SOIL CAPILLARY DEPRESSION IN LNAPL CONTAMINATED SOIL DUE TO FLUCTUATING GROUNDWATER TABLE STUDIES

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by

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ABSTRAK

Tumpahan minyak adalah kejadian tipikal yang berlaku di seluruh dunia. Semua sektor di Malaysia sebahagian besarnya bergantung kepada minyak sebagai sumber tenaga. Akibatnya, tumpahan minyak boleh berlaku dengan mudah semasa pengangkutan minyak, penyimpanan, pengeluaran, dan pemprosesan kerana saluran paip dan kebocoran tangki simpanan bawah tanah. Sebaik sahaja minyak sampai ke meja air bawah tanah, ia boleh mengubah sifat tanah dan mencemarkan air. Minyak yang kurang padat daripada air biasanya akan terapung di permukaan dan berhijrah dengan air bawah tanah. Tanah yang tercemar dan air bawah tanah akan memberi kesan kepada alam sekitar. Akibatnya, kerja pemulihan untuk membersihkan tanah yang tercemar dan air bawah tanah diperlukan. Kos rawatan pencemaran tanah biasanya agak besar. Teknik pengesanan untuk tumpahan minyak di kawasan yang luas juga kompleks dan mahal. Akibatnya, penghijrahan LNAPL di dalam tanah boleh disiasat. Selain daripada corak penghijrahan, kapilari tanah juga memainkan peranan penting untuk penghijrahan LNAPL. Kawasan tanah yang tercemar boleh dipulih setelah megetahui penghijrahan minyak di dalam tanah. Dengan ini, kerja pemulihan boleh dijalankan dengan yang lebih tepat. Ujian tangki dua dimensi digunakan untuk menyiasat penghijrahan diesel dalam kajian ini. Untuk mengkaji kemurungan kapilari di dalam tanah, beberapa corak turun naik muka air tanah telah disimulasikan. Di samping itu, hubungan muka air tanah isi padu tumpahan minyak telah disiasat dalam kajian ini. Kaedah Analisis Imej digunakan untuk memerhatikan profil LNAPL dan air dalam sampel tanah.

ABSTRACT

Oil spills are a typical occurrence that occurs all around the world. All sectors in Malaysia rely largely on oil as a source of energy. As a result, oil spills can happen easily during oil transportation, storage, production, and processing due to pipeline and underground storage tank leaks. Once the oil reaches the groundwater table, it can change the properties of the soil and pollute the water. The less-dense oil than water will usually float on the surface and migrate with the groundwater. Polluted soil and groundwater will have an impact on the environment. As a result, remedial work to clear the contaminated soil and groundwater is required. The cost of soil pollution treatment is typically considerable. The tracing technique for an oil spill over a vast area is also complex and costly. As a result, the migration of Light Non-Aqueous Phase Liquids (LNAPLs) in the soil can be investigated. Other than the migration pattern, the capillary fringe also plays an important role in LNAPL migration. The contaminated area of the ground may be predicted using knowledge of oil migration in soil, allowing for a more precise repair. Two-dimensional tank tests were used to investigate the lateral migration of diesel in this investigation. To investigate capillary depression in the soil, several groundwater table fluctuation patterns were simulated. In addition, the volume of oil spilled relationship was investigated in this study. Simplified Image Analysis Method was used to observe the saturation profile of LNAPL and water in the soil sample.

TABLE OF CONTENTS

APPENDIX A

APPENDIX B

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF PLATES

Page

LIST OF ABBREVIATIONS

NAPL	Non-Aqueous Phase liquid
LNAPL	Light Non-Aqueous Phase liquid
DNAPL	Dense Non-Aqueous Phase liquid
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
ASTM	American Society for Testing and Materials
SIAM	Simplified Image Analysis Method
BS	British Standard
USCS	Unified Soil Classification System
AASHTO	American Association of State Highway and Transportation Officials

CHAPTER 1

INTRODUCTION

1.1 Background

Groundwater contamination has been a problem because of the accelerated growth of industrialization, population, and urbanization. Non-aqueous phase liquid (NAPL) is one of the contamination types. NAPLs are hydrocarbon contaminants that are non-dissolvable by water, like oil or petroleum. NAPLs will affect the quality of soil and groundwater for a very long time. When NAPL is released into the ground, it will tend to migrate vertically downward the water table. The presence of NAPL in soil may fill up the soil pore space, either water or air. (Teramoto and Chang, 2020)Thus, it will affect the soil capillary depression.

The sources of NAPL contamination are from the leakage of petroleum from storage tanks or others transfer pipelines. The leaking hydrocarbon will migrate to the saturation zone and accumulate together as LNAPL. (Podgorski *et al.*, 2021) Generally, NAPL can be separated into two types: light non-aqueous phase liquid (LNAPL) and dense non-aqueous phase liquid (DNAPL). LNAPL is more delicate than water and non-soluble in the water, while DNAPL is thicker than water and does not dissolve. LNAPL will remain on top of the water table when migrating in the soil, but DNAPL will go below the water table due to its density. This type of LNAPL may exist in different forms: vapor phase in vadose zone pore spaces, vadose zone liquid residual LNAPL, free phase LNAPL in the water-unsaturated area, and entrapped LNAPL globules above and below the water table. (Azimi *et al.*, 2020)

The migration of LNAPL in the soil will be different for every area as the water table level of each particular soil is different. (Teramoto and Chang, 2020) The changes in the groundwater table will affect the subsurface distribution of the different LNAPL phases. As the water table increases or decreases, the free LNAPL may become entrapped or vice versa. LNAPL is absorbed by capillary force in a saturated area called entrapped when the water level rises. (Baedecker *et al.*, 2011) On the other hand, the water level drops will make the LNAPL get mobility and become free LNAPL.

Some research predicted that the relationship between the thickness of LNAPL monitored in the experiment well to the real thickness in groundwater aquifers. They found that the volume in monitoring well is more than the actual thickness of LNAPL. They assumed that the LNAPL saturation is changing with the depth of the soil and is a function of the LNAPL-water capillary pressure.

From the problems mentioned above, one of the most likely LNAPL contamination is the leakage of diesel from underground storage tank or diesel spillage. Therefore, diesel is chosen to be used in this research. This is to simulate the leakage of the underground storage tank or oil spillage.

1.2 Problem Statement

An important environmental concern is assessing the spatial-temporal transportation of LNAPLs in the unsaturated area because of surface or near-surface emission. Due to the multiple complex elements that govern the fate and behaviour of the emitted LNAPL, determining its future and behaviour could be difficult. A full study of all transport modalities, geologic processes, fluid thermodynamic parameters, rock medium properties, and fluid mechanics is required to build a model that explains and forecasts the fate and behaviour of LNAPL in the subsurface. This type of innovation is crucial in risk assessment, as it gives specialists a better grasp of the proper remedial techniques to apply. The model developed in the experiment can then be used to predict and simulate LNAPL activity in the subsurface area.

1.3 Objective

The objectives of this experimental study are:

1. To investigate the LNAPL migration in soil.

2. To study the effect of the water table on the soil capillary depression of LNAPL contaminated soil.

3. To study the effect of volume of LNAPL on the depth of LNAPL migration.

1.4 Scope of Work

In this study, diesel will be used as the sample of the experiment as the accessibility of diesel. Furthermore, diesel is safer due to its inflammable characteristics compared to others oil types. For the porous media, sand will be used due to high permeability to shorten the experiment period. To simulate different gradients of slopes, several widely used slopes were generated in the two-dimensional water tank. Various amounts of diesel were added to affect multiple levels of LNAPL pollution. The sample was subjected to image analysis to assess the saturation distribution of LNAPL contamination.

1.5 Expected Outcome

The expected outcome of this experimental study is to understand the migration behaviour of LNAPL in the soil. The flow of the migration will help in understanding the source of water contamination and can prevent it. The relation of the water table and soil capillary depression will be identified.

1.6 Dissertation outline

This dissertation contains five chapters. Chapter 1 is an introduction that includes the background of the study, problem statements, objectives, scope of works, and expected outcome of the study. Chapter 2 is literature, in which other authors' articles are used to explain more about the research. Chapter 3 is a research methodology, which discusses the procedures carried out in the study to achieve the objectives. To make the procedures more understandable, a flow chart was developed. Chapter 4 is the results and discussion. This chapter contains the findings of the study, discussion, and suggestions on the study. Finally, in Chapter 5, the study will be concluded and summarize all the things discussed in the previous chapters and draw conclusions on the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

NAPL, or non-aqueous phase liquid, is a hydrophobic substance that is insoluble in water. BTEX stands for benzene, toluene, ethylbenzene, and xylene, to name a few. Crude oil, fuel, and petroleum are likewise classed as NAPLs.

Light non-aqueous phase liquids (LNAPL) and dense non-aqueous phase liquids (DNAPL) are the two forms of NAPLs. Density is the difference between LNAPLs and DNAPLs. LNAPL has a lower density than water and will float, but DNAPL has a higher density and will sink and settle in the water. (Fagerlund, 2006)

Oil spills pose a serious hazard to coastal ecosystems, with immediate economic losses and long-term negative consequences on biological interactions. (Yang *et al.*, 2011) This is due to the densely crowded nature of the area. The presence of crude oil and waste lubricating oil in the soil harmed the soil's physical, chemical, and microbiological qualities, hampered crop seed germination, and inhibited crop growth. The impact of crude oil and used lubricating oil pollution on soil characteristics and plant growth is proportional to their concentrations. (I *et al.*, 2017)

As the oil contamination becomes more serious, the remediation work becomes important and has become a great study. (Mao *et al.*, 2015) The clean-up of petroleum-contaminated soil, which might occur due to an oil spill or an industrial leak, has gotten a lot of attention. Compared to lengthy carbon-chain hydrocarbons, such as heavy oil, short carbon-chain hydrocarbons are more volatile and biodegradable, making them easier to degrade, treat, and remediate. (Lee *et al.*, 2018) Different types of remediation work can be used to repair the soil, such as physical, chemical treatment, thermal remediation, biological remediation, and phytoremediation. (U.S. EPA, 2006)

For soil remediation, predicting the transit of LNAPL pollution is critical. Different parameters, such as permeability, saturation, density, viscosity, and others, will influence LNAPL migration.

2.2 Non-Aqueous Phase Liquid

Non-aqueous phase liquid, or in short NAPL, is a hydrophobic chemical that insoluble in water. (Tsai *et al.*, 2020) BTEX is one of the examples which stand for benzene, toluene, ethylbenzene, and xylene. Other than that, crude oil, diesel, and petroleum are also classified as NAPL. Generally, there are two types of NAPL: dense non-aqueous phase liquid (DNAPL) and light non-aqueous phase liquid (LNAPL). DNAPL is more viscous than water, while LNAPL is less dense than water. (Alazaiza *et al.*, 2021)

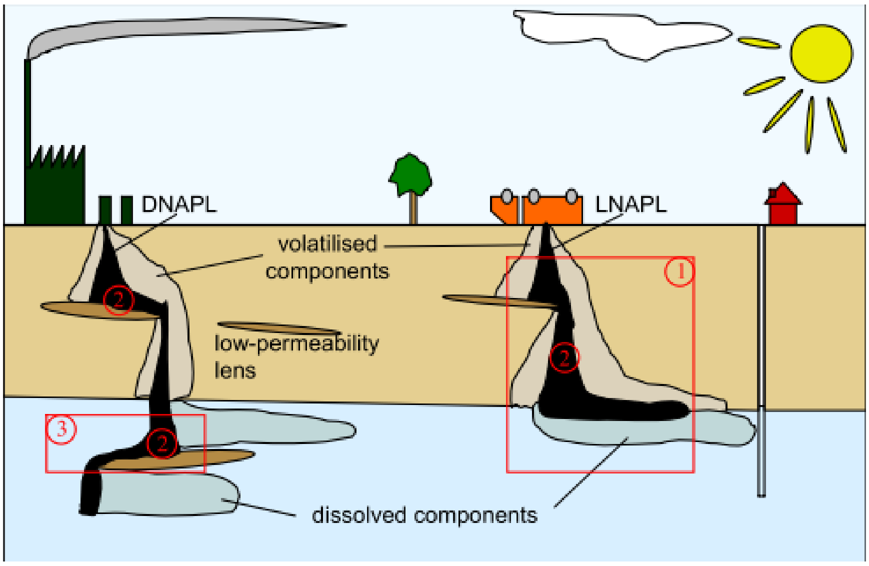

Figure 2.1: Illustration of typical movement of LNAPL and DNAPL (Source: Fagerlund, 2006)

2.2.1 Light Non-Aqueous Phase Liquid

Light non-aqueous phase liquid (LNAPL) is a contaminant found in groundwater insoluble in water and has a lower density than water. Some of the examples of LNAPL are BTEX, gasoline, diesel, and kerosene. LNAPL will contaminate the soil and groundwater for a long time of period. The release of petroleum to the ground subsurface resulted in unusable soil for construction. The petroleum products are full of multicomponent organic chemical compound which have varying of water solubility. The chemical component in the LNAPL has overthrown the early concept of LNAPL, which is LNAPL is insoluble in water. The different solubility affects the movement if LNAPL is subsurface and makes the migration is more complicated. Therefore, the LNAPL movement is needed to be known to have effective remediation work.

2.2.2 Dense Non-Aqueous Phase Liquid

Dense non-aqueous phase liquid (DNAPL) is the NAPL that is denser than water and is not soluble. DNAPL will sink deeply into the subsurface due to their high density until they enter a less permeable layer and form a non-aqueous reservoir. Due to soil heterogeneity, soil dispersion, and the considerable depth of contamination combined with gravity-driven finger movement, subsurface zones that DNAPLs have polluted are typically difficult to delimit. Thus, the remediation work of these pollutants in the groundwater is a complicated matter. (Philippe *et al.*, 2020)

DNAPL migration in the subsurface is influenced by several factors that can be divided into three categories: (i) porous media characteristics like soil structure, hydraulic conductivity, capillary pressure, and pore size; (ii) fluid properties like density, viscosity, wettability, and interfacial tension; and (iii) subsurface conditions like soil water content and groundwater flow rate. Many soil types have two distinct porosity scales in their natural state, giving rise to double-porosity soil structure. Double-porosity is a natural occurrence that happens when two different pore structures appear in the soil structure at the same time. Geomaterials that can exhibit double-porosity characteristics include rock aquifers, compacted soils, and top agricultural soil. (Alazaiza, Copty and Abunada, 2020)

2.3 Contamination of Soil Due to Oil Spill

Oil spills are described as the leakage and discharge of oil into the environment from petroleum extraction, storage, distribution, and refinement facilities, posing harm to the marine, coastal, and terrestrial ecosystems. (Salimnezhad, Soltani-Jigheh, and Soorki, 2021) Next, petroleum is a complex blend of organic chemicals found in various geological settings and over time. The majority of the elemental constitution is made up of carbon and hydrogen. Low amounts of sulphur, nitrogen, oxygen, and traces of some metals are all present. However, oil spills have caused serious environmental contamination and have become an impending worry due to the rise of petroleum exploitation and transportation. (Oliveira *et al.*, 2021)

According to statistics from The International Tanker Owners Pollution Federation Limited, 85 percent of spills are under 7 tonnes. In contrast, the number of accidents over 700 tonnes has reduced dramatically during the last three decades. On the other hand, large spills account for the majority of oil spilled each year, and they have significant environmental and economic implications. (Azevedo *et al.*, 2014) For example, at the end of the Gulf War, Kuwait's oil production infrastructure destruction resulted in huge ground pollution. Furthermore, previous oil exploitation and attendant tanker exploration, accidents, and petrochemical effluent have polluted Iran's southern coastal plain. (Kermani and Ebadi, 2012)

Petroleum compositions can influence and are disseminated in several environmental compartments following an oil leak incident, including sea water, rivers, groundwater, sediment, soil, and others. Most studies focus on the presence of total petroleum hydrocarbons (TPH), primarily aromatic hydrocarbons such as polycyclic aromatic hydrocarbons (PAH) and BTEX (benzene, toluene, ethylbenzene, and xylene), which account for between 10% and 35% of the hydrocarbon composition in light oils and between 15% and 40% in heavy oils; and aliphatic compounds, which account for representing 55% to 90% in light oils and 25% to 80%, in heavy oils. (Oliveira *et al.*, 2021)

2.4 Impact of Oil Spill

Several hydrocarbon components in crude oil are poisonous and water-soluble to some extent. Oil contamination poses a threat to wildlife, such as the poisoning of higher-ranking animals when they consume vast amounts of other organisms that have absorbed oil into their tissue. damage to red blood cells; inflammation; harm on adrenal tissue of birds, which affect the ability to maintain blood pressure and fluid concentration in their bodies, resulting in a reduction in egg shell thickness. (Kermani and Ebadi, 2012)

In the geotechnical part, the researcher did the triaxial experiments to determine the shear strength of motor oil contaminated quartz sand. They discovered a considerable drop in internal friction angle and a considerable rise in a volumetric strain of loose and dense sands. Due to oil pollution, Kuwaiti sand has a minor reduction in strength and permeability and increased compressibility. They discovered that the impacts of crude oil on soil strength metrics are stronger than those of light gas oil and benzene. The strength, permeability, maximum dry density (MDD), optimum moisture content (OMC), and Atterberg limits of CL (clay of low plasticity, lean clay), SM (silty sand), and SP (poorly graded sand) soils were all also reduced by oil contamination.

2.5 Soil Capillary

2.5.1 Formation of Capillary Fringe

The capillary fringe is a subsurface layer where groundwater attracts up from a water table and fills pores through capillary action. Tension saturation causes water to fill the pores at the base of the capillary fringe. In comparison to silt and clay, the capillary rise will be lower in the sand with a large pore size.

Table 2.1: Type of grain size and its capillary rise

Soil types	Grain size (mm)	Capillary rise (cm)
Silt	0.05-0.02	200
Coarse Silt	0.1-0.5	106
Fine Sand	0.2-0.1	43
Medium Sand	0.5-0.2	25
Coarse Sand	1.0-0.5	14
Very Coarse Sand	2.0-1.0	6.5
Fine Grave	5.0-2.0	2.5

2.5.2 Vadose Zone

The vadose zone is a section of the subsurface that is unsaturated and lies above the groundwater table. The vadose zone's soil and rock are not submerged in water; rather, the pores within them hold both air and water. The vadose zone is nonexistent in a few places, as is typical in areas with lakes and marshes, and it is several meters thick in others, as is usual in dry regions.

LNAPL can occur in four phases in the vadose zone of the subsurface: NAPL (immiscible liquid), aqueous (dissolved in water), gaseous, and solid-phase material partition.

The vadose zone is often the primary determinant of water flow from the land surface to the aquifer. As a result, it has a significant impact on the rate of aquifer recharge and is critical for groundwater utilization. The vadose zone's flow rates and chemical responses determine if, where, and how quickly contaminants enter groundwater supplies.

2.6 Remediation On Oil Contaminated Soil

2.6.1 Physical Remediation

The fastest and safest option is to excavate crude oil-contaminated soil, but this is not a sophisticated or inexpensive method. The polluted soil is collected and transferred to a landfill where it can be disposed of properly. Samples are taken from the excavated area's bottom and sidewalls to determine if the site is clean or not. Washing contaminated soil is another physical process. Washing the polluted soil with organic solvents such as ethanol-water mixture and ethyl acetate-acetone-water mixture resulted in substantial hydrocarbon removal. Soil cleaning not only removes heavy metals from the ground but also treats them for oil contamination. The addition of surfactants will improve the efficiency of washing. Both chemical and natural surfactants have been shown to aid in the removal of crude oil in studies. Different surfactants remove different crude oil fractions; for example, the artificial surfactant sodium dodecyl sulphate (SDS) removed aliphatic hydrocarbons from the polluted soil, while natural surfactants saponin and rhamnolipid removed polycyclic aromatic hydrocarbons. Physical treatment can be done either in situ or ex-situ. (Ahmad *et al.*, 2020)

The key benefit of in situ treatment is that it allows for soil remediation without excavating or transporting it. It also gets around limits on the re-deposition of treated soil on the property. In situ remediation usually necessitates a longer treatment period. It is even more difficult to ensure care uniformity due to the sub-surface's heterogeneity. In situ remediation must also be worried about preventing pollutants from spreading by causing contaminants to travel away from the polluted soil field. In situ physical remediation of organically polluted soil can be placed in three categories: air sparging, which forces air to bubble through groundwater to volatilize volatile organic compounds (VOCs), and soil flushing, which involves the flushing action of groundwater in pump-and-treat systems, are both methods for enhancing contaminant removal by vaporisation in the vadose region. Chemicals such as surfactants are also used to improve the removal efficiency of water flowing through polluted soil. (Lim, Lau and Poh, 2016)

2.6.2 Thermal Remediation

Thermal remediation is also normally known as incineration. The contaminated soil is burned at high temperatures under controlled conditions in an incinerator during incineration. After heating, the vaporized pollutants are collected or eliminated by pyrolysis. This is one of the simplest methods for removing oil from the soil. It has been demonstrated on a pilot-scale that at temperatures of about 800°C, almost all oil pollutants can be extracted from polluted soil using a combustor. On-site incineration is often used because it is a less expensive way of remediating contaminated soil. (Kusumawati and Mangkoedihardjo, 2021) However, it should be noted that this method is not environmentally friendly because crude oil contains volatile and flammable chemical compounds that can pollute the atmosphere. (Diphare and Muzenda, 2014) The cost of transportation to the incinerator may also make the procedure prohibitively costly. (Ball, Stewart and Schliephake, 2012) . Figure 2.2 shows the emissions of incineration, which will lead to secondary waste.

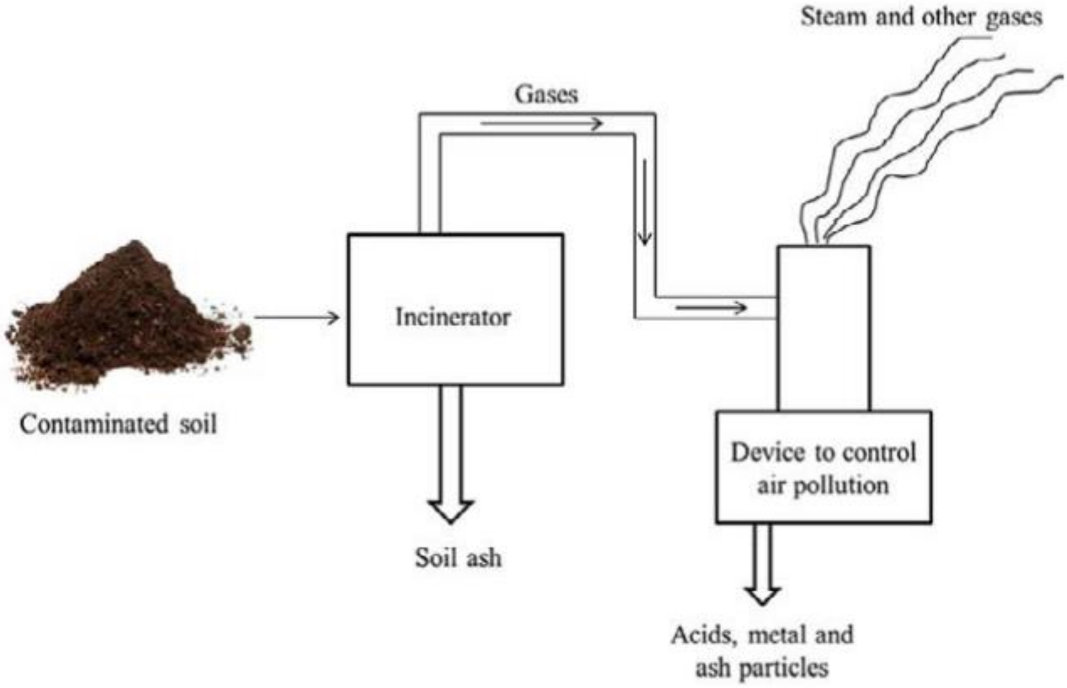

Figure 2.2 Incineration of contaminated soil (Kusumawati and Mangkoedihardjo, 2021)

2.6.3 Chemical Remediation

Chemical remediation of polluted soil generally through chemical oxidation reactions. Fenton's reagent, hydrogen peroxide, permanganate, persulfate, ozone, and peroxymonosulfate are some of these oxidants. Magnetite, Fe^{2+}, zero-valent iron, goethite, hematite, manganese oxide, and cobalt are claimed to act as catalysts when these chemical oxidants treat soil polluted with diesel and fuel oil. The pollutant removal effectiveness in this method ranged from 35 - 90 % depending on the chemical oxidant and catalyst utilized. The use of magnetite resulted in high crude oil clean-up efficiency (80%) for both oxidants. Under the same experimental circumstances, poor remediation efficiencies (10-15%) were observed when soluble Fe2+ was utilised alone. Chemical oxidation is an effective method for cleaning up petroleum oil-polluted soil since it is non-selective and unaffected by the pollutant's toxicity. This reduces the spread of contaminants and aids in the clean-up of crude oil pollution. This approach also benefits from being simple to use and operate, as it produces quick results at a cheap cost of operation. Excessive chemical oxidant dosage has a negative influence on the ecosystem. To safeguard the environment, only little amounts of chemical oxidant should be used. (Varjani, 2017)

Another remediation is electrochemical. Electrochemical remediation is based on applying an electric voltage to an electrode or a network of electrodes implanted in various configurations in polluted soil. When current travels through the soil, it creates multiple physical and chemical phenomena, such as electrolysis, electroosmosis, and electrophoresis, highlighting the technologies of continuous current (DCT), such as pH shifts and water hydrolysis. Electrokinetic transport, also known as electroosmosis, is a phenomenon that aids in the transport, mobilisation, and concentration of pollutants, while electro-oxidation is based on electrochemically driven redox reactions. (Streche *et al.*, 2018) As a consequence, voltage is created, causing the fluid medium to flow preferentially towards the cathode, dragging the pollutant along with the bulk flow. These methods are also utilised to investigate bacterial diversity in a crude oil-polluted environment. This method has the advantage of requiring less time and having reduced operational costs. The main disadvantage is that the electrolysis process generates thermal hot patches in the soil surrounding the electrodes, which affects soil pH over time. This has a negative impact on the environment. (Varjani, 2017)

2.6.4 Biological Remediation

Bioremediation is the technique of removing pollutants from the soil using biological microorganisms. Microbes are used to remove hydrocarbons such as oil. The toxins will be used as food and energy by the microbes, allowing them to multiply. The cost of implementing bioremediation will be cheaper. In most cases, there will be little to no residual treatment required once the remediation operation is completed because the microorganisms will totally break down the contamination, whereas, in physical/chemical treatment, the contaminants are generally only isolated. In situ, bioremediation and ex-situ bioremediation are the two types of bioremediations. Ex-situ bioremediation is typically used for heavier hydrocarbons, while in situ bioremediation is typically used for lighter or more volatile pollutants. (Xu *et al.*, 2016)

In situ bioremediation technologies are sustainable because they do not require transport and deposition of contaminated soil. Microorganisms and their work to detoxify or eliminate pollutants in the site are used in this technology. The capacity of microorganisms to break down contaminants into less dangerous by-products is influenced by their access to nutrients, electron donors, and acceptors. (EPA, 2013) Normally, the procedure will include passing the aqueous solution through naturally occurring microorganisms to break down organic molecules, which will provide oxygen and sustenance. Therefore, Contaminants in soil and ground water can be degraded by in situ bioremediation. (O'Niell and Nzengung, 2004) In situ bioremediation can be done using a variety of treatment methods. Air sparging, bioventing, and bio slurping are just a few examples.

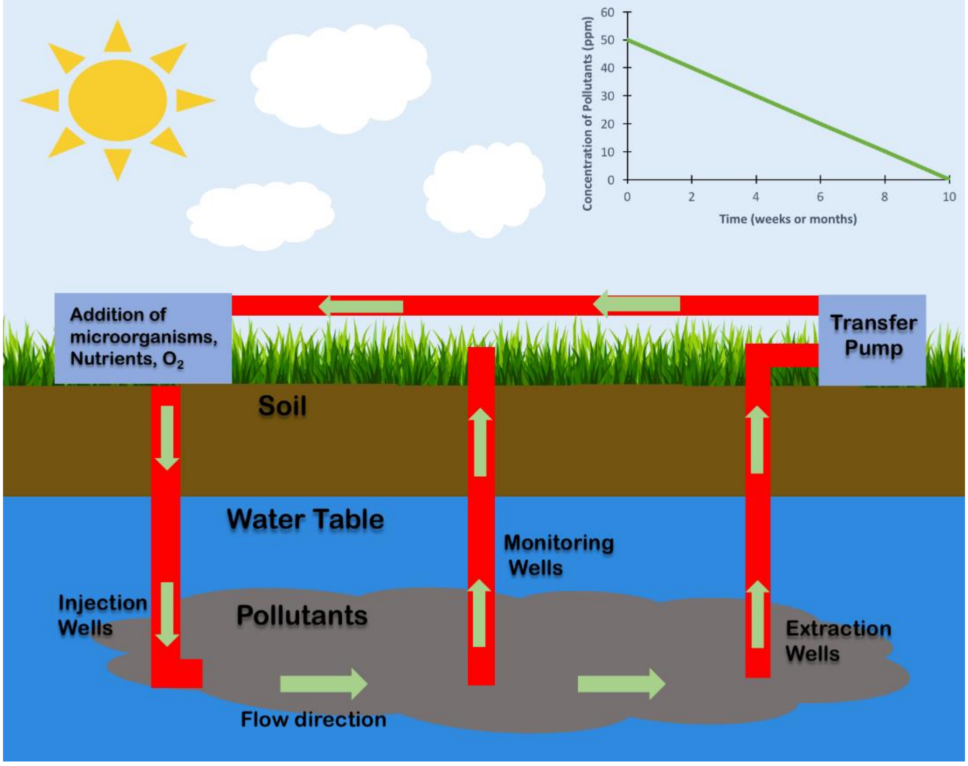

Figure 2.3: Process of in situ bioremediation

Ex-situ bioremediation is a sort of ex-situ remediation that removes toxins from the soil. Ex-situ bioremediation procedures typically necessitate soil excavation to remove contaminated material such as soil or water from the environment and bioremediation operations to be performed outside of the site area. Ex-situ bioremediation is faster than in-situ bioremediation because it can be applied to a vast area of contaminated soil. The efficiency of the remediation process can be readily controlled. This is due to the soil's propensity to homogenize and mix continuously. Furthermore, there are two types of ex-situ bioremediation: slurry phase soil treatment and solid-phase soil treatment. Slurry phase treatment involves mixing polluted soil with water and other additives in a bioreactor and mixing microorganisms to allow the microorganisms to digest the contaminants. The contaminated soils are treated above ground in the solid phase treatment area, and a collecting system is required to prevent contaminant escapes from the treatment area. Biodegradation rates can be accelerated by factors such as heat, nutrition, moisture, and oxygen. Treatment in the solid phase is easier than treatment in the slurry phase, but it takes longer. (U.S. EPA, 2001)

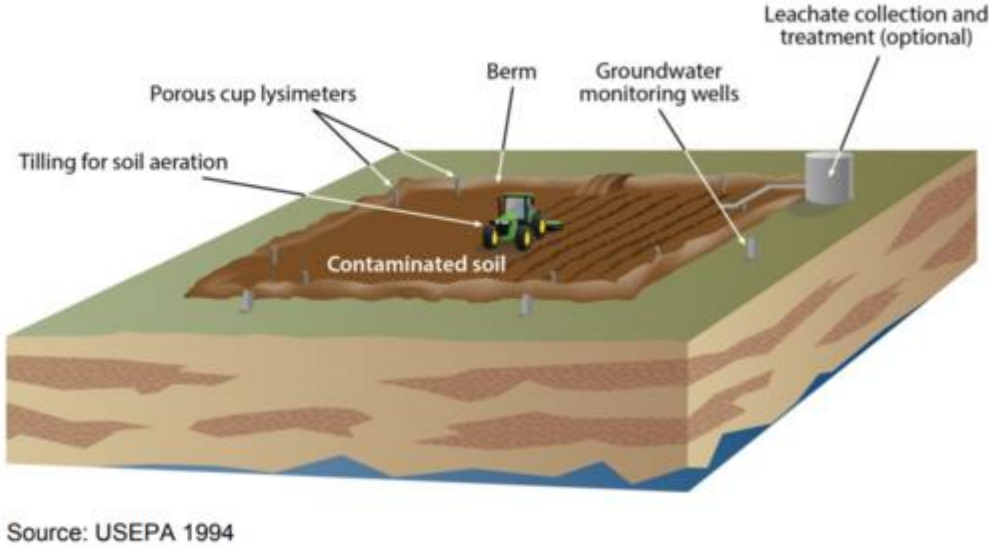

Figure 2.4: Example of ex-situ bioremediation, landfarming (U.S. EPA, 2001)

2.6.5 Phytoremediation

Phyto is a word that means "plant." Phytoremediation, then, is the practice of employing plants to remove or break down pollutants from the soil. Biodegradation will proceed at the plant's root. (Boer and Wagelmans, 2016) For this purpose, plants with extensive root systems, low water requirements, adaptability to a wide range of climatic conditions, and a rapid growth rate are an ideal selection. The selection of plant species, ambient circumstances, and rhizobacteria all influence phytoremediation efficacy.

The roots release nutrients into the soil to support the growth of microorganisms. The roots also help to loosen the soil, increase soil spacing, and improve water and aeration movement. This can make it easier for polluted water to travel to the lower saturated zone and be treated. (Ahmad *et al.*, 2020) Plants also manufacture enzymes that aid in catalysing breakdown, such as oxygenase. To assist the growth of microorganisms, the roots release nutrients into the soil. The roots also aid in soil loosening, increasing soil spacing, and improving water and aeration flow. Polluted water may be able to move to the lower saturated zone and be treated more easily. Plants also produce enzymes like oxygenase, which aid in catalysing breakdown.

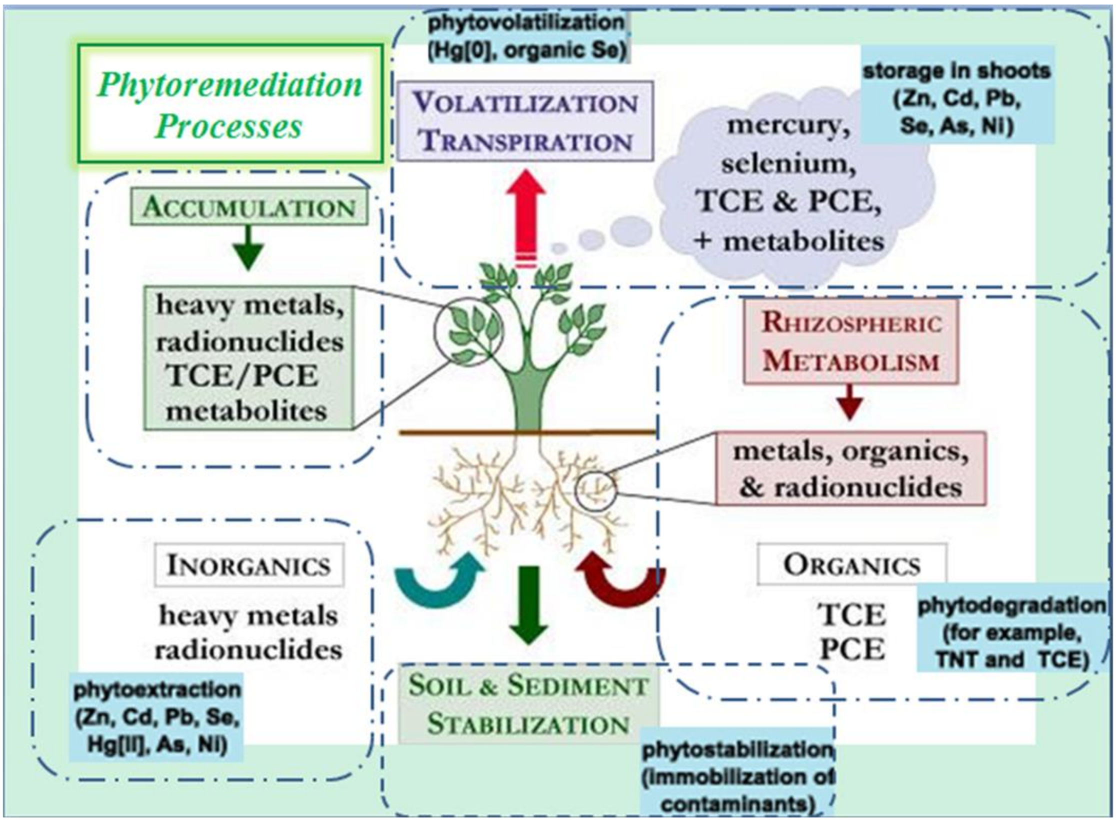

Figure 2.5: Phytoremediation process

2.7 Properties of LNAPL

2.7.1 Density

Mass of a substance over unit volume is known as density. The specific gravity (S.G.) is the mass ratio to a volume of substance at a constant temperature to the mass of the same volume of water at the same temperature and is one way to represent the density of a fluid. If a NAPL's S.G. is less than 1.0, it is less dense than water (LNAPL) and will stay on the water. It is denser than water if its S.G. is higher than water, usually larger than 1.0. (DNAPL). As the temperature rises, the density of most fluids drops.

As a result, during remedial efforts that contribute heat to the subsurface, the thickness of fluids deemed to be DNAPLs under natural subsurface circumstances will decrease. The density of DNAPLs with densities close to that of water may be reduced to where the DNAPL is temporarily converted to an LNAPL. The hydraulic conductivity of a porous media is determined by the liquid's density and viscosity. The hydraulic conductivity with regard to the liquid increases as density rises. (Newell *et al.*, 1995)

2.7.2 Viscosity

Viscosity is a fluid's inherent feature that affects its rate of movement in a porous medium. Internal friction within a vapor phase that causes flow resistance could be described as it. The higher the viscosity, the more difficult it is to flow. Temperature affects this resistance as well. As the temperature rises, the viscosity of most fluids decreases. As the viscosity of the fluid drops, the hydraulic conductivity increases.(Onaa, Olaobaju and Amro, 2021)

2.7.3 Interfacial Tension

Forces applying on the connection between two phases per unit area are known as interfacial tension. The phases involved could be fluids or solids; the energy needed to break the cohesive intermolecular bonds between the two phases is interfacial tension. It is measured in kilowatt-hours per square metre. The greater the interfacial tension, the more stable the interface between the liquids is in general. Temperature, pH changes, and the existence of surfactants and dissolved gases all influence interfacial tension. (Ryan and Dhir, 1996) The wettability of the phase affects interfacial tension. (Blunt, 2017)

2.7.4 Wettability

In the existence of other fluid with which it is immiscible, wettability is described as the overall tendency of one fluid to spread on or stick to a solid surface. At the pore scale, this idea has been utilised to relate to fluid distribution. The wetting fluid in a multiphase system preferentially coats (wets) solid surfaces and tends to occupy smaller pore volumes. When two-phase fluids come into contact with a solid, for example, the wetting phase prefers to cover the solid phase rather than the fluid phase, and this is commonly measured using contact angle. (Polini and Yang, 2017) Liquids, mainly water, preferentially moisten solid surfaces in the vadose zone, where air, water, and LNAPL are present. When there is air and LNAPL, LNAPL will cover mineral surfaces preferentially and displace air from pore spaces. When only water and LNAPL are present in the saturated zone, water will act as wetting fluid, kicking out LNAPL from pore spaces. Wettability is influenced by elements such as NAPL and aqueous-phase composition, the existence of organic matter, mineralogy, surfactants, and the porous medium's saturation history. (Newell *et al.*, 1995)

2.7.5 Capillary Pressure

The pressure difference across the interface between the wetting and non-wetting phases is known as capillary pressure, and it is commonly described as the height of an analogous water column. It establishes the maximum pore size in which an interface can form. It is a measurement of the attraction of a liquid's molecules to each other and to a solid surface. The trend of the porous material to attract wetting fluid while repelling non-wetting fluid is referred to as capillary pressure. Before the non-wetting fluid, which is NAPL, may enter the porous medium, the capillary pressure of the biggest pore gaps must be exceeded. The entry pressure is the minimum pressure necessary for the NAPL to enter the medium.

Generally, capillary pressure will be high if the pore volume decreases, initial moisture content drops, and interfacial tension rises. The configuration and magnitude of trapped residual NAPL are influenced by capillary circumstances. The preferred migration of LNAPL through coarse-grained materials rather than fine-grained materials has been observed in the field as a result of capillary pressure. (Wipfler, Ness and Breedveld, 2004)

2.7.6 Saturation

Saturation is the percentage of total pore volume in a representative volume of a porous media that contains a certain fluid. The relative permeability function describes how an LNAPL's mobility is connected to its saturation in the medium. LNAPL migration inside the vadose zone is similar to that of a dense non-aqueous phase liquid (DNAPL) discharge. (Kueper *et al.*, 2003) If only a small amount of LNAPL is released, migration will stop within the vadose zone due to retentive capillary pressures immobilising mass within soil pores. For larger separate leases, LNAPL will drain under the gravitational effect and spread because of the lithology of the overburden or bedrock geology structure. The saturated aquifer will impede, but not totally prevent, LNAPL migration deeper due to both increased water content and associated buoyant forces deriving from the LNAPL-water fluid density contrast, unlike DNAPLs, which sink as they hit the water table. The driving forces of an LNAPL discharge will penetrate below the water table, and the lateral spread of LNAPL near the water table inside the capillary fringe is mostly dictated by the LNAPL head gradient, which is initially greater than the water table gradient owing to the LNAPL release. The LNAPL gradient, on the other hand, will fade over time and finally stabilising the LNAPL footprint. Due to insufficient LNAPL head to exceed pore entry pressure, lower LNAPL saturations, and natural source ozone depletion (NSZD) processes, the LNAPL saturation at the leading edge will drop to below residual (i.e., a fraction of the pore space occupied by LNAPL that cannot be mobilised under an applied gradient) and through balances of factors, the leading edge will cease to migrate. (Tomlinson *et al.*, 2017)

2.7.7 Relative Permeability

Relative permeability is defined as the proportion of the effective permeability of a medium to a fluid at a certain saturation to the permeability of the medium to the fluid at 100 percent saturation. The relative permeability values vary from 0 to 1. The interaction of two fluids to limit mobility is depicted in a simplified relative permeability diagram for a hypothetical LNAPL/water system. However, unlike distinctive relative permeability, relative permeability does not have a single absolute value; rather, each -fluid phase saturation level has a separate relative permeability value. To comprehend the respective phase distribution in the media, the individual phase relative permeabilities are required.

Different forms of multiphase flow regimes can be described using relative permeability curves, all of which can exist at any given location. Zone I: LNAPL is a possibly movable, continuous phase with a high saturation level. Water can only pass through narrow pores. Water has a low relative permeability. Within huge mobile product accumulations, such circumstances can be observed. Zone II: LNAPL and water are both continuous phases. However, they do not share the same pore spaces in general. The saturation of the other fluid, on the other hand, considerably reduces the relative permeability of each fluid. Such conditions could be indicative of water table zones with reduced mobile product accumulations. Zone III: LNAPL is discontinuous and gets trapped in isolated pores as a residual. Flow, not LNAPL, is nearly entirely defined by the movement of water. Zones of residual LNAPL maintained below the water table are an example of such circumstances.

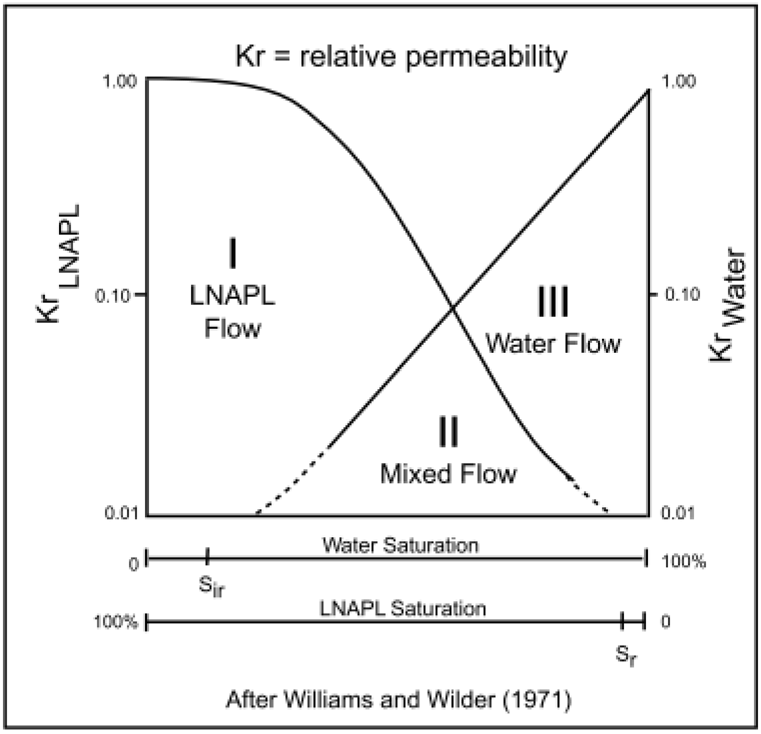

Figure 2.6: Relative permeability curves for water and an LNAPL in a porous medium (Newell *et al.*, 1995)

2.8 Behavior of LNAPL Transport in Fluctuating Water Table

LNAPL has a different phase when in transport. They can be either residual or mobile-free. Multiphase flow is the propagation of LNAPL via porous media. Density, viscosity, interfacial tensions, solubility, and vapour pressure of NAPL are significant in forecasting subsurface contamination and understanding NAPL transport. The geographic distribution of LNAPLs within an aquifer is influenced by changes in water table elevation, particularly in the vertical direction. LNAPLs migrate lower with the moving water when the water table and capillary fringe drop, leaving a residual proportion in the saturated zone. The reverse upward migration of the LNAPLs occurs as the water table rises. LNAPL and air entrapment under the water table can also occur as the water table rises. The presence of air provides an extra source of oxygen that can aid the biological breakdown of pollutants, but the presence of entrapped LNAPL beneath the water table causes the mobile, free-phase LNAPL within the capillary fringe to decrease. Water table fluctuations expand the vertical area of the source zone, which can lead to an increase in the interphase mass transfer of pollutants to groundwater. (Alazaiza *et al.*, 2020)

2.9 Simplified Image Analysis Method

The simplified image analysis method is a simple and cost-effective method for studying the effects of water fluctuation on LNAPL contaminants when spilled into the subsoil under controlled laboratory conditions. It can continuously measure the saturation distribution values as well as variations over time. To investigate the fluid characteristics and movement in soil and groundwater, non-invasive or fewer impact techniques such as gamma-ray, X-ray attenuation, and electrical conductivity probes have been utilised. Although these investigations have produced useful information on the fate and transit of NAPLs in medium, they have significant disadvantages, the most noteworthy of which is that they cannot observe the migration of fluid under dynamic conditions and across the whole domain of interest. Image analysis approaches such as light transmission visualisation, light reflection method, spectral image analysis technique, and simplified image analysis technique have attracted increased attention from researchers as a result of the aforementioned restrictions. (Alazaiza *et al.*, 2021) This method should be cost-effective and simple to calibrate, allowing experiments to be carried out under a variety of controlled conditions, and non-intrusive and non-destructive, allowing continuous testing under dynamic conditions without having to