.
	Black sand	Composed of basalt, andesite and volcanic glass. The minerals that give black colour to these rocks are predominantly pyroxenes (mostly augite), amphiboles (mostly hornblende) and iron oxides (mostly magnetite).
	Quartz sand	Quartz is the most common sand forming mineral. This sand type consists little else than this mineral.

2.5 Groundwater

Groundwater is the water present in subsurface soil pore spaces. An aquifer is a unit of rock or unconsolidated deposit from which an amount of usable water can be yielded. Water pressure in the saturated zone is greater than atmospheric pressure, and later generally fills the pore space. Water in this zone is called groundwater. Groundwater can be recharged and flow towards the surface naturally. From the Figure 2.5, basic groundwater structure is defined together with aquifer and aquitard.

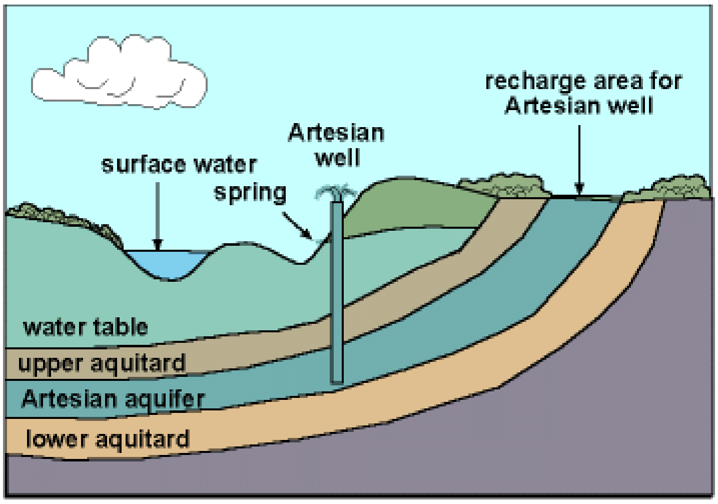

Figure 2.5 : Cross-section showing aquifer, aquitard and groundwater

2.5.1 Formation of Fluctuating Groundwater

The estimation of the Earth's hydrosphere has a huge amount of water about 1386 million cubic kilometres. However, 97.5 % of this amount are saline waters and only 2.5 % is fresh water as shown in Figure 2.6. Fresh water shows about 29.9 % as groundwater while the greater portion of this fresh water (68.7 %) is in the form of ice and permanent snow cover in the Antarctic, the Arctic, and in the mountainous regions. Only 0.26 % of the total amount of fresh waters on the Earth are concentrated in lakes, reservoirs and river systems where they are most easily accessible for our economic needs and vital for water ecosystems.

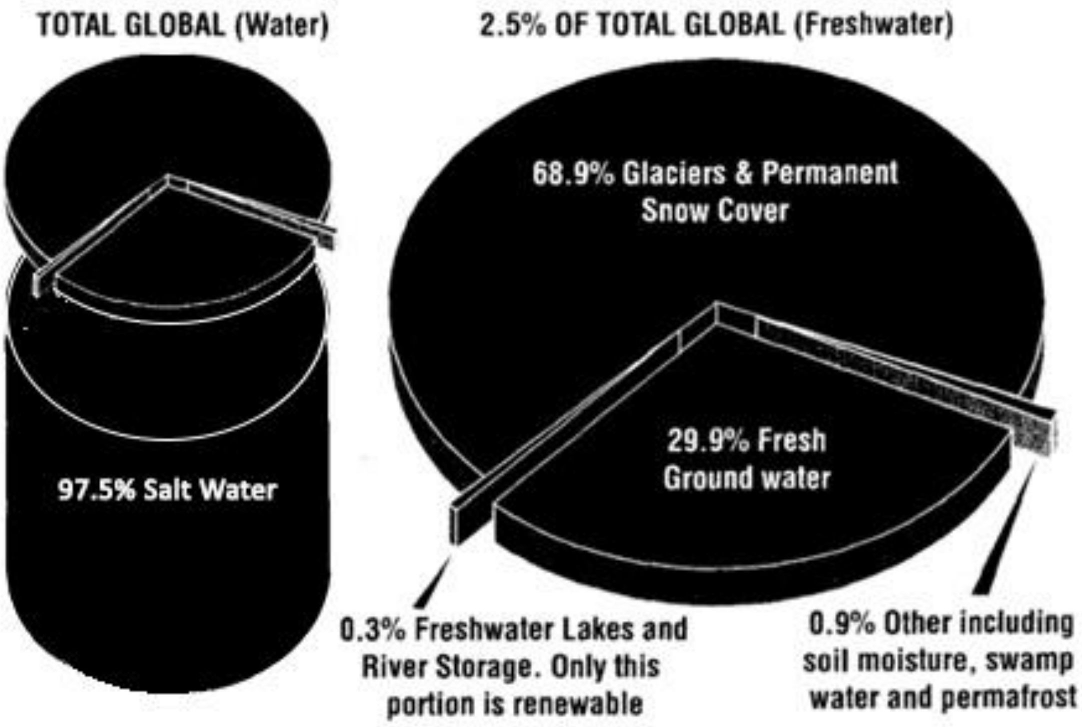

Figure 2.6 : Statistic report on global water and freshwater which taken from Shiklomanov (1998).

Groundwater is subsurface water that saturates the pores in soil and rocks. Groundwater is replenished by precipitation unevenly depending on local climate and geology. When rain falls, some of the water evaporates, some are transpired by plants, some flows overland and some infiltrates into pores of the soil. Water that enter soil may sometimes replaces water that has been evaporated or transpired through plants during dry period. Between the land surface and the aquifer water is an unsaturated zone. In this unsaturated zone, small openings of the soil and rock contains a little amount of water, whereas the larger openings usually contain air instead of water.

Water levels in aquifers show a dynamic balance between groundwater recharge, storage and discharge. When recharge exceeds discharge, the volume of groundwater will increase directly increasing the water levels; vice versa. Process of recharging and discharging happens unevenly in time and space, causing groundwater level to continuously fluctuate. Water levels in wells reflect these changes and provide the principal means of tracking changes in groundwater storage over time. The water level measurements are mostly affected by the hydrological stresses such as precipitation and pumping.

2.5.2 Impact of Groundwater Pollution by LNAPL

Groundwater accounts for more than 90% of freshwater resources in Malaysia. The total usable water is estimated approximately the sum of 10% of surface runoff and volume of groundwater recharge. However, not all groundwater can be abstracted due to difficulty in groundwater assessment, poor quality of water, uneconomical treatment of water required, intruded by saline water, etc.

Table 2.4 : The summary of water resources in Malaysia (Ismail, 2009)

Water resources	Quantity (Billion m3)
Annual rainfall	990
Surface runoff	566
Evapotranspiration	360
Groundwater recharge	64
Surface artificial storage	25
Groundwater storage	5000

Over-exploitation of groundwater may lead to ground subsidence, saltwater intrusion, threat to wetlands and an accelerated movement of pollutants. Groundwater should be protected from pollution for consumption and ecosystem. Major threats are from urbanisation, industrial waste, and discharge from agriculture activities (Chu, 2004). Accidental spillage of oil is one of the threats that causing NAPLs pollute groundwater. Due to its properties of low water solubility and toxicity, it can degrade in groundwater quality for years through dissolution. The fluctuation of groundwater level can cause vertical displacement and redistribution of LNAPL within the saturated and unsaturated zones. Initially, LNAPL tends to float over the capillary zone. A portion of LNAPL was retained in soil pores of the vadose zone as immobile globules due to interfacial forces and capillary forces when groundwater table falls. Entrapped LNAPL or residual is difficult to be displaced by water. When the groundwater table rises, floating LNAPL will again leaving some residual LNAPL within the saturated zone. Due to its behaviour, the contaminated zone may extend to full range of groundwater table and capillary fringe fluctuating zones (Fetter, 1999).

Crude oil contains poisonous chemical constituents that can harm to the environment, human as well as other species. Upon contact or consumption, oil poses danger to human in mental health, physical/physiological effects with its genotoxic, immunotoxic, and endocrine toxicity properties of oil (Laffon et al., 2016). Crude oil is made up of thousands of chemical compounds. Some of the lighter ones, including benzene and toluene, are known as volatile organic compounds (VOCs) and tend to evaporate soon after they reach the water's surface. These chemicals can cause respiratory problems as well as temporary central nervous system troubles. And some VOCs have been linked to cancers at high exposure levels. When oil or dispersants come into contact with skin, they can also cause dermatitis and other skin infections.

Therefore, this study experimentally investigates the effect of groundwater fluctuation on migration of LNAPL in subsurface. One-dimensional column test is used to study the effects of groundwater level fluctuation. From that, simplified image analysis method is used to measure the distribution of water and LNAPL saturation in porous media.

CHAPTER 3

METHODOLOGY

3.1 Overview

In this study, physical experiments were conducted for further analysis and relationship development. Physical experiments included soil properties tests and simulation test. Soil properties tests comprised proctor test, constant head test and direct shear test while simulation test is 1-D column test which was using simple image analysis method. With all methodology and objectives set, data collection was done to gather information from existing researches. Existing physical study was carried out to acquire further information on oil spill experiment method of the tests was studied to identify the importance of the tests and objective of acquiring properties. Then, physical experiments were done. Particle size analysis was done first to sieve the required particle size from 1.18 mm to 0.30 mm. For the following simulation test, medium used was sand with no presence of silt. Therefore, sand was extracted from the river sand sample. Then, proctor test was to determine the dry density of the sample so that the next experiments were applying with a fixed dry density. After obtaining soil properties, simulation of 1-D column test was done with simple image analysis method. Data and results were analysed and comparison were carried out to develop relationships.