CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Agrobiology, Food and Natural Resources

Department of Water Resources

Experimental Observation of Soil Porous Material Contamination during Multi-Phase Liquid Flow

Ph.D. Thesis

Ph.D. Student: Ing. Ayele Teressa Chala

Supervisor: Prof. Dr. Svatopluk Matula

Co-supervisor: Dr. František Doležal

Declaration

I declare that I have worked my dissertation on "*Experimental Observation of Soil Porous Material Contamination during Multi-Phase Liquid Flow"* independently and that I have used only the sources I quote and list in the References.

In Prague 2018 Signature _______________

Acknowledgement

First and foremost, I would like to thank my supervisor Prof. Dr. Svatopluk Matula for his guidance and support throughout my study. Thank you! I would also like to thank my co-supervisor the late Dr. František Doležal for his support. I am grateful to other stuff members of Department of Water Resources at FAPAZ of CZU who have supported me along the way. I am also grateful to my mother, brothers and sisters who have provided me through moral and emotional support in my life. Special thanks to my wife Mrs. Mestu Desalegn for her support and encouragement. Many thanks to my friend Dr. Chris Ash for the language correction of the dissertation.

Finally, I would like to thank Faculty of Agro-Biolgy Food and Natural Resources of Czech University of life Sciences Prague for giving me the opportunity to study PhD at the faculty.

Thank you!

Abstract

Subsurface contamination by Light Non-Aqueous Phase Liquid (LNAPL) and its remediation involves multi-component multi-phase liquid flow. Proper characterization and remediation of the contaminated sites require comprehensive understating of the behavior of LNAPLs in natural porous media. The aims of this work are to evaluate different methods for the quantification of porous media with respect to LNAPL and to evaluate the impact of different liquids and injection rates on the decontamination of the porous media and oil recovery. For these purposes there were two sets of experiments done on uniformly packed silica sand sample columns. In one set of the experiments, sample columns were subjected to different water to LNAPL ratios and in the other, sample columns were saturated with LNAPL only. Water and/or LNAPL were sampled using Activated Carbon Pellet (ACP), determined through gravimetric analysis method and water content was measured using soil moisture sensors. In the other set, LNAPL was displaced from the sample columns with water, ethanol and hexane at 200 ml/h and with water at 100, 400 and 800 ml/h flooding rates. The results show that ACP could sample water and LNAPL proportionally but with higher variance, though more liquid was sampled from sample columns subjected to only one liquid. It also shows that more water and LNAPL could be sampled from sample columns subjected to lower water to LNAPL ratios. On the other hand, results from soil moisture sensors and gravimetric analysis method were similar for higher applied water to LNAPL ratios. However, decreasing the ratio by increasing the amount of LNAPL affected water content from both methods. It affected gravimetric water content by increasing the oven dry solid mass and subsequently resulted in lower water content estimation. It resulted in over estimation of water content from soil moisture sensors through the modification of the bulk relative permittivity of the sample column, which in turn was used successfully in estimating LNAPL content using the dielectric mixing model. Results from the second set of experiments show that it could be possible to recover statistically significant amount of oil using hexane compared to water and ethanol. Results from water injection rates show that the amount of LNAPL recovered up to water breakthrough were statistically a significantly different even though the overall recovered oil were not statistically significant from each other. At the end of the experiment, it can be possible to recover 91%, 61% and 61% using hexane, ethanol and water at 200 ml/h, and 59, 61 and 63% using water at 100, 400 and 800 ml/h flooding rates respectively.

Table of Contents

List of Tables

List of Figures

List of Appendices

List of Symbols and Abbreviations

Abbreviations

AC	Activated carbon
ACP	Activated carbon pellet
ACPB	Activated carbon pellet from Brenntag, Ltd.
ACPT	Activated carbon pellet from Techpoint s.r.o.
ASTM	American Society for Testing Material
AWWA	American Water Works Association
BTEX	Benzene, toluene, ethylbenzene and xylenes
CFCs	chlorofluorocarbons
C-H	Carbon hydrogen bond
DNAPL	Dense non-aqueous phase liquid
EEA	European Environmental Agency
FFE	Fractional flow equation
GAC	Granular activated carbon
GC	Gas chromatography

GC-MS	Gas chromatography-Mass spectroscopy
HC	Hydrocarbons
HEM	Hexane extractable material
IA	Immunoassay
ITRC	Interstate Technology & Regulatory Council
IUPAC	International Union for Pure and Applied Chemistry
LNAPL	Light non-aqueous phase liquid
Marcol 82	Commercial name for medicinal grade white mineral oil used in this study
MTBE	Methyl tertiary butyl ether
NAPL	Non-aqueous phase liquid
NSZ	Natural source zone
PAC	Powdered activated carbon
PAH	polycyclic aromatic hydrocarbon
PHC	Petroleum Hydrocarbons
RS	Raman Spectroscopy
RTI	Research Triangle Institute
SC40	Commercial nam for activated carbon pellet used in this study
SPME	solid-phase microextraction
ST56	Commercial name for silica sand used in this study
TPH	Total petroleum hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Working Group
US EPA	United States Environmental protection Agency
UST	Underground storage tanks
VHC	Volatile hydrocarbon

Nomenclature

Symbol	Description	Dimension	SI Unit
A	Area	$[L^2]$	m^2
AOD	Mass of the sample after oven dry	[M]	kg
BOD	Mass of the sample before oven dry	[M]	kg
c	Concentration of the fluid (volumetric fraction)	$[L^3L^{-3}]$	m^3m^{-3}
C	Solute concentration	$[NL^{-3}]$	$Jkg^{-1}K^{-1}$
c_i	Initial concentration (volumetric fraction) of injected liquid	$[L^3L^{-3}]$	m^3m^{-3}
D	Diffusion-dispersion coefficient	[-]	-
EC	Electrical conductivity	$[L^{-3}M^{-1}T^3I^2]$	Sm^{-1}
E_D	Fluid displacement efficiency	$[L^3L^{-3}]$	m^3m^{-3}
E_R	Total oil recovery efficiency	$[L^3L^{-3}]$	m^3m^{-3}
F_{ax}	Advective flux of solute mass	$[MT^{-1}L^{-2}]$	$Kgs^{-1}m^{-2}$
f_o	fraction of oil flow	$[L^3TL^{-3}T^{-1}]$	$m^3sm^{-3}s^{-1}$
f_w	fraction of water flow (water cut)	$[L^3TL^{-3}T^{-1}]$	$m^3sm^{-3}s^{-1}$
g	Acceleration of gravity/gravity constant	$[LT^{-2}]$	ms^{-2}
h	Hydraulic/total head	[L]	m
i	intermediate wetting phase	[-]	-
k	Permeability	$[L^2]$	m^2
K	Saturated hydraulic conductivity	$[LT^{-1}]$	ms^{-1}
K_h	Henry's law constant	$[MT^2L^2N^{-1}]$	Pam^3mol^{-1}
K_i	Intrinsic permeability	$[L^2]$	m^2
K_o	Oil permeability	$[L^2]$	m^2
K_{ro}	Oil relative permeability	$[L^2L^{-2}]$	-
K_{rw}	Water relative permeability	$[L^2L^{-2}]$	-
K_w	Water permeability	$[L^2]$	m^2
L	Distance between two points	[L]	m
M	Mobility ratio	$[L^3T^2L^{-3}T^{-2}]$	-
m_i	Mass of injected liquid	[M]	kg
m_o	Mass of oil/LNAPL	[M]	kg

m_s	Oven-dry soil mass	[M]	kg
m_w	Mass of water	[M]	kg
n	non-wetting phase	-	-
N_c	Capillary number	$[T^2MLT^{-2}M^{-1}L^{-1}]$	-
n_e	Effective porosity	$[L^3L^{-3}]$	m^3m^{-3}
o	Oil or LNAPL	[-]	-
P	Pressure	$[MT^2L^{-1}]$	Pa
P_c	Capillary pressure	$[MT^2L^{-1}]$	Pa
P_{ciw}	P_c between intermediate and wetting phases	$[MT^2L^{-1}]$	Pa
P_{cni}	P_c between non-wetting and intermediate wetting phases	$[MT^2L^{-1}]$	Pa
P_{cnw}	P_c between non-wetting and wetting phases	$[MT^2L^{-1}]$	Pa
P_n	Non-wetting phase pressure	$[MT^2L^{-1}]$	Pa
P_{Nv}	Number of pore volume	$[L^3L^{-3}]$	-
P_o	Oil/LNAPL pressure	$[MT^2L^{-1}]$	Pa
P_v	Pore volume	$[L^3]$	m^3
P_w	Water/wetting phase pressure	$[MT^2L^{-1}]$	Pa
q	Specific discharge	$[L^3T^{-1}L^{-2}]$	ms^{-1}
Q	Discharge	$[L^3T^{-1}]$	m^3s^{-1}
q_i	Injection flow rate	$[L^3T^{-1}]$	m^3s^{-1}
q_o	Oil flow rate	$[L^3T^{-1}]$	m^3s^{-1}
q_p	Production flow rate	$[L^3T^{-1}]$	m^3s^{-1}
q_t	Total flow rate	$[L^3T^{-1}]$	m^3s^{-1}
q_w	Water flow rate	$[L^3T^{-1}]$	m^3s^{-1}
S	Degree of saturation	$[L^3L^{-3}]$	m^3m^{-3}
S_i	Intermediate wetting phase degree of saturation	$[L^3L^{-3}]$	m^3m^{-3}
S_n	Non-wetting phase degree of saturation	$[L^3L^{-3}]$	m^3m^{-3}
S_{oi}	Initial oil saturation	$[L^3L^{-3}]$	m^3m^{-3}
S_{or}	Residual oil saturation	$[L^3L^{-3}]$	m^3m^{-3}
S_w	Water/wetting phase degree of saturation	$[L^3L^{-3}]$	m^3m^{-3}
t	time	[T]	s

t_{bt}	Injected liquid breakthrough time	[T]	s
T_{soil}	Temperature of the soil	[Θ]	K
u	Darcy's velocity	[LT^{-1}]	ms^{-1}
v	Average linear velocity	[LT^{-1}]	ms^{-1}
V_i	Volume of injected liquid	[L^3]	m^3
V_o	Volume ov oil/LNAPL	[L^3]	m^3
V_p	Total volume of soil pore space	[L^3]	m^3
V_r	Total volume of recovered liquid	[L^3]	m^3
Vs	Bulk volume of the sample	[L^3]	m^3
V_t	Total volume	[L^3]	m^3
V_w	Volume of water	[L^3]	m^3
w	Gravimetric water/LNAPL content	[M]	kg
w	wetting phase or water	[-]	-
w_c	Cumulative volume of water injected	[$L^3T^{-1}T$]	m^3
x	Distance along direction of movement	[L]	m
z	Elevation head	[L]	m
α	angle made by the direction of flow with the horizontal	-	^{o}
α	An empirical parameter accounting for soil geometry	[-]	-
α	Different phases (*w,i,n* etc.)	[-]	-
γ	Oil-water interfacial tension	[MT^{-2}]	kgs^{-2}
σ_b	Bulk electrical conductivity of the porous media	[$L^{-3}M^{-1}T^3I^2$]	Sm^{-1}
σ_p	Pore water electrical conductivity	[$L^{-3}M^{-1}T^3I^2$]	Sm^{-1}
ε_a	Apparent relative permittivity	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	-
ε_{ab}	ε_b when bulk electrical conductivity is 0	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	-
εb	Real portion of the relative permittivity	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	-
ε_{air}	Relative permittivity of air	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	-
εo	Relative permittivity of oil/LNAPL	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	-
ε_p	Real portion of relative permittivity	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	-
ε_{raw}	unprocessed raw value of relative permittivity	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	
ε_s	Relative permittivity of soil/solid particles	[$ML^3T^4I^2ML^{-3}T^{-4}I^{-2}$]	-

ε_w	Relative permittivity of water	$[ML^{3}T^{4}I^{2}ML^{-3}T^{-4}I^{-2}]$	-
θ	Contact angle	[-]	^{o}
$\theta_{LNAP}L$	Volumetric LNNAPL/oil content	$[L^{3}L^{-3}]$	$m^{3}m^{-3}$
θ_w	Volumetric water content	$[L^{3}L^{-3}]$	$m^{3}m^{-3}$
λ	Fluid mobility	$[L^{3}MTL^{-3}M^{-1}T^{-1}]$	-
μ	Dynamic viscosity	$[ML^{-1}T^{-1}]$	$kgm^{-1}s^{-1}$
μ_o	Viscosity of oil	$[ML^{-1}T^{-1}]$	$kgm^{-1}s^{-1}$
μ_w	Viscosity of water	$[ML^{-1}T^{-1}]$	$kgm^{-1}s^{-1}$
ρ_b	Soil/sample column bulk density	$[ML^{-3}]$	kgm^{-3}
ρ_d	Soil/sample particle density	$[ML^{-3}]$	kgm^{-3}
ρ_i	Density of injected liduid	$[ML^{-3}]$	kgm^{-3}
ρ_{LNAPL}	Density of LNAPL/oil	$[ML^{-3}]$	kgm^{-3}
ρ_o	Density of oil/LNAPL	$[ML^{-3}]$	kgm^{-3}
ρ_w	Density of water	$[ML^{-3}]$	kgm^{-3}
$\emptyset$	Porosity of the sample	$[L^{3}L^{-3}]$	$m^{3}m^{-3}$

1. Introduction

Environmental pollution by both naturally occurring and man-made chemicals is a major concern on the global scale. Human activities worsen the condition through the production and utilization of a wide range of chemicals. One of these chemicals which is commonly used by humans in day-to-day activities is petroleum hydrocarbons (PHC). Speight (2015) indicates that 50% of today's energy source for human activity is from PHC. This extensive use needs a bulk production, transportation and storage of PHC. Speight (2014) states that it is almost impossible to carry out these activities without spills and losses. The author further specified that it is the soil, which is important for maintaining the ecological equilibrium, that suffers the most ecological damage.

Porous media can both store and transmit fluids with different phases. Pinder & Gray (2008) describe a phase as a solid, liquid or gas that is separated from another liquid, solid, or gas by an identifiable boundary. Fanchi & Seidle (2017) mentioned that the flow of non-wetting phase and wetting phase liquids through the porous media is one of the best examples of multiphase liquid flow. Contamination of vadose zone and ground water by non-aqueous phase liquids, here after NAPL, according to Schroth, et al. (1995) is a widespread problem, and there is a significant portion of contaminated groundwater and soil worldwide. Mayer, et al. (2005) and Interstate Technology & Regulatory Council, ITRC (2009a) among others described that NAPL is immiscible with water and forms a visible and separate oily phase. NAPLs could have densities that are lighter than water (light, LNAPLs), denser than water (dense, DNAPLs) or mixtures with a combined density close to that of water (neutral, NNAPLs) (Fetter, et al., 2018).

NAPLs contaminate soils in the vadose zone during their course to the saturated zone and groundwater depending on the amount of their release. Their migration at the macro scale is influenced mainly by capillary forces, viscous forces and gravity (Mayer, et al., 2005). Hence, multiphase fluids flow in natural porous media is the interest of many fields; and hydrology, contaminant clean-up and petroleum engineering are some of them (Arnold & Nishigak, 1999). Despite its wide applications, the study of the flow and transport through porous media is limited to macroscopic data regarding the inlet and outlet of the domain as the porous media itself is not transparent (Coutelieris & Delgado, 2012). The complexity of the porous media at local scale (heterogeneity) in addition to the more complex nature of multiphase and multicomponent flow through the porous media makes the study to be at macro scale. Because the data (result) at micro scale cannot represent the actual processes at field or macro scale, and the minimum sample used should represent the figure of the area. For example, Coutelieris and Delgado (2012) illustrated that the presence of a very thin (capillary) throat in porous media at the local level leads to extremely high velocity and Reynolds number at that location even with very low volumetric flow rate at macro scale.

The multicomponent multiphase flow and other processes occurring in the porous media pose serious problems in the context of soil and water contamination control. The occurrence and movement of contaminants in the environment are influenced by physical, chemical and biological entities they interact with (Selim, 2015). There are interactions between LNAPLs and water, and these multiphase liquids and porous media. They can be observed and recorded, using various physical procedures through indirect, non-destructive and continuous methods and are supported by chemical analyses. The hydraulic properties of a homogeneous porous media with respect to LNAPL can be quantified with sufficient adequacy with the help of laboratory column experiments.

For this study there will be two sets of experiments. For both sets of experiments silica sand will be repacked layer by layer to form uniform sample columns. In the first set of experiments, sample columns will be subjected to different water to LNAPL ratios, while in the second set of experiments, sample columns will be subjected to LNAPL only. To be consistent, one pore volume plus of the mentioned liquid(s) will be applied to the sample columns, and drained-out liquids will be collected and analyzed. After gravity drainage and redistribution, sample columns in the first set of experiments will be evaluated for their water and/or LNAPL content. First, the liquids will be sampled using Activated Carbon Pellet (ACP) and then water content will be measured using soil moisture sensors and volumetric oil content will be estimated using the Dielectric Mixing Model (DMM). Finally, water and LNAPL contents of the sample columns will be determined through gravimetric analysis method from destructed samples from sample columns. In the second set of the experiments, LNAPL will be displaced from the sample columns with water, ethanol and hexane at 200 ml/h flooding rates. Additionally, LNAPL will be displaced from sample columns using water at 100, 400 and 800 ml/h injection rates. Displaced liquid will be collected successively and the amount of recovered oil in each collected sample and the total amount of oil and liquids displaced will be analyzed.

The aim of this work is:

- to evaluate different methods for the quantification of porous media contaminated with LNAPL during multicomponent multiphase flow, through the experimentation using sample columns made from uniformly packed silica sand subjected to different water to LNAPL ratios
- to evaluate LNAPL recovery efficiency from uniformly packed sample columns and saturated with oil through water, ethanol and hexane flooding
- To assess the impact of water injection rates on the displacement of LNAPL from uniformly packed sand sample columns

2. Literature Review

The problem in general has been treated by several textbooks, journal publications and monographs, e.g., Schwille (1984; 1988); Domenico & Schwartz (1998); Mercer & Cohen (1990); Pankow & Cherry (1996) and Mayer, et al. (2005). Because of the importance and usage of different crude oil products, of which 50% to 98% is petroleum hydrocarbon (Speight, 2014), there are extensive literature on the exploration, recovery, transportation and storage of crude oil and its refined products, e.g., Goodger (1975); Jahn, et al. (2008), Speight (2011b); Dembicki (2017) are some of the handful of literature. Transportation, storage and usage of the products are not immune from the loss to the environment in one way or another (Speight, 2014) and there are also a handful of literature on the spills and leakage (release) of the products to subsurface e.g., MacDonald (1998); Winegardner & Testa (2000); Etkin (2001); Kvenvolden & Cooper (2003); Illangasekare, et al. (2005); National Research Council (2005); Schmidt-Etkin, (2011). Released oils/NAPLs flow downward under the force of gravity (Cheremisinoff, 2017) and the migration and distribution in subsurface media is a function of many factors, e.g. amount, type and mode of oil released, NAPL interaction with other fluids and porous media (Illangasekare, et al., 2005; Suthersan, et al., 2017). Behavior of NAPL in porous media is discussed by many authors e.g., by van Dijk, et al. (1995); Mukhopadhyay and Cushman (1998); Chao, et al. (2000); van Dijke and Sorbie (2002); Tavassoli, et al. (2005); Boyer, et al. (2010) and Agaoglu, et al. (2015) . Detection of the contaminants, and sampling and analysis of the contaminated samples for NAPLs are also discussed in much literature (Cohen, et al., 1992; Nadim, et al., 2000; Griffin & Watson, 2002; Speight, 2005; Keer, et al., 2008). Even though complete removal of NAPLs from contaminated media is not possible (Soga, et al., 2004), there are a handful of methods to clean up media contaminated with NAPLs (Hunt, et al., 1988; Riser-Roberts, 1998; Mulligan, et al., 2001; Henry & Warner, 2002; Khan, et al., 2004; Kovalick, 2008; Caliman, et al., 2011). The following sub-sections of this chapter focuses on the literature of the subject area in detail.

2.1. Theoretical background

Fluid flow through the media: be it structured, fractured or porous, is derived by the force or pressure gradient. Flow through the porous media is the most complex of the three due to the number of factors and their interplay to determine the flow of a fluid through the solid matrix.

Mayer, et al. (2005) among others listed the forces as pressure, gravitational, viscous, and inertial forces. For the flow where the flow rate through porous media is very slow and within Darcy's flow regime, the viscous force dominates over inertial forces (Kaviany, 2001). For practical purposes, inertial forces can be neglected for flow in the porous media (Mayer, et al., 2005). Flow of a fluid through soil and other porous media is generally best described by Darcy's Law (Wu, 2016). This empirical equation as stated by Hassanizadeh (2015) was designed for 1D steady-state flow of incompressible water in saturated homogeneous isotropic rigid sandy soil under constant temperature. Darcy's Law for a single-phase flow through fully saturated porous media is governed by pressure gradient and gravitational forces (Illangasekare & Frippiat, 2013) and is described as follows:

$$q = -\frac{k_i}{\mu}.(\nabla P - \rho g) \qquad [1]$$

Where: q is the specific discharge (L/T), k_i is the intrinsic/absolute permeability tensor (L^2), μ is the dynamic viscosity (M/LT), ∇P is change in fluid phase pressure (MT^2/L), ρ is the fluid mass density (M/L^3), g is the gravity vector (L/T^2)

However, over the course of time, the equation has been used for the single-phase flow of liquid other than water through porous media and water flow under different scenarios. The equation has been used to describe: 3D flow of water, which is much more complex than 1D flow, flow of water with any amount of dissolved/soluble matter, under non-isothermal condition, in heterogeneous anisotropic deformable porous media, unsteady flow of two or more compressible fluids (Hassanizadeh, 2015). The total/hydraulic head (h), Eq. [2] of the fluid in the porous media is the sum of the pressure head and the elevation head from the reference level. Fetter (2000) and Illangasekare & Frippiat (2013), among others, pointed out that kinetic energy head is not included as the flow of the liquid (water) in the subsurface porous media is very slow.

$$h = \frac{P}{\rho g} + z \qquad [2]$$

$$q = -k_i \frac{\rho g}{\mu} \nabla h = -K \nabla h \qquad [3]$$

Where: z is elevation head/the depth from a reference level (L), $K = k_i(\frac{\rho g}{\mu})$, (L/T) is saturated hydraulic conductivity; this shows that specific discharge is proportional to head loss and thus valid for laminar flow (Illangasekare & Frippiat, 2013). Darcy's Law has been extended to multiphase systems, Eq. [4] (Mayer, et al., 2005) based on the following assumptions:

- ✓ The driving force for a phase α determined by the gradient in the phase pressure and the gravitational force
- ✓ The relative permeability of the phase, $k_{r\alpha}$, is the function of saturation phases involved

$$q_\alpha = -\frac{k_{r\alpha}k}{\mu_\alpha}(\nabla P_\alpha + \rho_\alpha g \nabla z) \qquad \alpha = w, n \tag{4}$$

Where: subscript *α (= w, n)* refers to fluid phase under consideration, *w* for wetting phase and *n* for non-wetting phase, $k_\alpha = k_{r\alpha}$ k; k_α is effective permeability, $k_{r\alpha}$ is relative permeability and k is absolute permeability of the phase.

The new element which differs in Eq. [4][4] from Eq. [3] is the addition of the relative permeability $k_{r\alpha}$ (-), which scales the saturated intrinsic permeability k_i. Hassanizadeh (2015) explains that it is added for the consideration of the influence on the flow of one phase due to the presence of the other phases. The equation was derived on the assumption of the sole dependence of relative permeability of the porous media on the saturation. Saturation, on the other hand is governed by the law of conservation of mass Eq. [5] (Mayer, et al., 2005). The law of conservation of mass for incompressible fluid works for the conservation of the volume as the density of the fluid is constant, Eq. [6] (Hassanizadeh, 2015).

$$\emptyset\frac{\partial \rho_\alpha S_\alpha}{\partial t} + \nabla \rho_\alpha q_\alpha = 0 \tag{5}$$

$$\emptyset\frac{\partial S_\alpha}{\partial t} + \nabla q_\alpha = 0 \tag{6}$$

Where: $\emptyset$ is porosity of the porous media (-), S_α is the fluid phase saturation (-)

For the two-phase fluid flow in the porous media, one more equation is required to use with Eq. [4] and Eq. [5] or Eq. [6] depending on the compressibility. The supplemental equation for this purpose is capillary pressure (P_c) equation, which is the pressure difference between the non-wetting and wetting phase, Eq. [7] (Hassanizadeh, 2015). Capillary pressure depends on the contact angle of the wetting phase (θ), and proportional to the interfacial tension (γ) between the non-wetting and wetting phase. However, its relationship with the effective radius, *r*, is inverse (see Eq. [7]).

$$P_c(S_w) = P_n - P_w \quad [7]$$

If the flow consists of more fluid phases than two, Eq. [4] & Eq. [7] with Eq. [5] or Eq. [6] are repeated and used depending on the compressibility of the fluid for each additional phase by assuming as if there is no extra forces active, regardless of the number of phases that filled the pore (Hassanizadeh, 2015). However, Mayer, et al. (2005) derived a partial differential equation (PDE), Eq. [8] by substituting Eq. [4] in to Eq. [5] for incompressible porous media skeleton. Eq. [4] can be also substituted in Eq. [6] for incompressible fluids and gives Eq. [9] (Hassanizadeh, 2015).

$$\emptyset \frac{\partial \rho S_\alpha}{\partial t} = \nabla[\rho_\alpha \frac{k_{r\alpha}\, k_i}{\mu_\alpha} (\nabla P_\alpha + \rho_\alpha g \nabla z)] \quad [8]$$

$$\emptyset \frac{\partial S_\alpha}{\partial t} = \nabla[\frac{k_{r\alpha}\, k_i}{\mu_\alpha} (\nabla P_\alpha + \rho_\alpha g \nabla z)] \quad [9]$$

Eq. [8] is the more general form of PDE for multiphase fluids flow through porous media consisting of more than three fluid phases. By using this equation, it is possible to develop PDE for three phases and PDE can be coupled as the relative permeability and capillary pressure are the function of saturation (Mayer, et al., 2005). Assume that the basic fluid characteristics (density and viscosity) and porous media characteristics (intrinsic permeability, porosity and relative permeability) are known, six unknowns remain: saturation and pressure for each of the phases. To solve the coupled PDE, therefore, three more equations are required. Mayer, et al. (2005) suggested that the three equations required are one from the share of each three fluids in saturating the porous media or total volume balance for the phases, Eq. [10] and two equations from the capillary pressure (P_{ciw}) resulted between intermediate wetting and wetting fluids, Eq. [11] and the other capillary pressure (P_{cni}) resulted from the pressure developed between non-wetting and intermediate-wetting fluids, Eq. [12].

$$S_w + S_i + S_n = 1 \quad [10]$$

Where: S stands for saturation with the respective subscripts (w, i, n) for wetting, intermediate-wetting and non-wetting phases respectively.

$$P_{ciw}(S_w) = P_i - P_w \quad [11]$$

$$P_{cni}(S_t) = P_n - P_i \quad [12]$$

In the three fluid phases flow, the capillary pressure between the wetting and non-wetting phases (P_{cnw}) are independent. Nevertheless, it can be estimated by adding capillary pressure between intermediate-wetting and wetting phases (P_{ciw}), and non-wetting and intermediate-wetting phases (P_{cni}), Eq. [13] (Wu, 2016).

$$P_{cnw} = P_{ciw} + P_{cni} \qquad [13]$$

For the specified fluids and characterized porous media with respect to relative permeability functions, PDE, Eq. [8] for the simultaneous flow of three immiscible fluids can be coupled with Eq. [10], Eq. [11] & Eq. [12]. However, the equations are highly non-linear, especially for three-dimensional flow problems. Helmig (1997) recommended that a significant computational effort with advanced numerical simulation techniques are required to solve the problem.

The PDEs and coupled equations with them are for more complex scenarios that consist of more than two phases. In multiphase flow under natural condition, such as the spill and flow of NAPLs in vadose zone where water, oil, and soil air (gas) are fluids of interest, the flow can be reduced to two-phase fluid flow. Helmig (1997) reasoned that the gas phase is in contact with the atmosphere and its density, viscosity and pressure gradient are three, two and several orders of magnitude less than that of water and NAPL respectively. Mayer, et al. (2005) suggested that even it can be treated as a one-dimensional, single-phase flow problem for practical applicability with the following assumptions:

- ✓ The aqueous phase is at irreducible saturation and hence the intruding NAPL flows on the stationary aqueous phase while displacing air
- ✓ While it is the reasonable assumptions for all type of liquids flow by displacing gases, as both the density and viscosity of the liquids are much greater than that of gases, the air phase in unsaturated zone is at atmospheric pressure throughout the domain and hence no resistance to the flow of NAPL

On the basis of the above assumptions, only the PDE of NAPL needs to be solved (Mayer, et al., 2005) and the use of only PDE to solve for the flow of NAPL under the above assumptions make it analogous to Richards’ equation for unsaturated fluid flow, (see e.g., Celia & Bouloutas (1990) for the Richards’ equation).

2.1.1. Immiscible displacement

Immiscible displacement in porous media is a kind of multiphase flow through which one fluid displaces the other immiscibly. The most common examples of immiscible displacement are the displacement of oil by water and/or gas during secondary oil recovery from oil fields (Chen & Ewing, 1999; Constantinides & Payatakes, 2000; Ezekwe, 2011; Joekar-Niasar & Hassanizadeh, 2012; Speight, 2016; Wu, 2016), the displacement of NAPL by water from NAPL contaminated porous media during decontamination process (Francisca & Arduino, 2007; O'Carroll & Sleep, 2007a; Agaoglu, et al., 2015), pollution of groundwater aquifers by liquid wastes (Avraam & Payatakes, 1995), and fluid movement in air-water porous media in groundwater hydrology (Chen & Ewing, 1999). In strong water wet systems, the displacement of oil by water would be in a piston manner (Tiab & Donaldson, 2016). But, Lyons & Plisga (2005), among others, argue that the displacement from porous media is not even in a leaky piston manner. Rather it is better determined by relative permeability and wettability preference of the porous media towards the liquids (Tiab & Donaldson, 2016). Immiscible displacement of oil from porous media by water or gas can be described by the fractional flow equation (FFE), the frontal advance theory, proposed by Buckley Leverett (Buckley & Leverett, 1942; Lyons & Plisga, 2005; Satter, et al., 2008). Pinder & Gray (2008) indicated that the Buckley-Leverett method is the best-known analytical approach to solve two phases' fluids immiscible displacement problems from porous media.

The fractional flow of one phase during multiphase fluid flow through porous media is determined from the flow rate of the phase of interest divided by the total flow rate of all fluids combined (Fanchi, 2010). Hence, for two phases' fluid flow during the immiscible displacement of oil by water from porous media, where water is the wetting phase and oil is the non-wetting phase, the fractional flow for water is given as follows:

$$f_w = \frac{q_w}{q_t} = \frac{q_w}{(q_w + q_o)} \quad [14]$$

Where: f_w is fraction of water flow (water cut), q_w is water flow rate, q_o is oil flow rate, q_t is total flow rate. The fraction flow of water (f_w) and the fraction flow of oil (f_o) are related by f_w = 1- f_o.

Based on Darcy's equations for the flow of oil and water in porous media, (Leverett, 1941) developed FFE Eq. [18] (Lyons & Plisga, 2005; Dandekar, 2013). FFE is derived by considering the fractional contributions of each of the two phases to Darcian velocity (Pinder & Gray, 2008).

These fractional contributions equations Eqs. [15] & [16] are combined based on the expression of capillary pressure between the non-wetting phase (oil) and wetting phase (water), and gravity for a linear system for any angle from the horizontal alignment using Eq. [17] (Craig, 1971). However, FFE is formulated only based on the flow of the wetting phase without neglecting the dynamics of the non-wetting phase but neglecting porous media skeleton deformation, and compressibility of the fluids, Eq. [18] (Pinder & Gray, 2008). Eq. [21] is derived from Eqs. [15] & [16] after re-arranging them, Eqs. [19] & [20], by subtracting Eq. [16] from Eq. [15].

$$q_w = -\frac{k_w A}{\mu_w}\left(\frac{\partial P_w}{\partial x} + \rho_w g sin\alpha\right) \qquad [15]$$

$$q_o = -\frac{k_o A}{\mu_o}\left(\frac{\partial P_o}{\partial x} + \rho_o g sin\alpha\right) \qquad [16]$$

$$f_w = \frac{1 + \frac{Ak_o}{q_t \mu_o}\left(\frac{\partial P_c}{\partial x} - g\Delta\rho sin\alpha\right)}{1 + \frac{\mu_w}{\mu_o}\frac{k_o}{k_w}} \qquad [17]$$

Where: Subscripts o,w = oil and water, $K_{(o,w)}$ are effective permeability of oil and water respectively, $\mu_{(o,w)}$ are oil and water viscosity respectively, P_c is capillary pressure (P_o -P_w), x is distance along direction of movement, A is cross-sectional area normal to flow direction (cm^2), $\Delta\rho$ is water-oil density differences (ρ_w- ρ_o), α is angle made by the direction of flow with the horizontal

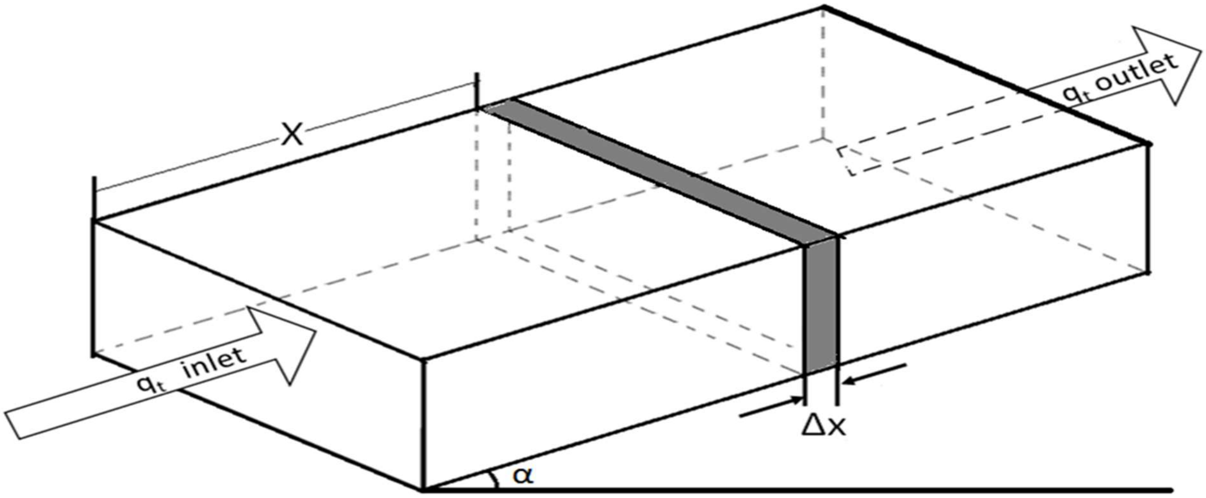


Fig. 1. 1-D displacment form porous media with angle α from the horizontal axis for the derivation of FFE

$$\frac{q_w \mu_w}{k_w A} = -\left(\frac{\partial P_w}{\partial x} + \rho_w g sin\alpha\right) \quad [18]$$

$$\frac{q_o \mu_o}{k_o A} = -\left(\frac{\partial P_o}{\partial x} + \rho_o g sin\alpha\right) \quad [19]$$

$$\frac{q_w \mu_w}{k_w A} - \frac{q_o \mu_o}{k_o A} = \left(\frac{\partial P_o}{\partial x} - \frac{\partial P_w}{\partial x}\right) - g(\rho_w - \rho_o) sin\alpha \quad [20]$$

From Eq. [7] above the capillary pressure between non-wetting phases, P_n, in this case oil, P_o, and wetting phase, P_w, here also, P_w, water gives the capillary pressure, P_c and differentiating the equation with respect to the distance gives:

$$\frac{\partial P_c}{\partial x} = \frac{\partial P_o}{\partial x} - \frac{\partial P_w}{\partial x} \quad [21]$$

From Eq. [14] it is possible to calculate q_o and q_w with respect to q_t and f_w as follows:

$$q_o = (1 - f_w) q_t; \qquad q_w = f_w q_t \quad [22]$$

Substituting Eqs. [22] & [23] into Eq. [21] and re-arranging gives Eq. [18], which Leverett (1941) developed; where $\Delta\rho = (\rho_w - \rho_o)$.

For two-phase fluids multiphase flow in porous media, relative permeability ratios k_{ro}/k_{rw} is equal to k_o/k_w, and water injection rate, i_w, is the same as total flow rate, q_t (Ahmed, 2010). Hence, Eq. [18] can be expressed both in relative permeability ratios and water injection rate. Eq. [18] shows that all the terms of the equation are defined by the characteristics of the porous media except for water-injection rate, viscosity of the displacing fluid and direction of the flow, considering the oil as the part of the porous media. Eq. [18] can be described in more generalized form for any displacing liquids by substituting the subscript with any fluid of interest.

Eq. [18] is the general equation derived for the displacement of oil by water, and it is the base for many equations. Since then, many equations have been derived from it based on different flow scenarios. Ezekwe (2011), among others, argue that even though there are effects from capillary and gravity forces, fractional flow of a fluid is mainly affected by relative permeability. The gradient of capillary pressure is generally small (Ahmed, 2010) and its effect on the displacement is neglected under practical usage (Lyons & Plisga, 2005) and hence Eq. [18] can be expressed as Eq. [24]. Although, the capillary pressure term is neglected from the FFE, however, Donaldson &

Alam (2008) indicated that the influence of wettability on the flow is expressed by relative permeability, as it is the function of overall porous media wettability. On the other hand, the effect of gravity on the horizontal immiscible displacement is zero as sin(0)=0 (Dandekar, 2013; Tiab & Donaldson, 2016) and Eq. [24] can be re-arranged as Eq. [25].

$$f_w = \frac{1 - \frac{Ak_{ro}}{i_w \mu_o}(g \Delta \rho sin\alpha)}{1 + \frac{\mu_w}{\mu_o}\frac{k_{ro}}{k_{rw}}} \qquad [23]$$

$$f_w = \frac{1}{1 + \frac{\mu_w}{\mu_o}\frac{k_{ro}}{k_{rw}}} \qquad [24]$$

The continuity equation applies for two phases as both liquids are considered incompressible, and Eq. [6] of conservation of volume with respect to time, t and flow length, x can be re-arranged for both phases, Eqs. [26] & [27]. FFE for each liquid is the function of individual liquid saturations as relative permeability and capillary pressure are both dependent on saturation (Lyons & Plisga, 2005). It is assumed that the porous media is fully saturated by the two liquids only, Eq. [28].

$$\frac{\partial q_w}{\partial x} = -\emptyset A \frac{\partial S_w}{\partial t} \qquad [25]$$

$$\frac{\partial q_o}{\partial x} = -\emptyset A \frac{\partial S_o}{\partial t} \qquad [26]$$

$$S_w + S_o = 1 \qquad [27]$$

The combination of Eq. [26] through Eq. [28] by adding Eqs. [26] & [27] after substituting the re-arranged form of Eq.[28] for the term S_o ($S_o = 1 - S_w$) gives Eq. [29]:

$$\frac{\partial}{\partial x}(q_w + q_o) = -\emptyset A \left(\frac{\partial s_w}{\partial t} + \frac{\partial}{\partial t}(1 - S_w) \right) = -\emptyset A \left(\frac{\partial S_w}{\partial t} - \frac{\partial S_w}{\partial t} \right) = 0 \qquad [28]$$

Neglecting both gravity and capillary pressure gradient from Eq. [21] and re-arranging it gives the fractional flow rate for oil, q_o, Eq. [30] (Satter, et al., 2008):

$$q_o = \frac{k_{ro}A}{\mu_o}\left(\frac{q_w \mu_w}{k_{rw}A}\right) \qquad [29]$$

Substituting Eq. [30] in to Eq. [14] gives Eq. [31].

$$f_w = \frac{q_w}{(q_w + \frac{k_{ro}A}{\mu_o}\left(\frac{q_w \mu_w}{k_{rw}A}\right))} = \frac{q_w}{q_w(1 + \frac{k_{ro}}{\mu_o}\left(\frac{\mu_w}{k_{rw}}\right))} = \frac{1}{(1 + (\frac{\mu_w k_{ro}}{k_{rw}\mu_o})} \qquad [30]$$

Eqs. [25] & [31] are the fractional flow equation for the displacement of oil by water for horizontal displacement by neglecting capillary pressure gradient (Dandekar, 2013).

Buckley and Leverret (1942) developed the basic flow equation known as frontal advance equation, here afterwards Buckley-Leverret Equation (BLE), Eq. [31], for describing an immiscible displacement of oil by water in one-dimensional two-phase fluid flow (Lyons & Plisga, 2005; Ahmed, 2010).

$$v = \frac{q_t}{\emptyset A}\left(\frac{\partial f_w}{\partial S_w}\right) \qquad [31]$$

Where: q_t is the flow rate (cm^3/s), A is the cross-sectional area (cm^2), $\emptyset$ is porosity of the media (-), v is the rate of advance or velocity (cm/s), $\partial f_w/\partial S_w$ is the slope of the curve of f_w vs S_w.

BLE was derived based on the principle of conservation of mass for the displacing fluid as it flows through any given element in the porous media (Ahmed, 2010) at a constant total flow rate (q_t constant) (Ezekwe, 2011). Assume water is an incompressible fluid (the density of the water, ρ_w is constant); the volume of the water is conserved and hence the volume of the fluid entering and leaving the element, makes the change in volume of the fluid in that element (Ahmed, 2010), see Eq. [32] and Fig. 1.

$$\begin{bmatrix} vol.\,of\ water\ flowing \\ into \\ element\ in\ time, \Delta t \end{bmatrix} - \begin{bmatrix} vol.\,of\ water\ flowing \\ out\ of \\ element\ in\ time, \Delta t \end{bmatrix} = \begin{bmatrix} Accumulation \\ of\ water \\ in\ element\ , \Delta x \end{bmatrix} \qquad [32]$$

The volume (*vol.*) of water injected into and out flow through a given element of the column, Δx, in each time interval, Δt, can be quantified from fractional flow equation. Eq. [32] can be expressed algebraically using fractional flow of water as:

$$(f_w q_t \Delta t)_x - (f_w q_t \Delta t)_{x+\Delta x} = (\emptyset A \Delta x S_w) \qquad [33]$$

Re-arranging Eq. [33] gives:

$$\frac{\emptyset A \Delta S_w}{q_t \Delta t} = -\frac{(f_w)_{x+\Delta x} - (f_w)_x}{\Delta x} \qquad [34]$$

Taking limits as Δt → 0 and Δx → 0 gives the continuity equation:

$$\frac{\emptyset A}{q_t}(\frac{\partial S_w}{\partial t})_x = -(\frac{\partial f_w}{\partial x})_t \qquad [35]$$

For constant fluid properties and flow rate, the fractional flow of water is a function of water saturation only (Lyons & Plisga, 2005; Ahmed, 2010; Tiab & Donaldson, 2016) and hence by applying chain rule on $f_w = f_w(S_w)$, the right hand term of Eq. [35] can be expressed as Eq. [36] and substitute Eq. [36] into Eq. [35] gives BLE, Eq. [37].

$$(\frac{\partial f_w}{\partial x})_t = (\frac{\partial f_w}{\partial S_w})_t (\frac{\partial S_w}{\partial x})_t \qquad [36]$$

$$(\frac{\partial S_w}{\partial t})_x = -\frac{q_t}{\emptyset A}(\frac{\partial f_w}{\partial S_w})_t (\frac{\partial S_w}{\partial x})_t \qquad [37]$$

Water saturation is a function of time at a given location ($S_w = S_w$ (x, t)) and Ezekwe (2011) presented that for any displacement, the distribution of water is a function of both location and time. Further re-arranging BLE, Eq. [37] gives Eq. [38].

$$(\frac{\partial x}{\partial t})_{S_w} = (v)_{S_w} = (\frac{q_t}{\emptyset A})(\frac{\partial f_w}{\partial S_w})_{S_w} \qquad [38]$$

Eq. [38] shows that the velocity of a plane of a given water saturation is directly proportional to the derivative of the water cut at that water saturation. Integrating the equation, according to Lyons & Plisga (2005), for the whole period from the beginning of the injection, the plane of the given water saturation moves some distance, x [39].

$$\int_0^x \partial x = \int_0^t (\frac{q_i}{\emptyset A}(\frac{\partial f_w}{\partial S_w}))\partial t => x = \frac{w_c}{\emptyset A}(\frac{\partial f_w}{\partial S_w}) \qquad [39]$$

Where t is time and integrating from time zero to end of the injection time, t; $q_i = q_t$ is water injection rate; and $w_c = q_i \times t$ is the cumulative volume of water injected. On the other hand, if x is the distance from the injector to producer (length of the column) the time of the displacing liquid breakthrough, t_{bt}, is given by:

$$t_{bt} = \frac{x}{\frac{q_t}{\emptyset A}(\frac{\partial f_w}{\partial S_w})} \qquad [40]$$

2.1.2. Fluid-fluid miscible displacement

Kirkham (2014) defines miscible displacement as a type of displacement through which one fluid mixes with and displaces another fluid. This type of flow often in groundwater flow is referred to as hydrodynamic dispersion (Bear, 1972). Though the process has many applications, and leaching of salts from a soil (Kirkham, 2014); displacement of oil from an oil reservoir with solvents and surfactants (Thomas, 2008; Hirasaki, et al., 2011) and CO_2 (Speight, 2011b); removing of organic contaminants like NAPL with surfactants and solvents from the porous media (Mulligan, et al., 2001; Mao, et al., 2015) are some of the examples. Contrary to the displacement of two immiscible fluids pumped through porous media, Dullien (1992) among others described that miscible fluids do not tend to flow in separate channels and do not keep their identity, rather the flow is the mixture of the fluids. Due to the strong wettability preference of the fluids, it is difficult to displace immiscible fluid completely from the porous media. However, it is possible to displace miscible fluid completely without leaving residual saturation in the porous media (Dullien, 1992). Unlike in immiscible displacement, in miscible displacement there is no capillary pressure between the fluids and the liquid mix with the process of diffusion and dispersion (Chen & Ewing, 1999).

Numerical simulations of miscible displacement of one fluid by another in a porous media can be formulated in an analogous way to two-phase immiscible multiphase flow displacement through porous media (Chen, et al., 2005). The basis for this analogy was well described in Lantz (1970) and Chen & Ewing (1999). The simulation uses the combination of the equation for the conservation of mass, Eq. [41] and Darcy's Law for the flow velocity of the fluid, Eq. [43], by describing the viscosity of the fluids with respect to the concentration, c, along the flow direction, x (x is within a range of porous media length for the range of flow time, t) as follows Eq. [43] (Chen & Ewing, 1999; Chen, et al., 2005).

$$\mathrm{A}.\left(\frac{K(x)}{\mu(c)}(\nabla p - \rho q z)\right) = q_p - q_i = \mathrm{A}.u = q \qquad [41]$$

$$\emptyset(x)\partial c_t - \mathrm{A}.(D(u)c) + u.\nabla c + q_i c = q_i c_i \qquad [42]$$

$$u = -\frac{k(x)}{\mu(c)}(\nabla P - \rho g \nabla z) \qquad [43]$$

Where: k and $\emptyset$ are the absolute permeability and porosity of the sample column respectively, ρ and μ are the density and viscosity of the fluid mixture, g *is* acceleration due to gravity, c is the concentration of the fluid (volumetric fraction), p is the pressure of the fluid, D is the diffusion-dispersion coefficient, c_i is the injection concentration, q_i and q_p the injection and production flow rate and u is the Darcy's velocity.

Eqs. [41] & [43] show that the viscosity is the function of the concentration of one of the fluids with respect to the other fluid during miscible displacement. The difference in concentration of the mixed fluid during the displacement results in viscosity and density differences at a different time and location.

2.1.3. Displacement efficiency

Most studies and technologies related to oil recovery from the reservoir are applicable to porous media contamination by NAPL and its decontamination, e.g. oil recovery technologies used for in-situ extraction of organic pollutants (Lake, 1989). Oil production through the injection of water into the oil reservoir (water flooding) and known as secondary oil recovery (SOR) accounts for more than one-half of worldwide and USA domestic oil production (Agbalaka, et al., 2008). Nevertheless, at the end of SOR almost 65-70% of residual oil remains in the reservoir (Shah, 1981; US National Research Council, 1988; Lake, 1989). Gharbi, et al. (1998) among others stated that enhanced oil recovery (EOR) which employs thermal, chemical or solvent method is used to recover as much as possible residual oil left after SOR. Ernst (2000) projected that EOR may extend the world oil supply to 125 years at the then consumption rate. To achieve the goal, many abandoned, matured oil fields have to be reutilized (Agbalaka, et al., 2008).

The overall oil recovery efficiency (E_R) from a reservoir is the product of displacement efficiency (E_D) and volumetric swept efficiency (E_V) (Fanchi, 2010). The displacement efficiency, according to Ezekwe (2011) is measured in terms of the effectiveness of the displacing fluid in displacing the oil from the reservoir while volumetric swept efficiency is the proportion of the reservoir contacted by the displacing liquid. If the displacing liquid could invade the whole volume of the reservoir, the fluid displacement efficiency and total oil recovery efficiency (E_R) are equal, Eq. [44] and calculated as follows:

$$E_R = E_D = 1 - \frac{S_{or}}{S_{oi}} \qquad [44]$$

Where: S_{or} and S_{oi} are residual and initial oil saturation in the invaded region respectively.

In practical cases, the recovery efficiency is less than one and Fanchi (2010), among others stated that if not for economic reason, in many cases, there is technology that improves it. Low salinity (Yildiz, et al., 1999; Agbalaka, et al., 2009) and increased temperature of the flooding liquid (Agbalaka, et al., 2009; Roosta, et al., 2015), among others, improvers the efficiency of the oil recovery. However, Soga et al. (2004) argue that it is impossible to remove the contaminant from NAPL contaminated sites completely. The authors argue that, the remediation efficiency should not be based on the reduction of NAPL mass from source zone only, but also on the reduction of risk achieved through the lowering of concentration of the dissolved components that could arise from the source zone.

2.2. Scale of the problem and role of human activities

Environmental contamination is a major concern and human activates aggravate it. Human activities from local concentrations of economic activates and large-scale industrial activities have the major share. Global warming, which is mainly the result of the venting and burning of fossil fuel (coal, petroleum and natural gas) is the main agenda of the 21st century. Methane and CO_2 are the significant contributor of greenhouse gasses and according to Jahn, et al. (2008) the level of CO_2 has increased from 288 ppm in the late 19th century to 375 ppm today. Griffin (2017) reported that 100 fossil fuel producing companies have produced 923 billion of tones of CO_2 emissions which is 52% of global industrial greenhouse gases since the Industrial Revolution. Production and utilization of fossil fuels are not only the cause of atmospheric pollution but also substantially contaminate soil and water resources (Zoller, 2009). Fossil fuels are the main sources of hydrocarbons and hydrocarbon liquids are NAPLs (Newell, et al., 1995). NAPL is one of the main contaminants to the environment and Schroth, et al. (1995) pointed out that contamination of the subsurface by NAPL is a widespread problem, and there is a significant portion of NAPL contaminated groundwater and soil across the globe.

The European Environmental Agency (EEA) stated that contamination occurs when massive amount of chemicals, which overwhelm the buffering capacity of the soil, are released to the environment (EEA, 2010). The damage is higher when contamination occurs to soil which is crucial media for agricultural production, and directly related to other natural resources, for example, ground and surface waters, forest and the biomass (Dupuis & Knoepfel, 2015).

According to Dupuis & Knoepfel (2015), their impact on human health is insidious and they can enter the human body through contaminated food consumption, inhalation, and ingestion of contaminated soil particles or through skin absorption. Although there had been an effort to remediate the contaminated sites, in 2007, EEA estimated that there will be 50% increment of contaminated sites which needs remediation until 2025 (EEA, 2007).

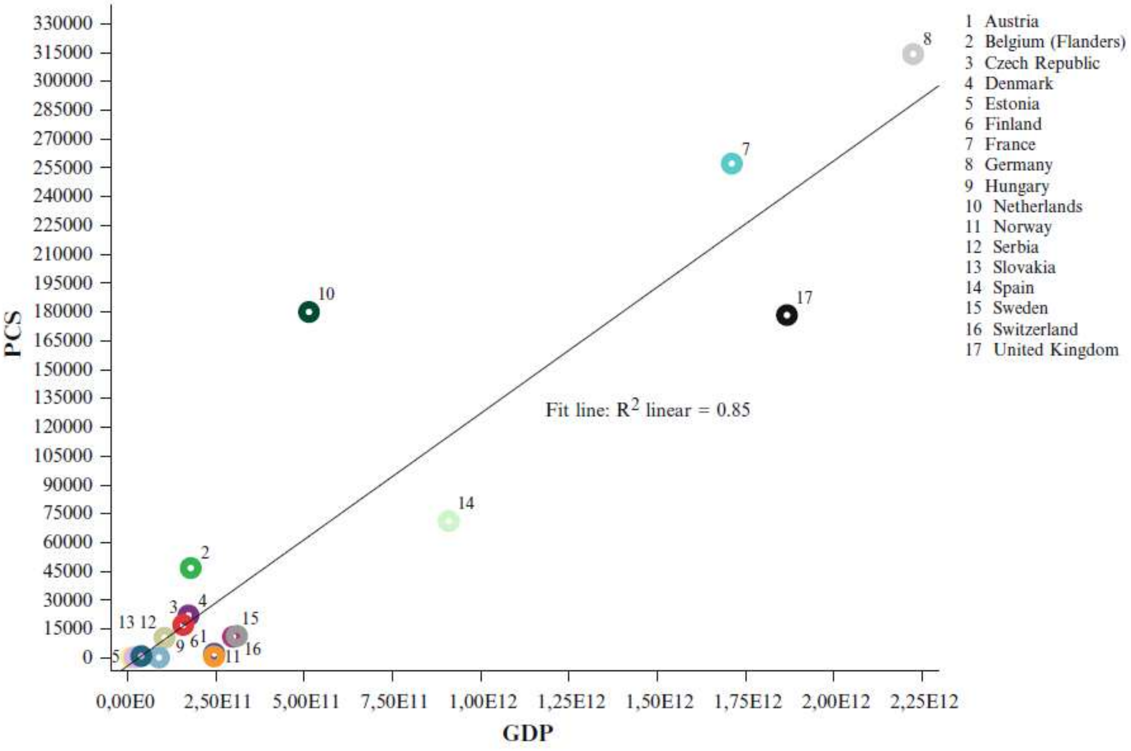


Fig. 2. The relationship between gross domestic product (GDP) and potentially contaminated sites (PCS) in 17 European Countries, taken from Dupuis & Knoepfel (2015)

In Europe alone, there are 1.2 million suspected contaminated sites, of which 127,000 have been confirmed (Dupuis & Knoepfel, 2015). However, it is only 45% of the confirmed sites that has already been remediated with slow progress and at extremely high cost (Dupuis & Knoepfel, 2015). The Commission of European Communities (2006) reported that Europe loses 38 billion euros every year due to soil degradation, of which around 50% is due to soil contamination. Dupuis & Knoepfel (2015) mentioned that the management of contaminated sites yearly costs Europe 6.5 billion euro. On average, 42% of the money for the management is financed through public expenditures (EEA, 2007), see Fig. 3. US EPA (2004), on the other hand, estimated that the cost of mitigating the hazards from 235,000 to 355,000 USA contaminated sites for the following 30 years could be more than $209 billion dollars. There is a disagreement on the number of contaminated sites and amount of money needed to remediate them. US National Academy of Sciences (2012) argued that both the number of proposed sites and the cost proposed for the identified sites in USA were underestimated. Meanwhile, it is difficult to get the data on the number of contaminated sites and degree of contamination from pollution haven countries even though it prevails itself in day to day activities, for instance smog due to air pollution in major Chinese cities. The major cause the problem of contamination, according to Dupuis & Knoepfel (2015) is the local concentration of economic activities where waste-intensive production and consumption patterns prevail, mainly population-intensive industries.

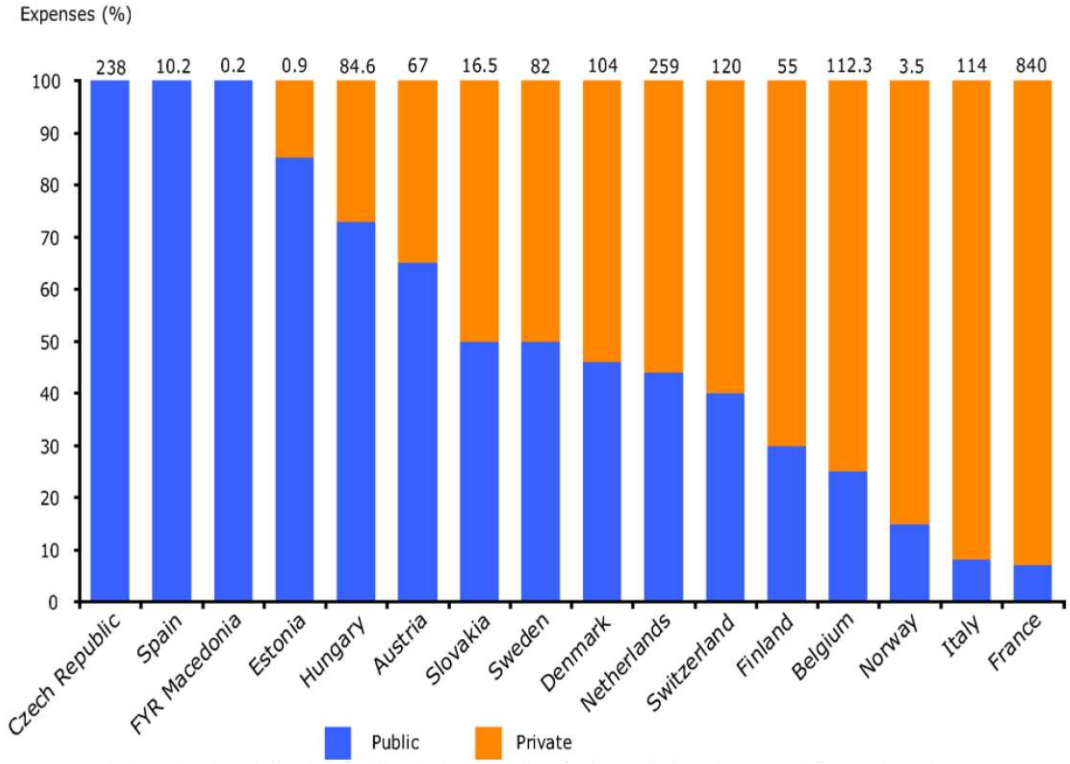


Fig. 3. Estimated allocation of public and private expenditures for management of contaminated sites by 16 European countries; values on the top indicate the total annual management expenditure in Million euro, taken from EEA (2007)

2.3. Chemical of concern

The estimate put that, in addition to naturally occurring chemicals, there are 6×10^6 chemical compounds created by humans, of which most of them created in 20th century and 1000 new ones added every year (Alloway & Ayres, 1997). In both industrialized and developing countries, chemicals are produced mainly for economic development. It affects directly or indirectly almost everybody's life through agriculture and food industry (fertilizers, pesticides food additives), pharmaceuticals, cleaning materials, fuels etc. However, a significant number of chemicals produced for the wellbeing of human beings are contaminants for the environments and further chemically hazard for both the human beings themselves and the environment. If they are released to the environment in mass above the buffering capacity of the soil, they will result in contamination. For the pollutants/contaminants to be harmful to the environment, there should be a source and a receptor with a pathway connecting the two (Alter, 2012). According to Swartjes (2011), contaminated sites have potentially dangerous amounts of pollutants: heavy metals, mono cyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, persistent organic pollutants, volatile organic contaminants, and other organochlorides.

Most of the chemical compounds listed above are made up of organic compounds and originated mainly from crude oil. Petroleum is used as an equivalent term for crude oil (Speight, 2005) and here after the term petroleum will be used through this work. The word petroleum is from two Latin words, *petra* and *oleum,* which means rock oil (Oxford English Dictionary , 2015). Crude oils according to Giles & Mills (2010) are a highly complex combination of hydrocarbons; heterocyclic compounds of sulfur, nitrogen and oxygen; organometalic compounds; inorganic sediment and water. Speight (2014) mentioned that 50 to 98% of crude oil is hydrocarbons and over 50% of its constituents according to Smith (1968) and Mango (1997) among others, is the light hydrocarbons.

Contamination from the use of fossil fuels in general and light hydrocarbons in particular is a main concern. Most of the carbon is stored deep in the Earth: 82% locked up as carbonate in limestones and dolomites, and about 18% occurs as organic carbon in coal, oil, and gas (Selley & Sonnenberg, 2014). It is only 0.1% of total carbon which used as carbon exchange (Romanova & Romanov, 2015). Burning of the fossil fuels releases CO_2 to the atmosphere which is the main cause for the global warming in addition to making the rain slightly acidic (pH 5.8) (Speight, 2005). Huang & McElroy (2012) stated that 89.3 Gt of carbon was added to the atmosphere between 1995 and 2007 due to the use of fossil fuels. Depending on the quality of the fuel and amount used with respect to nitrogen and sulfur content, however, their burning could make the rain more acidic, which can acidify the soil on which it falls. This could lead to the release of toxic elements such as aluminum from the soil (McElroy, 2002). Directly released hydrocarbons to the subsurface have a persistent nature and can contaminate large volumes of soil and groundwater. Kim & Corapcioglu (2003) showed that most of the released jet fuel remains as free LNAPLs after 20 years.

2.4. Hydrocarbons

Organic chemistry is a branch of chemistry dedicated to study hydrocarbons and their derivatives (Stoker, 2013). A hydrocarbon is a compound that contains only carbons and hydrogen atoms. Whereas its derivative is a compound that contains one or more additional elements as the functional group. Hydrocarbons and some common derivatives of them are presented under Appendix A. Fossil fuels (oil, gas and coal) are mainly made up of HCs (Olah & Molnár, 2003). It is likely that there are thousands of HC compounds occur in crude oil but around 600 different HCs have been positively identified (Giles & Mills, 2010). It is believed that there are six times as many different types of organic compounds (both manmade and natural), approximately 10 million (Raymond, 2014) as inorganic compounds, approximately 1.7 million (Stoker, 2013).

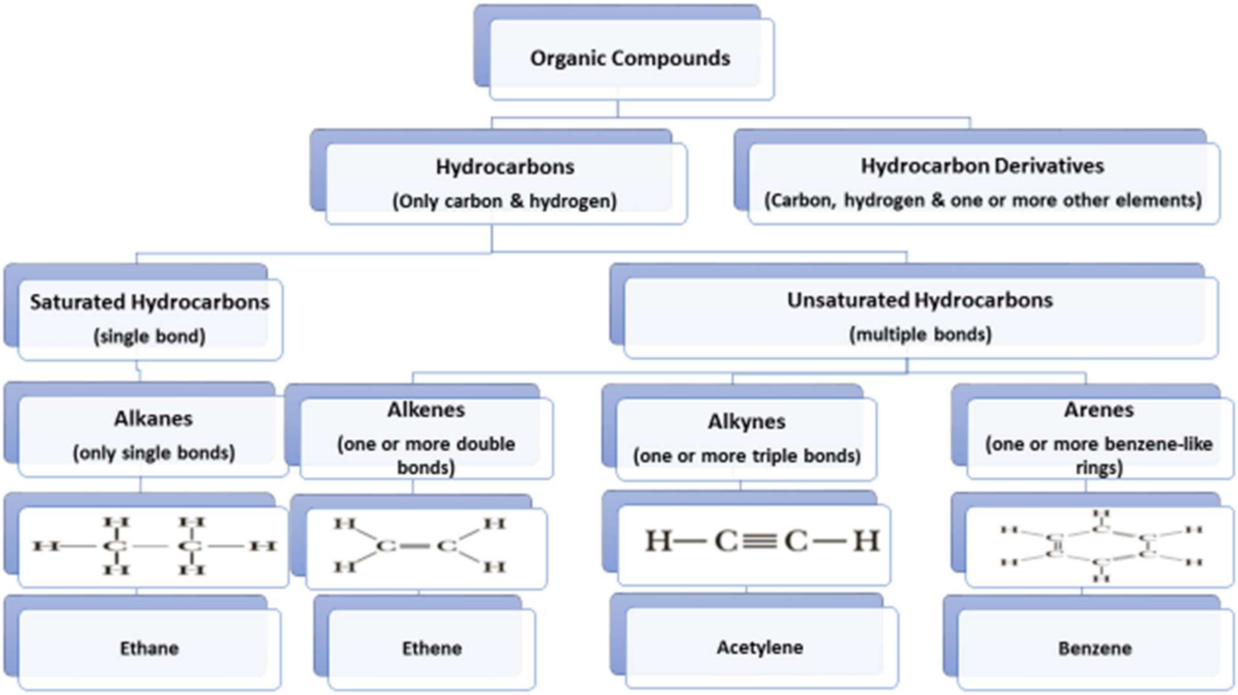


Fig. 4. Summary of organic compounds classification, from Stroker (2013) and Brown et al. (2017) and modified.

Hydrocarbons can be grouped under saturated and unsaturated hydrocarbons depending on the bonding type between carbons of a compound (Fig. 4). The bonding of a carbon atom can be to four other atoms through single bonds or to three other atoms through two single bonds and one double bond or to two other atoms through two double bonds or through one single bond and one triple bond (Stoker, 2013). Hydrocarbon compounds in which all carbon-to-carbon bonds bonded with single bonds are grouped under saturated hydrocarbons (alkanes) and the ones with at least one multiple bond are grouped under unsaturated hydrocarbons. Hydrocarbon compounds can be also grouped under four families depending on their bond formation and structural arrangement (Fig. 5). Hydrocarbons that contain only a single-bonded carbon atom are of the alkane family and those unsaturated hydrocarbons with at least one carbon-carbon double bond and at least one carbon-carbon triple bond as functional groups are categorized under alkene and alkyne families respectively. Alkanes can be further classified as paraffins and naphthenes (cycloalkane) (Gary, et al., 2007). Only paraffins from pentane (C_5H_{12}) to heptadecane ($C_{17}H_{32}$) (Simanzhenkov & Idem, 2003) and all naphthenes are liquid at room temperature and pressure (Selley & Sonnenberg, 2014). Simanzhenkov & Idem (2003) explained that, due to their high chemical activity, naturally unsaturated hydrocarbons are absent from crude oil but produced during the thermal or/and catalytic treatment of crude oil. The last family of hydrocarbon is aromatic hydrocarbon and members of this family have a ring of six carbon atoms bonded in alternative double and single bonds.

Hydrocarbon groups of organic compounds vary from the simplest methane (CH_4, molecular weight: 16) to thousands more different types of hydrocarbons that involves two or more carbon atoms bonded together and forms chains. The chain could be: straight, branched or ring (mono/polycyclic hydrocarbons). This broad range in molecular weights results in boiling points that range from –160°c to temperatures in excess of 1100 °C (Speight, 2015). Hydrocarbon compounds with a given molecular formula could have more than one arrangement (atomic connections) and form different types of isomers. In addtion to chains and netwoks forming properties of carbon atom links, isomerism is one of the main reasons for the existence of so many organic compounds (hydrocarbons) (Seager & Slabaugh, 2014). Generally, as the number of carbon atoms in the molecule increases so as the number of constitutional isomers (Dalton, 2011; Ouellette & Rawn, 2015). Isomers have different chemical properties (reactivity) and physical properties (melting point, boiling point and density). Bettelheim, et al. (2013) examplefied the boiling points of the isomers of butane (n-butane (butane) with -0.5 ºC and 2-Methylpropane (isobutane) with 11.6 ºC).

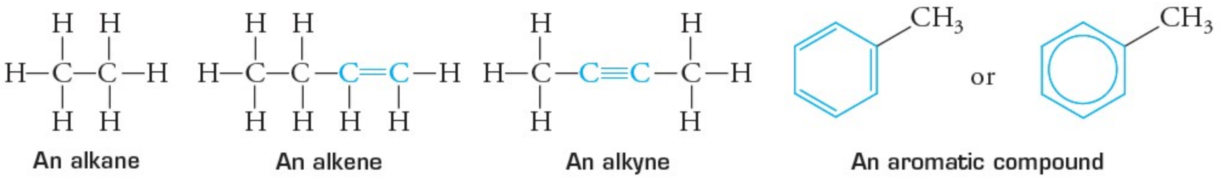


Fig. 5. Examples for hydrocarbon families, taken from Raymond (2014)

2.5. Uses of hydrocarbons

Petroleum hydrocarbon products have been known and used for centuries. Studies from archeological investigations show that petroleum had been extracted and utilized 5 to 6 centuries before Christ (Simanzhenkov & Idem, 2003). Sumerians in the Tigris-Euphrates valley frequently used bitumen or asphalt in construction and ornamental works (Speight, 2001). Herodotus, the ancient Greek historian, recorded that Mesopotamians in the 4th century before Christ had used Bitumen to caulk their ships (Giles & Mills, 2010). He also mentioned about the oil well of Zante (Henry, 1873). Giles & Mills (2010) mentioned that Egyptians were using the derivatives of crude oil in the mummification process. Seafarers used asphalt from natural oil seeps to caulk (seal) and waterproof their sailing vessels (Winegardner & Testa, 2000). In the fifteenth century, even Christopher Columbus used it to caulk his ship (Speight, 2001). The use of petroleum as a fuel for lamp was documented by Marco Polo in 1291 (Winegardner & Testa, 2000).

It is the pressure from the advent of the Industrial Revolution which required the efficient and sufficient energy supply in addition to the visible air pollution caused from using coal that forced to search for alternative energy sources (Winegardner & Testa, 2000). The energy source that joined the burning rock (coal) as part of 19th century energy portifollow (Fanchi & Christiansen, 2017) and dominated the 20th century energy source (Speight, 2011b) was petroleum (rock oil). It further evolved with the development of internal combustion engines (Winegardner & Testa, 2000). In today’s world transportation fuel is mainly from petroleum hydrocarbon (Demirbas, 2010). Petroleum hydrocarbon is the first trillion dollar industry and the largest single item balance of payments and exchanges between nations (Giles & Mills, 2010). Nowadays, hydrocarbons are used primarily as fuel to generate energy for heating, transportation and industry (Speight, 2015). A relatively small portion, up to 4%, of petroleum hydrocarbon products are used as a raw material in the production of plastics, textiles, pharmaceuticals and other products (Olah & Molnár, 2003).

Different fractions of crude petroleum are used for different purposes. Natural gas (C_1 - C_4) is a mixture of gaseous alkanes at room temperature and is mainly used as source of energy for heating, cooking and electric generation (Smil, 2015). This fraction of the hydrocarbons is the cleanest burning of all the fossil fuels (Chandra, 2006). Natural gas is also used as a raw material to produce paints, fertilizer, plastics, antifreeze, dyes, photographic film, medicines, and explosives (Speight, 2007). While gasoline (C_5 - C_{12}) and diesel and kerosene (C_{12} - C_{18}) are mixtures of liquid alkanes at room temperature and used as a fuel for different types of engines (Raymond, 2014). Riazi (2005) summarized the major fuel products as liquefied petroleum gases (LPG), gasoline, kerosene and jet fuel, diesel and heating oil, and residual fuel oil.

HCs have been used as fuels with different additives to improve the performance of engines and air quality. Lead was used as antiknock additives from 1920s to 1980s (Nriagu, 1990). The use of lead in the form of tetraethyl lead to increase the octane number of gasolines for the mentioned purpose was easy and economical (Leffler, 2008). Unfortunately, however, lead is toxic and even at lower concentration in vapor form can cause memory loss, blindness, or death (Leffler, 2008) and its use is banned since 1970s (Tong, et al., 2000; Järup, 2003). Since 1970s, methyl tertiary butyl ether (MTBE) was used as gasoline additive in the USA instead of lead (Davidson & Creek, 2000). It was added to the gasoline to boost octane number (Deeb, et al., 2000) and also to improve air quality (Squillace, et al., 1997; Fetter, 2014). However, this oxygenated additive has its own problem. Hartley, et al. (1999) among others mentioned that MTBE was a frequent contaminant of groundwater. Reports from thousands of USA wells indicate that leakage of USTs was the main cause for the contamination (Winegardner & Testa, 2000). Due to its higher solubility in water and low Henry's Law dimensionless constant (Fiorenza & Rifai, 2003) and polar characteristics of oxygenates (Deeb, et al., 2003), MTBE migrates through aquifer with minimal retardation and could contaminate large volumes of groundwater. After scientists and environmentalists found out the problem related to using MTBE, another oxygenate, ethanol has taken its place. Experiments by Song, et al. (2006) showed that gasoline used with ethanol additives brought about generally lower regulated engine-out emissions than MTBE did. Even though ethanol like MTBE is both an oxygenate and water-soluble additive, a study from Dakhel, et al. (2003) showed that ethanol is easily biodegradable from the aerobic groundwater compared to MTBE, which persisted beyond their experimental duration of six months. Even though lower molecular weights alcohols, esters, ketones and ethers are known to microbiologists as biodegradable, MTBE is notably resistant to it (US National Academy of Science, 2000). Demirbas (2010) argued that the production of grain-based ethanol for biofuel purposes is increasing in an unprecedented way. Competition with the food supply for the booming population of our planet, is therefore, the main question that the sustainability of ethanol production faces (Demirbas, 2008; Kessler, 2008; Balat & Balat, 2009; Twidell & Weir, 2015).

Leffler (2008) mentioned that in addition to lead, MTBE, and ethanol, other petrochemical additives, e.g., methanol, tertiary butyl alcohol (TBA), and ethyl tertiary butyl ether (ETBE) among others were used. Despite the additional contamination risk, they pose, Davidson & Creek (2000) mentioned that the use of a variety of additives at different times could help in identifying the source, time or number of gasoline spills at a site in forensic environmental investigations. Finally, Nadim, et al. (2001) predicted that in future, to solve the problems, hydrogen could substitute gasoline to power electrically driven motors in automobiles.

Petroleum hydrocarbons are used also for non-fuel purposes. The major non-fuel products are summarized by Riazi (2005) as solvents, lubricants, petroleum waxes, white oils, and coke. Except for the solvents which are in the light petroleum fraction (C_4-C_{14}) (Riazi, 2005) the other non-fuel use products consist of higher carbon molecules (Winegardner & Testa, 2000). Petroleum hydrocarbon solvents like other solvents are used to dissolve, suspend, or transport the other ingredients in industrial process and commercial formulation (Montemayor, 2010). Often water is taken as the universal solvent. But, though water is an environmentally friendly solvent, many organic compounds are not water soluble (Rogers & Seddon, 2003). Hydrocarbon solvents are used in paint, printing ink, polish, adhesives, perfumes, vegetable oils, varnish, dry cleaning, leather, fur, and tyre industries (Montemayor, 2010). Hexane is a good example of a hydrocarbon solvent. It is applicable in the extraction of edible oils from seeds and vegetables (Wan, et al., 1995; Johnson, 1997) and to extract oil and grease from contaminated water and soil for laboratory analysis (US EPA, 2010). It is also used as a cleaning agent/degreaser in the textile, leather and furniture industries and as a solvent additive in glues (rubber cement, adhesives), varnishes, and inks (US EPA, 2000a). Hexane is one of the additives of gasoline (C6 - C12) (Raymond, 2014). However, traditional industrial organic solvents are volatile organic compounds and a major source of environmental pollution (Rogers & Seddon, 2003). The authors reviewed the progress on the development of new ionic liquid solvents and concluded that, due to their versatility and "green" credentials, ionic liquid solvents will replace conventional organic solvents in the future.

Higher molecule hydrocarbon fractions are used for different purposes. Lubricants, for example are used primarily to reduce friction and wear to prolong the life and increase the efficiency of mechanical devices and are used for heat dissipation, corrosion protection, power transmission, and contaminant removal (Verdura, et al., 2003). The other higher molecular petroleum hydrocarbon fraction, petroleum wax, which is a class of mineral waxes and usually solid at room temperature (Chaudhuri, 2010) is used for many purposes. Mansoori, et al. (2003) mentioned the applications of petroleum waxes in coating of drinking cups; an adhesives additive; production of candles and rubber; as components of hot melts, inks, and coatings for paper; and they are also used in asphalt and caulks. Some products of petroleum hydrocarbons are not found in the crude oil from which the products are to be produced. But, they are thermally converted during the process of producing another product (Fahim, et al., 2010). One of the best examples is petroleum coke which is the result of thermal conversion of resins and asphaltenes from crude oil (Jones, 2006). It is produced from the destructive distillation of petroleum residue (Pillon, 2008). Coke is insoluble in organic solvents though its carbon content by mass is 90 to 95%, and it also does not pose the same potential environmental issues as other petroleum products (Speight, 2015). It has applications in electrode manufacturing, it is used for heating purpose as a fuel, used as a feedstock in coke ovens for the steel industry, and for the manufacturing of graphite (Gary, et al., 2007; Speight, 2015).

The other crude oil fraction which has many applications is white mineral oil. Stoker (2013) mentioned that mineral oil involves alkane in the range of C_{15} to C_{24}. It is a highly refined colorless, tasteless, odorless liquid hydrocarbon from petroleum distillates (Speight, 2015). Different refining stages including catalytic hydrogenation remove unnecessary constituents of crude oil including toxic polycyclic aromatics and heavy metals (Speight & Exall, 2014). Hence, white mineral oil is a refined complex mixture of saturated hydrocarbons from paraffin (alkane), naphthenes (cycloalkane) or a mixture of the two (Parkash, 2009). Depending on the degree of refining and type of the alkane source, mineral oils can be grouped under two categories: medicinal (pharmaceutical) and technical grade mineral oil (Speight, 2015). Speight (2014) mentioned that due to its high specific gravity and density, naphthenic source mineral oils are applicable in pharmaceutical use while paraffinic source mineral oil which has lighter specific gravity and lower viscosity are preferable for lubrication and other technical uses.

Generally, white mineral oils have a wide range of applications in medicine, pharmaceutical, cosmetics, lubricants, insecticides, vehicles, paper impregnation, food packaging, food contact and even food itself (Speight, 2015). Even though there is a wide use of petroleum hydrocarbon products in today's world, there are concerns for their continuity in future uses. Schobert (1990) sated the concern as environmental issues (air pollution from the burning of fossil fuels and soil and groundwater contamination from the spill of NAPLs) and sustainability of petroleum hydrocarbons sources. However, many studies have been done on how to improve both the production efficiency and burning quality of petroleum hydrocarbons.

HCs can be used in the study of laboratory-based modeling of LNAPL with respect to natural porous media. Due to its high quality and stability, white mineral oils under different commercial names have been used in the experimental study of LNAPL behavior in the porous media (Ma, et al., 1999; Duffield, et al., 2003; Francisca & Rinaldi, 2003; Fischer, et al., 2006; Francisca & Arduino, 2007; Hatiboglu & Babadagli, 2008; Francisca & Montoro, 2012; Báťková, et al., 2014; Baker, et al., 2015). Previous laboratory experiments by Cary, et al. (1989a; 1989b); Lenhard (1992); Schroth, et al. (1995; 1996; 1998a; 1998b); Ma, et al., (1999); Oostrom, et al. (1997); Oostrom & Lenhard (1998) and Kechavarzia, et al. (2005) used isoparaffin solvent with the commercial name Soltrol 220 (C_{13}-C_{17}) and Lenhard, et al. (1993) used Soltrol 170 (C_{12}-C_{14}) for such purposes. The hydrocarbon solvents were selected for the experiments for their negligible solubility in water, density (lighter than water), low volatility at room temperature and low health hazard (Schroth, et al., 1998a; Schmidt, et al., 2002). However, McKee, et al. (2005) mentioned that there is an occupational exposure limit for hydrocarbon solvents with up to 15 carbons, and a potential for solvents with more than 15 carbons to form aerosols. Different fractions of hydrocarbons and/or petrochemicals have also been used for study, e.g., in Zalidis, et al., (1991); Thomson, et al., (1992); Seagren, et al., (1999); Schmidt, et al., (2002); Agaoglu, et al., (2012).

2.6. Petroleum hydrocarbons production

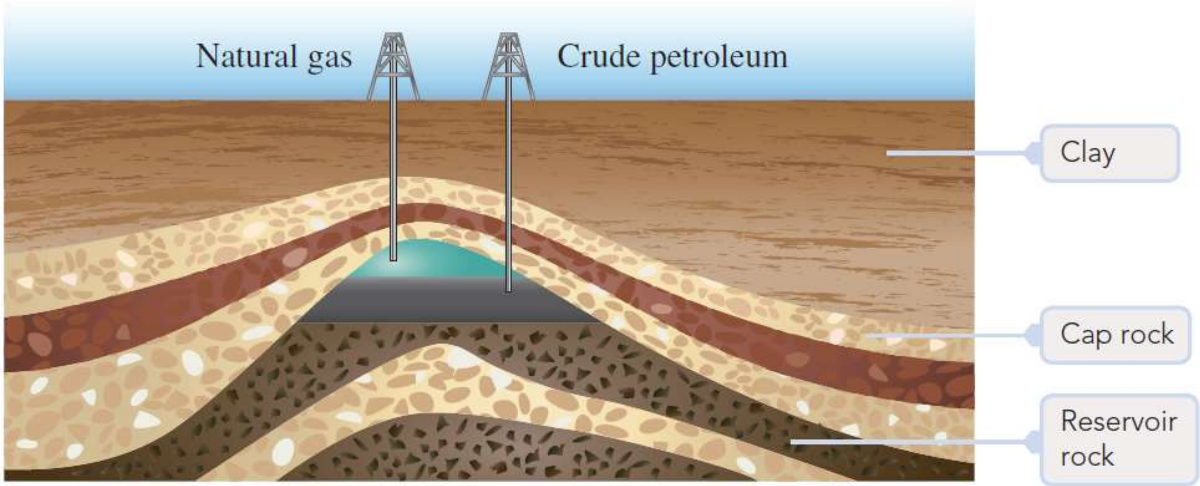


Fig. 6. Vertical profile of rock formation for crude petroleum and natural gas in subsurface, taken from Stroker (2013)

Naturally, crude petroleum (crude oil) and natural gas, which are the main sources of hydrocarbons are found dispersed in the porous rock formation of the subsurface (Stoker, 2013), see Fig. 6. With bases on either organic or inorganic origin, there are many scientific hypotheses on the origin of petroleum. The supporters of the organic-origin theories argue that petroleum is formed from sedimentary rock, once living organisms (plant and animals), while the opponents of the theories argue that it is formed by abiogenic process that occur within the Earth (Walters, 2006). The abiogenic origin theories were much discussed between 1950s and 1980s (Sylvester-Bradley & King, 1963). It is mainly supported by Russian-Ukrainian School of thoughts (Romanova & Romanov, 2015), and one of the theories of abiogenic origin of petroleum hydrocarbon is even known as Russian-Ukrainian theory (Glasby, 2006). Robinson (1966) among others supported the duplex origin of petroleum hydrocarbons. Simanzhenkov & Idem (2003) also concluded that it is almost impossible to answer them using only one theory. However, many recent studies support the biogenic/organic source of petroleum hydrocarbon (Glasby, 2006). Western scholars, except for astronomers and a few geochemists and petroleum geologists, like Thomas Gold who had developed his own theory on the abiogenic origin of hydrocarbons, support the biogenic origin of hydrocarbons (Glasby, 2006; Romanova & Romanov, 2015).

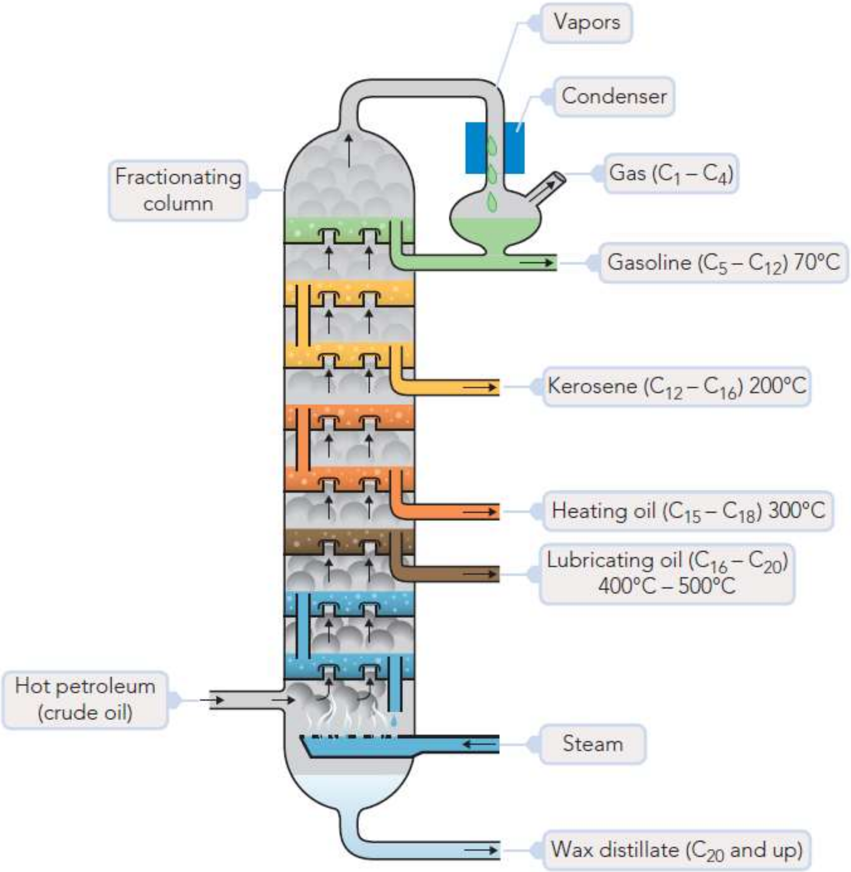


Fig. 7. Fractionating column for complex mixtures of petroleum hydrocarbon separations taken from Stroker (2013)

Experimental, geological and geochemical evidence supports the biogenic thermogenic hypothesis (Peters, et al., 2005). From laboratory heating experiments, Lewan et al. (1979), Lewan (1985; 1994) and Ruble, et al. (2001) among others showed that it could be possible to generate similar products to natural crude oil from potential source. Another piece of evidence that strengthens the theory is that above 99% of global crude oil reservoirs that has been discovered is found in sedimentary rock rather than in the basement igneous or metamorphic rocks (Peters, et al., 2005). Gold (1985; 2001), however, argues that the biomarker in crude oil reservoirs are from the dissolution of biogenic materials during upward migration of inorganic hydrocarbons that originate by polymerization of methane in the mantle based on the deep-Earth gas theory. The opponents of the deep-Earth gas theory as the origin of petroleum argue that the petroleum in the basement rocks could be from the downward migration of petroleum from organic-rich sedimentary rock (Peters, et al., 2005).

Table 1. Some petroleum hydrocarbon fractions produced from distilation column, taken from Riazi (2005)

Petroleum fraction	Approximate hydrocarbon range	Approximate boiling range (º C)
Light gases	C_2 - C_4	-90 - 1
Gasoline (light & heavy)	C_4 - C_{10}	-1 - 200
Naphtha (light & heavy)	C_4 - C_{11}	-1 - 205
Jet fuel	C_9 - C_{14}	150 - 255
kerosene	C_{11} - C_{14}	205 - 255
Diesel fuel	C_{11} - C_{16}	205 - 290
Light gas oil	C_{14} - C_{18}	255 - 315
Heavy gas oil	C_{18} - C_{28}	315 - 425
Wax	C_{18} - C_{36}	315 - 500
Lubricating oil	$> C_{25}$	> 400
Vacuum gas oil	C_{28} - C_{55}	425 - 600
Residuum	$> C_{55}$	> 600

Despite the arguments on the origin of petroleum hydrocarbons, there is no question on the vast investment on it in the last few centuries. There has been a lot of money invested on the deep subsurface exploration, production, transportation, storage and utilization of petroleum hydrocarbons as well as the study and cleanup of contaminated environments by released products. Henry (1873) mentioned that petroleum frequently occurred in the form of springs. Giles & Mills (2010) cited that 240 m deep oil wells were drilled in China in the year of 347 CE. The first industrial-scale crude oil production was from a 22 m deep well (Simanzhenkov & Idem, 2003). Today, however, most of the crude oil comes from deeper wells and data from U.S. Energy and Information Administration (US EIA) show that the average depth of crude oil exploratory wells drilled increased from 4,232 feet in 1949 to 7,778 feet in 2008 in USA (US EIA, 2015).

Crude oil is produced from the reservoir through different oil recovery mechanisms (primary, secondary and tertiary). Produced crude oil is a complex mixture of different hydrocarbons which differ in carbon contents and physical properties like boiling points. The separation process employs this difference in boiling points of each fraction and the fractional distillation method is used (Stoker, 2013), see the different fractions of petroleum HCs and employed temperature used for separation of different fractions under Fig. 7. There should be the transportation of produced oil from oil fields and refined products from refinery to different storage tanks. Giles & Mills (2010) mentioned that the daily production of petroleum hydrocarbon transported through more than one million km of pipe lines is sufficient to fill a string of railroad tank cars over 2100 km in length.

2.7. Production and utilization of PHC products and environment

Production of crude oil and use of its different end products are the main source of green-house gases: carbon dioxide and methane. In addition to carbon dioxide and methane, crude oil/petroleum is the source of other atmospheric contaminants: oxides of sulfur and nitrogen. Sulfur and nitrogen can be removed during the refining processes using different catalysts. Ancheyta (2013) indicated that nitrogen is less concentrated but more difficult to remove compared to sulfur of which 90% or more can be removed easily from the petroleum. The production of oxides during the processing and use of refined products depends on the refining quality. In moist air, the oxides of nitrogen and sulfur react to form their respective acids. These strong acids dissolve in water droplets and fall as acid rain/precipitation back to the land/water surfaces (Speight, 2014). Moreover, produced petroleum and its different end products can contaminate water bodies, surface and subsurface directly through spill and leakage.

The most common and widely known use of petroleum hydrocarbon is as fuel for energy, heating, transportation, and industry (Speight, 2015). Combustion of hydrocarbon fuel, both internal combustion in engines and burning in which a flame is formed during combustion, gives out energy upon oxidation reaction, see Eq. [45] for stoichiometric burning of hydrocarbon in oxygen (complete combustion) and Eq. [46] burning of hydrocarbon propane as an example. However, due to the lack of sufficient oxygen, the combustion of hydrocarbon fuel can result in an incomplete combustion and the product will be carbon monoxide, water and less energy compared to the complete combustion of equivalent hydrocarbon fuel, for the stoichiometric incomplete combustion of hydrocarbon fuel see Eq. [47], all the equations from Speight (2011a).

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right) H_2O \qquad [45]$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + energy \qquad [46]$$

$$zC_xH_y + \left(z\left(\frac{x}{2}+\frac{y}{4}\right)\right)O_2 \rightarrow\ z.xCO + \left(\frac{z.y}{2}\right)H_2O \qquad [47]$$

In addition to carbon dioxide and water the exhaust gases of petroleum hydrocarbon fuel can include other chemicals depending on the chemical combinations of the oxidizer alone. Speight (2011a) stated that the burning of hydrocarbon, gasoline in air where 21% is oxygen and 78% is nitrogen by volume may produce nitrogen oxides (NO_x). However, nitrogen is inert and cannot be oxidized at low combustion temperature, but thermodynamically favored only at high temperature in an excess of oxygen, see Eq. [48] for the stoichiometric combustion of hydrocarbon fuel at lower temperature.

$$\mathrm{C_xH_y} + \left(\mathrm{x}+\frac{\mathrm{y}}{4}\right)\mathrm{O_2} + \left(3.76\left(\mathrm{x}+\frac{\mathrm{y}}{4}\right)\right)\mathrm{N_2} \rightarrow \mathrm{xCO_2} + \left(\frac{\mathrm{y}}{2}\right)\mathrm{H_2O} + \left(3.76\left(\mathrm{x}+\frac{\mathrm{y}}{4}\right)\right)\mathrm{N_2} \qquad [48]$$

Complete combustion of hydrocarbon fuels produces carbon dioxide, water as steam and energy. However, if the supply of oxygen is insufficient, a heat sinks such as a solid surface or flame trap (Speight, 2011a), incomplete combustion of the fuel takes place (Hutter, 2008). Hamilton & Falkiner (2003) among others pointed out that the production of unburned or partially combusted fuel is from the absence of sufficient oxygen. In an incomplete combustion there can also be the production of carbon dioxide and water (Stoker, 2013). Complete combustion efficiency with 100% is not realistically achievable, even under complete combustion. Speight (2011a) valued 10% to 95% range for most common combustion processes. The efficiency increases with the increasing of temperature of the reactants, time that the reactants are in contact, vapor pressure, surface area, and stored chemical energy (Speight, 2011a). Despite their liquid or solid origin, hydrocarbon fuels combustion process takes places in gaseous phase (Hutter, 2008). Speight (2011a) among others indicated that for the combustion to happen the liquid hydrocarbon fuels should be in the vapor form above their flash point.

Liberman (2008) listed that industrial and internal engine combustion processes produce harmful emissions that includes: unburned hydrocarbon, carbon monoxide, oxides of nitrogen, sulfur dioxide and solid carbon particulates (soot). These emissions are environmental pollutants. In 1984, US Congress, Office of Technology Assessment (OTA) sorted out that oxides of nitrogen (NO_x) and sulfur dioxide are the main causes for acid precipitation and acid deposition (US OTA, 1984). On the other hand, hydrocarbons emitted during the combustion of the fuel, such as benzene and polycyclic aromatic hydrocarbons (PAHs) from gasoline powered vehicles are carcinogenic (Mendelsohn, et al., 2015). Flachsbart (2008) described that carbon monoxide is a colorless, tasteless, odorless gas without irritating behavior. It could enter blood stream through lung and compete for the oxygen of hemoglobin and eventually starve heart and brain of oxygen (Flachsbart, 2008). To modify the combustion both for the release quality and safety of the engine, a lot has been done. Many additives have been discovered for that matter which can improve the combustion efficiency, and some were discussed previously under the section 'uses of hydrocarbons'.

$$CH_3 - CH_2 - OH \xrightarrow{\text{yields}} H_2O + CO_2 + Enengy \qquad [49]$$

$$2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O + Energy \qquad [50]$$

The product of the burning of ethanol resulted in water vapor and carbon dioxide Eqs. [49] & [50]. On the other hand, even though saturated hydrocarbon alkane is the least reactive group of organic compounds (Stoker, 2013), they undergo two chemical reactions. The first and most important one is the exothermic reaction of the combustion of alkane that yields energy, carbon dioxide and water like ethanol. The second one is the halogenation of alkanes. Halogenation is the endothermic reaction by which the hydrogen of the alkane is substituted by halogens. This substitution reaction takes place in the presence of heat or light and undergo fluorination, chlorination, bromination or iodination specifically (Stoker, 2013). Brown, et al. (2017) described that all the densities of liquid bromoalkenes and iodoalkanes are greater than the density of water. The authors further described that even though the densities of monochloroalaknes are less than that of water, the densities of di- and polychloroalkanes are greater than that of water. Stoker (2013) stated the chlorination of alkanes does not stop at monochlorinated products but produces polychlorinated products (e.g., chlorinated methane with the presence of heat (h) or light (l), Eq. [51]). This reaction transforms alkanes which are LNAPLs to haloalkanes which are DNAPLs (Brown, et al., 2017).

$$CH_4 + Cl_2 \xrightarrow{h/l} CH_3Cl + HCl \xrightarrow{After\ 2\ more\ proc.} CHCl_3 + Cl_2 \xrightarrow{\text{h/l}} CCl_4 + HCl \qquad [51]$$

The other main problem concerning environmental contamination by petroleum hydrocarbons is from released petroleum hydrocarbons. Spill and leakage occur from crude oil production field to refinery during transportation, and underground storage tanks. Speight (2011b; 2014) among others pointed out that it is almost impossible to refine, deliver and store crude oil and its products without spills and losses. There are also occasions when petroleum hydrocarbons released to the environment intentionally. The release of petroleum from field production facilities and burning the oil wells by retreating Iraqi forces during Gulf War to slow advancing coalition forces (Karasik, 2002), the destruction of ISIS oil refining plants by Russian forces (RT, 2016) and the destruction of oil facilities including oil trucks by USA (Bender, 2015) to weaken the terrorist economically are some of the recent phenomenon.

In addition to the varying composition of crude oil and blends added prior to transportation to refinery, Speight (2014) stated that surfactants added to both blends, and to crude oil in aid of transportation, affect the physical properties when spilled and make the contamination more complex. Squillace, et al. (1997) reviewed that oxygenated gasoline with 10% MTBE by mass comes in to contact with water, up to 5000 mg/l MTBE can dissolve at 25 °C. Due to its higher water solubility, mobility in subsurface, and high vapor pressure in its pure form, MTBE can migrate both hydraulically down gradient and vertically downward through the saturated zone rapidly. Winegardner & Testa (2000) among others emphasized that thousands of USA groundwater wells have been contaminated with MTBE from underground storage tanks' gasoline leakage.

Historically, petroleum hydrocarbon is stored in underground in bulk for economical and safety purposes. Economically, the space used to store on the ground is used for another purpose, while underground storage is by far the safest approach as most petroleum hydrocarbon products are flammable (Winegardner & Testa, 2000). However, storing of petroleum hydrocarbon products in underground storage tanks has negative side effect as the leakage of petroleum hydrocarbon may happen without noticing and could contaminate large amount of adjacent soil. Dowd (1984) estimated that 10-30% of more than 3.5 million USTs used to store different products were suspected leaking. RTI (1999) among others indicated that the frequent cause for the contamination of environment by petroleum hydrocarbons in USA has been through the leaking of underground storage tanks (UST). Results from Chang & Lin (2006) shows that out of 242 storage tank accidents happened in 40 years, 74% of them happened in petroleum refineries, oil terminals or storage.

2.8. Characteristics and behavior of NAPLs in subsurface

Released NAPLs to the subsurface interacts with subsurface media: soil, water and gasses. In multiphase fluid system, one phase preferentially maintain contact with solid phase and spread over the solid surface compared to the other fluid depending on the chemistry of the solid in question. This preferential contact depends on the wettability of the media regarding each fluid (Ezekwe, 2011). In two-phase fluid system, soil and rock media are water wettability with respect to air (Mayer, et al., 2005), NAPL wettability with respect to air (van der Perk, 2006). In three-fluid phase system, air is non-wetting phase with respect to both water and NAPL (Mayer, et al., 2005). However, the wettability of the porous media with respect to water and NAPL in two-phase system and wetting phase and intermediate wetting phase in the presence of air depends on the wettability of the media with respect to water and NAPL. In the presence of little or absence of organic matter from the soil, the soil can be assumed water wettability with respect to NAPL, and a peat bog soil could be NAPL wettability with respect to water (Lowe, et al., 1999). The interaction of water, which is dipolar, to negatively charged clay is through hydrogen bonding. Tan (2011) described that organic compounds with functional groups of N–H, $–NH_2$, –OH, and –COOH groups also interacts through the formation of the hydrogen bonds between functional groups and the oxygen on the clay surface. However, NAPLs (HC compounds) are without those functional groups and they are nonpolar organic compounds (Berkowitz, et al., 2014). Organic compounds with nonpolar properties adsorbed to subsurface media with hydrophobic nature. During adsorption, according to Tan (2011) there is a competition with water molecules for the site and water is expelled.

2.8.1. Migration and distribution of NAPL in subsurface

Subsurface contamination due to NAPLs is frequently from the accidental spills and leakage of crude oil products. Migration and distribution of NAPLs depend: mainly on the volume of NAPL released (Schwille, 1984) and on area of infiltration, duration of the release, properties of the porous media it released to, and subsurface flow condition (Mercer & Cohen, 1990). When released to subsurface, NAPL migrates both downward by the force of gravity and laterally by the effect of capillary forces and porous media spatial variability (e.g., due to the layering of subsurface) (Helmig, 1997; ITRC, 2009a). Many studies show that migration and distribution are affected by the site heterogeneity (Kueper, et al., 1993; Fagerlund, et al., 2006; Yang, et al., 2013) in addition to the amount of NAPL released (Yong, et al., 2012). And even in relatively homogeneous media, micro-scale heterogeneity could exist concerning NAPL saturation (Dekker & Abriola, 2000). In the same manner, Davis, et al. (2003b) indicated that biodegradation of diesel from porous media with small-scale heterogeneity shows a high degree of variability. Lee, et al. (2001a) concluded that distribution of hydrocarbon contaminants in a shallow sand aquifer is affected by indigenous biodegradation, hydrostratigraphy, preliminary pump-and-treat remedy, recharge by rainfall, and subsequent water level fluctuation.

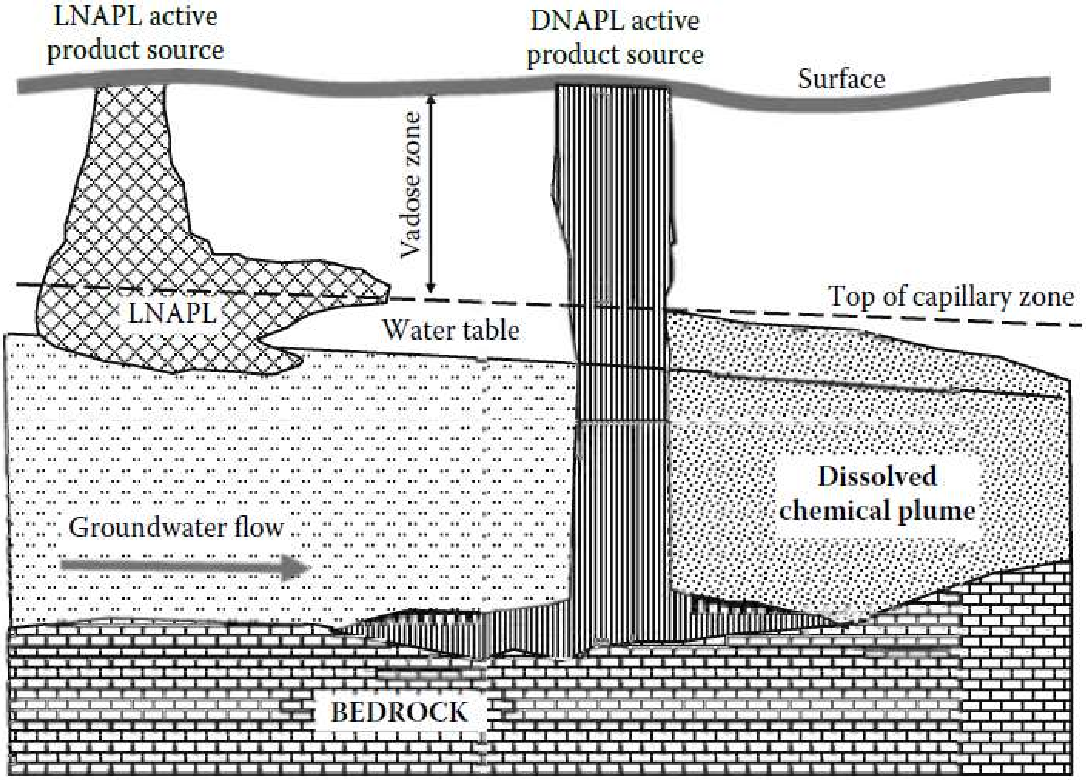


Fig. 8. Schematic illustration of LNAPL and DNAPL penetration plumes from active product sources, taken from Yong et al. (2012)

Migration of released NAPL in porous media is governed by the forces of gravity, viscous, and capillary (Mayer, et al., 2005); by permeability, viscous forces and capillary force (Ezekwe, 2011); and volume and viscosity of the released NAPL (ITRC, 2009a). Schwille (1988), Pankow & Cherry (1996) and Fountain (1998) among others described that the dense non-aqueous phase liquids (DNAPL) pass through the vadose zone downwards with relatively little spreading. It leaves low residual saturation behind compared to the light non-aqueous phase liquids (LNAPL) (e.g, petroleum hydrocarbon liquids (Charbeneau, et al., 2000; Johns, et al., 2003)). However, the entrapment of both LNAPL and DNAPL in the vadose zone are similar. Rubin (2013) indicated that they both occupy the pore volume free of residual water saturation. Once they reach the saturated zone DNAPLs keep in penetrating through it (Huling & Weaver, 1991; Redman, 2009), as they are denser than water, while LNAPLs end up on the top of the water table with the creation of LNAPL lens (Rubin, 2013). Carcione, et al. (2003) and Redman (2009) among others illustrated that DNAPL sink to the bottom of an aquifer until they get impermeable layer. Upon reaching the impervious layer, DNAPL accumulates above it in the form of a pool and moves in the direction of downward slope of the impervious surface (Bear & Cheng, 2010). Helmig (1997) mentioned that DNAPL can migrate againest groundwater flow depending on the heteroginities of the aquifer. Meanwhile, LNAPL accumulates and spreads over the surface of the saturated zone, predominantly in the direction of groundwater flow (ITRC , 2009b). Heiderscheidt, et al. (2011) described that LNAPLs tend to float on top of the water table depending upon their thickness, with some possible depression of the water table. Winegardner & Testa (2000) among others mentioned that LNAPL from water table close to ground surface will migrate back easily to the surface through vaporization and could contaminate surface water.

Groundwater table fluctuation redistribute LNAPL contaminants by partitioning them into the soil and ground water (Lee, et al., 2001a). The fluctuation creates a smear zone in the vicinity of groundwater table with LNAPL trapped in the pore spaces in the form of blobs or ganglia during rising in saturated zone (Reddi, et al., 1998) and leave behind residual fraction during falling in vadose zone (Lenhard, et al., 2004; Kechavarzia, et al., 2005). Reddi et al. (1998) and Lee, et al. (2001b) among others mentioned that smearing results in dissolution of LNAPL and contaminants mass loss through natural attenuation mainly through biodegradations. Works by Cassidy (2007) shows that the most attenuation of LNAPL in the study was around the smear zone. Lundegard & Johnson (2006) found that yearly mass loss rate from source zone above water table was two orders of magnitude higher than that of submerged part of the source zone through natural attenuation processes from formerly petroleum hydrocarbons contaminated site. Dobson, et al. (2007) argued that despite it increases biodegradation, groundwater fluctuations could increase the exposure of receptors down gradient.

Soil contamination by NAPL has been a growing concern and RTI (1999) pointed out that it can be a source of contamination to groundwater. NAPL contamination reduces the usability of land for development and above all, some petroleum hydrocarbon products may remain in the soil for years. Volatile hydrocarbons (VHCs $< C_{12}$) mainly benzene, toluene, ethylbenzene and xylenes and commonly known as BTEX are the main component of oil transported down gradient in contaminant plume (Baedecker, et al., 2011). On the other hand, hydrocarbons with carbon number greater the 12 are les soluble in water. They could remain in subsurface as contaminant plume for longer time and functions as a potentially long-lived source zone to adjacent soil, soil gas and groundwater (ITRC, 2009a). Result from Kim & Corapcioglu (2003) showed that most of the jet-fuel spilled mass remained as free LNAPL after 20 years. The existence and migration of LNAPL in subsurface for a long time will cause contamination to more groundwater and soil. ITRC (2009a) listed that sorption, dissolution and volatilization are the mechanisms by which petroleum hydrocarbon products released to the soil may be removed overtime. The behavior of NAPL changes overtime due to the degradation of its components in addition to the partitioning of its components to aqueous, gaseous and solid phases (Davis, et al., 2006).

2.8.2. Wettability and contact angle

Wettability of the media depends on the material from which the media itself made up of and the fluid in contact with. Therefore, porous media has different affinity for different fluids. In two phase fluids flow, one of the two phases readily wet the grain than the other one does. A force balance between adhesive and cohesive forces determines the degree of wetting (wettability) (Wu, 2016). In another way, Mayer, et al. (2005) explained that the wetting phase exhibits a stronger affinity for the particle(s) which costs the non-wetting phase the surface of the grains and removes it towards the interior of the pore spaces. The wettability of the grains surfaces of the soil that form pores revealed by the interfacial tension between the fluids in the pore (Delleur, 2003). Hence, the wettability of a solid surface towards two phases can be quantified by the contact angle between the solid and a fluid surrounded by a background reference phase. Hillel (1998); Mayer, et al. (2005); Ezekwe (2011) and Blunt (2017) among many other authors specified that, a contact angle of zero shows a perfect wetting, and of less than 90^o indicates the testing fluid is the wetting phase. The authors further described that a contact angle greater than 90^o shows the test fluid is non-wetting while 90^o is a neutral-wetting phase. However, as mentioned in van der Perk (2006), Anderson took 70° to 110° as neutral-wetting phase value. Meanwhile, rock in the oilfield can be categorized as strongly water-wet if the contact angle is 0-70°, strongly oil-wet if the contact angle is 110°-180° and has intermediate wettability if the contact angle is 70° -110° by using water as the testing fluid (Tiab & Donaldson, 2016; Schön, 2015; Dandekar, 2013).

Natural subsurface system consists of solids (soil grains or rock) are water wettability (Mayer, et al., 2005). Delleur (2003) and Mayer, et al. (2005) mentioned that, however, in very dry soil, NAPL can be the wetting liquid with respect to water and air. Carbonate materials and soils with high organic matter content under natural systems are NAPL wettable with respect to water (Mayer, et al., 2005). Roosta, et al. (2015) concluded that increasing temperature changes the wettability of carbonate rocks toward water wet. Lyons (2010) stated that pure and clean silica is water wettable with respect to any hydrocarbons. Domenico & Schwartz (1998) generalized that rock forming minerals are water wettable with respect to NAPLs while organic matter, such as humus in soil are NAPLs wettable with respect to water. On the other hand, particles in saturated zone are water wet with respect to NAPL (Mayer, et al., 2005). In the three-phase fluids system consisting air, water and NAPL (Fig. 9) and where water is a wetting fluid, air is a non-wetting fluid and NAPL is an intermediate wetting fluid (Mayer, et al., 2005). Hui & Blunt (2000) showed that, however, in strongly oil-wet meida gas could be an intermediate wetting phase.

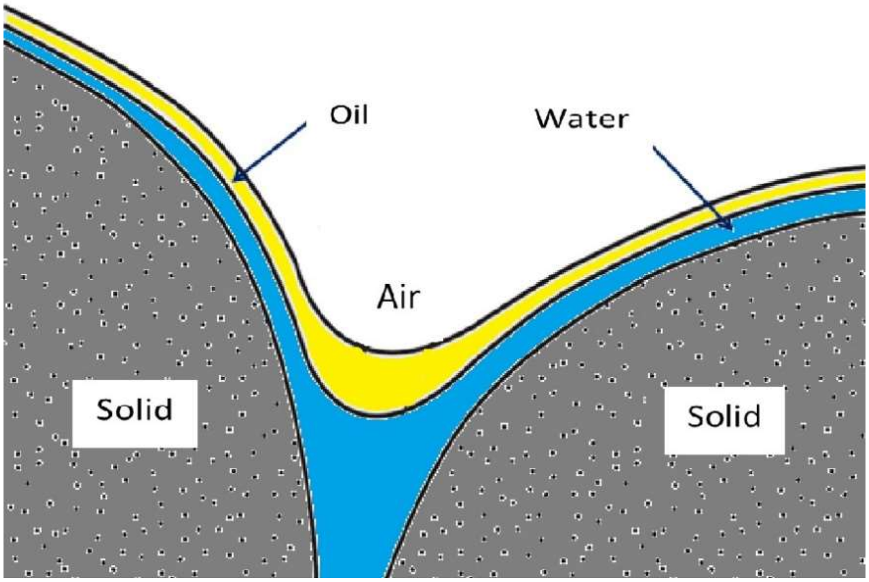


Fig. 9. Schematic pore cross-section with three fluid phases, taken from Bear and Cheng (2010) and modified.

2.8.3. Viscosity of the liquids

Flowing liquid faces resistance from both within the liquid itself and immediate environment in contact. The measure of this internal resistance to flow due to intermolecular forces is known as viscosity. It is a fundamental and non-equilibrium property of the liquid (Viswanath, et al., 2007). This drag force according to Viswanath, et al. (2007) and Bhushan (2013) among others is a measure of frictional properties of the fluid and a function of temperature and pressure. Fluids' viscosity which are dependent on only temperature and pressure are Newtonian fluids. Temperature has different impact on liquids and gases. In liquid, the increment of temperature decreases intermolecular forces due to the expansion which takes the molecules far apart results in the decrement of the viscosity of the liquid (Bhushan, 2013). When pressure increases, the molecules are forced closer together which resulted in the increment of intermolecular forces and that increases the viscosity of the liquid (Klaus & Tewksbury, 1988). The response of the viscosity of petroleum-based oil to the pressure is fast. Bhushan (2013) explained that it could be to several orders of magnitude and some oil become plastic at 200 MPa. For gas, however, the increment of the temperature increases the viscosity by increasing the transfer of momentum due to the increase in the velocity of the molecules (Klaus & Tewksbury, 1988) but fairly dependent on pressure (Compressed Gas Association, 2003). However, some types of fluids are dependent on shear rate and shear stress in addition to temperature and pressure, and such fluids are non-Newtonian fluids. The viscosity of the gas is only dependent on pressure and temperature and hence gas is purely Newtonian fluid (Compressed Gas Association, 2003). Most liquids including water and mineral oil fractions of hydrocarbons, and true solutions of lower molecular weights are Newtonian (Klaus & Tewksbury, 1988), while polymer solutions (Poling, et al., 2001), inorganic glasses, soap solutions, liquid crystal, and two-phase fluids (Bird & Wiest, 1999) are non-Newtonian fluids.

This property of fluids due to flow is unique for a fluid of single-phase flow at a given pressure, temperature and shear stress; but, viscosity of mixed liquids flow is dependent on the contribution of each components. However, Brennen (2005) considered homogenous or thoroughly mixed flow solution as single-phase flow by taking its effective density, effective viscosity and flow volume. But, Dullien (1992) argued that the concentration of the fluids during the miscible displacement of one fluid by another is dynamic with respect to time and location and hence it yields different viscosity and density of the fluid mixture at different time and location. For higher contrast in viscosities of the fluids flowing, Carlson (2006) described that miscible displacement could be sensitive to porous media heterogeneity and may form viscous fingering. In the case of multiphase flow in general and immiscible displacement, each of the fluids in the flow system tend to keep its identity by flowing in separate channels (Dullien, 1992).

Viscosity ratio of the liquids is one of the main factor which governs immiscible displacement of NAPLs in porous media (Saeedi, 2012) and affects the displacement efficiency of water flooding in oil recovery (Don & Paul, 1998). Viscosity ratio is the ratio between the liquid at a place (mostly oil) and advancing liquid (commonly water). Enhanced (tertiary) oil recovery methods are designed to reduce the viscosity of the crude oil (Speight, 2016). The viscosity ratio can be decreased either by increasing the viscosity of the injected water (by the addition of appropriate polymer) or by increasing the reservoir temperature (Chierici, 1995). Larson, et al. (1982); Dawe (1991); Wang, et al. (2011); Zou, et al. (2012); Wang (2013); Gou, et al. (2015); Wei, et al. (2017) and Weidong, et al. (2017) among others indicated that chemicals (e.g., polymers) improve the mobility ratio through favoring viscosity ratio. Hornof & Baig (1995) among others showed that keeping the viscosity of the displaced fluid below the viscosity of the displacing fluid increases the displacement efficiency through favoring mobility ratio. Unfavorable viscosity ratio (when advancing fluid displaces a more viscous fluid at a place) may give rise to viscous fingering due interfacial instability (Peters & Flock, 1981; Homsy, 1987; Bacri, et al., 1993; Jackson, et al., 2015). Viscous fingering affects fluid residual saturation and relative permeability (Saraf & McCaffery, 1985). It also reduces the sweep efficiency of the reservoir during oil recovery (Wang, 2013).

2.8.4. Interfacial tension and capillary pressure

In porous media, tension force is created at the contact area of two immiscible fluids. Ayirala & Rao (2008) explained that it is due to the imbalance between the molecular attractive and repulsive forces. The tension is usually referred as surface tension if it is between a liquid phase and a gas phase fluid, and interfacial tension if it is between two immiscible liquids (Donnez, 2007; Speight, 2014). Both tension forces are the function of temperature and pressure. Additionally, however, surface tension is a function of the phase compositions. The interface is sharp between the liquids, and hence, the properties of the phases are varying on either side of the interface created. Interfacial tension between two liquids of interest is less than the surface tension of the liquid with higher tension (Dimri, et al., 2012) and often between the values of surface tension of the two liquids (Lyons, 2010). The separation region between the two phases is not really a two-dimensional surface and Coutelieris and Delgado (2012) described it as very small but non-zero thickness with a few molecular radii (of the order of one hundredth of a micron). However, the presence of this very small area creates a pressure difference, known as capillary pressure across the contact surface (Donnez, 2007).

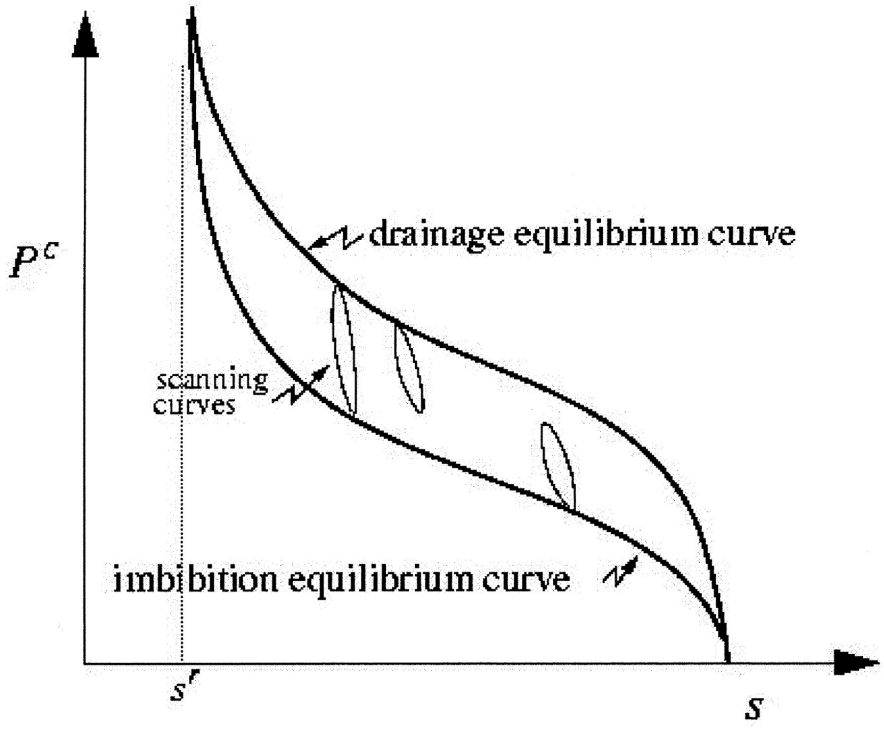


Fig. 10. Graph of typical capillary pressure vs. wetting phase saturation curve, taken from Hassanizadeh et al. (2002)

Capillary pressure is a function of interfacial tension and curvature of the interface (Lyons & Plisga, 2005) and contact angle of the wetting fluid (Dimri, et al., 2012). It is linearly proportional to interfacial tension and contact angle or wettability, but inversely proportional to the effective radius of curvature (Donnez, 2007). Wettability is an adhesive force while interfacial tension is a cohesive force. Dolson (2016), however, described that both forces work together, and overcoming capillary pressure means overcoming these two resistive forces. In the description of multiphase flow and unsaturated flow through porous media, capillary has the main role (Hassanizadeh, et al., 2002). For two-phase fluid system in porous media, pressure is high in non-wetting fluid than in wetting fluid. In water wettable media, for example, pressure is higher in oil than in water (Donnez, 2007). However, in big radius of curvatures, the interface is flat and pressures in both fluids are equal as wetting phase could not rise due to the distribution of wetting force over larger perimeter (Donnez, 2007). Petroleum products show little variations in surface tension (Speight, 2014). Lyons (2010) described that surface tension of hydrocarbon decreases both with increasing temperature and the presence of dissolved gases. The reduction of interfacial tension with increasing temperature compared to surface tension, however, is more noticeable (Lyons, 2010). On the other hand, Hjelmeland & Larrondo (1986) concluded that interfacial tension between the crude oil and reservoir brine decreases with increasing temperature under aerobic condition but increases under anaerobic condition; whereas under constant temperature interfacial tension increases with increasing pressure.

In porous media, capillary pressure works against the interfacial tension between NAPL and aqueous phase in squeezing out oil droplet through the pore throat. Dimri, et al. (2012) discussed that the impact is higher for a small pore diameter. They can be related and gives capillary number (Nc). Mwangi & Rao (2014) and Tiab & Donaldson (2016) among others defined the capillary number as the ratio of viscous force to capillary force that affects the flow of fluid in porous media. It reflects the balance between the two forces at pore level (Speight, 2017) and defined as Eq. [52]. At higher capillary number viscous force dominates while at lower capillary number capillary forces (the effect of interfacial tension between liquids) dominates over viscous force (Alvarado & Manrique, 2010). Capillary number can be increased either by increasing the velocity of the advancing liquid or by lowering the interfacial tension between the advancing liquid and liquid at a place by applying surfactant or alkaline flooding (Sharma & Shah, 1989; Sheng, 2011). Satter, et al. (2008) mentioned that increasing Nc through the injection of surfactants has a great significance on enhanced oil recovery. Dimri, et al (2012) explained that a saturating and wetting fluid can be displaced from porous media by invading fluid if the pressure of the invading fluid is at least equal to the capillary pressure of the largest pore; however, if the saturating fluid is non-wetting, it can be displaced spontaneously by evading fluid. Dong & Dullien (2006) stated that when the wetting phase displaces the non-wetting phase, the displacement is partially or fully driven by capillary pressure; otherwise it opposes the displacement.

$$N_c = \mu v / \gamma cos\theta \qquad [52]$$

Where: μ is the water viscosity, v is the linear advance rate, γ is the oil-water interfacial tension and θ is the contact angle.

2.8.5. Permeability

Most natural porous media store and transmit the liquid under pressure gradient. The property of the porous media (soil, sediment and rock) to allow the pass of the liquid through itself is known as permeability. Permeability of the porous media is the sole characteristics of the porous media irrespective of the type of liquid flow through it (Lyons & Plisga, 2005). However, this works only for the porous media with one fluid only. The saturation of the media could be 100% by the fluid of interest, and the permeability is known as absolute permeability (Buryakovsky, et al., 2012). Porous media also allow the flow of one fluid through itself in the presence of another fluid, and permeability under such condition is known as effective permeability (Lyons & Plisga, 2005). Theoretically, the absolute permeability of a given porous media is a unique number while that of effective permeability varies from zero to the value of absolute permeability depending on the amount of the other fluid present in the porous media during the flow. These two types of permeability can be related to each other by third form of permeability known as relative permeability. Relative permeability is the ratio of effective permeability to absolute permeability and its value varies between 0 and 1 (Satter, et al., 2008).

In most of the pores of porous media, for example in petroleum reservoir (Satter, et al., 2008), there is a simultaneous presence of different fluid phases. It could be the combination of two phases of gaseous, water or non-aqueous phase liquid or the existence of the three phases together. The concept of effective permeability implies that except one phase the other fluid phases of interest are mobile (Buryakovsky, et al., 2012). The presence of immobile phase affects the flow of the other fluid phases and Satter, et al. (2008) described that the mobile phase experiences the decrease in flow. Baker, et al. (2015) generalized that relative permeability depends on wettability and pore structure of the porous media, capillary to viscous forces ratio and interfacial tension of the fluids of interest, and saturation history.

The wettability preference of the porous media in which flow takes place towards phases determines the magnitude of effective permeability. Wetting phase occupies the surface of solid mineral of the porous media while non-wetting phase occupies the center of the pore (Mayer, et al., 2005; Buryakovsky, et al., 2012). In oil-wet porous media, according to Satter, et al. (2008), e.g., water has less affinity to the wall of the pores which makes it mobile phase at relatively less saturation and oil recovery from such fields are less optimistic. However, at relatively higher saturation the wetting phase can be displaced by non-wetting phase (drainage) while the displacement of non-wetting phase by wetting phase (imbibition) is possible even at relatively less saturation (Baker, et al., 2015). The relative permeability of a fluid increases non-linearly with an increase in the saturation of the phase (Satter, et al., 2008). The presence of isolated blobs of non-wetting phase in bigger pores inhibits the flow of the wetting phase. Mayer, et al. (2005) stated that the maximum relative permeability of the wetting phase is less than the maximum value of the non-wetting phase.

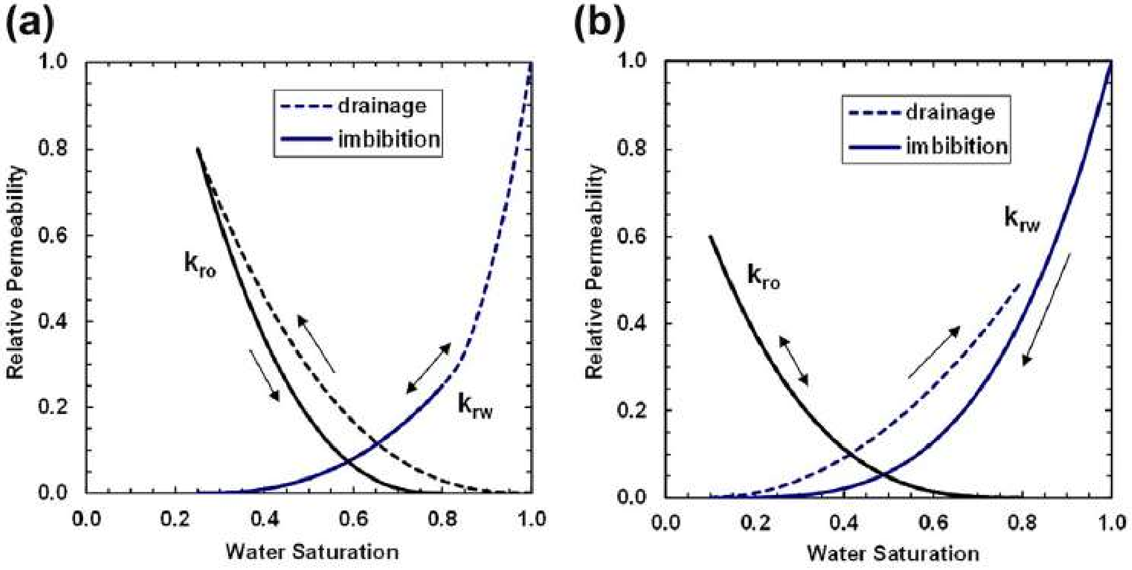


Fig. 11. Diagram of drainage and imbibition hysteresis in water-oil relative permeability data: (a) water-wet rock and (b) oil-wet rock, taken from Baker, et al. (2015)

The mobility of a fluid in a porous media can be described by the ratio of the permeability of the porous media to the viscosity of the fluid Eq. [53] (Lyons & Plisga, 2005; Fanchi, 2010).

$$\lambda = k/\mu \qquad [53]$$

Where: λ is fluid mobility (md/cp), k is effective permeability of the media (md) and μ is fluid viscosity (cp)

If the flowing fluids through the media are more than one, and one fluid displaces the other, the mobility is described by the mobility ratio (m) of the displacing to displaced fluids Eq. [54] (Satter, et al., 2008; Ezekwe, 2011; Sahimi, 2011). Usually oil is viscous and less mobile than water (Bedrikovetsky, 1993) and it results in unfavorable higher mobility ratio (Wang, 2013). The more mobile water tends not to displace oil (Bedrikovetsky, 1993). Kumar, et al. (2008) summarized that in higher mobility ratio, viscous fingering dominates and results in lower oil recovery efficiency. Satter, et al. (2008) among others stated that mobility ratio can be lowered by either lowering the viscosity of the oil or by increasing the viscosity of the displacing liquid (water). Methods used to increase viscosity ratio is used in favoring mobility ratio also. The mobility ratio is favorable if the mobility of the displacing fluid (water) is less than the mobility of the displaced fluid (oil). Fanchi (2010) mentioned that mobility ratio greater than one is unfavorable in displacement process.

$$\mathrm{M} = \frac{k_{rw}/\mu_w}{k_{ro}/\mu_o} = k_{rw}\mu_o/k_{ro}\mu_w \qquad [54]$$

Where: M is mobility ratio, k_{rw} and k_{ro} are relative permeability of water and oil respectively, μ_w and μ_o are water and oil viscosity respectively

2.8.6. Fate and transport of LNAPLs in subsurface

The phase state of the contaminant is a critical property when comes to its fate and transport in subsurface. Pepper, et al. (2006) stated that highly water-soluble chemicals are more readily transfer to aqueous phase and transported by water flow. The authors added that volatilization or evaporation could be the fate of the chemicals with moderate to high vapor pressure and transported as gaseous phase both in vadose zone and in atmosphere. Concerning NAPLs contaminated soils which are cross-media in nature (e.g., movement of NAPL in soils to groundwater) requires analysis of chemical fate and transport (Gustafson, et al., 1997). The fate and transport of NAPLs in subsurface is determined by many factors. It is mainly due to chemical and physical properties of the NAPL itself, geochemical conditions and hydrogeologic media into which the product has been released to (Day, et al., 2001).

Mass transfer of NAPL released to subsurface media (soil and water) takes place through the processes of volatilization, sorption, aqueous phase migration, retention (Winegardner & Testa, 2000) or it remains as blobs, ganglia or NAPL pool (Fitts, 2013). However, the share of each processes depends on the chemical composition of the released NAPL that could contribute to the individual processes. Volatile components of the released NAPL evaporates mainly in the vadose zone (Kresic, 2007). The dissolved portion of the released NAPL migrates as aqueous phase liquid through the processes of advection, dispersion and diffusion while the non-dissolved NAPL migrates as non-aqueous phase liquid (Winegardner & Testa, 2000). Mayer, et al. (2005) among others indicated that the non-aqueous phase could be the natural source zone and further contaminates down gradient media.

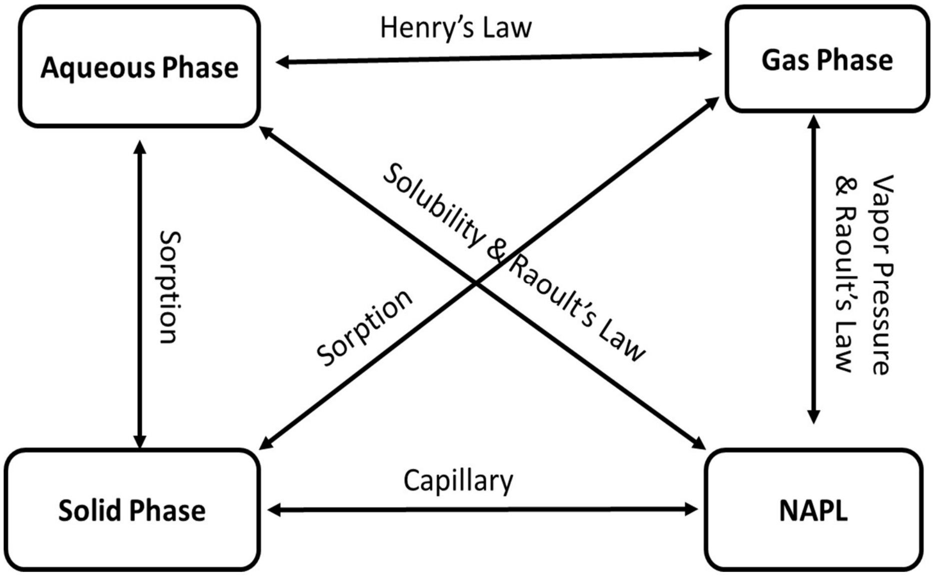


Fig. 12. Simplified conceptual view of phase equilibrium relationship used for interphase mass transfer of chemical/organic components in subsurface (Mayer, et al., 2005; Paspaliaris, et al., 2010)

2.8.6.1. Volatilization

PHCs from both contaminated groundwater and vadose zone migrate back to the upper subsurface by volatilization process through soil pores. Volatilization represents a source to subsurface vapor transport (Kresic, 2007). HCs forms two phase NAPL-water system in saturated zone and three phase NAPL-water-air in vadose zone (Petri, et al., 2014). Migration of HCs through volatilization in subsurface depends on the components of PHC itself and subsurface characteristics. Temperature is the driving force for the volatilization process under natural condition and according to Winegardner & Testa (2000) among many other authors, thermal energy enables the molecules in liquid or solid phases to overcome intermolecular forces in transferring them to vapor phase. Volatilization of NAPLs according to Cohen & Mercer (Cohen & Mercer, 1993) and Kresic (2007) are affected by many factors: vapor pressure, aqueous solubility, concentration of NAPL in the soil, soil moisture content, soil air movement, sportive and diffusive properties of the soil and bulk soil properties such as organic carbon content, porosity, density and clay content. NAPLs mass transfer rate through volatilization is limited in saturated zone (Braida & Ong, 1998; 2000) and decreases with increasing soil water in vadose zone (Yoon, et al., 2003; Oostrom, et al., 2005b). However, the vapor phase mass transfer increases with both pore gas velocity and grain size (Anwar, 2013) but inversely related to volumetric NAPL content of the porous media (Anwar, et al., 2003). The mass transfer through volatilization increases with the soil particle size, diffusivity of the NAPL and air velocity but inversely related to the Henry's law constant (Braida & Ong, 1998; Chao, et al., 2008) and decreases with the increase of soil bulk density and organic matter content (Hayden, et al., 1997).

At a given temperature, vapor pressure which is the equilibrium partial pressure in the atmosphere or air space surrounding the compound is a characteristic of any volatile liquid or solid. Winegardner & Testa (2000) mentioned that vapor pressure of a given substance at a given temperature is the same weather it is in the pore of the vadoze zone or in the atmosphere above an open disposal trench. The fate of volatilized HCs in subsurface could be escaping to the atmosphere following concentration gradient, adsorption to soil particles, destruction by biological activities, or re-solution by percolating water (Winegardner & Testa, 2000). Volatile HCs (VHCs) in subsurface can migrate and ultimately condense, sorb onto soil particles, dissolve in groundwater, degrade or escape to the atmosphere (Kresic, 2007).

Generally, the volatility of HC decreases with the increasing of the number of carbon atom per molecule. HCs with less than twelve carbon atoms per molecule commonly known as BTEX (benzene, toluene, ethylbenzene and xylenes) are Volatile. The potential for a chemical to volatilize from the water to the air space or atmosphere can be estimated by Henry's law. The law states that, in a very dilute solution, the vapor pressure of a chemical should be proportionate to its concentration, Eq. [55] and described as follows:

$$P = K_h C \qquad [55]$$

Where: P is vapor pressure, K_h is Henry's law constant and C is concentration of chemical in water

2.8.6.2. Sorption

In contaminated subsurface, molecules of the contaminants dissolved in water or from gas, often in the form of organic carbon, can be attached to the soil particles through sorption process. The process is the most significant factor attuning the movement of chemicals through the soil (Nicholis, 1991). However, even though this process could minimize the risk of groundwater from contamination through retardation, Albarrán, et al. (2003) mentioned that the less mineralization and longer persistence is the fate of some sorbet (organic chemicals) in the top soil. Sorption of HCs could be either through the attachment of the contaminant molecules to the surface of the soil particles (adsorption) or through incorporation of the contaminant molecules in to the structure of the soil particles (absorption) (Kresic, 2007). The sorption could be physical or chemical, and physical sorption which is the result of the van der Waals force is weaker compared to chemical sorption (Winegardner & Testa, 2000).

HCs tend to preferably adsorb onto organic carbon that could be found in the soil as film on individual soil grain, as discrete solids, or as a stringer of organic material in the soil (Kresic, 2007). Soil organic matter content is the determinant factor than other soil properties according to Nicholis (1991) for the sorption of non-ionized chemicals. However, organic matter plays only a minor role in vapor phase sorption at lower soil moisture content (Steinberg, et al., 1996). Ruiz, et al. (1998) argue that water affects the adsorption of VOCs by decreasing the retention of VOCs to a greater extent for aromatic and aliphatic compounds than for the polar compound. Significant amount of VOCs sorbed and stored in the upper part of the soil during dry season but released during subsquent increases in soil water content (Poulsen, et al., 1998). Due to their higher specific surface area, clay minerals could be also considered good sorbents for nonionic compounds in general and HCs in particular (Site, 2001). The larger the specific surface area, the greater the sorption (Winegardner & Testa, 2000). Clay minerals are dominant sorption sites in areas with high clay concetrations and low total organic carbon concetrations (Kresic, 2007).

2.8.6.3. Dissolution

Organic pollutants enter subsurface as slightly soluble NAPL or as dissolved solutes (Essaid, et al., 2015). If NAPLs were truly insoluble in water and remain as non-aqueous phase liquid as their name indicate, their impact on groundwater quality would be minimum (Mayer, et al., 2005). However, even though the solubility of NAPLs in water is in small amount and at low rate, Weiner (2013) mentioned that small volume of NAPLs could contaminate large amount of soil and groundwater due to their high toxicity. The solubility of NAPLs is higher than the acceptable drinking water standards (Redman, 2009). Hadley & Newell (2012) emphasized that it is very difficult to achieve drinking water standards at contaminated groundwater sites with the existing remediation technologies. Testa and Winegardner (2000) mentioned that dissolved constituents of LNAPL mainly BTEX are among the concerns related to the environment. Interstate Technology & Regulatory Council (ITRC, 2009a) defines free NAPL in subsurface as natural source zone (NSZ) and is the cause for further contamination to down gradient groundwater and soil. Solubility of NSZ is one of the causes of NAPL distribution mechanism by which aqueous phase HCs contaminate down gradient groundwater due to mass transfer from non-aqueous to aqueous phase through dissolution process.

Heyse, et al. (2002) summarized that dissolution of NAPLs in subsurface is influenced by the chemical composition and physical attributes (viscosity, density, hydrophobicity, etc.) of the NAPLs, water flow dynamics, aquifer-scale distribution of the NAPLs and the grain-scale geometry and heterogeneity of the subsurface matrix. Generally, solubility of HCs liquid from the same family (homologous) decreases with increasing the number of carbon atoms per molecule (Yaron, 1989; Verweij, 1993; Paradowski, 1995; Dembicki, 2017). Dembicki (2017) stated that for a given carbon number saturated compounds are less soluble than aromatic compounds and within saturated group the solubility increases from straight-chained to branched-chained alkanes while the ring one is the most soluble. Amirijafari & Campbell (1972) Showed that at the same temperature and pressure the solubilities of binary and ternary HCs mixtures are greater than that of the pure components. Results from Baedecker, et al. (2011) show that BTEX are the main components of PHC transported down gradient in oil contaminant plumes that resulted from the spill of crude oil. However, LNAPL with more carbon atoms per molecule are less soluble in water and remain in subsurface for longer time as LNAPL and be a natural source zone (ITRC, 2009a). Studies from Powers, et al. (1993) show that dissolution of NAPLs in saturated subsurface depends on the distribution of entrapped NAPL and aqueous phase velocity. Miller, et al (1990) showed that the mass transfer between the two phases directly related to aqueous phase velocity and non-aqueous phase fluid saturations in experimental column. Braida & Ong (2000) argue that dissolution rate of NAPLs is strongly affected by porous media particle size, with direct relationship during air sparging remediation process.

Physical distribution of NAPL components as aqueous phase liquid and biological break down are the main processes by which NSZ is depleted (ITRC , 2009b). Biodegradation in subsurface is a redox reaction that takes place through electron accepting processes and fermentation (Essaid, et al., 2015). Dissolved oxygen, nitrate, iron and manganese oxides, sulfate, and carbon dioxide are the most important electron acceptors under natural condition (McCarty & Criddle, 2012). Aerobic biodegradation of HCs is more important in unsaturated zone (Lahvis, et al., 1999) and very limited in saturated zone due to low solubility of oxygen and its slow replenishment (Essaid, et al., 2015). Another reason for the limit of oxygen in saturated zone could be the consumption of oxygen in aerobic biodegradation process above the water table (Ostendorf & Kampbell, 1991). Anaerobic biodegradation plays a major role in degrading HCs from crude oil spill site (Essaid, et al., 1995) and subsurface crude-oil reservoir (Jones, et al., 2008) compared with aerobic biodegradation. With the presence of hydrocarbon-degrading microbial populations, anaerobic biodegradation of HCs potentially depends on electron acceptors (Leahy & Colwell, 1990). Anaerobic biodegradation uses nitrate (Widdowson, et al., 1988; Coates, et al., 2001); manganese oxides (Mihelcic & Luthy, 1988; Lovely, et al., 1989); ferric oxy-hydroxides (Cho, et al., 1997; Lovely, et al., 1989; Chapelle, et al., 2002) or sulfate (Edwards & Grbić-Galić, 1992; Coates, et al., 1997; Anderson & Lovley, 2000) as electron acceptors.

In electron acceptor-depleted sites and conditions, HCs can be degraded to methane by methanogenic microbial consortia (Gray, et al., 2010). The process is responsible for the formation of heavy oil deposits and oil sands (Jiménez, et al., 2016) and biodegradation of 36% of crude oil spill (Essaid, et al., 1995). Result from Ng, et al. (2015) showed that methane and CO_2 (greenhouse gases) were responsible for 70% of crude-oil source zone carbon lose through unsaturated zone. Methanogenic HCs degradation is sustainable over geological time scales (Gray, et al., 2010), because CO_2 which is the only electron acceptor to sustain the intermediate steps of the whole process is a net product of the overall reaction (Jiménez, et al., 2016). Methane produced through methanogenic process in saturated zone exceeds the aqueous solubility (Essaid, et al., 2015) which causes the transport of methane through unsaturated zone (Amos, et al., 2005). During the transport, methane reacts with oxygen, and according to Molins & Mayer (2007) the reaction causes the downward advection of oxgen from the surface which enhance the reaction rate.

2.8.6.4. Aqueous phase transport

Groundwater table fluctuations and water infiltration dissolve NAPLs in unsaturated zone and transport them to the aquifer (Radilla, et al., 1998). Dissolved organic compounds from unsaturated zone with dissolved organic compounds in saturated zone in aqueous phase are transported through the aquifer by the physical processes of advection, hydrodynamic dispersion and molecular diffusion (Winegardner & Testa, 2000). Of the three transport processes, advection is the most important and active process for the transport of dissolved chemicals in subsurface (Heiderscheidt, et al., 2011). It is the process in which dissolved substances or solutes are transported along with the bulk movement of groundwater down gradient (Murgulet, 2017). The process can be described by Darcy's Law and its flow velocity can be determined from average saturated hydraulic conductivity (Domenico & Schwartz, 1998; Fetter, 2000), Eq. [56] and mass flux due to advection only (Fitts, 2013, Eq. [57]).

$$v_x = K/n_e(\Delta h/\Delta L) \qquad [56]$$

$$F_{ax} = qC \qquad [57]$$

Where: v_x is average linear velocity; K is saturated hydraulic conductivity; n_e is effective porosity, $\Delta h/\Delta L$ = hydraulic gradient, F_{ax} is the advective flux of solute mass in the x direction through the area normal to the flow direction, q is specific discharge and C is solute concentration.

Advection transport process does not only transport contaminants from one place to another but also spread or disperse them on the way (Fitts, 2013). Heiderscheidt, et al. (2011) described that the process is known as dispersion and it is mainly controlled by the heterogeneity of the subsurface. This mixing process due to the variation of the velocity in the porous media causes the spread out of the contaminants (Illangasekare, et al., 2011) and the dilution of the contaminants at the advancing age (Suthersan, et al., 2017). The dilution makes more oxygen available for NAPLs' aerobic degradation (Blanc, et al., 1996). However, even though the process employs the lateral spreading of the solute, Heiderscheidt, et al. (2011) generalized that the process is much more coincident with the direction of groundwater flow direction than to its transverse. It has two components, and mechanical dispersion results from differences in length flow paths or tortuosity of flow paths (Winegardner & Testa, 2000), while hydrodynamic dispersion results from local scale variations in advective velocities (Suthersan, et al., 2017). Nevertheless, the two components are not mutually exclusive (Vallero, 2004). Fetter (2000) illustrated that some fluid flows through longer pathways than other fluid, while fluids move faster at the center of the pore than its wall, and those fluids travel through larger pores' networks move faster than those through smaller pores' networks. The adsorptive behavior of individual contaminants with respect to the matrix affects overall dispersive processes as non-adsorbing contaminants move with groundwater while adsorbing contaminants are retarded (Logan, 2012).

In addition to the movement with groundwater through advection process following hydraulic gradient and the lateral spreading through mechanical and hydrodynamic dispersion (Fetter, 2000), dissolved chemicals including organic compounds according to Winegardner & Testa (2000) travel randomly from area of high solute concentration to lower concentration by the process of diffusion. This process is the result of kinetic energy of each molecule and driving force of entropy and hence the process may take place against hydraulic gradient. But, Heiderscheidt, et al. (2011) pointed out that diffusion process is the slowest of the three processes.

These processes are not independent of each other's, rather it is difficult to separate one from the other. For the advection and dispersion processes many equations have been developed. Ogata (1970), for example, developed an equation for advection-dispersion transport process based on the premise of the center of the mass of the solute is moving at the same rate as the average linear groundwater velocity with statistically normal distribution by spreading out both ahead of and behind the center of the mass. Heiderscheidt, et al. (2011) developed another equation for advection-dispersion transport process which describes the change in the concentration of the species over the time.

2.8.6.5. Free LNAPL in the subsurface

Fitts (2013) described that most organic contaminants start their trip to subsurface as NAPL. Released NAPL interacts with the subsurface media through the processes of volitalization, sorption, aqueous phase migration, and liquid phase migration and detention (Winegardner & Testa, 2000). Mercer & Cohen (1990); Haridy, et al. (2004); Francisca & Montoro (2014) and Comegna, et al. (2016) among others described that NAPL in the soil can be in the form of disconnected immobile gangila and blobs, or mobile pool. A significant amount of released HCs to subsurface remains as free LNAPL for longer time. Free LNAPL is the portion of LNAPL that is not entrapped as a residual saturation but mobile (Johns, et al., 2003). Kim & Corapcioglu (2001;

2003) showed that 20 years after the release to the subsurface, most of the spilled jet fuel mass remained as free NAPL (76.4%). NAPLs can be found in vadose zone separated from the main body of NAPL and trapped in the form of blobs and ganglia, and in saturated zone in the form of ganglia and NAPL pool (Chrysikopoulos, 2005). Blobs and ganglia in the vadose zone held in place by sorption and capillary forces while NAPL pool in contact with saturated zone is free and mobile (Weiner, 2013). Groundwater fluctuations and flow, and infiltration from rain and other surface water through blobs, ganglia and NAPL pool dissolve small fraction of NAPLs slowly into to the aqueous phase and forms contaminant plume downstream (Soga, et al., 2004). Chrysikopoulos (2005) notified that the dissolution of NAPLs from NAPL pool is less than that of from residual blobs due to the limited contact with ground water. Due to persistence of NAPL pools for longer time, they could be long-lasting NAPL source zone groundwater contaminant (Held & Celia, 2001; Chrysikopoulos, 2005).

2.8.6.6. Detection, characterization and monitoring of NAPL in subsurface

Released petroleum hydrocarbons to environment can be known at the time of the spill, through inventory monitoring or only after it appears in surface water or ground water wells (Charbeneau, et al., 2000). Under ideal condition, visual analysis of samples from contaminated site could be possible for the presence of NAPLs (Cohen, et al., 1992). The authors added that the method is difficult for samples where the NAPL is clear and colorless, present at low saturation or distributed heterogeneously. US EPA (1992) emphasized that inexpensive field method is very important for rapid detection of NAPL zones to characterize contaminated site. To understand the environmental conditions and the nature and extent of the contamination, and for the success of monitoring and cleanup, the contaminated site should be thoroughly and accurately characterized (Nielsen, et al., 2006). NAPLs contaminated site can be characterized using results from core sampling, cone penetrometer testing, geophysical logging, and tracer test methods (Jin, et al., 1995).

Kvapil & Mares (2003) suggests cone peneteration logging which is a combination of cone penetration test and geophysical logging for the detection of total petroleum hydrocarbon content from shallow unconsolidated soil material. Stewart & North (2006) showed that cone-penetrometer testing is suitable for the detection of the contaminants from saturated, unconsolidated soils contaminated with DNAPL. The presence, and potential for NAPLs and dissolved constituents of petroleum hydrocarbons presence in subsurface can be detected by drilling borings and subsequently installing monitoring wells (Winegardner & Testa, 2000).

Monitoring wells with tracers are used for the detection of contaminants in the subsurface. Several tracers have been tried to detect NAPLs in subsurface (Mariner, et al., 1999). After reviewing literature, Schuberta (2015) concluded that radon is an ideal tracer for the assessment of a wide range of subsurface NAPL contamination. Results from Hunkeler, et al. (1997) show that noble gas radon decreases significantly with the presence of NAPLs in the test porous media and monitoring wells. Ponsin, et al. (2015) among others indicated that radon has high affinity for NAPL. Schubert, et al. (2001; 2005) suggested that soil-gas radon concentration could be used as an indicator for subsurface NAPLs contamination. Fan, et al. (2007); Schubert, et al. (2007); García-González, et al. (2008) and Yoon, et al. (2013) among others concluded that noble gas radon can be used as a tracer for the detection of residual NAPL contamiantion. Davis, et al. (2003a) added that radon is inexpensive and accurate means for the monitoring of subsurface NAPL contamination.

Geophysical techniques (e.g., ground penetrating radar (GPR), galvanic resistivity, electromagnetic induction) has been used to detect pure LNAPL from homogeneous media (Monier-Williams, 1995). The discovery of new LNAPL contaminant plume by Bermejo, et al. (1997) using surface geophysical method (GPR) was a success for the method. Daniels et al. (1995); Maxwell & Schmok (1995) and Deeds & Bradford (2002) among others could also detect subsurface NAPL pool using GPR under certain conditions. It is also possible to detect sufficient concentration of residual NAPL (Chang & Lin, 2006). The method is based on the electromagnetic characteristics of the materials (Orlando, 2002). Results from Grumman & Daniels (1995); Kim, et al. (2000) and Orlando (2002) among others show that there is a potential in the future to use this non-invasive, non-destructive method for the detection and delineation of sites contaminated with NAPLs. The method could also be used for the assessment and monitoring of remediation technologies (Allen, et al., 2007; Cassidy, 2007; Che-Alota, et al., 2009). However, Redman (2009) argue that no study shows the applicability of the method for dissolved and vapor phase detection.

Core sampling and analysis method sometimes called the traditional method is used to characterize sites with respect to NAPL contamination (Jin, et al., 1995; Wilson & Mackay, 1995; Annable, et al., 1998). It is the appropriate method for the sampling and analysis (detection) of NAPL below the water-sediment interface for NAPL contaminated near-surface marine sediments (Abrams, 1996). Hunkeler, et al. (1997) mentioned that bore hole core sample is usually used for the detection and quantification of NAPLs in contaminated sites. The method gives direct evidence of NAPL saturation (US National Research Council, 1999). It can be used as a reference method for the other methods (Halihan, et al., 2005). However, Mayer & Miller (1992) argue that given the heterogeneity of natural subsurface porous media, the size of the core samples used are often too small to represent the contaminated media. Furthermore, Nelson & Brusseau (1996) argue that the possibility of sampling a localized NAPL zone from the wider area of interest is small as it provides discrete data of the contaminated area.

2.8.6.7. Remediation of LNAPL contaminated subsurface

Many technologies have been developed to remediate NAPL source zone and NAPL contaminated sites. Oostrom, et al. (2005a) listed some of the means and technologies used to remediate as for containment (capping, hydrodynamic isolation, solidification and vitrification), removal (pump and treat, and excavation), intercepting pollutants (reactive permeable barrier, and funnel and gate), inducing phase transfer (soil vapor extraction and air sparging), chemical flushing (surfactant-enhanced aquifer remediation), solvent flushing, chemical oxidation, thermally-enhanced extraction (steam injection and electrical resistance heating), and bioremediation (natural attenuation and engineered bioremediation). The technologies are well described in many literatures. Surfactant-enhanced aquifer remediation was described in West & Harwell (1992); Harwell, et al. (1999); Mulligan, et al. (2001) and Jayanti, et al. (2002) among many other authors. Pump and treat technology to remediate contaminated groundwater is presented in among others, Mackay & Cherry (1989); Cheremisinoff (1998) and Illangasekare & Reible (2001). Air sparging remediation technology is discussed in Johnson et al. (1993); Winegardner & Testa ; (2000) and Kuo (2014) and soil vapor extraction to remediate sites contaminated with volatile organic materials like VHCs is conferred in Mayer, et al. (2005). Biological remediation/bioremediation technology for NAPL contaminated sites (soil and groundwater) is elaborated in Langwaldt & Puhakka (2000) and Yadav & Hassanizadeh (2011); while chemical methods are discussed in Gates & Siegrist (1995); Knauss et al. (1997); Nelson et al. (2001) and Seol et al. (2001).

Treatment technologies employ different methods for the treatment. Pump-and-treat method employs hydraulic head difference to pull or push the contaminated water for capturing and pump to the surface for the treatment (Mercer, et al., 1990). Dissolution of residual saturation or desorption of strongly hydrophobic contaminants during conventional pump-and-treat method is difficult. Sabatini, et al. (1995) mentioned that, hence pump-and-treat method is often limited by mass transfer constraints. To solve the problem, additives (surfactants) which can desorb or solubilize the contaminants and enhance the efficiency of the treatment can be used (Fountain, et al., 1991; 1996; Pennell, et al., 1994; Harwell, et al., 1999; Mulligan, et al., 2001).

Aquifer contaminated with volatile contaminants can be remediated by using air sparginig method (van Dijke, et al., 1995; Johnson, 1998; Bass, et al., 2000). The method is used in remediating aquifer contaminated with volatile organic contaminants by injecting air into contaminated zone to encourage volatilization (Johnson, et al., 1993; Reddy, et al., 1995; Waduge, et al., 2004). The produced vapor from the saturated zone can be removed with another complementary remediation technology (e.g., soil vapor extraction, bioventing, horizontal wells, or heating) in vadose zone to eliminate the off-site migration of vapors (Johnson, et al., 1993; Reddy, et al., 1999; Mohamed, et al., 2007; Al-Maamari, et al., 2009). Likewise, soil vapor extraction method which can be used in conjunction with in situ air sparging method can be used alone or with another technology to remediate vadose zone contaminated with volatile organic compounds (Hutzier, et al., 1991; Kearl, et al., 1991; Travis & MacInnis, 1992; Rathfelder, et al., 1995). Bioremediation is an in-situ remediation method which employs biological treatment of contaminated media through which contaminants can be broken down to less/non-toxic forms by microbial (Atlas, 1995; Riser-Roberts, 1998; Boopathy, 2000; Vidali, 2001; Sarkar, et al., 2005)

In addition to physical and biological remediation technologies, contaminated media can be remediated using chemical methods. The media can be remediated by injecting oxidizing chemicals: e.g., hydrogen peroxide (Gates-Anderson, et al., 2001; Watts, et al., 2002; Goi, et al., 2009; Tsai & Kao, 2009); hydrogen peroxide with Fenton's reagent (Watts, et al., 1994; Kong, et al., 1998; Mclay, 1999; Lu, 2000; Chamarro, et al., 2001; Neyens & Baeyens, 2003; Pignatello, et al., 2006); potassium permanganate (Gates & Siegrist, 1995; Mclay, 1999; Gates-Anderson, et al., 2001; Nelson, et al., 2001; Seol, et al., 2001); hydrous pyrolysis/oxidation e.g., using dissolved oxygen with manganese dioxide (Knauss, et al., 1997; Leif, et al., 1998; US Department of Energy,

2000) to oxidize organic contaminants. Ram, et al. (1993) and Khaitan, et al. (2006) among others concluded that site heterogeneities, contaminant type, and the extent of the contamination are the main factors to choose the appropriate technology for NAPL contaminated site. Ram, et al. (1993); Riser-Roberts (1998) and Reddy, et al. (1999) included also regulatory requirements, time constraints and costs for the selection of appropriate technology.

Soga, et al., (2004) indicated that it is impossible to remove residual NAPL from contaminated sites completely due to the complexity of the entrapment. Meanwhile, US National Research Council (2000) concluded that engineered treatment technologies have limitations for subsurface cleanup. Nevertheless, Johnson et al. (2006) described that source zone natural attenuation processes can remove post-treatment residuals left after engineered remediation processes. Natural attenuation, e.g., both aerobic and anaerobic biodegradation, sorption, volatilization, oxidation, reduction, dispersion, dilution, and cometabolsim, (Lee & Lee, 2003; Mulligan & Yong, 2004; Sutherland, et al., 2004; Chen, et al., 2005) can be used alone or as a supplement for engineered remediation technologies. Yong & Mulligan (2004) mentioned that natural attenuation which is traditionally considered as exclusive remedial method is becoming the integral part of other remedial technologies. MacDonald (2000) argue that, however, in addition to their limited effectivenes, the high cost for the construction and operation of engineered technologies is the cause for the rush to use natural atteunetion. In the meantime, US National Research Council (2000) reported that natural atteunation remediation method is effective for few types of contaminants only. Long-term monitroing and associated costs with it, and long time it requires, and intermediate products of biodegradation (which could be tox) are some of the limitations of the natural attenuation method (Wiedemeier, et al., 1999).

2.8.6.8. Contamination of subsurface due to LNAPL residual Saturation

In many fields the main target is to reduce the residual saturation of the liquid of interest. The attempt to reduce the residual saturation of the oil in oil recovery (Joekar-Niasar & Hassanizadeh, 2012) and contaminants (e.g, LNAPL) in remediation of contaminated site (O’Carroll & Sleep, 2007b) are some of the common examples. In contrary to miscible displacement, in immiscible displacement the displacing fluid cannot displace the fluid at a place completely (Dullien, 1992). The fluid at a place (e.g., NAPL in the form of blobs and ganglia) is fully separated from its corresponding boundary reservoir (e.g., NAPL pool) and the displacing fluid cannot expel it from the porous media (Joekar-Niasar & Hassanizadeh, 2012). The corresponding saturation of the liquid at a place is referred to as residual saturation and is immobile due to capillary forces (Winegardner & Testa, 2000). Schwille (1984) among others described that the liquid at a place left after displacement can be transported later in an aqueous form depending on its solubility.

Winegardner & Testa (2000) and Joekar-Niasar & Hassanizadeh (2012) among others mentioned that contact angle, capillary number, viscosity ratio, aspect ratio, and interfacial tension are the main factors that affect the residual saturation of the liquid at a place. Results from Hughes & Blunt (2000) show that residual saturation of the non-wetting phase decreases with increasing contact angle due to the suppression of snap-off. Joekar-Niasar & Hassanizadeh (2012) explaind the matter in another way, as the decrease in contact angle of the non-wetting phase results possibly in increasing of the snap-off which leads to more disconnections of the phase (more trapping of the phase). Residual oil saturation increases with the decrease of contact angle. Constantinides & Payatakes (2000) found that wetting films cause substantial increase of the residual oil saturation (non-wetting phase).

Capillary forces are responsible for the entrapment of fluid whereas viscous forces are for displacing it from the porous media during immiscible displacement. Trapped residual oil can be mobilized if the viscous forces acting on it exceed the retaining capillary forces (Speight, 2017). Non-wetting phase residual saturation decreases with increasing capillary number (Hughes & Blunt, 2000; Sheng, 2013). Study by Koplik & Lasseter (1985) shows that the number of trapped blobs increases with the increase of capillary number while the size of the blobs decreases with the increase of capillary number. Meanwhile, the viscosity ratio of the displacing fluid to the displaced fluid is the determining factor on residual saturation reduction. Vizika, et al. (1994) found out that viscosity ratio plays a major role in the displacement of liquid from the porous media for the whole range of capillary numbers. The interfacial tension between the fluids also affects the displacement from the porous media. Mungan (1966); Wagner & Leach (1966) and Laha, et al. (2009) among others mentioned that the displacement efficiency can be increased by decreasing the interfacial tension. Decreasing the interfacial tension also increases both the capillary number and displacement efficiency (Xu, et al., 2014). Surfactants are used to decrease the interfacial tension between the liquids (Fountain, et al., 1991; Mulligan, et al., 2001). Paria

(2008) and Rosen & Kunjappu (2012) stated that ssurfactants are long chain molecule with both hydrophilic (head) and hydrophobic (tail) moieties. Surfactants replace the molecules of one of the fluids that form the interface. Rosen (2004) described that the hydrophilic group of the surfactants interact with water molecules while the hydrophobic groups interact with HCs across the interface and reduce the tension. However, there is a concern on the application of the surfactants for the contaminated site remediation from their toxicity and biodegradability point of view (Mulligan, et al., 2001). Residual saturation of a liquid does not depend only on the properties and interactions of the liquids and liquids with the matrix but also on the porous media topology and geometry (Joekar-Niasar & Hassanizadeh, 2012).

2.9. Analysis of porous media for water and LNAPL content

Liquid naturally occurs abundantly and widely in porous media is water. However, NAPLs could be found in porous media, e.g., at oil fields and NAPL contaminated porous media. The quantification of these liquids with respect to the porous media is very necessary. Porous media liquid content can be measured through direct or indirect methods. The direct method employs the change in mass of the porous media after the removal of the liquid either thermally or chemically. While, the indirect methods exploit certain variables that could change with the change of porous media liquid content. Many methods have been developed for soil and other porous media liquid content determination. In the following subsections, some of the commonly used methods for the porous media water as well as NAPL/HCs analysis will be reviewed.

2.9.1. Porous media water content analysis

The most commonly known porous media water content analysis is soil water content analysis. Soil can be analyzed broadly for storage and hydraulic properties with respective to water. Reynolds & Topp (2008) listed water content, water potential, and water desorption and imbibition characteristics under storage properties, and un/saturated hydraulic properties and capillary parameters under hydraulic property. There are two common ways of describing soil water content: mass and volume water content. Mass or gravimetric water content is expressed relative to the mass of oven dry soil sample, Eq. [58].

$$w = m_w/m_s \qquad [58]$$

Where: w is gravimetric water content (-), m_w is mass of water which is the difference of wet soil mass and oven-dry soil mass (m_s). Volumetric water content, on the other hand, is described as the volume of water per bulk volume of soil, Eq. [59] or it can be converted from gravimetric water content value using Eq. [60] if the dry bulk density of the soil sample is determined. Pikul (2008) suggested that sampling method that enables the simultaneous measurement of bulk density and gravimetric water content is necessary for the purpose. Volumetric soil water content also shows the depth of water to per unit depth of soil (Or, et al., 2012).

$$\theta_w = v_w / v_t \qquad [59]$$

$$\theta_w = \rho_b w / \rho_w \qquad [60]$$

Where: θ_w is volumetric water content (-), v_w is volume of water, v_t is bulk volume of the soil sample, ρ_b is dry bulk density of the soil sample and ρ_w is density of water. Porous media water content can be expressed in terms of the porous media degree of saturation, Eq. [61] (Hillel, 2004).

$$S = v_w / v_p \qquad [61]$$

Where: S is degree of saturation, v_w is volume of water-filled pore, and v_p is total volume of soil pore space. Soil water content can be determined through direct methods or measured through indirect methods. Note that: literature uses the term soil water content interchangeably with soil moisture content.

2.9.1.1. Direct methods for soil water content analysis

Direct method of soil water content determination is the classical soil water content measurement method through the separation of soil and water to determine the amount of water removed from the sample. Gardner (1986) described that the removal and determination could be achieved through one or more of the following methods: measurement of loss of weight of the sample, collection by distillation or absorption in a desiccant and measurement of the amount of water removed, extraction of the water with substances which will replace it in the sample and measurement of some physical or chemical property of the extracting material that is quantitatively affected by water content, or quantitative measurement of reaction products displaced from a sample. Topp & Ferré (2002) among others indicated that separation of the water from the soil matrix could be achieved by heating, chemical reaction or extracting and replacing by solvent. Measurement of the weight loss of the sample, commonly known as gravimetric method is the most commonly used direct methods (Reynolds & Topp, 2008). The amount of the change in the mass of the soil sample depends on the constituents of the solid and the liquid parts. The conventional protocol uses 105 °C oven temperature for 24 to 48h depending on sample size, wetness, and soil characteristics to get stable mass (Or, et al., 2012). It is International Standards Organization's (ISO) standard, and many organizations including European Standard (EN) and British Standard Institutions (BSI) among others adopt the method for gravimetric water content determination (British Standards Institution, 2014).

However, at 105 °C oven temperature, some clay may retain significant amount of adsorbed water (Hillel, 2004) or even water continues to be released from the soil up to 400 °C (Cooper, 2016). On the other hand, there may be an oxidation and decomposition of organic matter at oven temperature (Hillel, 2004) and the volatilization of organic compounds can happen above 50 °C temperature (Topp & Ferré, 2002) or below 105 °C that can cause the loss of mass (Cooper, 2016). While some organic matter may evaporate at oven-drying temperature (105 °C), there are certain organic liquids in the solid matrix e.g. non-volatile hydrocarbons that may not evaporate at this temperature (Mansur, et al., 2015).

Soils contaminated with oil has different geotechnical properties, e.g. lower dry bulk density and lower optimum water content compared to its non-contaminated counterpart (Khamehchiyan, et al., 2007; Rahman, et al., 2010; Kermani & Ebadi, 2012). Due to these problems it is not practical to specify a temperature for all soils that is suitable to evaporate off all water and ensure that no other losses (or gains) occur (Cooper, 2016). Topp & Ferré (2002) suggested that there should be a special precaution in adopting a reference condition for drying and interpreting the results for soils with high organic matter content, significant amounts of gravels or are salt-affected. Despite the problem related to oven temperature and drying time specifications, gravimetric method is the standard method for the calibrations of other methods (Gardner, 1986; Topp & Ferré, 2002; Cooper, 2016). However, the term "gravimetric water content" itself is not used by all authors, and "gravimetric water content", "soil moisture", "soil water content", "oven-dry water", and "soil water content (105 °C, 24h)" are the terms used by different authors and mentioned in Pikul (2008). Direct method is a destructive method that does not allow the repetitive measurement at the exact location (Verhoef & Egea, 2013) and it is not used extensively in the studies of hydrological processes (Topp, 2003). Additionally, it is time consuming, impractical for measuring at field

(Bittelli, 2011) and measuring method that could overcome the listed problems is needed for field soil water measurement.

2.9.1.2. Indirect methods for soil water content analysis

Soil water content can be measured indirectly using different methods and devices. Gardner (1986) made a review of the indirect and direct methods commonly used at the time: time domain reflectometry (TDR) and neutron moderations for field application, and the direct method: thermal gravimetric analysis for laboratory method. Roughly twenty years later Ferré & Topp (2005) made a review of five electromagnetic (EM) techniques which include two intrusive methods: TDR and capacitance measurement and three nonintrusive methods: ground penetrating radar (GPR), passive microwave and remote active microwave or radar, and two non-electromagnetic methods: thermos-gravimetric method and the indirect method, neutron thermalization or neutron moderation. A decade later, S.U., et al. (2014) critically reviewed over thirteen soil moisture measurement methods by categorizing them under classical (thermo-gravimetric and calcium carbide) method and modern techniques include neutron scattering, gamma attenuation, dielectric methods: TDR, capacitance and frequency domain reflectometer, electrical impedance, GPR, micro-electro mechanical system, soil resistivity sensor, thermal dissipation block, heat flux sensor, tensionmetric and optical techniques: polarized light, fiber optic sensor and near infrared optical techniques. This shows that the number of soil water content measuring methods are increasing rapidly in the last few decades. Even though, there are a lot of modern methods available for soil water content measurement, still classical technique, thermo-gravimetric analysis method is the standard reference for soil water content determination (S.U., et al., 2014; Cooper, 2016). And it is used widely for the calibration of the other methods (Reynolds, 1970; McGarry, 2006).

Unlike direct method, indirect method measures variable that is affected by the amount of soil water content. The variable changes with the change of soil water content (Bittelli, 2011). Variables that are used by different methods include but not limited to relative permittivity (dielectric constant), electrical conductivity and resistivity, thermal property/heat capacity, hydrogen content, and magnetic susceptibility (Reynolds & Topp, 2008). All the methods that employ EM technique to measure soil water content are based on the high relative permittivity of the water (Topp, 2003). The relative permittivity of water is about 80 (Robinson, et al., 1999) and the other soil materials range from 1 to 7 (Topp, 2003). The relative permittivity of some common materials is air 1, quartz 4, mica 6 and mineral oil 3 (Silva, 2010). Relative permittivity of most NAPLs are much lower than that of water. Redman (2009) listed the values for kerosene, gasoline and crude oil as 2.1, 2.2 and 2.2 respectively. Methanol and ethanol which are hydrocarbon derivatives of alcohol group have 33 and 24 relative permittivity at 25 °C temperature (Brown, et al., 2011). The differences in relative permittivity values between water and other soil components makes the relative permittivity of the soil much sensitive to change in soil water content (Bittelli, 2011). The widely used EM based soil water content measuring sensors are Time domain reflectometry (TDR) (Topp, et al., 1980; Baker & Allmaras, 1990; Brisco, et al., 1992; Yu, et al., 1999; Topp & Ferré, 2002) and capacitance/frequency domain reflectometry (FDR) (Thomas, 1966; Bell, et al., 1987; Dean, et al., 1987; Robinson & Dean, 1993; Mohamed, et al., 1997; Wu, 1998; Fares, et al., 2011).

On the other hand, methods that use resistivity techniques to measure soil water content are based on the principle of the resistivity of the soil that changes depending on soil water content. The electrical conductivity of a soil increases with the water content of the soil while the resistivity is the inverse of it (Cooper, 2016). Water in the pore space is the main reason for the electrical conductivity of the soil which is associated with the ion and its mobility (Annan, 2009). According to Bittelli (2011) among others, the resistivity value of the soil is measured from the change in voltage from a current transferred into the soil by electrodes. Meanwhile, neutron scattering methods use the collision of high-energy neutron with atoms of soil components. The collision of this high-speed neutron with nuclei of similar mass atom, hydrogen, slowdown some neutrons (Cooper, 2016). All the hydrogen atoms participate in collision is assumed to be from water molecules in the pore space and the amount of the collision depends on soil water content (Bittelli, 2011). However, Cooper (2016) among others mentioned that there could be other sources of hydrogen in the soil that can change the measurement of the water content. The method measures the quantity of neutrons returned to the detectors with in a given period (Ferré & Topp, 2005). Methods depend on the thermal properties exploit the change of the thermal properties due to soil water variation (Bittelli, 2011). The technique uses heat source and temperature sensor to measure water content and increase in temperature due to instantaneous heat application has inverse relation with volumetric heat capacity, which has direct relation with volumetric water content (S.U., et al., 2014). In the similar way, the other remaining methods e.g. optical method utilize some variables that could change with the amount of soil water.

There are a lot of soil moisture sensors developed over the last few decades depending on different variables. However, of all the methods developed to measure soil water content, electromagnetic (EM) based methods have received the most attention (Kizito, et al., 2008). They use the advantage of higher relative permittivity of the water (80) compared to other soil constituents (1-7). Hence, it is the change of soil water content that changes the relative permittivity of the soil decidedly (Ferré & Topp, 2005). Baumhardt, et al. (2000); Seyfried & Murdock (2001; 2004) and Gong, et al. (2003) among others, argue that soil water content measurement is affected by soil bulk density, texture, temperature, and electrical conductivity. Despite many efforts and recommendations made for further investigations using respective methods (Phogat, et al., 1991; Ochsner, et al., 2001; Boluwade & Madramootoo, 2016), convincing simultaneous measurement of soil bulk density and soil water content using soil water sensors or otherwise are not realized. The main problem is field level bulk density estimation to acceptable level of accuracy. However, Yang, et al. (2016) improved the kriging method estimated bulk density by cokriging with estimated soil water content. On the other hand, it is possible to measure water content with soil temperature (Seyfried & Murdock, 2001; Decagon Devices, 2017a) or bulk electrical conductivity (Dasberg & Dalton, 1985; Zegelin, et al., 1989; Noborio, 2001; Thomsen, et al., 2007) or all the three simultaneously (Balendonck & Hilhorst, 2001; Valente, et al., 2006; Kizito, et al., 2008; Decagon Devices, 2010; Skierucha, et al., 2012; Decagon Devices, 2017b). The advantage of measuring all the three at the same time and place were summarized by Kizito, et al. (2008) as: allowing examination of the nature of their interdependency, eliminating the need for interpolating different measurement types, and the inclusion of the other two measurements allows correction for the soil water content measurements, if required.

Among the commonly used devices that could measure temperature, electrical conductivity and volumetric water content (θ_w) simultaneously are sensors which are the family of ECH$_2$O sensors (EC-5, ECH$_2$O-TE and 5TE) (Decagon Devices Inc., Pullman, USA) (Decagon Devices, 2008; Decagon Devices, 2010; Kizito, et al., 2008). Both 5TE and ECH$_2$O-TE sensors use 70 MHz frequency to minimize textural and salinity effects that makes the sensor to measure the soil water content in most soils (Decagon Devices, 2008; Decagon Devices, 2010). Though both are based on the same theory, 5TE sensor is the improved and latest version of the two sensors and it uses stainless screws instead of gold traces that is used by ECH$_2$O-TE for the EC measurement (Decagon Devices, 2016; Decagon Devices, 2017b). It measures the water content based on the relative permittivity of the media using capacitance/frequency domain technology (Decagon Devices, 2010). Electrical conductivity and temperature measurements of the sensor are calibrated at factory for all soils while soil water content for mineral soil is calculated based on Topp, et al. (1980) equation [62] (Decagon Devices, 2017b).

$$\theta_w = 4.3 \times 10^{-6} {\varepsilon_a}^3 - 5.5 \times 10^{-4} {\varepsilon_a}^2 + 2.92 \times 10^{-2} \varepsilon_a - 5.3 \times 10^{-2} \qquad [62]$$

Where: θ_w is volumetric water content, ε_a is apparent relative permittivity. However, Topp, et al. (1980) uses K_a for the apparent relative permittivity. The accuracy of the equation for θ_w measurement is ±3% and if better accuracy is required or the measurement is for other types of soil which has high electrical conductivity, or non-normal mineralogy, soil specific calibration is necessary (Decagon Devices, 2010). However, Decagon's ProCheck reader, DataTrac3, or ECH$_2$O utility convert raw relative permittivity values based on Eq. [62] if mineral soil calibration option is chosen (Decagon Devices, 2016). The option works for mineral soil with saturation extract electrical conductivity < 10 dS/m (Decagon Devices, 2010). Saturation extract electrical conductivity can be determined through the steps recommended by Hilhorst (2000) using Eq. [63].

$$\sigma_p = \varepsilon_p \sigma_b / (\varepsilon_b - \varepsilon_{ab=0}) \qquad [63]$$

Where: σ_p is the pore water (the water that can be extracted from the soil) electrical conductivity (dS/m), ε_p is the real portion of relative permittivity of the soil pore water (-), σ_b is the bulk electrical conductivity (dS/m) which is measured directly by the sensor, ε_b is the real portion of the relative permittivity of the bulk soil (-) and $\varepsilon_{\sigma b=0}$ is the real portion of the relative permittivity of the soil when bulk electrical conductivity is 0 (-). ε_p can be calculated from soil temperature using a simple formula, Eq. [64] (Decagon Devices, 2016).

$$\varepsilon_p = 80.3 - 0.37 \times (T_{soil} - 20) \qquad [64]$$

Where: T_{soil} is temperature of the soil measured by the sensor (°C). ε_b can be calculated using Eq. [65] from the raw relative permittivity used in calculating volumetric water content (θ_w) under Eq. [62] as follows:

$$\varepsilon_b = \varepsilon_{raw} / 50 \qquad [65]$$

Where: ε_{raw} is unprocessed raw value of relative permittivity reported by sensors. However, recent sensors, e.g. 5TE report the value of θ_w, and ε_b in this case ε_a under Eq. [62] can be calculated from the reported value of θ_w using Eq. [62]. On the other hand, there are two recommendations for the value of $\varepsilon_{\sigma b=0}$: Hilhorst (2000) recommends 4.1 as the generic value offset, while researchers at Decagon Devices Inc. reccomend 6 for their sensors for the accurate determeination of σ_p in all soil types (Decagon Devices, 2016).

2.9.2. Sample Analysis for hydrocarbons content

Unlike water there are thousands of different HCs existed in crude oil, though around 600 of them only positively identified so far (Giles & Mills, 2010). Ahmed (2010) among others indicated that HCs can occur in gaseous, liquid or solid states. They vary from methane which is a gas at room temperature with boiling point of -160 °C to those HCs with many carbons per molecule and boiling points more than 1100 °C (Speight, 2015). These different HCs have different physical properties e.g., density, solubility in water, melting and boiling points and chemical properties (reactivity) (Speight, 2011b). Even isomers of a HC compound have different such properties (Bettelheim, et al., 2013). These make difficult to develop specific method and technique for the detection and analysis of them at field level, or sampling, sample handling and above all to come up with a single laboratory or field based analytical method for the entire range (Speight, 2015).

There are many analytical methods available for the analysis of HCs in the contaminated samples, however. Samples can be analyzed for the content of total petroleum hydrocarbon (TPH), petroleum group type and individual compound (Farrell-Jones, 2003). TPH is a term used to describe a large family of several hundred chemical compounds made mainly from hydrogen and carbon originated from crude oil (US EPA, 2005). It is not usually practical to measure each of these chemical compounds in PHC contaminated samples (RTI, Research Triangle Institute, 1999). But, TPH amount is necessary to indicate the level of the contamination. TPH method is a good indicator, but it doesn’t show the components. Therefore, it is very important to group PHCs into petroleum hydrocarbon fractions that act alike in soil or water (US EPA, 2005). Dividing TPHs in to fractions enables to identify the component which is harmful to people and environment, and their fate in the environment (RTI, Research Triangle Institute, 1999). Each fraction may contain many individual compounds. However, in practical world it is mostly a refined product for intended use that causes the contamination. Hence, it is not common to find all these petrochemicals in analyzed sample from contaminated soil or water for TPH. Samples with the same amount of TPH could be from different sources based on the constituents of their sources (Speight, 2015). On the other hand, samples from different contaminated sites could be originated from the same source based on TPH and its constituents (Wang, et al., 2002). Speight & Arjoon (2012) mentioned that the composition of HCs released to the environment changes overtime. Physical, chemical, and biological processes change the location and concentration of hydrocarbons at any site (RTI, Research Triangle Institute, 1999).

Different methods use different means of separation of HCs from the sample and has different detection range, and hence measure different subsets of HCs. The selection of the most appropriate method hence depends on these factors (Nelson, 2003; Smith & Cresser, 2003; Speight, 2005; Speight, 2015). Even though there are a lot of analytical methods for the environmental sample analysis, there are four most commonly used analytical methods for TPH: gas chromatography (GC), infrared spectrometry (IR), gravimetric analysis and immunoassay (Speight, 2014; 2015). All but immunoassay are laboratory methods of TPHs analysis (Speight, 2015). All the three methods involve the extraction of HCs from soil matrix or water sample, and solvent extracted sample can be analyzed for TPH gravimetrically after removing the solvent or determined from the purified extracts with IR or GC (Falcó, 2014). Extraction procedures for the methods includes, among others, classic procedures using soxhlet extraction with non-polar solvents (Soxhlet, 1879; US EPA, 1986; 1996b), microwave assisted extraction (Ganzler, et al., 1986; Ganzler & Salgó, 1987; Lopez-Avila, et al., 1994; Daghbouche, et al., 1996; US EPA, 2007a), supercritical CO_2 extraction (Eckert-Tilotta, et al., 1993; Janda, et al., 1993; US EPA, 1996c; Morselli, et al., 1999; Hartonen, et al., 2002; Liang & Tilotta, 2003) and ultrasonic extraction (Marvin, et al., 1992; Lombas-García, et al., 1998; Banjoo & Nelson, 2005; US EPA, 2007b; Couto, et al., 2014).

GC method is the most preferred laboratory method of the three laboratory methods for TPH analysis due to selectivity and sensitivity offered by its many detector systems and range (Speight, 2005). It is also the only of the three methods according to Total Petroleum Hydrocarbon Criteria Working Group (1998); Farrell-Jones (2003) and Speight (2014) which enables both the quantification and identification of individual constituents, including the type of the fuel present and the presence or absence of toxic molecules. For analysis, the method simulates distillation of crude oil refinery for petroleum fractions which are produced based on differences in vapor pressure of different fractions (Smith, et al., 2004). Depending on the column temperature, molecules with different chemical and physical properties leave the stationary phase and carried to the detector by mobile gas phase for analysis. However, it can analyze commonly from nC_6 (compounds below it is highly volatile, and interference occur from the solvent (hexane) peak) to nC_{40} (Speight, 2005; Yang, et al., 2015). Even though the share of HC compounds below nC_6 in gasoline is as much as 25% (Speight, 2005), their content in samples contaminated from gasoline spill is very much reduced over time (Baedecker, et al., 2011). The whole gasoline spilled can evaporate completely in a few hours (Yang, et al., 2015) and might not be found in a sample. However, on the other side, many lubricating oils has more than nC_{40} HCs and crude oil has even more than nC_{100} HCs. Even though there are specialized gas chromatographs that can analyze possibly up to nC_{60} (615 °C) using two-dimensional high-temperature GC (Dutriez, et al., 2009), the higher-molecular-weight HCs are beyond the detection range of the common GC. Speight (2014) stated that the higher boiling points of HCs undergo molecular fragmentation through thermal decomposition and produces non-indegineous volitile products above 350 °C.

IR and gravimetric methods often preferable over GC to analyze higher-molecular-weight HCs (Speight, 2005). As they could not reach the detector because they are too reactive to pass through gas chromatograph, the method falls short to analyze polar constituents (compounds with nitrogen, oxygen, and sulfur content) of the crude oil (Speight, 2005). And hence analysis of samples contaminated with oxygenated fuels (ethers e.g. by methyl tertiary butyl ether (MTBE) which used to be a common blending component of gasoline and alcohols e.g. ethanol which is the current blend to increase the octane number) using GC used for HC analysis is not efficient (Speight, 2005). However, they can be analyzed by GC with oxygen selective flame ionization detector (Speight, 2005).

Sample extracted with a suitable solvent (i.e., a solvent with no C-H bonds) and not removed by silica gel can be analyzed by IR method (Speight, 2005). Even though the target is to remove biogenic polar material, according to Total Petroleum Hydrocarbon Criteria Working Group (1998) some polar PHCs can be removed during the cleaning of the extract with silica gel. Regardless of the structure of the rest of the molecules, certain groups of chemical bonding give rise to bands at or near the same frequency (Aske, et al., 2001). Farrell-Jones (2003) among others mentioned that different functional groups and bond types have different infrared absorption frequencies and intensities. Hence, IR method measures the stretching and bending (vibration) that arises when a molecule absorbs energy (heat) in the infrared region of electromagnetic spectrum typically of specific frequency 2930 cm^{-1} (Okparanma & Mouazen, 2013). The value which is used in USA, corresponds to the stretching of aliphatic CH_2 groups; while multiple frequencies: 2960 cm^{-1} for CH_3 groups and 2900 to 3000 cm^{-1} for aromatic C-H bonds use in Europe (Total Petroleum Hydrocarbon Criteria Working Group, 1998). The absorbance of silica gel treated extract measured which is the result of all the compounds present, is compared to the absorbance of standards of known PHC concentration.

The method is simple, rapid, inexpensive and reproducible with common detection limit compared to GC (Total Petroleum Hydrocarbon Criteria Working Group, 1998; Lambert, et al., 2001; Speight, 2005). The standard method proposed by US EPA, Method 418.1 was even faster according to Forrester, et al. (2013) but ozone-depleting halogenated solvent, Freon 113 was used as a soil extract and the subsequent analysis of the extracts. On the other hand, ASTM (2011) under ASTM D7066-04 Method officially approved another halogenated solvent, chlorotrifluoro-ethylene (S-316) as the replacement of Freon 113. But, the regulation forbids the use of these halogenated solvents for such purposes (Falcó, 2014) and other solvents, i.e., hexane, methanol and methylene chloride consist of C-H bonds (Total Petroleum Hydrocarbon Criteria Working Group, 1998). Any of the molecule with even one C-H bond contributes to the measurement. Hence one of the problems to use the method is, hence, to find the appropriate solvent which cannot interfere with the C-H bond absorption of TPH from the sample.

Minty, et al. (1996; 2000) and Ramsey (2008) used liquid CO_2 for the supercritical fluid extraction and IR quantification for oil-in-water analysis. Liang & Tilotta (1998) used argon for the extraction of petroleum hydrocarbons from soil samples and had similar recovery and reproducibility with using CO_2 but with the longer operation time. Even though the using of CO_2 instead of halogenated solvents makes the method environmentally clean (Ramsey, et al., 2010), the overall method is comparatively bulky and involves the handling of high pressure liquid CO_2. Hawthorne, et al. (1994) showed that the recovery of HC alkane by CO_2 depends on the temperature of extraction, and at 65 °C it could be possible to extract up to nC_{25}, but the number increases with the temperature of extraction. However, Guiliano, et al. (2000) showed that the extraction of nC_{14} to

nC_{30} mainly alkanes from crude oil asphaltenes using CO_2 was influenced by pressure not by operating temperature between 40 to 50 °C. Speight (2014) among others stated that IR method suffers from detection limit (1 mg/L in water and 10 mg/kg in soil), poor accuracy and precision for heterogeneous soil samples. Additionally, TPHCWG (1998) mentioned that measuring alkyl C-H group absorbance underestimates the TPH in the sample if the sample contain benzene and naphthalene which do not contain alkyl C-H group.

Extracts that are not removed during solvent evaporation at 70 to 85 °C temperature and capable of being weighed can be analyzed by gravimetric analysis method (Speight, 2005). Like IR method there may be a cleanup of the extracts with silica gel depending on the source of the sample. Total Petroleum Hydrocarbon Criteria Working Group (1998) categorized that if it involves clean up step, it is considered as TPH method, otherwise it is considered as oil and grease method. It is simple and rapid (Speight, 2014), and inexpensive (Villalobos, et al., 2008) method of TPH analysis for sample containing heavy molecular-weight hydrocarbons (Okparanma & Mouazen, 2013). However, it has detection limits and its limit is 5 to 10 mg/L in water (US EPA, 2010) and 50 mg/kg in soil (Speight, 2005). The method is not suitable for the analysis of HC with low boiling point ($< nC_{15}$) that could evaporate below the mentioned temperature (Okparanma & Mouazen, 2013). However, this analytical method is used to analyze oily sludge, samples containing heavy-molecular-weight hydrocarbons, aqueous samples when hexane is the preferred solvent (Speight, 2005).

There are various extracting methods and clean up steps of the extracts in gravimetric analysis method. US EPA Method 9071B (1998) and Method 1664B (2010) gravimetric analysis methods for hexane extractable material (HEM) are the commonly used methods for samples from solid matrix and water respectively (Speight, 2015). The methods use normal hexane (n-hexane) for the extraction. However, Okparanma & Mouazen (2013) mentioned that n-hexane is not a good solvent for higher-molecular-weight PHCs. Hence, the analysis could be inaccurate for sample contaminated with higher-molecular-weight HCs. The method is suitable specifically for non-volatile and fully n-hexane extractable PHCs (US EPA, 1998). The method faces limitations on the both sides: on the lower side, HCs with lower boiling point ($< nC_{15}$) evaporate before being weighed, while on the upper side n-hexane is not a good solvent for higher-molecular-weight HCs. The older version of the US EPA methods uses ozone-depleting chlorofluorocarbons (CFCs), Freon 113 (US EPA, 1994a; 1994b). Even though the extraction efficiency in certain cases is higher using Freon 113 compared to n-hexane (US EPA, 2000a), the production and importing of ozone depleting substances including CFCs was banned under the Clean Air Act Amendments of 1990 (US EPA, 1994a).

There are many more laboratory methods with their limitations for PHC analysis. However, field detection and analysis method are very limited. The frequently used method for both field and laboratory analytical tool is Immunoassay (IA) (US EPA, 1996a). Total Petroleum Hydrocarbon Criteria Working Group (1998) among others specified that IA method relies on the specific interactions between antibodies and antigens to measure PHCs and other environmental contaminants. The method is fast, sensitive and cost-effective analysis method (Płaza, et al., 2005). There are a variety of IA test tool kits available on the market that are developed to test different compounds. Aga & Thurman (1997) mentioned that US EPA alone had 11 commercially available tool kits under SW-846 Methods for different tests. The sensitivity of the tool kit, hence, depends on the binding of the target analyte to the antibodies it is developed for. For e.g., the tool kit on which EPA Method 4030 developed for the analysis of TPH is sensitive most to the small aromatic compounds (US EPA, 1996a).

Even though, the method is rapid and economical both in terms of time and money, it may produce positive or negative results. Popek (2003) argue that it produces positive results if the sample has different compound that is same chemical class with the target compound, and negative results in a case when natural attenuation occurs in the environment, e.g. fuel petroleum depletion. The accuracy of the method is lower than the standard laboratory methods for TPH analysis (Total Petroleum Hydrocarbon Criteria Working Group, 1998). The method is mostly used as a supplement to other methods as screening technique (Płaza, et al., 2005). Unlike the conventional laboratory analytical methods, IA analytical method may not produce a single result, rather it gives qualitative or semi-quantitative data that can be described as a range of value or in comparison to a standard value (US EPA, 1996a). However, the result can be quantified to a single value, if configured with a calibration curve constructed from a serious of reference standards (Popek, 2003). Even though IA is field analytical method, it is not recommended to use its tool kit above 27 °C and under direct sunlight (Total Petroleum Hydrocarbon Criteria Working Group, 1998).

Typical detection limit of the method is from 10 to 500 mg/kg in soil and 200 to 500 µg/L in water (Total Petroleum Hydrocarbon Criteria Working Group, 1998).

There are also some field based HC analysis methods. Fluorescence Spectroscopy (FS), Raman Spectroscopy (RS), Visible and Near-Infrared Spectroscopy and Field-Portable Gas Chromatography–Mass Spectrometry (GC-MS) are among mentioned methods in Okparanma & Mouazen (2013). Harris (2002) indicated that 2001 terrorist attack (9/11) and the anthrax incidents followed it, was the alarming bell to the scientists for the detection of biological as well as chemical warfare agents (CWA). GC-MS is an appropriate tool for the detection and analysis of volatile and semi-volatile compounds from the surrounding environment. Smith, et al. (2004) described that volatile compounds can be analyzed while in the atmosphere, but sample from solid-phase microextraction (SPME) should be done in nearby clean area with stationary GC-MS. Results from Zhang, et al. (2016a) show that SPME of polychlorinated biphenyls from soil matrix can be analyzed using portable GC-MS at field level. Barreira, et al. (2015), on the other hand, used SPME even for in situ gaseous organic compounds sampling from the atmosphere and analyzing using GC-MS. However, Nagashima, et al. (2015) showed that there is a reduction of sensitivity for sarin and soman due to gasoline which was used as an interfering matrix in the identification and analysis of field based volatile chemical warfare agents using sarin, soman, tabun and cyclohexylsarin. Except for its size and portability, field-based GC-MS is similar in analysis procedure to its laboratory-based counterparts. Nevertheless, due to its size there is a compromise in its quality. Harris (2002) stated that the smaller the size, the greater the sacrifice in sensitivity, separating and identifying powers.

RS in particular and spectroscopy methods in general can be used in in-situ detection and quantification of HCs. However, Kwon, et al. (2012) among others, indicated that due to its low scattering cross section inherited, RS has limited application in trace chemical analysis. But, Smith & Dent (2005) and Vandenabeele (2013) among others argue that the problem can be solved through either surface or resonance signal enhancement. Surface enhanced RS (SERS) has been in use in many current researches for in situ analysis. Zhang, et al. (2016a) used the method to detect and analyze organic compounds from solid matrix sampled by SPME. On the other hand, Fräulin, et al. (2014) could detect and analyze simultaneously the concentration of HCs, dissolved molecular oxygen and oxidized products of HCs with in a micro channel reactor during liquid-phases reaction. Klavarioti, et al. (2014) projected that using near-infrared spectroscopy methods for in situ HC detection and analysis in soil matrix could be possible. Meanwhile, by considering the portability of the tool, Forrester, et al. (2010) suggested that in situ measurement of soil contaminants using Mid Infrared Spectroscopy has become more feasible.

2.9.3. LNAPL and water content of a porous media

A lot has been done to model multiphase liquid flow through porous media. Aqueous phase (water) and non-aqueous phase (NAPL) are the target liquids. Parker, et al. (1987) developed a model for two and three (including air) phase fluids that describe relative permeability-saturation-fluid pressure functional relationship. Leverett (Leverett, 1941); Buckley & Leverett (1942); Douglas, et al. (1959); Tek (1961); Morel-Seytoux (1973); Wooding & Morel-Seytoux (1976); Yortsos & Fokas (1983); Dullien (1988) ; McWhorter & Sunada (1990); Kueper & Frind (1991); Porcelli & Binder (1994); Celia, et al. (1995); Russell (1995); Knight & Mitchell (1996); Dillard, et al. (1997); Oostrom, et al. (1997); Wanfang, et al. (1997); Schroth, et al. (1998b); Lenhard, et al. (2004) ; Helmig, et al. (2006); Fagerlund, et al. (2008); Francisca & Montoro (2012) among many others discussed about multiphase flow through the porous media. In concurrent steady two-phase flow in porous media, two fluids flow in the same channel or in different channels (Dullien, 1988; Dullien, 1992; Dullien, 2000; Dong & Dullien, 2006; Fanchi & Seidle, 2017) under different condition (Dullien, 1988). In steady flow there is no displacement of one fluid by the other and immiscible displacement is unsteady multiphase flow (Dullien, 1992). The author further discussed that contrary to miscible displacement, in immiscible displacement there is residual or irreducible saturation of the displaced liquid left behind in the porous media. After both steady and unsteady multiphase liquid flow, different amounts of both liquids could remain in the porous media.

Different analytical methods mentioned previously can be used to analyze individual liquids (water or oil) from contaminated porous media. But, simultaneous detection or analysis of the two liquids is not common. But, there is one USA Patent No. 5,095,271 by Ohkawa (1992) supposed to measure in situ soil moisture, salinity and HCs. Nevertheless, there is no information about it since then. Thermo-gravimetric method specifically and direct method generally is used as standard reference for other soil water content measurements. But there is no single method that can be used to measure the entire range of HCs. The lower molecule HCs can evaporate easily or even some of them are gaseous at ambient temperature while the higher molecules are semi-volatile or nonvolatile even at higher temperature. These wide variations in boiling points among other properties make HCs analytical methods, e.g. gravimetric method or chromatographic methods, which look better to be a nominee for reference method, difficult. Due to the variation in chemical and physical properties of LNAPL components (HCs), it is difficult to design a single analytical method (Speight, 2015) let alone developing a specific characteristics or variable that could be detected and analyzed with that of water simultaneously.

Water, on the other hand, is a unique substance compared to other constituents of the soil in terms of its relative permittivity, thermal property and electrical conductivity. The indirect methods use its unique variables to measure soil water content while thermos-gravimetric method uses its boiling point for the separation from soil matrix. But, the boiling points of HCs varies from roughly -160 to over 1000 °C which is difficult for practical application. On the other hand, relative permittivity of HCs or crude oil are more or less similar to solid components of the soil, thermal properties are not specified and hydrocarbons are non-polar organic compounds which are not solvents for ionic compounds and hence they are not good electrical conductivity in solid matrix. Due to these factors, it is difficult to get a sharp and unique HCs' variable that can be utilized in indirect porous media HCs content measurement. Darayan, et al. (1998) compared electrical conductivity, resistivity and relative permittivity of diesel contaminated soil with non-contaminated counterpart and the result shows that the difference was small. Haridy, et al. (2004) showed that there is no difference in electrical conductivity due to the amount of LNAPL in the soil.

The main natural components of the soil, non-magnetic mineral soil has 4-8 relative permittivity value (Hillel, 1998; Ajo-Franklin, et al., 2006) while water and air have 81 and 1 respectively (Jackson & Schmugge, 1989). The relative permittivity of mineral oil (Ross, 1980; Taslak, et al., 2015) and dry silica sand (Fredlund, et al., 2012) are around 2.2. Francisca & Rinaldi (2003) concluded that soil porosity and mineralogy have a large influence on the relative permittivity (dielectric constant) of the mixture than the relative permittivity of the organic fluid. Since the solid matrix is constant, the relative permittivity of the porous media changes with the change of its fluid content, mainly water. Under natural condition, pores of the porous media are generally occupied by air and/or water (Birdwell & Marrero, 2011; Hunt, et al., 2014). Water-saturated soils could have the relative permittivity values up to 25 (Ye, 2013), 30 (Clement & Ward, 2008) or 30 (for wet sandy soil) (Cassidy, 2009) depending on the degree of saturation. However, Ajo-Franklin, et al. (2004; 2006) indicated that there is a potential to use dielectric properties among other geophysical properties of the NAPLs to detect them in the subsurface.

The relative permittivity of the porous media can be modified to some extent if HCs (LNAPLs) which have the relative permittivity values commonly around 2.2 (Panuganti, et al., 2016) displace air. Halogenated HCs could have the relative permittivity values more than 10 (Maryott & Smith, 1951; Ajo-Franklin, et al., 2006) and the modification would be even higher with such NAPLs. Abdelgwad & Said (2016) recommended that high frequency electromagnetic sensors, e.g. GPR are required to detect organic contaminants in the contaminated soil. Results from LiangTong, et al. (2013) show that, however, the change in relative permittivity was insignificant when diesel (LNAPL) displaced only air, but water. On the other hand, Haridy. et al. (2004) used relative permittivity in three-phase (oil-air-sand) system in modeling LNAPL, and it worked for the three-phase system but not four-phase system that included water. However, it is impractical under field condition to find solid matrix (porous media) without water of some amount.

Many researchers have tried to deal with organic pollutants, especially NAPLs in the porous media by using the relative permittivity of the pollutants (Persson & Berndtsson, 2002; Haridy, et al., 2004; Olchawa & Kumor, 2008; Wilson, et al., 2009; Francisca & Montoro, 2012; Comegna, et al., 2013; 2016). Geophysical techniques (e.g., TDR, GPR) are used to discriminate volumetric NAPL content and porous media water content (Persson & Berndtsson, 2002; Comegna, et al., 2016). Effective relative permittivity of a porous media depends on its pore volumetric fluid content (Francisca & Montoro, 2012). Porous media could be occupied by single or multiphase fluid. Persson & Berndtsson (2002); Francisca & Montoro (2012); Comegna et al. (2013; 2016) utilized DMM to estimate porous media volumetric water and NAPL contents.

The relative permittivity measured from the porous media is the bulk relative permittivity contributed by each soil components (Persson & Berndtsson, 2002). The bulk relative permittivity of a porous media is predominated by its water content (80) compared to its air content (1). Topp, et al. (1980) developed an emperical equation Eq. [62] that relates the meausred relative permittivity of the soil with θ_w for mineral soils. Others used physical DMM to explain bulk relative permittivity measured based on the composite relative permittivity and volume fraction of each components. Even though there are several DMMs, mixing model, Eq. [66] proposed by Birchak, et al. (Birchak, et al., 1974) is the most commonly used model (Persson & Berndtsson, 2002; Haridy, et al., 2004).

$$\varepsilon_a^{\alpha} = \sum_i \theta_i \varepsilon_a^{\alpha} \qquad [66]$$

Where: ε_a is the bulk relative permittivity of the multiphase system, θ_i and ε_i are the volume fraction and the relative permittivity of component i, respectively and α is an empirical parameter accounting for soil geometry. The value for α is 1 if the electrical field is parallel to the layers of the media and −1 if the field is perpendicular to the layer. Birchak, et al. (1974) proposed 0.5 for an isotropic medium. Rinaldi & Francisca (2006) described the mixing model for water- saturated porous meda as:

$$\varepsilon_{Sw}^{\alpha} = (1-\emptyset)\varepsilon_s^{\alpha} + S\emptyset\varepsilon_w^{\alpha} + \emptyset(1-S)\varepsilon_{air}^{\alpha} \qquad [67]$$

Where: ε_{sw} is the relative permittivity of the soil–water mixture, ε_s, ε_w, and ε_{air} are the relative permittivity of soil particles, water, and air, respectively, S is the effective water saturation; and $\emptyset$ is the porosity of the sample. Eq. [67] can be for LNAPL saturated medium by substituting the parameters of LNAPL instead of water. For four phase systems where the media is saturated with both water and LNAPL, the mixing model can be described as:

$$\varepsilon_a^{\alpha} = (1-\emptyset)\varepsilon_s^{\alpha} + S_w\emptyset\varepsilon_w^{\alpha} + S_o\emptyset\varepsilon_o^{\alpha} + \emptyset(1-S)\varepsilon_{air}^{\alpha} \qquad [68]$$

Where: S_w and S_o are effective water and LNAPL saturation and ε_o is the relative permittivity of LNAPL. In another way, $S_w\emptyset$ and $S_o\emptyset$ are θ_w and $\theta LNAPL$ or volumetric water and LNAPL content respectively and Eq. [68] can be written as follows:

$$\varepsilon_a^{\alpha} = (1-\emptyset)\varepsilon_s^{\alpha} + \theta_w\varepsilon_w^{\alpha} + \theta_o\varepsilon_o^{\alpha} + \emptyset(1-S)\varepsilon_{air}^{\alpha} \qquad [69]$$

From the measured/calculated bulk relative permittivity, porosity of the media and relative permittivity of the constituents, it could be possible to estimate the volumetric LNAPL content. Volumetric water content of the media can be estimated from the calibration curve constructed using gravimetric water content and water content measured using soil moisture sensors. The overall degree of saturation of the porous media is the sum of the degree of saturation by water and LNAPL, Eq. [70].

$$\varepsilon_a^\alpha = (1-\emptyset)\varepsilon_s^\alpha + \theta_w\varepsilon_w^\alpha + \theta_o\varepsilon_o^\alpha + (\emptyset - (\theta_w + \theta_o))\varepsilon_{air}^\alpha \quad [70]$$

Matula, et al. (2008) and Báťková, et al. (2014), on the other hand, sampled non-volatile LNAPL and water simultaneously from porous media using activated carbon pellet (ACP) and analyzed them using thermo-gravimetric analysis method. Activated carbon (AC) in the form of pellet was used in different experiments involving adsorption of organic compounds (Cho, 1995; Cho & Choi, 1996; Sarkar & Bose, 1997; Moon, et al., 1998; Inomata, et al., 2002). AC is the most widely used sorbent and has a wide applications (Yang, 2003). It is used as adsorbent due to its extended surface area, high adsorption capacity, microporous structure and special surface reactivity (Nevskaia, et al., 1999; Khalili, et al., 2000; Ania, et al., 2002). It is mainly usedd for the adsorbation purposes; e.g., for air purification, waste water treatment, solvent recovery, to remove color, odor, taste, and other organic and inorganic impurities including chlorine from drinking water (Marsh & Rodriguez-Reinoso, 2006); in food processing, chemical industry, for the removal of color from sugar syrup, oil and fat, in the purificaation of many chemical, food and pharmaceutical products (Bansal & Goyal, 2005). AC can be used in powdered (PAC), granular (GAC) or pelletized (ACP) form (Elsayed, et al., 2014). Powdered form is used through batch-contact treatment (measured amount of powdered activated carbon mixed with the substance to be treated and subsequently separated by filtration) (Hassler, 1963). However, with granular and pelletalized carbon the substance to be purified passes continuously through a bed packed with activated carbon (Chowdhury, et al., 2013; Wang, et al., 2013). GAC is commonly used for the treatment of contaminated water (AWWA, 2013) and also used in gas phase applicatins (Cheremisinoff, 2002). ACP mainly used in gas-phase application due to its lower pressure drop, high mechanical strength and low dust content (Cheremisinoff, 2002; Serp & Machado, 2015).

Before the industrial scale application of highly developed porous AC, a partially devolatilized carbonaceous materials commonly known as wood char or coal char were used as an adsorbent for many years, date back 3750 BC (Menendez-Diaz & Martln-Gullonb, 2006). The use of AC has gotten an attention due to its purification capacity. Menendez-Diaz & Martln-Gullonb (2006) stated that the first application of AC in industrial sector was in England in 1794 as decolorizing agent for sugar production. Since then it has been used in many industrial applications. Hassler (1963); Bansal & Goyal (2005) and Marsh & Rodriguez-Reinoso (2006) among others discussed the application of AC in a wide areas of household, municipal and industrial products. But, according to Hassler (1963), it was the use of chlorine gas against the Allied Forces by the order of German Command during World War I that brought the fame to AC. The author described that neither of the forces had the protective cover when German forces used the gas for the first time and had German forces had the protective mask, the history of the World War I would be different. However, the German forces couldn't use the gas fro more times and turned to study for another means of gas warfare and that gap was an opportunity window for Allied Forces to come up with the protective mask made from hard GAC (Faust & Aly, 1998).

Marsh & Rodriguez-Reinoso (2006) defines AC as porosity enclosed by carbon atoms. It has high porosity with high specific surface area between 300 to 4000 m^2/g approximately (Yang, 2003). The porosity and adsorption capacity of ACP made from different sources are different depending on the raw materials used to manufacture them (Hassler, 1963) and the processes of activation (Wu, et al., 2005) Hassler (1963) and Aktaş & Çeçen (2012) listed the raw material from which AC can be manufactured as: wood, pecan shells, coconut shells, bones, bituminous coal, lignite, peat, pulp mill back-ash, petroleum base residues etc. Yang & Yu (1998) classified the source as plant origin (e.g., coconut shell and wood), mineral origin (e.g., coal and asphalt) and synthetic fiber (e.g., scrap tires). The manufacturing of AC from raw materials takes through two steps. The first step is the carbonization of the source material by which drying and heating to remove undesirable by-products that includes tar and other hydrocarbon, and followed by the second process, activation of the resulting char (Aktaş & Çeçen, 2012). Activation which is basically means the manufacturing of more porous materials from non-porous or less-porous materials through chemical reaction can be through chemical activation (Ahmadpour & Do, 1997; Hayashi, et al., 2000; Jin, et al., 2011) or physical activation with steam (Arriagada, et al., 1997; Bouchelta, et al., 2008; Fu, et al., 2013). Method and level of activation affect the adsorption capacity. The level of activation affects the percentage of micro, meso and macro pores and the size of the pore increases with the activation. Inagaki & Tascón (2006) and Inagaki (2009) among others, described that based on IUPAC definition the pores of AC could be micro, meso or macro with the radius of less than 2 nm, 2 to 50 nm and greater than 50 nm respectively. Sorption of fluids takes place in micro and meso pores while macro pores are used for the transport (Bansal & Goyal, 2005). In addition to controlling access of the adsorbate, macropores serves as place for its deposition (Yang & Yu, 1998).

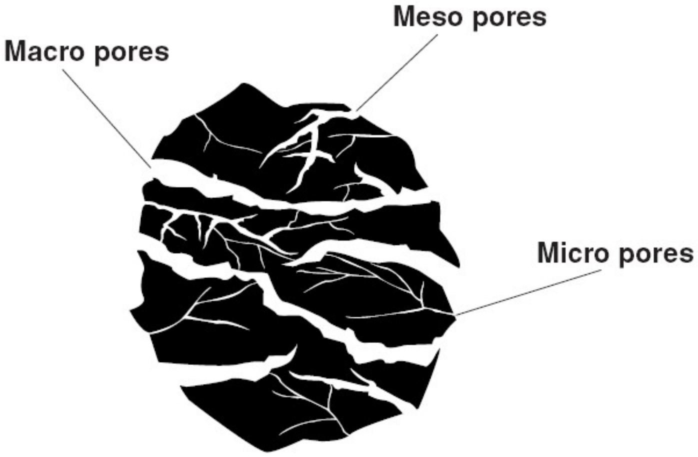


Fig. 13. Pore structure of activated carbon pellet, taken from Adib, et al. (2016)

A pure carbon surface is hydrophobic and affinity for water is very low (Parkyns & Sing, 1975). Yang (2003) argue that, however, even though weakly polar or nonpolar compounds preferentially adsorbed to AC, taking AC as hydrophobic material is incorrect as water can be adsorbed to it at higher vapor pressure. Hydrophobicity of carbon decreases and becomes increasingly hydrophilic as the amount of oxygen associated with its surface increases (Bansal & Goyal, 2005). In addition to oxygen, nitrogen content also affects the hydrophobicity of the AC (Li, et al., 2002). The presence of nitrogen reported to be effective for the adsorption of acid gases: H_2S, SO_2 and CO_2 (Adib, et al., 2000; Bagreev, et al., 2002; Plaza, et al., 2009). Generally, the nature of adsorbate (Ania, et al., 2002) and the nature of adsorbent such as surface chemistry (Plaza, et al., 2009; Shafeeyan, et al., 2010) and texture (Plaza, et al., 2009) affects the adsorption capacity of AC. Adib, et al. (2000) mentioned that the presence of oxygen, nitrogen, hydrogen and phosphorous governs surface chemistry.

Results from Yener, et al. (2008) show that sorption rate and capacity of PAC were greater than the corresponding value of GAC in removing dyes and pigments from wastewater. Bansal & Goyal (2005) presented that, despite the difficulty in handiling it, the size of PAC permits faster adsorption. Serp & Machado (2015) discussed that PAC presents bigger external surface area compared to GAC. Cheremisinoff (2002) indicated that using finer particle size AC improves adsorption efficiency through improving the diffusion rate to its surface. Meanwhile, Báťková, et al. (2014) showed that the diameter of the ACP significantly affects the amount of liquid adsorbed to it. Similarly, results from Elsayed, et al. (2014) show that ACP dimensions (both diameter and length) affect the adsorption kinetics.

AC can be used up to exhaustion (Cheremisinoff, 2002) and even depending on the nature of the adsorbate, it can be reused many times after regeneration/reactivation (cleaning/desorption) (Przepiorski, 2006). Adsorbate saturated AC loses its adsorption capacity and it should be either replaced or regenerated to restore the function (Sabio, et al., 2004). In addition to the prohibition of the direct disposal of the used AC (if adsorbents are considered as hazardous waste) in many countries, regeneration is generally cheaper than replacement (Lu, et al., 2011). Yang (2003) stated that stripping of the adsorbed molecule relatively easier and requires lower energy during regeneration to overcome non-specific, Van der Walls or London dispersion forces of adsorption. The spent AC can be regenerated through thermal desorption, pressure swing, extraction, thermal reactivation, chemical, or electrochemical processes (Cooney, et al., 1983; Newcombe & Drikas, 1993; Narbaitz & Cen, 1994; Moreno-Castilla, et al., 1995; Zhang, 2002; Sabio, et al., 2004; Przepiorski, 2006; Weng & Hsu, 2008). Adsorbates that are not volatile or soluble enough to be desorbed and removed through pressure reduction, elevation of temperature, or extraction with solvents can be thermally reactivated with the presence of steam or CO_2 (Przepiorski, 2006). Generally, spent AC can be regenerated either through desorption (e.g., thermal such as using inert gas, steam, or hot water, or nonthermal such as using solvent extraction, surfactant enhancement, or supercritical fluid extraction) or decomposition (e.g., microbial, electrochemical, or chemical) of the adsorbate (Sheintuch & Matatov-Meytal, 1999). Selection of the appropriate regeneration method depends on the nature of the adsorbate and economic, and environmental aspects. The regeneration efficiency of AC is not only depending on the percent of adsorbate removed but also on the reloading/adsorption capacity of the AC towards the same adsorbate after that (Narbaitz & Cen, 1997). Resluts from Bagreev; et al. (2001) show that eventhough it could be possible to desorbe 100% of the adsorbate, AC could be regenerated to 30% only. Meanwhile, Gómez-Serrano, et al. (2000) concluded that the surface chemistry and physical properties of regenerated AC used to remove H_2SO_4 from aqueous solution was not changed.

3. Materials and Methods

3.1. Experimental Setup

There were two different sets of experiments done for the study. For both sets of experiments, sample columns were packed manually. One set of the prepared sample columns were subject to different LNAPL to water ratios and the other set were saturated with oil only. LNAPL and/or water content of the first set of the experiments were analyzed using three different methods. While, LNAPL/oil was displaced from the second set of experiments by flooding the columns with three different liquids in mimic of decontamination. The purpose of the first set of the experiment was to create and verify a comprehensive but relatively simple methodology for quantification of properties of porous materials with respect to LNAPL after experimentation using water and medicinal grade white mineral oil moving through uniformly packed porous media. The purpose of the second set of experiment was to evaluate the impact of different liquids in remediating LNAPL contaminated media and the efficiency of LNAPL/oil recovery using different liquids.

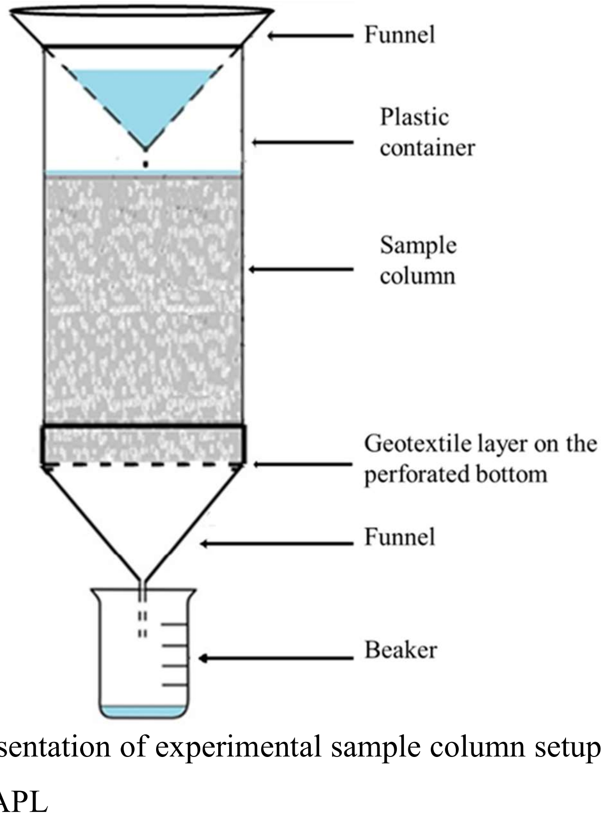


Fig. 14. Schematic representation of experimental sample column setup for the set saturated with water and/or LNAPL

The experiments were done in the laboratory under controlled temperature and relative humidity: with temperature range from 20 to 22 ºC and relative humidity 24 to 30%. For this purpose, sample columns were prepared in the laboratory using silica sand. The sand was packed layer by layer through gentle compaction to have uniformly packed sample column with 1.5 g/cm^3 bulk density. LNAPL and/or water for the first set of experiments and only LNAPL for the second set of experiments were applied to the prepared sample columns from the top and drained down and redistributed by gravity for over 24 hours, see Fig. 14 and Fig. 15 for the experimental setup. Drained out applied liquids from the sample columns were collected and analyzed.

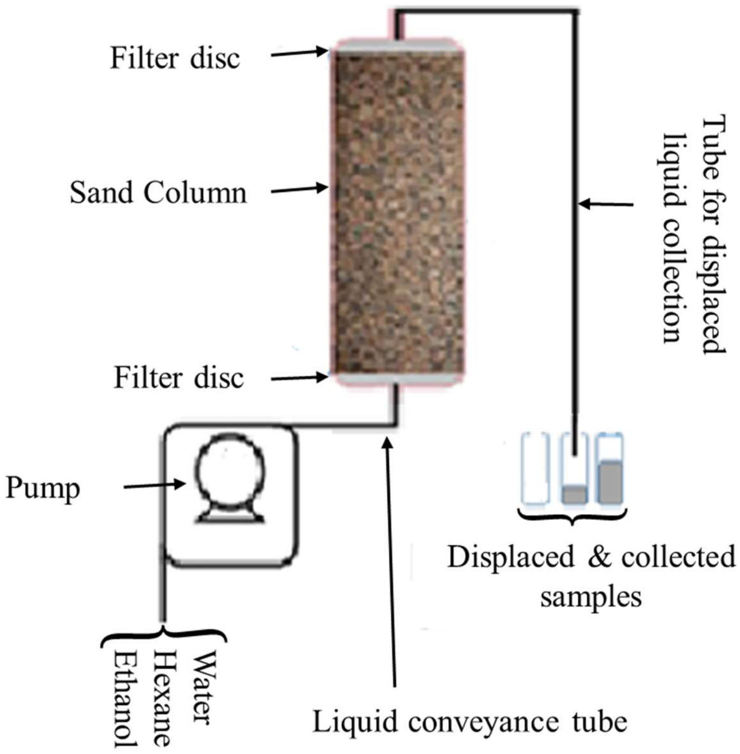


Fig. 15. Schematic representation of experimental sample column setup for the displacement of LNAPL from sample column

3.2. Materials used

Silica sand was packed in to transparent plastic tube for the sampling of LNAPL and Water from sample columns subject to different LNAPL to water ratios. For the set of the experiments used to study the impact of different liquids on the displacement of LNAPL from the porous media, the sand was packed in to transparent Plexiglas tube. Medicinal grade white mineral oil and water were applied from the top and distributed and drained downward using gravity for 24 hours before subject to the experimentations. The liquids were sampled from the porous media using activated carbon pellets and then LNAPL and water content of the sample column was determined using direct gravimetric analysis method from destructed sample. Water content of the sample columns was measured through indirect method using soil moisture sensors. For the group of the experiment used to study the displacement of oil from the sample columns, water, ethanol and hexane were supplied to the sample columns from the bottom against gravity. The displaced liquids were collected and analyzed for the content of the oil and injected liquid using gravimetric analysis method.

3.2.1. Silica sand

Porous media used to prepare sample column for this study was foundry silica sand commercially known as ST56 (Sklopísek Střeleč, a.s., Újezd pod Troskami, the Czech Republic). ST56 has narrow and uniform particle size distribution. And its particle size distribution ranges from 0.063 to 0.40 mm in diameter with effective grain size, d10, of 0.085 mm. The sand has a median grain size, d50, of 0.143 mm and a uniformity coefficient, Cu=d60/d10, of 1.82. Fetter (2014) described that a sample with Cu value less than 4 is well sorted sample, see Fig. 16 for its particle size distribution curve. ST56 is free from stones, gravel and very coarse sand (Table 2).

Chemically, ST56 is composed of silicon dioxide (SiO_2) (98.9%), Fe_2O_3 (0.07%), ($K_2O + Na_2O$) (0.02%) and ($CaO + MgO$) (0.02%). Almost 99% of ST56 sand is silica dioxide. British Geological Survey (2009) among others classified sand with silicon dioxide content greater than 95% as silica sand. Sklopisek Střeleč, a.s. (2015) company's sheet shows that ST56 has an average PH value of 8.0 with particle density 2.65 g/cm^3. Sklopísek Střeleč, a.s. produces different types of silica sand for different purposes and ST56 is produced for sport pitch surfaces cover. The company provides ST56 both in dry and wet conditions. The sand for the experiment was supplied packed and in oven-dry condition. However, to use for the experiment, it was evaluated for its water content. Its water content was determined using gravimetric analysis method. Ten samples from 10 to 20 g each were oven dried for 24h at 105 °C. Its average water content was 0.0% by mass (Table 3).

ST56 according to the producer's information sheet is free from organic matter. However, hexane was used in this study as a solvent in extracting oil from disturbed sample and as displacing liquid in displacing oil from sample column. Hexane is organic solvent and it could dissolve all hexane extractable material (HEM) and displace them with Marcol 82 oil from the sample column. HEM from ST56 could affect the analysis result for oil extracted or displaced from the sample column. Therefore, ST56 was tested for HEM content following Method 9071B (US EPA, 1998) and Method 1664B (US EPA, 2010) among other methods.

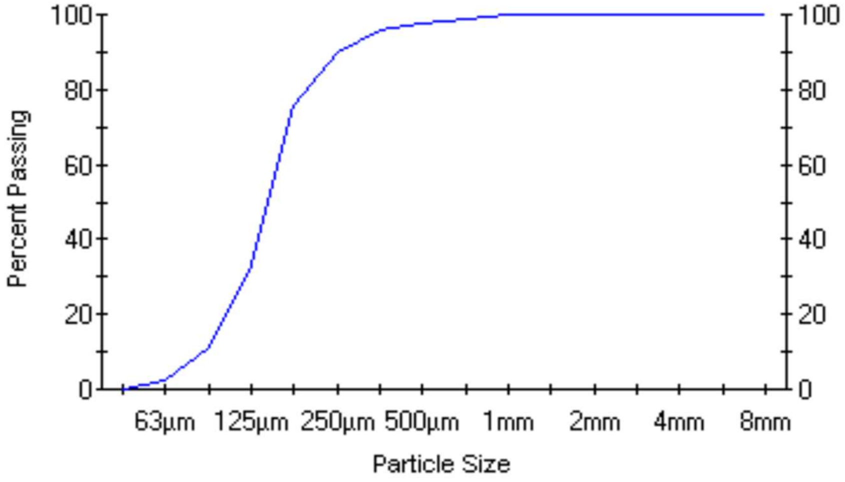


Fig. 16. Silica sand ST56 particle size distribution curve

Table 2. Textural contents of silica sand ST56

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

All the experiments consisting of hexane were done in well aerated room following the recommendations of the methods. Five 15 to 20 g oven-dried (to remove water) samples of ST56 were taken and 30 ml of n-hexane with 95% concentration by volume was added to each of them and shaken for 10 to 20 minutes and left for 10 more minutes. The extract was flittered using Whitman 40 filter paper and collected. The extraction was done three times from each sample following the same steps. Extraction funnel including filter paper was rinsed and cleaned before the filtering of the extracts begun with 10 ml of hexane and the same amount of hexane was applied at the end of filtering the extracts to collect down HEM from filtering system. The filtered extracts and the sand were oven dried at 80 °C for four hours and cooled down in a desiccator. The result from measured mass showed that there was no any extract left after evaporation and also there was no change in mass of ST56 used. Therefore, ST56 is free from HEM that could affect the value of the displaced oil from the sample columns.

Table 3. Initial Moisture Content of Silica Sand ST56

No	Mass of sand before oven dry	Mass of sand A fter oven dry	Mass of water (g)	Water content (%)
1	19.59	19.58	0.01	0.05
2	19.77	19.77	0.00	0.00
3	20.59	20.58	0.01	0.05
4	11.49	11.48	0.01	0.09
5	12.06	12.06	0.00	0.00
6	12.31	12.30	0.01	0.08
7	12.95	12.95	0.00	0.00
8	19.49	19.49	0.00	0.00
9	21.17	21.16	0.01	0.05
10	20.12	20.11	0.01	0.05

3.2.2. Liquids used

Four different liquids: three organics (ethanol, hexane and mineral oil) and one inorganic liquid, water was used in this study. Water and mineral oil were used in the experiments used for the quantification of water and LNAPL from porous media subject to different LNAPL to water ratios. All the four liquids were used in the experiments for the displacement of oil from sample columns. Additionally, the liquids were used in sampling liquids using activated carbon pellet (ACP) from free liquids pool for the selection of appropriate ACP for the experiment. Drinking quality tap water was used throughout the experiment. Some common properties of the liquids used are presented in

Table 4. The dielectric constant (relative permittivity) of the ethanol, n-hexane and ethanol is from Wohlfahrt (1991; 2008) and Marcol 82 mineral oil is from Ross (1980) and Taslak, et al. (2015).

Table 4. Some properties of liquids used in the experiment

Liquid	CV	ρ	BP	μ	AS	n	ε
Water	100	1	100	1.00[a]	-	1.333	80
Marcol 82	100	0.855	150 - 350	27 – 37 [a]	immiscible	1.464 – 1.470	2.2
Ethanol	96.6	0.789	78	1.08 [b]	miscible	1.360	25
n-hexane	95	0.659	67- 69	0.30[b]	9.5 – 13[c]	1.376	1.9
n-hexane	99	0.659	68 - 70	0.30[b]	95 – 13[c]	1.375	1.9

[a] 20 °c., [b] 25 °c., [c] in distilled water @ 20 °c.

Where: CV is content by volume (%), ρ is density at 20 °C, BP is boiling point (°C), μ is dynamic viscosity (mPa.s), AS is aqueous solubility (g/L), n is Refractive index (-) and ε is relative permittivity (-) at 20 °C.

3.2.2.1. Oil

Oil used in this study as LNAPL was medicinal grade white mineral oil with commercial name Marcol 82 (Lubstar, The Czech Republic). The oil is also known by another name, and International Nomenclature of Cosmetic Ingredients, Europe (INCI) calls it Paraffinum Liquidum, while The USA Cosmetic, Toiletry and Fragrance Associations (CTFA) calls it simply Mineral Oil. The number of carbons per molecule of mineral oil ranges from 15 to 40. Speight (2014) stated that mineral oils are grouped in to aromatic, naphtenic and paraffinic three main groups. However, medicinal grade white mineral oil is a mixture of saturated hydrocarbons with carbon content from C15 to C24 per molecule (Stoker, 2013). According to Exxonmobil (2016), Marcol 82 is the result of several refining stages including catalytic hydrogenation to remove aromatic group of hydrocarbons and other unnecessary constituents of the crude oil. Hence, Marcol 82 is a purified mixture of liquid saturated hydrocarbons. Lubstar (2015) described that the percentage of paraffinic, naphthenic, and aromatic content of Marcol 82 is 67, 33 and 0 respectively. Hence, Marcol 82 is free from toxic polycyclic aromatics and heavy metals. On top of that, high temperature during the production of Marcol 82 destructs germs completely. It is chemically inert and has better oxidative stability compared to most mineral and vegetable oils (Exxonmobil, 2016).

Due to its superior quality, Marcol 82 has a wide application in cosmetic industry, pharmaceuticals and even in a verity of food-contact materials but not used as food additives or in nasal, oral or lip care products (Exxonmobil, 2016). Some of the usage of Marcol 82 in cosmetic industry includes but not limited to baby products (shampoos, baby oils and bath oils), hair care products, emollients, moisturizers, antiperspirant and deodorant sticks and in pharmaceuticals used as ingredients in the production of topical ointments and petroleum jellies and also used as a pelletizer aid, and in the manufacture of gelatine capsules (Lubstar, 2015).

Marcol 82, like pure water is colorless, odorless and tasteless. However, Marcol 82 is lighter than water and incapable of mixing with water and it is immiscible liquid with respect to water. Some basic properties of Marcol 82 is given in

Table 4. Stability, higher boiling point compared to water, absence of toxic materials, colorlessness, odourlessness and tastelessness as well as its density and immiscibility with water were some of the considerations to select it for this study following Matula, et al. (2008) and Báťková, et al. (2014).

Marcol 82 oil was tested for evaporation loss to the maximum oven temperature used during the experiment, 105 °C for 24h. Boiling point of the hydrocarbons depends on the number of carbon content per molecule and for similar structural arrangements of hydrocarbons, boiling points increases with the number of carbon contents (Bettelheim, et al., 2013). Marcol 82 is a medicinal grade mineral oil and medicinal grade mineral oil is a mixture of $C_{15}H_{32}$ to $C_{24}H_{50}$ alkanes (Stoker, 2013) and the boiling point of pentadecane is 270.6 °C. However, there might be evaporation loses at any temperature and hence, Marcol 82 oil was tested for used maximum oven temperature evaporation loss. Fifteen samples of 10 ml (8.55 g) each were oven dried at 105 °C for 24h and the loss to evaporation was determined. The previous study by Matula, et al. (2008) showed that the oil is stable with respect to 105 °C oven temperature. The result from this experiment also confirmed that the oil is stable up to 105 °C oven temperature and the loss was only 0.08% by mass in average with 0.04 standard deviation.

3.2.2.2. Hexane

Another liquid used in this experiment is hexane (C_6H_{14}) from Penta s.r.o., the Czech Republic. It was used in testing the sorption capability of ACP, for the extraction of oil from destructed sample from the sample column, and to displace oil from the sample column. Hexane is a saturated hydrocarbon with five isomers which are all liquid at room temperature (Mackay, et al., 2006). Even though hexane has five isomers, International Union for Pure and Applied Chemistry (IUPAC) nomenclatures only n-hexane as hexane and named the rest four as the methylated derivatives of pentane and butane (Raymond, 2014). All isomers of hexane are acyclic alkane, but n-hexane has both melting and boiling points higher than the other four hexane isomers (Brown, et al., 2017). The hexane used in this experiment is normal hexane (n-hexane) and here afterwards in this document as hexane unless to identify n-hexane from the other isomers of hexane.

The most excellent use of n-hexane is as a solvent and is a major solvent in the extraction of edible oils from seeds and vegetables (Johnson & Lusas, 1983; Johnson, 1997); and to extract oil and grease from contaminated water and soil for laboratory analysis (US EPA, 2010). It is also used as a cleaning agent/degreaser in the textile, leather and furniture industries and as a solvent additive in glues (rubber cement, adhesives), varnishes, and inks (US EPA, 2000b). Hexane is one of the additives of gasoline (C6 - C12) (Raymond, 2014). Hexane was used as an extracting liquid in this study based on n-hexane extractable materials (HEM) of US EPA (1998) Method 9071B and US EPA (2010) Method 1664. Additionally, it was used as an adsorbate for the evaluation of different sources of activated carbon pellets' adsorption capacity. Hexane was also used in the displacement of oil from the sample column. There were 95 and 99% by volume of hexane used in this study. Hexane with 95% concentration was used in the evaluation of activated carbon pellet's sorption capability and for displacing of the oil from the sample column. But, for the extraction of oil from destructed sample both 95 and 99% concentration of hexane were used. The hexane has boiling point from 67 °C to 70 °C, density of 0.659 g/ml and immiscible with water, for some more common properties of the hexane, see Table 4. Hexane like Marcol 82 oil, is a light non-aqueous phase liquid. However, in this work the term oil and LNAPL refer Marcol 82 oil only.

3.2.2.3. Ethanol

Ethanol was one of the liquids used as an adsorbate for the evaluation of activated carbon pellet's sorption capability. It was also used for displacing oil/LNAPL from sample column. Ethanol used for this experiment was technical grade bio ethanol from Biointerier s.r.o, the Czech Republic, and here afterwards in this paper referred as ethanol. See Table 4 for some properties of ethanol used in this experiment. Ethanol is known also as ethyl alcohol, drinking alcohol or simply as alcohol is the member of a large family of organic compounds, alcohol group. Alcohol group is the derivative of hydrocarbon organic compounds group with hydroxyl (-OH) functional group that is covalently bonded to saturated hydrocarbons (alkanes). This group of organic compounds has both polar and non-polar character. The hydroxyl group presents as polar and the alkyl group presents as nonpolar (Bettelheim, et al., 2013). However, the non-polarity character dominates its polarity as the number of carbon atoms per molecule increases. Stoker (2013), among others, mentioned that the first three members of the group including ethanol are totally water soluble while water solubility of the other members of the group dramatically decreases with increasing carbon numbers.

The wide and commonly known use of ethanol is for drinking as an alcoholic beverage. However, the largest single end use of ethanol according to Stoker (2013) is as a fuel for motor vehicles. Ethanol is used as a fuel after blended with gasoline. It boosts the octane number of the gasoline (Lucius, et al., 1992) and results in cleaner fuels and little pollution (Yüksel & Yüksel, 2004). The ethanol content of the fuel could be up to 85% by volume for modern vehicles or even up to 100% for flex-fuel cars (McElroy, 2010). However, Karpov (2007) indicated that problems with starting carburetor engines below 10 °C and poor evaporation of alcohol at higher load make the use of higher load of alcohol undesireable. Ethanol used in this experiment was bio ethanol with 96.6% ethanol content by volume, see Eq. [66] for bio ethanol production from sugar (glucose) through fermentation process. However, the bio ethanol used was denatured with less than 1% of 2-butanon by volume to make it for the use of technical purposes only and unfit for drinking. On the other hand, most technical ethanol used in industrial application is the denatured ethanol prepared from hydrocarbon, ethene via a hydration reaction (Stoker, 2013), see Eq. [72] for industrial ethanol production from ethene via a hydration reaction.

$$C_6H_{12}O_6 \xrightarrow[Fermentation]{Yeast} 2CH_3 - CH_2 - OH + CO_2 \qquad [71]$$

$$CH_2 = CH_2 + H_2O \xrightarrow{Catalyst} CH_3 - CH_2 - OH \qquad [72]$$

3.2.3. Activated carbon pellet (ACP)

Material used as an adsorbent to sample water and/or LNAPL from the sample column was pelletized activated carbon Silcarbon SC40. To choose better ACP for the purpose, two different sources of SC40, from Brenntag, Ltd., Prague, the Czech Republic and Techpoint s.r.o, the Czech Republic were compared for their adsorption capacities. Both used SC40 have an average diameter of 4 mm and length in the range of 7.5 to 12.0 mm. The dimensions of the pellets were measured using a digital sliding gauge EXTOL® Premium, Všestary, the Czech Republic with an accuracy of 0.01 mm. ACP from both sources were evaluated for their adsorption capacities using different liquid pools. Other qualities (e.g., time to settle at the bottom of the liquid pool and strength among others) were also used to choose SC40 with better performance for the sampling of water and/or LNAPL from the sample columns.

Table 5. Main characteristics of ACPs used

Name	Aspect	Media diameter	Specific area	Apparent density	Initial water content
*SC40	pellet	4 mm	1100 m^2/g	450 ± 25 kg/m^3	< 6%
**SC40	Pellet	4 mm	1100 m^2/g	-	< 4%

Where: * is ACP from Brenntag Ltd. and ** ACP from Techpoint S.r.o.

3.2.3.1. Initial water content of ACP

Initial water content of SC40 from both sources was tested. The producers' fact sheets show that the water content at packing was less than 4% and 6% by mass for ACP from Techpoint and Brenntag respectively, Table 5. American Water Works Association, AWWA (2012) indicated that up to 8% water content by mass for GAC is acceptable for waste water treatment. 20 ACPs from each source were oven dried at 105 ^{O}C for 24h and water content was determined through gravimetric analysis method, see **Error! Not a valid bookmark self-reference.** for the summarized result. The results show that water contents of ACPs from both sources are in the specified range set by the producers and recommended for water treatment use by AWWA (2012).

Table 6. Statistical summary of ACPs' water content at packing

	ACP from Techpoint (g)				ACP from Berrentag (g)			
	Mass BOD	Mass AOD	Δ	WC (%)	Mass BOD	Mass AOD	Δ	WC (%)
Mean	0.1529	0.1510	0.0019	1.2	0.0719	0.0708	0.0011	1.5
Median	0.1568	0.1545	0.0018	1.2	0.0706	0.0693	0.0008	1.1
Standard Dev.	0.0088	0.0088	0.0006	0.4	0.0104	0.0096	0.0009	1.1
Minimum	0.1362	0.1344	0.0007	0.5	0.0490	0.0490	0.0000	0.0
Maximum	0.1634	0.1617	0.0029	2.1	0.0941	0.0904	0.0037	4.1
Count	20	20	20	20	20	20	20	20

Where: Standard Dev. is for standard deviation, BOD and AOD are before and after oven dry respectively, and Δ is their mass difference.

3.2.3.2. Initial water content and adsorbed liquid to ACP from free liquid pool

The relationship between ACPs' initial water content and amount of liquid adsorbed to them were evaluated. Forty for Brenntag and thirty for Techpoint oven-dried ACPs were used for each four types of liquids used. They were kept in water, Marcorl 82, ethanol, and hexane pools with the depths of 1.5, 1.8, 1.9 and 2.3 cm respectively for thirty minutes. The mass gained, or the amount of adsorbed liquid was analyzed using gravimetric analysis method. The results are plotted as Fig. 17 for both ACP sources and liquids used. The plots show that ACP from Brenntag has more initial water content than ACP from Techpoint. Furthermore, the adsorptive capacity is less in ACP from Techpoint compared to the one from Brenntag. However, the correlation between initial water content and adsorbed liquid for all the four pairs shows that there is no strong link between the initial water content and the amount of any adsorbed liquid to either of the ACP used ($R < 0.5$). The coefficient of determination ($R^2 = 0.24, 0.23$) revealed that maximum 24% and 23% of the variance in adsorption test were explained by initial water content of ACPT and ACPB respectively for water, and for many of them the values were below 5% (Fig. 17).

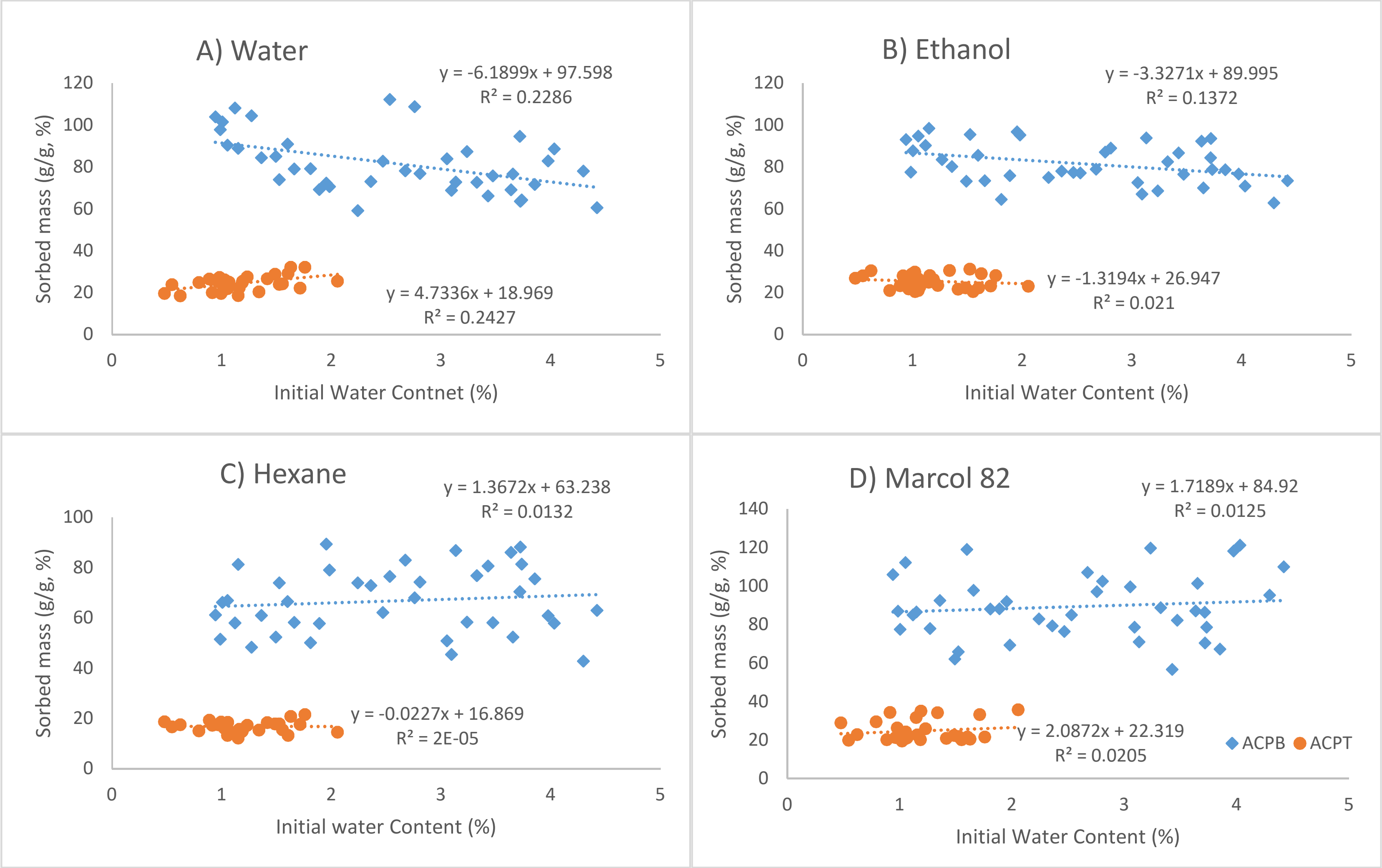


Fig. 17. Graph of adsorbed liquid to ACP vs its initial water content

Where: ACP is activated carbon pellet, ACPB and ACPT are activated carbon pellets from Brenntag and Techpoint respectively

3.2.3.3. Adsorption capacity of ACPs from liquid pool

Adsorption capacity of ACPs produced from different source raw materials and even from the same but different techniques of production/activation could be different (Laine & Yunes, 1992; XiangLan, et al., 2012; Shuahua, et al., 2017). Adsorption performances of ACPs from Berrentag and Techpoint were evaluated for their adsorption capacity in different types of free liquid pools. Liquids used were drinking quality tap water, ethanol, hexane, and medicinal grade white mineral oil (Marcol 82). Thirty ACPs from Techpoint and sixty-five from Berrentag for each liquid used were oven dried at 105 °C for 24h. The oven-dried pellets were placed in water, Marcol 82, ethanol and hexane pools at the depths of 1.5, 1.8, 1.9 and 2.3 cm respectively for thirty minutes. The masses of the ACPs were measured before and after adsorption and analyzed using gravimetric method. The results show that for any liquid types used, over 70% by mass or 85% by volume of adsorbed liquid to mass of ACP were adsorbed to ACP from Brenntag. Meanwhile, the amount of adsorbed liquids to ACPs from Techpoint were not more than 40% by mass for any of the liquids used (Fig. 18).

In most literature, the amount of adsorbed liquids to activated carbon is reported in mass bases (McKay, et al., 1985; Ying, et al., 1990; Karanfil, et al., 1996; Aygün, et al., 2003; Ayotamuno, et al., 2006; Apul, et al., 2013). However, most of the surface area of AC, especially in granular and pelletized forms, is found on the pore surfaces. Hence, it seems logical to report the amount of the adsorbed liquid with the volume of adsorbed liquid to the mass of ACP. Mangun, et al. (1998) reported by the volume of adsorbed liquid to the mass of AC. Liquids used in the experiment: water, ethanol, hexane and Marcol 82 have 1, 0.789, 0.659 and 0.855 g/ml densities respectively. Graph under Fig. 18 shows the percentage of adsorbed liquids to ACPs both in mass and volume basis. The change in reporting unit does not change the amount for water adsorbed, while it affects the lest dense liquid, hexane the most. Results from adsorbed liquids to ACP mainly to ACP from Brenntag clearly show that there were differences in amount of three organic liquids adsorbed when reported in mass basis, while the difference is not visible from the graph when reported in volume bases (Fig. 18). However, many authors, e.g., Daifullah & Girgis (2003) and Li, et al. (2012) concluded from mass basis analysis that AC adsorption increases with increasing the molecular weight of an adsorbate.

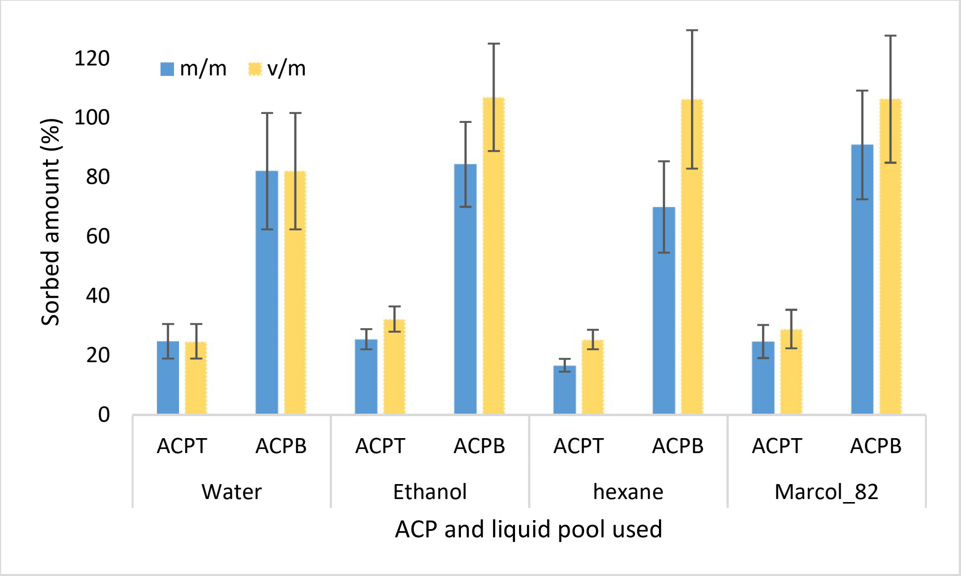


Fig. 18. Amount of adsorbed liquids to ACP from free liquid pools

Where: blue and yellow show in mass and volume basis respectively and ACPT and ACPB are activated carbon pellet from Techpoint and Berrentag respectively

In addition to the adsorption test, time taken for ACP released at the surface of the water pool to settle at the bottom of the pool and strength difference were compared. ACP from Brenntag looks like stronger than the ones from Techpont and less fragile. Thirty ACPs from each source were selected randomly and released at the top of 1000 ml graduated cylinders filled with water. Time taken to the individual ACP to sink and settle at the bottom of the water pool was recorded. The results show that it was somewhere between 4 to 9 seconds for the ACP from Techpoint to settle at the bottom of the water pool. However, it can take even more than 4 minutes for the ACP from Brenntag to settle at the bottom the pool. No settlement recorded before 10 seconds for ACP from Brenntag (Fig. 19). It indicates that ACP from Techpoint is denser or less porous than ACP from Brenntag. On the other hand, even though most of the wastewater treatment using AC is by gravity filtration through fixed-bed made from AC (US EPA, 2000b; Çeçen & Aktaş, 2012), dissolved contaminants could be found throughout the water while LNAPL contaminants mainly floats on the surface of the contaminated water. Based on its performance and recommendation made by Matula, et al. (2008), ACP from Brenntag was chosen for the sampling of LNAPL/Water from sample column. And here after wards in this work the abbreviation ACP is used for the activated carbon pellet from Brenntag only.

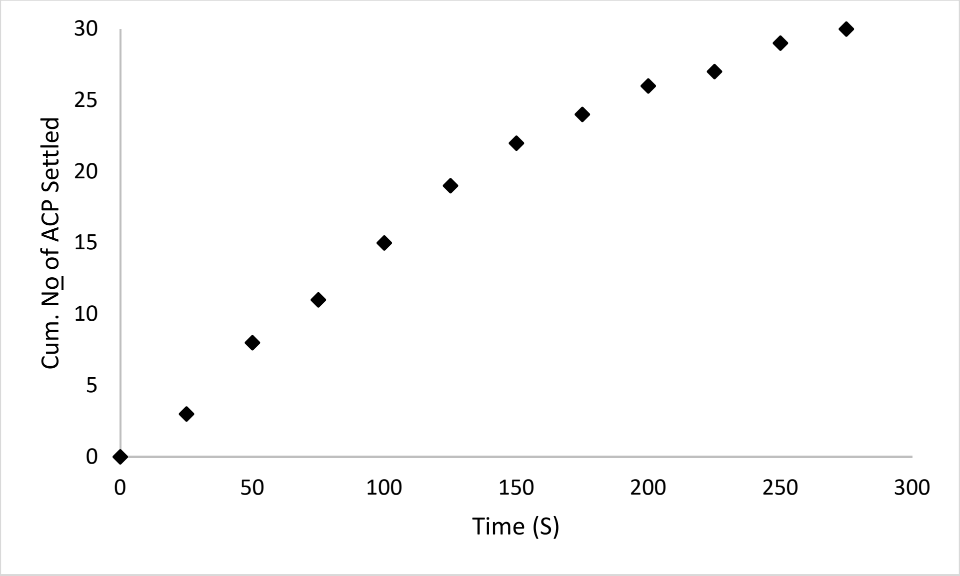


Fig. 19. Graph of cumulative ACP settled at the bottom of water pool

The apparent density of ACP used for the experiment is 450 ± 25 kg/m^3 with the specific surface area approximately 1100 m^2/g (Table 5). Its initial water content at packing was less than 6% by mass (Fig. 17). The iodine adsorption number of the pellet is greater than 1050 mg/g. The average mass of the pellets used for the experiment was about 0.08 g with 0.4683 standard deviation. The mass of a pellet depends on the dimension of the pellet. The average diameter and length of the pellets used were 4 and 9 mm respectively with 0.0095 and 1.711 respective standard deviations. All the handlings of the pellets were taken in small Petri Dishes. ACPs were dried out to constant mass at 105 °C oven temperature for 24h before all the experiments involving ACPs. ACPs with small Petri Dishes were stored in desiccator to cool down for the measurement and to keep the mass constant throughout the experiment.

3.3. Sample column preparation

Sample columns were prepared from silica sand for two different sets of experiments. The first set of the sample columns were prepared for the analysis of sample columns' Water/LNAPL content through different methods. While the second set of the sample columns were prepared for the displacement of oil/LNAPL from porous media. The two sets used different sizes of the sample columns but from the same sand and LNAPL. The Sample columns were packed with bulk density of 1.5 g/cm^3 from silica sand ST56 with particle density 2.65 g/cm^3. Porosity and pore volume of the sample columns were calculated following Singh and Kanwar (1991) from bulk density-particle density-porosity relationship, Eq. [73], as follows:

$$\emptyset = 1 - (\rho_b/\rho_d) \qquad [73]$$

Where, $\emptyset$ is porosity, ρ_b is bulk density, and ρ_d is particle density

However, Vogeler, et al. (2001) among others consider a pore volume as the volume of a porous media in question saturated by a fluid. The values from both methods could be the same if and only if all the pores of the prepared sample column would be water saturated pores. To be consistent, however, porosity and a pore volume of the sample columns throughout this work were calculated based on Singh and Kanwar (1991) Eq. [73]. Hence, the porosity of the sample columns for both sets of experiments was 43.4%. But they had different one pore volume since the total volume of the sample columns for the two sets are different. A pore volume (Pv) of a sample column was calculated from total volume of the sample column and its porosity, Eq. [75]. The number of pore volumes of a liquid passes through the sample column was calculated using Eq. [74] from the total volume of liquid passes through the sample column divided by its pore volume (Kirkham, 2014).

$$P_{Nv} = Q * t/P_v \qquad [74]$$

$$P_v = \emptyset * V_s \qquad [75]$$

Where: Pv is one pore volume, ϕ is porosity of the media, V_s is the total volume of the sample column, P_{Nv} is number of pore volume, Q is discharge, and t is time

3.3.1. Sample column for the sampling of LNAPL/water from porous media

Sample columns were prepared from silica sand ST56 in to transparent plastic container with inner diameter of 11.3 cm to the height of 8 cm. The container was perforated at the bottom to allow free drainage of the applied liquids to the sample columns, with geotextile at the bottom to keep the sand from loss. Sand with initial water content less than 0.05% in average was used, Table 1. Some liquid (LNAPL or water) was applied to a loose sand to make packing suitable. The sand and liquid were mixed thoroughly and packed uniformly layer by layer. The height of the column was divided in to four equal parts, each 2 cm. For each layers of the column 300 g of silica sand and 10 to 20% Pv of liquid was added and mixed thoroughly. The mixtures were repacked layer by layer to have uniform sample column. The column dry sand content was approximately 4×300 g = 1200 g and its volume was $\pi\times (11.3/2)^2\times 8\ \text{cm}^3 = 800\ \text{cm}^3$. One Pv of the sample column was $800\ \text{cm}^3\times 0.434 = 347\ \text{cm}^3$. For consistency and uniform distribution of the liquids across the sample column, one pore volume plus of water and /or LNAPL were applied to simulate gravity assisted multiphase flow. Through the experiment, the total amount of liquid applied to a sample column was ≥ 365 ml.

Table 7. Amount of water and LNAPL applied to the sample columns

Water to LNAPL ratio	Amount of liquid applied during sample column preparation		Amount of liquid applied from the top to prepared sample column	
	amount (ml)	Liquid	amount (ml)	Liquid
100:0	80	water	285	water
90:10	40	LNAPL	325	water
75:25	88	LNAPL	277	water
65:35	80	water	125 + 160	LNAPL + water
50:50	80	LNAPL	180 + 105	water + LNAPL
35:65	80	LNAPL	125 + 160	water + LNAPL
25:75	88	water	277	LNAPL
10:90	40	water	325	LNAPL
0:100	80	LNAPL	285	LNAPL

The applied ratios were 100:0, 90:10, 75:25, 65:35, 50:50, 35:65, 25:75, 10:90 and 0:100 by volumes in three replications each. For 100:0 and 0:100, 4×20 mL = 80 ml of water and LNAPL were applied respectively to wet dry sand during packing. The rest (365^{+} ml – 80 ml ≥ 285 ml) of the water and LNAPL were applied to the respective repacked sample columns from the top, and drained and distributed downward by gravity. The amount of liquid used during packing and applied from the top to repacked sample columns for the rest of water to LNAPL ratios are presented under Table 7. Drained outflow of liquid from the sample columns were collected and analyzed. The mass of sample column immediately after packing, after drained by gravity for 24 hours, and the mass of drained out liquid were measured, see Table 8 for the values. The sample columns were covered both at the bottom and top to avoid evaporation loss during the sampling of water and/or LNAPL using ACP and other experimentations.

Table 8. Average mass of sample column, its liquid content, and drained-out liquid

Water to LNAPL Ratio	Sample column and its liquid content mass (g)			Drained-out liquid mass (g)		
	AP	AD	LC	BOD	AOD	Loss
100:0	1279.23	1514.03	314.03	8.10	0.00	8.10
90:10	1235.53	1511.18	311.18	6.53	0.01	6.52
75:25	1275.23	1507.61	307.61	6.89	6.83	0.06
65:35	1280.41	1536.59	336.59	19.23	19.23	0.00
50:50	1268.36	1483.50	283.50	40.21	40.19	0.02
35:65	1269.41	1465.09	265.09	44.27	44.24	0.03
25:75	1287.11	1501.46	301.46	7.18	7.12	0.05
10:90	1241.03	1492.09	292.09	8.89	8.86	0.03
0:100	1268.53	1455.59	255.59	31.66	31.64	0.02

where: AP is after packing, AD is after drainage, LC is liquid conetent of the sample column, BOD and AOD are before and after oven dry of the drained out liquids, and loss is loss to evaportion

3.3.2. Sample column for the displacement of LNAPL

Silica sand ST56 was packed into plexiglass tube with 4.5 cm diameter to 15.5 cm height. A filter disk (Filtrak 390) was fitted to either ends of the sample column and small inert glass marbles were used to fill the space between the upper filter disk and the column outlet. Sample column was prepared from uniformly packed 377.25 g of silica sand ST56. It was repacked layer by layer in five layers, each 3.1 cm thick. The porosity and a pore volume of the sample column were 43.4% and 107 ml respectively Eqs. [73] & [75]. More than one Pv of oil was applied (110 ml) to the sample column and 25 ml of it was used during sample column packing whereas the rest 85 ml was applied to the prepared sample column from the top in mimicking contamination. The applied LNAPL was drained down and distributed with gravity for over twenty-four hours to achieve equilibrium condition. The drained-out oil was collected and determined. Both ST56 and Marcol 82 oil are chemically inert and hence the loss of the oil due to microbial activity during the experimentation was assumed to be negligible. In mimic of decontamination, oil saturated sample columns were flooded with ethanol and hexane at 200 ml/h, and water at 100, 200, 400 and 800 ml/h. Sample columns were prepared in three replications for each liquids and flooding rates.

Table 9. Basic descriptive statistics of sample columns prepared, amount of oil drained out and amount of oil in the sample columns

	saturated Sample column (g)	Drained out oil (g)	Drained out oil (ml)	oil in sample column (g)	oil in sample column (ml)
Mean	459.05	11.94	13.96	81.80	95.68
Median	459.08	11.79	13.78	81.83	95.70
Standard Deviation	0.81	0.82	0.96	0.81	0.95
Range	2.91	2.82	3.30	2.91	3.41
Minimum	457.62	10.73	12.55	80.37	93.99
Maximum	460.53	13.55	15.85	83.28	97.40

Table 9 shows that the average mass of saturated sample columns prepared was 459.05 g with standard deviation 0.81. The average amount of applied oil that drained out from the sample columns over twenty-four hours was 11.94 g with standard deviation 0.82. The amount of oil in saturated sample columns were calculated from the amount of applied oil and drained out oil. The amount of LNAPL applied was 110 ml to each sample column and the average volume of drained out oil was 13.96 ml and hence the average volume of the oil in saturated sample columns could be 96.04 ml (110 ml – 13.96 ml). The difference between the two values, 0.36 ml (96.04 ml – 95.68 ml) is very small compared to the total amount of oil in the sample columns. Therefore, we can use the maximum value, and the average amount of oil in saturated sample column for the displacement experiment was taken 96.04 ml.

3.3.3. Sample column water and/or LNAPL content

Total sample column's liquid content can be estimated roughly from the amount of applied liquid, drained-out liquid and mass of the sample column by assuming the loss of the sand during sample column preparation was negligible. Based on this assumption, the amount of dry sand in each sample columns were 4×300 g = 1200 g and the additional weight of the sample column were only of the liquid applied to it (Table 8). However, under practical condition it is difficult to avoid the loss of both sand and liquid (e.g., evaporation loss) during sample column preparation. In this experiment water and /or LNAPL were sampled from sample columns saturated with different water to LNAPL ratios using ACP. Sample columns were also analyzed for its water and LNAPL content using direct gravimetric analysis method and indirect methods using soil moisture sensors.

3.3.3.1. Sampling of liquids from the sample columns using ACP

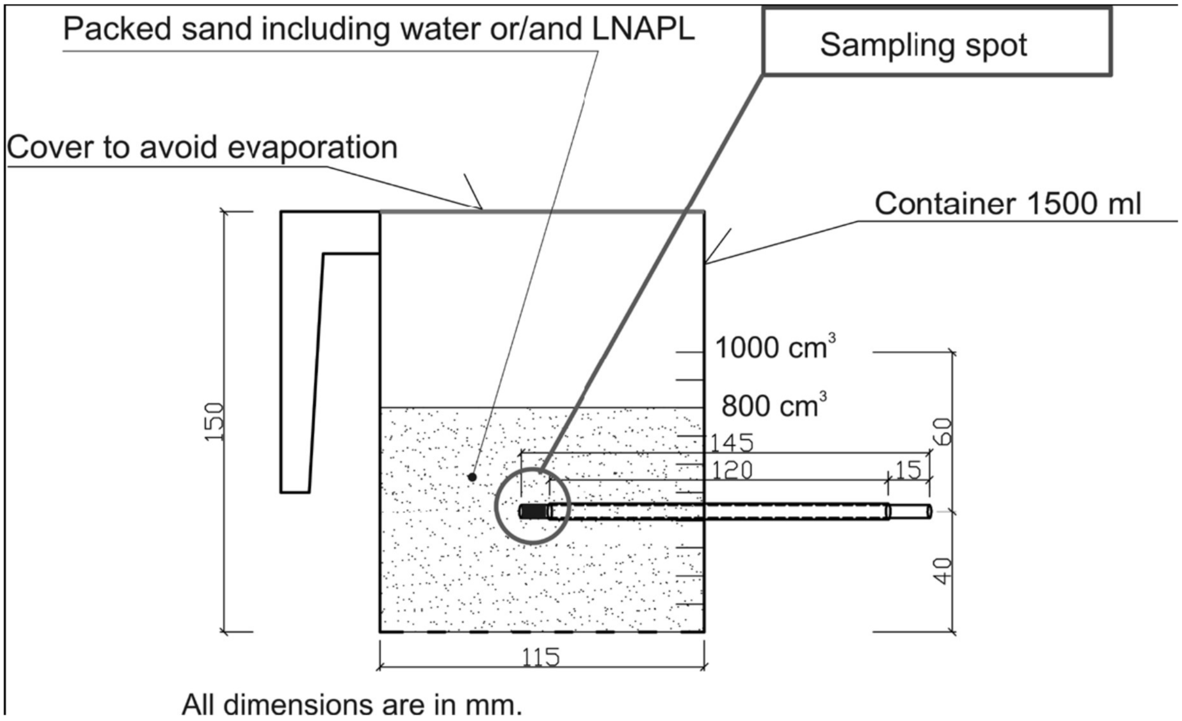


Fig. 20. Schematic of the experimental setup for sampling of water and/or LNAPL from sample column, taken from Báťková, et al. (2014)

Water and/or LNAPL were sampled from the sample columns through adsorption using ACP. The sampling was taken place from the center of the sample column. ACP was placed in to the sampling point using a lab-built metal sampler and left there for thirty minutes. A total of six for one water to LNAPL ratios were taken by sampling twice from each prepared sample columns. The methodology and materials followed Matula, et al. (2008) and Báťková, et al. (2014). The experimental setup, which is taken from Báťková, et al. (2014) is shown as Fig. 20. ACP after sampling liquids from porous media were oven dried at 105 ^{O}C for 24 hours to separate water from LNAPL. The mass of ACP before sampling, immediately after sampling, and after oven drying were measured using digital balance. The amount of adsorbed liquids was determined using gravimetric analysis method. Except at the sampling time, ACPs were kept in small heat resistant, transparent Petri Dishes. The Petri Dishes were used in handling ACPs through the experiment e.g., during measuring, oven drying and cooling down to constant mass in desiccator.

3.3.3.2. Measuring water content using soil moisture sensors

Water contents of the sample columns from which water and/or LNAPL were sampled using ACPs were measured through indirect method using soil moisture sensors. Soil moisture sensors used for the measurement were 5TE and ECH$_2$O-TE, both from Decagon Devices, Inc., USA. 5TE and ECH$_2$O-TE sensors have almost the same prong length which are 5.2 and 5.3 cm respectively. Approximately water content of the top 6 cm of 8 cm long sample column was measured, see Fig. 21. The readings were taken at the midway of 11.3 cm diameter of the core sample columns three times and their average was taken as the water content of the top 6 cm of a sample column.

Fig. 21. Soil moisture sensors used in the experiments: 5TE top and ECH2O-TE, taken from Decagon device, Inc.

The idealized water content measurement using 5TE sensor is given under Fig. 22. In addition to volumetric water content, both sensors give the readings of electric conductivity and temperature of the sample column. The sensors give water content in volumetric basis from the bulk relative permittivity of the sample columns based on Eq. [62] of Topp, et al. (1980). Bulk dielctric permitvity of the sample columns were calculated from the equation and optimized using

Microsoft Excel Solver. The calculated bulk relative permitivty was used for the estimation of volumeteric LNAPL content of the sample columns using Eq. [71] and to evaluate DMM for the estimation of water and LNAPL.

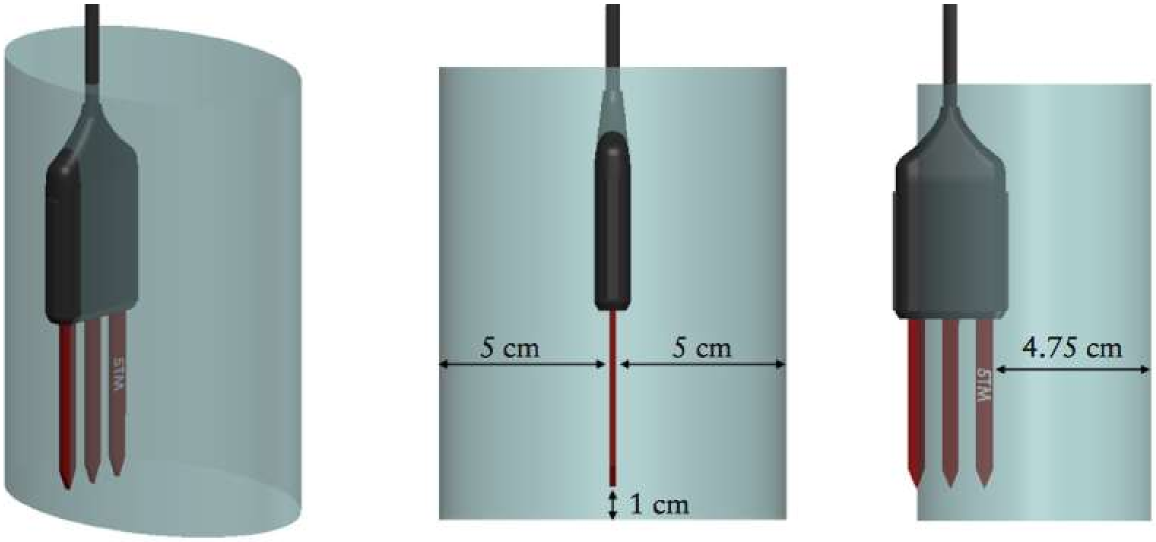


Fig. 22. Idealized measurement volume of Decagon 5TE, taken from Decagon Devices, Inc.

3.3.3.3. Water and LNAPL content analysis through gravimeteric method

Sample column water and LNAPL contents were determined through direct method by taking destructed samples from the sample columns. 10 to 20 g of disturbed sample were taken from three positions: top, middle and bottom of the sample columns. The samples were oven dried for 24h at 105 °C to determine the water content. The mass of the oven-dried samples was taken and LNAPL was extracted from the sand using hexane following Method 9071B (US EPA, 1998) and Method 1664B (US EPA, 2010) among other methods for hexane extractable material (oil and grease) and here afterwards HEM. LNAPL was first extracted using hexane with 99% concentration and then twice with n-hexane with 95% concentration by volume. 30 ml of hexane with 99% concentration was added to the oven-dried sample and shaken for 10 to 20 minutes and left stand for 10 minutes. The extract was flittered using Whitman 40 filter paper and eluted through glass column with 3 mm in diameter and 15 cm high and packed with 3 to 5 g oven-dried (for 12 hours at 140 °C) anhydrous sodium sulfate. The extract was collected and again 20 ml of hexane with 95% concentration was added to the sand and shaken for 10 to 20 minutes and left for 10 minutes and eluted through the column and the extract was collected. Extracting were repeated for the third time with 20 ml of hexane with 95% concentration and eluted through the same column. The column with anhydrous sodium sulfate and filter paper were rinsed with 10 ml n-hexane at the beginning and finally 10 ml of hexane used to collect LNAPL from column packed with sodium sulfate granular and filtering paper. The extracts were oven dried at 80 ^{O}C for three to four hours while the sand was oven dried for 24 hours at 105 ^{O}C. The same procedure was used for the calibration of the method to extract known amount of LNAPL mixed with a given mass of the sand, Fig. 23.

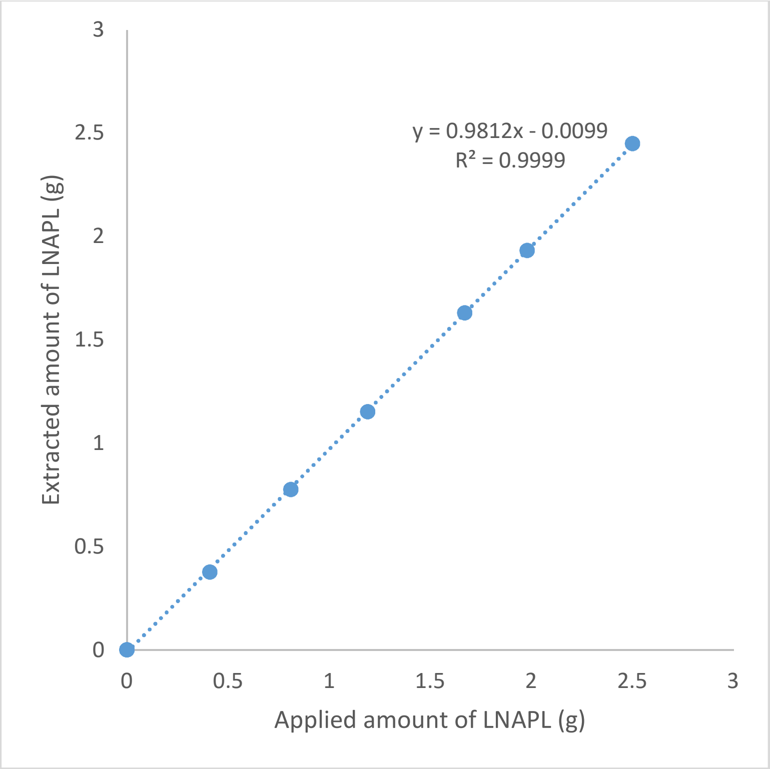


Fig. 23. Graph of extracted and measured LNAPL values from silica sand against known amount of applied LNAPL to the sand

The mass of tare and both tare with LNAPL and tare with sand was measured using digital balance Denver Instrument SI-234A. Gravimetric water and LNAPL contents of the sand were calculated from the result. Gravimetric water and LNAPL contents were converted to their equivalent volumetric continents using the bulk density of the sand column and densities of water and LNAPL using Eq. [76]. Sample columns were packed with bulk density of 1.5 g/cm^3 while densities of water and LNAPL are 1.0 and 0.855 g/cm^3 respectively at 20 $^{\circ}$C.

$$\theta_w = w(\rho_b/\rho_w) \qquad [76]$$

Where: θ_w is volumetric water content, w is gravimetric water content, ρ_b is bulk density of the sand column and ρ_w is water density. Note: volumetric LNAPL content (θ_{LNAPL}) for the sample column can be calculated from gravimetric LNAPL content by substituting LNAPL density (ρ_{LNAPL}) in a place of density of the water in Eq. [76].

3.3.4. Recovering oil/LNAPL from sample column

LNAPL/oil recovery from the sample columns was performed by flooding the sample columns with water, ethanol or hexane. Sample columns were saturated with oil and displacing liquid was applied from the bottom against gravity following Rinaldi & Francisca (2006). However, liquids were introduced to the sample columns using pump instead of variable head pressure to apply constant injection and flow rates. Pump used for the experiment was a peristaltic pump. Liquids were applied to the sample columns at a rate of 200 ml/h for 90 minutes. Additionally, water was applied at rates of 100, 400 and 800 ml/h for 180, 45 and 22.5 minutes respectively. Displacement of oil by hexane was done in well ventilated room following the recommendation of the US EPA (2010) in Method 1664 for hexane extractable materials. Displaced liquids were collected successively every three minutes into glass bottles of 100 ml targeting for the collection of 10 ml in each bottle for the 200 ml/h pumping rate and 6, 1.5 and 0.75 minutes for the water flooding rates of 100, 400 and 800 ml/h respectively. The calibration/adjustment of the pump was in volume basis, but it was the mass of the recovered liquids that was measured immediately after the collection. However, the mass was converted to its equivalent volume after the separation of the oil from the collected liquid. It was converted using Eq. [77] based on mass-volume-density relationship as follows:

$$V_r = V_o + V_i = (m_o/\rho_o + m_i/\rho_i) \qquad [77]$$

Where: V_r is total volume of recovered liquid, V_o, m_o and ρ_o are volume, mass and density of the oil respectively, and V_i, m_i and ρ_i are volume, mass and density of injected liquid espectively (water, ethanol or hexane).

3.3.4.1. Amount of liquids pumped through liquid conveyance tube

All three liquids used: water, ethanol and hexane were pumped through the same diameter of plastic tube used for the main experiment for the displacement of oil from porous media. The liquids were pumped for 30 minutes to the same 50 cm height against gravity at 200 ml/h pumping rate. The pumped liquids were collected successively every three minutes and the mass of the liquids were measured. The mass was converted to volume using mass-volume-density relationship using the densities of the respective liquids (

Table 4). The result shows that the pump delivered more than the value (more than 10 ml every three minutes) it was calibrated for. However, even though the difference in densities of the liquids used resulted in mass difference of the pumped and collected liquids every three minutes, the volume of all three liquids pumped and collected are not statistically significantly different (**Error! Not a valid bookmark self-reference.**).

Table 10. Statistical Anova: single factor for the analysis of volume of liquids pumped through liquid conveyance tube

Source of Variation	*SS*	*df*	*MS*	*F*	*P-Value*	*F crit.*
Between Groups	0.043496	2	0.021748	0.238437	0.790	3.354131
Within Groups	2.462667	27	0.09121			

where: *SS* is sum of squares, *df* is degree of freedom, *MS* is mean squares, *F* is the Fisher F statistic, *P-value* is probability value and *F crit.* is F critical

3.3.4.2. Oil in recovered liquid

To separate oil, form the displacing liquids and quantify it, recovered liquids were oven dried. To remove water, ethanol and hexane, recovered liquids were oven dried at 105 °C for 24 hours, 85 °C for five hours, and 80 °C for four hours respectively. Before taking the mass, oven-dried samples were stored in a desiccator and cooled down to constant mass. The oil content of the recovered liquids was determined using gravimetric analysis method. Before carrying out the displacement experiment, efficiency of the separation method was evaluated by oven drying approximately 10 ml of known mixture of water, ethanol or hexane with LNAPL (oil) at different ratios to respective temperature and time mentioned above for the liquids used. Fig. 24 C & D show that the oven-dry method works perfectly for the separation and quantification of oil displaced with hexane and ethanol.

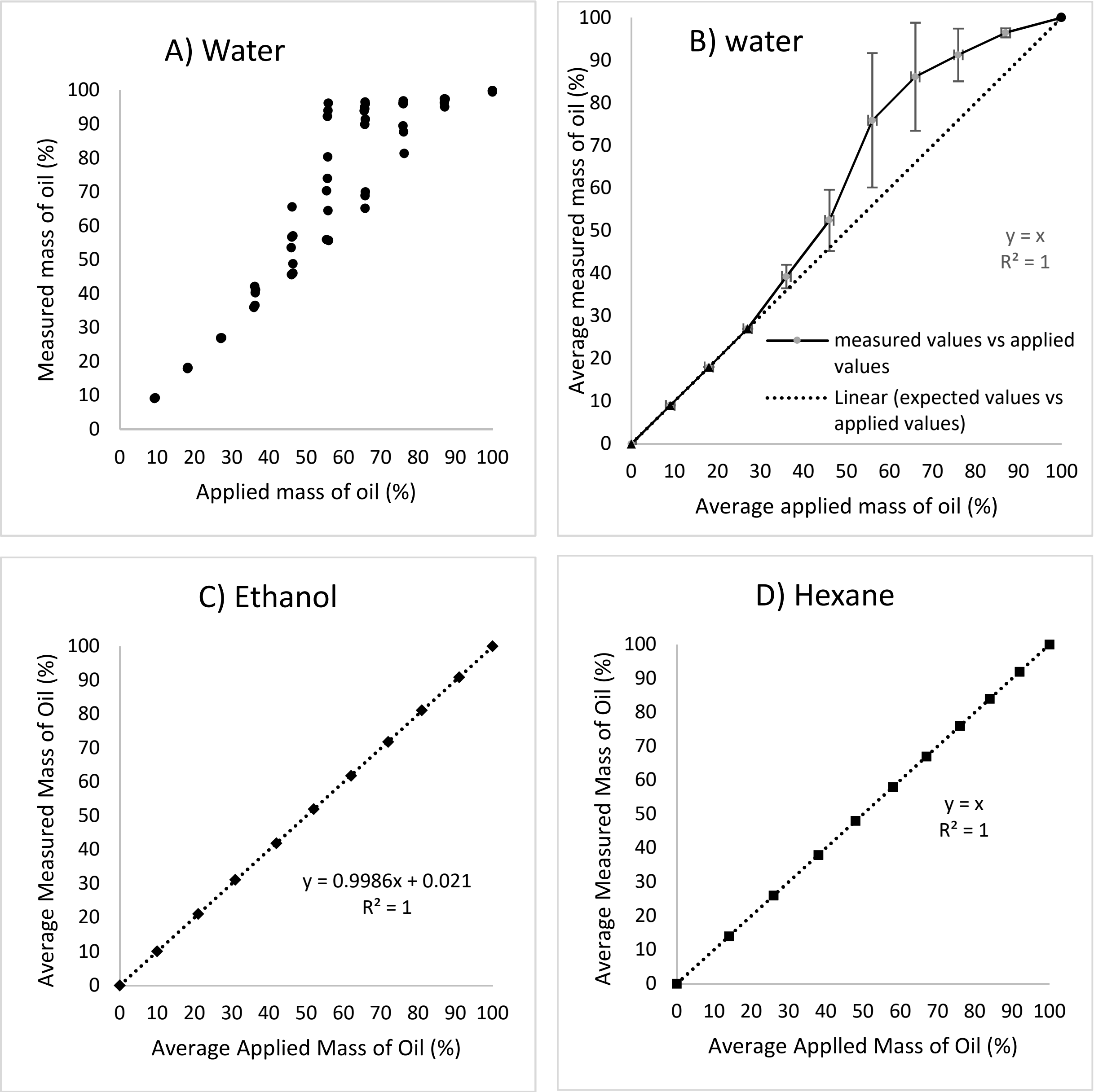


Fig. 24. Graphs of measured values of oil after oven-dry separation from oil mixed with water, ethanol or hexane at different ratios

On the other hand, even though the method works perfectly for up to 30% oil content by mass, it is difficult to remove water from oil using the same drying bottle if the percentage of the oil in the recovered sample is greater than 30% (Fig. 24 A & B). Rather, the amount of measured values after oven drying were beyond the expected values of oil for 30% to 100% applied oil to water ratios by mass (Fig. 24 A & B). However, from the trial experiment and visual analysis, almost in all 10-ml collected samples from sample columns subjected to 100 and 200 ml/h water flooding rates, the percentage of oil was either 100% or less than 30%. For 400 and 800 ml/h water flooding rates the first few samples were pure oil and the rest were the mixture of LNAPL and water. The first up to three of the mixture had oil greater than 30% by mass while the rest had LNAPL less than 30% by mass. To solve the separation problem, 10 ml displaced liquid with greater than 30% oil content was collected into more than one bottles, and oven dried separately. Results from individual bottles were added and used for the analysis.

3.4. Data analysis

Mass of the ACPs at all courses of the experiment as well as mass of the displaced and collected samples before and after oven dried and mass of destructed sample for gravimetric water and oil content analysis were measured using digital balance Denver Instrument SI-234A, Orville, USA that has the precision of 0.0001 g. The oven-dried samples were stored in desiccator at room temperature and cooled down to constant mass. The amount of adsorbed liquids to ACP, water content of destructed samples from the sample column and displaced LNAPL/oil were calculated based on the mass differences between before and after oven drying. The amount of oil content was determined from the amount of oil extracted from oven-dried samples.

After the separation and quantification of oil from adsorbed liquid to ACP and displaced liquid from the sample columns, and gravimetric water and oil contents of the sample column were determined the values will be used for the assessment of:

- The applicability of ACP in the study of multiphase flow. Activated carbon has been used to treat polluted water and air, mainly by organic pollutants. However, in this study, pelletized activated carbon will be used to sample LNAPL and water from porous media saturated with different water to LNAPL ratios. The values will be used for the assessment of ACP efficiency in sampling different water to LNAPL ratios.
- The comparison of water and oil contents obtained from different methods. Water content measured using soil moisture sensors, and water and oil contents determined through gravimetric analysis methods will be used to evaluate DMM for the estimation/separation of LNAPL and water from porous media.

- The efficiencies of the water, ethanol and hexane in displacing oil from porous media. The displacement of oil from porous media is applicable in oil recovery from oil fields and remediating oil contaminated subsurface. The amount of oil displaced from the sample columns will be used to assess the efficiency of the three liquids used in the displacement of oil from the sample columns. Additionally, the amount of displaced LNAPL by different water flooding rates will be used to evaluate the impact of flooding rates on immiscible oil displacement from the porous media. Furthermore, the displacement pattern of LNAPL components will be generally presented from displaced pure LNAPL.

Collected data will be analyzed using Microsoft Excel 2016 and Microsoft Excel 2016 integrated with QI Macros 2015 and IBM SPSS computer statistical program. Most of the analysis procedures using IBM SPSS will be based on the recommendations by Field (2013).

4. Results and Discussion

4.1. Sample columns prepared, drained out liquids and silica sand ST56

Silica Sand ST56 used for the experiment was dry with average water content of 0.04% by mass (Table 3). It was repacked in to plastic and glass containers with some added liquid (water or LNAPL) for the convenience of packing. In addition to the liquid used for repacking, additional liquids were applied to the packed sample column from the top and drained down and distributed by gravity. In total, one pore volume plus (more than one pore volume) of water and/or LNAPL with different ratios for one set of experiments and one pore volume plus only LNAPL for the other set of experiments were applied to the sample columns. Sample columns subjected to the liquid(s) were left stand for 24h to get the equilibrium condition through gravity drainage and redistribution. Some amount of either water or LNAPL was drained out from sample columns after 24h.

From sample columns subjected to different water to LNAPL ratios except from 100:0 and 90:10, LNAPL was the only drained out liquid by gravity, Table 8 and Table 9. Mayer, et al. (2005), Delleur (2003), van der Perk (2006), and Rubin (2013) among many authors stated that wetting fluid spread over solid particles at the expense of the non-wetting fluid. In gas-liquid multiphase system, gas/air is always non-wetting phase (Schön, 2015)and hence air is non-wetting phase with respect to Water and NAPL in three-phase fluid system. During the experiment, drainage took place depending on the ratio of the applied liquids. For the applied 100:0 water to LNAPL ratio, water was the only applied and drained out liquid from the sample columns. In the same way, from the sample columns subjected to LNAPL only, LNAPL was the only drained out liquid from the sample columns from both sets of the experiments.

Sample columns subjected to 90:10 water to LNAPL ratio were the only sample columns where water was the only drained out liquid, Table 8. The amount of LNAPL in the applied ratio was small (10%) compared to that of water (90%). LNAPL was applied during sample columns preparation while water was applied from the top. From the rest of the sample columns subjected to different water to LNAPL ratios: 75:25, 65:35, 50:50: 35:65, 25:75, 10:90 and 0:100, LNAPL was the only drained out liquid. Zhang, et al. (2004) described that during the imbibition and drainage of the liquids, wetting phase displaces non-wetting phase from the porous media.

Moreover, Domenico & Schwartz (1998) generalized that water is a wetting fluid with respect to NAPLs on rock forming minerals. However, Delleur (2003) and Mayer, et al. (2005) stated that very dry natural soil could be NAPL wettable with respect to water. Soil in natural subsurface system is water wettable with respect to NAPLs; while NAPLs can be a wetting fluid in carbonate material, soil with high organic matter content, such as humus and a peat bog soil (Domenico & Schwartz, 1998; Lowe, et al., 1999; Mayer, et al., 2005). But, silica sand ST56 that was used in this experiment is chemically inert mineral sand (approximately 99% $SiO_{2)}$ which is free from organic matter. Hence, it shows that ST56 is water wettabile with respect to oil/LNAPL used.

4.2. The amount of water and/or LNAPL in sample columns

Sample columns' liquid content can be roughly estimated from the amount of liquid applied to the sample column and drained out. This could be possible by assuming the loss of sand and liquid during sample column preparation was zero. The amount of dry sand in forming each sample column could be 4×300 g = 1200 g for one set of the experiments and 5×75.45 g = 377.25 g for the other set of the experiments, see the section under sample column preparation. However, it is difficult to avoid the losses during sample column preparation. Sample columns' liquid (Water and LNAPL) content was sampled using ACP, measured using soil moisture sensors and determined through gravimetric analysis method. Both water and LNAPL contents of the sample columns were determined using thermo-gravimetric analysis method. Water content of the sample columns was measured using soil moisture sensors and LNAPL continent was estimated using DMM.

4.2.1. Water and LNAPL sampled from porous media using ACP

Water and LNAPL were sampled using ACP from the center of the sample columns saturated with different water to LNAPL ratios. The summary from thermo-gravimetric analysis method of the adsorbed water and LNAPL is presented as a graph (Fig. 25). The results show that ACP could sample Water and LNAPL proportionally from the sample columns saturated with different water to LNAPL ratios. Nevertheless, the graph shows that more liquid was sampled when the sample columns were saturated either by LNAPL or water compared to when both liquids where used to saturate a sample column. Additionally, the amount of adsorbed liquid (LNAPL + water) increased with the amount of LNAPL in the ratio increased. In this paper, here afterwards the first value in the ratio of applied liquids to the sample column will be the value of LNAPL unless stated. Porous media used to form the sample column has different affinity for water and LNAPL/oil. One reason for the increment of the amount of sampled liquid with the ratio of applied LNAPL to water could be due to the wettability preference of the sand particles.

The wetting phase has stronger affinity for the soil solid particles which expels the other phase towards the center of the pore spaces (Jensen & Falta, 2005). Lyons (2010) stated that pure and clean sillica sand is water wettable with resperct to any hydrocarbons. Domenico & Schwartz (1998) generalized that rock forming minerals are water wettable with respect to NAPLs. Results from drained out liquids from all sample columns subjected to different LNAPL to water ratios where LNAPL was a part show that all the drained-out liquid was LNAPL except from 10:90 which was only water, Table 8. It shows that ST56 is water wettable with respect to LNAPL. In water wettable porous media, large pores are LNAPL wettable while small pores are water wettable (Abdallah, et al., 2007) which resulted in the draining out of excess non-wetting phase from macro pores. Hence, the presence of non-wetting phase in the larger pores could give adsorption opportunity for the non-wetting phase over the wetting phase. The other reason, from the trend of the graph in general and the comparison between the amount of LNAPL sampled compared to water from the sample columns saturated with only one liquid, could be due to the stronger affinity of ACP itself for organic compounds compared to water. The graph under Fig. 18 shows that ACP could sample more organic liquids (in volume basis) compared to water from free respective liquids pools. The graph also shows that the pellet could sample even more Marcol 82 oil when reported in mass base even though water is denser than the oil used as LNAPL. Zhang (2004) and Tan (2014) associated the affinity of activated carbon for organic compounds with the affinity of silica gel for water or air moisture. However, result from Karanfil & Kilduff (1999) shows that adsorption of hydrophobic organic compounds to AC decreases with increasing surface polarity of AC (e.g., increasing surface acidity of AC).

Fig. 25 shows that more liquids were sampled from sample columns saturated with either water or LNAPL compared to sample columns saturated with both water and LNAPL despite there were other sample columns with higher liquid content (Table 8). In the sample columns saturated with both liquids, there was capillary pressure between the phases (Fig. 10) while there was no such a capillary pressure when only one liquid used to saturate the sample columns. Hence, the other reason why ACP could sample less liquids from sample columns saturated with two liquids compared to when only one liquid type used could be due to the presence of capillary pressure between two immiscible liquids.

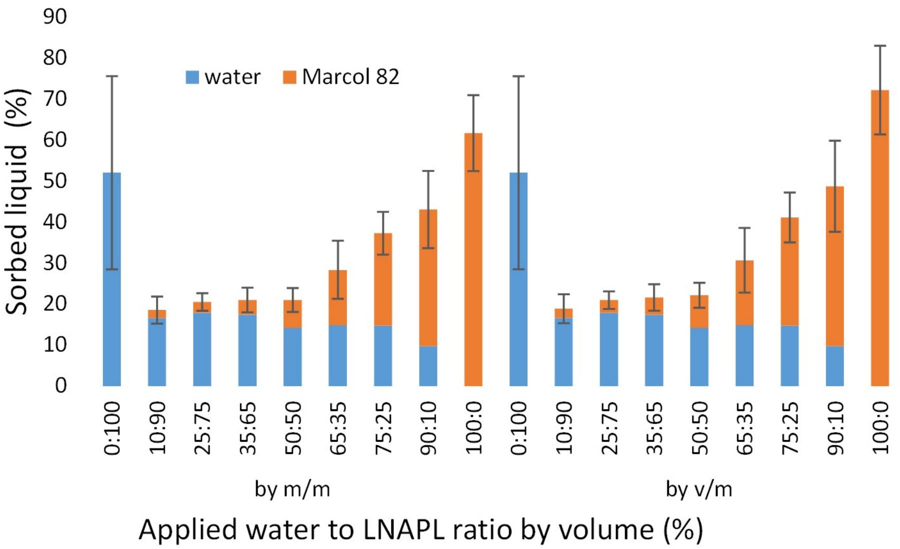


Fig. 25. Amount of water and LNAPL sampled using ACP from sample columns saturated with different LNAPL to water ratios

Where: m/m is sampled mass (g) per mass (g) of activated carbon pellet (ACP) and v/m is sampled volume (ml) per mass of ACP

4.2.2. Water content from soil moisture sensors

After water and LNAPL were sampled from the sample columns using ACP, sample column volumetric water content (θ_w) was measured using 5TE and ECH$_2$O-TE soil moisture sensors from the top 6 cm approximately. Measured θ_w, bulk sample column electric conductivity (EC), calculated extract solution EC using Eq. [63], and bulk relative permittivity calculated from θ_w measured using Eq. [62] are presented in Fig. 26. The graph shows that both 5TE and ECH$_2$O-TE soil moisture sensors responded to sample columns' water content pretty good with a slight difference in measuring the water content between them. From the graph of average measured water content with standard deviation, individual sensors measured water contents with low variance which shows both the quality of the sensors used and the uniformity of the prepared sample columns for the experiment. However, ± 3% for water content values is expected using Topp, et al. (2003) model used for both sensors (Decagon Devices, 2008; Decagon Devices, 2010).

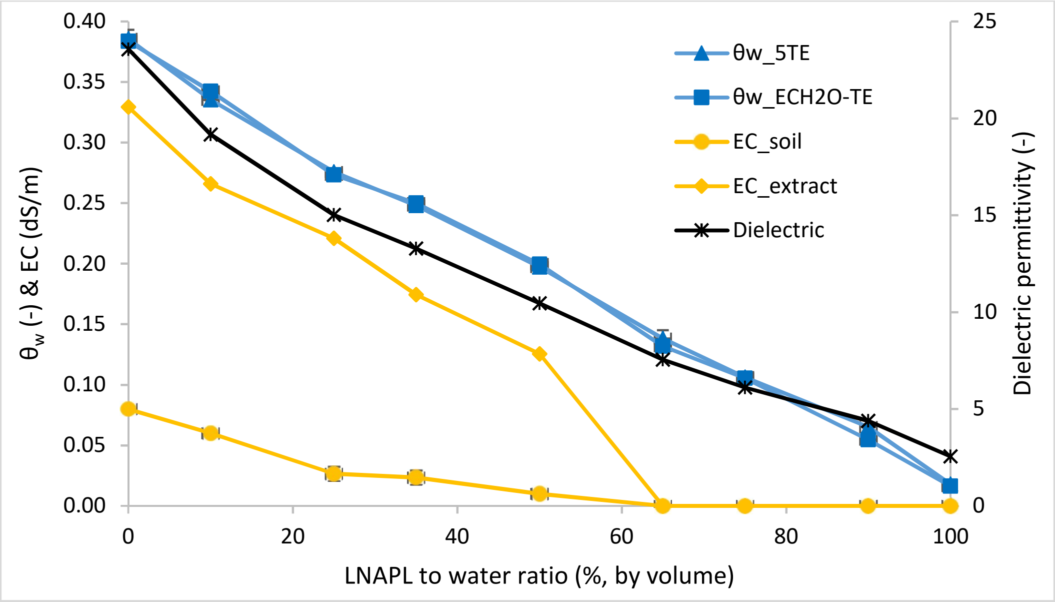


Fig. 26. Graph of θ_w, EC bulk and EC extracted solution and bulk relative permittivity using 5TE and ECH_2O-TE from sample columns subjected to different LNAPL to water ratios

On the other hand, both sensors responded to the bulk sample column EC in the same way and gave almost the same values. Therefore, only the values from one sensor, 5TE which were used for the construction of the graph were also used to calculate EC for the extract solution. Extract solution EC was calculated using 4.1 as the generic value offset recommended by Hilhorst (2000). The calculated extract solution EC varied from 0 to 0.33 dS/m and all the values were within the recommended value for the extract solution EC (< 10 dS/m) by Decagon Devices (2016) to use the sensors for better mineral soil water content measurement.

Graphs under Fig. 26 show that both bulk sample column and extract solution EC are zero at higher LNAPL to water ratios. Pollitt (1943) mentioned mineral oil as the chief dielectric or insulating liquid used in oil-filled transformers and oil switches. Result from Kolay, et al. (2016) shows that resistivity of the kaolinite and kaolinite-sand mixtures increases with the increasing of NAPL applied. However, Schwartz, et al. (2012) showed that increasing polar compound containing NAPL can increase the electrical conductivity of a porous media through adsorbing to the mineral surface and releasing of inorganic ion to pore water. However, LNAPL (mineral oil) and silica sand ST56 used in this study were inert and the oil without polar compounds.

4.2.3. Water content determined through gravimetric analysis method

Sample column water content was determined using direct thermo-gravimetric analysis method from destructed samples. Samples were taken from top, mid and bottom positions of the sample columns. The obtained values of the samples' water content were in gravimetric/mass basis using Eq. [58] and converted to respective volumetric water content for the sample columns using Eq. [60]. The average values for the sample columns, the top, middle and bottom positions, and the average values for top and middle (Tomi) positions of sample columns subject to different LNAPL to water ratios are presented as Fig. 27. The graph shows that θ_w from different positions are almost the same for sample columns subjected to either LNAPL or water only and the same for sample columns subjected to higher LNAPL to water ratios. However, for the intermediate or lower applied LNAPL to water ratios, there was the difference in θ_w from different positions and the lower position had lower θ_w compared to the upper one for 90:10, 75:25 and 65:35. Except for 25:75 and 10:90 the bottom position had the lowest θ_w compared to the other two positions for all applied ratios where water was the part. The middle position had the θ_w value between the values of the top and the bottom positions except for 50:50 ratio where the position had the higher value compared to the other two positions. Nevertheless, results from Kruskal-Wallis Nonparametric Test show that there is no statistically significant difference between θ_w for three positions of the sample columns where water was used ($p = 0.906$) and water was used alone ($p = 0.230$) to saturate the sample columns.

The slight difference in water contents at different positions could be due to the interactions of liquids with each other's and with the solid matrix. The main reason for the difference in θ_w from different positions could be the order of liquids application to the sample columns (Table 7). Liquid with lower volume in the ratios was used either during the sample column preparation in wetting dry and loose sand to make the repacking suitable or applied first to the prepared sample columns from the top and then followed by the liquid with higher volume in the ratio. Draining and redistribution took place downward by gravity and there could be a chance for the bottom part of the sample column to be saturated with liquids applied first. The sand to which water and/or LNAPL applied was water wettable with respect to the LNAPL. Macro pores of the sample columns could be occupied by LNAPL which made the downward redistribution of LNAPL easier compared to water could occupy the micro pores. The other result that could support this reasoning was that, from all sample columns subjected to different LNAPL to water ratios where LNAPL was the part except from 10:90, it was only LNAPL that was drained out from the sample columns (Table 8). However, from 10:90 it was only water that was drained out. Additionally, θ_w was calculated from gravimetric water content which in turn determined from the difference in mass before and after oven dry divided by the mass of oven dried sand. The oil used as LNAPL is stable at 105 °C and could affect what was taken as a dry sand mass which could decrease the calculated water contents from different positions. The impact of the oil on thermos-gravimetric water content analysis will be discussed in the following sections in comparisons to θ_w from the soil moisture sensors and determined LNAPL content (θ_{LNAPL}) of the sand columns through gravimetric analysis method.

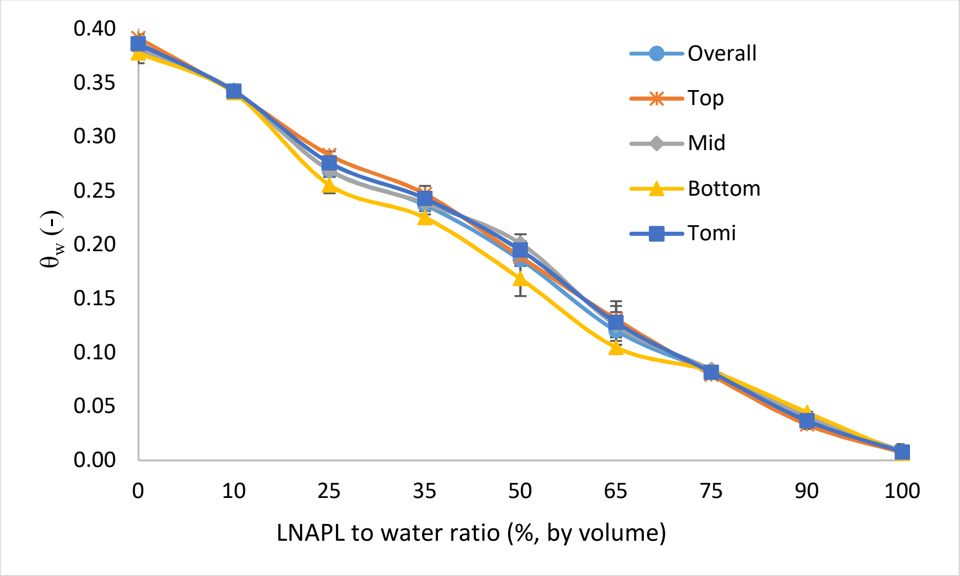


Fig. 27. Graph of average θ_w for different positions of sample columns subjected to different LNAP to water ratios

Where: Top, Mid and Bottom are top, middle and bottom positions of the sample column respectively, overall is the average for the three positions, and Tomi is the average for the top and middle positions of the sample column

4.2.4. θ_w from gravimetric method and measured using soil moisture sensors

Values of θ_w measured through indirect method using soil moisture sensors: 5TE and ECH$_2$O-TE and θ_w directly determined through thermo-gravimetric analysis method are presented in Fig. 28 for comparison. Soil moisture sensors used for the experiment measured the water content of the top 6 cm of 8 cm long sample columns (Fig. 22). For the comparison, average θ_w from the top and middle positions (Tomi) of the sample columns determined through gravimetric analysis method were calculated. The graph under Fig. 27 shows that θ_w from all the three were almost the same for 0:100 through 50:50 LNAPL to water ratios and from sample columns subjected to only one liquid. However, the values were a bit different, mainly between the values obtained using direct and indirect methods for the higher percentage of LNAPL in applied liquid. The θ_w values from 5TE sensor reading were the highest compared to the other two while the values from gravimetric methods was the lowest. In contrary to the result, higher values from gravimetric analysis could be expected if there were a loss of LNAPL to evaporation which could give higher θ_w estimation if it had happened. However, the oil used as LNAPL is nonvolatile and the loss to oven-dry temperature was tested and it was almost negligible (Báťková, et al., 2014).

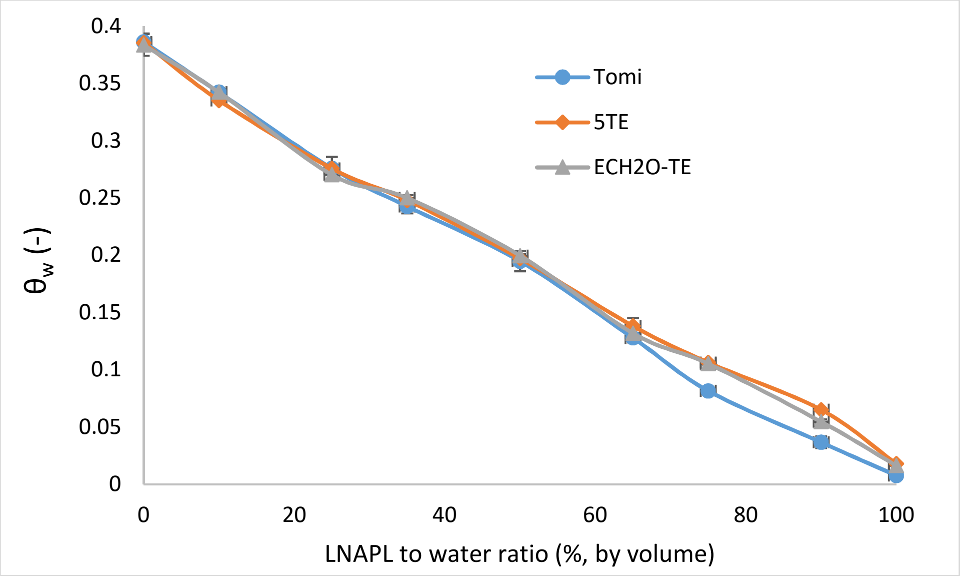


Fig. 28. Graph of θ_w (-) measured by soil moisture sensors and determined using gravimetric method from sample columns subjected to different LNAPL to water ratios

The boiling point of the lowest molecule in the medicinal mineral oil constituent, C_{15} (Speight, 2014) or C_{18} (Stoker, 2013) is roughly above 200 °C for both cases (Bettelheim, et al., 2013). Gardner (1986); Topp & Ferré (2002); Hillel (2004) and Mansur, et al. (2015) among others, on the other hand argue that thermo-gravimetric analysis method could be affected both by the oven dry loss of non-water substances which could cause the over estimation of the water content, and by the retaining of some water in heavy clay sample or the presence of non-volatile organic liquids in the sample of interest at oven temperature which could be resulted in under estimation of water content. Result from Kruskal-Wallis Nonparametric Test show that there is no statistically significant difference ($p = 0.864$) between θ_w from gravimetric analysis method and measured soil moisture sensors for the sample columns subjected to water only. Result from the analysis method shows that, however, there is statistically significant difference between ($p = 0.044$) θ_w obtained through gravimetric analysis method and measured using soil moisture sensors for the sample columns subject to oil/LNAPL only. The difference is between the gravimetric analysis methods and the sensors mainly with 5TE sensor.

4.2.5. LNAPL content determined through gravimetric analysis method

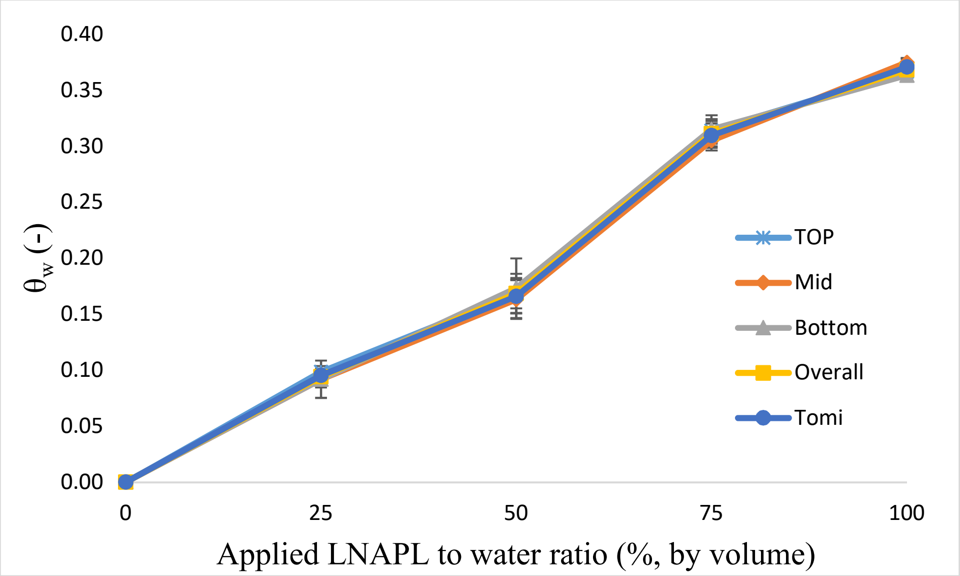


Fig. 29. Graph of θ_{LNAPL} from different positions and their average for sample columns subjected to different LNAPL to water ratios

Oil/LNAPL content (θ_{LNAPL}) was determined from the destructed sample for the sample columns subjected to 0:100, 25:75, 50:50, 75:25 and 100:0 LNAPL to water ratios. LNAPL was extracted from oven-dried destructed samples taken from different positions of the sample columns. The amount of extracted LNAPL from the sample was first calibrated with the calibration curve (Fig. 23) and θ_{LNAPL} was calculated from the mass LNAPL content using Eq. [60] by using the density of the oil instead of the density of water (

Table 4). LNAPL content of the sample columns: average, top, mid, and bottom positions, and the average for the top and mid positions (Tomi) are presented as a graph (Fig. 29). The graph shows that θ_{LNAPL} content for different positions were almost the same with small differences. Results from Kruskal-Wallis Nonparametric Test show that there is no statistically significant difference between θ_{LNAPL} from three positions for the sample columns' LNAPL content analyzed using gravimetric analysis method and where LNAPL and water used ($p = 0.974$) and LNAPL used alone for the saturation ($p = 0.177$).

4.2.6. The effect of the oil on thermos-gravimetric water content analysis

Graph under Fig. 28 shows that gravimetric analysis method gave lower θ_w content compared to soil water content measured using soil moisture sensors where the ratios of LNAPL in applied liquid was higher. The reason could be due to the inclusion of non-volatile oil (LNAPL) as a part of the dry sand particle in the determination of gravimetric water content. To evaluate the effect of non-volatile LNAPL on the gravimetric water content analysis method, extracted oil from the sand sample was used to determine the mass of the dry sand and subsequently to determine the water content of the sand.

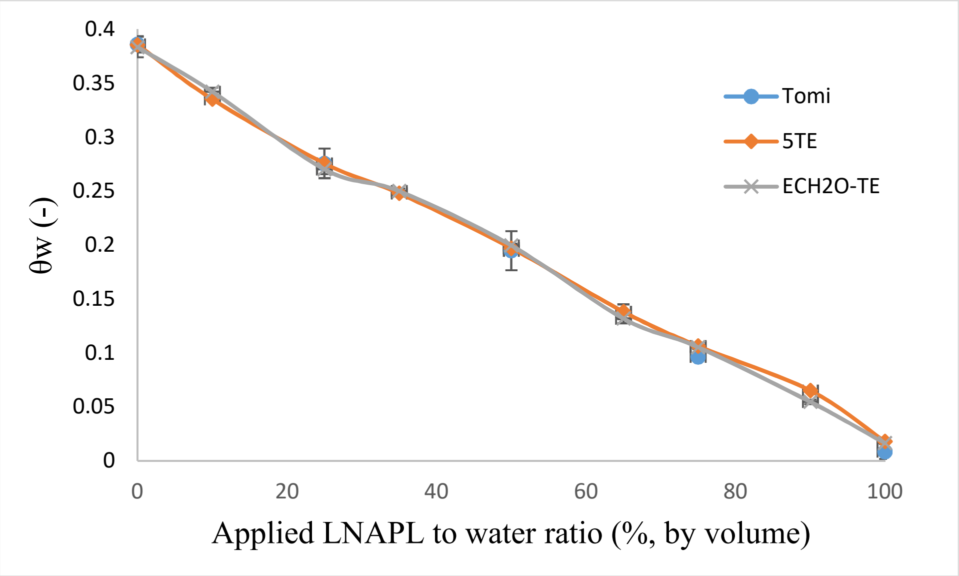


Fig. 30. Graph of θ_w (-) from soil moisture sensors and gravimetric analysis method from sample columns subjected to different LNAPL to water ratios

Note: the values are for the top 6 cm of sample columns and Tomi was determined after the oil was excluded from the dry sand mass

Gravimetric water content and its corresponding value of volumetric water content was determined from the mass of water and dry sand without the oil (Fig. 30). Both graphs under Fig. 28 & Fig. 30 show that all methods gave same θ_w for the sample columns where water was the only applied liquid. However, for the sample columns subjected to both liquids, gravimetric analysis method gave lower θ_w (Fig. 28) when oil was the part of the dry sand mass (solid phase of the soil). However, excluding the oil/LNAPL in calculating the mass of the solid phase could improve gravimetric analysis method. Fig. 30 shows that the difference between θ_w measured using soil moisture sensors and θ_w determined through gravimetric analysis method after excluding the oil from the mass of the solid phase is lower compared to considering the oil as the part of solid phase of the porous media (Fig. 28). From all the three measurements, θ_w for the sample columns where LNAPL was the only liquid applied were close to zero. Nonetheless, θ_w from gravimetric analysis method was the lowest and statistically significantly different from θ_w obtained using soil moisture sensors ($p = 0.038$, from Kruskal-Wallis Test). It indicates that the loss of the oil to oven temperature during gravimetric analysis method was negligible. Hence, in contrary to what might be expected, the oil was not resulted in the over estimation of θ_w using gravimetric analysis method as the oil was stable at oven temperature used (at 105 °C for 24h). Rather the presence of the oil resulted in θ_w under estimation from gravimetric analysis method.

Meanwhile, the presence of LNAPL could affect the result from soil moisture sensors through the modification of the bulk relative permittivity of the sample column. While many studies focus on the loss of non-water components with water during thermos-gravimetric analysis method due to the oxidation and evaporation of non-water components (e.g., Topp & Ferré, 2002; Hillel, 2004; Cooper, 2016), less or no attention has been given for the impact of non-volatile non-aqueous phase liquid on the thermos-gravimetric water content determination. Graph under Fig. 31 shows that overall average water content of the sample columns saturated either by water or LNAPL did not change whether the oil was considered as the part of solid phase or not. Sample columns saturated only with water were free of oil while the water content of the sample columns saturated only with LNAPL were zero. Meanwhile, the graph shows that water content determined by excluding oil from the mass of the solid phase were greater than that of determined by considering oil as part of the solid phase.

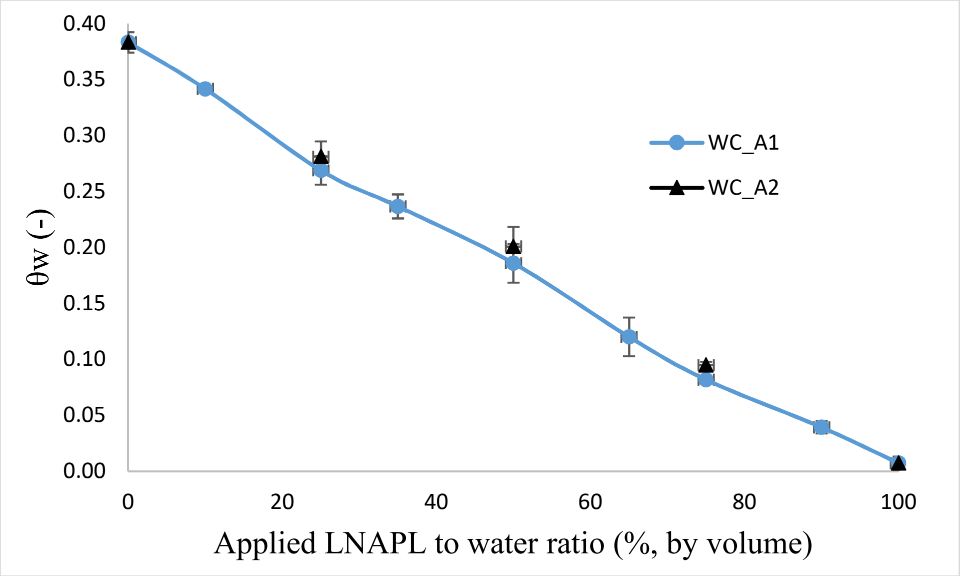


Fig. 31. Graph of θ_w (-) from sample columns subjected to different LNAPL to water ratios determined using gravimetric analysis method

Where: WC_A1 and WC_A2 before and after oil was excluded from the dry solid mass respectively and the values are average for sample columns subjected to a given ratio

4.2.7. Comparison of liquid contents from the three methods

Graph under Fig. 32 shows that ACP could sample more liquids from sample columns subjected to one liquid only compared to the other two methods. It could sample the liquids with high standard deviation from the means compared to the other methods also. Given that the method has not been used for the quantification and analysis of porous media with respect to its liquid content, let alone the sampling and analysis of its multiphase liquids content, ACP used for the experiment responded to the amounts of liquids in the different ratios proportionally (Fig. 32). For the application of ACP in the sampling and analysis of porous media's liquid content, more must be done to improve its quality (to have ACPs with uniform adsorption quality) and ACPS with uniform dimensions (length and diameter) to minimize the variations in sampling.

Gravimetric analysis method and soil moisture sensors responded to different LNAPL to water ratios by far in a better way compared to sampling using ACP. The difference between water content from gravimetric analysis method and measured using soil moisture sensors were smaller for the lower LNAPL ratio in applied liquid. But, the differences were visible and statistically significant for the higher applied LNAPL to water ratios. After the oil was excluded from the oven-dry solid mass through the extraction, the differences were minimized significantly. Fig. 32 shows that water content from soil moisture sensor, 5TE, and gravimetric analysis method for the top 6 cm (GMT), and average for the whole sample column (GMA) were the same for applied LNAPL to water ratio. Nevertheless, in most cases soil moisture sensor gave more θ_w for applied LNAPL to water ratios.

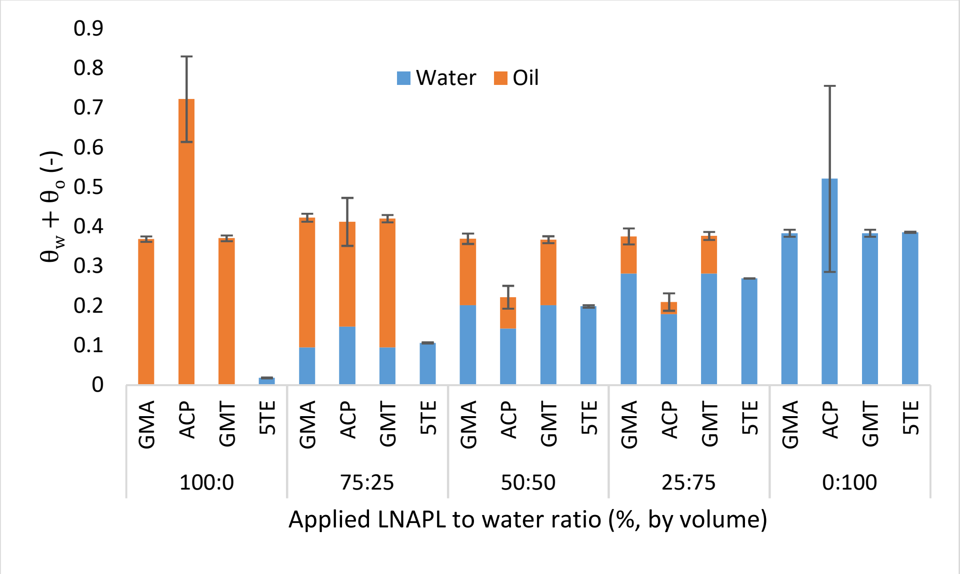


Fig. 32. Graph of θ_w and θ_{LNAPL} (-) measured using different methods from sample columns subjected to different LNAPL to water ratios

Where: GMA & GMT are gravimetric analysis method for sample columns average and average for the top and mid positions of the sample columns respectively, the values for both gravimetric method and soil moisture sensor (5TE) in volume basis while the value using activated carbon pellet (ACP) was based on the volume of water and oil adsorbed to one gram of ACP (%)

4.2.8. LNAPL content estimated using DMM

Volumetric water content (θ_w) determined through gravimetric analysis method was lower than that of measured using soil moisture sensors (Fig. 28), and even after excluding oil from the dry sand mass (Fig. 30). Some research works have utilized this small difference to estimate porous media LNAPL content (Persson & Berndtsson, 2002; Haridy, et al., 2004; Olchawa & Kumor, 2008; Wilson, et al., 2009; Francisca & Montoro, 2012; Comegna, et al., 2013; 2016). It was indicated that the presence of LNAPL modifies the relative permittivity of the porous media compared to the same porous media with the same amount of water but differ in LNAPL content. In this study, at higher applied LNAPL to water ratios, θ_w were different for direct and indirect methods. Two reasons were identified for the differences. The first reason was that gravimetric analysis method could under estimate the water content of the sample columns due to the inclusion of non-volatile LNAPL as part of the oven-dry sand mass. The differences could be minimized by excluding the oil from the dry sand mass. The other reason could be due to the over estimation of θ_w from soil moisture sensors due to the modification of sample columns bulk relative permittivity due to the presence of LNAPL. Results from many studies show that the presence of NAPLs in the porous media could modify the bulk relative permittivity of the porous media.

Fig. 28 shows that the presence of higher non-volatile LNAPL content affected θ_w measured using soil moisture sensors through the modification of bulk relative permittivity of the porous media (ε_a). Modified ε_a can be used to estimate θ_{LNAPL} using DMM, Eq. [70]. θ_w measured using soil moisture sensors (Fig. 26), and θ_w and θ_{LNAPL} determined through gravimetric analysis method were used to estimate α for the model and then the applicability of DMM for the estimation of porous media LNAPL content was assessed. Persson & Berndtsson (2002) and Haridy et al. (2004) among others estimated θ_{LNAPL} from dielectric and electrical conductivity (EC) values measured from the samples. However, measured EC values for applied LNAPL to water ratios greater than 65:35 were zero. On the other hand, most contaminants exist in the subsurface in lower amounts while θ_w from the direct and indirect methods are significantly different at higher θ_{LNAPL} content.

DMM for the estimation of LNAPL and water was evaluated based on the relative permittivity of the materials used (from literature, see the literature review part), silica sand 2.2, water 81, mineral oil 2.2, air 1. From measured values of θ_w and θ_{LNAPL}, α was fitted and optimized using Solver in Excel program. The α value was different for different phase systems used. The value was 0.67 for three-phase system (sand, water and air) and 0.50 for sand-LNAPL-air three-phase system (Table 11). For four-phase system (sand, water, LNAPL and air) the value was between 0.62 and 0.64 (Table 11). The values are in the ranges of 0.46 to 0.67 for three-phase system and 0.39 to 0.81 for four-phase system mentioned by Persson & Berndtsson (2002). The model was tested for θ_{LNAPL} content using the α values and θ_{LNAPL} content for other sample columns were estimated (Table 11).

Table 11. Estimated values of α and θ_{LNAPL} from measured values of ε_a, θ_w and θ_{LNAPL} using DMM

$\varepsilon_{a\ (-)}$	EC(dS/m)	θ_w^{*} (cm^3/cm^3)	θ_w^{**} (cm^3/cm^3)	θ_{LNAPL}^{***} (cm^3/cm^3)	α (-)	θ_{LNAPL}^{****} (cm^3/cm^3)
23.57	0.07	0.39	0.38	0.00	0.67	0.00
19.17	0.05	0.34	-	-	0.64	0.04
15.02	0.02	0.28	0.28	0.09	0.62	0.09
13.29	0.02	0.25	-	-	0.62	0.13
10.45	0.01	0.20	0.20	0.17	0.62	0.17
7.55	0.00	0.14	-	-	0.63	0.22
6.12	0.00	0.11	0.09	0.29	0.63	0.29
4.39	0.00	0.07	-	-	0.62	0.34
2.55	0.00	0.02	0.01	0.37	0.50	0.37

Where: ε_a is bulk relative permittivity, EC is electrical conductivity, α is an empirical parameter accounting for soil geometry, * is θ_w from soil moisture sensor, ** is θ_w from gravimetric analysis method, *** is θ_{LNAPL} from gravimetric analysis method and **** is θ_{LNAPL} estimated using DMM

It could be concluded that the presence of significant amount of LNAPL in porous media could affect water content determination through thermos-gravimetric analysis. The presence of non-volatile LNAPL results in underestimation of the water content, otherwise resulted in overestimation of the water content from non-water evaporation loss due to the presence of volatile LNAPL.

4.3. Recovered oil from sample columns flooded with different liquids

Sample columns saturated with 0.9 Pv volume of medicinal grade white mineral oil used as LNAPL was subjected to water, ethanol and hexane at 200 ml/h flooding rate. Additionally, water at 100, 400 and 800 ml/h flooding rates were used to recover oil and decontaminate the sample columns manually saturated with 90% degree of saturation in mimic of contamination. Displaced liquids were collected successively and analyzed for recovered liquid and oil amounts. Statistical analysis shows that significant amount of liquid (hexane + oil) and oil were displaced using hexane as flooding liquid compared to using water and ethanol at 200 ml/h flooding rate for 90 minutes experimental duration. On the other hand, even though less significant amount of liquid (water + LNAPL) were displaced by water at 100 ml/h statistically compared to 200, 400 and 800 ml/h flooding rates at the end of respective experiments, the amount of LNAPL displaced by water at these four flooding rates are not statistically significantly different from each other. However, the amount of pure LNAPL displaced using different water injection rates were statistically significant.

4.3.1. Amount of liquid recovered from sample columns

Oil was displaced from oil saturated sample columns with water, ethanol or hexane flooding at the rate of 200 ml/h against gravity for 90 minutes. Water was used also to flood the sample columns at 100, 400, and 800 ml/h. The displaced liquids were collected successively every six and three minutes for 100 and 200 ml/h flooding rates respectively and every 90 and 45 seconds for 400 and 800 ml/h application rates respectively. The recovered liquid samples were only oil or a mixture of oil and flooding liquid. The amount of collected displaced liquid was measured by mass and converted to the equivalent volume using Eq. [60] based on mass-volume-density relationship after quantifying the amount of the oil in recovered liquid. Table 13 and Table 13 show descriptive statistics of the recovered liquid (volume) by flooding the sample columns with water, ethanol and hexane at 200 ml/h and with water at 100, 200, 400 and 800 ml/h respectively.

Table 12. Descriptive statistics of recovered liquids (ml) from sample columns subjected to different liquids at 200 ml/h flooding rate

	N	Range	Minimum	Maximum	Mean	Std. Deviation
Hexane	30	2.286	9.468	11.754	10.80241	.714263
Ethanol	30	.922	9.478	10.400	9.95317	.247468
Water	30	1.67	9.20	10.87	10.0640	.43806

Table 13. Descriptive statistics of recovered liquids (ml) from sample columns subjected to different water flooding rates

	N	Range	Minimum	Maximum	Mean	Std. Deviation

100 ml/h	30	1.540	9.010	10.550	9.71833	.395004
200 ml/h	30	1.670	9.200	10.870	10.06400	.438057
400 ml/h	30	1.350	9.420	10.770	10.13600	.375514
800 ml/h	30	1.590	9.090	10.680	10.01667	.434125

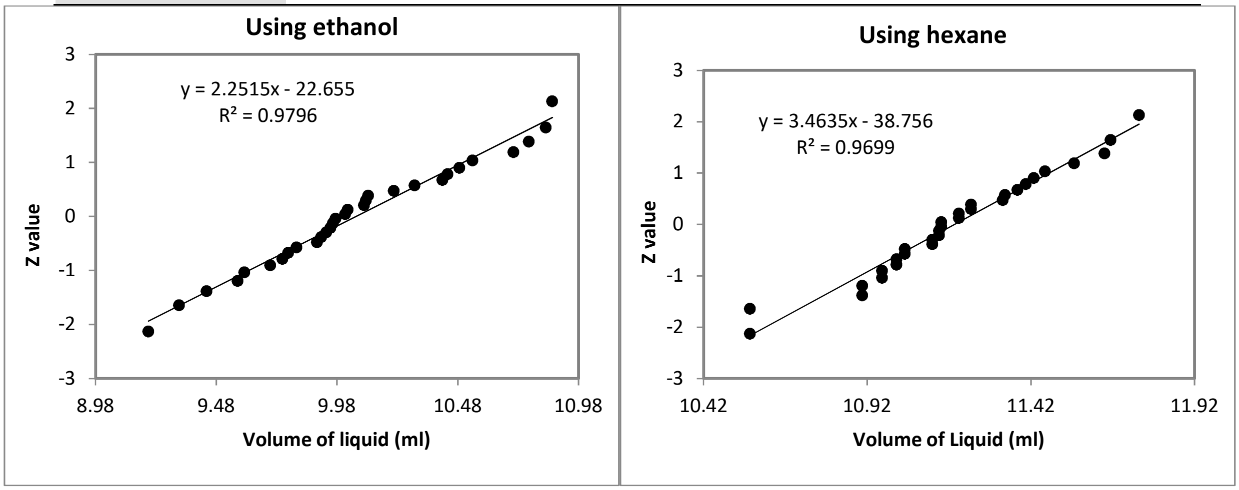


Fig. 33. Probability plot of recovered liquid every three minutes using ethanol and hexane where Z is a standardized normal distribution

A Shapro-Wilk's test, p-values for water, ethanol and hexane were 0.602, 0.414 and 0.486 respectively ($p > 0.05$) and a visual inspection of their histogram and box plots from QI Macros showed that the recovered volumes of liquids every three minutes were approximately normally distributed for all the three displacing liquids, see Fig. 33 for the probability plots using QI Macros. Q-Q plots under

Fig. 34 show that the distribution of liquid volume displaced at different water flooding rates are normally distributed. Leven's Test for homogeneity of variance using SPSS software program shows that the error variance of the volume of recovered liquid is equal across the flooding rates and the difference is statistically insignificant.

Results from statistical analysis using Anova: single factor at $\alpha = 0.05$ show that there was statistically significant difference between the groups of data (p-value < 0.05) for both between the mean of the liquids used at 200 ml/h (Table 15) and between the mean of water flooding rates (Table 15). Furthermore, to identify a group different from the others, the Post Hoc analysis was carried out for both sets of the data. Results from Post Hoc test show that the mean volume of liquid collected from the sample columns subjected to hexane flooding were statistically significantly different ($p < 0.05$) from the other two, whereas the difference between the other two groups of data: water and ethanol flooding were not statistically significantly different from each other ($p > 0.05$). The analysis also shows with strong observed power, 1.00 (> 0.8), that 36.7% of the variability is due to the type of liquid used for flooding.

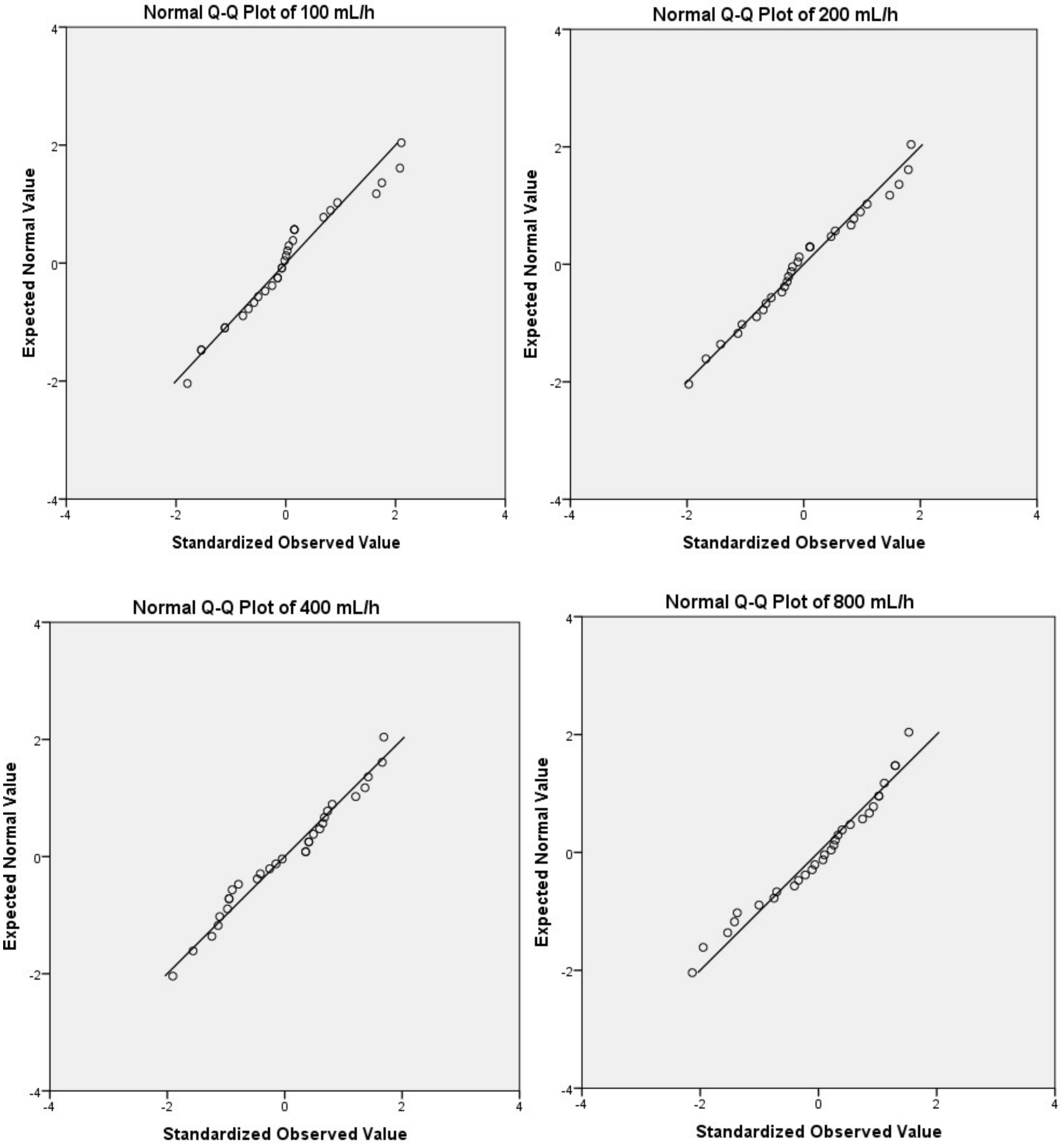


Fig. 34. Normal Q-Q plot for the recovered liquid every three minutes using different water flooding rates

where: Q-Q is Quantile-Quantile

Meanwhile, results from different water flooding rates show that the mean volume of liquid collected from the sample columns subjected to 100 ml/h was statistically significantly different ($p < 0.05$) from the volume of liquids from the sample columns subjected to 200, 400 and 800 ml/h water flooding rates. While the volume of liquids from the sample columns subjected to 200, 400 and 800 ml/h flooding rates are not statistically significantly different from each other ($p > 0.05$). The analysis also shows with strong observed power, 0.952 (> 0.8), that only 13.4% of the variability in the volume of liquid displaced is due to the water flooding rates.

Table 14. Statistical analysis using Anova: single factor for amount of liquid recovered from sample columns subjected to different liquids at 200 ml/h flooding rate

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	12.813	2	6.407	25.189	.000
Within Groups	22.128	87	.254		
Total	34.942	89			

Table 15. Statistical analysis using Anova: single factor for the amount of recovered liquid from sample columns subjected to different water flooding rates

	SS	df	MS	F	Sig.
Between Groups	3.034	3	1.011	5.973	.001
Within Groups	19.645	116	.169		
Total	22.679	119			

4.3.2. Amount of oil recovered from sample columns

Each collected volume of displaced liquids was oven dried to remove the displacing liquids: water, ethanol and hexane and to quantify the amount of oil displaced (recovered). The displacement of the oil/LNAPL from the sample column is immiscible with respect to water, miscible with respect to hexane, and somewhat intermediate with respect to ethanol. From the visual observation of the interface formed between oil and displacing liquids, some of the first collected samples by using water and ethanol flooding were pure oil, while the rest were the mixture of oil and water, and oil and ethanol respectively. On the other hand, due to the absence of interface formation between the two liquids, it was difficult to identify visually whether the displaced liquid by hexane flooding was pure oil or a mixture of oil and hexane, as oil and hexane are miscible liquids. However, after removing hexane by means of oven drying the samples, it was possible to quantify the amount of oil and hexane in each recovered sample. In respect of the oven-dry results, all thirty samples collected from the sample columns using hexane as a flooding liquid were the mixture of oil and hexane (Fig. 35 A & C). The oven-dry results of the displaced liquids from the sample columns using water and ethanol also confirmed that the visual observations concerning the contents of the recovered liquids were correct (Fig. 35). The graphs show that some of the collected samples using water and ethanol flooding were pure oil while most them were the mixture of the oil and the flooding liquid. Two of the thirty samples with ethanol flooding, and 5, 5, 4 and 3 of each from thirty samples with water flooding at 100, 200, 400 and 800 ml/h respectively were pure oil/LNAPL and the rest were the mixture of water and LNAPL/oil. The result also shows that the number of pure volumes of LNAPL collected decreases with increasing the flooding rates. The total volume of pure LNAPL displaced by water flooding were also decreases with increasing the flooding rates (Fig. 40). However, the overall recovered oil increases with increasing flooding rates and 59, 61, 61 and 63% of LNAPL could be recovered from 0.89 Pv of average sample columns oil content at 100, 200, 400 and 800 ml/h flooding rates respectively.

At the end of the experiment, 302 ml (2.82 Pv) of liquid were recovered from the sample column using water, 299 ml (2.80 Pv) of liquid were recovered using ethanol, and 324 ml (3.03 Pv) of liquid was recovered using hexane at 200 ml/h flooding rate. Meanwhile, 291 ml (2.72 Pv), 304 mL (2.82 Pv) and 301 ml (2.81 Pv) of liquids were recovered at the end of the experiments by flooding the sample columns with water at 100, 400 and 800 ml/h injection rates. The total amounts in Pv of oil recovered at the end of the experiment using water, ethanol and hexane at 200 ml/h flooding rate were 0.55, 0.55 and 0.82 respectively. On the other hand, 0.53, 0.54 and 0.56 Pv of oil/LNAPL were recovered through water flooding at 100, 400 and 800 ml/h respectively. The average degree of oil saturation for the sample columns prepared for the experiment was 89.4%. From 0.89 Pv of oil in the sample column, it would be possible to recover 61%, 61% and 91% using water, ethanol and hexane at 200 ml/h flooding rate at the end the experiment. In the meantime, 59, 61 and 63% of the oil could be recovered using water at 100, 400 and 800 ml/h flooding rates.

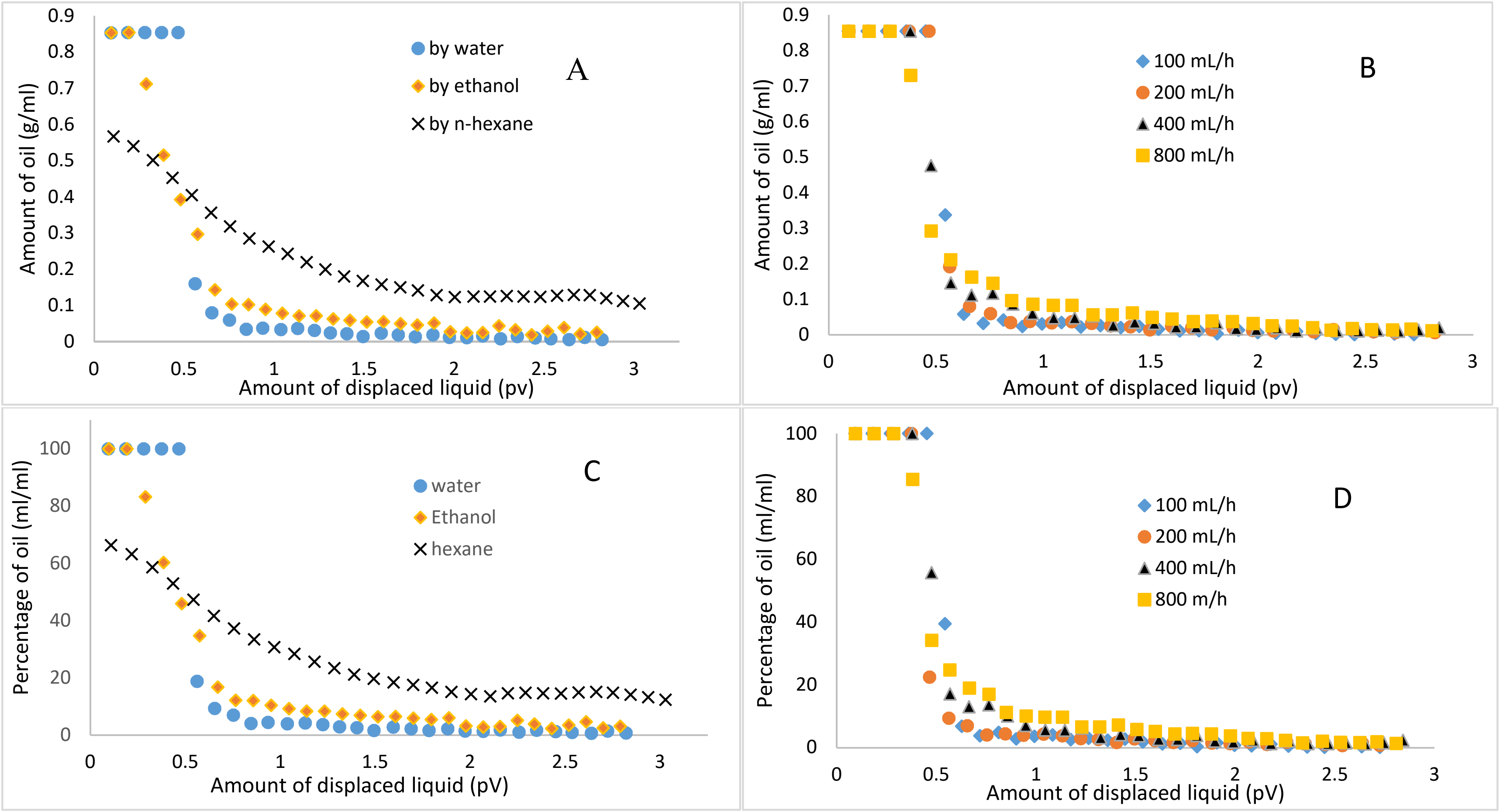


Fig. 35. Graph of recovered oil in each collected sample against Pv of recovered liquid

Where: A & C are from flooded with water, hexane, and ethanol at 200 ml/h and B & D with water at 100, 200, 400, and 800 ml/h, Pv is pore volume

The trends of the graphs under Fig. 35 A & C and Fig. 36 A & C show that it would be possible to recover more significant amounts of oil using hexane beyond the 90 minutes. On the other hand, there were more, and significant amounts of oil remained in the sample columns (approximately 40%) flooded by ethanol at 200 ml/h and water at different flooding rates compared to oil in the sample column flooded with hexane (less than 20%). Graphs under Fig. 35 show that, however, the displacements of the oil using water and ethanol were approaching zero and hence further recovery of significant amounts of oil was not expected compared to using hexane as flooding liquid. The significance of hexane in displacing oil was due to the solubility and miscibility effect of the liquids as both Marcol 82 oil and hexane are non-polar organic liquids. Following the principle of "like dissolves like" hexane could dissolve and then displace a significant amount of oil. Though ethanol is an organic liquid with both non-polar and polar characters, it could not displace significant amount of oil compared to using water (Fig. 37). Stoker (2013) among others described that the polar portion of ethanol structure dominates its non-polar part. Ethanol is completely water soluble but has a limited solubility in organic solvent, such as hexane. Yüksel & Yüksel (2004) mentioned that fuel phase separation is one of the main problems for the successful application of ethanol-gasoline blend as a homogenous liquid phase motor fuel.

The interfacial force and capillary pressure develpoed between water and oil, and ethanol and oil could be one of the main reasons for the less recovery of oil using water and ethanol flooding compared to hexane flooding. Alvarado & Manrique (2010) among others argue that the interfacial force, commonly known as capillary pressure, between the invading liquid and oil limits the amount of oil displaced. Study by O'Carroll & Sleep (2007b) showed that hot water flooding significantly increases NAPL mass recovery compared to ambient temperature water flushing through the reduction of NAPL's viscosity and interfacial tension between water and NAPL which decreases capillary pressure. Ezekwe (2011) among others mentioned that in immiscible displacement displacing liquid flows through the interconnected macro pores will keep flowing through it due to interfacial force and capillary pressure from micro pores. Graphs under Fig. 35 show that the percentage of recovered LNAPL in cumulative displaced liquid through different water flooding rates are not different from each other after one Pv of liquid recovered.

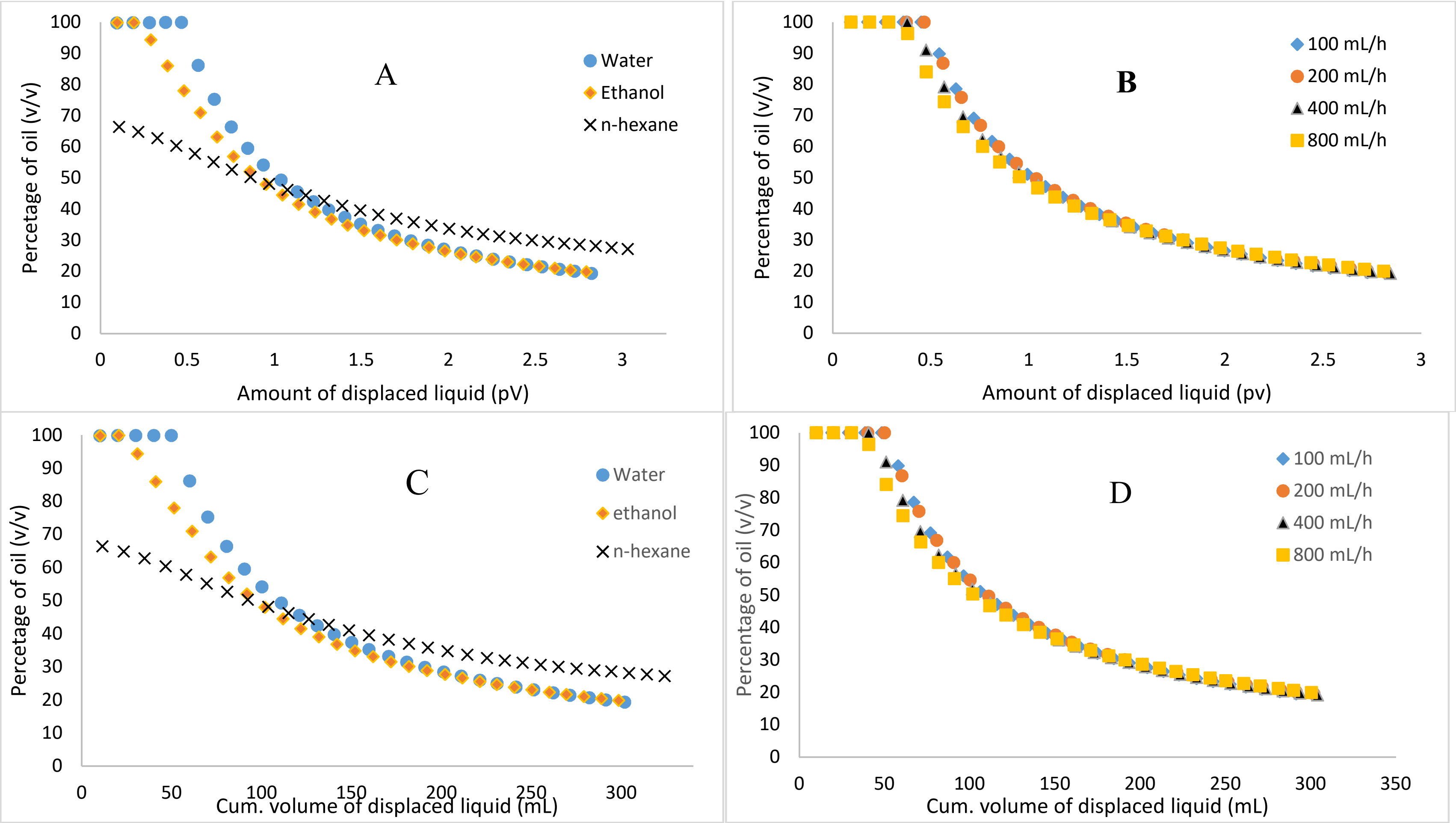


Fig. 36. Graph of recovered oil in total recovered liquid

Where: Graph A & B in pore volume (Pv) and C & D in ml

The cumulative recovered LNAPL through different flooding rates (Fig 37) shows that the total recovered LNAPL are not different from each other though the amount of LNAPL from 100 ml/h was lower than the others. Kruskal-Wallis Non-Parametric test shows that there is no statistically significant difference ($p > 0.05$) between the mean of the oil displaced at the end of the experiments by different flooding rate. Sharma & Shah (1989) and Sheng (2011) among others indicated that increasing the flooding rate increases the capillary number which could increase the displacement efficiency and decrease residual oil saturation.

The breakthrough curves for the three liquids (Fig. 39) also shows that the relative concentration of water and ethanol in the displaced liquid became constant after the first pore volume of displaced liquid. However, the curve for hexane flooding shows that the relative concentration was increasing beyond one pore volume and the curve is far below the unit value at which hexane could not displace more oil. Kruskal-Wallis Non-Parametric Test shows that there is statistically significant difference ($p < 0.05$) between the mean of the oil displaced at the end of the experiments using hexane, ethanol and water flooding.

Out of the total 0.55 pore volume of oil recovered using water at 200 ml/h flooding rate, 0.47 Pv of the oil was displaced in the first 15 minutes of the 90 minutes displacement time (see graphs under Fig. 37 A and B). However, the amount of recovered oil in the remaining 75 minutes was only 0.08 Pv. On the other hand, the amounts of oil recovered during the first 15 minutes using ethanol and hexane were 0.37 and 0.31 Pv respectively. While the amount of oil recovered in the remaining 75 minutes was 0.18 and 0.60 Pv for using ethanol and hexane respectively. The total recovered oil during the first one Pv of displaced liquid using water, ethanol and hexane were 0.52, 0.46 and 0.50 respectively. The values for the first two pore volumes of recovered liquid were 0.54, 0.53 and 0.69 Pv using water, ethanol and hexane respectively. The result shows that 85% of the recovered oil using water was in the first 0.5 Pv of the displaced liquid. However, there were only 34% and 67% of the recovered oil by hexane and ethanol in the first 15 minutes respectively.

Meanwhile, 0.53, 0.55, 0.55 and 0.56 Pv of oil was recovered at the end of the experiments using water at 100, 200, 400 and 800 ml/h flooding rates respectively. The breakthrough was 50.2, 49.8, 44.2 and 38.5 ml of oil using 100, 200, 400 and 800 ml/h water injection rates. In the first pore volume of the displaced liquid 0.51, 0.52, 0.50 and 0.49 Pv of oil could be recovered using 100, 200, 400 and 800 ml/h water flooding rates respectively.

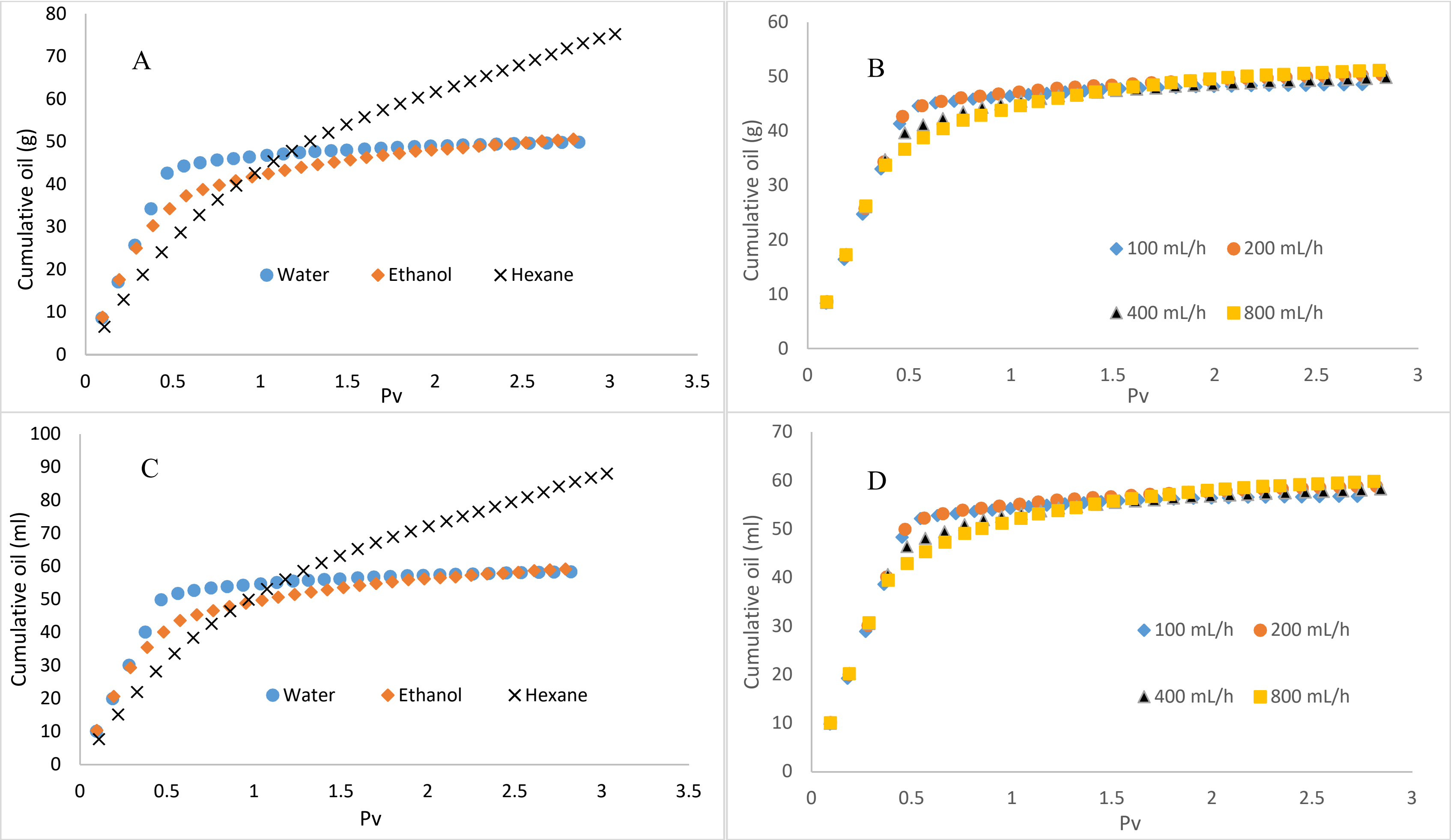


Fig. 37. Graph of cumulative recovered oil

Where: Graphs A & C from using different liquids at 200 ml/h and B & D using water at different flooding rates

The amount of oil recovered in the first five collected samples were 0.45, 0.47, 0.43 and 0.40 Pv for 100, 200, 400 and 800 water flooding rates. The amount of oil recovered in the remaining 25 samples was only 0.08, 0.08, 0.11 and 0.16 Pv using 100, 200, 400 and 800 ml/h water flooding rates respectively. These show that after one Pv of displaced liquid almost double amount of oil could be recovered using 800 ml/h compared to 100 and 200 ml/h flooding rates. 0.53, 0.54, 0.53 and 0.54 Pv of oil could be recovered using 100, 200, 400 and 800 ml/h water flooding rates respectively. The result showed that 85, 85, 80 and 72% of the recovered oil using 100, 200, 400 and 800 water flooding rates respectively were in the first five collected samples. The values for at the end of the first and second Pv displaced liquid respectively were 96.3, 93.8, 91.3 and 87.3%, and 99.5, 98.4, 97.8 and 97.4% with 100, 200, 400 and 800 ml/h flooding rates respectively. These show that most of the oil was recovered with the first pore volume of the displaced liquids. Significant amount of oil was recovered using 800 ml/h water flooding rate compared to 100 and 200 ml/h in the second Pv of the displaced liquid. However, only below 3% of the oil was recovered in the third and final Pv of displaced liquid using different water flooding rates. Break through curves under Fig. 39 show it could not be possible to recover significant amount of LNAPL using different water flooding rates as the curves approach unity even though significant amount of applied oil was remained in the sample columns (approximately 0.35 Pv). It could be possible to recover in average 62% of the oil from the sample columns using different water injection rates.

From 85% degree of oil saturation, O'Carroll & Sleep (2007b) were able to recover 75% and 64% of the oil using hot and cold water flooding in a laboratory experiment. However, according to Gates, et al. (2010) due to both geological and fluid heterogenities, it would be possible to recover only 5% to 15% using cold water and 30% to 80% using steam in situ/field scale processes. Although hot water reduced the high level of oil saturation, O'Carroll & Sleep (2007b) concluded that it did not result in lowering the NAPL residual saturation.

During the displacement of oil from the sample columns, all the three liquids invaded the whole volume of the column and the total recovery efficiency as well as liquid displacement efficiency for the 90-minute displacement was calculated using Eq. [44]. For this experiment it could be calculated simply by dividing the amount of oil recovered from the sample column by the total amount of oil that was initially in the sample column. The average volume of the oil in the prepared sample columns was 96.51 ml. The average amount of oil displaced by water, ethanol and hexane at the end of a 90-minute experiment were 58.35, 59.16 and 87.99 ml respectively. Therefore, the total recovery efficiency for using water, ethanol and hexane were 60%, 61% and 91% respectively. On the other hand, However, 56.71, 58.35, 58.35 and 59.92 ml of oil were recovered using 100, 200, 400 and 800 ml/h water flooding rates respectively.

The total recovery efficiency using 100, 200, 400 and 800 ml/h flooding rates were 59, 61, 61 and 62 % respectively. To recover oils both using different liquids and water with different flooding rates, different amounts of the liquids were injected into the oil saturated sample columns. At the end of 90 minutes 244, 240 and 236 ml of water, ethanol and hexane were recovered respectively. Meanwhile, 234, 246 and 241 ml of water were recovered from 100, 400 and 800 ml/h water injection rates at the end of respective flooding rates' experiment. On the other hand, from the economic, environmental and other points of view these liquids have different values.

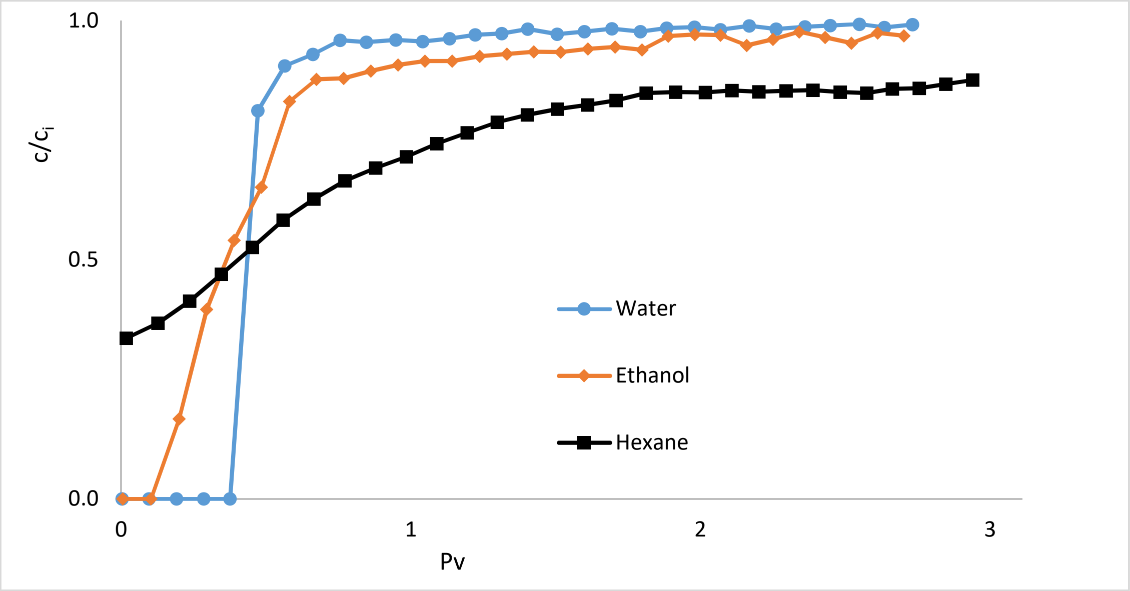


Fig. 38. Breakthrough curves for different liquids injected into sample columns at 200 ml/h

where c is the concentration of the fluid (volumetric fraction) (ml/ml) and c_i is the initial concentration (volumetric fraction) of the injected liquid (ml/ml)

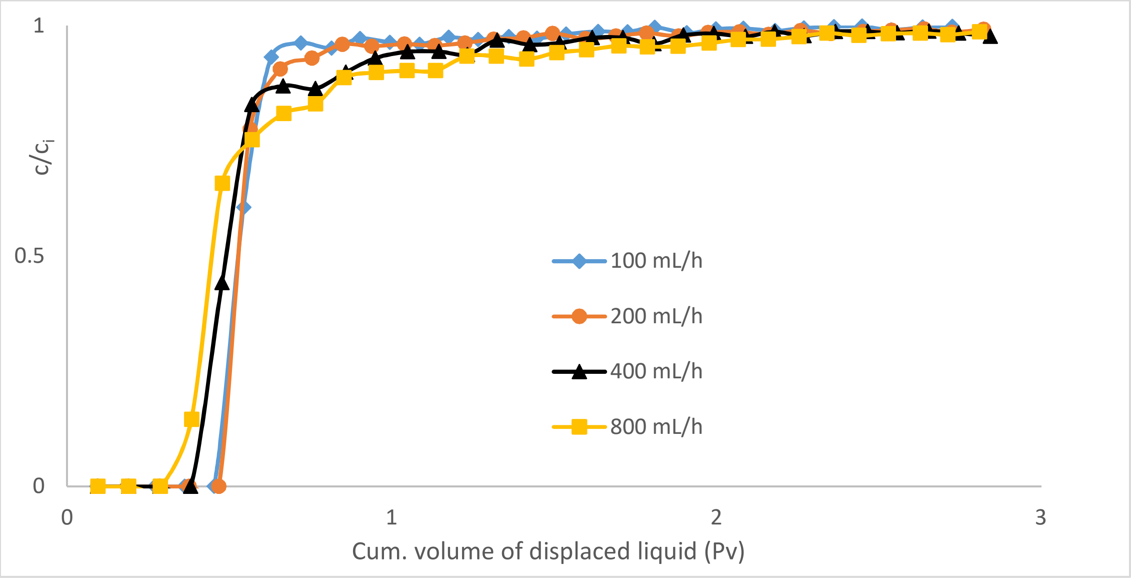


Fig. 39. Breakthrough curves for water injected in to sample columns at different flooding rates

Note: for both Figs. 39 and 40, the breakthroughs are for the sample columns packed from silica sand ST56 at 1.5 g/cm^3 and saturated with 0.9 Pv of Marcol 82 oil

4.4. Amount of pure LNAPL recovered

Recovered liquid samples from the sample columns flooded with water, ethanol and hexane were either pure oil/LNAPL or the mixture of the injected liquid and oil. All the collected samples from the sample columns flooded with hexane were a mixture of hexane and oil (Fig. 36 A & C). Nevertheless, some of the collected liquid samples at the beginning of the displacement from sample columns subjected to ethanol and water were pure LNAPL (Fig. 36). The breakthrough for hexane was at the first 10 ml recovered liquid sample and for ethanol it was at the third recovered sample. The breakthrough for 100, 200, 400 and 800 ml/h water injection rates were after 5, 5, 4 and 3 recovered samples respectively. Therefore, the first two samples collected from the sample columns flooded with ethanol, and 5, 5, 4 and 3 of the samples collected from the sample columns flooded with water at 100, 200, 400 and 800 ml/h flooding rates respectively were pure LNAPL. These show that significant amount of LNAPL displaced by water injection were recovered before water breakthrough. Hence, it is important to evaluate the pattern of the recovered pure LNAPL from the sample columns flooded with water.

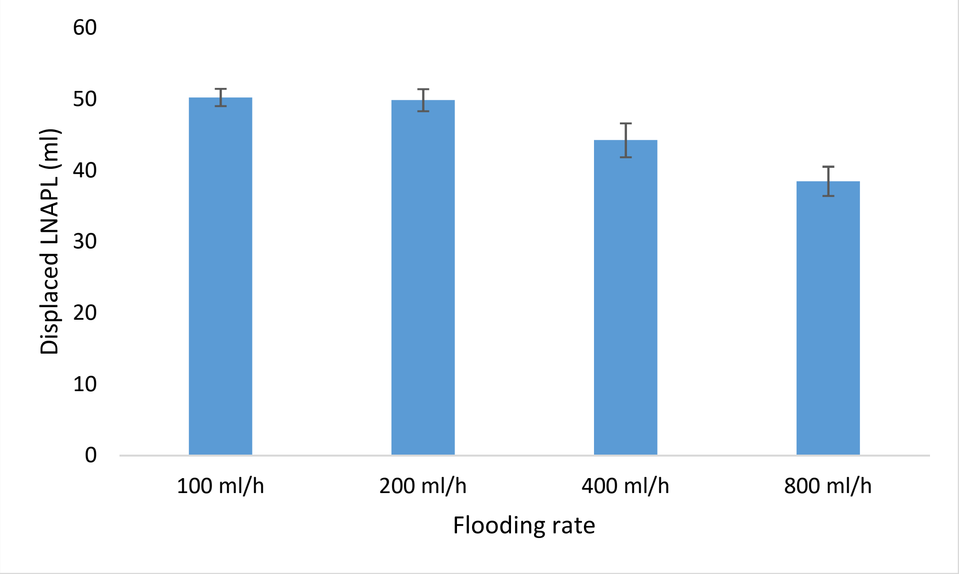


Fig. 40. Graph of total volume of pure LNAPL recovered from sample columns subjected to different water injection rates

The amount of LNAPL recovered from sample columns before breakthrough with different water injection rates varied between the applied rates and decreases with increasing flooding rates (Fig. 40). It could be possible to recover 50.2, 49.8, 44.2 and 38.5 ml of pure LNAPL in average before water breakthrough using 100, 200, 400 and 800 ml/h injection rates respectively. Nonparametric Kruskal-Wallis Test showed that there was statistically significantly difference (P = 0.025) between the mean of the pure LNAPL recovered before water breakthrough with different injection rates, with mean rank: 9.67, 9.33, 5.00 and 2.00 for 100, 200, 400 and 800 ml/h flooding rates respectively.

Table 16. Basic statistics of oven dried sequentially recovered pure LNAPL with water flooding

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
Displaced 1st	39	99.6323	.09705	.01554	99.6008	99.6638	99.47	99.90
Displaced 2nd	39	99.8177	.04416	.00707	99.8034	99.8320	99.74	99.91
Displaced 3rd	26	99.8612	.03798	.00745	99.8458	99.8765	99.79	99.93
Displaced 4th	13	99.8777	.03632	.01007	99.8557	99.8996	99.82	99.93
control	13	99.9123	.04106	.01139	99.8875	99.9371	99.86	99.98
Total	130	99.7862	.12225	.01072	99.7650	99.8074	99.47	99.98

The amount of LNAPL retained after oven drying the displaced and collected pure LNAPL samples were done for pure LNAPL collected successively every 6, 3, 1.5 and 0.75 minutes at 100, 200, 400 and 800 ml/h flooding rates respectively. The average recovered pure oil before water breakthrough was calculated from three sample columns for each flooding rates. However, a total of over 39 sample columns were subjected to different water flooding rates, and only 39 of them were selected for the pattern of recovered LNAPL. The number of samples collected, and oven dried under fifth order was comparatively small and left out of the analysis.

Table 17. Result from Anova: single factor Post Hoc Test for the amount of recovered pure LNAPL

LSD	0.028276			
HSD	0.039571			
Scheffe	0.137688			
Post Hoc	1st	2nd	3rd	4th
2nd	**0.184597**			
3rd	**0.228634**	0.044037		
4th	**0.244628**	0.060032	0.015994	
control	**0.278887**	0.094291	0.050253	0.034259

Where: Colored cells have significant mean differences, LCD is least significant difference test, HSD is Tukey's honestly significant difference, and Scheffe is Scheffe test

Successively displaced pure LNAPL approximately 10 ml each from 39 sample columns, and thirteen each approximately 10 ml LNAPL samples (as a control from oil used in the study) were oven dried at 105 °C for 24h. The loss of LNAPL used in this experiment to oven temperature showed that the average percentage of the oil to evaporation loss was 0.08 with 0.04 standard deviation. Table 16 Shows that the maximum loss of the oil was from the samples recovered first with 0.37 and 0.097, mean and standard deviation respectively. Under both conditions, however, the loss of the oil was less than 0.5% and cannot affect the overall result of the study. Additionally, displaced oil in pure form could be analyzed without oven drying. Successively recovered and oven-dried pure oil shows that as the recovered sample closes to the breakthrough, the difference with the control decreases and the difference is statistically insignificant (Table 16).

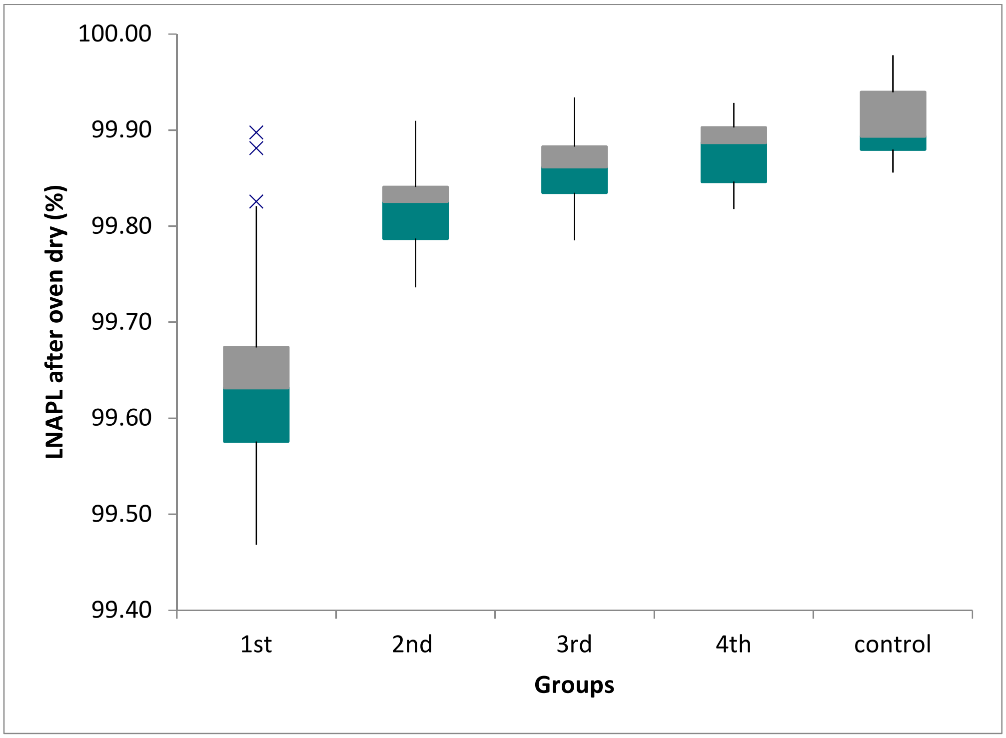


Fig. 41. Box and Whisker plot for oven-dried recovered pure LNAPL and control

Where: the end of the whiskers shows the maximum and minimum values, the upper and lower sides of the box are the medians of the upper half and the lower half respectively, and the green and grey parts of the box (separated by the median) are the second and third quartiles of the data respectively

Result from ANOVA single factor analysis using SPSS showed that there was statistically significant difference between the mean of the percentage of pure LNAPL left after oven drying. It showed that, order of the recovery had statistically significant impact on the type/pattern of LNAPL displacement from porous media ($p < 0.001$). To show where the difference(s) lie, Post Hoc test using Games-Howell method (for different sample number among the groups used with different variances from Leven's test of equality of error of variances, $p < 0.001$) was done. The results show that there was statistically significant difference between the mean of the first, second and third recovery orders ($p \leq 0.001$). Again, the mean of the first and the second recovered samples were statistically significantly different from the mean of the fourth order and the control ($p < 0.001$). The mean of the LNAPL recovered at third order was also statistically significantly different from the mean of the control used (p = 0.008). However, there was no statistically significant difference between the mean of the third and fourth recovered samples (p = 0.682), as well as between the fourth and control (p = 0.188). The analysis also showed that 73.9% of the variation between the means were due to the order of the displacement with strong observed power, 1.00.

ANOVA single factor analysis using Excel integrated QI Macros confirmed that the analysis results from SPSS program (Table 17). All the pair wise mean comparison through Post Hoc Test using QI Macros were similar with that of SPSS except the mean difference between the percentage of LNAPL displaced at 4th order and the control (Table 16; Fig. 41). In QI Macros, the Post Hoc test was done using three procedures. All the pair of the mean statistically significantly different from each other were at least true using two procedures except the mean of the pure LNAPL displaced 4th with the control. Therefore, given the analysis result from IBM SPSS, the mean difference between the 4th and the control is not strongly supported. Even though it is not supported by qualitative analysis, the quantitative analysis of the oil may indicate that displaced LNAPL sample before water breakthrough were displaced somehow based on their carbon content per molecule. Mineral oil range used hydrocarbons with lower molecules displaced first and then followed by intermediate and higher molecules. However, qualitative analysis of the samples is very important to make such conclusion.

5. Conclusions and Recommendations

Multicomponent multiphase liquid flow through porous media has many applications. Contamination by NAPLs and the remediation of the contaminated subsurface as well oil recovery from oil fields involves multiphase multicomponent liquid flow. Proper characterization and remediation of the contaminated sites require comprehensive understating of the behavior of NAPLs in natural porous media. In subsurface porous media, released NAPLs interact with gaseous phase, aqueous phase and solid phase. In saturated zone, the interaction could be between four phases while in vadose zone it could be minimized to three phases as the air pressure in the vadose zone is atmospheric pressure. In this work, sample columns subjected to different LNAPL to water ratios in mimic of porous media contamination during multiphase multicomponent liquid flow was studied. Sample columns' liquid content was sampled with ACP, measured using soil moisture sensors and determined through gravimetric analysis method. Additionally, in separate experiment, sample columns saturated with LNAPL were flooded with different types of liquids in mimic of the decontamination of the porous media contaminated by LNAPL/oil. Hexane, ethanol and water were injected to the sample columns at 200 ml/h flooding rates and water also injected to sample columns at 100, 400 and 800 ml/h.

ACPs from different sources and/or produced through different activation methods have different sorption capacity and ACPs used in this study showed that ACPs from different sources could have different adsorption capacities. ACP from Brenntag had performed better compared to the one from Techpoint and chosen for the sampling of water and/or LNAPL from the porous media. The study also found that it could be possible to select ACP with better sorption quality based on its density, dust content, strength, time taken for freely released pellet to settle at the bottom of water pool. ACP from Brenntag used in the experiment could sample both LNAPL and water from sample columns saturated with different LNAPL to water ratios proportionally. The pellet sampled more liquids from sample columns subjected to one liquid only compared to sample columns subjected to both liquids. More liquids were sampled also from sample columns where the amount of applied LNAPL was higher compared to sample columns subjected to liquids where the amount of LNAPL was lower in the ratio. In all cases, it could sample both liquids with higher standard deviations/variance. Therefore, to use ACP for the quantification of porous with respect to water and LNAPL, more must be done to improve the quality of the pellets, e.g., production of pellets with uniform quality and dimensions (both length and diameter).

LNAPL and water contents of the sample columns were also analyzed using soil moisture sensors and gravimetric analysis method. The results show that for the sample columns subjected to only one liquid, and at the lower LNAPL to water ratio the result from gravimetric analysis method and soil moisture seniors were the same. Nevertheless, at higher LNAPL to water applied ratios, water content from both methods were different. Two reasons were identified for the differences. The first reason was that gravimetric analysis method could under estimate the water content of the sample columns due to the inclusion of nonvolatile LNAPL as part of the oven-dry sand mass. The difference could be minimized significantly after excluding the oil from the dry solid mass. The other reason for the difference in water content estimation between the two methods could be from the over estimation of water content measured by soil moisture sensors due to the modification of porous media bulk relative permittivity from the presence of LNAPL. Results from many studies show that the presence of NAPLs in the porous media could modify the bulk relative permittivity of the porous media. It could be concluded that the presence of significant of LNAPL in porous media could affect water content determination through thermos-gravimetric analysis method. The presence of non-volatile LNAPL results in underestimation of the water content, otherwise resulted in overestimation of the water content from non-water evaporation loss due to the presence of volatile LNAPL.

Many studies have showed that it could be possible to use DMM to estimate porous media NAPLs and water contents. Water contents can be measured using soil moisture sensors and also can be determined through gravimetric analysis methods effectively. Bulk relative permittivity of the porous media can be modified if NAPLs displaces air from the pores given that the bulk density, soil solid particles and water contents are constant. If the porosity and degree of saturation of the porous media is known, NAPLs content of the porous media can be estimated effectively. This study shows that DMM can be used to estimate LNAPL content of the porous media. The study used non-volatile oil to quantify exactly the amount of LNAPL in the porous media otherwise it could be difficult to determine LNAPL and water contents using conventional thermos-gravimetric analysis method from the same sample. On the other hand, the use of volatile LNAPL for such purpose could be difficult as the LNAPL evaporates at oven temperature which could result in over estimation of water but under estimation of LNAPL.

Water, hexane and ethanol at 200 ml/h flooding rate were used to displace oil from the sample columns. Results show that significant amount of oil could be recovered using hexane as a flooding liquid compared to water and ethanol at 200 ml/h flooding rate. However, the amount oil recovered by ethanol and water were not statistically significantly different from each other. The main reason for the hexane to displace significant amount of oil was because hexane both dissolved and displaced the oil from the porous media as hexane is miscible with and a solvent for most hydrocarbons. On the other hand, the oil is immiscible with both water and ethanol and interfacial tension and capillary pressure could develop when they contact. The interfacial tension, viscosity differences and capillary pressure hinders the displacement of oil by water and ethanol. Even though ethanol has both polar and non-polar character it could not displace significant amount of oil compared to water.

Many literatures indicated that increasing flooding rates increases capillary number which could increase displacement efficiency through decreasing residual oil saturation. But, results from water injection rates show that increasing the flooding rates from 100 to 200 to 400 to 800 ml/h did not increase the overall displacement efficiency. This shows that for the flooding rates and sample columns used it could not possible to displace significant amount of oil by increasing the flooding rates for the experimental duration. In contrary, before water breakthrough, statistically significant amount of pure oil could be recovered at lower injection rates than at higher injection rates. Results from oven dried pure LNAPL recovered show that the evaporation loss decreases sequentially. It can be concluded that HC components relatively with lower carbon content per molecules could be displaced first. However, to derive concrete conclusion, qualitative analysis should be done to observe the pattern of displacement.

Finally, evaluation of methods for oil separation from injected liquids: water, ethanol and hexane indicated that oven drying 10 ml sample worked perfectly for the separation of oil from hexane and ethanol for the whole range with $R^2 = 1$. The method worked perfectly also to separate oil form water for up to 30% by mass of oil in the displaced liquid sample with $R^2 = 1$. However, for the percentage of the oil in the displaced sample greater than 30%, it was difficult to separate oil from the displacing water using the same drying bottle. The problem was tackled for the sample with greater than 30% by mass in each 10 ml displaced liquid through collecting displaced liquid into more than one bottle. The collected samples were oven dried separately but the amount of oil in each bottle were added. Additionally, the method of oil extraction using hexane was evaluated and the result shows that hexane extracted the oil used in the study from the porous media used perfectly, with $R^2 = 1$.

6. References

Abdallah, W., Buckley, J.S., Carnegie, A., Edwards, J., Herold, B., Fordham, E., Graue, A., Habashy, T., Selezne, N., Signer, S., Hussain, S., Montaron, B., Ziauddin, M. 2007. Fundamentals of Wettability. Oilfield Review. 19(2). 44-61.

Abdelgwad, A.H., Said, T.M. 2016. Measured dielectric permittivity of contaminated sandy soil at microwave frequency. J. Microw. Optoelectron. Electromagn. Appl. 15(2). 115-122.

Abrams, M.A. 1996. Distribution of Subsurface Hydrocarbon Seepage in Near-Surface Marine Sediments. In Schumacher, D., Abrams, M.A. (eds): Hydrocarbon Migration and Its Near-surface Expression. Tulsa, USA. American Association of Petroleum Geologists Memoir 66. p. 1-14. ISBN 0-89181-345-4.

Adib, F., Bagreev, A., Bandosz, T.J. 2000. Adsorption/oxidation of hydrogen sulfide on nitrogen-containing activated carbons. Langmuir. 16(4). 1980-1986.

Aga, D.S., Thurman, E.M. 1997. Environmental Immunoassays: Alternative Techniques for Soil and Water Analysis. In Aga, D.S., Thurman, E.M. (Eds): Immunochemical Technology for Environmental Applications. Washington DC, USA. American Chemical Society Symposium Series 657. p. 1-20. ISBN 0-8412-3487-6.

Agaoglu, B., Copty, N.K., Scheytt, T., Hinkelmann, R. 2015. Interphase mass transfer between fluids in subsurface formations: A review. Advances in Water Resources. 79. 162-194.

Agaoglu, B., Scheytt, T., Copty, N.K. 2012. Laboratory-scale experiments and numerical modeling of cosolvent flushing of multi-component NAPLs in saturated porous media. Journal of Contaminant Hydrology. 140-141. 80-94.

Agbalaka, C.C., Dandekar, A.Y., Patil, S.L., Khataniar, S., Hemsath, J. 2008. The effect of wettability on oil recovery: A review. Society of Petroleum Engineers. 1-13.

Agbalaka, C.C., Dandekar, A.Y., Patil, S L., Khataniar, S., Hemsath, J.R. 2009. Core flooding studies to evaluate the impact of salinity and wettability on oil recovery efficiency. Transport Porous Media. 77. 77–94.

Ahmadpour, A., Do, D.D. 1997. The preparation of activated carbon from macadamia nutshell by chemical activation. Carbon. 35(12). 1723-1732.

Ahmed, T. 2010. Reservoir Engineering Handbook. Burlington, USA. Gulf Professional Publishing. P. 1454. ISBN 978-1-85617-803-7.

Ajo-Franklin, J.B., Geller, J.T., Harris, J.M. 2004. The dielectric properties of granular media saturated with DNAPL/water mixtures. Geophysics Res. Lett. 31(17). L17501.

Ajo-Franklin, J.B., Geller, J.T., Harris, J.M. 2006. A survey of the geophysical properties of chlorinated DNAPLs. Journal of Applied Geophysics. 59(3). 177-189.

Aktaş, Ö., Çeçen, F. 2012. Activated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment. Weinheim, Germany. WILEY-VCH Verlag GmbH & Co. KGaA. p. 388. ISBN 978-3-527-32471-2.

Albarrán, A., Celis, R., Hermosín, M.C., López-Piñeiro, A., Ortega-Calvo, J.J., Cornejo, J. 2003. Effects of solid olive-mill waste addition to soil on sorption, degradation and leaching of the herbicide simazine. Soil Use and Management. 19(2). 150-156.

Allen, J.P., Atekwana, E.A., Atekwana, E.A., Duris, J.W., Werkema, D.D., Rossbach, S. 2007. The microbial community structure in petroleum-contaminated sediments corresponds to geophysical signatures. Applied and Environmental Microbiology. 73(9). 2860-2870.

Alloway, B.J., Ayres, D.C. 1997. Chemical Principles of Environmental Pollution. London, UK. Chapman & Hall. P. 395. ISBN 0-7514-0380-6.

Al-Maamari, R.S., Hirayama, A., Sueyoshi, M.N., Abdalla, O.A., Al-Bemani, A.S., Islam, M.R. 2009. The application of air-sparging, soil vapor extraction and pump and treat for remediation of a diesel-contaminated fractured formation. Energy Sources, Part A. 31(11). 911-922.

Alter, B. 2012. Environmental Consulting Fundamentals: Investigation and Remediation. Boca Raton, USA. CRC Press. p. 373. ISBN 978-1-4398-6891-1.

Alvarado, V., Manrique, E. 2010. Enhanced Oil Recovery: Field Planning and Development Strategies. Burlington, USA. Gulf Professional Publishing. p. 192. ISBN 978-1-85617-855-6.

Amirijafari, B., Campbell, J. 1972. Solubility of gaseous hydrocarbon mixtures in water. Society of Petroleum Engineers Journal. 12(01). 21-27.

Amos, R.T., Mayer, K.U., Bekins, B.A., Delin, G.N., Williams, R.L.2005. Use of dissolved and vapor-phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface. Water Resour. Res. 41(2). W02001.

Ancheyta, J. 2013. Modeling of Processes and Reactors for Upgrading of Heavy Petroleum. Boca Raton, USA. Taylor & Francis Group, LLC. p 524. ISBN 978-1-4398-8046-3.

Anderson, R.T., Lovley, D.R. 2000. Anaerobic bioremediation of benzene under sulfate-reducing conditions in a petroleum-contaminated aquifer. Environ. Sci. Technol. 34(11). 2261-2266.

Ania, C.O., Parra, J.B., Pis, J.J. 2002. Effect of texture and surface chemistry on adsorptive capacities of activated carbons for phenolic compounds removal. Fuel Processing Technology. 77-78. 337-343.

Annable, M.D., Rao, P.S., Hatfield, K., Graham, W.D., Wood, A.L., Enfield, C.G. 1998. Partitioning tracers for measuring residual NAPL: field-scale test results. Journal of Environmental Engineering. 124(6). 498-503.

Annan, A.P. 2009. Electromagnetic Principles of Ground Penetrating Radar. In Jol, H.M. (ed): Ground Penetrating Radar Theory and Applications. Oxford, UK. Elsevier B.V. p. 4-40. ISBN 978-0-444-53348-7.

Anwar, A.H.M. F. 2013. Mass transfer characteristics of nonaqueous phase liquid based on air–liquid interfacial area in variably saturated porous media. Water, Air & Soil Pollution. 224 (1567). 1-11.

Anwar, A.H.M.F., Tien, T. H., Inoue, Y., Takagi, F. 2003. Mass transfer correlation for nonaqueous phase liquid volatilization in porous media. Environ. Sci. Technol. 37(7). 1277-1283.

Apul, O.G., Wang, Q., Zhou, Y., Karanfil, T. 2013. Adsorption of aromatic organic contaminants by graphene nanosheets: Comparison with carbon nanotubes and activated carbon. Water Research. 47(4). 1648-1654.

Arnold, W., Nishigak, M. 1999. Mass- and Energy Migration in Low Pervious. In B. Scholz-Reiter, B., Stahlmann H.D., Nethe, A. (eds): Process Modelling. Berlin, Germany. Heidelberg: Springer-Verlag. p. 480-496. ISBN 978·3·641-6426S-4.

Arriagada, R., García, R., Molina-Sabio, M., Rodriguez-Reinoso, F. 1997. Effect of steam activation on the porosity and chemical nature of activated carbons from Eucalyptus globulus and peach stones. Microporous Materials. 8(3-4). 123-130.

Aske, N., Kallevik, H., Sjöblom, J. 2001. Determination of saturate, aromatic, resin, and asphaltenic (SARA) components in crude oils by means of infrared and near-infrared spectroscopy. Energy & Fuels. 15(5). 1304-1312.

Atlas, R.M. 1995. Petroleum biodegradation and oil spill bioremediation. Marine Pollution Bulletin. 31(4-12). 178-182.

Avraam, D.G., Payatakes, A.C. 1995. Generalized relative permeability coefficients during steady-state two-phase flow in porous media, and correlation with the flow mechanisms. Transport in Porous Media. 20(1-2). 135-168.

AWWA 2012. Granular Activated Carbon. Denver, USA. American Water Work Association.

AWWA 2013. Reactivation of Granular Activated Carbon. Denver, USA. American Water Works Association.

Aygün, A., Yenisoy-Karakaş, S., Duman, I. 2003. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Microporous and Mesoporous Materials. 66(2-3). 189-195.

Ayirala, S.C., Rao, D.N. 2008. Mechanistic Modeling of Dynamic Vapor-Liquid Interfacial Tension in Complex Petroleum Fluids. In Mittal K.L. (ed): Contact Angle, Wettability and Adhesion: Volume 5. Boca Raton, USA. CRC Press. p. 73-94. ISBN 978-9-04-742999-9.

Ayotamuno, M.J., Kogbara, R. B., Ogaji, S.O.T., Probert, S.D. 2006. Petroleum contaminated ground-water: Remediation using activated carbon. Applied Energy. 83(11). 1258-1264.

Bacri, J.C., Rakotomalala, N., Salin, D., Wouméni, R. 1993. Non-Linear Three Dimensional Miscible Viscous Fingering in Porous Media. In Gouesbet G., Berlemont, A. (eds): Instabilities in Multiphase Flows. New York, USA. Springer. p. 297-307. ISBN 978-1-4899-1596-2.

Baedecker, M.J., Eganhouse, R.P., Bekins, B.A., Delin, G.N. 2011. Loss of volatile hydrocarbons from an LNAPL oil source. Journal of Contaminant Hydrology. 126(3-4). 140-152.

Bagreev, A., Bashkova, S., Bandosz, T.J. 2002. Adsorption of SO2 on activated carbons: The effect of nitrogen functionality and pore sizes. Langmuir. 18(4). 1257-1264.

Bagreev, A., Rahman, H., Bandosz, T.J. 2001. Thermal regeneration of a spent activated carbon previously used as hydrogen sulfide adsorbent. Carbon. 39(9). 1319-1326.

Baker, J.M., Allmaras, R.R. 1990. System for automating and multiplexing soil moisture measurement by time-domain reflectometry. Soil Sci. Soc. Am. J. 54(1). 1-6.

Baker, R.O., Yarranton, H.W., Jensen, J.L. 2015. Practical Reservoir Engineering and Characterization. Waltham, USA. Gulf Professional Publishing. p. 521. ISBN 978-0-12-801811-8.

Balat, M., Balat, H. 2009. Recent trends in global production and utilization of bio-ethanol fuel. Applied Energy. 86. 2273–2282.

Balendonck, J., Hilhorst, M.A. 2001. Application of an intelligent dielectric sensor for soil water content, electrical conductivity and temperature. Proceedings of the 18th IEEE Instrumentation and Measurement Technology Conference. Rediscovering Measurement in the Age of Informatics. 21-23 May 2001. Budapest Convention Centre, Institute of Electrical and Electronics Engineers, Budapest, Hungary. Proceedings of IEEE. V. 3. p. 1817-1822. ISBN 0-7803-6646-8.

Banjoo, D.R., Nelson, P.K. 2005. Improved ultrasonic extraction procedure for the determination of polycyclic aromatic hydrocarbons in sediments. Journal of Chromatography. 1066(1-2). 9-18.

Bansal, R.C., Goyal, M. 2005. Activated Carbon Adsorption. Boca Raton, USA. Taylor & Francis Group. p. 472. ISBN 0-8247-5344-5.

Barreira, L.M., Parshintsev, J., Kärkkäinen, N., Hartonen, K., Jussila, M., Kajos, M., Kulmala, M., Riekkola, M.L. 2015. Field measurements of biogenic volatile organic compounds in the atmosphere by dynamic solid-phase microextraction and portable gas chromatography-mass spectrometry. Atmospheric Environment. 115. 214-222.

Bass, D.H., Hastings, N.A., Brown, R.A. 2000. Performance of air sparging systems: a review of case studies. Journal of Hazardous Materials. 72(2-3). 101-119.

Báťková, K., Matula, S., Miháliková, M., Chala, A.T., Barradas, J.M., Mekonnen, G.B. 2014. Testing of Activated Carbon for Water and Non-volatile LNAPL Quantitative Determination in Porous Media under Laboratory Conditions. Soil & Water Res. 9(4). 161-168.

Baumhardt, R.L., Lascano, R.J., Evett, S.R. 2000. Soil material, temperature, and salinity effects on calibration of multisensor capacitance probes. Soil Sci. Soc. Am. J. 64(6). 1940-1946.

Bear, J. 1972. Dynamics of Fluids in Porous Media. New York, USA. Dover Publications. p. 756. ISBN 0-186-65675-6.

Bear, J., Cheng, A.H.D. 2010. Modeling Groundwater Flow and Contaminant Transport. New York, USA. Springer. p. 834. ISBN 978-1-4020-6681-8.

Bedrikovetsky, P. 1993. Mathematical Theory of Oil and Gas Recovery with Applications to ex-USSR Oil and Gas Fields. Dordrecht, the Netherlands. Springer. p. 576. ISBN 978-90-481-4300-9.

Bell, J.P., Dean, T.J., Hodnett, M.G. 1987. Soil moisture measurement by an improved capacitance technique, part II: Field techniques, evaluation and calibration. Journal of Hydrology. 93(1-2). 79-90.

Bender, J. 2015. The US just destroyed 280 ISIS oil trucks [Online]. [Cited on 16. 4. 2017]

Available at <http://www.businessinsider.com/us-isis-oil-trucks-2015-11>.

Berkowitz, B., Dror, I., Yaron, B. 2014. Contaminant Geochemistry: Interactions and Transport in the Subsurface Environment. Berlin, Germany. Springer-Verlag. p. 577. ISBN 978-3-642-54776-8.

Bermejo, J.L., Sauck, W.A., Atekwana, E.A. 1997. Geophysical discovery of a new LNAPL plume at the former Wurtsmith AFB, Oscoda, Michigan. Groundwater Monitoring & Remediation. 17(4). 131-137.

Bettelheim, F.A., Brown, W.H., Campbell, M.K., Farrell, S.O., Torres, O.J. 2013. Introduction to Organic and Biochemistry. Belmont, USA. Brooks/Cole. p. 1968. ISBN 1-133-10508-4.

Bhushan, B. 2013. Introduction to Tribology. New York, USA. John Wiley & Sons. p.711. ISBN 978-1-119-94453-9.

Birchak, J., Gardner, C., Hipp, J., Victor, J. 1974. High dielectric constant microwave probes for sensing soil moisture. Proceedings of the IEEE. 62(1). 93-98.

Bird, R.B., Wiest, J.M. 1999. Non-Newtonian Fluids. In Schetz, J.A., Fuhs, A.E. (eds): Fundamentals of Fluid Mechanics. New York, USA. John Wiley & Sons. p. 223-277. ISBN 0-471-34856-2.

Birdwell, J.E., Marrero, T.R. 2011. Estimating Molecular Diffusivities in Environmental Media. In Thibodeaux, L.J., Mackay, D. (eds): Handbook of Chemical Mass Transport in the Environment. Boca Raton, USA. CRC Press. p. 71-101. ISBN 978-1-4200-4755-4.

Bittelli, M. 2011. Measuring soil water content: A Review. HortTechnology. 21(3). 293-300.

Blunt, M. J. 2017. Multiphase Flow in Permeable Media: A Pore-Scale Perspective. Cambridge, UK. Cambridge University Press. p. 498. ISBN 978-1-107-09346-1.

Boluwade, A., Madramootoo, C.A. 2016. Independent principal component analysis for simulation of soil water content and bulk density in a Canadian Watershed. International Soil and Water Conservation Research. 4(3). 151.158.

Boopathy, R. 2000. Factors limiting bioremediation technologies. Bioresource Technology. 74(1). 63-67.

Bouchelta, C., Medjram, M.S., Bertrand, O., Bellat, J.P. 2008. Preparation and characterization of activated carbon from date stones by physical activation with steam. Journal of Analytical and Applied Pyrolysis. 82(1). 70-77.

Boyer, F., Lapuerta, C., Minjeaud, S., Piar, B. 2010. Cahn–Hilliard/Navier–Stokes Model for the simulation of three-phase flows. Transport in Porous media. 82. 463-483.

Braida, W.J., Ong, S.K. 1998. Air sparging: Air-water mass transfer coefficients. Water Resources Research. 34(12). 3245-3253.

Braida, W., Ong, S.K. 2000. Influence of porous media and airflow rate on the fate of NAPLs under air sparging. Transport in Porous Media.38. 29-42.

Brennen, C.E. 2005. Fundamentals of Multiphase Flow. New York, USA. Cambridge University Press. p. 345. ISBN 0-521-84804-0.

Brisco, B., Pultz, T.J., Brown, R.J., Topp, G.C., Hares, M.A., Zebchuk, W.D. 1992. Soil moisture measurement using portable dielectric probes and time domain reflectometry. Water Resources Research. 28(5). 1339-1346.

British Geological Survey 2009. Mineral Planning Factsheets: Silica sand [online]. [cited on 22. 3.2014] Available at <http://www.bgs.ac.uk/mineralsUK/>.

British Standards Institution 2014. Geotechnical investigation and testing - Laboratory testing of soil: Part 1: Determination of water content. London, UK. BSI Standards Limited. p 10. ISBN 978 0-580-81882-0.

Brown, W.H., Foote, C.S., Iverson, B.L., Anslyn, E. 2011. Organic Chemistry. Belmont, USA. Brooks Cole. p. 1242. ISBN 0-538-49675-4.

Brown, W.H., Iverson, B.L., Anslyn, E., Foote, C.S. 2017. Organic Chemistry. Boston, USA. Brooks Cole. p. 1413. ISBN 978-1-305-86554-9.

Buckley, S.E., Leverett, M.C. 1942. Mechanism of fluid displacement in sands. Journal of society of petroleum engineers. 107-106.

Buryakovsky, L., Chilingar, G.V., Rieke, H.H., Shin, S. 2012. Fundamentals of the Petrophysics of Oil and Gas Reservoirs. Hoboken - Massachusetts, USA. John Wiley & Sons. - Scrivener Publishing. p. 374. ISBN 978-1-118-34447-7.

Caliman, F.A., Robu, B.M., Smaranda, C., Pavel, V.L., Gavrilescu, M. 2011. Soil and groundwater cleanup: benefits and limits of emerging technologies: A review. Clean Techn Environ Policy. 13. 241-268.

Carcione, J.M., Seriani, G., Gei, D. 2003. Acoustic and electromagnetic properties of soils saturated with salt water and NAPL. Journal of Applied Geophysics. 52. 177-191.

Carlson, M.R. 2006. Practical Reservoir Simulation: Using, Assessing, and Developing Results. Tulsa, USA. PennWell Corporation. P. 552. ISBN 0-87814-803-5.

Cary, J.W., McBride, J.F., Simmons, C.S. 1989a. Observations of water and oil infiltration into soil: Some simulation challenges. Water Resources Research. 25(1). 73-80.

Cary, J.W., Simmons, C.S., McBride, J.F. 1989b. Predicting oil infiltration and redistribution in unsaturated soils. Soil Science Society of America Journal. 53(2). 335-342.

Cassidy, N.J. 2007. Evaluating LNAPL contamination using GPR signal attenuation analysis and dielectric property measurements: Practical implications for hydrological studies. Journal of Contaminant Hydrology. 94(1-2). 49-75.

Cassidy, N.J. 2009. Electrical and Magnetic Properties of Rocks, Soils and Fluids. In Jol, H.M. (ed): Ground Penetrating Radar: Theory and Applications. Amsterdam, The Netherlands. Elsevier Science. p. 41-72. ISBN 978-0-444-53348-7.

Çeçen, F., Aktaş, Ö. 2012. Activated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment. Weinheim, Germany. Wiley-VCH Verlag & Co. KGaA. p. 388. ISBN 978-3-527-32471-2.

Celia, M.A., Bouloutas, E.T. 1990. A general mass-conservative numerical solution for unsaturated flow equation. Water Resources Research. 26(7). 1483-1496.

Celia, M.A., Reeves, P.C., Ferrand, L.A. 1995. Recent advances in pore scale models for multiphase flow in porous media. Reviews of Geophysics. 33(S2). 1049-1057.

Chamarro, E., Marco, A., Esplugas, S. 2001. Use of fenton reagent to improve organic chemical biodegradability. Water Research. 35(4). 1047-1051.

Chandra, V. 2006. Fundamentals of Natural Gas: An International Perspective. Tulsa, USA. PennWell. p. 163. ISBN 1-59370-088-1.

Chang, J.I., Lin, C.C. 2006. A study of storage tank accidents. Journal of Loss Prevention in the Process Industries. 51-59.

Chao, K.P., Ong, S.K., Huang, M.C. 2008. Mass transfer of VOCs in laboratory-scale air sparging tank. Journal of Hazardous Materials. 152(3). 1098–1107.

Chao, W.L., Parlange, J.Y., Steenhuis, T.S. 2000. An analysis of the movement of wetting and nonwetting fluids in homogeneous porous media. Transport in Porous media. 41(2). 121-135.

Chapelle, F.H., Bradley, P.M., Lovley, D.R., O'Neill, K., Landmeyer, J.E. 2002. Rapid evolution of redox processes in a petroleum hydrocarbon-contaminated aquifer. Ground Water. 40(4). 353-360.

Charbeneau, R.J., Johns, R.T., Lake, L.W., McAdams, M.J. 2000. Free-product recovery of petroleum hydrocarbon liquids. Groundwater Monitoring & Remediation. 20(3). 147-158.

Chaudhuri, U.R. 2010. Fundamentals of Petroleum and Petrochemical Engineering. Boca Raton, USA. CRC Press. p. 380. ISBN 978-1-4398-5160-9.

Che-Alota, V., Atekwana, E.A., Atekwana, E.A., Sauck, W.A., Werkema, D.D.2009. Temporal geophysical signatures from contaminant-mass remediation. The Leading Edge. 74(4). B113-B123.

Chen, K.F., Kao, C.M., Hsieh, C.Y., Chen, S.C., Chen, Y.L. 2005. Natural biodegradation of MTBE under different environmental conditions: microcosm and microbial identification studies. Bulletin of Environmental Contamination and Toxicology. 74. 356-364.

Chen, Z., Ewing, R. 1999. Mathematical analysis for reservoir models. SIAM J. Math. Anal. 30(2). 431 - 453.

Cheremisinoff, N.P. 1998. Groundwater Remediation and Treatment Technologies. Westwood, USA. Noyes Publications. p. 395. ISBN 0-8155-1411-5.

Cheremisinoff, N.P. 2002. Handbook of Water and Wastewater Treatment Technologies. Boston, USA. Butterworth-Heinemann. p.636. ISBN 0-7506-7498-9.

Cheremisinoff, N.P. 2017. Groundwater Remediation: A Practical Guide for Environmental Engineers. Hoboken, USA. Scrivener Publishing. p. 393. ISBN 978-1-119-40757-7.

Chierici, G.L. 1995. Principles of Petroleum Reservoir Engineering. Berlin, Germany. Springer-Verlag. p. 398. ISBN 978-3-642-78245-9.

Cho, J.S., Wilson, J.T., DiGiulio, D.C., Vardy, J.A., Choi, W. 1997. Implementation of natural attenuation at a JP-4 jet fuel release after active. Biodegradation. 8(4). 265-273.

Cho, S.Y. 1995. A study on adsorption of trichloromonofluoroethane by an activated carbon pellet. Carbon. 1184-1186.

Cho, S.Y., Choi, D.K. 1996. Langmuir parameters for adsorption of two halogenated chemicals on an activated carbon pellet. Korean Journal of Chemical Engineering. 13(4). 409-411.

Chowdhury, Z.K., Summers, R.S., Westerhoff, G.P., Leto, B.J., Nowack, K.O., Corwin, C.J., Passantino, L.B. 2013. Activated Carbon: Solutions for Improving Water Quality. Denver, USA. American Water Works Association. p. 318. ISBN 1-58321-907-2.

Chrysikopoulos, C.V. 2005. Nonaqueous Phase Liquid Pool Dissolution in Subsurface Formations. In Kassim, T.A. (ed): Environmental Impact Assessment of Recycled Wastes on Surface and Ground Waters: Volume 3 - Engineering Modeling and Sustainable. Heidelberg, Germany. Springer-Verlag Berlin Heidelberg. p. 97-132. ISBN 3-540-23585-x.

Clement, W.P., Ward, A.L. 2008. GPR Surveys across a Prototype Surface Barrier to Determine Temporal and Spatial Variations in Soil Moisture Content. In Allred, B., Daniels, J.J., Ehsani, M.R. (eds): Handbook of Agricultural Geophysics. Boca Raton, USA. CRC Press. p. 305-315. ISBN 978-0-8493-3728-4.

Coates, J.D., Chakraborty, R., Lack, J.G., O'Connor, S.M., Cole, K.A., Bender, K.S., Achenbach, L.A. 2001. Anaerobic benzene oxidation coupled to nitrate reduction in pure culture by two strains of Dechloromonas. Nature. 411. 1039-1043.

Coates, J.D., Woodward, J., Allen, J., Philp, P., Lovley, D.R. 1997. Anaerobic degradation of polycyclic aromatic hydrocarbons and alkanes in petroleum-contaminated marine harbor sediments. Appl. Environ. Microbiol. 63(9). 3589-3593.

Cohen, R.M., Bryda, A.P., Shaw, S.T., Spalding, C.P. 1992. Evaluation of visual methods to detect NAPL in soil and water. GWMR. 12(4). 132-141.

Cohen, R.M., Mercer, J.W. 1993. DNAPL Site Evaluation. Sterling, USA. Geotrans, Inc. p. 396.

Comegna, A., Coppola, A., Dragonetti, G., Sommella, A. 2013. Dielectric response of a variable saturated soil contaminated by non-aqueous phase liquids (NAPLs). Procedia Environmental Sciences. 19. 701-710.

Comegna, A., Coppola, A., Dragonetti, G., Sommella, A. 2016. Estimating nonaqueous-phase liquid Content in variably saturated soils using time domain reflectometry. Vadose Zone J. 15(5).

Commission of the European Communities 2006. Thematic Strategy for Soil Protection: Impact Assessment of the Thematic Strategy on Soil. Brussels, Belgium. p. 130.

Compressed Gas Association 1999. Handbook of Compressed Gases. Boston, USA. Kluwer Academic Publishers. p. 698. ISBN 0-412-78230-8.

Constantinides, G.N., Payatakes, A.C. 2000. Effects of precursor wetting films in immiscible displacement through porous media. Transport in Porous Media. 38(3). 291-317.

Cooney, D.O., Nagerl, A., Hines, A.L. 1983. Solvent regeneration of activated carbon. Water Res. 17(4). 403-410.

Cooper, J.D. 2016. Soil Water Measurement: A Practical Handbook. Hoboken, USA. John Wiley & Sons. p. 358. ISBN 978-1-405-17676.7.

Coutelieris, F.A., Delgado, J.M.P.Q. 2012. Transport Processes in Porous Media. Berlin, Germany. Springer Science+Business Media. p. 236. ISBN 978-3-642-27909-6.

Couto, M.N., Borges, J.R., Guedes, P., Almeida, R., Monteiro, E., Almeida, C.M., Basto, M.C.P., Vasconcelos, M.T. 2014. An improved method for the determination of petroleum hydrocarbons from soil using a simple ultrasonic extraction and fourier transform infrared spectrophotometry. Petroleum Science and Technology. 32(4). 426-432.

Craig, F.F. 1971. The Reservoir Engineering Aspects of waterflooding. Dallas, USA. Millet the Printer. p. 134. ISBN 0-89520-202-6.

Daghbouche, Y., Garrigues, S., de la Guardia, M. 1996. Flow injection-fourier transform infrared spectrometric determination of oil and greases: preliminary microwave-assisted extraction studies. Analyst. 121(8). 1031-1036.

Daifullah, A.A.M., Girgis, B.S. 2003. Impact of surface characteristics of activated carbon on adsorption of BTEX. Colloids and Surfaces A. 214(1-3). 181-193.

Dakhel, N., Pasteris, G., Werner, D., Höhener, P. 2003. Small-volume releases of gasoline in the vadose zone: impact of the additives MTBE and ethanol on groundwater quality. Environmental Science & Technology. 37(10). 2127-2133.

Dalton, D.R. 2011. Foundations of organic chemistry: unity and diversity of structures, pathways, and reactions. Hoboken, USA. Wiley. p. 1414. ISBN 978-1-118-00539-2.

Dandekar, A.Y. 2013. Petroleum Reservoir Rock and Fluid Properties. Boca Raton, USA. CRC press. p. 502. ISBN 978-1-4398-7645-9.

Daniels, J.J., Roberts, R., Vendl, M. 1995. Ground penetrating radar for the detection of liquid contaminants. Journal of Applied Geophysics. 33(1-3). 195-207.

Darayan, S., Liu, C., Shen, L.C., Shattuck, D. 1998. Measurement of electrical properties of contaminated soil. Geophysical Prospecting. 46(5). 477-488.

Dasberg, S., Dalton, F.N. 1985. Time domain reflectometry field measurements of soil water content and electrical conductivity. Soil Sci. Soc. Am. J. 49(2). 293-297.

Davidson, J.M., Creek, D.N. 2000. Using the gasoline additive MTBE in forensic environmental investigations. Environmental Forensics. 1(1). 31-39.

Davis, B.M., Semprini, L., Istok, J. 2003a. Development of Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL in the Subsurface. Corvallis, USA. U.S. Department of Energy Report. p. 121.

Davis, C., Cort, T., Dai, D., Illangasekare, T.H., Munakata-Marr, J. 2003b. Effects of heterogeneity and experimental scale on the biodegradation of diesel. Biodegradation. 14(6). 373–384.

Davis, G.B., Merrick, N.P., Mclaughlan, R. 2006. Protocols and Techniques for Characterizing Sites with Subsurface Petroleum Hydrocarbons- A Review. Salisbury South, Australia. CRC CARE Pty Ltd. p. 51. ISBN 978-1-921431-10-4.

Dawe, R.A. 1991. Enhancing oil recovery. Journal of Chemical Technology & Biotechnology. 51(3). 361-393.

Day, M.J., Reinke, R.F., Thomson, J.A. M. 2001. Fate and transport of fuel components below slightly leaking underground storage tanks. Environmental Forensics. 2(1). 21-28.

De Blanc, P.C., McKinney, D.C., Speitel, G.E. 1996. Modeling Subsurface Biodegradation of Non-aqueous Phase Liquids. In Corapcioglu, M.Y. (ed): Advances in Porous Media. Amsterdam, the Netherlands. Academic Press. p. 1-86. ISBN 0-444-82500-2.

De Silva, C.W. 2010. Mechatronics: A Foundation Course. Boca Raton, USA. CRC Press. p. 867. ISBN 978-1-4200-8212-8.

Dean, T.J., Bell, J.P., Bat, A. J.B. 1987. Soil moisture measurement by an improved capacitance technique, Part I. Sensor design and performance. Journal of Hydrology. 93(1-2). 67-78.

Decagon Devices 2008. ECH2O-TE/EC-TM: Water Content, EC and Temperature Sensors (Operator's Manual) [on line]. [cited on 13. 2. 2016] Available at <https://www.decagon.com/>.

Decagon Devices 2010. 5TE: Water Content, EC and Temperature Sensors (Operator's Manual). Pullman [on line]. [cited on 22. 3. 2016] Available at <https://www.decagon.com/>.

Decagon Devices 2016. 5TE: Water Content, EC and Temperature Sensor [on line]. [cited on 5. 8. 2017] Available at <https://www.decagon.com/>.

Decagon Devices 2017a. 5TM Soil Moisture & Temperature Sensor [on line]. [cited on 13. 10. 2017] Available at <https://www.decagon.com/>.

Decagon Devices 2017b. SENSOR 5TE Soil Moisture, Temperature, & Electrical Conductivity [online]. [cited on 13. 10. 2017] Available at <https://www.decagon.com/>.

Deeb, R.A., Chu, K., Shih, T., Linder, S., Suffet, I., Kavanaugh, M.C., Alvarez-Cohen, L. 2003. MTBE and other oxygenates: Environmental sources, analysis, occurrence, and treatment. Environmental Engineering Science. 20(5). 433-447.

Deeb, R.A., Scow, K.M., Alvarez-Cohen, L. 2000. Aerobic MTBE biodegradation: An examination of past studies, current challenges and future research directions. Biodegradation. 11(2-3). 171-186.

Deeds, J., Bradford, J. 2002. Characterization of an aquitard and direct detection of LNAPL at Hill Air Force Base using GPR AVO and migration velocity analyses. SPIE. 323-329.

Dekker, T.J., Abriola, L.M. 2000. The influence of field-scale heterogeneity on the infiltration and entrapment of dense nonaqueous phase liquids in saturated formations. Journal of Contaminant Hydrology. 42(2-4). 187–218.

Delleur, J.W. 2003. Groundwater Engineering. In Chen, W F., Liew, J.Y.R. (eds): The Civil Engineering Handbook. Boca Raton, USA. CRC Press. p. 34.1- 34.27. ISBN 0-8493-0958-1.

Dembicki, H. 2017. Practical Petroleum Geochemistry for Exploration and Production. Amsterdam, Netherlands. Elsevier. p. 331. ISBN 978-0-12-803350-0.

Demirbas, A. 2008. Present and future transportation fuels. Energy Sources Part A. 30(16). 1473–1483.

Demirbas, A. 2010. Future fuels for internal combustion engines. Energy Sources, Part A. 32. 1273-1281.

Dillard, L.A., Essaid, H.I., Herkelrath, W.N. 1997. Multiphase flow modeling of a crude-oil spill site with a bimodal permeability distribution. Water Resources Research. 33(7). 1617-1632.

Dimri, V.P., Srivastava, R.P., Vedanti, N. 2012. Fractal Models in Exploration Geophysics: Applications to Hydrocarbon Reservoirs. Amsterdam, Netherlands. Elsevier Science. p. 165. ISBN 978-0-08-045158-9.

Dobson, R., Schroth, M.H., Zeyer, J. 2007. Effect of water-table fluctuation on dissolution and biodegradation of a multi-component, light nonaqueous-phase liquid. Journal of Contaminant Hydrology. 94(3-4). 235-248.

Dolson, J. 2016. Understanding Oil and Gas Shows and Seals in the Search for Hydrocarbons. Cham, Switserland: Springer International Publishing. p486. ISBN 978-3-319-29708-8.

Domenico, P.A., Schwartz, F.W. 1998. Physical and Chemical Hydrogeology. New York, USA. John Wiley & Sons, lnc. p543. ISBN 0471-59762-7.

Donaldson, E.C., Alam, W. 2008. Wettabillty. Houston, USA. Gulf Publishing Company. p. 355. ISBN 1-933762-29-2.

Dong, M., Dullien, F.A.L. 2006. Porous Media Flows. In Crowe C.T. (ed): Multiphase Flow Handbook. Boca Raton, USA. CRC Press. p. 10 (1-55). ISBN 0-8493-1280-9.

Don, G., Paul, W. 1998. Enhanced Oil Recovery. Richardson, USA. Society of Petroleum Engineers. p. 545. ISBN 1-55563-077-4.

Donnez, P. 2007. Essentials of Reservoir Engineering. Paris, France. Editions Technip. p. 387. ISBN 978-2-7108-0892-3.

Douglas, J., Peaceman, D., Rachford, H.H. 1959. A method for calculating multidimensional immiscible displacement. AIME. 216. 297-308.

Dowd, R.M. 1984. Leaking underground storage tanks. Environ. Sci. Technol. 18(10). 309A.

Duffield, A.R., Ramamurthy, R.S., Campanelli, J.R. 2003. Surfactant Enhanced Mobilization of Mineral Oil within Porous Media. Water, Air & Soil Pollution. 143(1-4). 111-122.

Dullien, F.A.L. 1988. Two-phase flow in porous media. Chemical Engineering & Technology. 11(1). 407-424.

Dullien, F.A.L. 1992. Porous Media: Fluid Transport and Pore Structure. San Diego, USA. Academic Press. p. 574. ISBN 0-12-223651-3.

Dullien, F.A.L. 2000. Capillary and Viscous Effects in Porous Media. In Vafai, K. (ed): Handbook of Porous Media. New York, USA. Marcel Dekker Inc. p. 53-111. ISBN 0-8247-8886-9.

Dupuis, J., Knoepfel, P. 2015. The Politics of Contaminated Sites Management. Lausanne, Switzerland. Springer. p 159. ISBN 978-3-319-11306-7.

Dutriez, T., Courtiade, M., Thiébaut, D., Dulot, H., Bertoncini, F., Vial, J., & Hennion, M.C. 2009. High-temperature two-dimensional gas chromatography of hydrocarbons up to nC60 for analysis of vacuum gas oils. Journal of Chromatography. 1216(14). 2905–2912.

Eckert-Tilotta, S.E., Hawthorne, S.B., Miller, D.J. 1993. Supercritical fluid extraction with carbon dioxide for the determination of total petroleum hydrocarbons in soil. Fuel. 72(7). 1015-1023.

Edwards, E.A., Grbić-Galić, D. 1992. Complete mineralization of benzene by aquifer microorganisms under strictly anaerobic conditions. Appl. Environ. Microbiol. 58(8). 2663-2666.

EEA (European Environment Agency) 2007. Progress in management of contaminated sites [Online]. [cited on 18. 05. 2017] Available at <https://www.eea.europa.eu/>.

EEA 2010. The European environment state and outlook 2010: Soil. Copenhagen, Denmark. European Environment Agency and JIR. p. 44. ISBN 978-92-9213-157-9.

Elsayed, A., Mahmoud, S., Al-Dadah, R., Bowen, J., Kaialy, W. 2014. Experimental and numerical investigation of the effect of pellet size on the adsorption characteristics of activated carbon/ethanol. Energy Procedia. 61. 2327-2330.

Ernst, W.G. 2000. Earth Systems: Processes and Issues. Cambridge, UK. Cambridge University Press. p. 576. ISBN 978-0-521-47323-1.

Essaid, H.I., Bekins, B.A., Cozzarelli, I.M. 2015. Organic contaminant transport and fate in the subsurface: Evolution of knowledge and understanding. Water Resources Research. 51(7). 1-42.

Essaid, H.I., Bekins, B.A., Godsy, E.M., Warren, E., Baedecker, M.J., Cozzarelli, I.M. 1995. Simulation of aerobic and anaerobic biodegradation processes at a crude oil spill site. Water Resour. Res,.31(12). 3309-3327.

Etkin, D.S. 2001. Analysis of oil spill trends US and worldwide. International Oil Spill Conference Proceedings. 1291-1300.

Exxonmobil 2016. Marcol82 [Online]. [Accessed 10. 11. 2016]. Available at <https://www.exxonmobil/>.

Ezekwe, N. 2011. Petroleum Reservoir Engineering Practice. Westford, USA. Pearson Education, Inc.p. 770. ISBN 0-13-715283-3.

Fagerlund, F., Illangasekare, T.H., Niemi, A. 2006. Nonaqueous-phase liquid infiltration and immobilization in heterogeneous media: Application to stochastically heterogeneous formations. Vadose Zone Journal. 6(3). 483-495.

Fagerlund, F., Niemi, A., Illangasekare, T.H. 2008. Modeling of nonaqueous phase liquid (NAPL) migration in heterogeneous saturated media: Effects of hysteresis and fluid immobility in constitutive relations. Water Resources Research. 44(3). W03409:1-18.

Fahim, M.A., Al-Sahhaf, T.A., Elkilani, A. 2010. Fundamentals of Petroleum Refining. Amsterdam, Netherlands. Elsevier Science. p. 496. ISBN 978-0-444-52785-1.

Falcó, I.P.R. 2014. Petroleum Hydrocarbon Analysis. In Nollet, L.M.L., De Gelder, L.S.P. (eds): Handbook of Water Analysis. Boca Raton, USA. Taylor & Francis Group. p. 845-868. ISBN 978-1-4398-8966-4.

Fanchi, J.R. 2010. Integrated Reservoir Asset Management: Principles and Best Practices. Burlington, USA. Gulf Professional Publishing. p. 361. ISBN 978-0-12-382088-4.

Fanchi, J.R., Christiansen, R. L. 2017. Introduction to Petroleum Engineering. Hoboken, USA. John Wiley & Sons, Inc. p. 335. ISBN 978-1-119-19361-6.

Fanchi, J.R., Seidle, J.P. 2017. Multiphase Flow in Porous Media. In Michaelides, E., Crowe, C.T., Schwarzkopf, J.D. (eds): Multiphase Flow Handbook. Boca Raton, USA. CRC Press. p. 685-728. ISBN 978-1-4987-0100-6.

Fan, K., Kuo, T., Han, Y., Chen, C., Lin, C., Lee, C. 2007. Radon distribution in a gasoline-contaminated aquifer. Radiation Measurements. 42(3). 479-485.

Fares, A., Abbas, F., Maria, D., Mair, A. 2011. Improved calibration functions of three capacitance probes for the measurement of soil moisture in tropical soils. Sensors. 11(5). 4858-4874.

Farrell-Jones, J. 2003. Petroleum Hydrocarbons and Polyaromatic Hydrocarbons. In Thompson, K.C., Nathanail C.P. (eds): Chemical Analysis of Contaminated Land. Boca Raton, USA. CRC Press. p. 132-176. ISBN 0–8493–2810–1.

Faust, S.D., Aly, O.M. 1998. Chemistry of Water Treatment. Boca Raton, USA. CRC Press. p. 506. ISBN 0-409-90000-1.

Ferré, T.P. & Topp, G.C., 2005. Measuring Soil Water Content. In Anderson, M.G., McDonnell, J.J. (eds): Encyclopedia of Hydrological Sciences. Chichester, England. John Wiley & Sons Ltd. p. 1077-1088. ISBN 0-471-49103-9.

Fetter, C.W. 2000. Applied Hydrogeology. Upper Saddle River, USA. Prentice Hall. p. 598. ISBN 0-13-088239-9.

Fetter, C.W. 2014. Applied Hydrogeology. Harlow, UK. Pearson Education Limited. p. 610. ISBN 1-292-02290-6.

Fetter, C.W., Boving, T., Kreamer, D. 2018. Contaminant Hydrogeology. Long Grove, USA. Waveland Press. p. 647. ISBN 1-4786-3279-8.

Field, A. 2013. Discovering Statistics Using IBM SPSS Statistics. London, UK. SAGE Publications. p. 915. ISBN 978-1-4462-4917-8.

Fiorenza, S., Rifai, H.S. 2003. Review of MTBE Biodegradation and Bioremediation. Bioremediation Journal. 7(1). 1-35.

Fischer, H., Wo, S., Morrow, N.R. 2006. Modeling the effect of viscosity ratio on spontaneous imbibition. SPE. 102641 (1-20).

Fitts, C.R. 2013. Groundwater Science. Waltham, USA. Academic Press. p. 639. ISBN 978-0-12-384705-8.

Flachsbart, P.G. 2008. Exposure to Ambient and Microenvironmental Concentrations of Carbon Monoxide. In Penney, D. G. (ed): Carbon Monoxide Poisoning. Boca Raton, USA. Taylor & Francis. p. 5 - 41. ISBN 0-8493-8417-6.

Forrester, S.T., Janik, L.J., McLaughlin, M.J., Soriano-Disla, J.M., Stewart, R., Dearman, B. 2013. Total petroleum hydrocarbon concentration prediction in soils using diffuse reflectance infrared spectroscopy. Soil Sci. Soc. Am. J. 77(2). 450-460.

Forrester, S., Janik, L., McLaughlin, M. 2010. An infrared spectroscopic test for total petroleum hydrocarbon (TPH) contamination in soils. In Robert, G. (ed):19th World Congress of Soil Science, Soil Solutions for a Changing World, 1 - 6 August 2010. Brisbane, Australia, International Union of Soil Sciences, DVD., p. 13-16. ISBN 978-0-646-53783-2.

Fountain, J.C. 1998. Technologies for Dense Nonaqueous Phase Liquid Source Zone Remediation. Pittsburgh, USA. Ground-Water Remediation Technologies Analysis Center. TE-98-02. p. 62.

Fountain, J.C., Klimek, A., Beikirch, M.G., Middleton, T.M. 1991. The use of surfactants for in situ extraction of organic pollutants from a contaminated aquifer. Journal of Hazardous Materials. 28(3). 295-311.

Fountain, J.C., Starr, R.C., Middleton, T., Beikirch, M., Taylor, C., Hodge, D. 1996. A controlled field test of surfactant-enhanced aquifer remediation. Groundwater. 34(5). 910-916.

Francisca, F.M., Arduino, P. 2007. Immiscible displacement model for anisotropic and correlated porous media. International Journal of Geomechanics. 7(4). 311-317.

Francisca, F.M., Montoro, M.A. 2012. Measuring the dielectric properties of soil–organic mixtures using coaxial impedance dielectric reflectometry. Journal of Applied Geophysics. 80. 101-109.

Francisca, F.M., Montoro, M.A. 2014. Influence of particle size distribution and wettability on the displacement of LNAPL in saturated sandy soils. Journal of Environmental Engineering. 141(6). 04014091:1-12.

Francisca, F.M., Rinaldi, V.A. 2003. Complex Dielectric Permittivity of Soil–Organic Mixtures (20 MHz–1.3 GHz). Journal of Environmental Engineering. 129. 347-357.

Fräulin, C., Rinke, G., Dittmeyer, R. 2014. Characterization of a new system for space-resolved simultaneous in situ measurements of hydrocarbons and dissolved oxygen in microchannels. Microfluidics and Nanofluidics. 16(1-2). 149-157.

Fredlund, D.G., Rahardjo, H., Fredlund, M.D. 2012. Unsaturated Soil Mechanics in Engineering Practice. Hoboken, USA. Wiley-Interscience. p. 926. ISBN 978-1-118-13359-0.

Fu, K., Yue, Q., Gao, B., Sun, Y., Zhu, L. 2013. Preparation, characterization and application of lignin-based activated carbon from black liquor lignin by steam activation. Chemical Engineering Journal. 228. 1074-1082.

Ganzler, K., Salgó, A. 1987. Microwave-extraction -a new method superseding traditional Soxhlet extraction. European Food Research and Technology. 184(4). 274-276.

Ganzler, K., Salgó, A., Valkó, K. 1986. Microwave extraction: A novel sample preparation method for chromatography. Journal of Chromatography. 371. 299-306.

García-González, J.E., Ortega, M.F., Chacón, E., Mazadiego, L.F., Miguel, E.D. 2008. Field validation of radon monitoring as a screening methodology for NAPL-contaminated sites. Applied Geochemistry. 23(9). 2753-2758.

Gardner, W.H. 1986. Water Content. In Klute, A. (Ed): Methods of Soil Analysis: Part 1-Physical and Mineralogical Methods. Madison, USA. American Society of Agronomy - Soil Science Society of America. p. 493-544. ISBN 0-89118-088-5.

Gary, J.H., Handwerk, G.E., Kaiser, M.J., 2007. Petroleum Refining: Technology and Economics. Boca Raton, USA. CRC Press. p. 465. ISBN 978-0-203-90792-4.

Gates-Anderson, D.D., Siegrist, R.L., Cline, S.R. 2001. Comparison of potassium permanganate and hydrogen peroxide as chemical oxidants for organically contaminated soils. Journal of Environmental Engineering. 127(4). 337-347.

Gates, D.D., Siegrist, R.L. 1995. In situ chemical oxidation of trichloroethylene using hydrogen peroxide. Journal of Environmental Engineering. 121(9). 639-644.

Gates, I.D., Adams, J.J., Larter, S.R. 2010. The Impact of Oil Viscosity Heterogeneity on Production from Heavy Oil and Bitumen Reservoirs: Geotailoring Recovery Processes to Compositionally Graded Reservoirs. In Chopra, S., Lines, L.R., Schmitt, D.R., Batzle, M.L. (eds): Heavy Oils: Reservoir Characterization and Production Monitoring. Tulsa, USA. Society of Exploration Geophysicists. p. 265-273. ISBN 978-1-56080-222-8.

Gharbi, R., Peters, E., Elkamel, A. 1998. Scaling miscible fluid displacements in porous media. Energy & Fuels. 12(4). 801-811.

Giles, H.N., Mills, C.O. 2010. Crude Oils: Their Sampling, Analysis, and Evaluation. West Conshohocken, USA: ASTM International. p. 51. ISBN 978-0-8031-7014-8.

Glasby, G.P. 2006. Abiogenic origin of hydrocarbons: An historical overview. Resource Geology. 56(1). 83-96.

Goi, A., Trapido, M., Kulik, N. 2009. Contaminated soil remediation with hydrogen peroxide oxidation. International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering. 3(4). 209-213.

Gold, T. 1985. The origin of natural gas and petroleum and the prognosis for future supplies. Energy. 10. 53-77.

Gold, T. 2001. The Deep Hot Biosphere: The Myth of Fossil Fuels. New York, USA. Springer. p. 243. ISBN 978-0-387-95253-6.

Gómez-Serrano, V., Acedo-Ramos, M., Valenzuela-Calahorro, C., López-Peinado, A.J. 2000. Regeneration of activated carbon after contact with sulfuric acid solution. Journal of Chemical Technology and Biotechnology. 75(9). 835-839.

Gong, Y., Cao, Q., Sun, Z. 2003. The effects of soil bulk density, clay content and temperature on soil water content measurement using time-domain reflectometry. Hydrological Processes. 17(18). 3601–3614.

Goodger, E.M. 1975. Hydrocarbon Fuels: Production, Properties and Performance of Liquids and Gases. London, UK. The Macmillan Press Ltd. p. 270. ISBN 978-1-349-02654-8.

Gou, S., Yin, T., Yan, L., Guo, Q. 2015. Water-soluble complexes of hydrophobically modified polymer and surface active imidazolium-based ionic liquids for enhancing oil recovery. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 471. 45-53.

Gray, N.D., Sherry, A., Hubert, C., Dolfing, J., Head, I.M. 2010. Methanogenic degradation of petroleum hydrocarbons in subsurface environments remediation, heavy oil formation, and energy recovery. Adv. Appl. Microbiol. 72. 137-161.

Griffin, P. 2017. The Carbon Majors Database. London, UK. CDP Report. p. 15.

Griffin, T.W., Watson, K.W. 2002. A comparison of field techniques for confirming dense nonaqueous phase liquids. GWMR. 22(2). 48-59.

Grumman, D.L., Daniels, J.J. 1995. Experiments on the detection of organic contaminants in the vadose zone. Journal of Environmental and Engineering Geophysics. 1(A). 31-38.

Guiliano, M., Boukir, A., Doumenq, P., Mille, G., Crampon, C., Badens, E., Charbit, G. 2000. Supercritical fluid extraction of Bal 150 crude oil asphaltenes. Energy & Fuels. 14(1). 89-94.

Gustafson, J., Griffith Tell, J., Orem, D. 1997. Total Petroleum Hydrocarbon Criteria Working Group Series: Volume 3 - Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Amherst, USA. Amherst Scientific Publishers. p. 102. ISBN 1-884-940-12-9.

Hadley, P.W., Newell, C.J. 2012. Groundwater remediation: The next 30 years. Groundwater. 50(5). 1-10.

Halihan, T., Paxton, S., Graham, I., Fenstemaker, T., Riley, M. 2005. Post-remediation evaluation of a LNAPL site using electrical resistivity imaging. Journal of Environmental Monitoring. 7(4). 283-287.

Hamilton, B., Falkiner, R.J. 2003. Motor Gasoline. In Totten, G.E., Westbrook, S.R., Shah, R.J. (eds): Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing. West Conshohocken, USA. Astm Intl. p. 61-88. ISBN 0-8031-2096-6.

Haridy, S.A., Persson, M., Berndtsson, R. 2004. Estimation of LNAPL saturation in fine sand using time-domain reflectometry. Hydrological Sciences Journal. 49(6). 987-1000.

Harris, C.M. 2002. Product review: GC to go. Analytical Chemistry. 74(21). 585 A -589 A.

Hartley, W.R., Englande, A.J., Harrington, D.J. 1999. Health risk assessment of groundwater contaminated with methyl tertiary butyl ether (MTBE). Water Science and Technology. 305-310.

Hartonen, K., Bøwadt, S., Dybdahl, H. P., Nylund, K., Sporring, S., Lund, H., Oreld, F. 2002. Nordic laboratory intercomparison of supercritical fluid extraction for the determination of total petroleum hydrocarbon, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in soil. Journal of Chromatography. 958(1-2). 239-248.

Harwell, J.H., Sabatini, D.A., Knox, R.C. 1999. Surfactants for ground water remediation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 151(1-2). 255-268.

Hassanizadeh, S.M. 2015. Advanced Theories of Two-Phase Flow in Porous Media. In Vafai, K, (ed): Handbook of Porous Media. Boca Raton, USA. CRC Press. p. 47-62. ISBN 978-1-4398-8557-4.

Hassanizadeh, S.M., Celia, M.A., Dahle, H.K. 2002. Dynamic effect in the capillary pressure-saturation relationship and its impacts on unsaturated flow. Vadose Zone Journal. 1(1). 38-57.

Hassler, J.W. 1963. Activated Carbon. New York, USA. Chemical Publishing Company, Inc. p. 397.

Hatiboglu, C.U., Babadagli, T. 2008. Pore-scale studies of spontaneous imbibition into oil-saturated porous media. Physical Review E. 77(6). 066311: 1-11.

Hawthorne, S.B., Hegvik, K.M., Yang, Y., Miller, D.J. 1994. Determination of heavy hydrocarbon contamination using supercritical fluid extraction with infrared detection. Fuel. 73(12). 1876-1879.

Hayashi, J., Kazehaya, A., Muroyama, K., Watkinson, A.P. 2000. Preparation of activated carbon from lignin by chemical activation. Carbon. 38(13). 1873-1878.

Hayden, N.J., Voice, T.C., Wallace, R.B. 1997. Residual gasoline saturation in unsaturated soil with and without organic matter. Journal of Contaminant Hydrology. 25(3-4). 271-281.

Heiderscheidt, J.L., Illangasekare, T.H., Borden, R.C., Thomson, N.R. 2011. Principles of ISCO Related Subsurface Transport and Modeling. In Siegrist, L.R., Crimi, M., Simpkin, T.J. (eds): In Situ Chemical Oxidation for Groundwater Remediation. New York, USA. Springer-Verlag. p. 233 - 284. ISBN 978-1-4419-7825-7.

Held, R.J., Celia, M.A. 2001. Pore-scale modeling and upscaling of nonaqueous phase liquid mass transfer. Water Resources Research. 37(3). 539-549.

Helmig, R. 1997. Multiphase Flow and Transport Processes in the Subsurface: A Contribution to the Modeling of Hydrosystems. Berlin, Germany. Springer-Verlag. p. 367. ISBN 3-540-62703-0.

Helmig, R., Miller, C.T., Jakobs, H., Class, H., Hilpert, M., Kees, C.E., Niessner, J. 2006. Multiphase Flow and Transport Modeling in Heterogeneous Porous Media. In Bucchianico, A.D., Mattheij, R.M.M., Peletier, M.A. (eds): Progress in Industrial Mathematics at ECMI 2004. Berlin, Germany. Springer-Verlag. p. 449-488. ISBN 3-540-28072-3.

Henry, J.T. 1873. The Early and Later History of Petroleum. Philadelphia, USA. APRP Co. p. 607.

Henry, S.M., Warner, S.D. 2002. Chlorinated Solvent and DNAPL Remediation: Innovative Strategies for Subsurface Cleanup. Washington DC, USA. American Chemical Society. p. 330. ISBN 0-8412-3793-X.

Heyse, E., Augustijn, D., Rao, P.S.C., Delfino, J.J. 2002. Nonaqueous phase liquid dissolution and soil organic matter sorption in porous media: Review of system similarities. Critical Reviews in Environmental Science and Technology. 32(4). 337-397.

Hilhorst, M.A. 2000. A pore water conductivity sensor. Soil Sci. Soc. Am. J. 64(6). 1922-1925.

Hillel, D. 1998. Environmental Soil Physics. San Diego, USA. Academic Press. p. 771.

ISBN 0-12-348-525-8.

Hillel, D. 2004. Introduction to Environmental Soil Physics. San Diego, USA. Academic Press. p. 494. ISBN 0-12-348655-6.

Hirasaki, G.J., Miller, C.A., Puerto, M. 2011. Recent advances in surfactant EOR. SPE Journal. 16(04). 889-907.

Hjelmeland, O.S., Larrondo, L.E. 1986. Experimental investigation of the effects of temperature, pressure, and crude oil composition on interfacial properties. SPE Reservoir Engineering. 1(04). 321-328.

Hofstee, C., Dane, J.H., Hill, W.E. 1997. Three-fluid retention in porous media involving water, PCE and air. Journal of Contaminant Hydrology. 25. 235-247.

Homsy, G.M. 1987. Viscous fingering in porous media. Annual Review of Fluid Mechanics. 19. 271-311.

Hornof, V., Baig, F.U. 1995. Influence of interfacial reaction and mobility ratio on the displacement of oil in a Hele-Shaw cell. Experiments in Fluids. 18(6). 448-453.

Huang, J., McElroy, M.B. 2012. The contemporary and historical budget of atmospheric CO2. Canadian Journal of Physics. 90(8). 707-716.

Hughes, R.G., Blunt, M.J. 2000. Pore scale modeling of rate effect in imbibition. Transport in Porous Media, 40(3). 295-322.

Hui, M.H., Blunt, M.J. 2000. Effects of wettability on three-phase flow in porous media. J. Phys. Chem. 104(16). 3833-3845.

Huling, S.G., Weaver, J.W. 1991. Ground Water Issue: Dense Nonaqueous Phase Liquids. Ada, USA. EPA: Superfund Technology Support Center for Ground Water. p. 21.

Hunkeler, D., Hoehn, E., Höhener, P., Zeyer, J. 1997. 222Rn as a partitioning tracer to detect diesel fuel contamination in aquifers: Laboratory study and field observations. Environ. Sci. Technol. 31(11). 3180–3187.

Hunt, A., Ewing, R., Ghanbarian, B. 2014. Percolation Theory for Flow in Porous Media. New York, USA. Springer Cham Heidelberg. p. 447. ISBN 978-3-319-03770-7.

Hunt, J.R., Sitar, N., Udell, K.S. 1988. Nonaqueous phase liquid transport and cleanup: 1. Analysis of mechanisms. Water Resources Research. 24(8). 1247-1258.

Hutter, G. 2008. Application of Warnings and Labels for Carbon Monoxide Protection. In Penney, D.G. (ed): Carbon Monoxide Poisoning. Boca Raton, USA. CRC press. p. 198-232. ISBN 978-0-8493-8417-2.

Hutzier, N.J., Murphy, B.E., Gierke, J.S. 1991. State of technology review: Soil vapor extraction systems. Journal of Hazardous Materials. 26(2). 225-230.

Illangasekare, T.H., Frippiat, C.C. 2013. Miscible and Immiscible Pollutants in Subsurface Systems. In Fernando, H.J.S. (ed): Handbook of Environmental Fluid Dynamics, Volume Two. Boca Raton, USA. CRC Press. p. 257-271. ISBN 978-1-4665-5604-1.

Illangasekare, T.H., Frippiat, C.C., Fučík, R. 2011. Dispersion and Mass Transfer in Groundwater Near-Surface Geologic Formations. In Thibodeaux L. J., Mackay, D. (eds): Handbook of Chemical Mass Transport in the Environment. Boca Raton, USA. CRC Press. p. 414-451. ISBN 978-1-4200-4755-4.

Illangasekare, T.H., Jensen, K.H., Javandel, I., Mayer, A.S. 2005. Migration and Distribution. In Mayer A.S., Hassanizadeh, S.M. (eds): Soil and Groundwater Contamination: Nonaqueous Phase Liquids-Principles and Observations. Washington DC, USA. American Geophysical Union. p. 47-95. ISBN 0-87590-420-3.

Illangasekare, T.H., Reible, D.D. 2001. Pump-and-Treat for Remediation and Plume Containment: Applications, Limitations, and Relevant Processes. In Kaluarachchi, J.J. (ed): Groundwater Contamination by Organic Pollutants: Analysis and Remediation. Reston: ASCE. p. 79-119. ISBN 0-7844-0527-1.

Inagaki, M. 2009. Pores in carbon materials-importance of their control. New Carbon Materials. 24(3). 193-232.

Inagaki, M., Tascón, J M.D. 2006. Pore Formation and Control in Carbon Materials. In Bandosz, T.J. (ed): Activated Carbon Surfaces in Environmental Remediation. San Diego, USA. Academic Press. p. 49-105. ISBN 0-12-370536-3.

Inomata, K., Kanazawa, K., Urabe, Y., Hosono, H., Araki, T. 2002. Natural gas storage in activated carbon pellets without a binder. Carbon. 40(1). 87-93.

ITRC (Interstate Technology & Regulatory Council) 2009a. Evaluating Natural Source Zone Depletion at Sites with LNAPL. LNAPL-1. Washington, D.C., USA. Interstate Technology & Regulatory Council, LNAPLs Team. www.itrcweb.org.

ITRC (Interstate Technology & Regulatory Council) 2009b. Evaluating LNAPL Remedial Technologies for Achieving Project Goals. LNAPL-2. Washington, D.C., USA. Interstate Technology & Regulatory Council, LNAPLs Team. www.itrcweb.org.

Jackson, S.J., Stevens, D., Power, H., Giddings, D. 2015. A boundary element method for the solution of finite mobility ratio immiscible displacement in a Hele-Shaw cell. International Journal for Numerical Methods in Fluids. 78(9). 521-551.

Jackson, T.J., Schmugge, T.J. 1989. Passive microwave remote sensing system for soil moisture: some supporting research. IEEE Transactions on Geoscience and Remote Sensing. 27(2). 225-235.

Jahn, F., Cook, M., Graham, M. 2008. Hydrocarbon Exploration and Production. Oxford, UK: Elsevier. p. 444. ISBN 978-0-444-53236-7.

Janda, V., Bartle, K.D., Clifford, A.A. 1993. Supercritical fluid extraction in environmental analysis. Journal of Chromatography. 642(1-2). 283-299.

Järup, L. 2003. Hazards of heavy metal contamination. British Medical Bulletin. 68. 167–182.

Jayanti, S., Britton, L.N., Dwarakanath, V., Pope, G.A. 2002. Laboratory evaluation of custom-designed surfactants to remediate NAPL source zones. Environmental Science & Technology. 36(24). 5491-5497.

Jensen, K.H., Falta, R.W. 2005. Fundamentals. In Mayer, A., Hassanizadeh, S.M. (eds): Soil and Groundwater Contamination: Nonaqueous Phase Liquids-Principles and Applications. Washington DC, USA. American Geophysical Union. p. 5-45. ISBN 0-87590-420-3.

Jiménez, N., Richnow, H.H., Vogt, C., Treude, T., Krüger, M. 2016. Methanogenic hydrocarbon degradation: Evidence from field and laboratory studies. J. Mol. Microbiol. Biotechnol. 26(1-3). 227-242.

Jin, M., Delshad, M., Dwarakanath, V., McKinney, D.C., Pope, G.A., Sepehmoori, K., Tilburg, C.E., Jackson, R.E. 1995. Partitioning tracer test for detection, estimation, and remediation performance assessment of subsurface nonaqueous phase liquids. Water Resources Research. 31(5). 1201-1211.

Jin, X.J., Yu, Z.M., Yan, G.J., Yu, W. 2011. Preparation of activated carbon of lignin from straw pulping by chemical activation using potassium carbonate. Materials Science Forum. 704-705. 517-522.

Joekar-Niasar, V., Hassanizadeh, S.M. 2012. Analysis of fundamentals of two-phase flow in porous media using dynamic pore-network models: A review. Critical Reviews in Environmental Science and Technology. 42(18). 1895-1976.

Johns, R.T., Lake, L.W., Obigbesan, A.B., Bermudez, L., Hassan, M.R., Charbeneau, R.J. 2003. Analytical solutions for free-hydrocarbon recovery using skimmer and dual-pump wells. Groundwater Monitoring & Remediation. 23(1). 97-106.

Johnson, L.A. 1997. Theoretical, Comparative and Historical Analyses of Alternative Technologies for Oilsseeds Extraction. In Wan, P.J., Wakelyn, P.J. (eds): Technology and Solvents for Extracting Oilseeds and Nonpetroleum Oils. Champaign: Amer Oil Chemists Society. p. 4-47. ISBN 978-0-935-31581-3.

Johnson, L.A., Lusas, E.W. 1983. Comparison of alternative solvents for oils extraction. Journal of the American Oil Chemists' Society. 60(2). 229-242.

Johnson, P.C. 1998. Assessment of the contribution of volatilization and biodegradation to in situ air sparging performance. Environmental Science and Technology. 32(2). 276-281.

Johnson, P., Lundegard, P., Liu, Z. 2006. Source zone natural attenuation at petroleum hydrocarbon spill sites—I: Site-specific assessment approach. Ground Water Monitoring & Remediation. 26(4). 82-92.

Johnson, R.L., Johnson, P.C., McWhorter, D.B., Hinchee, R.E., Goodman, I. 1993. An overview of in situ air sparging. Groundwater Monitoring & Remediation. 13(4). 127-135.

Jones, D.M., Head, I.M., Gray, N.D., Adams, J.J., Rowan, A.K., Aitken, C.M., Bennett, B, Huang, H., Brown, A., Bowler, B.F.J., Oldenburg, T., Erdmann, M., Larter, S.R. 2008. Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. Nature. 451. 176-180.

Jones, D.S.J. 2006. Quality Control of Products in Petroleum Refining. In Jones, D.S.J., Pujadó, P. (eds): Handbook of Petroleum Processing. Dordrecht, The Netherlands. Springer. p. 705-737. ISBN 1-4020-2819-9.

Karanfil, T., Kilduff, J.E. 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 1. priority pollutants. Environ. Sci. Technol. 33(18). 3217-3224.

Karanfil, T., Kilduff, J.E., Schlautman, M.A., Weber, W. 1996. Adsorption of organic macromolecules by granular activated carbon. 1. Influence of molecular properties under anoxic solution conditions. Environmental Science & Technology. 30(7). 2187-2194.

Karasik, T.W., 2002. Toxic Warfare. Santa Monica, USA. RAND. p. 52. ISBN 0-8330-3207-0.

Karpov, S.A. 2007. Ethanol as a high-octane, environmentally clean component of automotive fuels: Current aspects of use. Chemistry and Technology of Fuels and Oils. 43(5). 355-347.

Kaviany, M. 2001. Principles of Heat Transfer in Porous Media. New York, USA. Springer Science+Business Media. p. 707. ISBN 978-1-4419-2894-8.

Kearl, P.M., Korte, N.E., Gleason, T.A., Beale, J.S. 1991. Vapor extraction experiments with laboratory soil columns: Implications for field programs. Waste Management. 11(4). 231-239.

Kechavarzia, C., Soga, K., Illangasekare, T.H. 2005. Two-dimensional laboratory simulation of LNAPL infiltration and redistribution in the vadose zone. Journal of Contaminant Hydrology. 76(3-4). 211 – 233.

Keer, I.V., Bronders, J., Touchant, K., Verhack, J., Wilczek, D. 2008. Detection and Measurement Techniques to Identify the Presence of NAPLs in the Field. In Annable, M.D., Teodorescu, M., Hlavinek, P., Diels, L. (eds): Methods and Techniques for Cleaning-up Contaminated Sites. Dordrecht, The Netherlands. Springer. p. 59-69. ISBN 978-1-4020-6873-7.

Kermani, M., Ebadi, T. 2012. The effect of oil contamination on the geotechnical properties of fine-grained soils. Soil and Sediment Contamination. 21(5). 655–671.

Kessler, E. 2008. Our Food and Fuel Future. In Pimentel, D. (ed): Biofuels, Solar and Wind as Renewable Energy Systems: Benefits and Risks. Dordrecht, The Netherlands. Springer. p. 259-294. ISBN 978-1-4020-8653-3.

Khaitan, S., Kalainesan, S., Erickson, L.E., Kulakow, P., Martin, S., Karthikeyan, R., Hutchinson, S.L.L., Davis, L.C., Illangasekare, T.H., Ng'oma, C. 2006. Remediation of sites contaminated by oil refinery operations. Environmental Progress. 25(1). 20-31.

Khalili, N.R., Pan, M. Sandí, G. 2000. Determination of fractal dimensions of solid carbons from gas and liquid phase adsorption isotherms. Carbon. 38(4). 573-588.

Khamehchiyan, M., Charkhabi, A.H., Tajik, M. 2007. Effects of crude oil contamination on geotechnical properties of clayey and sandy soils. Engineering Geology. 89(3-4). 220–229.

Khan, F.I., Husain, T., Hejazi, R. 2004. An overview and analysis of site remediation technologies. Journal of Environmental Management. 71. 95-122.

Kim, C., Daniels, J.J., Guy, E.D., Radzevicius, S.J., Holt, J. 2000. Residual hydrocarbons in a water-saturated medium: A detection strategy using ground penetrating radar. Environmental Geosciences. 7(4). 169-176.

Kim, J., Corapcioglu, M.Y. 2001. Sharp interface modeling of LNAPL spreading and migration on the water table. Environmental Engineering Science. 18(6). 359-367.

Kim, J., Corapcioglu, M.Y. 2003. Modeling dissolution and volatilization of LNAPL sources migrating on the groundwater table. Journal of Contaminant Hydrology. 65(1-2). 137-158.

Kirkham, M.B. 2014. Principles of Soil and Plant Water Relations. Waltham, USA. Academic Press. p. 579. ISBN 978-0-12-420022-7.

Kizito, F., Campbell, C.S., Campbell, G.S., Cobos, D.R., Teare, B.L., Carter, B., Hopmans, J.W. 2008. Frequency, electrical conductivity and temperature analysis of a low-cost capacitance soil moisture sensor. Journal of Hydrology. 352(3-4). 367– 378.

Klaus, E.E., Tewksbury, E.J. 1988. Liquid Lubricants. In Booser, E.R. (ed): CRC Handbook of Lubrication: Theory and Practice of Tribology, Volume II: Theory and Design. Boca Raton, USA. CRC Press. p. 229-254. ISBN 0-8493-3902-2.

Klavarioti, M., Kostarelos, K., Pourjabbar, A., Ghandehari, M. 2014. In situ sensing of subsurface contamination-part I: near-infrared spectral characterization of alkanes, aromatics, and chlorinated hydrocarbons. Environ Sci Pollut Res. 21(9). 5849-5860.

Knauss, K.G., Aines, R.D., Dibley, M.J., Leif, R.N., Mew, D.A. 1997. Hydrous Pyrolysis/Oxidation: In-Ground Thermal Destruction of Organic Contaminants. Livermore, USA. Lawnmce Livermore National Laboratory. p. 18.

Knight, M.A., Mitchell, R.J. 1996. Modelling of light nonaqueous phase liquid (LNAPL) releases into unsaturated sand. Can. Geotech. J. 33(6). 913-925.

Kolay, P.K., Burra, S.G., Kumar, S. 2016. Effect of salt and NAPL on electrical resistivity of fine-grained soil-sand mixtures. International Journal of Geotechnical Engineering. 1-7.

Kong, S.H., Watts, R.J., Choi, J.H. 1998. Treatment of petroleum-contaminated soils using iron-mineral-catalyzed hydrogen peroxide. Chemosphere. 37(8). 1473-1482.

Koplik, J., Lasseter, T.J. 1985. Two-phase flow in random network models of porous media. Society of Petroleum Engineers Journal. 25(01). 89-100.

Kovalick, W. W. 2008. Review of Characterization and Remediation Technologies for NAPL's in Groundwater. In Annable, M.D., Teodorescu, M., Hlavinek P., Diels, L. (eds): Methods and Techniques for Cleaning-up Contaminated Sites. Dordrecht, The Netherlands. Springer. p. 165-175. ISBN 978-1-4020-6873-7.

Kresic, N. 2007. Hydrogeology and Groundwater Modeling. Boca Raton, USA. CRC Press. p. 807. ISBN 0-8493-3348-2.

Kueper, B.H., Frind, E.O. 1991. Two-phase flow in heterogeneous porous media: 1. Model development. Water Resources Research. 27(6). 1049-1057.

Kueper, B.H., Redman, D., Starr, R.C., Reitsma, S., Mah, M. 1993. A field experiment to study the behavior of tetrachloroethylene below the water table: Spatial distribution of residual and pooled DNAPL. Groundwater. 31(5). 756-766.

Kumar, M., Hoang, V.T., Satik, C., Rojas, D.H. 2008. High-mobility-ratio-waterflood performance prediction: Challenges and new insights. SPE Reservoir Evaluation & Engineering. 11(01). 186-196.

Kuo, J. 2014. Practical Design Calculations for Groundwater and Soil Remediation. Boca Raton, USA. CRC Press. p. 296. 9ISBN 78-1-4665-8524-9.

Kvapil, J., Mares, S. 2003. Cone penetration logging for the direct detection of LNAPLs contamination. Near Surface Geophysics. 157-160.

Kvenvolden, K.A., Cooper, C.K. 2003. Natural seepage of crude oil into the marine environment. Geo-Mar Lett. 23. 140–146.

Kwon, Y.H., Sowoidnich, K., Schmidt, H., Kronfeldt, H.D. 2012. Application of calixarene to high active surface-enhanced Raman scattering (SERS) substrates suitable for in situ detection of polycyclic aromatic hydrocarbons (PAHs) in seawater. J. Raman Spectrosc. 43(8). 1003-1006.

Laha, S., Tansel, B., Ussawarujikulchai, A. 2009. Surfactant–soil interactions during surfactant-amended remediation of contaminated soils by hydrophobic organic compounds: A review. Journal of Environmental Management. 90(1). 95-100.

Lahvis, M.A., Baehr, A.L., Baker, R.J. 1999. Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions. Water Resour. Res. 35(3). 753-765.

Laine, J., Yunes, S. 1992. Effect of the preparation method on the pore size distribution of activated carbon from coconut shell. Carbon. 30(4). 601-604.

Lake, L.W. 1989. Enhanced Oil Recovery. Englewood Cliffs, USA. Prentice Hall Inc. p. 550. ISBN 0-132-81601-6.

Lambert, P., Fingas, M., Goldthorp, M. 2001. An evaluation of field total petroleum hydrocarbon (TPH) systems. Journal of Hazardous Materials. 83(1-2). 65-81.

Langwaldt, J.H., Puhakka, J.A. 2000. On-site biological remediation of contaminated groundwater: a review. Environmental Pollution. 107(2). 187-197.

Lantz, R.B. 1970. Rigorous calculation of miscible displacement using immiscible reservoir simulators. Trans. SPE AIME. 249. 192-202.

Larson, R.G., Davis, H.T., Scriven, L.E. 1982. Elementary mechanisms of oil recovery by chemical methods. Society of Petroleum Engineers of AIME. 34(02). 243-258.

Leahy, J.G. Colwell, R.R. 1990. Microbial degradation of hydrocarbons in the environment. Microbiol. Rev. 54(3). 305-315.

Lee, C.H., Lee, J.Y., Cheon, J.Y., Lee, K.K. 2001b. Attenuation of petroleum hydrocarbons in smear zones: A case study. Journal of Environmental Engineering. 127(7). 639-647.

Lee, J.Y., Cheon, J.Y., Lee, K.K., Lee, S.Y., Lee, M.H. 2001a. Factors affecting the distribution of hydrocarbon contaminants and hydrogeochemical parameters in a shallow sand aquifer. Journal of Contaminant Hydrology. 50(1-2). 139 - 158.

Lee, J.Y., Lee, K.K. 2003. Viability of natural attenuation in a petroleum-contaminated shallow sandy aquifer. Environmental Pollution. 126(2). 201-212.

Leffler, W.L. 2008. Petroleum Refining in Nontechnical Language. Tulsa, USA. PennWell. p. 279. ISBN 978-1-59370-158-1.

Leif, R.N., Chiarappa, M., Kumamoto, G., Aines, R.D., Newmark, R.L., Knauss, K.G. 1998. Semivolatile Organic (GC-MS) and Inorganic Analyses of Groundwater Samples During the

Hydrous Pyrolysis/Oxidation (HPO): Field Test in Visalia, California, 1997. Livermore, USA. Lawrence Livermore National Laboratory. p. 57.

Lenhard, R.J. 1992. Measurement and modeling of three-phase saturation-pressure hysteresis. Journal of Contaminant Hydrology. 9(3). 243-269.

Lenhard, R.J., Johnson, T.G., Parker, J.C. 1993. Experimental observations of nonaqueous-phase liquid subsurface movement. Journal of Contaminant Hydrology. 12(1-2). 79-101.

Lenhard, R.J., Oostrom, M., Dane, J.H. 2004. A constitutive model for air–NAPL–water flow in the vadose zone accounting for immobile, non-occluded (residual) NAPL in strongly water-wet porous media. Journal of Contaminant Hydrology. 71(1-4). 261-282.

Leverett, M.C. 1941. Capillary behavior in porous solids. Journal of Society of Petroleum Engineers. 152-169.

Lewan, M.D. 1985. Evaluation of petroleum generation by hydrous phrolysis experimentation. Philosophical Transactions of the Royal Society of London, A. 315(1531). 123-134.

Lewan, M.D. 1994. Assessing natural oil expulsion from source rocks by laboratory pyrolysis. In Magoon, L.B., Dow, W.G. (eds): The Petroleum System - From Source to Trap. Tulsa, USA. The American Association of Petroleum Geologists. p. 201-210. ISBN 978-1-629-81092-8.

Lewan, M.D., Winters, J.C., McDonald, J.H. 1979. Generation of oil-like pyrolyzates from organic-rich shales. Science. 203(2). 897-899.

Liang, S., Tilotta, D.C. 1998. Extraction of petroleum hydrocarbons from soil using supercritical argon. Anal. Chem. 70(3). 616-622.

Liang, S., Tilotta, D. C. 2003. Determination of total petroleum hydrocarbons in soil by dynamic on-line supercritical fluid extraction with infrared photometric detection. Journal of Chromatography. 986(2). 319-325.

LiangTong, Z., QingYi, M., YunMin, C., RenPeng, C. 2013. Experimental study on applicability of using time-domain reflectometry to detect NAPLs contaminated sands. Sci China Tech Sci. 56(6). 1534-1543.

Liberman, M. 2008. Introduction to Physics and Chemistry of Combustion: Explosion, Flame, Detonation. Berlin, Germany. Springer-Verlag Berlin Heidelberg. p. 360. ISBN 978-3-540-78758-7.

Li, L., Quinlivan, P.A., Knappe, D.R.U. 2002. Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. Carbon. 40(12). 2085-2100.

Li, L., Sun, Z., Li, H., Keener, T.C. 2012. Effects of activated carbon surface properties on the adsorption of volatile organic compounds. Journal of the Air & Waste Management Association. 62(10). 1196-1202.

Logan, B.E. 2012. Environmental Transport Processes. Hoboken, USA. John Wiley & Sons Inc.p. 479. ISBN 978-0-470-61959-9.

Lombas-García, E., Gans, O., Krska, R., Grasserbauer, M. 1998. Supercritical fluid extraction versus ultrasonic extraction for the analysis of polycyclic aromatic hydrocarbons from reference sediment. International Journal of Environmental & Analytical Chemistry. 72(4). 289-300.

Lopez-Avila, V., Young, R., Beckerl, W.F. 1994. Microwave-assisted extraction of organic compounds from standard reference soils and sediments. Analytical Chemistry. 66(7). 1097-1106.

Lovely, D.R., Baedecker, M.J., Lonergan, D.J., Cozzarelli, I.M., Phillips, E.J., Siegel, D.I. 1989. Oxidation of aromatic compounds coupled to microbial iron reduction. Nature. 339. 297-299.

Lowe, D.F., Oubre, C.L., Ward, C.H. 1999. Surfactants and Cosolvents for NAPL Remediation: A Technology Practices Manual. Boca Raton, USA. CRC Press. p. 448. ISBN 978-0-849-34117-5.

Lubstar 2015. Marcol 82. [On line]. [Accessed on 05. 12. 2015] Available at <www.lubstar.cz/>.

Lucius, J.E., Olhoeft, G.R., Hill, P.L., Duke, S.K. 1992. Properties and Hazards of 108 Selected Substances. Denver, USA. U.S. Dept. of the Interior - Geological Survey. p. 554.

Lu, M.C. 2000. Oxidation of chlorophenols with hydrogen peroxide in the presence of goethite. Chemosphere. 40(2). 125-130.

Lundegard, P.D., Johnson, P.C. 2006. Source zone natural attenuation at petroleum hydrocarbon spill sites - II: Application to a former oil field. Ground Water Monitoring & Remediation. 26(4). 93-106.

Lu, P.J., Lin, H.C., Yu, W.T., Chern, J.M. 2011. Chemical regeneration of activated carbon used for dye adsorption. Journal of the Taiwan Institute of Chemical Engineers. 42(2). 305-311.

Lyons, W. 2010. Working Guide to Reservoir Engineering. Burlington, USA. Elsevier Inc. p. 316. ISBN 978-1-85617-824-2.

Lyons, W.C., Plisga, G.J. 2005. Standard Handbook of Petroleum & Natural Gas Engineering. Oxford, UK. Gulf Professional Publishing. p. 1565. ISBN 0-7506-7785-6.

MacDonald, I.R. 1998. Natural oil spills. Scientific American. 279(5). 57-61.

MacDonald, J.A. 2000. Evaluating natural attenuation for groundwater cleanup. Environmental Science & Technology. 34(15). 346 A-353 A.

Mackay, D.M., Cherry, J.A. 1989. Groundwater contamination: pump-and-treat remediation. Environmental Science & Technology. 23(6). 630-636.

Mackay, D., Shiu, W.Y., Ma, K.C., Lee, S.C. 2006. Handbook of physical-chemical Properties and Environmental Fate for Organic Chemicals: Volume I - Introduction and Hydrocarbons. Boca Raton, USA. CRC Press. p. 4182. ISBN 1-56670-687-4.

Mango, F.D. 1997. The light hydrocarbons in petroleum: A critical review. Organic Geochemistry. 26(7-8). 417-440.

Mangun, C.L., Daley, M.A., Braatz, R.D., Economy, J. 1998. Effect of pore size on adsorption of hydrocarbons in phenolic-based activated carbon fibers. Carbon. 36(1-2). 123-129.

Mansoori, G.A., Barnes, H.L., Webster, G.M. 2003. Petroleum Waxes. In Totten, G.E., Westbrook, S.R., Shah, R.J. (eds): Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing. West Conshohocken, USA. ASTM International. p. 525-556. ISBN 0-8031-2096-6.

Mansur, A.A., Pannirselvam, M., Al-Hothaly, K.A., Adetutu, E.M., Ball, A.S. 2015. Recovery and characterization of oil from waste crude oil tank bottom Sludge from Azzawiya Oil Refinery in Libya. J Adv Chem Eng. 5(1).

Mao, X., Jiang, R., Xiao, W., Yu, J. 2015. Use of surfactants for the remediation of contaminated soils: A review. Journal of Hazardous Materials. 285. 419-435.

Mariner, P.E., Jin, M., Studer, J.E., Pope, G.A. 1999. The First Vadose zone partitioning interwell tracer test for nonaqueous phase liquid and water residual phase liquid and water residual. Environmental Science & Technology. 33(16). 2825-2828.

Marsh, H., Rodriguez-Reinoso, F. 2006. Activated Carbon. Amsterdam, The Netherlands. Elsevier Science. p. 554. ISBN 978-0-080-44463-5.

Marvin, C.H., Allan, L., McCarry, B. E., Bryant, D.W. 1992. A comparison of ultrasonic extraction and soxhlet extraction of polycyclic aromatic hydrocarbons from sediments and air particulate material. International Journal of Environmental & Analytical Chemistry. 49(4). 221-230.

Maryott, A.A., Smith, E.R. 1951. Table of Dielectric Constant of Pure Liquids. Washington DC, USA. United States Department of Commerce - National Bureau of Standards. p. 44.

Ma, S., Zhang, X., Morrow, N.R. 1999. Influence of fluid viscosity on mass transfer between rock matrix and fractures. Journal of Canadian Petroleum Technology. 38(7). 25-30.

Matula, S., Kabát, A., Špongrová, K. 2008. Laboratory scale modelling and observation of LNAPL transport in porous media. Vienna Technical University, Vienna, University of Natural Resources and Applied Life Sciences (BOKU), CD, Abstract, p. 175–176.

Maxwell, M., Schmok, J. 1995. Detection and mapping of an LNAPL plume using GPR: A case study. 8th EEGS Symposium on the Application of Geophysics to Engineering and Environmental Problems, Tulsa, USA, 23 April 1995, Environment and Engineering Geophysical Society. p. 15-23. ISSN 1554-8015.

Mayer, A.S., Hassanizadeh, S.M., Falta, R.W., Illangasekare, T.H., Javandel, I., Jensen, K.H., Oostrom, M. 2005. Soil and Groundwater Contamination: Nonaqueous Phase Liquids-Principles and Observations. Washington, DC, USA. American Geophysical Union. p. 216. ISBN 0-87590-420-3.

Mayer, A.S., Miller, C.T. 1992. The influence of porous medium characteristics and measurement scale on pore-scale distributions of residual nonaqueous-phase liquids. Journal of Contaminant Hydrology. 11(3-4). 189-213.

McCarty, P.L., Criddle, C.S. 2012. Chemical and biological processes: The need for mixing. In: Kitanidis, P.K., McCarty, P.L. (eds): Delivery and Mixing in the Subsurface: Processes and Design Principles for In Situ Remediation. New York, USA. Springer. p. 7-52. ISBN 978-1-4614-2238-9.

McElroy, M.B. 2002. The Atmospheric Environment: Effects of Human Activity. Princeton, USA. Princeton University Press. p. 344. ISBN 978-0-691-00691-8.

McElroy, M.B. 2010. Energy: Perspectives, Problems, and Prospects. New York, USA. Oxford University Press. p. 409. ISBN 978-0-19-538611-0.

McGarry, D. 2006. Comparison of Four Soil Water Measurement Methods. In Lal, R. (ed): Encyclopedia of Soil Science. Boca Raton, USA. CRC Press. p. 317-325. ISBN 978-1-439-87062-4.

McKay, G., Bino, M.J., Altamemi, A.R. 1985. The adsorption of various pollutants from aqueous solutions on to activated carbon. Water Research. 19(4). 491-495.

McKee, R.H., Medeiros, A.M., Daughtrey, W.C. 2005. A Proposed methodology for setting occupational exposure limits for hydrocarbon solvents. Journal of Occupational and Environmental Hygiene. 2(10). 524–542.

Mclay, D. 1999. Overview of remediation technologies for dense nonaqueous phase liquids. Environmental Claims Journal. 11(4). 97-107.

McWhorter, D.B., Sunada, D.K. 1990. Exact integral solution for two-phase flow. Water Resources Research. 26(3). 399-413.

Mendelsohn, J., Howley, P.M., Israel, M.A., Gray, J.W., Thompson, C.B. 2015. The Molecular Basis of Cancer. Philadelphia, USA. Saunders. p. 863. ISBN 978-1-4557-4066-6.

Menendez-Diaz, J.Á., Martln-Gullonb, I. 2006. Types of Carbon Adsorbents and Their Production. In Bandosz, T.J. (ed): Activated Carbon Surfaces in Environmental Remediation. Amsterdam, The Netherlands. Elsevier. p. 1-47. ISBN 0-12-370536-3.

Mercer, J.W., Cohen, R.M. 1990. A review of immiscible fluids in the subsurface: Properties, models, characterization and remediation. Journal of Contaminant Hydrology. 6(2). 107-163.

Mercer, J.W., Skipp, D.C., Giffin, D. 1990. Basics of Pump and Treat Ground Water Remediation Technology. Cincinnati, USA. US EPA. p. 66.

Mihelcic, J.R., Luthy, R.G. 1988. Degradation of polycyclic aromatic hydrocarbon compounds under various redox conditions in soil-water systems. Appl. Environ. Microbiol. 54(5). 1182-1187.

Miller, C.T., Poirier-McNeil, M.M., Mayer, A.S. 1990. Dissolution of trapped nonaqueous phase liquids: Mass transfer characteristics. Water Resour. Res. 26(11). 2783–2796.

Minty, B., Ramsey, E.D., Davies, I., 2000. Development of an automated method for determining oil in water by direct aqueos supercritical fluid extraction coupled on-line with infrared spectroscopy. Analyst. 125(12). 2356–2363.

Minty, B., Ramsey, E.D., Lewis, R. 1996. Hydrocarbons in water: analysis using on-line aqueous supercritical fluid extraction–fourier transform infrared spectroscopy. Analytical Communications. 203-2004.

Mohamed, A.M.I., El-menshawy, N., Saif, A.M. 2007. Remediation of saturated soil contaminated with petroleum products using air sparging with thermal enhancement. Journal of Environmental Management. 83(3). 339-350.

Mohamed, S.O., Bertuzzi, P., Bruand, A., Raison, L., Bruckler, L. 1997. Field evaluation and error analysis of soil water content measurement using the capacitance probe method. Soil Sci. Soc. Am. J. 61(2). 399-408.

Molins, S., Mayer, K. U. 2007. Coupling between geochemical reactions and multicomponent gas and solute transport in unsaturated media: A reactive transport modeling study. Water Resour. Res. 43(5). W05435.

Monier-Williams, M. 1995. Properties of light non-aqueous phase liquids and detection using commonly applied shallow sensing geophysical techniques. 8th EEGS Symposium on the Application of Geophysics to Engineering and Environmental Problems, Tulsa, USA, 23 April 1995, Environment and Engineering Geophysical Society. p. 1-15. ISSN 1554-8015.

Montemayor, R.G. 2010. Petroleum Solvents. In Rand, S.J. (ed): Significance of Tests for Petroleum Products. West Conshohocken, USA. ASTM International. p. 173-183. ISBN 978-0-8031-7001-8.

Moon, D.J., Chung, M.J., Cho, S.Y., Ahn, B.S., Park, K.Y., Hong, S.I. 1998. Adsorption equilibria of chloropentafluoroethane and pentafluoroethane on activated carbon pellet. Journal of Chemical & Engineering Data. 45(3). 861-864.

Morel-Seytoux, H.J. 1973. Two-Phase Flow in Porous Media. In Chow, V. T. (ed): Advances in Hydroscience. San Diego, USA. Academic Press. p. 120-202.

Moreno-Castilla, C., Rivera-Utrilla, J., Joly, J.P., López-Ramón, M.V., Ferro-García, M.A., Carrasco-Marín, F. 1995. Thermal regeneration of an activated carbon exhausted with different substituted phenols. Carbon. 33(10). 1417-1423.

Morselli, L., Setti, L., Iannuccilli, A., Maly, S., Dinelli, G., Quattroni, G. 1999. Supercritical fluid extraction for the determination of petroleum hydrocarbons in soil. Journal of Chromatography. 845(1-2). 357-363.

Mukhopadhyay, S., Cushman, J.H. 1998. Diffusive Transport of Volatile Pollutants in Nonaqueous-Phase Liquid Contaminated Soil: A Fractal Model. Transport in Porous Media. 30(2). 125–154.

Mulligan, C.N., Yong, R.N. 2004. Natural attenuation of contaminated soils. Environment International. 30(4). 587 - 601.

Mulligan, C.N., Yong, R.N., Gibbs, B.F. 2001. Surfactant-enhanced remediation of contaminated soil: a review. Engineering Geology. 60(1-4). 371-380.

Mungan, N. 1966. Interfacial effects in immiscible liquid-liquid displacement in porous media. Society of Petroleum Engineers Journal. 6(03). 247-253.

Murgulet, D. 2017. Groundwater Contaminant Transport Mechanisms and Pollution Prevention. In Chen, D. H. (ed): Sustainable Water Management and Technologies: Sustainable Water Technologies. Boca Raton, USA. CRC Press. p. 23-52. ISBN 978-1-482-21510-6.

Mwangi, P.M., Rao, D.N. 2014. An Overview of Surfactants in Enhanced Oil Recovery. In Romsted, L.S. (ed): Surfactant Science and Technology: Retrospects and Prospects. Boca Raton, USA. CRC Press. p. 489-505. ISBN 978-1-4398-8296-2.

Nadim, F., Hoag, G.E., Liu, S., Carley, R.J., Zack, P. 2000. Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview. Journal of Petroleum Science and Engineering. 26(1-4). 169-178.

Nadim, F., Zack, P., Hoag, G.E., Liu, S. 2001. United States experience with gasoline additives. Energy Policy. 29(1). 1-5.

Nagashima, H., Kondo, T., Nagoya, T., Ikeda, T., Kurimata, N., Unoke, S., Seto, Y. 2015. Identification of chemical warfare agents from vapor samples using a field-portable capillary gas chromatography/membrane-interfaced electron ionization quadrupole mass spectrometry instrument with Tri-Bed concentrator. Journal of Chromatography. 1406. 279-290.

Narbaitz, R.M., Cen, J. 1994. Electrochemical regeneration of granular activated carbon. Water Research. 28(8). 1771-1778.

Narbaitz, R.M., Cen, J. 1997. Alternative methods for determining the percentage regeneration of activated carbon. Water Research. 31(10). 2532-2542.

National Research Council 2005. Contaminants in the Subsurface: Source Zone Assessment and Remediation. Washington DC, USA. The National Academies Press. p. 358. ISBN 0-309-54664-8.

Nelson, M.D., Parker, B.L., Al, T. A., Cherry, J.A., Loomer, D. 2001. Geochemical reactions resulting from in situ oxidation of PCE-DNAPL by KMnO4 in a sandy aquifer. Environmental Science and Technology. 35(6). 1266-1275.

Nelson, N.T., Brusseau, M.L. 1996. Field study of the partitioning tracer method for detection of dense nonaqueous phase liquid in a trichloroethene- contaminated aquifer. Environmental Science & Technology. 30(9). 2859-2863.

Nelson, P. 2003. Index to EPA Test Methods. Boston, USA. EPA New England Region 1 Library. p. 82.

Nevskaia, D.M., Santianes, A., Muñoz, V., Guerrero-Ruíz, A. 1999. Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study. Carbon. 37(7). 1065-1074.

Newcombe, G., Drikas, M. 1993. Chemical regeneration of granular activated carbon from an operating water treatment plant. Water Research. 27(1). 161-165.

Newell, C.J., Acree, S.D., Ross, R.R., Huling, S.G. 1995. Light Nonaqueous Phase Liquids. Washington, DC, USA. U.S. Environmental Protection Agency, EPA/540/S-95/500 (NTIS 95-267738).

Neyens, E., Baeyens, J. 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials. 98(1-3). 33-50.

Ng, G.H., Bekins, B.A., Cozzarelli, I.M., Baedecker, M.J., Bennett, P.C., Amos, R.T., Herkelrath, W. N. 2015. Reactive transport modeling of geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN. Water Resour. Res. 51(6). 4156–4183.

Nicholis, P.H. 1991. Organic Contaminants in Soils and Groundwaters. In Jones, K.C. (ed): Organic Contaminants in the Environment: Environmental Pathways & Effects. New York, USA. Elsevier Science. p. 87-132. ISBN 978-94-010-8424-6.

Nielsen, D.M., Nielsen, G.L., Preslo, L.M. 2006. Environmental Site Characterization. In Nielsen, D. M. (ed): Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring. Boca Raton, USA. CRC Press. p. 35-205. ISBN 1-56670-589-4.

Noborio, K. 2001. Measurement of soil water content and electrical conductivity by time domain reflectometry: A review. Computers and Electronics in Agriculture. 31(3). 213–237.

Nriagu, J.O. 1990. The rise and fall of leaded gasoline. The Science of the Total Environment. 92. 13-28.

O'Carroll, D.M., Sleep, B.E. 2007a. Role of NAPL thermal properties in the effectiveness of hot water flooding. Journal of Transport in Porous Media. 91(3-4). 393–405.

O'Carroll, D.M., Sleep, B. E. 2007b. Hot water flushing for immiscible displacement of a viscous NAPL. Journal of Contaminant Hydrology. 91(3-4). 247-266.

Ochsner, T.E., Horton, R., Ren, T. 2001. Simultaneous water content, air-filled porosity, and bulk density measurements with thermo-time domain reflectometry. Soil Sci. Soc. Am. J. 65(6). 1618–1622.

Ogata, A. 1970. Theory of Dispersion in a Granular Medium. Washington, DC, USA. United States Government Printing Office. Geological Survey Professional Paper 411-1. p. 36.

Ohkawa, T. 1992. Compact open NMR systems for in situ measurement of moisture, salinity, and hydrocarbons. San Diego, USA. Patent No. 5,095,271. p. 12.

Okparanma, R.N., Mouazen, A.M. 2013. Determination of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbon (PAH) in soils: A review of spectroscopic and nonspectroscopic techniques. Applied Spectroscopy Reviews. 48(6). 458–486.

Olah, G.A., Molnár, Á. 2003. Hydrocarbon Chemistry. Hoboken, USA. Wiley. p. 871. ISBN 0-471-41782-3.

Olchawa, A., Kumor, M. 2008. Time domain reflectometry (TDR) - Measuring dielectric constant of polluted soil to estimate diesel oil content. Archives of Hydro-Engineering and Environmental Mechanics. 55(1-2). 55-62.

Oostrom, M., Dane, J.H., Wietsma, T.W. 2005b. Removal of carbon tetrachloride from a layered porous medium by means of soil vapor extraction enhanced by desiccation and water table reduction. Vadose Zone Journal. 4(4). 1170–1182.

Oostrom, M., Falta, R.W., Mayer, A.S., Javandel, I., Hassanizadeh, S.M. 2005a. Remediation. In Mayer A., Hassanizadeh, S. M. (eds): Soil and Groundwater Contamination: Nonaqueous Phase Liquids-Principles and Observations. Washington DC, USA. American Geophysical Union. p. 141-189. ISBN 0-87590-420-3.

Oostrom, M., Hofstee, C., Dane, J.H. 1997. Light nonaqueous-phase liquid movement in a variably saturated sand. Soil Science Society of America Journal. 61(6). 1547-1554.

Oostrom, M., Lenhard, R.J. 1998. Comparison of relative permeability-saturation-pressure parametric models for infiltration and redistribution of a light nonaqueous-phase liquid in sandy porous media. Advances in Water Resources. 21(2). 145-157.

Or, D., Wraith, J.M., Robinson, D.A., Jones, S.B. 2012. Soil Water Content and Water Potential Relationships. In Huang, P.M, Li, Y., Sumner, M.E. (eds): Handbook of Soil Sciences: Properties and Processes. Boca Raton, USA. CRC Press. p. 4.1-4.28. ISBN 978-1-4398-0306-6.

Orlando, L. 2002. Detection and analysis of LAPL using the instantaneous amplitude and frequency of ground-penetrating radar data. Geophysical Prospecting. 50. 27-41.

Ostendorf, D.W., Kampbell, D.H. 1991. Biodegradation of hydrocarbon vapors in the unsaturated zone. Water Resour. Res. 27(4) 453-462.

Ouellette, R.J., Rawn, J.D. 2015. Principles of Organic Chemistry. Oxford, UK. Elsevier. p. 485. ISBN 978-0-12-802444-7.

Oxford English Dictionary 2015. Petroleum [Online]. [Accessed on 15. 05. 2015] Available at <https://en.oxforddictionaries.com/definition/petroleum>.

Pankow, J.F., Cherry, J.A. 1996. Dense Chlorinated Solvents and other DNAPLs in Groundwater: History, Behavior, and Remediation. Portland, USA. Waterloo Press. p. 522.

Panuganti, S.R., Wang, F., Chapman, W.G., Vargas, F.M. 2016. A simple method for estimation of dielectric constants and polarizabilities of nonpolar and slightly polar hydrocarbons. Int J Thermophys. 37. 75 (1-24).

Paradowski, H. 1995. Methods for the Calculation of Hydrocarbon Physical Properties. In Wauquier, J. (ed): Petroleum Refining: Crude Oil, Petroleum Products, Process Flowsheets. Paris, France. Editions Technip. p. 86-175. ISBN 978-2-71 08-0685-1.

Paria, S. 2008. Surfactant-enhanced remediation of organic contaminated soil and water. Advances in Colloid and Interface Science. 138(1). 24-58.

Parkash, S. 2009. Petroleum Fuels Manufacturing Handbook: Including Specialty Products and Sustainable Manufacturing Techniques. New York, USA. The McGraw-Hill Companies. p. 444. ISBN 978-0-07-163241-6.

Parker, J.C., Lenhard, R.J., Kuppusamy, T. 1987. A parametric model for constitutive properties governing multiphase flow in porous media. Water Resources Research. 23(4). 618-624.

Parkyns, N.D., Sing, K.S.W. 1975. Adsorption at the Gas/Solid Interface. In Everett, D.H. (ed): Colloid Science: A Specialist Periodical Report - Colloid Science, Volume 2. London, UK. The Chemical Society. p. 1-51. ISBN 0-85186-518-0.

Paspaliaris, I., Papassiopi, N., Xenidis, A., Hung, Y.T. 2010. Soil Remediation. In Wang, L.K., Hung, Y., Shammas, N.K. (eds): Handbook of Advanced Industrial and Hazardous Wastes Treatment. Boca Raton, USA. CRC Press. p. 519-570. ISBN 978-1-4200-7219-8.

Pennell, K.D., Jin, M., Abriola, L.M., Pope, G.A. 1994. Surfactant enhanced remediation of soil columns contaminated by residual tetrachloroethylene. Journal of Contaminant Hydrology. 16(1). 35-53.

Pepper, I.L., Gerba, C.P., Brusseau, M.L. 2006. Environmental & pollution science. Boston, USA. Academic Press. p. 532. ISBN 978-0-12-551503-0.

Persson, M., Berndtsson, R. 2002. Measuring nonaqueous phase liquid saturation in soil using time domain reflectometry. Water Resources Research. 38(5). 22-1–22-8.

Peters, E.J., Flock, D.L. 1981. The onset of instability during two-phase immiscible displacement in porous media. Society of Petroleum Engineers Journal. 21(02). 249-258.

Peters, K.E., Walters, C.C., Moldowan, J.M. 2005. The Biomarker Guide: Volume 1 - Biomarkers and Isotopes in the Environment Human History. Cambridge, UK. Cambridge University Press. p. 471. ISBN 0-521-78158-2.

Petri, B.G., Fučík, R., Illangasekare, T.H., Smits, K.M., Christ, J.A., Sakaki, T., Sauck, C.C. 2014. Effect of NAPL source morphology on mass transfer in the vadose zone. Groundwater. 53(5). 1-14.

Phogat, V.K., Aylmore, L.A.G., Schuller, R.D. 1991. Simultaneous measurement of the spatial distribution of soil water content and bulk density. Soil Sci. Soc. Am. J. 55(4). 908-915.

Pignatello, J.J., Oliveros, E., MacKay, A. 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Critical Reviews in Environmental Science and Technology. 36(1). 1-84.

Pikul, J.L. 2008. Soil Water Measurement: Gravimetric. In Trimble, S.W. (ed): Encyclopedia of Water Science: Volume I-II. Boca Raton, USA. CRC Press. p. 1063-1066. ISBN 978-0-8493-9627-4.

Pillon, L.Z. 2008. Interfacial Properties of Petroleum Products. Boca Raton, USA. CRC Press. p. 361. ISBN 978-1-4200-5100-1.

Pinder, G.F., Gray, W.G. 2008. Essentials of Multiphase Flow in Porous Media. Hoboken, USA. John Wiley & Sons. p. 257. ISBN 978-0-470-31762-4.

Płaza, G.A., Ulfig, K., Tien, A.J. 2005. Immunotechniques as a Tool for Detection of Hydrocarbons. In Margesin, R., Schinner, F. (eds): Manual for Soil Analysis: Monitoring and Assessing Soil Bioremediation. Berlin, Germany. Springer-Verlag. p. 121-130. ISBN 978-3-540-28904-3.

Plaza, M.G., Pevida, C., Arias, B., Fermoso, J., Casal, M.D., Martín, C.F., Rubiera, F., Pis, J.J. 2009. Development of low-cost biomass-based adsorbents for post combustion CO2 capture. Fuel. 88(12). 2442-2447.

Poling, B.E., Prausnitz, J.M., O'Connell, J.P. 2001. The properties of Gases and Liquids. New York, USA. The McGraw-Hill Companies. p. 752. ISBN 978-0-071-18971-2.

Pollitt, A.A. 1943. Mineral oils for transformers and switchgear. The Journal of the Institution of Electrical Engineers. 90(13). 15-22.

Ponsin, V., Chablais, A., Dumont, J., Radakovitch, O., Höhener, P. 2015. 222Rn as natural tracer for LNAPL recovery in a crude oil-contaminated aquifer. Groundwater Monitoring & Remediation. 35(2). 30-38.

Popek, E.P. 2003. Sampling and Analysis of Environmental Chemical Pollutants: A Complete Guide. San Diego, USA. Academic Press. p. 356. ISBN 978-0-12-803202-2.

Porcelli, P.C., Binder, M.S. 1994. Simulation and transport phenomena of a ternary two-phase flow. Transport in Porous Media. 14(2). 101-122.

Poulsen, T.G., Moldrup, P., Yamaguchi, T., Massmann, J.W., Hansen, J.A. 1998. VOC vapor sorption in soil: Soil type dependent model and implications for vapor extraction. Journal of Environmental Engineering. 124(2). 146-155.

Powers, S.E., Abriola, L.M., Weber, W.J. 1993. An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: Steady state mass transfer rates. Water Resources Research. 28(10). 2691 - 2705.

Przepiorski, J. 2006. Activated carbon filters and their industrial applications. In Bandosz, T. J. (ed): Activated Carbon Surfaces in Environmental Remediation. Oxford, UK. Elsevier Ltd. p. 421-474. ISBN 978- 0-12-370536-5.

Radilla, G., Aigueperse, A., Quintard, M., Bertin, H. 1998. Theoretical Study and Experimental Validation of Transport Coefficients for Hydrocarbon Pollutants in Aquifers. In Crolet J. M., Hatri, M. E. (eds): Recent Advances in Problems of Flow and Transport in Porous Media: Theory and Applications of Transport in Porous Media. Dordrecht, The Netherlands. Springer. p. 143-152. ISBN 978-90-481-4989-6.

Rahman, Z.A., Hamzah, U., Taha, M.R., Ithnain, N.S., Ahmad, N. 2010. Influence of oil contamination on geotechnical properties of basaltic residual soil. Am. J. Applied Sci. 7(7). 954-961.

Ram, N.M., Bass, D.H., Falotico, R., Leahy, M. 1993. A decision framework for selecting remediation technologies at hydrocarbon-contaminated sites. Journal of Soil Contamination. 2(2). 167-189.

Ramsey, E.D. 2008. Determination of oil-in-water using automated direct aqueous supercritical fluid extraction interfaced to infrared spectroscopy. J. of Supercritical Fluids. 44(2). 201-210.

Ramsey, E.D., Sun, Q., Zhang, Z., Guo, W., Liu, J.Y., Wu, X.H. 2010. Sustainable oil-in-water analysis using a supercritical fluid carbon dioxide extraction system directly interfaced with infrared spectroscopy. Journal of Environmental Sciences. 22(9). 1462–1468.

Rathfelder, K., Lang, J.R., Abriola, L.M. 1995. Soil vapor extraction and bioventing: Applications, limitations, and future research directions. Reviews of Geophysics. 33(S2). 1067-1081.

Raymond, K.W. 2014. General, organic, & Biological Chemistry: An Integrated Approach. Hoboken, USA. John Wiley & Sons, Inc. p. 676. ISBN 978-1-118-35258-8.

Reddi, L.N., Han. W., Banks, M.K. 1998. Mass loss from LNAPL pools under fluctuating water table conditions. Journal of Environmental Engineering. 124(12). 1171-1177.

Reddy, K.R., Adams, J.A., Richardson, C. 1999. Potential technologies for remediation of Brownfields. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management. 3(2). 61-68.

Reddy, K.R., Koski, S., Zhou, J. 1995. A review of in-situ air sparging for the remediation of VOC-contaminated saturated soils and groundwater. Hazardous Waste and Hazardous Materials. 12(2). 97-118.

Redman, J.D. 2009. Contaminant Mapping. In Jol, H. M. (ed): Ground Penetrating Radar Theory and Applications. Amsterdam, The Netherlands. Elsevier Science. p. 247-269. ISBN 978-0-444-53348-7.

Reynolds, S.G. 1970. The gravimetric method of soil moisture determination: Part I - A study of equipment, and methodological problems. Journal of Hydrology. 11(3). 258-273.

Reynolds, W.D., Topp, G.C. 2008. Soil Water Analyses: Principles and Parameters. In Carter, M.R., Gregorich, E.G. (eds): Soil Sampling and Methods of Analysis. Boca Raton, USA. CRC Press. p. 913-937. ISBN 978-0-8493-3586-0.

Riazi, M.R. 2005. Characterization and Properties of Petroleum Fractions. Philadelphia, USA. ASTM International. p. 407. ISBN 0-8031-3361-8.

Rinaldi, V.A., Francisca, F.M. 2006. Removal of immiscible contaminants from sandy soils monitored by means of dielectric measurements. Journal of Environmental Engineering. 132(8). 931-939.

Riser-Roberts, E. 1998. Remediation of petroleum contaminated soils: biological, physical, and chemical processes. Boca Raton, USA. Lewis Publishers. p. 576. ISBN 978-0-873-71858-5.

Robinson, D.A., Gardner, C.M.K., Cooper, J.D. 1999. Measurement of relative permittivity in sandy soils using TDR, capacitance and theta probes: comparison, including the effects of bulk soil electrical conductivity. Journal of Hydrology. 198-211.

Robinson, M., Dean, T.J. 1993. Measurement of near surface soil water content using a capacitance probe. Hydrological Processes. 7(1). 77-86.

Robinson, R. 1966. The origins of petroleum. Nature. 212(5068). 1291-1295.

Rogers, R.D., Seddon, K.R. 2003. Ionic Liquids--Solvents of the Future?. Science. 302(5646). 792-793.

Romanova, U.G., Romanov, G.V. 2015. The Origin of Petroleum: The Mystery Remains. Geoscience New Horizons GeoConvention 2015, Calgary, Canada, 4 – 8 May 2015, GeoConvention 2015: New Horizons. p. 1-5.

Roosta, A., Roostaee, A.R., Rahbar, M. 2015. Temperature effect on wettability and oil recovery efficiency during spontaneous imbibition. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 37(18). 1988-1995.

Rosen, M.J. 2004. Surfactants and Interfacial Phenomena. Hoboken, USA. Wiley-Interscience. p. 444. ISBN 0-471-47818-0.

Rosen, M.J., Kunjappu, J.T. 2012. Surfactants and Interfacial Phenomena. Hoboken, USA. Wiley. p. 600. ISBN 978-0-470-54194-4.

Ross, J.F. 1980. Handbook for Radio Engineering Managers. London, Uk. Butterworth & Co. Ltd. p. 947. ISBN 0-408-00424-X.

RT (Russian Television) 2016. Russian fighter jets destroy ISIS oil facilities [Online]. [Accessed on 18. 07. 2017] Available at: <https://www.rt.com/news/345267-russia-jets-oil-isis-turkey/>.

RTI (Research Triangle Institute) 1999. Toxicological profile for Total Petroleum Hydrocarbons (TPH). Atlanta, USA. Agency for Toxic Substances and Disease Registry Division of Toxicology/Toxicology Information Branch. p. 334.

Rubin, H. 2013. Soil and Aquifer Management. In Fernando. H.J.S. (ed): Handbook of Environmental Fluid Dynamics: Overview and Fundamentals. Boca Raton, USA. CRC Press. p. 91 - 106. ISBN 978-1-4398-1670-7.

Ruble, T.E., Lewan, M.D., Philp, R.P. 2001. New insights on the Green River petroleum system in the Uinta basin from hydrous pyrolysis experiments. American Association of Petroleum Geologists Bulletin. 85(8). 1333-1371.

Ruiz, J., Bilbao, R., Murillo, M.B. 1998. Adsorption of different VOC onto soil minerals from gas phase: Influence of mineral, type of VOC, and air humidity. Environ. Sci. Technol. 32(8). 1079-1084.

Russell, T.F. 1995. Modeling of multiphase multicontaminant transport in the subsurface. Reviews of Geophysics. 33(S2). 1035-1047.

S.U., S.L., Singh, D.N., Baghini, M.S. 2014. A critical review of soil moisture measurement. Measurement. 54. 92-105.

Sabatini, D.A., Knox, R.C., Harwel, J.H. 1995. Emerging Technologies in Surfactant-Enhanced Subsurface Remediation. In Sabatini, D.A., Knox, R.C., Harwell, J.H. (eds): Surfactant-Enhanced Subsurface Remediation: Emerging Technologies. Washington DC, USA. American Chemical Society. p. 1-8. ISBN 0-8412-3225-3.

Sabio, E., González, E., González, J.F., González-García, C.M., Ramiro, A., Gañan, J. 2004. Thermal regeneration of activated carbon saturated with p-nitrophenol. Carbon. 42(11). 2285-2293.

Saeedi, A. 2012. Experimental Study of Multiphase Flow in Porous Media during CO2 Geo-Sequestration Processes. Berlin, Germany. Springer-Verlag. p. 184. ISBN 978-3-642-25040-8.

Sahimi, M. 2011. Flow and Transport in Porous Media: From Classical Methods to Modern Approaches. Weinheim, Germany. WILEY-VCH Verlag GmbH & Co. KGaA. p. 709. ISBN 978-3-527-40485-8.

Saraf, D.N., McCaffery, F.G. 1985. Relative Permeabilities. In Donaldson, E.C., Chilingarian, G.V., Yen, T.F. (eds): Enhanced Oil Recovery, I: Fundamentals and Analyses. Amsterdam, The Netherlands. Elsevier Science. p. 75-118. ISBN 0-444-42206-4.

Sarkar, D., Ferguson, M., Datta, R., Birnbaum, S. 2005. Bioremediation of petroleum hydrocarbons in contaminated soils: Comparison of biosolids addition, carbon supplementation, and monitored natural attenuation. Environmental Pollution. 136(1). 187-195.

Sarkar, S.C., Bose, A. 1997. Role of activated carbon pellets in carbon dioxide removal. Energy Conversion and Management. 38. S105-S110.

Satter, A., Iqbal, G.M., Buchwatter, J.L. 2008. Practical Enhanced Reservoir Engineering. Tulsa, USA. PennWell Corporation. p. 688. ISBN 1-59370-056-3.

Schmidt-Etkin, D. 2011. Spill Occurrences: A World Overview. In Fingas, M. (ed): Oil Spill Science and Technology: Prevention, Response, and Cleanup. Burlington, Oxford, UK. Gulf Professional Publishing. p. 7- 48. ISBN 978-1-85617-943-0.

Schmidt, R., Gudbjerg, J., Sonnenborg, T.O., Jensen, K.H. 2002. Removal of NAPLs from the unsaturated zone using steam: prevention of downward migration by injecting mixtures of steam and air. Journal of Contaminant Hydrology. 55(3-4). 233-260.

Schobert, H.H. 1990. The Chemistry of Hydrocarbon Fuels. London, UK. Butterworth & Co Ltd. p. 348. SBN0-408-03825-X.

Schön, J.H. 2015. Physical Properties of Rocks: Fundamentals and Principles of Petrophysics. Amsterdam, The Netherlands. Elsevier B.V. p. 497. ISBN 978-0-08-100404-3.

Schroth, M.H., Ahearn, S.J., Selker, J.S. Istok, J.D. 1996. Characterization of miller-similar silica sands for laboratory hydrologic studies. Soil Sci. Soc. Am. J. 60(5). 1331-1339.

Schroth, M.H., Istok, J.D., Ahearn, S.J., Selker, J.S. 1995. Geometry and position of light nonaqueous-phase liquid lenses in water-wetted porous media. Journal of Contaminant Hydrology. 19. 269-287.

Schroth, M.H., Istok, J.D., Selker, J.S. 1998a. Three-phase immiscible fluid movement in the vicinity of textural interfaces. Journal of Contaminant Hydrology. 32(1-2). 1-23.

Schroth, M.H., Istok, J.D., Selker, J.S., Oostrom, M., White, M.D. 1998b. Multifluid flow in bedded porous media: laboratory experiments and numerical simulations. Advances in Water Resources. 22(2). 169-183.

Schubert, M. 2015. Using radon as environmental tracer for the assessment of subsurface Non-Aqueous Phase Liquid (NAPL) contamination - A review. The European Physical Journal Special Topics. 224(4). 717-730.

Schubert, M., Freyer, K., Treutler, H.C., Weiß, H. 2001. Using the soil gas radon as an indicator for ground contamination by non-aqueous phase-liquids. Journal of Soils and Sediments. 1(4). 217-222.

Schubert, M., Paschke, A., Lau, S., Geyer, W., Knöller, K. 2007. Radon as a naturally occurring tracer for the assessment of residual NAPL contamination of aquifers. Environmental Pollution. 145(3). 920-927.

Schubert, M., Peña, P., Balcázar, M., Meissner, R., Lopez, A., Flores, J.H. 2005. Determination of radon distribution patterns in the upper soil as a tool for the localization of subsurface NAPL contamination. Radiation Measurements. 40(2-6). 633-637.

Schwartz, N., Huisman, J.A., Furman, A. 2012. The effect of NAPL on the electrical properties of unsaturated porous media. Geophysical Journal International. 88(3). 1007-1011.

Schwille, F. 1984. Migration of Organic Fluids Immiscible with Water in the Unsaturated Zone. In Yaron, B., Dagan, G., Goldshmid, J. (eds): Pollutants in Porous Media: The Unsaturated Zone Between Soil Surface and Groundwater. Berlin, Germany. Springer-Verlag. p. 27-48. ISBN 978-3-642-69587-2.

Schwille, F. 1988. Dense Chlorinated Solvents in Porous and Fractured Media: Model Experiments. Chelsea: Lewis Publishers. p. 146. ISBN 0-87371-121-1.

Seager, S.L., Slabaugh, M.R. 2014. Chemistry for Today: General, Organic, and Biochemistry. Belmont, USA. Cengage Learning. p. 960. ISBN 1-133-60227-4.

Seagren, E.A., Rittmann, B.E., Valocchi, A.J. 1999. An experimental investigation of NAPL pool dissolution enhancement by flushing. Journal of Contaminant Hydrology. 37(1-2). 111-137.

Selim, H.M. 2015. Transport & Fate of Chemicals in Soils: Principles & Applications. Boca Raton, USA. CRC Press. p. 326. ISBN 978-1-4665-5795-6.

Selley, R.C., Sonnenberg, S.A. 2014. Elements of Petroleum Geology. San Diego, USA. Academic Press. p. 526. ISBN 978-0-123-86031-6.

Seol, Y., Schwartz, F.W., Lee, S. 2001. Oxidation of binary DNAPL mixtures using potassium permanganate with a phase transfer catalyst. Groundwater Monitoring & Remediation. 21(2). 124-132.

Serp, P., Machado, B. 2015. Nanostructured Carbon Materials for Catalysis. Cambridge, UK. The Royal Society of Chemistry. p. 555. ISBN 978-1-84973-909-2.

Seyfried, M.S., Murdock, M.D. 2001. Response of a new soil water sensor to variable soil, water content, and temperature. Soil Sci. Soc. Am. J. 65(1). 28-34.

Seyfried, M.S., Murdock, M.D. 2004. Measurement of soil water content with a 50-MHz soil dielectric sensor. Soil Sci. Soc. Am. J. 68(2). 394–403.

Shafeeyan, M.S., Daud, W.M.A.W., Houshmand, A., Shamiri, A. 2010. A review on surface modification of activated carbon for carbon dioxide adsorption. Journal of Analytical and Applied Pyrolysis. 89(2). 143-151.

Shah, D.O. 1981. Surface Phenomena in Enhanced Oil Recovery. New York, USA. Springer. p. 874. ISBN 978-1-4757-0339-9.

Sharma, M.K., Shah, D.O. 1989. Use of Surfactants in Oil Recovery. In Donaldson, E.C., Chilingarian G.V., Yen, T.F. (eds): Enhanced Oil Recovery, II: Processes and Operations. Amsterdam, The Netherlands Elsevier Science. p. 255-315. ISBN 0-444-42933-6.

Sheintuch, M., Matatov-Meytal, Y.I. 1999. Comparison of catalytic processes with other regeneration methods of activated carbon. Catalysis Today. 53(1). 73-80.

Sheng, J.J. 2011. Modern Chemical Enhanced Oil Recovery: Theory and Practice. Burlington, USA. Gulf Professional Publishing. p. 617. ISBN 978-1-85617-745-0.

Sheng, J.J. 2013. Surfactant-Polymer Flooding. In Sheng, J. (ed): Enhanced Oil Recovery Field Case Studies. Waltham, USA. Gulf Professional Publishing. p. 117-142. ISBN 978-1-12-386545-8.

Shuahua, H.W.W., Meixia, W., Qiaoli, X., Mei, N. 2017. The comparison of different activation techniques to prepare activated carbon materials from waste cotton fabric. Autex Research Journal. 17(3). 287-294.

Simanzhenkov, V., Idem, R. 2003. Crude Oil Chemistry. New York, USA. Marcel Dekker. p. 409. ISBN 0-8247-4098-X.

Singh, P., Kanwar, R.S. 1991. Preferential solute transport through macropores in large undisturbed saturated soil columns. J. Environ. Qual. 20(1). 295 - 300.

Site, A.D. 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. J. Phys. Chem. Ref. Data, 30(1). 187-439.

Skierucha, W., Wilczek, A., Szypłowska, A., Sławiński, C., Lamorski, K. 2012. A TDR-based Soil moisture monitoring system with simultaneous measurement of soil temperature and electrical conductivity. Sensors. 12(10). 13545-13566.

Sklopisek Střeleč 2015. Sand for Sport Surfaces: ST 56 [Online].

[Accessed on 12. 12. 2016] Available at < https://en.glassand.eu/our-sands/by-type/sport-sands>.

Smil, V. 2015. Natural Gas: Fuel for the 21st Century. Chichester, UK. Wiley. p. 251. ISBN 978-1-119-01286-3.

Smith, E., Dent, G. 2005. Modern Raman Spectroscopy - A Practical Approach. Chichester, UK. John Wiley & Sons Ltd. p. 201. ISBN 0-471-49794-0.

Smith, H.M. 1968. Qualitative and Quantitative Aspects of Crude Oil Composition. Washington DC, USA. US Dept. of the Interior, Bureau of Mines. p. 136.

Smith, K.A., Cresser, M.S. 2003. Soil & Environmental Analysis: Modern Instrumental Techniques. New York, USA. Marcel Dekker. p. 576. ISBN 0-8247-0991-8.

Smith, P.A., Lepage, C.R.J., Koch, D., Wyatt, H.D.M., Hook, G.L., Betsinger, G., Erickson, R.P., Eckenrode, B.A. 2004. Detection of gas-phase chemical warfare agents using field-portable gas chromatography–mass spectrometry systems: instrument and sampling strategy considerations. Trends in Analytical Chemistry. 23(4). 296-306.

Soga, K., Page, J.W.E., Illangasekare. T.H. 2004. A review of NAPL source zone remediation efficiency and the mass flux approach. Journal of Hazardous Materials. 110. 13-27.

Song, C.L., Zhang, W.M., Pei, Y.Q., Fan, G.L., Xu, G.P. 2006. Comparative effects of MTBE and ethanol additions into gasoline on exhaust emissions. Atmospheric Environment. 40(11). 1957–1970.

Soxhlet, F. 1879. Soxhlet, über gewichtsanalytische Bestimmung des Milchfettes. Dingers Polytech. J. 232. 461-465.

Speight, J.G. 2001. Handbook of Petroleum Analysis. Toronto, Canada. Wiley-Interscience. p. 519. ISBN 0-471-36167-4.

Speight, J.G. 2005. Environmental Analysis and Technology for the Refining Industry. Hoboken, USA. Toronto, Canada. Wiley & Interscience. p. 349. ISBN 0-471-67942-9.

Speight, J.G. 2007. Natural Gas: A Basic Handbook. Houston, USA. Gulf Publishing Company. p. 250. ISBN 1-933762-14-4.

Speight, J.G. 2011a. Handbook of Industrial Hydrocarbon Processes. Oxford, UK. Gulf Professional Publishing. p. 641. ISBN 978-0-7506-8632-7.

Speight, J.G. 2011b. An Introduction to Petroleum Technology, Economics, and Politics. Hoboken – Massachusetts, USA. Wiley-Scrivener, John Wiley & Sons. p. 320. ISBN 978-1-118-01299-4.

Speight, J.G. 2014. The Chemistry and Technology of Petroleum. Boca Raton, USA. CRC Press. p. 913. ISBN 978-1-4398-7390-8.

Speight, J.G. 2015. Handbook of Petroleum product Analysis. Hoboken, USA. John Wiley & Sons, Inc. p. 345. ISBN 978-1-118-36926-5.

Speight, J.G. 2016. Introduction to Enhanced Recovery Methods for Heavy Oil and Tar Sands. Cambridge, USA. Oxford, UK. Gulf Professional Publishing. p.563. ISBN 978-0-12-849906-1.

Speight, J.G. 2017. Rules of Thumb for Petroleum Engineers. Hoboken - Beverly, USA. Wiley - Scrivener. p. 753. ISBN 978-1-118-59526-8.

Speight, J.G., Arjoon, K.K. 2012. Bioremediation of Petroleum and Petroleum Products. Salem - Hoboken, USA. Wiley - Scrivener. p. 567. ISBN 978-0-470-93849-2.

Speight, J.G., Exall, D.I. 2014. Refining Used Lubricating Oils. Boca Raton, USA. CRC Press. p. 442. ISBN 978-1-4665-5150-3.

Squillace, P.J., Pankow, J.F., Korte, N.E., Zogorski, J.S. 1997. Review of the environmental behavior and fate of methyl tert-butyl ether. Environmental Toxicology and Chemistry. 16(9). 1836-1844.

Steinberg, S.M., Schmeltzer, J.S., Kreamer, D.K. 1996. Sorption of benzene and triehioroethylene (TCE) on a desert Soil: Effects of moisture and organic matter. Chemosphere, 33(5). 961-980.

Stewart, M., North, L. 2006. A borehole geophysical method for detection and quantification of dense, non-aqueous phase liquids (DNAPL) in saturated soils. Journal of Applied Geophysics. 60(2). 87-99.

Stoker, H.S. 2013. General, Organic, and Biological Chemistry. Belmont, USA. Brooks/Cole. p. 1045. ISBN 1-133-10394-4.

Sutherland, J., Adams, C., Kekobad, J. 2004. Treatment of MTBE by air stripping, carbon adsorption, and advanced oxidation: technical and economic comparison for five groundwaters. Water Research. 38(1). 193-205.

Suthersan, S.S., Horst, J., Schnobrich, M., Welty, N., McDonough, J. 2017. Remediation Engineering: Design Concepts. Boca Raton, USA. CRC Press. p. 603. ISBN 978-1-4987-7327-0.

Swartjes, F.A. 2011. Introduction to contaminated site management. In Swartjes F.A. (ed): Dealing with Contaminated Sites: From Theory towards Practical Application. Dordrecht, The Netherlands: Springer. p. 3-89. ISBN 978-90-481-9757-6.

Sylvester-Bradley, P.C., King, R.J. 1963. Evidence for abiogenic hydrocarbons. Nature. 198(4882). 728-731.

Tan, K.H. 2011. Principles of Soil Chemistry. Boca Raton, USA. CRC Press. p. 362. ISBN 978-1-4398-1395-9.

Tan, Z. 2014. Air Pollution and Greenhouse Gases: From Basic Concepts to Engineering Applications for Air Emission Control. Singapore. Springer. p. 481. ISBN 978-981-287-211-1.

Taslak, E., Kocatepe, C., Arıkan, O., Kumru, C.F. 2015. Electrical analysis of corn oil as an alternative to mineral oil in power transformers. World Academy of Science, Engineering and Technology. 9(8). 873-877.

Tavassoli, Z., Zimmerman, R.W., Blunt, M.J. 2005. Analytic Analysis for Oil Recovery During Counter-Current Imbibition in Strongly Water-Wet Systems. Transp Porous Med. 58. 173–189.

Tek, M.R. 1961. Multiphase flow of water, oil and natural gas through vertical flow strings. Journal of Petroleum Technology. 13(10). 1029-1036.

Thomas, A.M. 1966. In situ measurement of moisture in soil and similar substances by `fringe' capacitance. Journal of Scientific Instruments. 43(1). 21-27.

Thomas, S. 2008. Enhanced oil recovery - An overview. Oil & Gas Science and Technology. 63(1). 9-19.

Thomsen, A., Schelde, K., Drøscher, P., Steffensen, F. 2007. Mobile TDR for geo-referenced measurement of soil water content and electrical conductivity. Precision Agric. 8(4-5). 213–223.

Thomson, N.R., Graham, D.N., Farquhar, G.J. 1992. One-dimensional immiscible displacement experiments. Journal of Contaminant Hydrology. 10(3). 197-223.

Tiab, D., Donaldson, E.C. 2016. Petrophysics: Theory and Practice of Measuring Reservoir Rock and Fluid Transport Properties. Waltham, USA. Elsevier Inc. p. 894. ISBN 978-0-12-803188-9.

Tong, S., von Schirnding, Y.E., Prapamontol, T. 2000. Environmental lead exposure: a public health. Bulletin of the World Health Organization. 78(9). 1068-1077.

Topp, G.C. 2003. State of the art of measuring soil water content. Hydrological Processes. 17(14). 2993-2996.

Topp, G.C., Davis, J.L., Annan, A.P. 1980. Electromagnetic determination of soil water content: Measurements in coaxial transmission lines. Water Resources Research. 16(3). 574-582.

Topp, G.C., Ferré, P.A. 2002. Water Content: General Information. In Dane J. H., Topp, G. C. (eds): Methods of Soil Analysis: Part 4 - Physical Methods. Madison, USA. Soil Science Society of America. p. 417- 446. ISBN 978-0-891-18841-4.

Total Petroleum Hydrocarbon Criteria Working Group 1998. Total Petroleum Hydrocarbon Criteria Working Group Series: Volume 1- Analysis of Petroleum Hydrocarbons in Environmental Media. Amherst, USA. Amherst Scientific Publishers. p. 98. ISBN 1-884-940-14-5.

Travis, C.C., MacInnis, J.M. 1992. Vapor extraction of organics from subsurface soils. Is it effective?. Environmental Science & Technology. 26(10). 1885-1887.

Tsai, T.T., Kao, C.M. 2009. Treatment of petroleum-hydrocarbon contaminated soils using hydrogen peroxide oxidation catalyzed by waste basic oxygen furnace slag. Journal of Hazardous Materials. 170(1). 466-472.

Twidell, J., Weir, T. 2015. Renewable Energy Resources. New York, USA. Routledge. p. 784. ISBN 978-0-415-58437-1.

US Department of Energy 2000. Hydrous Pyrolysis Oxidation/Dynamic Underground Stripping. Visalia, USA. US Department of Energy. Innovative Technology Summary Reports. p. 22.

US EIA 2015. https://www.eia.gov/dnav/ng/hist/e_ertwo_xwde_nus_fwa.htm. [Online]

Available at: https://www.eia.gov/dnav/ng/hist/e_ertwo_xwde_nus_fwa.htm

US EPA 1986. Method 8100: Polynuclear Aromatic Hydrocarbons. US Environmental Protection Agency. Washington DC, USA.

US EPA 1992. Dense Nonaqueous Phase Liquids: A Workshop Summary. EPA/600/R-92/030, US Environmental Protection Agency. Washington DC, USA.

US EPA 1994a. Method 1664: N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons). EPA-821-B-94-004, US Environmental Protection Agency. Washington DC, USA.

US EPA 1994b. Method 9071A: Oil and Grease Extraction Method for Sludge and Sediment Samples. US Environmental Protection Agency. Washington DC, USA.

US EPA 1996a. Method 4030: Soil Screening for Petroleum Hydrocarbons by Immunoassay. US Environmental Protection Agency. Washington DC, USA.

US EPA 1996b. Method 3540C: Soxhlet Extraction. US Environmental Protection Agency. Washington DC, USA.

US EPA 1996c. Method 8440: Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry. United States Environmental Protection Agency. Washington DC, USA.

US EPA 1998. EPA Method 9071B: n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples.: US Environmental Protection Agency. Washington DC, USA.

US EPA 2000a. Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136). EPA/821-R-00-003, US Environmental Protection Agency. Washington DC, USA.

US EPA 2000b. Wastewater Technology Fact Sheet: Granular Activated Carbon Adsorption and Regeneration. EPA 832-F-00-017, US Environmental Protection Agency. Washington DC, USA.

US EPA 2004. Cleaning Up the Nation's Waste Sites: Markets and Technology Trends. EPA 542-R-04-015, US EPA/National Service Center for Environmental Publications (NSCEP). Cincinnati, USA.

US EPA 2005. A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL). EPA 542-R-04-011, US EPA National Service Center for Environmental Publications. Cincinnati, USA.

US EPA 2007a. Method 3546: Microwave Extraction. US Government: US Environmental protection Agency. Washington DC, USA.

US EPA, 2007b. Method 3550C: Ultrasonic Extraction. US Government: United States Environmental Protection Agency. Washington DC, USA.

US EPA, 2010. Method 1664 Revision B: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry. EPA-821-R-10-001, US Environmental protection Agency. Washington DC, USA.

US National Academy of Science 2000. Natural Attenuation for Groundwater Remediation. Washington DC, USA. National Academy Press. p. 274. ISBN 0-309-51645-5.

US National Academy of Sciences 2012. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. Washington DC, USA. The National Academies press. p. 326. ISBN 978-0-309-27874-4.

US National Research Council 1988. Frontiers in Chemical Engineering: Research Needs and Opportunities. Washington DC, USA. National Academies Press. p. 223. ISBN 0-309-55519-1.

US National Research Council 1999. Groundwater & Soil Cleanup: Improving Management of Persistent Contaminants. Washington DC, USA. National Academy Press. p. 285. ISBN 0-309-51961-6.

US National Research Council 2000. Natural Attenuation for Groundwater Remediation. Washington DC, USA. National Academy Press. p. 274. ISBN 978-0-309-06932-8.

US OTA, 1984. Acid Rain and Transported Air Pollutants: Implications for Public Policy. Washington DC, USA. OTA-O-204, US Congress, Office of Technology Assessment. US Government Printing Office. p. 323.

Valente, A., Morais, R., Tuli, A., Hopmans, J.W., Kluitenberg, G.J. 2006. Multi-functional probe for small-scale simultaneous measurements of soil thermal properties, water content, and electrical conductivity. Sensors and Actuators A. 132(1). 70-77.

Vallero, D.A. 2004. Environmental Contaminants: Assessment and Control. San Diego, USA. Academic Press. p. 801. ISBN 0-12-710057-1.

van der Perk, M. 2006. Soil and Water Contamination: From Molecular to Catchment Scale. London, UK. CRC Press. p. 402. ISBN 0-415-40943-8.

van Dijke, M.I.J., Sorbie, K.S. 2002. Pore-scale network model for three-phase flow in mixed-wet porous media. Physical Review E. 66(4). 046302: 1-14.

van Dijke, M.I.J., van der Zee, S.E.A.T.M., van Duijn, C.J. 1995. Multi-phase flow modeling of air sparging. Advances in Water Resources. 18(6). 319-333.

Vandenabeele, P. 2013. Practical Raman spectroscopy: an introduction. Chichester, UK. John Wiley & Sons. p. 167. ISBN 978-0-470-68318-7.

Verdura, T.M., Brunette, G., Shah, R. 2003. Lubricating Greases. In Totten, G.E., Westbrook, S.R., Shah. R.J (ed): Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing. West Conshohocken, USA. ASTM International. pp. 557-572. ISBN 0-8031-2096-6.

Verhoef, A., Egea, G. 2013. Soil Water and Its Management. In Gregory, P.J., Nortcliff, S. (eds): Soil Conditions and Plant Growth. Chichester, UK. Wiley-Blackwell. p. 269-322. ISBN 978-1-4051-9770-0.

Verweij, J.M. 1993. Hydrocarbon Migration Systems Analysis. Amsterdam, The Netherlands. Elsevier Science Publishers. p. 276. ISBN 0-444-89103-X.

Vidali, M. 2001. Bioremediation. An overview. Pure & Applied Chemistry. 73(7). 1163-1172.

Villalobos, M., Avila-Forcada, A.P., Gutierrez-Ruiz, M.E. 2008. An improved gravimetric method to determine total petroleum hydrocarbons in contaminated soils. Water Air Soil Pollut. 194(1-4). 151-161.

Viswanath, D.S., Ghosh, T.K., Prasad, D.H., Dutt, N.V., Rani, K.Y. 2007. Viscosity of Liquids: Theory, Estimation, Experiment, and Data. Dordrecht, The Netherlands. Springer. p. 660. ISBN 978-1-4020-5481-5.

Vizika, O., Avraam, D.G., Payatakes, A.C. 1994. On the role of the viscosity ratio during low-capillary-number forced imbibition in porous media. Journal of Colloid and Interface Science. 165(2). 386-401.

Vogeler, I., Green, S.R., Clothier, B.E., Kirkham, M.B., Robinson, B.H. 2001. Contaminant Transport in the Root Zone. In Iskandar I.K., Kirkham, M.B. (eds): Trace Elements in Soil: Bioavailability, Flux, and Transfer. Boca Raton, USA: Lewis Publishers. p. 175 - 197. ISBN 1-56670-507-X.

Waduge, W.A.P., Soga, K., Kawabata, J. 2004. Effect of NAPL entrapment conditions on air sparging remediation efficiency. Journal of Hazardous Materials. 110(1-3). 173-183.

Wagner, O.R., Leach, R.O. 1966. Effect of Interfacial Tension on Displacement Efficiency. Society of Petroleum Engineers Journal. 6(04). 335-344.

Walters, C.C. 2006. The Origin of Petroleum. In Hsu, C.S., Robinson, P.R. (eds): Practical Advances in Petroleum Processing. New York, USA. Springer. p. 79-101. ISBN 0-387-25811-6.

Wanfang, Z., Wheater, H.S., Johnston, P.M. 1997. State of the art of modelling two-phase flow in fractured rock. Environmental Geology. 31(3-4). 157-166.

Wang, C., Yuan, W., Qi, H. 2013. Study on the Associated Removal of Pollutants from Coal-Firing Flue Gas Using Biomass Activated Carbon Pellets. In Qi, H., Zhao, B. (eds): Cleaner Combustion and Sustainable World. New York, USA. Springer-Verlag Berlin Heidelberg and Tsinghua University Press. p. 433-439. ISBN 978-3-642-304446.

Wang, D. 2013. Polymer Flooding Practice in Daqing. In Sheng, J. (ed): Enhanced Oil Recovery Field Case Studies. Waltham: Gulf Professional Publishing. p. 83-116. ISBN 978-0-12-386545-8.

Wang, Y., Lu, Z., Han, Y., Feng, Y., Tang, C. 2011. A Novel thermoviscosifying water-soluble polymer for enhancing oil recovery from high-temperature and high-salinity oil reservoirs. Advanced Materials Research. 306-307. 654-657.

Wang, Z., Fingas, M., Sigouin, L. 2002. Using multiple criteria for fingerprinting unknown oil samples having very similar chemical composition. Environmental Forensics. 3(3-4). 251-262.

Wan, P.J., Pakarinen, D.R., Hron, R.J., Richard, O.L., Conkerton, E.J. 1995. Alternative hydrocarbon solvents for cottonseed extraction. JAOCS. 72(6). 653-659.

Watts, R.J., Kong, S., Dippre, M., Barnes, W. 1994. Oxidation of sorbed hexachlorobenzene in soils using catalyzed hydrogen peroxide. Journal of Hazardous Materials. 39(1). 33-47.

Watts, R.J., Stanton, P.C., Howsawkeng, J., Teel, A.L. 2002. Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide. Water Research. 36(17). 4283-4292.

Wei, B., Lu, L., Pu, W., Jiang, F., Li, K., Sun, L., Jin, F. 2017. From phase behavior to understand the dominant mechanism of alkali-surfactant-polymer flooding in enhancing heavy oil recovery. Journal of Surfactants and Detergents. 20(2). 355-366.

Weidong, L., Litao, L., Guangzhi, L., Luo, Z., Yunyun, W., Wei, J. 2017. Experimental study on the mechanism of enhancing oil recovery by polymer – surfactant binary flooding. Petroleum Exploration and Development. 44(4). 636-643.

Weiner, E. R., 2013. Applications of Environmental Aquatic Chemistry: A Practical Guide. Boca Raton, USA. CRC Press. p. 580. ISBN 978-1-4398-5333-7.

Weng, C.H., Hsu, M.C. 2008. Regeneration of granular activated carbon by an electrochemical process. Separation and Purification Technology. 64(2). 227-236.

West, C.C., Harwell, J.H. 1992. Surfactants and subsurface remediation. Environmental Science & Technology. 26(12). 2324-2330.

Widdowson, M.A., Molz, F.J., Benefield, L.D. 1988. A numerical transport model for oxygen- and nitrate-based respiration linked to substrate and nutrient availability in porous media. Water Resour. Res. 24(9). 1553-1565.

Wiedemeier, T.H., Rifai, H.S., Newell, C.J., Wilson, J.T. 1999. Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. New York, USA. John Wiley & Sons, Inc. p. 617. ISBN 0-471-19749-1.

Wilson, R.D., Mackay, D.M. 1995. Direct determination of residual nonaqueous phase liquids in the saturated zone using SF6 as a partitioning trace. Environmental Science & Technology. 29(5). 1255-1258.

Wilson, V., Power, C., Giannopoulos, A., Gerhard, J., Grant, G. 2009. DNAPL mapping by ground penetrating radar examined via numerical simulation. Journal of Applied Geophysics. 69(3-4). 140-149.

Winegardner, D.L., Testa, S.M. 2000. Restoration of Contaminated Aquifers: Petroleum Hydrocarbons and Organic Compounds. Boca Raton, USA. CRC Press. p. 446. ISBN 1-56670-320-4.

Wohlfahrt, C. 1991. Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures. Berlin, Germany. Springer-Verlag. p. 473. ISBN 3-540-54417-8.

Wohlfarth, C. 2008. Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures. Berlin, Germany. Springer-Verlag Berlin Heidelberg. p. 1658. ISBN 978-3-540-75505-0.

Wooding, R.A., Morel-Seytoux, H.J. 1976. Multiphase fluid flow through porous media. Annual Review of Fluid Mechanics. 8. 233-274.

Wu, K. 1998. Measurement of soil moisture change in spatially heterogeneous weathered soils using a capacitance probe. Hydrological Processes. 12(1). 135-146.

Wu, Y.S. 2016. Multiphase Fluid Flow in Porous and Fractured Reservoirs. Waltham, USA. Elsevier Inc. p. 401. ISBN 978-0-12-803848-2.

XiangLan, Z., Yan, Z., Qiong, L., Wei, Z. 2012. Surface properties of activated carbon from different raw materials. International Journal of Mining Science and Technology. 22(4). 483-486.

Xu, W., Ok, J.T., Xiao, F., Neeves, K.B., Yin, X. 2014. Effect of pore geometry and interfacial tension on water-oil displacement efficiency in oil-wet microfluidic porous media analogs. Physics of Fluids. 26(9). 093102:1-16.

Yadav, B.K., Hassanizadeh, S.M. 2011. An overview of biodegradation of LNAPLs in coastal (semi)-arid environment. Water Air Soil Pollut. 220(1-4). 225-239.

Yang, C., Wang, Z., Hollebone, B.P., Brown, C.E., Yang, Z., Landriault, M. 2015. Chromatographic Fingerprinting Analysis of Crude Oils and Petroleum Products. In Fingas, M.(ed): Handbook of Oil Spill Science and Technology. Hoboken, USA. John Wiley & Sons, Inc. p. 95-163. ISBN 978-0-470-45551-7.

Yang, M.C., Yu, D.G. 1998. Influence of activation temperature on the properties of polyacrylonitrile-based activated carbon hollow fiber. Journal of Applied Polymer Science. 68(8). 1331-1336.

Yang, Q., Luo, W., Jiang, Z., Li, W., Yuan, D. 2016. Improve the prediction of soil bulk density by cokriging with predicted soil water content as auxiliary variable. J Soils Sediments. 16(1). 77–84.

Yang, R.T. 2003. Adsorbents: Fundamentals and Applications. Hoboken, USA. Wiley-Interscience. p. 410. ISBN 0-471-29741-0.

Yang, Z., Zandin, H., Niemi, A., Fagerlund, F. 2013. The Role of Geological Heterogeneity and Variability in Water Infiltration on Non-aqueous Phase Liquid Migration. Environmental Earth Science. 68. 2085–2097.

Yaron, B. 1989. On the Behavior of Petroleum Hydrocarbons in the Unsaturated Zone: Abiotic Aspects. In Gerstl, Z., Chen, Y., Mingelgrin, U., Yaro, B. (eds): Toxic Organic Chemicals in Porous Media. Berlin, Germany. Springer-Verlag. p. 211-230. ISBN 978-3-642-74470-9.

Yener, J., Kopac, T., Dogu, G., Dogu, T. 2008. Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon. Chemical Engineering Journal. 144(3). 400-406.

Ye, Y. 2013. Development of the Experiment Detection Technique. In Ye, Y., Liu, C. (eds): Natural Gas Hydrates: Experimental Techniques and Their Applications. Dordrecht, The Netherlands. Springer. p. 19-87. ISBN 978-3-642-31100-0.

Yildiz, H.O., Valat, M., Morrow, N.R. 1999. Effect of brine composition on wettability and oil recovery of a Prudhoe Bay crude oil. Journal of Canadian Petroleum Technology. 38(1). 26-31.

Ying, W.C., Dietz, E.A., Woehr, G.C. 1990. Adsorptive capacities of activated carbon for organic constituents of wastewaters. Environmental Progress & Sustainable Energy. 9(1). 1-9.

Yong, R.N., Mulligan, C.N. 2004. Natural Attenuation of Contaminants in Soils. Boca Raton, USA. CRC Press. p. 319. ISBN 0-203-59150-X.

Yong, R.N., Nakano, M., Pusch, R. 2012. Environmental Soil Properties and Behavior. Boca Raton, USA. CRC Press. p. 432. ISBN 978-1-4398-4530-1.

Yoon, H., Valocchi, A.J., Werth, C.J. 2003. Modeling the Influence of Water Content on Soil Vapor Extraction. Vadose Zone Journal. 2(3). 368–381.

Yoon, Y.Y., Koh, D.C., Lee, K.Y., Cho, S.Y., Yang, J.H., Lee, K.K. 2013. Using 222Rn as a naturally occurring tracer to estimate NAPL contamination in an aquifer. Applied Radiation and Isotopes. 81. 233-237.

Yortsos, Y.C., Fokas, A.S. 1983. An analytical solution for linear waterflood including the effects of capillary pressure. Society of Petroleum Engineers Journal. 23(01). 115-124.

Young, R.N., Thomas, H.R. 2004. Geoenvironmental Engineering: Integrated Management of Groundwater and Contamination Land. London, UK. Thomas Telford Publishing. p. 599. ISBN: 0-7277-3277-3.

Yu, C., Warrick, A.W., Conklin, M.H. 1999. Derived functions of time domain reflectometry for soil moisture measurement. Water Resources Research. 35(6). 1789-1796.

Yüksel, F., Yüksel, B. 2004. The use of ethanol–gasoline blend as a fuel in an SI engine. Renewable Energy. 29(7). 1181-1191.

Zalidis, G.C., Annable, M.D., Wallace, R.B., Hayden, N.J., Voice, T.C. 1991. A laboratory method for studying the aqueous phase transport of dissolved constituents from residually held NAPL in unsaturated soil columns. Journal of Contaminant Hydrology. 8(2). 143-156.

Zegelin, S.J., White, I., Jenkins, D.R. 1989. Improved field probes for soil water content and electrical conductivity measurement using time domain reflectometry. Water Resources Research. 25(11). 2367-2376.

Zhang, H. 2002. Regeneration of exhausted activated carbon by electrochemical method. Chemical Engineering Journal. 85(1). 81-85.

Zhang, M., Kruse, N.A., Bowman, J.R., Jackson, G.P. 2016a. Field analysis of polychlorinated biphenyls (PCBs) in soil using solid-phase microextraction (SPME) and a portable gas chromatography-mass spectrometry system. Applied Spectroscopy. 70(5). 785-793.

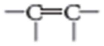
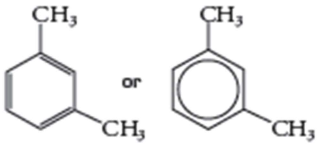
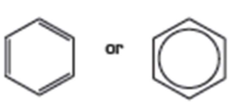
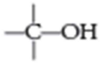
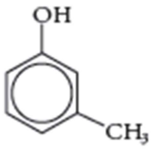
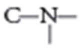
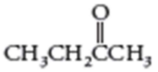
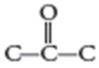
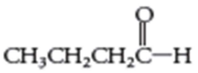
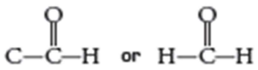
Zhang, S., Howard, K., Otto, C., Ritchie, V., Sililo, O.T., Appleyard, S. 2004. Sources, Types, Characteristics and Investigation of Urban Gorundwater Pollutants. In Lerner, D. N. (ed): Urban Groundwater Pollution. Lisse, The Netherlands. Swets & Zeitlinger B.V. p. 53 - 107. ISBN 0-203-97132-9.

Zhang, Y. 2004. Indoor Air Quality Engineering. Boca Raton, USA. CRC Press. p. 601. ISBN 978-0-203-48855-3.

Zoller, U. 2009. Application of Surfactants in Environmental Remediation. In Zoller, U. (ed): Handbook of Detergents: Part E. Applications. Boca Raton, USA. CRC Press. p. 363-373. ISBN 978-1-57444-757-6.

Zou, C., Ge, J., Zhao, P., Cui, C., Zhang, L. 2012. β -Cyclodextrin and methacrylic acid octyl phenols poly (ethylene oxide) ester modified acrylamide polymer for enhancing oil recovery. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry. 49(2). 171-177.

Appendix A. Important Families of Organic Compounds, taken from Raymond (2014), P.138

Family	Example	Functional group	Description
Alkane	$CH_3CH_2CH_2CH_3$		Hydrocarbons in which carbon atoms are joined only by single bonds.
Alkene	$CH_2{=}CHCH_2CH_3$	 $-\underset{\mid}{C}{=}\underset{\mid}{C}-$	Contain at least one carbon–carbon double bond.
Alkyne	$HC{\equiv}CCH_2CH_3$	$-C{\equiv}C-$	Contain at least one carbon–carbon triple bond.
Aromatic			Cyclic compounds in which rings have alternating double and single bonds.
Alcohol	$CH_3CH_2CH_2CH_2OH$	 $-\underset{\mid}{\overset{\mid}{C}}-OH$	Have an —OH group attached to an alkane-type carbon atom (a carbon atom that is singly bonded to carbon or hydrogen atoms).
Phenol			Contain an —OH group attached to an aromatic ring.
Ether	$CH_3CH_2OCH_2CH_3$	$C-O-C$	Contain a C—O—C linkage in which the carbon atoms are alkane-type or aromatic.
Thiol	$CH_3CH_2CH_2CH_2SH$	$C-SH$	Have an —SH group attached to an alkane-type or aromatic carbon atom.
Sulfide	$CH_3CH_2SCH_2CH_3$	$C-S-C$	Contain a C—S—C linkage in which the carbon atoms are alkane-type or aromatic.
Disulfide	$CH_3CH_2SSCH_2CH_3$	$C-S-S-C$	Contain a C—S—S—C linkage in which the carbon atoms are alkane-type or aromatic.
Amine	$CH_3CH_2NHCH_2CH_3$	 $C-\underset{\mid}{N}-$	Contain a nitrogen atom attached to one, two, or three carbon atoms, excluding C=O carbon atoms.
Alkyl halide	$CH_3CH_2CH_2Br$	$C-X$ $X = F, Cl, Br, I$	Have a halogen atom attached to an alkane-type carbon atom.
Ketone	 $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$	 $C-\overset{\overset{O}{\|}}{C}-C$	Contain a carbonyl group in which the carbonyl carbon is attached to two other carbon atoms.
Aldehdye	 $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-H$	 $C-\overset{\overset{O}{\|}}{C}-H$ or $H-\overset{\overset{O}{\|}}{C}-H$	Contain a carbonyl group in which the carbonyl carbon is attached to one carbon atom and one hydrogen atom or to two hydrogen atoms.

Note: Carboxlic acid, Ester and Amide are also improtant families of organic compuonds but left out of the Appendix due to the lack of enough space

Appendix B. Some basic properties of Marcol 82 used in the experiment, taken from www.exxonmobil.com

Property	Test Method	Typical	Min	Max
Appearance	Visual	-	Clear & Bright	
Odour	Olfactory	-	Odorless	
Color, Saybolt	ASTM D 6045	-	30	
Kinematic Viscosity @ 40ºC, mm²/s	ASTM D 445	-	14.5	17.5
Kinematic Viscosity @ 100ºC, mm²/s	ASTM D 445	3.6		
Dynamic Viscosity @ 20ºC, mPa.s	Calculated	-	27	37
Density @ 15ºC, kg/m3	ASTM D 4052	-	845	858
Relative Density @ 20ºC/20 °C	ASTM D 4052	-	0.843	0.857
Relative Density @25 °C/25 °C	ASTM d 4052	-	0.841	0.855
Pour Point, ºC	ASTM D 5950	-	-	-6
Flash Point, ºC	ASTM D 92	-	182	-
Refractive Index, nD^{20}	ASTM D 1218	-	1.464	1.47
Carbon Type, % and Paraffinic / Naphthenic / Aromatic	am-s 1805	65/ 35 / 0	-	-

Appendix C. Table that shows gravimetric water contents of packed activated carbon pellets (ACP) from Techpoint and Berrentag

ACP No	Techpoint ACP				Berrentag ACP			
	mass (g) of ACP			water content (%)	mass (g) of ACP			water content (%)
	BOD	AOD	Water		BOD	AOD	Water	
1	0.1362	0.344	0.0018	1.3	0.0722	0.0714	0.008	1.1
2	0.1434	0.1421	0.0013	0.9	0.0768	0.0760	0.0008	1.1
3	0.1603	0.1576	0.0027	1.7	0.0941	0.0904	0.0037	4.1
4	0.1479	0.1461	0.0018	1.2	0.0699	0.0688	0.0011	1.6
5	0.1585	0.1567	0.0018	1.1	0.0680	0.0673	0.0007	1.0
6	0.1614	0.1595	0.0019	1.2	0.0636	0.0630	0.0006	1.0
7	0.1440	0.1411	0.0029	2.1	0.0816	0.0804	0.0012	1.5
8	0.1439	0.1417	0.0022	1.6	0.0643	0.0637	0.0006	0.9
9	0.1610	0.1593	0.0017	1.1	0.0490	0.0490	0.0000	0.0
10	0.1550	0.1534	0.0016	1.0	0.0615	0.0611	0.0004	0.7
11	0.1393	0.1371	0.0022	1.6	0.0708	0.0689	0.0019	2.8
12	0.1576	0.1554	0.0022	1.4	0.0735	0.0723	0.0012	1.7
13	0.1634	0.1617	0.0017	1.1	0.0810	0.0786	0.0024	3.1
14	0.1618	0.1608	0.0010	0.6	0.0674	0.0671	0.0003	0.4
15	0.1592	0.1578	0.0014	0.9	0.0745	0.0735	0.0010	1.4
16	0.1620	0.1592	0.0028	1.8	0.0819	0.0805	0.0014	1.7
17	0.1560	0.1535	0.0025	1.6	0.0602	0.0599	0.0003	0.5
18	0.1422	0.1408	0.0014	1.0	0.0703	0.0696	0.0007	1.0
19	0.1470	0.1463	0.0007	0.5	0.0894	0.0864	0.0030	3.5
20	0.1580	0.1564	0.0016	1.0	0.0682	0.0675	0.0007	1.0

Appendix D. Table that shows sampled water and LNAPL from sample columns using ACP from Berrentag

Water : LNAPL	Mass (g) of ACP	Mass (g) of adsorbed			Adsorbed (%) of		
		water	LNAPL	Sum	water	LNAPL	Sum
100:0	0.0781	0.0562	0.0000	0.0562	71.96	0.00	71.96
100:0	0.0590	0.0367	0.0000	0.0367	62.20	0.00	62.20
100:0	0.0744	0.0211	0.0000	0.0211	28.36	0.00	28.36
100:0	0.0742	0.0577	0.0000	0.0577	77.76	0.00	77.76
100:0	0.0745	0.0148	0.0000	0.0148	19.87	0.00	19.87
100:0	0.0867	0.0463	0.0000	0.0463	53.40	0.00	53.40
90:10	0.0698	0.0109	0.0008	0.0117	15.62	1.17	16.79
90:10	0.0784	0.0113	0.0007	0.0120	14.41	0.90	15.31
90:10	0.0677	0.0125	0.0015	0.0140	18.46	2.25	20.71
90:10	0.0734	0.0124	0.0026	0.0150	16.89	3.51	20.40
90:10	0.0728	0.0141	0.0037	0.0178	19.37	5.14	24.51
90:10	0.0786	0.0119	0.0007	0.0126	15.14	0.89	16.03
75:25	0.0959	0.0143	0.0044	0.0187	14.91	4.63	19.55
75:25	0.0905	0.0165	0.0020	0.0185	18.23	2.20	20.43
75:25	0.0770	0.0131	0.0014	0.0145	17.01	1.82	18.84
75:25	0.0697	0.0113	0.0023	0.0136	16.21	3.36	19.57
75:25	0.0850	0.0178	0.0023	0.0201	20.94	2.75	23.69
75:25	0.0811	0.0163	0.0028	0.0191	20.10	3.46	23.56
65:35	0.0749	0.0118	0.0034	0.0152	15.75	4.53	20.28
65:35	0.0696	0.0116	0.0015	0.0131	16.67	2.18	18.85
65:35	0.0821	0.0168	0.0055	0.0223	20.46	6.70	27.16
65:35	0.0659	0.0112	0.0022	0.0134	17.00	3.37	20.37
65:35	0.0862	0.0139	0.0025	0.0164	16.13	2.85	18.97
65:35	0.0752	0.0136	0.0041	0.0177	18.09	5.44	23.53
50:50	0.0997	0.0152	0.0085	0.0237	15.25	8.56	23.81
50:50	0.0911	0.0154	0.0095	0.0249	16.90	10.40	27.30
50:50	0.0812	0.0134	0.0043	0.0177	16.50	5.33	21.83
50:50	0.0807	0.0113	0.0054	0.0167	14.00	6.67	20.67
50:50	0.1031	0.0116	0.0087	0.0203	11.25	8.39	19.65
50:50	0.0785	0.0090	0.0061	0.0151	11.46	7.75	19.21
35:65	0.0737	0.0073	0.0071	0.0144	9.91	9.68	19.59
35:65	0.0736	0.0107	0.0064	0.0171	14.54	8.74	23.28
35:65	0.0796	0.0124	0.0120	0.0244	15.58	15.13	30.71
35:65	0.0807	0.0121	0.0133	0.0254	14.99	16.52	31.52
35:65	0.0930	0.0167	0.0223	0.0390	17.96	24.02	41.98
35:65	0.0799	0.0120	0.0152	0.0272	15.02	19.03	34.05
25:75	0.0674	0.0089	0.0125	0.0214	13.20	18.57	31.77
25:75	0.0688	0.0090	0.0216	0.0306	13.08	31.45	44.53
25:75	0.0788	0.0113	0.0165	0.0278	14.34	20.93	35.27

25:75	0.0779	0.0145	0.0170	0.0315	18.61	21.77	40.38
25:75	0.1008	0.0164	0.0303	0.0467	16.27	30.05	46.32
25:75	0.0895	0.0110	0.0302	0.0412	12.29	33.72	46.01
10:90	0.0657	0.0063	0.0200	0.0263	9.59	30.44	40.03
10:90	0.0886	0.0071	0.0465	0.0536	8.01	52.54	60.55
10:90	0.0862	0.0106	0.0337	0.0443	12.30	39.08	51.37
10:90	0.0839	0.0074	0.0439	0.0513	8.82	52.28	61.10
10:90	0.0674	0.0076	0.0174	0.0250	11.28	25.86	37.13
10:90	0.0892	0.0078	0.0264	0.0342	8.74	29.63	38.38
0:100	0.0721	0.0010	0.0426	0.0436	1.39	59.05	60.43
0:100	0.0918	0.0012	0.0701	0.0713	1.31	76.32	77.62
0:100	0.0797	0.0008	0.0605	0.0613	1.00	75.87	76.87
0:100	0.0796	0.0012	0.0460	0.0472	1.51	57.74	59.25
0:100	0.0746	0.0011	0.0620	0.0631	1.47	83.09	84.57
0:100	0.0870	0.0016	0.0690	0.0706	1.84	79.32	81.16

Appendix E. Table that shows mass of prepared sample columns at different stages and drained out applied liquids

Applied Water to LNAPL Ratio	Mass of sample column and liquid applied (g)			Mass of drained out liquid from samplecolumn (g)		
	immediately after repacking	after applied water drained	Liquid in sample column	before oven dry	after oven dry	Loss
100:0	1278.23	1512.56	312.56	8.63	0.00	8.63
100:0	1279.17	1514.82	314.82	8.06	0.00	8.06
100:0	1280.29	1514.72	314.72	7.61	0.00	7.61
90:10	1235.25	1509.97	309.97	7.11	0.01	7.10
90:10	1235.70	1510.33	310.33	7.31	0.01	7.30
90:10	1235.65	1413.24	213.24	5.17	0.00	5.17
75:25	1273.47	1505.99	305.99	7.12	7.05	0.07
75:25	1276.03	1506.91	306.91	8.63	8.57	0.06
75:25	1276.20	1509.92	309.92	4.93	4.88	0.05
65:35	1279.65	1538.75	338.75	20.79	20.76	0.03
65:35	1281.00	1534.71	334.71	20.30	20.27	0.03
65:35	1280.57	1536.32	336.32	16.59	16.56	0.03
50:50	1267.65	1480.56	280.56	42.58	42.56	0.02
50:50	1269.02	1486.53	286.53	36.67	36.65	0.02
50:50	1268.40	1483.41	283.41	41.38	41.37	0.01
35:65	1269.02	1464.13	264.13	43.71	43.69	0.02
35:65	1269.25	1469.09	269.09	42.75	42.73	0.02
35:65	1269.95	1462.05	262.05	46.34	46.31	0.03
25:75	1287.77	1496.96	296.96	5.46	5.41	0.05
25:75	1286.86	1502.93	302.93	7.05	6.99	0.06
25:75	1286.70	1504.50	304.50	9.02	8.97	0.05
10:90	1240.69	1489.86	289.86	10.99	10.97	0.02
10:90	1241.54	1495.09	295.09	5.71	5.66	0.05
10:90	1240.86	1491.31	291.31	9.96	9.94	0.02
0:100	1268.13	1454.66	254.66	32.05	32.03	0.02
0:100	1268.75	1454.79	254.79	30.34	30.31	0.03
0:100	1268.71	1457.32	257.32	32.60	32.58	0.02

Appendix F. Table that shows average amount of liquid displaced every three minutes and oil recovered with it from sample colmuns subjected to 200 ml/h hexane flooding rate

	Amount of Liquid Recovered			Oil Recovered		
No	mass (g)	STDA	Volume (ml)	Mass (g)	STDA	Volume (ml)
1	9.1179	0.3273	11.5553	6.5562	0.3101	7.6681
2	9.2021	0.4312	11.7536	6.3533	0.4949	7.4308
3	9.0295	0.2923	11.6671	5.8491	0.1911	6.8410
4	8.8866	0.2341	11.6485	5.2791	0.1800	6.1744
5	8.6208	0.2436	11.4668	4.6422	0.2082	5.4294
6	8.4682	0.2618	11.4324	4.0755	0.3459	4.7666
7	8.3043	0.2519	11.3441	3.6140	0.3265	4.2268
8	8.2649	0.1852	11.4074	3.2603	0.2500	3.8132
9	8.1870	0.2517	11.3826	2.9920	0.2627	3.4994
10	8.1027	0.2419	11.3378	2.7529	0.3503	3.2198
11	7.9734	0.3163	11.2408	2.4677	0.4080	2.8862
12	7.8962	0.3498	11.2035	2.2383	0.3991	2.6179
13	7.7911	0.3429	11.1226	2.0122	0.3642	2.3535
14	7.7773	0.3738	11.1499	1.8737	0.3644	2.1914
15	7.6739	0.4638	11.0385	1.7429	0.3666	2.0385
16	7.7263	0.6554	11.1425	1.6723	0.3764	1.9559
17	7.3060	0.6191	10.5647	1.5001	0.2680	1.7544
18	7.5831	0.5199	11.0124	1.4216	0.1984	1.6627
19	7.4945	0.4697	10.9077	1.3363	0.1284	1.5630
20	7.5194	0.5093	10.9683	1.2708	0.0694	1.4863
21	6.8091	0.2517	9.9030	1.2345	0.3697	1.4439
22	6.8172	0.2419	9.9080	1.2556	0.2116	1.4685
23	6.8583	0.6554	9.9732	1.2475	0.3657	1.4591
24	6.8743	0.4697	9.9996	1.2413	0.2587	1.4518
25	6.8692	0.3322	9.9812	1.2719	0.4529	1.4876
26	6.8100	0.4566	9.8893	1.2779	0.3656	1.4946
27	6.7533	0.2896	9.4675	1.4431	0.4522	1.6878
28	6.7965	0.5458	9.8982	1.1935	0.3657	1.3959
29	6.7443	0.5969	9.8474	1.1119	0.4526	1.3005
30	6.7358	0.2557	9.8584	1.0430	0.3697	1.2199

Appendix G. Table that shows average amount of liquid displaced every three minutes and oil recovered with it from sample colmuns subjected to 200 ml/h ethanol flooding rate

	Amount of Liquid Recovered			Oil Recovered		
No	mass (g)	STDA	Volume (ml)	Mass (g)	STDA	Volume (ml)
1	8.7697	0.3243	10.2925	8.7829	0.2721	10.2724
2	8.7279	0.2759	10.3505	8.8395	0.3294	10.3386
3	8.8502	0.3790	10.3998	7.4047	0.7307	8.6604
4	8.4756	0.1055	10.1769	5.2486	0.5808	6.1387
5	8.3192	0.2356	10.2037	4.0048	1.2534	4.6839
6	8.1385	0.2834	10.0574	2.9894	0.4062	3.4963
7	8.2140	0.0655	10.3158	1.4821	0.3343	1.7334
8	7.9573	0.2958	10.0190	1.0437	0.2916	1.2207
9	7.9512	0.3006	10.0107	1.0307	0.1321	1.2055
10	7.9880	0.2180	10.0851	0.9014	0.1319	1.0543
11	7.9263	0.3692	10.0119	0.7905	0.0904	0.9246
12	7.8797	0.2155	9.9665	0.7159	0.1284	0.8373
13	7.9154	0.2606	10.0013	0.7161	0.0800	0.8375
14	8.0210	0.1590	10.1103	0.6387	0.0367	0.7470
15	7.8613	0.2996	10.0332	0.5957	0.0907	0.6967
16	7.9112	0.2113	9.9491	0.5469	0.1797	0.6397
17	7.8407	0.3249	9.9145	0.5529	0.1723	0.6467
18	8.0333	0.3009	10.1265	0.5089	0.1158	0.5952
19	7.9215	0.2025	10.0298	0.4652	0.1987	0.5442
20	7.8284	0.3471	9.9249	0.5132	0.0966	0.6002
21	7.6367	0.2324	9.6531	0.2647	0.0326	0.3096
22	7.7268	0.3636	9.7699	0.2376	0.0246	0.2779
23	7.4967	0.2569	9.4779	0.2415	0.0600	0.2825
24	7.7178	0.3546	9.7401	0.4261	0.0951	0.4984
25	7.6283	0.4012	9.6374	0.3162	0.0615	0.3698
26	7.7114	0.3696	9.7550	0.1903	0.0.237	0.2226
27	7.5118	0.2365	9.4933	0.2794	0.0260	0.3268
28	7.7244	0.3990	9.7524	0.3859	0.1003	0.4513
29	7.6471	0.3695	9.6717	0.2091	0.0370	0.2446
30	7.6455	0.2541	9.6651	0.2560	0.0211	0.2994

Appendix H. Table that shows average amount of liquid displaced every three minutes and oil recovered with it from sample colmuns subjected to 200 ml/h water flooding rate

	Amount of Liquid Recovered			Oil Recovered		
No	mass (g)	STDA	Volume (ml)	Mass (g)	STDA	Volume (ml)
1	8.6441	0.4307	10.1101	8.6441	0.4307	10.1101
2	8.4684	0.2677	9.9045	8.4684	0.2677	9.9045
3	8.6419	0.2373	10.1074	8.6419	0.2373	10.1074
4	8.5671	0.2799	10.0200	8.5671	0.2799	10.0200
5	8.3661	0.1504	9.7850	8.3661	0.1504	9.7850
6	9.9396	0.9946	10.2744	1.9744	0.5564	2.3092
7	9.8310	0.5702	9.9665	0.7990	0.2431	0.9345
8	10.3350	0.5152	10.4410	0.6252	0.2352	0.7312
9	9.8966	0.3832	9.9550	0.3443	0.2195	0.4027
10	9.6442	0.6712	9.7067	0.3681	0.2980	0.4306
11	10.7852	1.2396	10.8477	0.3684	0.1148	0.4308
12	9.9152	0.2989	9.9772	0.3655	0.0951	0.4274
13	9.8842	0.5028	9.9379	0.3166	0.0808	0.3703
14	9.4023	0.3704	9.4420	0.2346	0.1121	0.2743
15	9.7779	0.7959	9.8153	0.2202	0.0484	0.2576
16	9.5761	0.5263	9.5994	0.1373	0.0135	0.1606
17	10.8301	0.5047	10.8742	0.2603	0.0843	0.3045
18	9.9940	0.7559	10.0266	0.1923	0.0374	0.2249
19	10.0888	0.3846	10.1123	0.1385	0.0449	0.1620
20	10.4550	1.0070	10.4893	0.2021	0.0831	0.2364
21	9.7361	0.2689	9.7570	0.1231	0.0343	0.1439
22	10.2843	1.6082	10.3038	0.1153	0.0733	0.1348
23	9.5461	0.9412	9.5717	0.1511	0.0357	0.1767
24	10.5278	0.1397	10.5433	0.0913	0.0642	0.1067
25	9.8933	1.2939	9.9176	0.1431	0.0612	0.1674
26	10.6948	0.5441	10.7138	0.1120	0.0205	0.1310
27	9.3148	0.7104	9.3282	0.0791	0.0518	0.0925
28	10.7664	0.5372	10.7771	0.0629	0.0473	0.0736
29	9.1829	0.9338	9.2014	0.1093	0.0614	0.1278
30	10.4076	0.3152	10.4187	0.0653	0.0133	0.0764

Appendix I. Table that shows average amount of liquid displaced every six minutes and oil recovered with it from sample colmuns subjected to 100 ml/h water flooding rate

	Amount of Liquid Recovered			Oil Recovered		
No	Mass (g)	STDA	Volume (ml)	mass (g)	STDA	Volume (ml)
1	8.3611	0.3633	9.7791	8.3611	0.3633	9.7791
2	8.0471	0.2091	9.4118	8.0471	0.2091	9.4118
3	8.2827	0.2284	9.6874	8.2827	0.2284	9.6874
4	8.3055	0.2366	9.7140	8.3055	0.2366	9.7140
5	8.3135	0.1964	9.7234	8.3135	0.1964	9.7234
6	9.2187	0.7060	9.7779	3.2971	0.6658	3.8563
7	9.0211	0.5439	9.1108	0.5285	0.2742	0.6181
8	9.6834	0.2774	9.7365	0.3128	0.1841	0.3658
9	9.9681	0.2628	10.0388	0.4170	0.1971	0.4878
10	9.4158	0.6627	9.4538	0.2242	0.0780	0.2622
11	9.7267	0.3457	9.7775	0.2999	0.1382	0.3507
12	9.7092	1.3895	9.7659	0.3345	0.2288	0.3912
13	9.6197	0.6318	9.6551	0.2087	0.1618	0.2441
14	9.6507	0.7313	9.6926	0.2474	0.0541	0.2893
15	10.0581	0.1456	10.0922	0.2015	0.1387	0.2357
16	9.2411	0.3556	9.2778	0.2166	0.1178	0.2533
17	9.5962	1.0045	9.6218	0.1513	0.0657	0.1770
18	10.5226	0.3896	10.5414	0.1111	0.0368	0.1299
19	9.6386	1.1127	9.6573	0.1102	0.0669	0.1288
20	9.0064	0.5073	9.0109	0.0265	0.0114	0.0310
21	10.5270	0.2436	10.5508	0.1404	0.1186	0.1642
22	9.5558	0.7206	9.5658	0.0589	0.0247	0.0689
23	9.0977	0.7283	9.1052	0.0442	0.0427	0.0517
24	10.3548	0.9667	10.3710	0.0952	0.0956	0.1114
25	9.4792	1.5753	9.4858	0.0391	0.0432	0.0457
26	9.9911	0.7464	9.9937	0.0150	0.0127	0.0175
27	9.2789	0.5569	9.2801	0.0070	0.0047	0.0082
28	9.5113	0.4906	9.5239	0.0739	0.1235	0.0865
29	10.4092	0.5642	10.4134	0.0243	0.0381	0.0285
30	9.7265	0.5777	9.7281	0.0092	0.0127	0.0108

Appendix J. Table that shows average amount of liquid displaced every ninty seconds and oil recovered with it from sample colmuns subjected to 400 ml/h water flooding rate

	Amount of Liquid Recovered			Oil Recovered		
No	Mass (g)	STDA	Volume (ml)	mass (g)	STDA	Volume (ml)
1	8.5179	0.6526	9.9625	8.5179	0.6526	9.9625
2	8.7804	0.4293	10.2694	8.7804	0.4293	10.2694
3	8.7951	0.4454	10.2867	8.7951	0.4454	10.2867
4	8.6517	0.2927	10.1189	8.6517	0.2927	10.1189
5	9.5207	0.9556	10.3580	4.9371	2.4233	5.7744
6	9.5336	0.5382	9.7760	1.4291	0.2882	1.6714
7	10.0968	0.4866	10.2916	1.1489	0.3108	1.3437
8	10.4389	0.4322	10.6496	1.2428	0.4636	1.4536
9	9.8972	0.6862	10.0445	0.8685	0.2386	1.0158
10	9.6257	0.8145	9.7249	0.5847	0.1578	0.6838
11	10.5051	0.7535	10.5916	0.5104	0.2125	0.5970
12	10.3067	0.2274	10.3908	0.4956	0.0222	0.5796
13	9.3335	0.9399	9.4188	0.5028	0.0929	0.5881
14	9.7298	0.6117	9.7745	0.2635	0.0910	0.3081
15	10.7034	0.8962	10.7674	0.3770	0.0874	0.4409
16	9.7462	0.3794	9.7992	0.3125	0.1151	0.3655
17	10.7196	1.2982	10.7602	0.2393	0.0612	0.2799
18	10.0394	0.7075	10.0770	0.2221	0.0724	0.2598
19	10.2105	1.0176	10.2686	0.3423	0.1436	0.4003
20	9.6848	1.4119	9.7135	0.1692	0.0446	0.1979
21	9.9597	0.7666	9.9843	0.1450	0.0626	0.1696
22	10.4036	0.5691	10.4386	0.2065	0.0017	0.2415
23	9.5284	1.1819	9.5463	0.1056	0.0561	0.1235
24	9.7503	0.5825	9.7813	0.1829	0.1422	0.2139
25	10.2990	0.7093	10.3175	0.1090	0.0794	0.1275
26	10.6534	0.5961	10.6733	0.1172	0.0921	0.1371
27	9.6488	0.8469	9.6703	0.1272	0.0494	0.1488
28	10.3912	1.5161	10.4086	0.1026	0.0315	0.1200
29	9.8163	0.5737	9.8386	0.1318	0.1085	0.1542
30	10.3431	1.6380	10.3781	0.2062	0.1234	0.2411

Appendix K. Table that shows average amount of liquid displaced every fourty-five seconds and oil recovered with it from sample colmuns subjected to 800 ml/h water flooding rate

	Amount of Liquid Recovered			Oil Recovered		
No	Mass (g)	STDA	Volume (ml)	mass (g)	STDA	Volume (ml)
1	8.6032	0.2463	10.0622	8.6032	0.2463	10.0622
2	8.6733	0.2933	10.1442	8.6733	0.2933	10.1442
3	8.9418	0.3194	10.4582	8.9418	0.3194	10.4582
4	8.9786	0.6570	10.2479	7.4846	1.7065	8.7540
5	9.6273	0.6013	10.1299	2.9637	0.7322	3.4663
6	9.4919	0.3915	9.8449	2.0814	0.1623	2.4343
7	10.1083	0.4027	10.3950	1.6905	0.2325	1.9772
8	10.2442	0.2624	10.5029	1.5256	0.2177	1.7843
9	9.1979	0.3159	9.3507	0.9011	0.0590	1.0539
10	10.5211	0.9679	10.6779	0.9247	0.3096	1.0815
11	9.9074	0.8265	10.0497	0.8390	0.0881	0.9813
12	9.2904	0.1426	9.4231	0.7824	0.1785	0.9151
13	10.2454	0.1485	10.3443	0.5833	0.1188	0.6822
14	9.6021	0.3828	9.6947	0.5465	0.1627	0.6391
15	9.8695	0.5306	9.9745	0.6194	0.2427	0.7245
16	9.8377	0.4713	9.9215	0.4938	0.0365	0.5776
17	9.7935	0.4598	9.8683	0.4412	0.0269	0.5161
18	10.5080	0.6596	10.5752	0.3958	0.1471	0.4629
19	9.3356	0.6937	9.3978	0.3667	0.1387	0.4289
20	10.0937	1.9273	10.1590	0.3848	0.2129	0.4500
21	10.1335	0.8789	10.1894	0.3291	0.0535	0.3850
22	9.5356	0.7938	9.5774	0.2463	0.1382	0.2881
23	9.9427	0.5876	9.9850	0.2496	0.0254	0.2920
24	10.0708	1.3892	10.1050	0.2021	0.0607	0.2363
25	9.1513	1.1108	9.1723	0.1242	0.0583	0.1453
26	10.5444	0.0559	10.5769	0.1916	0.1912	0.2241
27	9.6837	0.9561	9.7081	0.1437	0.1102	0.1680
28	10.4392	1.0893	10.4634	0.1426	0.1190	0.1668
29	9.0690	0.0575	9.0942	0.1489	0.0561	0.1741
30	10.4037	0.6653	10.4238	0.1189	0.0414	0.1390

Appendix L. Table that shows amount of LNAPL left (%) after oven dry (105 °C, 24h) from successively recovered pure LNAPL from sample columns

No	LNAPL left after oven dry (%) in successive displacement					
	1st	2nd	3rd	4th	5th	control
1	99.52	99.77	99.83	99.84	99.89	*99.87*
2	99.64	99.80	99.86	99.90	99.90	99.98
3	99.66	99.84	99.88	99.89	99.84	99.97
4	99.67	99.84	99.87	99.90	99.91	99.89
5	99.66	99.83	99.90	99.92	99.81	99.94
6	99.56	99.85	99.88	99.91	99.86	99.88
7	99.49	99.76	99.82	99.83		99.89
8	99.62	99.81	99.81	99.85		99.89
9	99.68	99.86	99.86	99.87		99.92
10	99.54	99.79	99.84	99.82		*99.97*
11	99.68	99.81	99.86	99.90		99.92
12	99.57	99.84	99.86	99.85		99.86
13	99.73	99.88	99.93	99.93		99.88
14	99.59	99.83	99.86			
15	99.83	99.91	99.93			
16	99.67	99.87	99.90			
17	99.52	99.76	99.80			
18	99.69	99.84	99.88			
19	99.63	99.80	99.83			
20	99.56	99.80	99.80			
21	99.60	99.76	99.89			
22	99.47	99.74	99.79			
23	99.88	99.89	99.88			
24	99.70	99.87	99.90			
25	99.62	99.83	99.85			
26	99.63	99.84	99.88			
27	99.58	99.82				
28	99.73	99.88				
29	99.48	99.75				
30	99.51	99.77				
31	99.59	99.80				
32	99.70	99.84				
33	99.67	99.83				
34	99.59	99.83				
35	99.65	99.81				
36	99.90	99.79				

Appendix M. Table that shows Post Hoc Test result using Games-Howell in SPSS for the oven-dried pure LNAPL displaced at different order

(I) Order	(J) Order	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Displaced 1st	Displaced 2nd	-.1854*	.01707	.000	-.2336	-.1372
	Displaced 3rd	-.2288*	.01723	.000	-.2775	-.1802
	Displaced 4th	-.2454*	.01852	.000	-.2978	-.1929
	control	-.2800*	.01927	.000	-.3347	-.2253
Displaced 2nd	Displaced 1st	.1854*	.01707	.000	.1372	.2336
	Displaced 3rd	-.0435*	.01027	.001	-.0724	-.0146
	Displaced 4th	-.0600*	.01231	.000	-.0962	-.0238
	control	-.0946*	.01340	.000	-.1344	-.0548
Displaced 3rd	Displaced 1st	.2288*	.01723	.000	.1802	.2775
	Displaced 2nd	.0435*	.01027	.001	.0146	.0724
	Displaced 4th	-.0165	.01253	.682	-.0533	.0202
	control	-.0512*	.01361	.008	-.0915	-.0109
Displaced 4th	Displaced 1st	.2454*	.01852	.000	.1929	.2978
	Displaced 2nd	.0600*	.01231	.000	.0238	.0962
	Displaced 3rd	.0165	.01253	.682	-.0202	.0533
	control	-.0346	.01520	.188	-.0795	.0102
control	Displaced 1st	.2800*	.01927	.000	.2253	.3347
	Displaced 2nd	.0946*	.01340	.000	.0548	.1344
	Displaced 3rd	.0512*	.01361	.008	.0109	.0915
	Displaced 4th	.0346	.01520	.188	-.0102	.0795

Based on observed means.

The error term is Mean Square (Error) = .004.

*. The mean difference is significant at the .05 level.

Appendix N. Photo that shows: A) sampling of liquids from free liquid pool using activated carbon pellet (ACP), B) ACP used in the experiment, C) taking the mass of ACP, and D) measuring settling time of ACP

Appendix O. Photo that shows: A) sampling of water & LNAPL Porous media using ACP, B) soil moisture sensor and porous media for liquid content measurement, C) sample from sample column for gravimetric water & LNAPL content analysis, and D) sample prepared for the extraction of oil/LNAPL

Appendix P. Photo that shows: A) extraction of oil/LNAPL from destructed sample, and B) one of the sample columns prepared for the recovery of oil/LNAPL through injecting different liquids