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Water/LNAPL sampling and quantification from differently saturated porous media under laboratory conditions

Diploma Thesis

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Acknowledgements

Declaration

I declare that the Diploma Thesis on the theme " Water/LNAPL sampling and quantification from differently saturated porous media under laboratory conditions " is my own work and all the sources I cited in it are listed in Bibliography.

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Abstract

Soil and groundwater contamination due to accidental spills of hydrocarbons is a serious environmental problem that threatens groundwater. The presence of such product as a Non-Aqueous Phase Liquid (NAPL) near the water table, or as a trapped residual in the porous media, represents a continuous contamination source that keeps contributing to groundwater contamination for a very long time.

The main goal of the diploma thesis is to identify if it is possible to quantify proportionally the amount of water and Light Non-Aqueous Phase Liquid (LNAPL) in the porous media via adsorption of water/LNAPL to the activated carbon pellet, and with no dependence on degree of saturation of the porous media.

Sample columns were prepared artificially from porous media under laboratory conditions. Porous media which was used consists of Silica Sand commercially known as ST56 with defined chemical and physical properties. Equal proportion of LNAPL/water content by mass was applied during columns preparation. 5%, 15% and 25% liquid content of which 50% is water and the other 50% LNAPL were used with 3 replications. Water/LNAPL applied to column was sampled/taken using activated carbon pellets at 20 min., 45 min., 70 min. and 90 min. and quantified gravimetrically using 4 decimal digital balance. From measured data, both water and LNAPL could be sampled for 15% and 25% of liquid contents. However, only water could be sampled from 5% of liquid content porous media. Adsorbed water/LNAPL at different times and liquid contents were evaluated using Microsoft Excel computer program.

Key words: *NAPL, LNAPL,water/LNAPL, activated carbon, porous media, silica sand*

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1. INTRODUCTION

Gasoline, oil, lubricants, and diesel fuel are all common compounds in our daily lives. These substances are fuels that run today`s complex society. However, when spilled on the ground, they can cause massive problems in the environment. Such releases usually are followed by an assessment of the soil, and the degree and extent of environmental contamination (O`Shay and Hoddinott, 1994). The physical processes governing the flow and transport of immiscible organic liquid in a variably-saturated porous medium is a research area which has received a great deal of attention.

Soil and groundwater contamination due to accidental spills of hydrocarbons represents a serious environmental problem that threatens groundwater. The presence of such product as a non-aqueous phase liquid near the water table, or as a trapped residual in the porous media, creates a continuous contamination source that keeps contributing to groundwater contamination for a very long time (Al-Suwaiyan, 2007).

Petroleum products such as gasoline, diesel fuel, transmission fluid, engine oil, and other lubricants (referred to oil) are lighter than and nearly immiscible with water. In case of spills or leaks, most of the oil would exist in the liquid phase within and above the zone of water-table fluctuation which makes it easier for cleaning up of free oil. The EPA (1996) recognized recovery of a product placed above the water-table is a routine operation. On the other side the recovery of a product from below the ground is usually much more difficult to treat.

The theoretical part of the Diploma thesis is providing a brief review to the basic issues related to soil and groundwater contamination by NAPLs with a focus on LNAPLs and general concepts of their migration patterns, behavior in the porous media, transport properties and remediation techniques.

The practical part of the Diploma thesis is providing general description of the laboratory experiment performed on artificially packed sample column of silica sand with known properties and applying water and oil representing a non-volatile LNAPLs. The main aim of the experiment was to saturate the prepared columns of silica sand with known proportions of water/LNAPL and then sample the liquids using activated carbon pellets to evaluate amount of water and LNAPL adsorbed to it gravimetrically. The mass of adsorbed liquid before and after oven dry is taken using digital balance; water is evaporated while the representative oil remains adsorbed to the activated carbon.

2. AIMS AND OBJECTIVES

The study aims to characterize adsorption of water/LNAPL through the use of existing laboratory techniques. The aim of the thesis is to verify sampling method for water/LNAPL from porous media via adsorption to activated carbon proposed by Matula et al. (2008) to quantify water/LNAPL content. The hypothesis of this work was to state if it is possible to quantify proportionally the amount of water and non-volatile LNAPL in the porous media via adsorption of water/LNAPL to the activated carbon, and with no dependence on degree of saturation of the porous media. To achieve this aim, the following specific objectives were performed:

- Checking initial moisture content of Silica sand and activated carbon pellet
- Checking the evaporation loss of tap and distilled water as well oil used as LNAPL
- Comparing the oil used for previous study with the oil used for this study
- Comparing length and diameter of activated carbon pellets
- Packing of sand columns with specified proportions of water/LNAPL
- Inserting activated carbon pellets for specified time intervals (20, 45, 70 and 90 minutes)
- Drying of activated carbon pellets, to ensure all water will evaporate
- Taking weights and data selection, evaluation with statistical tool

3. LITERATURE REVIEW

3.1. Introduction to petroleum constituents

Many pollutants are present in liquids that are immiscible with water either than in the aqueous phase or sorbed to soils (Riser-Roberts, 1998). Petroleum liquids are complex mixtures of hundreds of different hydrocarbons, with minor amounts of nitrogen, oxygen, sulfur, and some metals. Nearly all petroleum compounds are nonpolar and not very soluble in water. The behavior of these compounds in a groundwater environment depends on the physical and chemical nature of the particular hydrocarbon blend as well as their particular soil environment. Hydrocarbons and their components are commonly called non-aqueous phase liquids (NAPLs). Gasoline and diesel fuels, oils, chlorinated solvents, and pesticides are examples (Weiner, 2013).

3.1.1. Classification of Petroleum constituents

The first step in refining crude oil into petroleum products is usually fractional distillation, a process that separates the crude oil components according to their boiling points. The resulting products are groups of mixtures, or fractions, each of which has boiling points within a specified range. All but the lightest fractions (lowest boiling temperature ranges) can contain hundreds of different hydrocarbon compounds. The fractions are often classified into general groups described in Table 1. In addition, several pure petrochemicals may be produced during fractional distillation, such as butane, hexane, benzene, toluene, and xylene, for use as solvents, production of plastics and fibers, and reblending into fuel mixtures. Refined petroleum products are further modified by catalytic cracking, blending, and reformulation processes to enhance desirable properties (Weiner, 2013).

Table 1 - Principal petroleum fractions from fractional distillation[1] (Weiner, 2013)

Boiling Range (°C)	Dominant Composition Range	Fraction	Uses
-160 to +30	C1-C4	Gases	LPG, methane, gaseous fuels, feedstock for plastics
30-60	C5-C7	Petroleum ether	Solvents, gasoline additives
90-130	C6-C9	Ligroin,naphtha	Solvents
40-200	C4-C12	Gasoline	Motor fuel
60-200	C7-C12	Mineral spirits	Solvents
150-300	C10-C16	Kerosene	Jet fuel, diesel fuel, lighter fuel oils
300-350	C16-C18	Fuel oil	Diesel oil, heating oil, cracking stock
>350	C18-C24	Lubricating stock	Lubricating oil, mineral oil, cracking stock
Solid residue	C25-C40	Paraffin wax	Candles, toiletries,wax paper
Solid residue	> C40	Residuum	Rooting tar,road asphalt

3.2. NAPLs

Non-Aqueous Phase Liquid (NAPL) is a term used to denote any liquid which is immiscible with water (Reddi and Inyang, 2000). Differences in the physical and chemical properties of water and NAPL result in the formation of a physical interface between the liquids which prevents the two fluids from mixing. NAPLs are typically classified as either LNAPLs which have densities less than that of water, or Dense Non-Aqueous Phase Liquids DNAPLs which have densities greater than that of water (Newell et al., 1995).

NAPLs are organic liquids that are immiscible with water and form a visible, separate oily phase in the subsurface. Their migration is governed by gravity, viscous forces, and capillary forces. If NAPLs were truly insoluble in water, their impact on groundwater quality would be very limited. But, NAPL components can dissolve in water in very small amounts and at very low rates. As a result, given the high toxicity of NAPL components, a small volume of NAPL in soil can form a long-term threat to the groundwater quality. Thus, unless

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[1] Note: The notation used here gives the range of carbon atoms in the fraction compounds. For example, C5-C7 means the petroleum fraction that contains mostly hydrocarbon compounds containing between 5 and 7 carbon atoms. This table indicates that as the number of carbon atoms in a hydrocarbon molecule increases, so do its boiling temperatureand its viscosity. Volatility decreases as the number of carbon atoms in a compound increases

properly managed, NAPLs can exist in the subsurface for decades and can contaminate large volumes of groundwater. However, it is very difficult to design effective remediation schemes, due to the complex behavior of NAPLs in the subsurface. In fact, the presence of NAPL has been shown to be a significant limiting factor in site remediation (EPA, 2003). This is partly due to hydrogeologic factors, such as complex heterogeneity patterns, and the presence of low permeability zones. But more importantly, and tied with hydrogeologic factors, it is because of the very complex nature of the various processes that affect the migration of NAPLs and transport of their dissolved components (Mayer and Hassanizadeh, 2005).

3.2.1. LNAPL

Petroleum chemicals (mainly benzene, toluene, xylene, and benzene derivatives) categorized as light non-aqueous phase liquids (LNAPLs) tend to form pools and spread laterally because of their low densities (Lesage and Jackson, 1992).

Light non-aqueous phase liquid (LNAPL) refers to an organic compound that is immiscible with, and lighter than, water (e.g., crude oil, gasoline, diesel fuel, heating oil). When an LNAPL is released to the subsurface, it can migrate downward under the force of gravity and laterally at the water table. Larger LNAPL releases may migrate to the water table while leaving residual, immobile LNAPL along the migration path (ITRC, 2009).

With a diagrammatic representation in Figure 1 it is shown how the NAPL spill is moving under the force of gravity, nearly vertically from the source locations which are usually at the land surface to the water table. During the downward migration, small droplets, or blobs as they are sometimes called, are left behind, trapped in the pores. All three phases-water, air and LNAPL are represented. Contaminants that have moved from the fluid phases to the solid surfaces of the grains are also represented as sorbed contaminants. Once the NAPL has reached the water table, it begins to form a pancake-layer on the water table. Because it is lighter than water it floats. And so such NAPLs have come to be known as LNAPLs (Pinder and Celia, 2006).
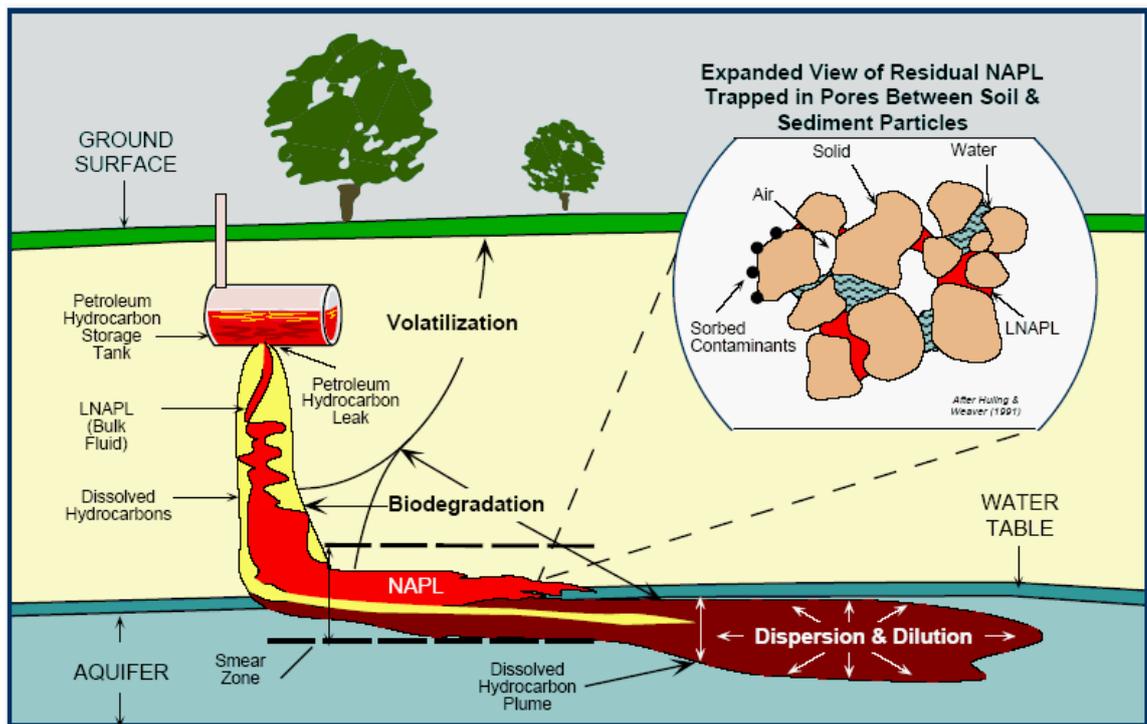
Figure 1 - Groundwater contamination as a result of petroleum spillage[2] (Pinder and Celia, 2006)

3.2.2. DNAPL

High contamination of groundwater occurs as a result of significant dissolved plumes generated from these DNAPL source zones that vary in size and complexity depending on site characteristics and DNAPL properties and distribution. Risk and liability management, consistent with regulatory compliance requirements, could involve remediation of the source zone as well as management of the dissolved plume (EPA, 2003).

Many of the halogenated hydrocarbons are characterized DNAPLs. Their densities exceed that of water, but they have lower viscosities. Their solubility in water is in the range of 100-500 mg/L (Lesage and Jackson, 1992).

When the NAPL which is entering the subsurface is heavier than water, it is called a DNAPL. Figure 2. illustrates the complex physical-chemical behavior of this type of contaminant. Like LNAPL, DNAPL moves vertically downward through the vadose zone under the influence of gravity and may volatilize in transit. Unlike LNAPL, DNAPL does not accumulate at the water table because it has a density greater than that of water. Rather, it will continue its vertical movement until it encounters a geological formation that exhibits the

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[2] Note: Petroleum migrates to the water table, where it begins to spread and move in the direction of the slope of the water table. Being slightly soluble, the components of the petroleum dissolve in the groundwater as shown. The dissolved component moves in the direction of groundwater flow

physical-chemical characteristics to impede its flow. Because a DNAPL is generally less attracted to soil grains than water, the DNAPL must overcome the resistance of the water, which prefers to occupy the pores, in order to displace it (Pinder and Celia, 2006).
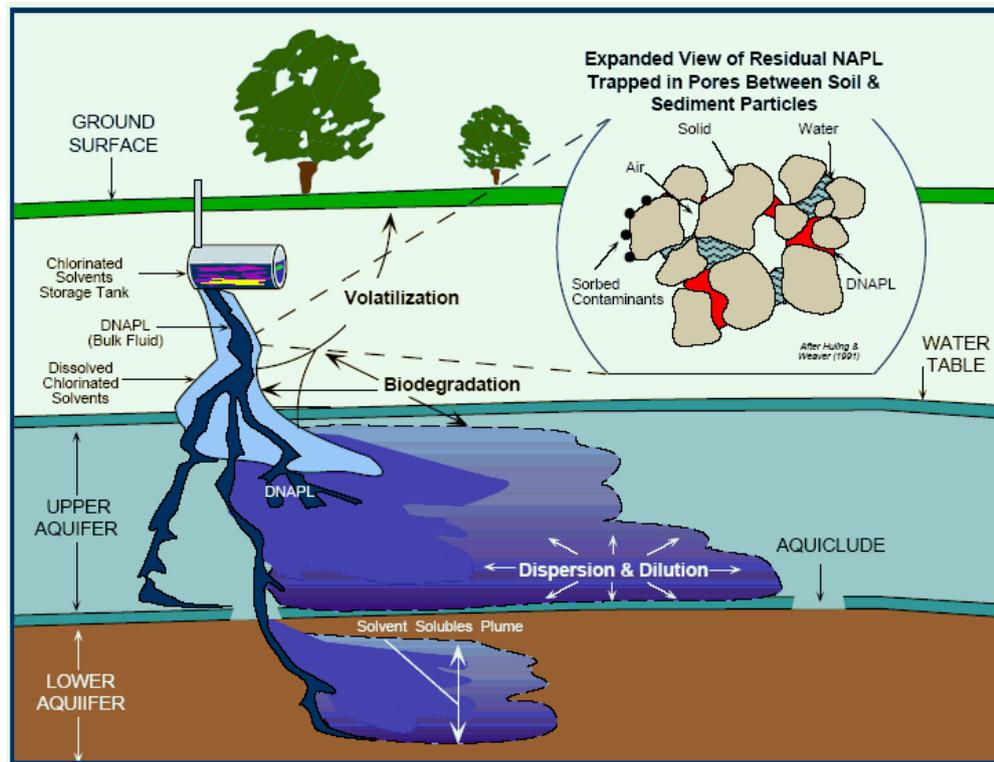
Figure 2 – Vertically downward movement of DNAPL[3]. (Pinder and Celia, 2006)

3.2.3. Crucial difference between LNAPLs and DNAPLs

It is customary to divide the wide range of NAPLs commonly encountered in geoenvironmental engineering into two general categories, LNAPLs and DNAPLs. This categorization is based on their specific gravity. According to Lowe et al. (1999) LNAPL migration through the unsaturated zone will be similar to DNAPL migration, except in the vicinity of the water table. LNAPLs have a specific gravity less than water, and DNAPLs have a specific gravity greater than water. In the Table 2 and Table 3 is a list of common types of LNAPLs and DNAPLs, respectively, along with some of their properties, which will be referred in subsequent sections. The difference in density of a NAPL with respect to water governs some important aspects of its transport in the subsurface. Therefore, it is useful to recognize this categorization at the outset (Reddi and Inyang, 2000).

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[3] A slightly soluble liquid with a density greater than that of water enters the subsurface and moves verticaly downward trough the water table to contaminate both and upper and a lower aquifer

Table 2 - Chemicals typically associated with LNAPLs (Reddi and Inyang, 2000)

LNAPLs	Specific gravity	Water solubility (mg/liter)	Interfacial tension (mN/m)
Benzene	0.88	1.75×10^3	35.0
Ethyl benzene	0.87	1.52×10^2	35.5
Styrene	0.91	3.00×10^2	35.5
Toluene	0.86	5.35×10^2	36.1
Methyl ethyl ketone	0.81	-	-
m-Xylene	0.86	1.30×10^2	36.4
o-Xylene	0.88	1.75×10^2	36.06
p-Xylene	0.86	1.98×10^2	37.8
Vinyl chloride	0.91	-	-
Crude oil	0.7-0.98	-	-
Diesel fuels	0.80-0.85	-	50
Gasoline	0.73	-	50
Fuel oils	0.81-0.85	-	48
Mineral oils	0.82	-	47
Petroleum distillates	0.71-0.75	-	50
n-Heptane	0.68	-	50.2
n-Hexane	0.66	-	51.0

Table 3 - Chemicals typically associated with DNAPLs (Reddi and Inyang, 2000)

DNAPLs	Specific gravity	Water solubility (mg/liter)	Interfacial tension (mN/m)
Carbon tetrachloride	1.56	7.57×10^2	45.0
Chloroform	1.48	8.20×10^3	32.8
Methylene chloride	1.33	2.00×10^4	28.3
Ethylene chloride	1.24	-	-
Bromobenzene	1.49	4.46×10^2	36.5
Chlorobenzene	1.11	4.66×10^2	37.4
Hexachlorobenzene	1.60	-	-
Chlorotoluene	1.10	3.30×10^3	30
Trichloroethylene	1.46	1.10×10^3	34.5
1,1,1-Trichloroethane	1.34	1.50×10^3	45
Tetrachloroethylene	1.62	1.50×10^2	44.4
Phenol	1.07	-	-
2-Chlorophenol	1.26	2.90×10^4	-
Pentachlorophenol	1.98	-	-
Naphthalene	1.03	-	-
Creosete	1.05-1.10	-	20
1,2-Dichlorethane	1.24	8.50×10^3	30

3.3.   Mechanism of NAPL distribution

A conceptual illustration of surface release, actually generated NAPL migration in the vadose, capillary fringe and aquifer zones is provided in Figure 3. There are three fundamental mechanisms for NAPL migration. First, the NAPL infiltrates into the soil and migrates both vertically and laterally under the influence of gravitational and capillary forces. The distribution of the NAPL liquid is a function of fluid properties (density, viscosity, interfacial tension, wetting potential and variable chemical composition), soil properties (grain size distribution, mineral content, moisture content, porosity, hydraulic conductivity and spatial heterogeneity), and system forcing history. If the source is periodic in nature, then during drying periods, not all the NAPL will drain from the pore space, leaving behind an immobile residual, held in place by capillary forces. If the NAPL is denser than water, it will migrate through the capillary fringe and continue its vertical migration until either the

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mobility becomes zero or the NAPL front encounters an impenetrable geologic horizon. The second contaminant transport mechanism is dissolution and consequent advection in the downward-flowing water phase, with precipitation providing the water source in the vadose zone. In the case of a DNAPL, flowing ground water picks up dissolved NAPL constituents. The third transport mechanism is transport as a vapour NAPL constituent in the soil gas, where the increased gas phase density induces downward movement. Partitioning between the gas and water-phase contaminants further enhances the migratory potential of the NAPL constituents (Guarnaccia et al., 1997).
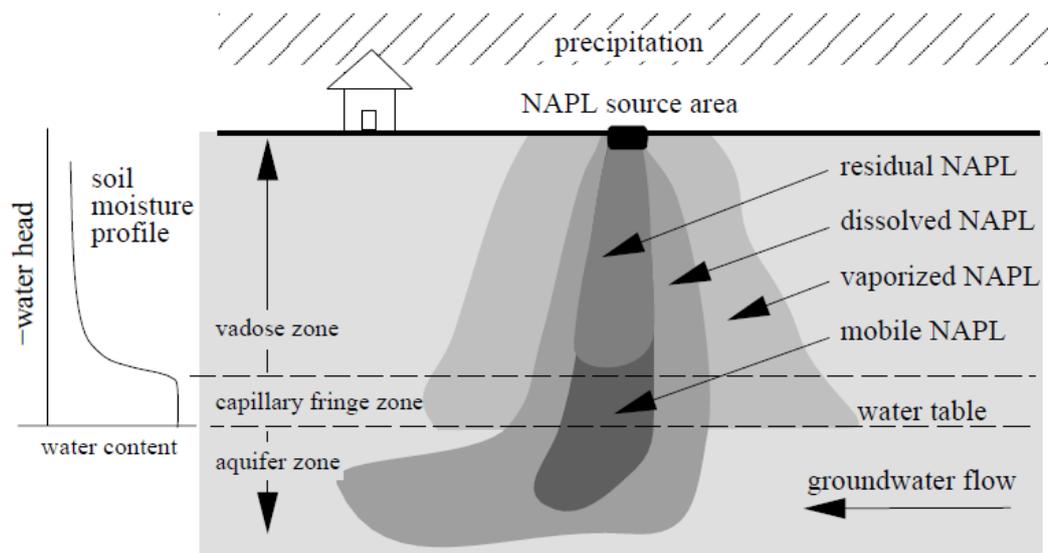
Figure 3 - Definition illustration of NAPL contamination in near-surface soils due to an intermittent release (Guarnaccia et al., 1997)

3.4. Distribution of LNAPL

The purpose of this text is to provide background information on LNAPL behavior in the subsurface environment. The movement and distribution of LNAPLs in the capillary zone are mainly lateral because of the spreading effect obtained as the LNAPLs come to rest on top of the water table. A lense effect is produced when more and more product arrives, at which time some penetration of the LNAPLs into the water table may occur. Since LNAPLs are lighter than water, buoyant forces are important. They serve to maintain the water level by keeping the product on top of the surface. The characteristic shape of the LNAPL movement in the capillary zone is often called LNAPL pancake, the configuration and extend of which are dependent on the permeability of the soil, the percolation rate, and the degree of water saturation. In general, the greater the permeability of the soil, the greater will be the lateral spread of the product and the thinner will be the pancake (Yong et al., 2012).

LNAPL may occur as either residual LNAPL or as free-phase LNAPL within the subsurface environment. LNAPL that is retained by soil capillary forces and that is trapped within pore spaces is relatively immobile and termed as residual LNAPL. Free phase LNAPL occurs when the LNAPL saturation exceeds the residual saturation, and a continuous LNAPL phase exists among interconnected pores in the soil matrix. The free phase LNAPL volume may move vertically or laterally within soil in response to gravity or, less commonly, viscous forces. Over time, dissolution of LNAPL components and volatilization will deplete the LNAPL, reducing saturation and mobility (API, 2007).

3.4.1. LNAPL distribution parameters

Characteristics of the LNAPL and subsurface materials govern transport at both the pore scale and field scale. At the pore scale, the following transport and fate parameters control LNAPL migration and distribution. At the field scale, LNAPL migration is much more difficult to predict due to such factors as complex release history and, most importantly, subsurface heterogeneity and pore scale principles is necessary for development of conceptual models incorporating observations made at the field scale (Newell et al., 1995).

3.4.2. Density

The most common way to define density is as the mass of a substance per unit volume. One way to express density of a fluid is the specific gravity which is the ratio of the mass of a given volume of substance at a specified temperature to the mass of the same volume of water at the same temperature. Consequently, the density of fluids considered to be DNAPLs under normal subsurface conditions may decrease during remedial actions which impart heat to the subsurface. A decrease in density of DNAPLs which have densities near that of water may result in sufficient reduction to temporarily convert the DNAPL to an LNAPL. Density not only affects the buoyancy of a liquid but also the subsurface mobility. The hydraulic conductivity of a porous medium is a function of the density and viscosity of the liquid. As the density increases, the hydraulic conductivity with respect to the liquid also increases (Newell et al., 1995).

3.4.3. Viscosity

Viscosity is the resistance of a fluid to flow. Dynamic, or absolute viscosity is expressed in units of mass per unit length per unit time. This resistance is also temperature dependent. The viscosity of most fluids will decrease as the temperature increases. The lower the

viscosity, the less energy required for a fluid to flow in a porous medium. The hydraulic conductivity increases as the fluid viscosity decreases (Newell et al., 1995).

According to Coutelieris and Delgado (2012) fluid density creates similar effects to fluid viscosity. In a displacement with a denser fluid above the less-dense fluid, gravity forces cause redistribution of the fluids. However, if a denser fluid is on the bottom, usually, a stable displacement occurs.

Fluid forces acting on the NAPL phase consist of due to capillary pressure gradients, which in turn depend on the soil texture distribution and the fluid saturations, buoyancy, which acts upward when NAPL density is less than the water density, and forces associated with water or air phase movement. When the first two terms balance, there is no vertical fluid movement. In this case LNAPL can only move laterally induced by the flow of water or air. This is one of the primary assumptions of the LNAPL recovery model (API, 2007).

3.4.4. Saturation, wetting and nonwetting fluid

When NAPL is present in the unsaturated zone, there are three phases that can occupy the pores: air, water, and NAPL. In the saturated zone, two phases can be present: water and NAPL. Saturation is a parameter for describing the relative abundance of each phase. The saturation S_i is the fraction of the pore space that phase *i* occupies (Fitts, 2013).

When multiple immiscible fluids are present in the pores, the fluid with the strongest molecular attraction for the solid surface will coat the surfaces, while the other fluids occupy the central parts of pores, away from the solid surfaces. The fluid that wets the solid surfaces is called the wetting fluid and the other(s) are called the nonwetting fluid(s). In most situations, both in the unsaturated and saturated zones, water will be the wetting fluid, while air and/or NAPL are nonwetting fluids. If the saturated zone is completely devoid of water, NAPL is the wetting fluid and air is the nonwetting fluid. The Figure 4 shows some example distributions of phases in both the saturated and unsaturated zone pores.
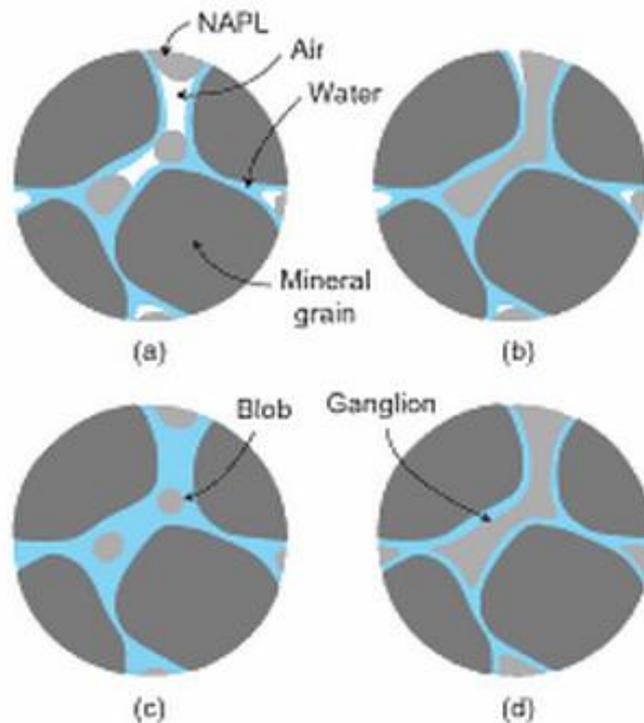
Figure 4 – Distribution of phases in the unsaturated zone (a and b) and the saturated zone (c and d)[4]

(Fitts, 2013)

Wettability is defined as the overall tendency of one fluid to spread on or adhere to a solid surface in the presence of another fluid with which it is immiscible. This concept has been used to describe fluid distribution at the pore scale. In a multiphase system, the wetting fluid will preferentially coat (wet) the solid surfaces and tend to occupy smaller pore spaces. The non-wetting fluid will generally be restricted to the largest interconnected pore spaces (Figure 5). In the vadose zone, where air, water, and LNAPL are present, liquids, usually water, preferentially wet solid surfaces as shown in Table 4 and Table 5, (EPA, 1995).

Table 4 - Typical wettability orders for different phase combinations (Mayer and Hassanizadeh, 2005)

Two-phase system	Wetting phase	Non-wetting phase
Water-Air	Water	Air
NAPL-Air	NAPL	Air
Water-NAPL	Water	NAPL

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[4] Water is the wetting fluid in each case. NAPL saturation increases from (a) to (b) and from (c) to (d)

Table 5 - Typical wettability orders for different phase combinations (Mayer et al., 2005)

Three-phase system	Wetting phase	Intermediate wetting phase	Non-wetting phase
Water-LNAPL-Air	Water	LNAPL	Air
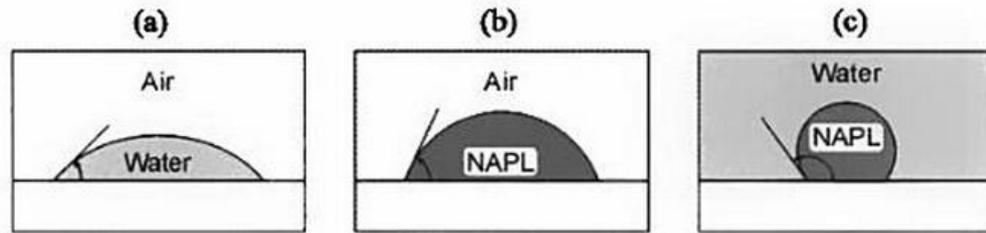
Figure 5 - Typical wettability preferences for combinations of water, NAPL and air

(Mayer and Hassanizadeh, 2005)

3.4.5. Interfacial tension and capillary pressure

Interfacial tension is the surface energy at the interface that results from differences in the forces of molecular attraction within the fluids and at the interface (Mercer and Cohen, 1990).

Figure 6 shows an interface where NAPL and water contact each other. Molecules in the NAPL have a greater attraction for themselves than they do for water molecules, and water molecules are more attracted to themselves than to NAPL molecules. One fluid typically has greater self-attraction than the other. Molecules near the interface are drawn away from the interface towards the interior of the fluid by these molecular forces. Interfacial tension is a property that measures the amount of imbalance in molecular attractions at an interface between two fluids. It has dimensions of energy/area, or equivalently, for/length. For most common NAPLs and water, the interfacial tension is in the range of 20-50 mN/m. Interfacial tension is so named because the interface looks as if there is some elastic membrane in tension stretched across the interface. The interface tends to contract around the nonwetting fluid, minimizing the surface area of the interface (Fitts, 2013).
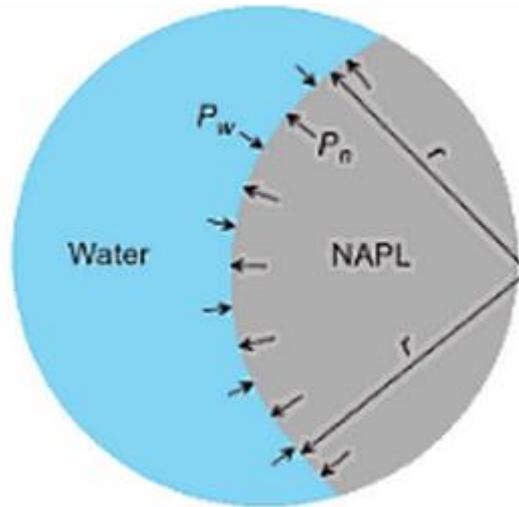
Figure 6– Close-up of an interface between NAPL (nonwetting fluid) and water (wetting fluid)

(Fitts, 2013)

An important characteristic of a porous medium is the relationship between the capillary pressure and wetting fluid saturation (Hillel, 1998).

Figure 7 shows a typical cycle of saturation vs. capillary pressure for an NAPL spill into the saturated zone. As NAPL saturation increases and water drains during NAPL invasion, it follows a drainage curve like the one labeled in the figure below. Eventually, the NAPL pulse moves through and NAPL saturations decreases as water reclaims some of the pore space taken up by NAPL. The wetting curve is always displaced toward higher NAPL saturation compared to the drainage curve, at the same capillary pressure (Fitts, 2013).
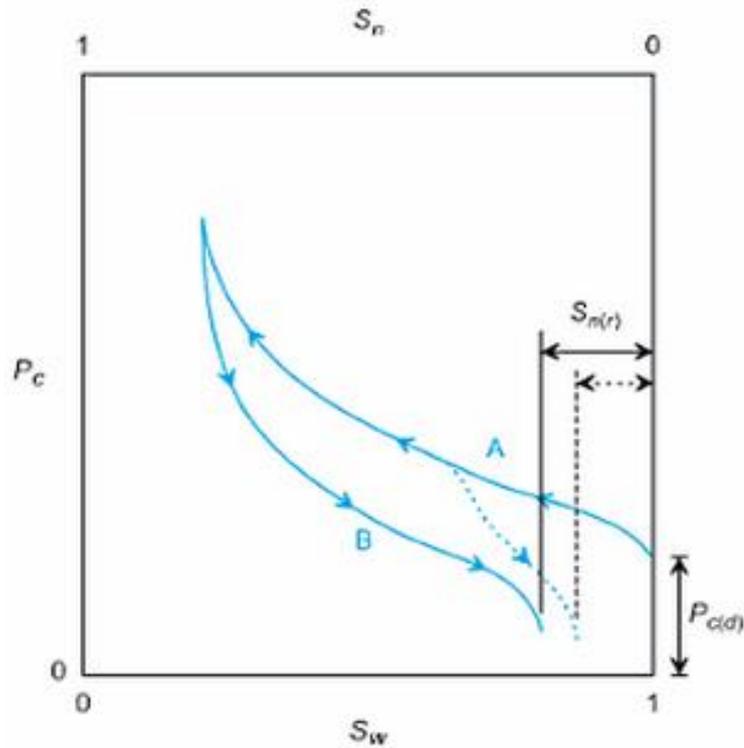
Figure 7 - Capillary pressure P_c vs. water saturation S_w and NAPL saturation S_n [5] (Fitts, 2013)

3.4.6. Influence of Tidal effect on LNAPL mobility

The tidal influence on LNAPL movement is a subject poorly studied with limited literature available. Tidal fluctuations along shorelines create a unique condition where the migration of LNAPLs is buffered and often mitigated from discharging into an open water body. A site investigation has been conducted in an area with presence of LNAPL located close to a major tidal river. The objective of the study (Davit et al., 2010) was to assess the influence of the tide upon the distribution and mobility of a separated LNAPL body migrating toward the river. The investigation area is strongly tidal influenced and in a continuous transient state, and therefore the vertical equilibrium is never reached. Baildown tests were performed at high and low tide in wells where LNAPL was present for assessing the physical characteristics of the LNAPL body. The baildown tests showed in general a low to very low recovery, generally not very affected by tidal fluctuation, since the recovery time is in general much longer than the tidal cycle. Tidal influence appears to have a limited impact on

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[5] During drainage (curve A), NAPL discplaces water. During wetting (curve B), water displaces NAPL. The displacement pressure is the minimum capillary pressure needed for NAPL to begin invading the medium. The residual NAPL saturation is the saturation at which the NAPL becomes immobile. The dashed wetting curve shows what would happen if wetting began after limited drainage.

measured NAPL thickness in the wells over time, but affects strongly the gradients, increasing locally the potential for NAPL mobility. The LNAPL body appears to be slowly migrating towards the river.

3.5.   LNAPL phase distribution in subsurface

Upon release to the environment, LNAPL migrates vertically until residual saturation depletes the liquid or until the capillary fringe is reached (Norris et al., 1994).

The constituents, or chemicals, that compose the LNAPL may be removed over time by various mechanisms, such as sorption, volatilization, and dissolution. If not removed, the LNAPL "body" can function as a potentially long-lived source zone for secondary impacts to adjacent soil, soil gas, and groundwater (ITRC, 2009).

According to Newell et al., (1995) LNAPL constituents can be in four phases in the subsurface. These phases are:

1) Air-Phase vapour in the pore space
2) Aqueous Phase- dissolved in water
3) Liquid Phase-free or mobile phase non-aqueous LNAPL
4) Adsorbed Phase-sorbed to subsurface solid

In the unsaturated zone, LNAPL may exist in all four phases. In the saturated zone, LNAPL may exist in aqueous, free phase and adsorbed phases.

3.5.1.   Volatilization

Volatilization refers to mass transfer from liquid and soil to the gaseous phase. Chemicals in the vadose zone gas may be derived from either the presence of NAPL dissolved chemicals, or adsorbed chemicals. Chemical properties affecting volatilization include vapour pressure and aqueous solubility described in the Table 6. Other factors influencing volatilization rate are concentration of contaminant in soil, soil moisture content, soil air movement, sorptive and diffusive characteristics of the soil, soil temperature, and bulk properties of the soil such as organic carbon content, porosity, density, and clay content (Krešić, 2007).

Table 6 - Selected properties of some common LNAPL chemicals and Gasoline Additives (Krešić, 2007)

Chemical	Solubility (mg/L)	Vapour pressure (nm Hg)
Benzene	1780	76-95.2
Toluene	535	28.4
Ethyl benzene	161	9.5
m-Xylene	146	8.3
Ethanol	Miscible	49-56.5
Methanol	Miscible	121.6
TBA	Miscible	1.57
MTBE	43,000-54,300	245-2560
ETBE	26,000	152
TAME	20,000	68.3
DIPE	2039-9000	149-151

3.5.2. Dissolution

When a contaminant is highly soluble or completely miscible in water, such as many salts and considerable number of compounds the rate of dissolution by groundwater flowing through the source zone is not limited. The time required to completely deplete the source zone is theoretically instantaneous: as soon as the contaminant comes in contact with water, it is dissolved and carried away by the groundwater flux (flow). The same is true when sources of miscible constituents in the vadose zone or at the land surface are exposed to the infiltrating water. The flux of the contaminant entering the subsurface will depend only on the infiltration rate. This is illustrated schematically in Figure 8. If the contaminant is not retarded by any of the processes in the unsaturated zone, and if the loading of the contaminant at the land surface is constant, the concentration arriving at the water table will eventually become constant as well. In such a case, the concentration can be calculated by dividing the mass of the contaminant at the surface with the volume of the infiltrating water. In case of low-solubility, immiscible compounds such as LNAPLs, the dissolution rate is limited and it depends on various factors including groundwater flow velocity, effective solubility, contact area between the NAPL body and the flowing water, dispersivity, diffusion and porosity (Krešić, 2007).

In general, higher dissolution rates may be associated with higher ground-water velocities, higher LNAPL saturation in the subsurface, increased contact area between

LNAPL and water, and LNAPLs with a high fraction of soluble components (Newell et al., 1995).
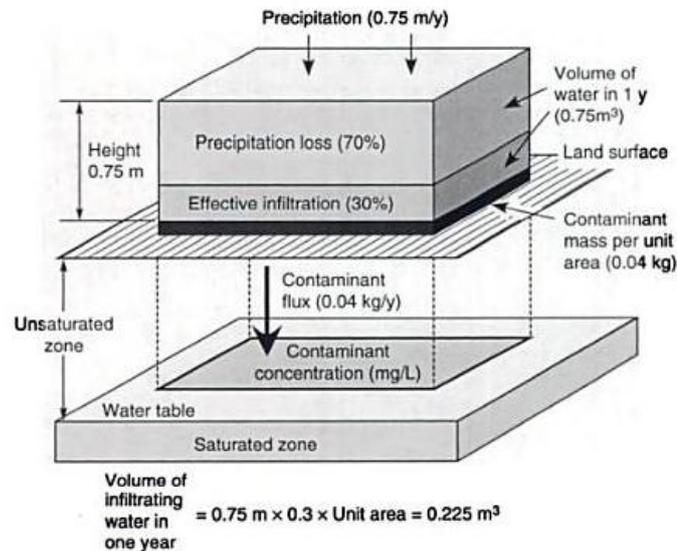
Figure 8 - Determination of the flux of infinitely soluble contaminant entering the vadose zone, as it is being dissolved by the infiltrating water[6] (Krešić, 2007)

3.5.3. Sorption

Sorption is defined as the interaction of a contaminant with a solid. In soil or aquifer material contaminated with LNAPL, contaminants from the LNAPL will partition onto solid phase material. The primary pathway in which this process occurs is through the water phase, as indicated in Figure 9 (Newell et al., 1995).
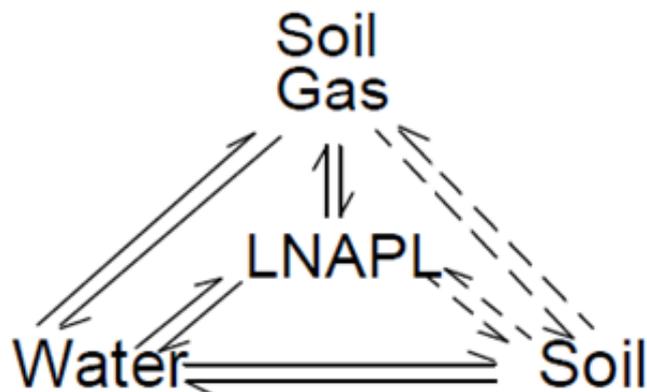
Figure 9 - Partitioning of LNAPL among the four phases potentially found in the unsaturated zone (Newell et al., 1995)

Boulding (1996) has revealed that adsorption/desorption of organic solutes by aquifer materials can be significantly rate limited. The rate-limiting mechanism apparently involves

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[6] Note: Assume miscible contaminant (unlimited dissolution), no retardation, no degradation, constant annual loading at the land surface,"very shallow water table"

constrained diffusion within the sorbent matrix. The validity of the local equilibrium assumption is dependent, in part, upon the hydrodynamic residence time of the contaminant in the velocity, as is done in pump-and-treat, can cause or enhance non-equilibrium conditions as a result of reduced residence time. Non-equilibrium will produce aqueous-phase concentration values lower than those obtained under ideal, equilibrium conditions. Thus, tailing will occur and removal by flushing will take longer.

3.5.4.   Biodegradation

Biodegradation of LNAPL source zones via microbial activity in the aqueous phase and vapour phase has been described and documented. However, there is less literature on the subject of direct biodegradation of the non-aqueous phase in the subsurface. Although it is commonly assumed that biodegradation or mineralization of source zone constituent mass is limited by the rate of partitioning from the LNAPL to aqueous phase, several laboratory studies have shown that rates of mineralization of target constituents dissolved into solvents (NAPLs) have exceeded the measured rates of partitioning. These studies propose various mechanisms for bacteria to enhance biodegradation of the LNAPL constituents (ITRC, 2009).

Many of the LNAPL-related compounds are amenable to biological degradation in the aqueous phase by naturally occurring microorganisms in the subsurface. However, there is an important distinction between aqueous-phase and NAPL biodegradation. The distinction is the inability to create and maintain conditions that are conducive to microbial activity within a NAPL. In brief, biodegradation of pure phase hydrocarbon does not appear to be practical and has not been demonstrated. Considerable research has focused on evaluating aerobic and anaerobic biodegradation and transformation processes. These processes play an important role in the ultimate fate of LNAPLs in the subsurface, both in the form of naturally occurring and actively engineered remediation processes (Norris et al., 1994).

3.6.   Conceptual Model of LNAPL movement in the subsurface

Movement of LNAPLs in the subsurface is controlled by several processes described in the following simplified scenario Figure 10. Upon release to the environment, NAPL (i.e., LNAPL or DNAPL) will migrate downward under the force of gravity. If a small volume of NAPL is released to the subsurface, it will move through the unsaturated zone where a fraction of the hydrocarbon will be retained by capillary forces as residual globules in the soil pores, thereby depleting the contiguous NAPL mass until movement ceases (API, 2002).
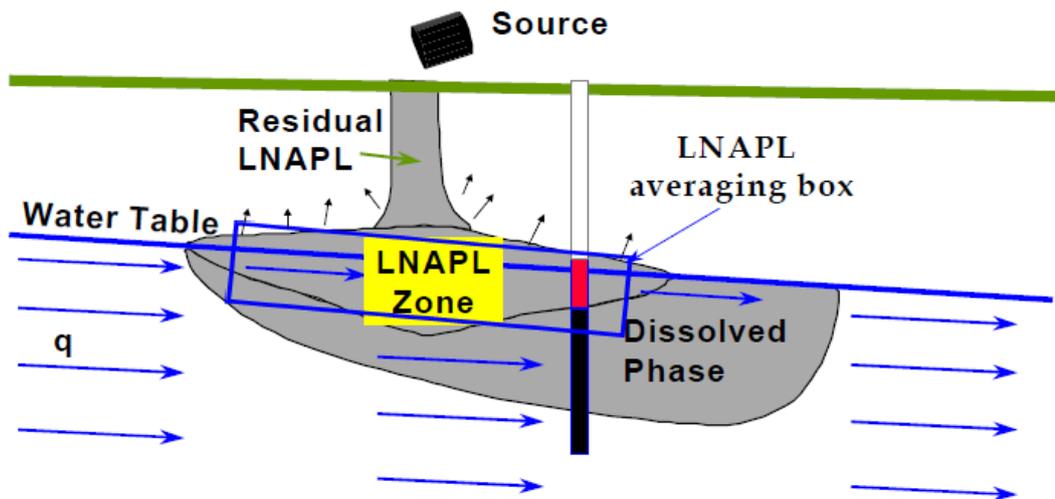
Figure 10 - Idealized Conceptualization of LNAPL in a well and adjacent formation (API, 2002)

3.6.1. Pancake conceptualization

The early conceptual model for LNAPL remediation developed in the 1980s was based on a "pancake" conceptualization for LNAPL distribution and migration (Figure 11). In this conceptualization, it was assumed that LNAPL released within the unsaturated zone migrates vertically under gravitational force until the water table is reached, at which time the LNAPL spreads horizontally as a continuous single-phase fluid. The LNAPL was assumed to "float" as a separate layer on the water table (or capillary fringe) in the shape of a "pancake" and remain as one interconnected mass. It was assumed that the LNAPL filled essentially the entire pore space (i.e., near 100 percent saturation) within the porous medium over a thickness comparable to (or some percentage of) the product thickness observed in monitoring wells. This inaccurate conceptualization ignored the critical influence of capillarity and commonly resulted in over predictions of the volume of product in the formation and recoverability (SABCS, 2006).
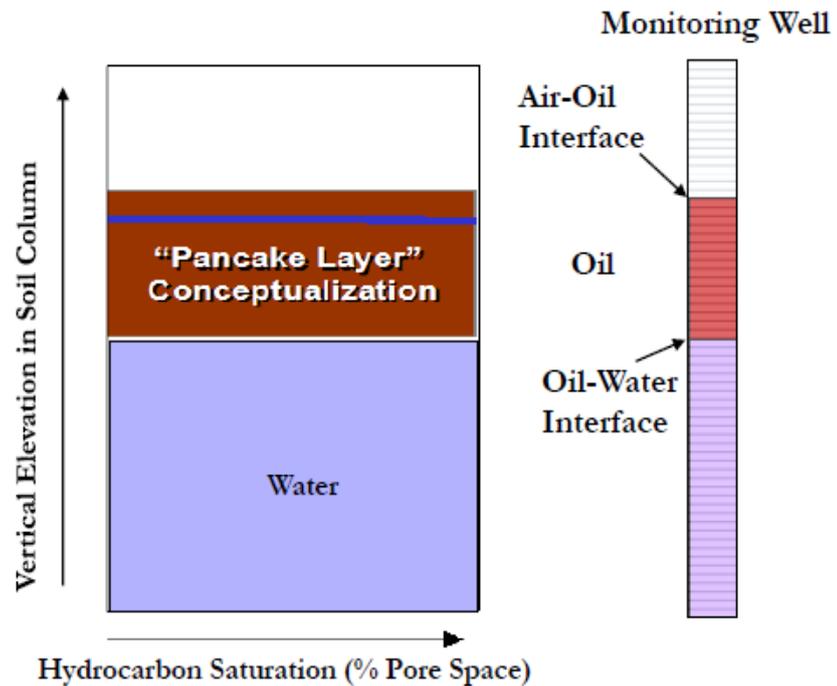
Figure 11 - Pancake conceptualization for LNAPL distribution (API, 2004)

One of the EPA (1996) technical guidance manual describing LNAPL estimation methods presented a comparison of a number of approaches to estimating actual product thickness. As documented in this manual, the Pancake Model approach appeared to be the most successful in predicting actual LNAPL thickness available in 1996. The Ballestero conceptual model assumes the LNAPL is in the form of a 100% LNAPL pancake sitting on top of the capillary fringe. The approach, however, also considers that LNAPL in the observation wells is not a direct reflection of the LNAPL layer in the subsurface. In the conceptualization the difference between LNAPL thickness observed in a well, and actual LNAPL thickness in soil, follow (EEE, P.C., 2010):

- Where an observation well intercepts the LNAPL layer, LNAPL suspended above the capillary fringe, flows down the well to the water table;

- LNAPL accumulates in the well and its weight further depresses the water table in the well, thereby making room for additional LNAPL. Eventually, a balance is established between the amount of LNAPL in the well and the amount of water displaced by LNAPL;

- The result is that LNAPL thickness observed in a well can be as much as four times greater than actual LNAPL thickness in the surrounding soil.

The Ballestero model takes into account an additional complication in that as the thickness of the free product (LNAPL) sitting on top of the capillary fringe increases, the degree to which it penetrates the capillary fringe increases, see Figure 12, thus somewhat decreasing the difference between apparent and actual thicknesses (EEE, P.C., 2010).
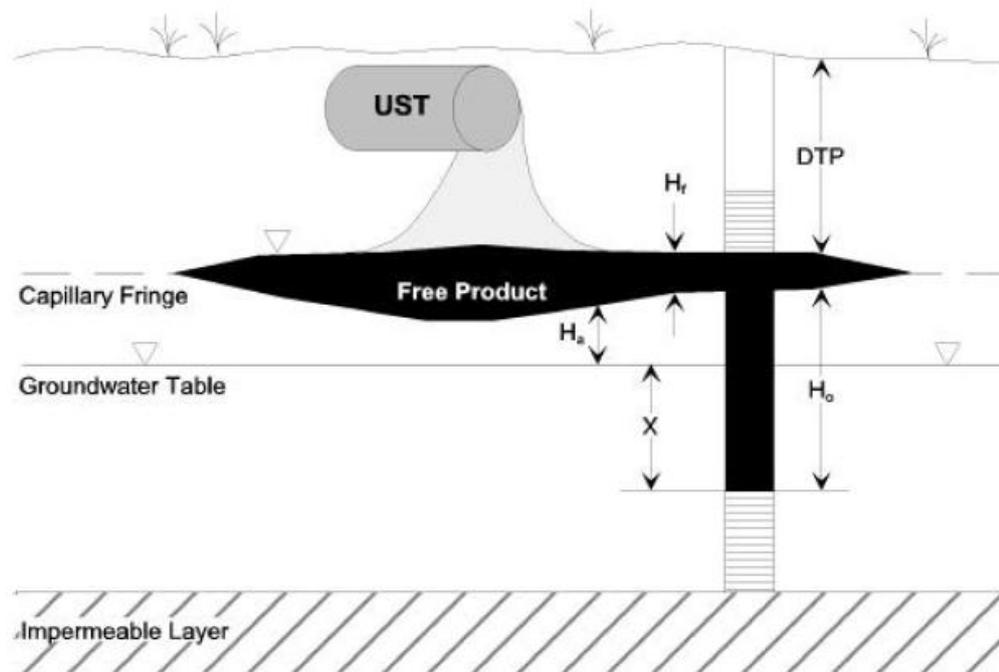
Figure 12 - The LNAPL spreads horizontally as a pancake after reaching the water table (EEE, P.C., 2010)

3.6.2. Multiphase conceptualization

An updated paradigm that is representative of typical soil capillary conditions is termed the "multiphase model" as shown in Figure 13. In this conceptualization, LNAPL does not migrate laterally as a separate layer (pancake) only above the water-saturated zone but, instead, rests like an iceberg at sea, largely submerged. Movement of LNAPL in the saturated zone is constrained by the capillary pressures needed to displace water from the pores at the margins of the LNAPL. Under the multiphase conceptualization, LNAPL, water and air coexist in zones of LNAPL saturation, and LNAPL saturations will decrease with depth in the porous medium, below the equilibrium elevation of the LNAPL/air interface observed in a monitoring well. The distribution of the LNAPL saturation in the porous medium over the depth interval between the LNAPL/water interface and the air/LNAPL interface observed in a monitoring well, is a function of the water-LNAPL capillary pressure (LNAPL is generally the non-wetting fluid compared to water). The distribution of the LNAPL saturation above the

air/LNAPL interface is a function of the LNAPL-air capillary pressure, where LNAPL is the wetting fluid compared to air. The complete LNAPL saturation profile can be obtained from having both the water-LNAPL and LNAPL-air capillary pressure curves (SABCS, 2006).
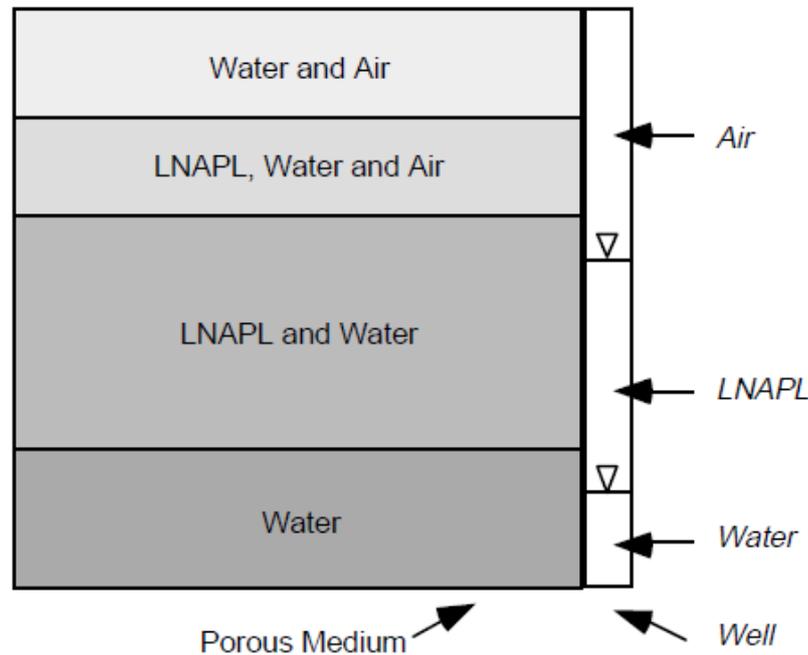
Figure 13 - Conceptualization of a multiphase fluid distribution in porous medium and monitoring well screened within the medium (Newell et al., 1995)

3.7. Forces in multiphase fluid systems

Newtonian fluids which are water, NAPL and air will not move unless there is force acting on them. The principle forces causing fluid movement are pressure gradients and gravity. If there is a balance between the vertical pressure gradient and gravity in each fluid phase, then a condition of hydrostatics (vertical equilibrium) exists, and there will be no motion in the vertical direction. Even under conditions of vertical equilibrium, there can be lateral gradients resulting in horizontal fluid movement (API, 2007).

3.7.1. LNAPL Migration in the Vadose Zone

When entering the subsurface, LNAPLs will migrate as a distinct phase downward through the unsaturated zone under the influence of gravity. Because of less density, LNAPLs travels much slower as compared to DNAPLs under the influence of gravity. The vertical migration will also be accompanied to some extent by the lateral spreading because of the effect of capillary forces. The advective groundwater effect also promotes the lateral spreading, thus in an ideal porous and homogeneous media the LNAPL plume is bound to

follow groundwater flow direction. In the unsaturated zone, the LNAPL contaminant can exist in all four distinct phases (Huling and Weaver, 1991). Figure 14 shows the possible existence all four LNAPL phases; gas, free, dissolved phases and residual entrapped LNAPLs in the soil pores (Gomo, 2009).
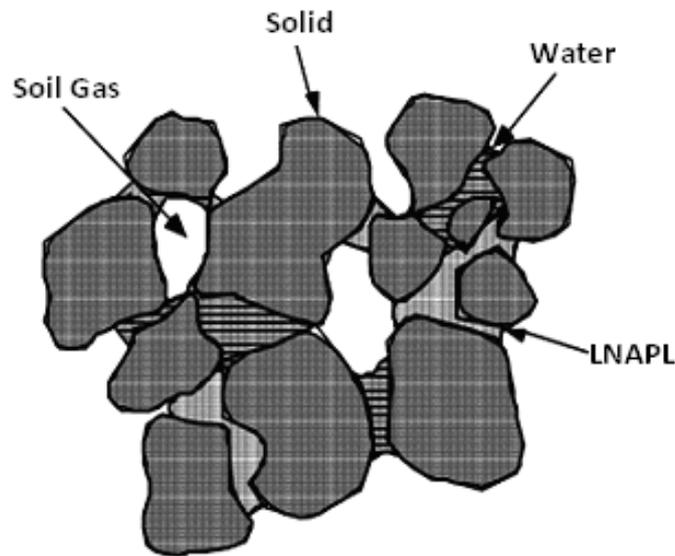
Figure 14 - LNAPL phases in the unsaturated zone (Huling and Weaver, 1991)

As the LNAPL descend through the unsaturated zone, the free phase volume decreases because the immobile LNAPL is left behind in the soil column as residual entrapped LNAPLs in the pore spaces. This entrapment of residual LNAPL is due to the surface tension effects which are a function of grain structure, texture and size among other factors. According to Brost and DeVaull (2000) the migration of LNAPL may also be limited by physical barriers such as low permeability layers. This fact seems to suggest that various permeability materials exhibit different retention capacities for LNAPLs. In addition to the migration of the non-aqueous phase, some of the LNAPL may volatilize and form a gaseous envelope of organic vapour extending beyond the main zone of contamination (Gomo, 2009).

3.7.2. LNAPL Migration in the Saturated Porous Media

On reaching the water table, the LNAPL behavior is chiefly dependent on its lighter density property and will spread laterally along the capillary fringe forming a lens or pancake. It may also depress natural groundwater levels during the lateral spreading. During interaction with the advective flowing groundwater, soluble components may dissolve to form a contaminant plume (Figure 15). The dissolved LNAPL phase can then migrate under the influence hydraulic gradients present in the aquifer (Newell et al., 1995). It is important to

highlight that both natural and artificial gradients has great potential to mobilize LNAPL contaminants.
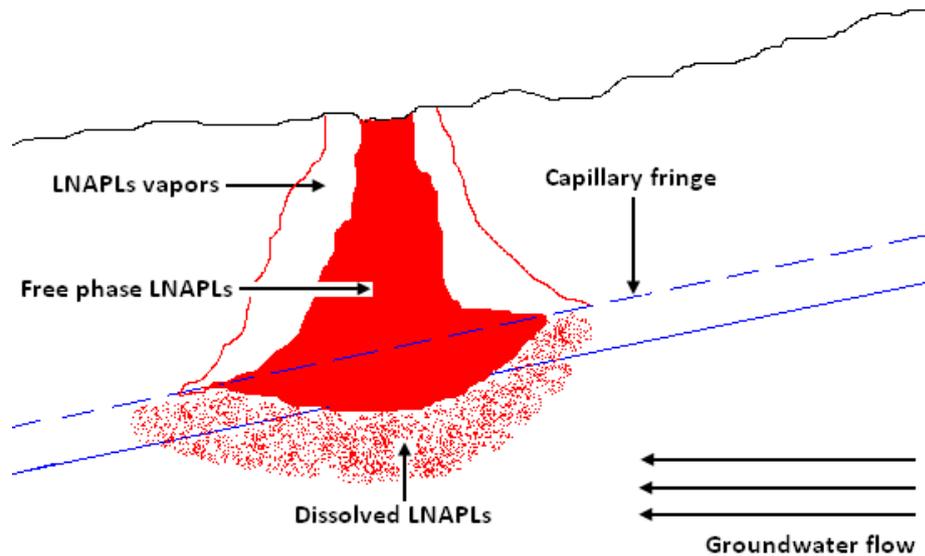
Figure 15 - Simple conceptual model of LNAPL migration in the subsurface (Mercer and Cohen, 1990)

Accumulated LNAPLs at or near the water table are subject to "smearing" as a result of changes in the water table elevation due to seasonal changes and or abstraction regimes. Seasonal changes could be due to recharge or discharge or tidal influence close to coastal environments. Mobile LNAPL floating above the water saturated zone will move vertically as the groundwater elevation fluctuates. As the water table rises or falls, LNAPLs will be retained in the soil pores, leaving behind a residual LNAPL "smear zone". If smearing occurs during a decline in the groundwater elevations, residual free phase LNAPLs may be trapped below the water table as groundwater elevations rise (Newell et al., 1995). Entrapment of the free phase LNAPLs below the water table elevations can lead to a wrong impression that the free phase contaminant has depleted. (Gomo, 2009).

3.7.3. LNAPL Migration in the Fractured Media

The behavior of LNAPL within a fractured rock media is a function of the properties of the immiscible fluid, geometry of the fracture network, rock matrix properties, and the groundwater flow regime. In other words, the LNAPL behavior is completely different in fractured rocks as compared to porous media. Fractured rock sites are among the most complex because of their considerable geologic heterogeneity and the nature of fluid flow and

contaminant transport through fractured media, see Figure 16. Complex geology poses a great challenge to site characterization (Gomo, 2009).
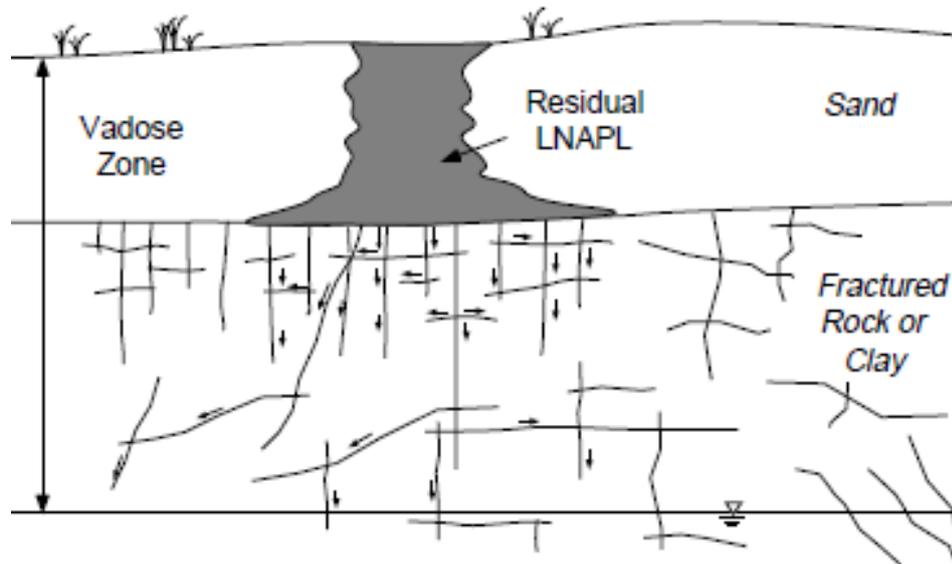
Figure 16 - Potential LNAPL migration in fractured medium (EPA, 1995)

3.8.   Risks and concerns associated with LNAPLs

There is a big number of potential risks or concerns linked to LNAPL in the subsurface that are discussed below. These are important to consider when developing remedial objectives and end-points for management of LNAPL at contaminated sites. LNAPL has the ability to migrate significant distances if the release source is not eliminated. Depending on site conditions, migrating free-phase LNAPL may have the potential to impact surface water bodies, water supply wells, and underground utilities that intercept the release. LNAPL may be released from soil during excavations that occur within LNAPL areas. Enlargement of the LNAPL zone will affect the distribution and extent of associated solute plumes. Vapours released from LNAPL may migrate into utilities or other confined spaces and accumulate at concentrations representing an explosion hazard. Elevated vapour concentrations may also occur during excavations within LNAPL source zones (SABCS, 2006).

There is a very important concept connected to LNAPL which is left in the soil pores and risk is the idea of ″near infinite mass″. Because of generally small mass in daughter phases, it does not take much LNAPL to saturate the surrounding water or vapour filled pore space. Because the LNAPL source is often exceedingly large compared to the dependent dissolved and vapour phase, two clearly related but separate aspects of risk are at issue. Any

concentration reduction through remediation or natural processes reduces longevity of risk by removing mass from the system, but does not necessarily reduce magnitude of risk over that shortened life span (Becket and Lundegard, 1997).

Gasoline components in the dissolved-phase may migrate away from the LNAPL zone, and have the potential to contaminate surface water bodies and water supply wells, and may pose human health and ecological risks through direct exposure pathways such as ingestion or dermal contact. A dissolved plume may also act as a source of soil vapour contamination which may migrate to indoor air (SABCS, 2006).

3.9.   LNAPL assessment

LNAPL management presents some of the greatest corrective action and clean-up compliance challenges to petroleum manufacturing, storage, and handling facilities such as refineries, bulk product terminals, gas stations, airports, and military bases. Once in the subsurface according to ITRC (2009), LNAPLs can be difficult to adequately assess and recover and thus can be a long-term source of:

- risk and exposure issues (e.g., vapour, groundwater and soil contamination)
- acute-risk concerns (e.g., explosive conditions)
- LNAPL mass concerns (e.g., regulations that require recovery of "free-product," "free-phase hydrocarbon," or "liquid-phase hydrocarbon"; for aesthetics or mass reduction reasons; or for potential LNAPL migration)

Not all LNAPL sites, however, pose the same concerns and, therefore, may not warrant the same level of management. Figure 17 presents an LNAPL management paradigm. The simple concept is to first identify the specific LNAPL composition and saturation concerns the particular LNAPL site conditions pose, if any. Next, apply the appropriate LNAPL remedial technology(ies) to abate those concerns. After all are addressed and any necessary actions with long-term stewardship are completed, the site should be eligible for no further action (NFA) status, if such status is applicable (ITRC, 2009).
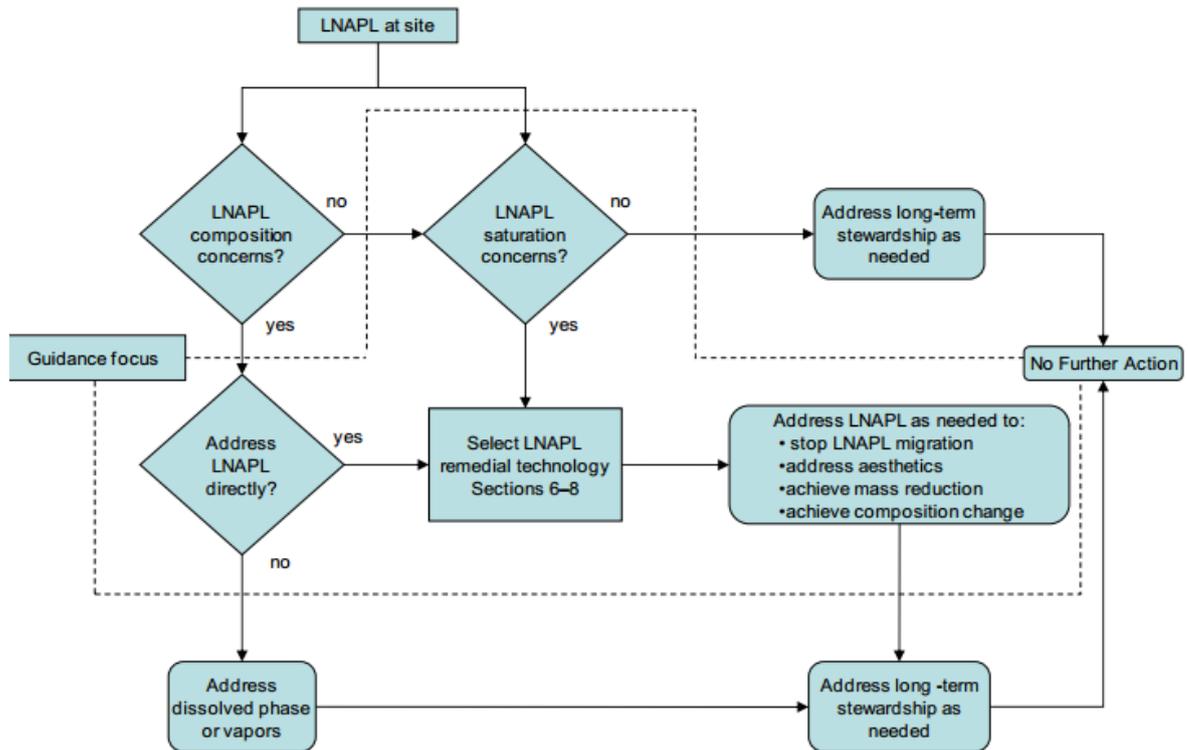
Figure 17 - Generalized LNAPL management overview (ITRC, 2009)

3.10. LNAPL remediation

Determination of physical and chemical properties of LNAPL obtained from wells or separated from soil samples will often be required to evaluate many aspects of LNAPL site characterization and remedial design. For example, information concerning physical properties such as density and viscosity may be used to assess LNAPL mobility and distribution and potential extraction designs. Analyses of LNAPL will be necessary to determine the chemical composition which may be used to compute the effective solubility of LNAPL components, identify potential LNAPL sources, and evaluate applicability of certain remedial technologies such as soil vapour extraction (Newell et al., 1995).

It is a tricky business trying to determine the location and amount of NAPL present in the subsurface. Conventional drilling and sampling methods often miss the thin, irregular threads of residual NAPL and the isolated pools where mobile NAPL has accumulated. Drilling itself is a hazardous activity that can create pathways where NAPLs can migrate deeper horizons. NAPL that pools at the top of a fine-grained layer can penetrate through the layer with the help of a poorly constructed borehole. If the borehole is left open or has coarse backfill, the NAPL will be able to move into the backfill and migrate down through the backfill and possibly into the well casing through the screen (Fitts, 2013).

The most frequently applied technologies according to Mayer and Hassanizadeh (2005) are:

1. Hydraulic removal of LNAPL: extraction of LNAPLs via wells or trenches, based on the manipulation of LNAPL and/or water gradients to drive mobile NAPL towards extraction points.

2. Pump-and-treat: Dissolution of NAPL components and extraction of ground-water containing dissolved NAPL components via extraction wells

3. Soil vapour extraction: Volatilization of NAPL components and extraction of vapour phase containing volatilized NAPL components via vapour-phase extraction wells

3.10.1. Hydraulic removal of LNAPL

Hydraulic removal of LNAPL relies on the extraction of LNAPLs via wells or trenches, based on the manipulation of LNAPL and/or water gradients to drive free LNAPL towards extraction points. Extraction wells or trenches are installed and operated to remove lighter-than-water NAPL (LNAPL) from the top of the water table. However, extraction efforts are not capable of removing all of the LNAPL from the aquifer. The primary benefit that can be achieved with this technology is limiting future migration of LNAPL, due to reduce LNAPL mobility or transmissivity (Mayer and Hassanizadeh, 2005).

3.10.2. Pump-and-treat

The pump-and-treat approach is limited in the presence of non-aqueous phase liquids, particularly after the pumps are switched off. For this reason, in the case of LNAPL a separate extraction is feasible by using specialized technologies. Firstly, the LNAPL can be removed with a metallic skimmer technology according to Meuser (2013) which comes into contact with the floating phase, adsorbs it and moves it upwards (Figure 18).

In case of a simultaneous pumping of groundwater and LNAPL a depression cone develops, in which non-aqueous phase liquids merge. During the pumping operation, when the LNAPL level decreases in response to pumping, the slurp may extract vapour. The extracted liquids (oil and water) and vapour must be differentiated above ground using the oil-water seperator and liquid-vapour separator technique, which is also required for the bioslurping technique (Meuser, 2013).
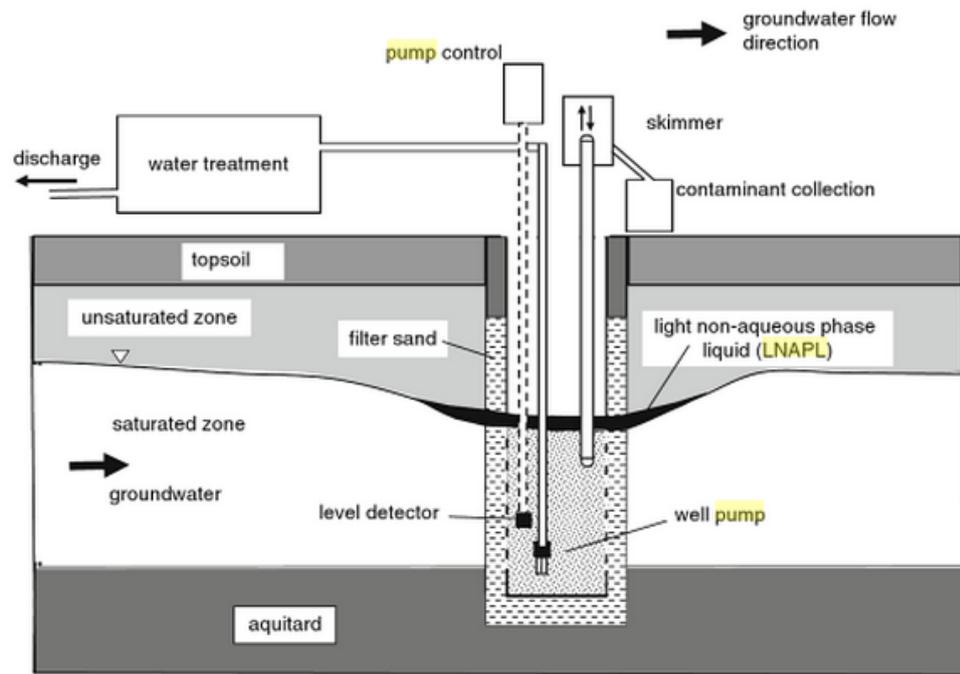
Figure 18 - Well system for separate extraction of contaminated water (pump system) and LNAPL (skimmer technology) (Meuser, 2013)

3.10.3. Soil vapour extraction

Most NAPL spills leave a trail of residual NAPL in the unsaturated zone. With organic NAPLs, the nearby pore gases will contain high concentrations of the volatile compounds in the NAPL. A good way to extract contaminant mass from the subsurface is to pump these gases from the unsaturated zone, a technique known as Soil Vapour Extraction (SVE). The SVE system commonly consist of wells that are screened in the unsaturated zone, or trenches with perforated pipe much like a horizontal well as shown in Figure 19, (Fitts, 2013).
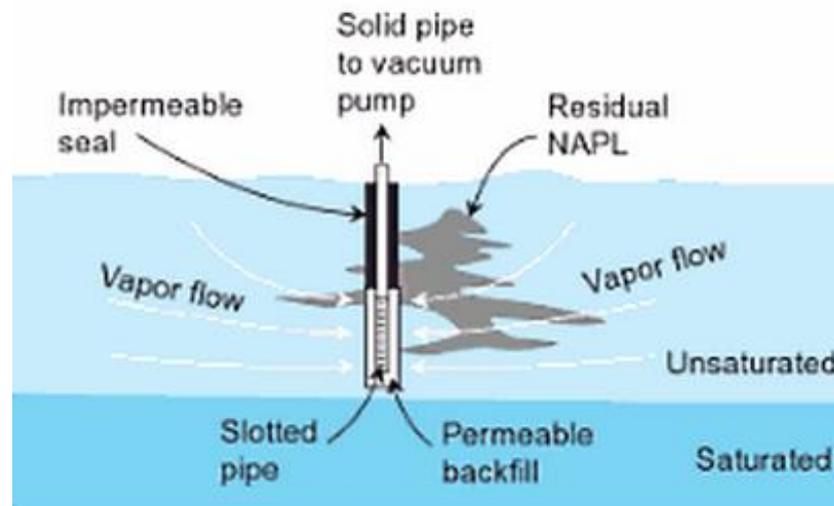
Figure 19 – Typical SVE system with one extraction well (Fitts, 2013)

3.10.4. The FACT System

The FACT (FLUTe[7] Activated Carbon Technique) is a method developed by FLUTe for mapping the distribution of contamination in the pore space and fractures of a borehole wall. The technique incorporates a 0.125 x 1.5 inch strip of activated carbon felt into the typical hydrophobic cover of the NAPL FLUTe system normally used for mapping the subsurface presence of a wide variety of NAPLs. The NAPL FLUTe cover is typically installed into a borehole on the outside of an everting FLUTe blank liner. The installation of a NAPL FLUTe cover with the added activated carbon strip (Figure 20) allows one to draw, by diffusion, the dissolved contaminants from the formation into the activated carbon. Recovery of the liner by inversion prevents the carbon from contact with any other portion of the borehole wall. At the surface, the carbon is then sectioned for chemical analysis. With the combination of the NAPL cover and the FACT, one can map both the NAPL and the dissolved phase of many other contaminants (FLUTe, 2010).
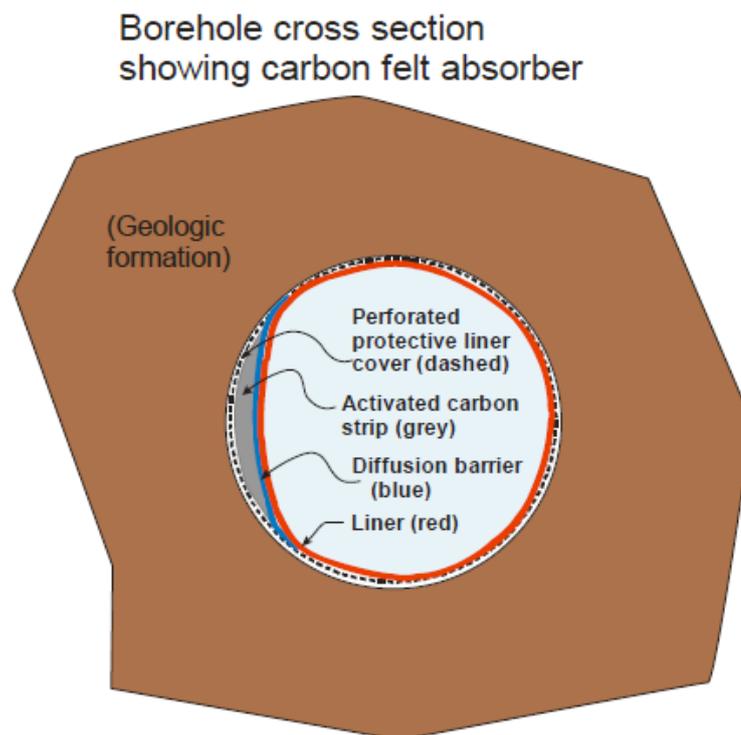
Figure 20 – Components of FACT (FLUTe, 2010)

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[7] Flexible Liner Underground Technologies, Ltd.L.C.

3.10.5. Measuring thickness of LNAPL and monitoring wells

At sites with petroleum hydrocarbons contamination, some monitoring wells and direct-push tools may contain a separate phase layer of product (LNAPL), which must be measured in addition to the water level. The thickness of this layer is referred to as the "apparent product thickness", which reflects the amount of hydrocarbon that has accumulated in the well - not the actual thickness of product in the formation. To measure the thickness of LNAPL, one of three methods can be used according to Nielsen and Nielsen (2007):

- An electronic oil-water interface probe
- Hydrocarbon-sensitive and water-sensitive paste applied to a measuring tape
- A clear, acrylic hydrocarbon bailer

3.10.6. LNAPL Modeling

Several multiphase flow models have been developed which are capable of simulating LNAPL transport. Such models have been used in site characterization to simulate potential contaminant distribution and LNAPL recovery system design. However, multiphase flow is a complex problem, particularly in a heterogeneous environment. Models incorporate simplifying assumptions to facilitate utility. Recognition of the underlying assumptions and evaluation of the site-specific applicability of the model is required. Data requirements may also be extensive. Certain parameters may not be readily measured in the field due to site characterization technology limitations. Many of the models are sensitive to parameters such as permeability, porosity, and LNAPL spill history that are often unknown or poorly defined. Thus, significant uncertainty in the accuracy of the results may exist, even at relatively well characterized sites (Newell et al., 1995).

4. MATERIALS AND METHODS

4.1. Brief description of experiment

The experiment was conducted in the laboratory at room temperature with small temperature and relative humidity fluctuations to sample and quantify multiphase liquids from porous media. Porous media used for the study is Silica Sand. The sand was packed manually and subjected to different amounts of multiphase liquids. Liquids used for the purpose were tap water for aqueous phase liquid and medicinal grade white mineral oil as LNAPL. The liquids were sampled (taken) from the porous material using Activated carbon Pellet and quantified using Digital balance and oven drying. The table below shows properties for the sand, water and oil used for the experiments.

4.2. Laboratory conditions

The experiment was performed in a laboratory with minimum variations of temperature and air humidity. The average temperature was 23°C and of air humidity was 38%. The single values of temperature and air humidity for each experiment were observed and recorded. Table 7 below shows values of temperature and air humidity during each experiments.

Table 7 – Temperature and air humidity conditions while performing experiments

Experiment	Temperature (°C)	Air Humidity (%)
1	23.1	43
2	22.8	35.5
3	22.8	35.5
Average	22.9	38

4.3. Silica sand

Porous media used for this experiment was silica sand with commercial name ST 56 from Střeleč area in East Bohemia and improved natural raw materials by Sklopisek Střeleč, a.s., Czech Republic. Chemically, according to the producer, the sand is composed of 98.9% SiO_2, 0.07% Fe_2O_3, 0.2% $K_2O + Na_2O$ and 0.2% $CaO + MgO$ and hence could be called silica sand. The sand is chemically inert. It has an average value of pH 8.0 and particle density 2.65 g/cm^3. Physically, it has uniform particle size and its particle size distribution ranges from

0.063 mm - 0.40 mm with middle grain size (d50) of 0.15 mm. However, it can have very few silt and or clay up to 2.2 %, but free from very coarse sand, gravel or stones, see Table 8.

Table 8 - Textural Contents of Silica Sand ST 56 (according to Sklopisek Střeleč, a.s.)

Category	Diameter (mm)	% Retained
Stones	>8	0
Coarse Gravel	8 to 4	0
Fine Gravel	4 to 2	0
Very Coarse Sand	2 to 1	0
Coarse Sand	1.0 - 0.5	2.1
Medium Sand	0.5 - 0.25	8
Fine Sand	0.25 - 0.125	56.9
Very Fine Sand	0.125 - 0.063	30.8
Silt/Clay	<0.063	2.2

According to Vašát (2006) it is recommended to use a porous media which has preferably the same size (dimensional and geometrically) of the grains. The same size of the grains is a guarantee of the same size of the pores in all depths and directions. Time aspect, optimally selected size and grains, porosity and hydraulic conductivity of the porous media should assure conditions for optimum length of the experiment, so that the experiment would not last too long or too short. The porous media should be chemically inert and unsuitable for survival and growth of microorganisms. It is also very important that the material is simply accessible in the case of repetition or continuing of the experiment.

4.4.   Light Non-Aqueous Phase Liquid

Liquid used as Light Non-Aqueous Phase Liquid (LNAPL) is medicinal grade white mineral oil commercially known as Marcol 82. It is a purified mixture of liquid saturated hydrocarbons obtained from petroleum by vacuum distillation with subsequent refining stages including an ultimate purification by catalytic hydrogenation (ExxonMobil, 2014).

The oil could be chosen and used for the study due to its desired chemical and physical properties over many oils available on market in addition to its superior quality in offering a high level of safety to work with. It is chemically inert and hence highly stable when contact with water, air, sand etc. It is insoluble in water and lighter than water with a

density around 0.85 g/cm^3. It is non-volatile at room temperature, and even at the boiling point of water and hence safe and appropriate for the objective.

Marcol 82, according to Lubstar (2014), is manufactured according to purity specifications more severe than the requirements of pharmacopoeias and hence a crystal clear, water-white product that contains no toxic impurities. It has a higher stability than most mineral, chemical and vegetable products and has excellent chemical inertness.

This medicinal grade white oil could be used in a variety of cosmetic and pharmaceutical applications depending on laws and regulations in each country (ExxonMobil, 2014). In cosmetic products, Marcol 82 can be used as a component in: emollients and moisturizers, baby products (shampoos, baby oils, and bath oils), hair care products, bath cubes, anti-perspirant, deodorant sticks, neutral and protective diluent for other cosmetic ingredients etc. Marcol 82 is an ingredient of pharmaceutical topical ointments and petroleum jellies. It is free from toxic polycyclic aromatics, heavy metals due to high level of purification methods and high temperature manufacturing process destroys germs completely (Lubstar, 2014).

Table 9 - Properties of Marcol oil 82 according to Exxonmobil, 2003

Property	Test Method	Typical	Min	Max
Appearance	Visual	-	Clear and Bright	Clear and Bright
Odour	Olfactory	-	Absent	Absent
Color, Saybolt	ASTM D 156	-	+ 30	-
Kinematic Viscosity (40ºC, mm²/s)	ASTM D 445	-	14.5	17.5
Kinematic Viscosity (100ºC, mm²/s)	ASTM D 445	3.7	-	-
Dynamic Viscosity (20ºC, mPa.s)	Calculated	-	27	37
Density (15ºC, kg/m3)	ASTM D 4052	-	845	858
Density (20ºC, kg/m³)	ASTM D 4052	-	842	855
Pour Point, (ºC)	ASTM D 97	-	-	6
Flash Point, (ºC)	ASTM D 92	-	182	-
Refractive Index, (nD²º)	ASTM D 1218	-	1.464	1468
Carbon Type, Paraffinic / Naphthenic / Aromatic (%)	ASTM D 2140	65/ 35 / 0	-	-

4.5. Activated carbon pellet

Activated carbon is an amorphous carbon based materials prepared in such a manner that they exhibit a high degree of porosity and an extended surface area (Çeçen and Aktaş, 2012). Activation creates pores in a non-porous material that gives the activated carbon an excellent sorption capacity for a wide range of organic compounds. Activation of the carbon is done both chemically and physically (thermal).

The term 'adsorption' was first used in 1881 by Kayser to describe the uptake of gases by chars. At about the same time, activated carbon material, as it is known nowadays, was discovered by R. von Ostrejko, who is considered the father and/or inventor of activated carbon. In 1901, he patented two different methods of producing activated carbons: The carbonization of lignocellulosic materials with metal chlorides (the basis of chemical

activation) and the mild gasification of chars with steam or carbon dioxide at red temperatures as it is mentioned by Bandosz (2006).

According to Strand (2001) carbon pores consist of:

1) Micro pores with a radius of less than 1 nm (small pores)
2) Meso pores with a radius of 1 – 25 nm (medium pores)
3) Macro pores with a radius larger than 25 nm (large pores)

Large pores are used for the transport of liquid through the carbon, and absorption occurs in the medium and and small pores. The activation basically means that pores are created in a non-porous material by means of chemical reactions. The figure below shows the pores size of activated carbon (Strand, 2001).
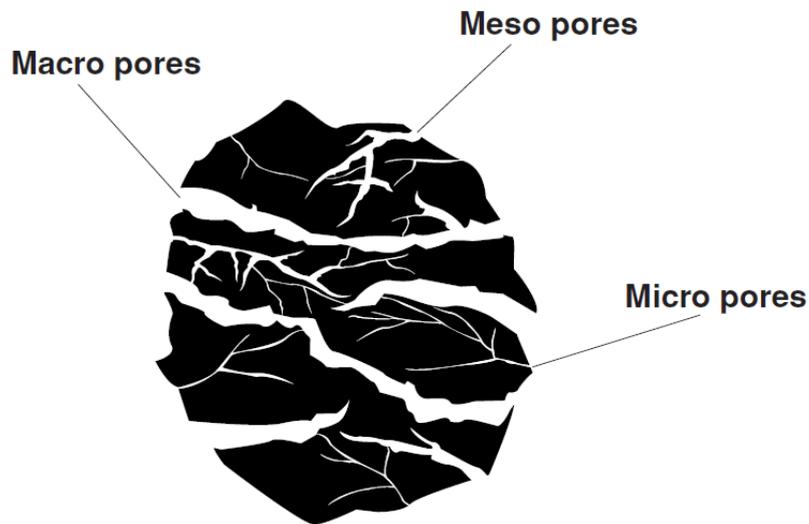
Figure 21- Pore size of activated carbon (Strand, 2001)

Large pores are used for the transport of liquid (Figure 21) while medium and small pores are for adsorption. Due to its coordination chemistry and ability to react with other heteroatoms, activated carbon is used in many specialized areas (Bandosz, 2006). Nowadays, the biggest application of activated carbon is in purification of water. However, it is used in many areas. Some among many are: in air purification to control potentially harmful, environmentally damaging or unpleasant odors; for decolorization of sugar, purify organic compounds, chlorine removal, decaffeination and others in food and beverages industry and medicinal areas. Activated carbon SC 40 is designed primarily to capture the solvents from a gas or liquid phase.

4.6. Porous material packing

To mimic natural soil profile, silica sand was packed layer by layer into circular container with the volume of 800 cm^3, height of 80 mm. For each liquid content 3 replicates were prepared. Applied multiphase liquids (water and LNAPL) were sampled following Matula (2008) through adsorption to activated carbon pellets. The pellets were inserted to the packed porous material using hollow stainless steel rod from the center horizontally.

Silica sand was packed in to each container as per the recommended bulk density for this sand according to the secondary data from Sklopisek Střeleč, a.s., which is 1.5 g/cm^3. Hence mass of the sand was calculated, 1.5 g/cm^3 density multiply by the volume of the container (Figure 22), 800 cm^3; which makes 1200 g (Digital balance used for this process was Kern 572 with measuring capacity up to 810 g). The sample for every 200 cm^3 was mixed with water/LNAPL uniformly in ceramic ball and packed layer by layer to get uniformly distributed soil column with uniformly distributed liquids, both water and LNAPL. The mass of dry soil in each layer was 1200 g/4=300 g. Samples with 5%, 15% and 25% by mass of liquids, of which 50% water and 50% LNAPL, were prepared.

Figure 22 – Packed silica sand columns for experiment

4.7.   Sampling and quantification of liquids

To sample the applied water and LNAPL from porous material, oven-dried activated carbon pellets were used. They were inserted into the packed sample column horizontally at the center, at 40 mm height, using hollow stainless steel rod (to keep activated carbon pellet at place). On each rods 3 activated carbon pellets were inserted with a tweezer at a distance of 15 mm (Figure 23). Activated carbon pellets were introduced into the prepared sample for 20, 45, 70 and 90 minutes. Activated carbon pellets were oven dried at 105°C for 24 hours before and after sampling the liquids to remove the water. Mass of activated carbon pellets before placing into packed sample, immediately after taking out from and the oven-dried one were measured by Digital balance, Denver Instrument SI-234A with d = 0.0001 g precision, measuring capacity from 0.01 g to 230 g and e = 0.001 g.

Data obtained from adsorbed and oven dry loss mass were used to compare and plot the amount of water and LNAPL adsorbed to the activated carbon pellet at different time scale. Microsoft Excel computer program and other suitable computer programmes were employed for this purpose.

Figure 23 – Stainless steel tubes ready for inserting of activated carbon

5. RESULTS

5.1. Initial water content of silica sand activated carbon pellet and evapoartion loss of Liquids used

To achieve the objective, materials mentioned in the Materials and Methods part of this study were tested. The main materials used were silica sand ST 56, tap water, Marcol 82 oil and activated carbon pellet SC 40 (to sample the liquids from packed silica sand). To sample and quantify water and oil from packed porous material with known amount and ratio of liquids, the principle is to evaporate water from liquids that adsorbed to activated carbon pellets following Matula (2008). Hence, before starting the main experiment, it was necessary to test some of the qualities of the materials.

Porous material that was used for the study was Silica sand ST 56 from Sklopisek Střeleč, a.s. Czech Republic. The company supply dry and packed sand. However, it is useful for the work to know the initial water content. Sample was taken and oven dried for 24 hours at 105 °C temperature, see Table 10 for the result.

Table 10 - Initial water content of Silica sand ST56 (Sklopisek Střeleč, a.s.)

No	Mass (g) of			Water content %
	Sand before oven dry	Sand after oven dry	Evaporation loss	
1	64.27	64.26	0.01	0.01
2	67.74	67.73	0.01	0.01
3	62.78	62.77	0.01	0.01
4	62.40	62.38	0.02	0.02
5	63.64	63.63	0.01	0.01

Distilled water, tap water and Lubstar Marcol 82 white mineral oil was oven dried to check the amount of liquid loss to evaporation at 105 °C for 24 hours, see Table 11.

Table 11- Mass lose of distilled water, tap water and white mineral oil after oven dry for 24 hours at 105 °C

Liquid	Weight of petri dish	Liquid+petri dish	Oven dry mass	Mass of liquid	Mass of evaporation loss	% of lost by oven drying
Distilled water	15.6978	16.9212	15.6978	1.2234	1.2234	100.00
	16.0950	17.3150	16.0950	1.2200	1.2200	100.00
	15.7353	16.9515	15.7354	1.2161	1.2162	99.99
	15.3071	16.5319	15.3070	1.2249	1.2248	100.01
	15.4409	16.6671	15.4408	1.2263	1.2262	100.01
	15.5721	16.5811	15.5720	1.0091	1.0090	100.01
Tap water	16.1272	17.3640	16.1274	1.2366	1.2368	99.98
	15.7731	17.0106	15.7732	1.2374	1.2375	99.99
	15.4859	16.7237	15.4861	1.2376	1.2378	99.98
	15.4824	16.7162	15.4825	1.2337	1.2338	99.99
	15.3891	16.4106	15.3895	1.0211	1.0215	99,96
	15.6134	16.8462	15.6137	1.2325	1.2328	99.98
White oil	16.0434	16.9973	16.9582	0.0391	0.9539	4.10
	15.4439	16.4164	16.3832	0.0332	0.9725	3.41
	16.4590	17.4047	17.3669	0.0377	0.9456	3.99
	15.6717	16.6038	16.5746	0.0292	0.9321	3.13
	15.7970	16.7024	16.6715	0.0309	0.9054	3.41
	15.8047	16.7535	16.7203	0.0331	0.9488	3.49

On the other hand, Marcol 82 used for the previous study, Esso white mineral oil, by Matula et al. (2008) and the other white mineral oil, Marcol 82 Lubstar, for this study were compared in terms of evaporation loss from free oil and from adsorbed oil to activated carbon pellet. Mass of oil before and after oven dry at 150°C for 24 hours were taken to determine the percentage of evaporation loss from free oil, see Table 11 for the result. Mean while, oven dried activated carbon pellets were kept in these two types of oil for 5 hours and mass of activated carbon pellets before and after adsorption as well as mass of oven dried activated carbon pellets after adsorption were taken to determine the evaporation loss from activated carbon pellet, see Table 12.

Table 12 - Evaporation loss from free oil Marcol 82 after oven dried at 150 ^{0}C for 24 hours

Marcol 82	Mass of oil (g)		Evaporation loss (g)	Evaporation loss (%)
	Before oven dry	After oven dry		
Lubstar	0.9648	0.9279	0.0369	3.82
	0.9222	0.8922	0.0300	3.25
	0.9822	0.9505	0.0317	3.23
	0.9674	0.9307	0.0367	3.79
	0.9631	0.9329	0.0302	3.14
	0.9702	0.9380	0.0322	3.32
	0.9840	0.9517	0.0323	3.28
Esso	0.2832	0.2629	0.0203	7.17
	0.3361	0.3147	0.0214	6.37
	0.3576	0.3357	0.0219	6.12
	0.3665	0.3451	0.0214	5.84
	0.2861	0.2675	0.0186	6.50
	0.3895	0.3635	0.0260	6.68
	0.3544	0.3337	0.0207	5.84

Table 13- Evaporation loss from adsorbed Marcol 82 to activated carbon pellets after oven dried at 150 ^{0}C for 24 hours

Oil type	Mass (g)					Oil lost (%) of adsorbed oil
	ACP[8]	Adsorbed oil + ACP	Adsorbed oil + ACP after oven dry	Oil adsorbed	Oil lost to evaporation	
Lubstar	0.0903	0.1704	0.1642	0.0801	0.0062	7.74
	0.0812	0.1660	0.1600	0.0848	0.0060	7.08
	0.0861	0.1869	0.1798	0.1008	0.0071	7.04
	0.1055	0.1959	0.1868	0.0904	0.0091	10.07
	0.0915	0.1704	0.1636	0.0789	0.0068	8.62
	0.0863	0.1666	0.1592	0.0803	0.0074	9.22
	0.0865	0.1605	0.1541	0.0740	0.0064	8.65
Esso	0.1233	0.2261	0.2190	0.1028	0.0071	6.91
	0.0852	0.1662	0.1604	0.0810	0.0058	7.16
	0.0845	0.1703	0.1610	0.0858	0.0093	10.84
	0.1050	0.2064	0.1970	0.1014	0.0094	9.27
	0.0936	0.1800	0.1734	0.0864	0.0066	7.64
	0.1099	0.1901	0.1822	0.0802	0.0079	9.85
	0.0874	0.1578	0.1529	0.0704	0.0049	6.96

According to the company that supply activated carbon pellet, see Materials and Methods part of this work, activated carbon pellet is packed with up to 5% by mass of moisture content. To check this, initial and oven-dry masses of activated carbon pellets were taken, see Table 14.

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[8] Activated Carbon Pellet

Table 14 - Initial moisture content (g) of activated carbon pellets SC 40 after oven dried at 150 ^{0}C for 24 hours

No	Mass (g)					Moisture content (%)
	Petri dish	ACP + Petri dish	Oven dry ACP + Petri dish	ACP	Evaporation loss	
	15.2800	15.3767	15.3754	0.0954	0.0013	1.36
	16.1064	16.1909	16.1905	0.0842	0.0004	0.44
	15.7469	15.8172	15.8158	0.0689	0.0014	2.03
	15.7499	15.8390	15.8369	0.0870	0.0021	2.41
	16.2167	16.3016	16.3009	0.0841	0.0007	0.87
	15.3467	15.4192	15.4175	0.0708	0.0017	2.40
	15.1637	15.2446	15.2438	0.0801	0.0007	0.92
	15.3992	15.4676	15.4666	0.0674	0.0010	1.48
	15.3090	15.3761	15.3755	0.0665	0.0006	0.90
	15.8432	15.9227	15.9224	0.0792	0.0003	0.42
	16.1335	16.2065	16.2049	0.0714	0.0016	2.24
	16.2564	16.3629	16.3613	0.1049	0.0016	1.53
	16.4045	16.4967	16.4960	0.0915	0.0007	0.80
	15.4490	15.5492	15.5465	0.0975	0.0027	2.77
	15.3179	15.4004	15.3996	0.0817	0.0008	0.98
	15.4211	15.5211	15.5190	0.0979	0.0021	2.15
	15.9154	16.0266	16.0237	0.1083	0.0029	2.68

5.2. Length and diameter of activated carbon pellets

Activated carbon pellets were selected according to length and diameter. They were supposed to be almost the same. Small irregularities were observed within each particular pellet. The diameter was not exactly the same within the whole length of a pellet and also uneven edges occurred quite often. Table 15 shows the Standard deviation for length 0.228564 mm and for the diameter 0.0342783 mm. From length and diameter, volume was calculated and averages of carbon pellets were taken into account. Figure 24 bellow shows that the volumes differ from 460 to 520 mm^3 with standard deviation 0.000844 mm^3.

Table 15 – Sum, mean and standard deviation for activated carbon pellets

	Length (mm)	Diameter (mm)	Volume (mm^3)
Sum	117.06	48.42	862199.9
Mean	9.755	4.035	498.9583
S. Deviation	0.228564	0.0342783	0.000844
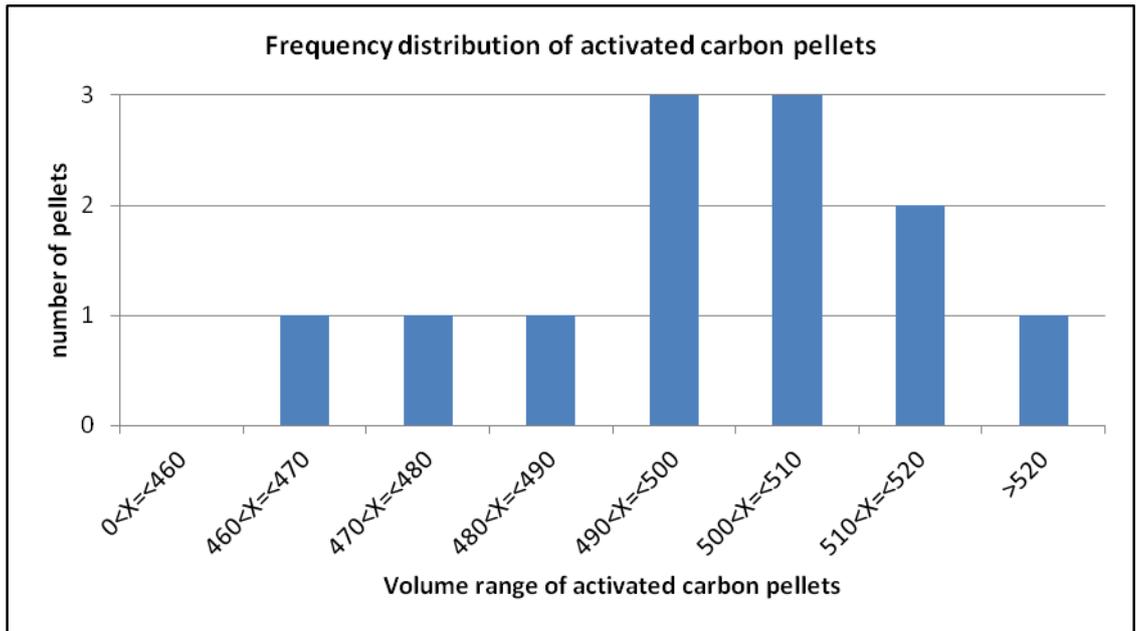
Figure 24 – Volume range of activated carbon pellets

5.3. Experiment I – Adsorption of water/LNAPL (from 5% by mass)

An Experiment with 5% liquid content of which 50% is water and the other 50% is Lubstar oil Marcol 82 used as LNAPL (2.5% by mass of water and 2.5% by mass of LNAPL) was done. Water, LNAPL and total liquid adsorbed to activated carbon pellets after 20, 45, 70 and 90 minutes from packed soil column with mentioned liquids are summarized in Table 16 and Figure 25 as follows and for more information see the Appendix.

Table 16 - Adsorbed amount of LNAPL and water (g) and (%) from 5% liquid content of sample column

Time (min)	Total adsorbed Liquid (g)	Adsorbed water (g)	Adsorbed LNAPL (g)	Total Liquid content (%)	LNAPL Content (%)	Water Content (%)
20	0.0106	0.0105	0.0000	11.22	0.00	11.22
45	0.0125	0.0127	0.0000	12.97	0.00	12.97
70	0.0185	0.0185	0.0000	18.70	0.00	18.70
90	0.0232	0.0242	0.0000	25.92	0.00	25.92
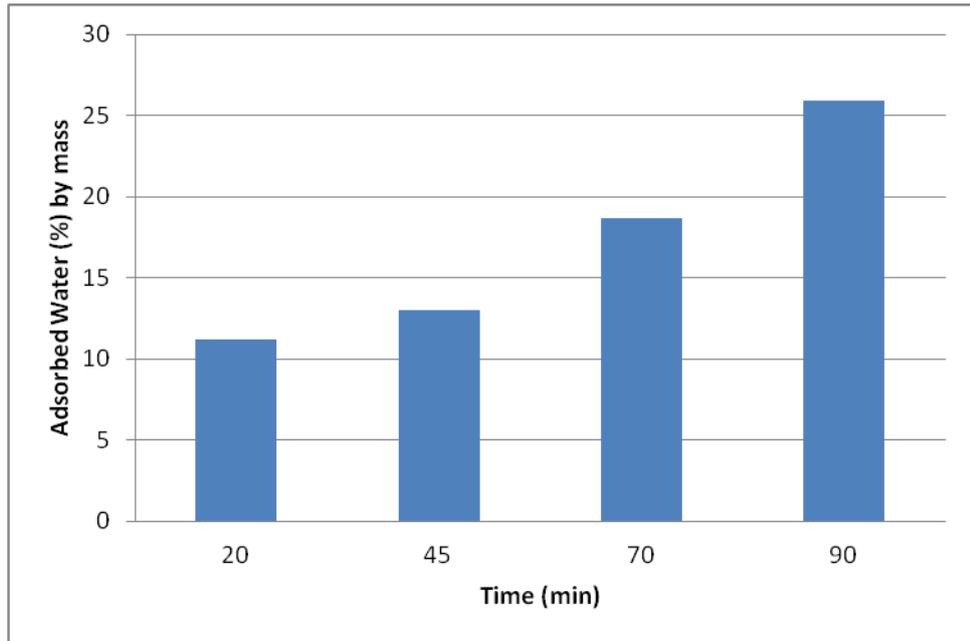
Figure 25- Graph of adsorbed water (%) to activated carbon pellets at different times (min)

5.4. Experiment II – Adsorption of water/LNAPL (from 15% by mass)

An Experiment with 15% liquid content of which 50% is water and the other 50% is Lubstar oil Marcol 82 used as LNAPL (7.5% by mass of water and 7.5% by mass of LNAPL) was done. Water, LNAPL and total liquid adsorbed to activated carbon pellets after 20, 45, 70 and 90 minutes from packed soil column with mentioned liquids are summarized in Table 17 and Figure 26 as follows and for more information see the Appendix.

Table 17 - Adsorbed amount of LNAPL and water (g) and (%) from 15% liquid content of sample column

Time (min.)	Total adsorbed liquid (g)	Adsorbed water (g)	Adsorbed LNAPL (g)	Total Liquid content (%)	LNAPL Content (%)	Water Content (%)
20	0.0133	0.0078	0.0055	14.29	**6.055**	**8.23**
45	0.0293	0.0190	0.0103	32.47	**11.29**	**21.18**
70	0.0380	0.0235	0.0146	44.53	**16.51**	**28.02**
90	0.0417	0.0260	0.0158	50.74	**19.58**	**31.15**
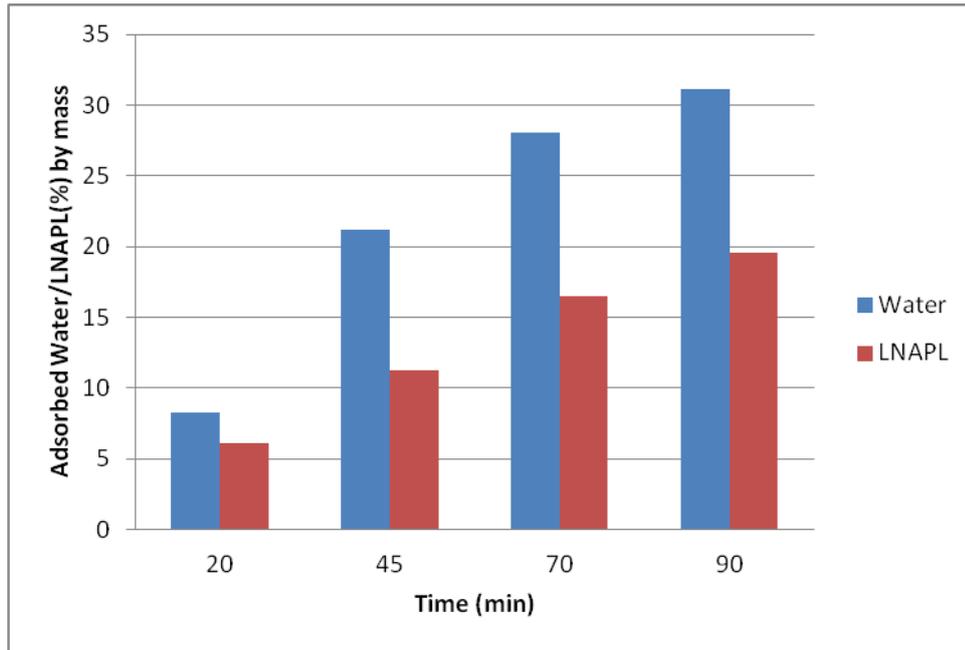
Figure 26- Graph of adsorbed water/LNAPL (%) to activated carbon pellets at different times (min) from 15% liquid content of sample column

5.5. Experiment III – Adsorption of water/LNAPL (25% by mass)

An Experiment with 25% liquid content of which 50% is water and the other 50% is Lubstar oil Marcol 82 used as LNAPL (12.5% by mass of water and 12.5% by mass of LNAPL) was done. Water, LNAPL and total liquid adsorbed to activated carbon pellets after 20, 45, 70 and 90 minutes from packed soil column with mentioned liquids are summarized in Table 18 and Figure 27 as follows and for more information see the Appendix.

Table 18 - Adsorbed amount of LNAPL and water (g) and (%) from 25% liquid content of sample column

Time (min.)	Total adsorbed liquid (g)	Adsorbed water (g)	Adsorbed LNAPL (g)	Total Liquid content(%)	LNAPL Content (%)	Water Content (%)
20	0.043	0.017	0.026	30.28	**17.56**	**12.72**
45	0.032	0.019	0.013	33.06	**19.76**	**13.30**
70	0.041	0.026	0.015	43.69	**27.41**	**16.27**
90	0.053	0.025	0.028	55.35	**26.25**	**29.11**
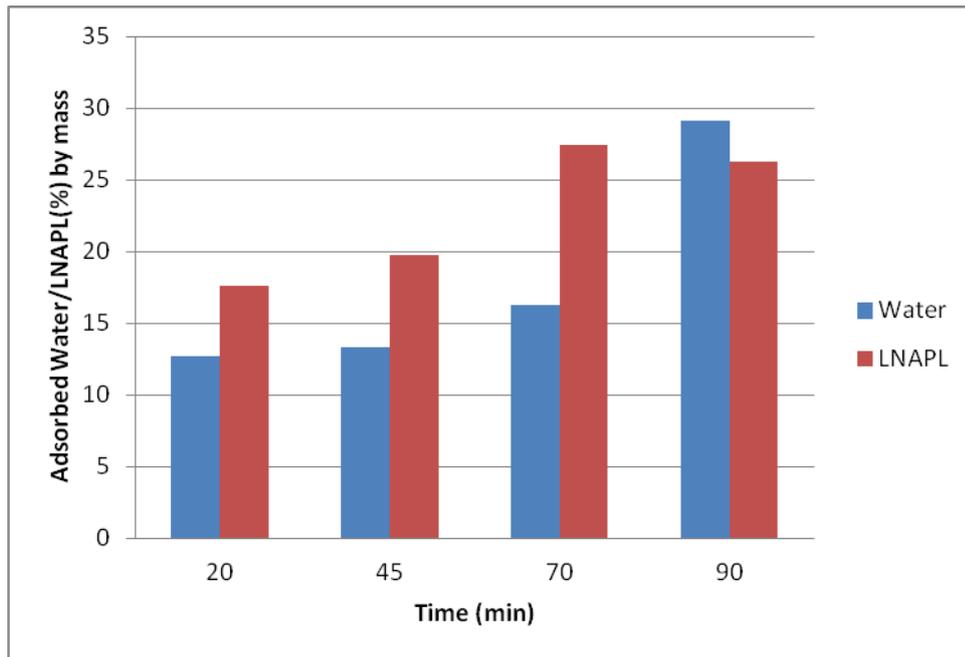
Figure 27- Graph of adsorbed water/LNAPL (%) to activated carbon pellets at different times (min) from 25% liquid content of sample column

6. DISCUSSION

Initial water content of silica sand ST56 used as porous material was below 1% by mass, see Table 10. However, for the main experiment the sand was oven dried for 4 hours at 105°C to remove even this small amount of water.

All distilled water (100%) and almost all tap water (99.98%) were evaporated while only small portion (3.59%) from white oil, Lubstar Marcol 82 i.e LNAPL was evaporated in average, see Table 11. This shows that only small fraction of this LNAPL is lost through evaporation at 105 °C for 24 hours, see Figure 28. Hence, tap water and Lubstar Marcol 82 is suitable for the study and they were used.
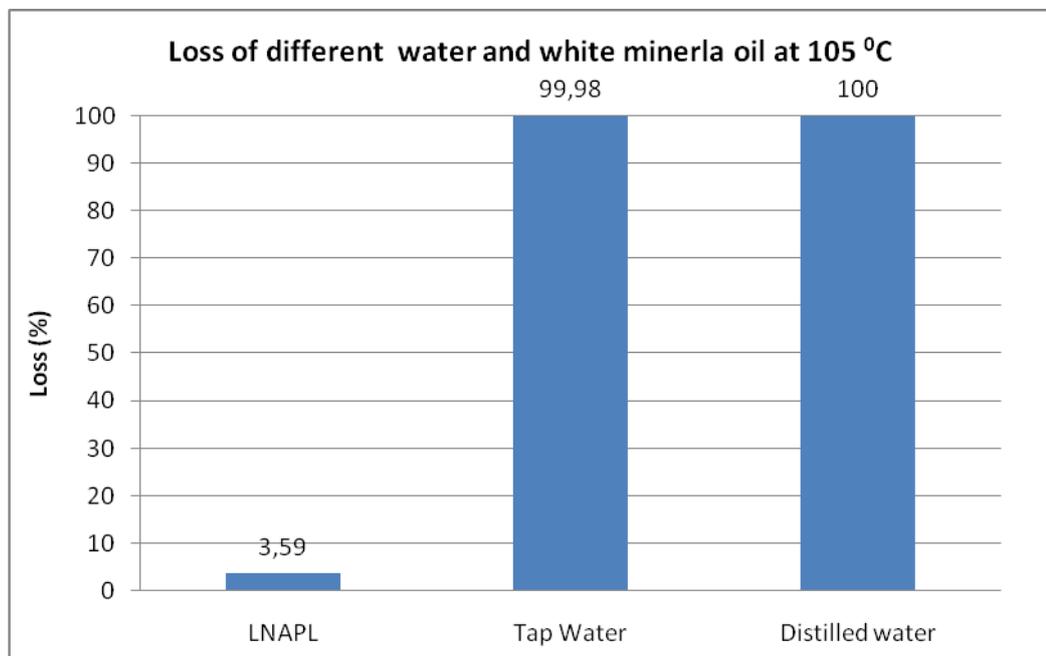
Figure 28 - Loss of different water and white oil at 105°C

The evaporation loss of oil from the oil used for the previous study, Esso Marcol 82 from free oil is almost as double as from the one which is used for the current study, Lubstar Marcol 82, see Table 12. However, the evaporation loss from oil Adsorbed to Activated Carbon Pellets (AACP), see Table 13 and Figure 29, are almost the same and within 95% confidence interval. Hence, studies using both marks of oil don't have significant differences.
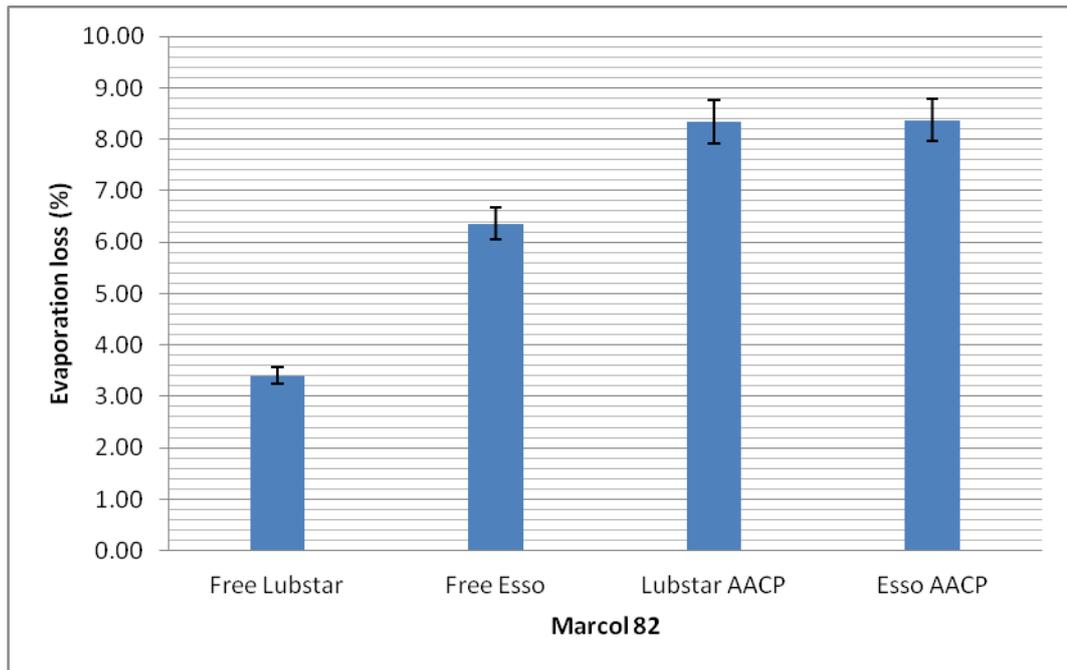
Figure 29 - Mean evaporation loss of Lubstar and Esso Marcol 82 from free and adsorbed to activated carbon pellets oven dried at 150 ^{0}C for 24 hours, where AACP is adsorbed to activated carbon pellet

Activated carbon pellets SC 40 were tested for initial water content and the result shows that none of the pellet tested has value for moisture content greater than 5% by mass, see Table 14. Hence the pellet is defined very well and good for use. To remove the initial water from every activated carbon pellet that was used for the main experiment, pellets were oven dried at 150 ^{0}C for 24 hours.

Matula et al. (2012) presented impact of diameter and length of activated carbon pellet SC 40 on sampling of water/LNAPL from porous media by adsorption. The results of one way ANOVA analysis of the diameter of activated carbon pellets used against the percentage of respective water/LNAPL adsorbed to them confirmed that the amount of adsorbed water/LNAPL significantly decreases with increasing of pellets' diameter. Up on their finding, activated carbon pellets with almost similar diameter and length were selected and used for this experimental work, see Table 15 and Figure 24.

In the Experiment I, 5% liquid content (2.5% water and 2.5% LNAPL by mass) the percentage of LNAPL adsorbed to activated carbon pellets SC 40 at 20, 45, 70 and 90 minutes are too small and insignificant. The amount of liquid (water/LNAPL) in the sand column is too low, 2.5% by mass each and LNAPL used is immobile compared to water and or exist only in liquid form not gaseous state at experimaetal condition. Evaporation loss from free

LNAPL used for the study, Lubstar Marcol 82, at 105 °C for 24 hours is too small, see Figure 29, and there is no chance for this oil to exist in vapour form at room temperature and 40% relative humidity. On the other hand, there is adsorption of water at all time intervals used in the study and adsorption increase with increase in duration of activated carbon pellet in the porous media for adsorption, see Figure 30. The smallest values of adsorbed water were observed at 20 minutes and the highest at 90 minutes as expected. The smallest amount of water adsorbed for 20 minutes (11.22%, see Table 17) duration of activated carbon pellet SC 40 in porous media is higher than that of the porous media with 2.5% by mass of water. However, from previous study by Matula et al. (2012) 10% by mass of water from porous media saturated to 20% by mass (10% water and 10% Esso Marcol 82) was reached around cca. 20 minutes. Marcol 82 used for these studies are different; Matula et al. (2012) used Esso Marcol 82 while Lubstar Marcol 82 used for this experiment.
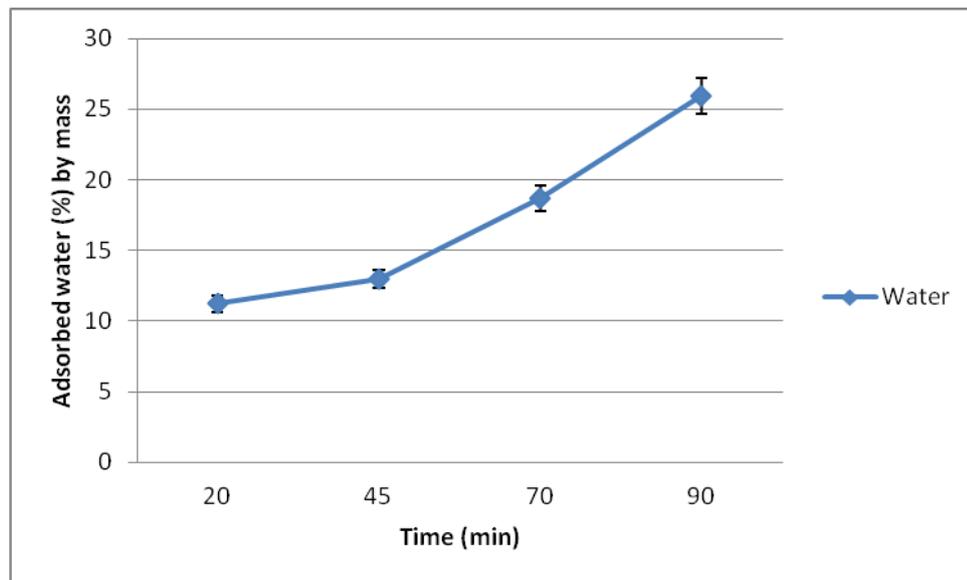
Figure 30 - Graphically demonstrated adsorbed amount of water (%) by mass to activated carbon pellet SC 40 at different times from 5% by mass of liquid content sample column

In Experiment II, where the liquid content of porous material packed, silica sand ST56, is 15% by mass of which 50% is water and the other 50% is LNAPL used for the study, there is an adsorption of both liquids to activated carbon pellet SC 40. The amount of both water and LNAPL adsorbed to the pellets increases with time, minimum at 20 minutes; 8.2% for water and 6.1% for LNAPL and maximum at 90 minutes; 31.2% for water and 19.6% for

LNAPL for the time used for the study [20, 90] minutes, see Figure 31 and 32. Water content portion of 7.5% of 15% saturation (7.5% water + 7.5% LNAPL) by mass was sampled using pellets around 20 minutes for water and between 20 and 45 minutes for LNAPL. The result is similar with Matula et al. (2012) for water sampling as tried to be discussed under Experiment I of this study. However, their study does not show proportional sampling time for LNAPL.
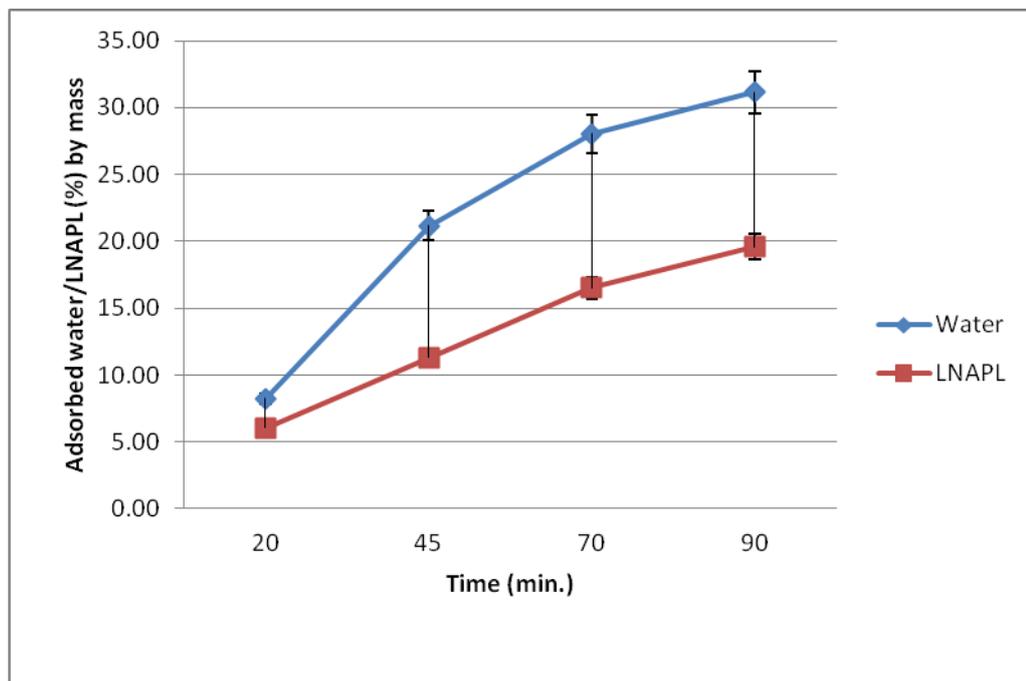
Figure 31- Graphically demonstrated adsorbed amount of water/LNAPL (%) by mass to activated carbon pellet SC 40 at different times from 15% by mass of liquid content sample column
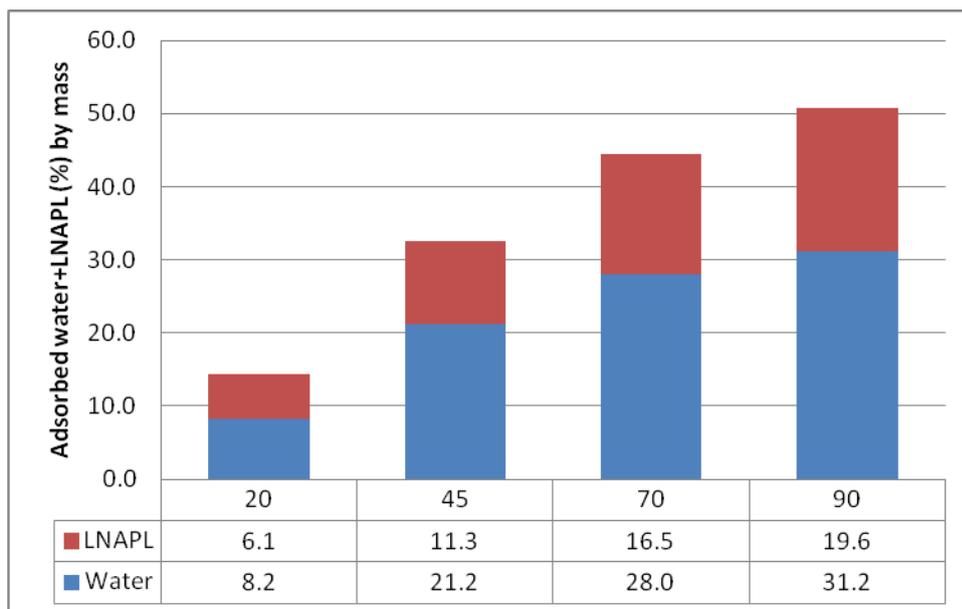
Figure 32 - Graphical and tabular overview of water + LNAPL adsorbed to activated carbon pellets from 15% liquid content of sample column at different times (minute)

In Experiment III, where the liquid content of porous material packed, silica sand ST56, is 25% by mass of which 50% is water and the other 50% is LNAPL used for the study, there is an adsorption of both liquids to activated carbon pellet SC 40. The amount of both water and LNAPL adsorbed to the pellets increases with time except some decrement for LNAPL between 70 and 90 minutes, minimum at 20 minutes; 12.7% for water and 17.6% for LNAPL and maximum for water at 90 minutes; 29.1% and maximum for LNAPL at 70 minutes 27.4% while at 90 minutes 26.2% for it; the time used for the study was [20, 90] minutes, see Figure 33 and 34. Water content portion of 12.5% of 25% saturation (12.5% water + 12.5% LNAPL) by mass was sampled using pellets again for this liquid content around 20 minutes for water and for LNAPL, it sampled 17.6% which is above the proportion of LNAPL, 12.5%, at 20 minutes, see Figure 33 and 34. The result is similar with Matula et al. (2012) for water sampling as tried to be discussed under experiment I and II of this study. However, their study does not show proportional sampling time for LNAPL. Additionally, the previous study use the same activated carbon pellet for different time series from the same packed porous materials with a given degree of saturation while this experiment used different pellets for 20, 45, 70 and 90 minutes of time.
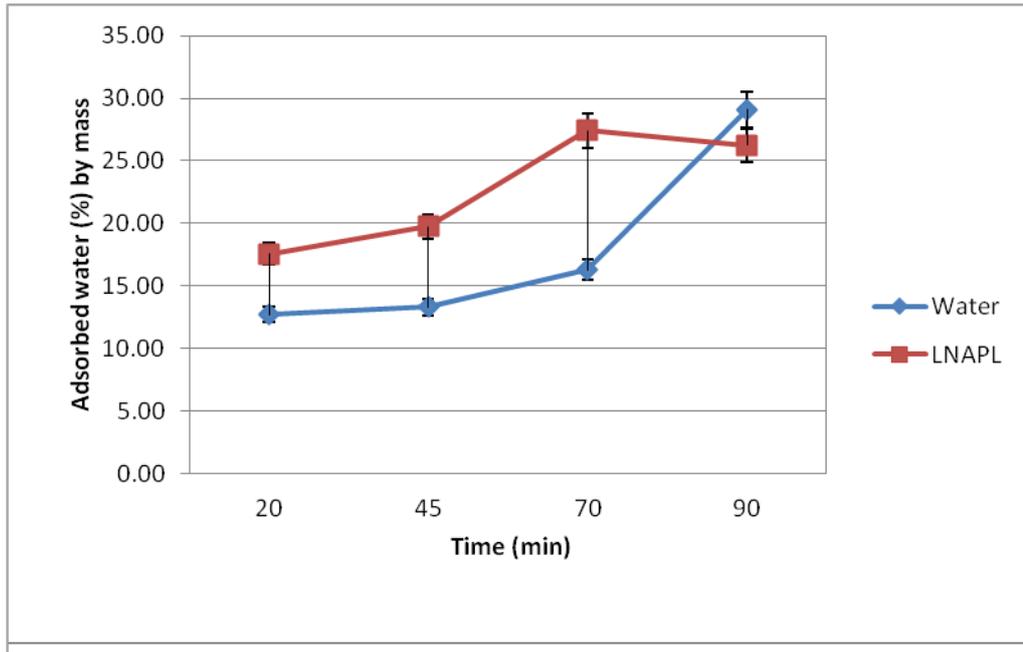
Figure 33 - Graphically demonstrated adsorbed amount of water/LNAPL (%) by mass to activated carbon pellet SC 40 at different times from 25% by mass of liquid content sample column

	20	45	70	90
LNAPL	17.6	19.8	27.4	26.2
Water	12.7	13.3	16.3	29.1
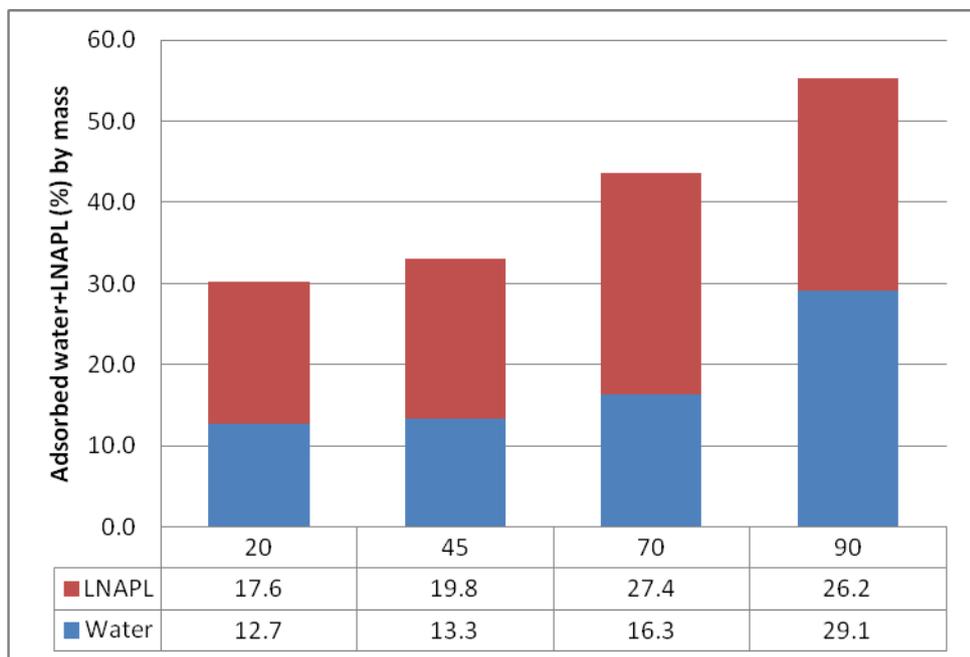
Figure 34 - Graphical and tabular overview of water + LNAPL adsorbed to activated carbon pellets from 25% liquid content of sample column at different times (minute)

7. CONCLUSION AND RECOMMENDATION

7.1.   Conclusion

The experiment was done in laboratory under little variation of temperature and relative humidity. The materials used for the study: silica sand ST 56, tap water, Lubstar Marcol 82 white medicinal grade oil and activated carbon pellet SC 40 were checked for desired properties to carry out the experiment. All the materials used for the previous study (Matula et al., 2012) are suitable for this experiment. Initial water content of the sand was below 1% by mass; however, it was oven-dried for the main experiment. Initial water content of activated carbon pellet SC 40 fell in the recommended range by the company that supply it and it was also oven-dried to remove the water.

Activated carbon pellet SC 40 that has been used following Matula et al. (2008) to sample for water/LNAPL is a suitable method for the study. The followings two are the main outcomes of this study:

The first hypothesis which says that "It is possible to quantify the amount of water and LNAPL proportionally from porous media via adsorption of water/LNAPL to activated carbon has been proven." And it is possible to sample them proportionally.

The second hypothesis which says that "There is no dependence when sampling proportionally on degree of saturation from the porous media." Experiments have shown that the degree of saturation of the porous medium has a great influence on adsorption of both water and LNAPL. Experiment with 5% saturation by mass is the best example where almost no LNAPL was sampled from the porous medium.

7.2.   Recommendation

The way forward is to do more experiments in range where sampling of both water and LNAPL is possible under stable laboratory condition. From Experiment I with 5% liquid content it is clear that it is difficult to sample LNAPL at lower LNAPL content and hence better to do experiments on the porous material with more degree of saturation.

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APPENDIX

Appendix A: Pictures taken during the experiment

Figure 35 - Homogenization of silica sand and water/LNAPL for sand columns
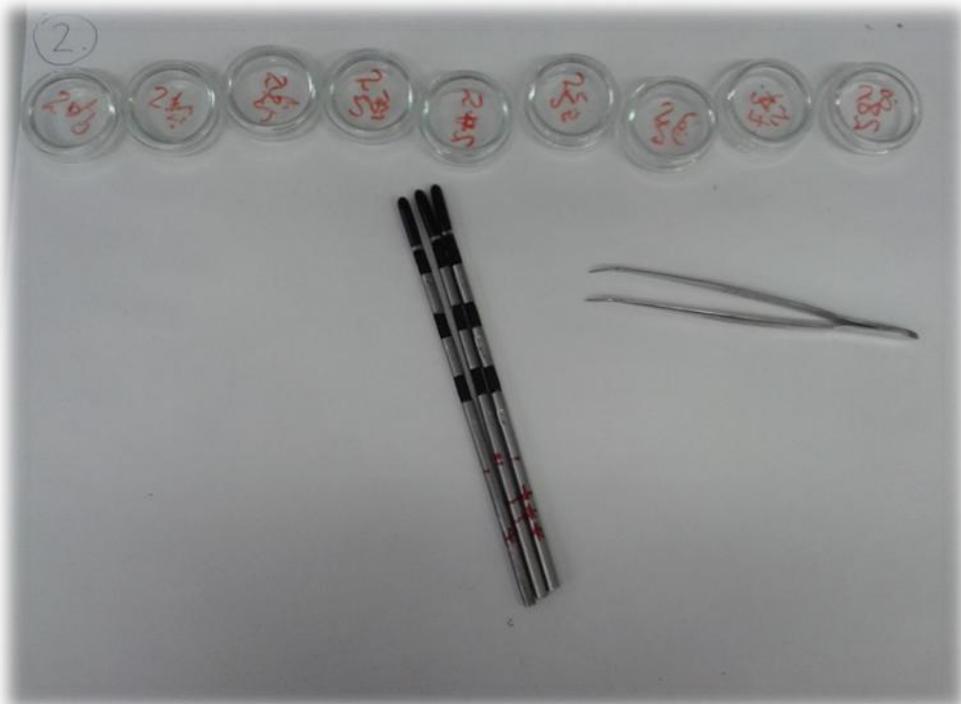
Figure 36 - Stainless steel tubes with inserted activated carbon pellets taken from the petri dishes

Figure 37 - Inserting stainless steel tube with activated carbon pellets into the silica sand column
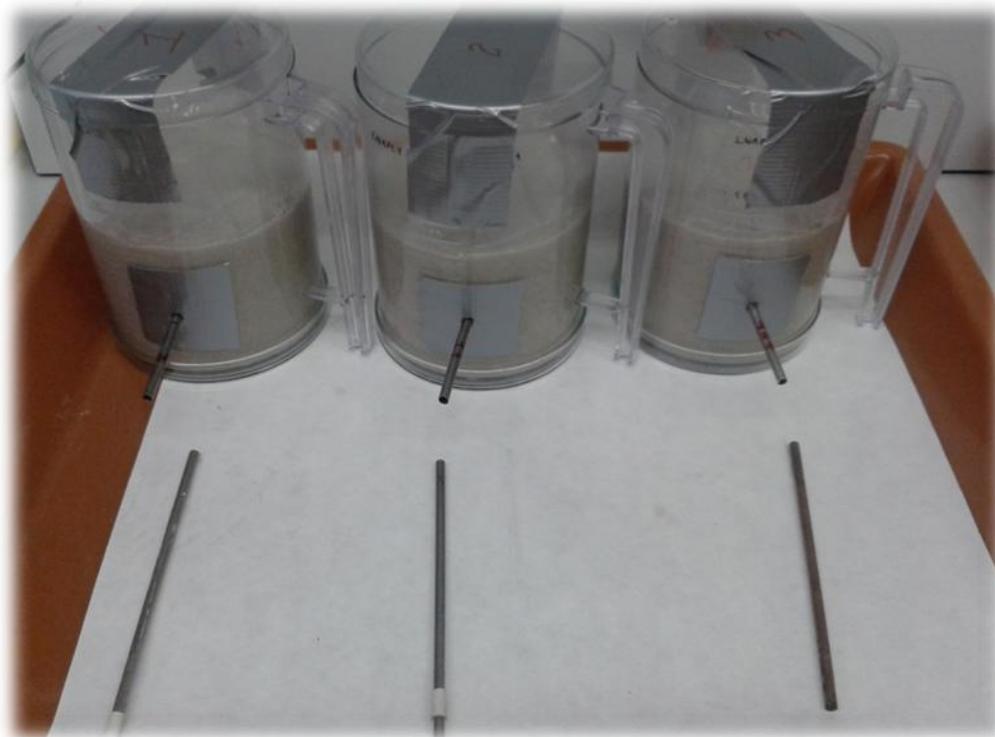

Figure 38 - Adsorption of water/LNAPL into activated carbon pellets

Figure 39 - Taking weight of activated carbon pellets after drying

Appendix B: Measured data for experiments

Mass of petridhish (g)	Mass of petridish and Activated Carbon before first oven dry (G)	Mass of Petridish and Activated Carbon After first oven dry (g)	Mass of Petridish and Activated Carbon after adsorption (g)	Mass of Petridish and Activated Carbon after second oven dry (g)	Mass of Activated Carbon before first oven dry (g)	Mass of Activated Carbon after first oven dry (g)
15.6273	15.7171	15.7165	15.7203	15.7163	0.0898	0.0892
15.3665	15.4642	15.4624	15.4773	15.4670	0.0976	0.0958
16.1064	16.1909	16.1905	16.2089	16.2008	0.0845	0.0842
15.7448	15.8536	15.8499	15.8571	15.8505	0.1088	0.1051
16.1432	16.2465	16.2452	16.2558	16.2507	0.1033	0.1020
15.4577	15.5517	15.5504	15.5802	15.5729	0.0939	0.0926
16.2167	16.3016	16.3009	16.3088	16.3035	0.0849	0.0841
15.2676	15.3804	15.3777	15.3895	15.3775	0.1128	0.1101
15.4422	15.5316	15.5306	15.5458	15.5346	0.0894	0.0884
15.7081	15.8042	15.8027	15.8160	15.8082	0.0961	0.0946
15.9908	16.0696	16.0680	16.0876	16.0674	0.0788	0.0772
16.2975	16.3902	16.3890	16.4155	16.3965	0.0927	0.0915
15.6325	15.7296	15.7283	15.7545	15.7342	0.0971	0.0958
15.1637	15.2446	15.2438	15.2644	15.2467	0.0809	0.0801
15.7403	15.8256	15.8246	15.8575	15.8413	0.0853	0.0843
15.3361	15.4213	15.4206	15.4690	15.4548	0.0852	0.0845
15.0401	15.1599	15.1582	15.2002	15.1758	0.1199	0.1181
15.7100	15.8034	15.8018	15.8226	15.8025	0.0934	0.0918
15.9426	16.0306	16.0299	16.0564	16.0372	0.0881	0.0874
15.6504	15.7416	15.7405	15.7697	15.7507	0.0913	0.0901
16.1348	16.1982	16.1976	16.2189	16.2000	0.0634	0.0629
15.5838	15.6642	15.6633	15.7200	15.6994	0.0804	0.0796
16.0024	16.0795	16.0781	16.1155	16.0920	0.0770	0.0757
15.9634	16.0286	16.0281	16.0491	16.0289	0.0652	0.0647
15.9329	16.0251	16.0231	16.0573	16.0308	0.0922	0.0902
16.0097	16.0931	16.0916	16.1284	16.1037	0.0834	0.0818
15.8444	15.9491	15.9470	15.9837	15.9543	0.1047	0.1025
16.3378	16.4426	16.4398	16.4973	16.4754	0.1048	0.1020
15.7686	15.8772	15.8738	15.9147	15.8893	0.1086	0.1052
15.9531	16.0397	16.0381	16.0761	16.0526	0.0866	0.0850
15.1646	15.2561	15.2557	15.2859	15.2564	0.0915	0.0911
15.8432	15.9227	15.9224	15.9702	15.9503	0.0795	0.0792
15.8765	15.9526	15.9524	16.0134	15.9959	0.0760	0.0759

15.8188	15.8933	15.8930	15.9242	15.8943	0.0745	0.0742
15.6866	15.7733	15.7723	15.8283	15.8093	0.0867	0.0857
15.3985	15.4820	15.4816	15.5350	15.5134	0.0835	0.0830
15.1740	15.2604	15.2592	15.2901	15.2593	0.0864	0.0852
15.9302	16.0138	16.0128	16.0446	16.0126	0.0835	0.0826
16.4045	16.4967	16.4960	16.5292	16.4958	0.0923	0.0915
15.6997	15.7834	15.7828	15.8245	15.7986	0.0838	0.0832

Mass of petridhish (g)	Mass of petridish and Activated Carbon before first oven dry (G)	Mass of Petridish and Activated Carbon After first oven dry (g)	Mass of Petridish and Activated Carbon after adsorption (g)	Mass of Petridish and Activated Carbon after second oven dry (g)	Mass of Activated Carbon before first oven dry (g)	Mass of Activated Carbon after first oven dry (g)
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16.1064	16.1909	16.1905	16.2089	16.2008	0.0845	0.0842
15.7448	15.8536	15.8499	15.8571	15.8505	0.1088	0.1051
16.1432	16.2465	16.2452	16.2558	16.2507	0.1033	0.1020
15.4577	15.5517	15.5504	15.5802	15.5729	0.0939	0.0926
16.2167	16.3016	16.3009	16.3088	16.3035	0.0849	0.0841
15.2676	15.3804	15.3777	15.3895	15.3775	0.1128	0.1101
15.4422	15.5316	15.5306	15.5458	15.5346	0.0894	0.0884
15.7081	15.8042	15.8027	15.8160	15.8082	0.0961	0.0946
15.9908	16.0696	16.0680	16.0876	16.0674	0.0788	0.0772
16.2975	16.3902	16.3890	16.4155	16.3965	0.0927	0.0915
15.6325	15.7296	15.7283	15.7545	15.7342	0.0971	0.0958
15.1637	15.2446	15.2438	15.2644	15.2467	0.0809	0.0801
15.7403	15.8256	15.8246	15.8575	15.8413	0.0853	0.0843
15.3361	15.4213	15.4206	15.4690	15.4548	0.0852	0.0845
15.0401	15.1599	15.1582	15.2002	15.1758	0.1199	0.1181
15.7100	15.8034	15.8018	15.8226	15.8025	0.0934	0.0918
15.9426	16.0306	16.0299	16.0564	16.0372	0.0881	0.0874
15.6504	15.7416	15.7405	15.7697	15.7507	0.0913	0.0901
16.1348	16.1982	16.1976	16.2189	16.2000	0.0634	0.0629
15.5838	15.6642	15.6633	15.7200	15.6994	0.0804	0.0796
16.0024	16.0795	16.0781	16.1155	16.0920	0.0770	0.0757
15.9634	16.0286	16.0281	16.0491	16.0289	0.0652	0.0647
15.9329	16.0251	16.0231	16.0573	16.0308	0.0922	0.0902
16.0097	16.0931	16.0916	16.1284	16.1037	0.0834	0.0818
15.8444	15.9491	15.9470	15.9837	15.9543	0.1047	0.1025
16.3378	16.4426	16.4398	16.4973	16.4754	0.1048	0.1020
15.7686	15.8772	15.8738	15.9147	15.8893	0.1086	0.1052
15.9531	16.0397	16.0381	16.0761	16.0526	0.0866	0.0850
15.1646	15.2561	15.2557	15.2859	15.2564	0.0915	0.0911
15.8432	15.9227	15.9224	15.9702	15.9503	0.0795	0.0792
15.8765	15.9526	15.9524	16.0134	15.9959	0.0760	0.0759
15.8188	15.8933	15.8930	15.9242	15.8943	0.0745	0.0742
15.6866	15.7733	15.7723	15.8283	15.8093	0.0867	0.0857
15.3985	15.4820	15.4816	15.5350	15.5134	0.0835	0.0830
15.1740	15.2604	15.2592	15.2901	15.2593	0.0864	0.0852
15.9302	16.0138	16.0128	16.0446	16.0126	0.0835	0.0826
16.4045	16.4967	16.4960	16.5292	16.4958	0.0923	0.0915
15.6997	15.7834	15.7828	15.8245	15.7986	0.0838	0.0832

Mass of petridish (g)	Mass of petridish and Activated Carbon before first oven dry (G)	Mass of Petridish and Activated Carbon After first over dry (g)	Mass of Petridish and Activated Carbon after adsorption (g)	Mass of Petridish and Activated Carbon after second oven dry (g)	Mass of Activated Carbon before first oven dry (g)	Mass of Activated Carbon after first oven dry (g)
15.0128	16.0167	16.0132	16.0390	16.0260	1.004	1.000
-	-	-	-	-	-	-
15.0788	15.1772	15.1848	15.2415	15.2033	0.098	0.106
15.5294	15.6321	15.6300	15.6768	15.6629	0.103	0.101
15.0026	15.3978	15.3970	15.4420	15.4389	0.395	0.394
15.6877	15.7908	15.7893	15.8192	15.8058	0.103	0.102
15.7009	15.7985	15.7970	15.8390	15.8278	0.098	0.096
15.0407	15.9310	15.9299	15.9806	15.9662	0.890	0.889
15.5771	15.6754	15.6747	15.7179	15.7008	0.098	0.098
-	-	-	-	-	-	-
15.3994	15.4801	15.4796	15.4951	15.4795	0.081	0.080
15.3092	15.4018	15.4010	15.4265	15.4097	0.093	0.092
16.1336	16.2492	16.2441	16.2699	16.2482	0.116	0.110
16.2564	16.3629	16.3613	16.3814	16.3618	0.107	0.105
15.4490	15.5492	15.5465	15.5824	15.5624	0.100	0.098
15.4211	15.5211	15.5190	15.5449	15.5202	0.100	0.098
15.2804	15.3898	15.3863	15.4088	15.3883	0.109	0.106
15.7476	15.8311	15.8305	15.8936	15.8812	0.083	0.083
15.7501	15.8551	15.8541	15.9092	15.8875	0.105	0.104
15.6385	15.7378	15.7358	15.7680	15.7488	0.099	0.097
15.5083	15.5920	15.5909	15.6145	15.5914	0.084	0.083
15.8608	15.9526	15.9517	16.0037	15.9815	0.092	0.091
16.1043	16.2065	16.2010	16.2417	16.2138	0.102	0.097
15.3593	15.4494	15.4484	15.4788	15.4495	0.090	0.089
16.2771	16.3616	16.3606	16.4040	16.3772	0.084	0.084
15.2377	15.3283	15.3275	15.3657	15.3426	0.091	0.090
15.5224	15.6287	15.6259	15.6568	15.6329	0.106	0.104
15.9154	16.0266	16.0237	16.0783	16.0473	0.111	0.108
15.8291	15.9283	15.9266	15.9806	15.9571	0.099	0.098
15.7349	15.8304	15.8285	15.8693	15.8437	0.096	0.094
15.1854	15.2719	15.2711	15.3045	15.2716	0.087	0.086
15.3477	15.4518	15.4480	15.4941	15.4643	0.104	0.100
15.5571	15.6436	15.6429	15.7063	15.6921	0.086	0.086
15.4857	15.5953	15.5937	15.6447	15.6145	0.110	0.108
15.7368	15.8288	15.8277	15.8756	15.8468	0.092	0.091
15.3179	15.4004	15.3996	15.4676	15.4512	0.082	0.082
15.6311	15.7407	15.7390	15.7762	15.7422	0.110	0.108
15.9421	16.0539	16.0513	16.1125	16.0925	0.112	0.109
15.7326	15.8213	15.8203	15.8866	15.8679	0.089	0.088
15.5485	15.6453	15.6437	15.6965	15.6715	0.097	0.095