Advanced Phytoremediation using Soil Solarization enhanced with Biosurfactant as a Novel Approach for Sustainable Remediation of Contaminated Land in the Niger Delta, Nigeria

By

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A PROJECT REPORT SUBMITTED TO THE FACULTY OF SCIENCE AND TECHNOLOGY, DEPARTMENT OF NATURAL SCIENCES, MIDDLESEX UNIVERSITY, LONDON, UK.

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DOCTOR OF PHYLOSOPHY (PhD) IN ENVIRONMENTAL SCIENCE.

Middlesex University London

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ABSTRACT

This PhD research was carried out to study soil solarization integration with phytoremediation enhanced with biosurfactant as a sustainable remediation option to hydrocarbon contaminated land and to evaluate sustainability feasibility in the Niger Delta contaminated land clean-up. A pilot study showed that native *C. odorata*, preliminary selected from a case study site in the region, produced higher biomass than *M. sativa* - a proven and well established phytoremediation plant. Rhamnolipid biosurfactant significantly reduced the PAHs in all amended treatments of both plants in the pilot study. *C. odorata* was employed to investigate the effect of soil solarization enhanced with biosurfactant (500 mg/kg) on phytoremediation of aged PAH contaminated soil (240 mg/kg). Solarization was carried out for 28 days before introducing seedlings of *C. odorata* for a 84 day phytoremediation period using a 4 x 4 and 2 x 4 cells microcosm to simulate the region's sub-tropical conditions for vegetated and un-vegetated treatments respectively. Soil solarization resulted in significant PAH reduction ($p \leq 0.01$) after the 28 days solarization period. Post-solarization significantly reduced ($p \leq 0.01$) PAHs in all solarized treatments compared to their non-solarized counterparts while biosurfactant did not contribute significantly ($p \geq 0.05$), due to possible denaturing by the relatively high soil temperatures recorded. The number of total soil/rhizosphere heterotrophic microorganisms increased in all solarized treatments but the increase was not statistically significant ($p \geq 0.05$). To ascertain the potential of phytoremediation in the region, a total of 32 stakeholder participants completed a questionnaire and five were further interviewed. The stakeholders scrutinized most of the default remediation techniques including covering with clean soil, excavation & disposal, thermal treatment (open burning) and concluded they were unsustainable, suggesting perceived sustainability and awareness of the different remediation techniques applicable or applied in the region. Phytoremediation and bioremediation were seen as the most sustainable remediation techniques due to being perceived as the least hazardous with high community acceptance. A holistic approach coupled with integrated sustainable remediation techniques of the type investigated in this study were seen as sustainable reparation to mitigate the current environmental, social and economic challenges to sustainability feasibility in remediation of contaminated land in the region. The novel and successful integration of soil solarization and phytoremediation using indigenous *C. odorata* as a combined techniques to treat even the most recalcitrant form of hydrocarbons-PAHs together with the technology acceptance by the local communities, open up new possibilities for a sustainable approach to remediate contaminated land in the oil rich Niger Delta region, Nigeria.

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LIST OF ABBREVIATIONS

B[a]P	Benzo[a]pyrene
CEC	Cation Exchange Capacity
CFU/g	Colony Forming Units per gram
CMC	Critical Micelle Concentration
CO_2	Carbon dioxide
DCM	Dichloromethane
Defra	Department for Environment Food & Rural Affairs
DHO	Dehydrogenase
DI	Deionize Water
EC_{50}	Half Maximal Effective Concentration
EPA	Environmental Protection Agency
EU	European Union
GC-FID/MS	Gas Chromatograph – Flame Ionization Detector/Mass Spectroscopy
GPS	Global Positioning System
GYEA	Glycerol Yeast Extract Agar
HPLC	High Pressure Liquid Chromatography
MJm^{-2}	Mega Joule per Square Meter
Mg/g	Milligram per gram
Mg/kg	Milligram per Kilogram
NO_3^- - N	Nitrate
NNPC	Nigerian National Petroleum Corporation
PAHs	Polycyclic Aromatic Hydrocarbons
POPs	Persistent Organic Pollutants
SDA	Sabouraud Dextrose Agar
SPDC	Shell Petroleum Development Company
SuRF-UK	Sustainable Remediation Forum UK

TTC	Tetrazolium Chloride
TSA	Tryptic Soya Agar
UNEP	United Nation Environmental Program
URE	Urease
USEPA	United State Environmental Protection Agency
WCED	World Commission on Environment and Development

GLOSSARY

Amended soil: The addition of biosurfactant to contaminated soil in order to improve the degradation of the soil's contaminants.

Biosurfactants: These are surface-active agents synthesized by microbes such as *Pseudomonas aeruginosa* with the ability to reduce surface tension and interfacial tensions between two immiscible liquids.

Microcosm: This is a bespoke growth chamber in miniature of the Niger Delta, Nigeria subtropical region to simulate contaminated land conditions.

Non-solarized soil: Soil treatment without transparent polythene sheets for 4 weeks solarization period.

Palliative Remediation: This is a type of remediation carried out by sub-standard contractors on the surface of impacted sites without actually removing the contaminants or cleaning the contaminated site to required or target values.

Phytoremediation: Phytoremediation is the application of plants to extract, degrade, contain, remove, sequester or immobilize contaminants in soil, water and other contaminated media.

Polycyclic Aromatic Hydrocarbon: Polycyclic aromatic hydrocarbons (PAHs) are a class of chemicals that consist of fused aromatic rings occurring naturally in crude oil, coal, and are produced as byproducts of incomplete combustion. As a pollutant, they are of concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic.

Rhizosphere: Rhizosphere is the region of the soil closest to the roots of plants and as a result under the direct influence of the root system.

Sustainable Remediation: Sustainable practices result in cleanups minimizing the environmental and energy 'footprints' of all actions taken during a project life.

Solarization: Soil solarization is a non-chemical soil treatment that uses radiation from the sun and a thin transparent film normally made of polyethylene to heat the soil to temperature range of 38 to 50^{o}C to a depth of about 10 to 20 cm for soil sterilization.

Solarized soil: Soil treatment covered with transparent polythene sheets for 4 weeks solarization period.

Un-amended soil: This is the opposite of "Amended" i.e. biosurfactant is not added to contaminated soil in order to improve the degradation of the soil's contaminants.

Weathered (Aged) PAH-contaminated soil: This is an artificially contaminated PAH soil, oven treated at 30 ^{o}C for 14 days to simulate the Niger Delta region's aged contaminated land exposed to subtropical environmental conditions

ACKNOWLEDGEMENT

I convey my deepest appreciation to my Supervisory Team, Professor Diane Purchase, Director of Studies and Dr. Huw Jones, Supervisor for their unfeigned support and commitment throughout this period. And for stimulating my interest and facilitating the opportunity of a life time. I will continue to be grateful to you and never could have had anyone better.

This research was jointly funded by Middlesex University UK/EU Research Studentship Award 2014 and Niger Delta Development Commission (NDDC) Foreign Postgraduate Scholarship Award 2014. Technical support were provided by Redloop Design and Innovation Centre and Eco-Remediation Technologies & Consultants Ltd. I am grateful to all my Research Group Members, Professor Hemda Garelick, Professor Diane Purchase, Dr. Huw Jones, Dr. Dirk Wildeboer, Dr. Khadija Isimekhai, Dr. Solomon Popoola, Job, Obed Amabogha and Priya.

I wish to express my profound and heartfelt gratitude to my family and friends for their inspiration, support and prayers. To my wonderful mum, Patience Erewa-Futughe, you are the best gift I ever had, this wouldn't have been possible without you. My brothers, Emmanuel Futughe, David Futughe and Michael Futughe and sister, Comfort Futughe-Etchie. To Mr. Sunny Mene for his timely assistance, Sam Aghomi who accompanied me around the Niger Delta region in particular through the creeks while I held my breath, and everyone too numerous to mention. Thank you! To a soul mate of eternal proportion, Mrs Oghomwen Lizzy Futughe, for her inestimable support, patience, love and endurance "…things were good when we were young…" Thank you for the love we share! To a very special friend, Engr. Nahid Bakri Bashir for grand inspiration. When I am with you, I can forget about the academic battlefield, drop my pen, switch off and unwind.

To my eldest brother, hero and mentor of blessed memory, Engr. Sampson Toritseju Futughe, who had since his departure being a great source of strength, motivation and inspiration. You prepared the stage for me, sadly you were not there to see me act out the scripts. No thanks to the cold hands of death. I only hope you would be proud of the actor I have become. Thank you for not given up on me even when I had given up on myself. To my disciplinarian, loving and intelligent dad, late Isaac Besigiwa Futughe, I see you through the mirror of myself. Thank you for the exceptional genes. Couldn't have asked for anything more!

Finally, He goes by so many names, Oritse, God, Allah, Jehovah, perhaps the '*God Particle*'. Hope they find *'It'* with the Large Hadron Collider at CERN. *'He'* gives and takes… To '*Him'* I am eternally grateful to be alive and well. Thank you.

DEDICATION

This PhD research is dedicated to the living memory of Kenule Beeson "Ken" Saro-Wiwa (10 October 1941 – 10 November 1995). A Nigerian writer, television producer, environmental activist, and winner of the Right Livelihood Award for "exemplary courage in striving non-violently for civil, economic and environmental rights" and the Goldman Environmental Prize. He was a voice against environmental degradation and pollution in the Niger Delta and Ogoniland in particular. Ken Saro-Wiwa non-violent campaign against multinational oil companies especially the Royal Dutch Shell and outspoken criticism of the Nigerian government, led to his death by hanging in 1995 after being found guilty by a special military tribunal of the gruesome murder of Ogoni chiefs at a pro-government meeting. His execution by the military dictator of General Sani Abacha, provoked international outrage and led to the suspension of Nigeria from the Commonwealth for over three years. According to Ken Saro-Wiwa environmental degradation and pollution:

> ***"is an ecological war in which no blood is spilled, no bones are broken, no one is maimed, so few are alarmed but men, women and children die, flora, fauna and fish perish, air, soil and water are poisoned: and finally, the land and its inhabitants die."***

Chapter 1

Introduction

CHAPTER ONE

1.0 INTRODUCTION

The Niger Delta in Nigeria is the world's second largest delta, third largest wetland and the largest in Africa (Awosika, 1995; Powell *et al.,* 1985). Since the advent of crude oil discovery in 1956, the Niger Delta region has been Nigeria's economic backbone with an estimated $600 billion revenue generated from oil accounting for over 90% of the country's total foreign exchange revenue (NDRMP, 2006; Shell, 2008a; Export, 2019). However, the region has been suffering many unpleasant environmental consequences associated with oil development that were not fully anticipated (Garrity and Levings, 1990; McGuiness, 1990; Burns *et al*., 1993; and Gesamp, 1993). Nigeria's growth and advancement in the oil industry in addition with the unchecked population proliferation and lack of pro-active environmental regulations resulted in large-scale damage to the environment, particularly in the Niger Delta region (Badejo and Nwilo, 2005b). According to Amnesty International (2009) the poorest and those who depend on traditional livelihoods such as fishing and agriculture are the most affected in the region. Ongoing activities including vandalization of oil pipelines by indigenous inhabitants; corrosion due to ageing pipelines; oil blow out from flow station; sabotage coupled with oil theft and illegal bunkering; inadequate care in loading and offloading of oil vessel etc. in the region, continue to release substantial amounts of crude oil, heavy metals and refined products into the fragile ecosystems. Crude oil spill pollution is a major threat to the region and if a state of emergency is not declared in relation with effective management and pragmatic remediation strategies, the productive but fragile ecosystem of the region may be annihilated due to continuous pollution and increasing energy demand (UNEP, 2011).

Generally, environmental pollution from crude oil spill especially in the Niger Delta is difficult to assess and often under-reported due to it being intensely extensive (Steiner, 2008). The Federal Government of Nigeria and the multinational oil companies, maintain their own data on spills, but since they are both limiting their legal liability for commensurate claims and compensations from oil spill damages, their own data cannot be considered to be reliable (Steiner, 2010). A summary of some of the major oil spills, actual and potential impact on the Niger Delta environment is presented in Table 1. Others include the 1970 Bomu II blowout; the 1985 Okoma pipeline spillage; the 2004 Oloibiri Well 14 oil spill (Zabbey, 2009; Ugochukwu and Ertel 2008). Most commonly, oil spillages are seldom reported or worst still under-reported by merely branding it minor without any contingent plan such as minimum post-spill containment, recovery and remediation strategies (Zabbey, 2009).

Globally, remediation of contaminated land presents enormous challenges. Various conventional remediation techniques such as excavation and landfilling, thermal desorption and incineration, sparging and venting, soil washing etc. consume energy and water, and often result in the incomplete contaminant or pollutant removal. These conventional methods also generate waste, pollute the atmosphere with toxic pollutants, produce greenhouse gases, and may have negative impact on the quality of life. In addition, manyof these techniques are expensive, labour intensive and result in extensive alteration to the physical, chemical and biological features of the treated soil (EU 2006; US EPA 2008; Schroder *et al*., 2008 and Futughe, 2012).

1.1 Background of the research

Environmental pollution in Nigeria, Niger Delta in particular from incidents spanning more than 50 years is far more pervasive than previously acknowledged and has generated global attention. According to a BBC report by Duffield (2010) Nigeria was branded the *'world oil pollution capital'.* The quality of life in the region is far below standard and increasingly unbearable as a result of the adverse impacts of oil spill. Majority of the population in the Niger Delta live in abject poverty and are susceptible to a number of health hazards and socio-economic constraints which for long has been the misfortune of the region. The region has been described as suffering from *"administrative neglect, crumbling social infrastructure and services, high unemployment, social deprivation, abject poverty, filth and squalor, and endemic conflict."* (UNDP, 2006). Some findings show water contamination exceeding 900 times the WHO standards and some communities have been observed to be using water from community wells far in excess of the safe limit (UNEP, 2011); these communities are still suffering the adverse health and environmental effects till date. From the records of the Department of Petroleum Resources (DPR), a total of 4,647 incidents gave rise to oil spill of 2,369,470 barrels into the Niger Delta environment between 1976 and 1996. Out of these huge quantities, it was estimated that 1,820,410.5 barrels (approximately 77%) were unrecovered from the environment and record showed that about 6%, 25%, and 69% of total oil spilled were in land, swamp and offshore respectively for this period (Badejo and Nwilo, 2005a). Pollution from oil spills in the region has become a phenomenon that reoccurs regularly and consequently become the bane of the Niger Delta, significant tension and agitation emerge between the host community indigenes and the multinational oil companies operating in the region (UNEP, 2006 and 2011).

Table 1: Summary of some oil spills in the Niger Delta region

Year	Activity/Event	Niger Delta State	Quantity in barrels	Environmental damages (actual and potential)
1978	GOCON's Escravos oil spill	Delta	300,000	Environmental pollution, drying up of vegetation and deprivation of plant and animal life. Large mortality of many species of invertebrates, turtles and fishes; Fresh surface water and groundwater impacted; Social tension arising from compensation disagreement.
July, 1978	SPDC's Forcados terminal tank failure oil spills	Rivers	580,000	Destruction of farmland, fishery, aquatic resources and mangrove ecosystem; Surface and groundwater pollution; Social tension over compensation claims and counter-claims
Jan, 1980	Texaco Funiwa- 5 well blowout	Rivers	400,000	Environmental pollution, drying up of vegetation and deprivation of plant and animal life. Oily sheen was observed in wells dug along beaches due to crude oil percolation. Fresh surface water and groundwater impacted
May, 1980	Oyakama oil spillage	Rivers	10,000	Destruction of farmland, fishery, and aquatic resources and mangrove ecosystem; Social tension arising from compensation disagreement.
Nov, 1982	System 2c pipeline rupture	Warri-Kaduna	18,000	Destruction of farmland; Social tension arising from compensation disagreement.
August, 1983	Oshika oil spill	Rivers	10,000	Destruction of farmland, fishery, and aquatic resources and mangrove ecosystem; Social tension arising from compensation disagreement.
Jan, 1998	Mobile Idoho oil spill	Akwa-Ibom	40,000	Death of over 90 % of mangrove seedlings among other plants on the shoreline within 14 days of exposure to the toxic oil film (Ajiboye, 1998)
1998	Jones Creek	Delta	21,548	Destruction of farmland, fishery, and aquatic resources and mangrove ecosystem; Social tension arising from compensation disagreement.

Oct, 1998	Jesse oil spill/fire incident	Delta	10,000	About 1,000 people burnt alive; Social tension over compensation claims and counter-claims
1998	Abudu pipeline spill	Edo	18,818	Destruction of farmland, fishery, and aquatic resources and mangrove ecosystem; Social tension arising from compensation disagreement.
Dec, 2011	Bonga oil spill	Delta (120 km offshore)	40,000	Community shoreline pollution, contaminated fishing gears, contaminated fishing grounds; adverse health effects on humans exposure to thousands of tons of chemical surfactants

1.2 Sustainable remediation

Over the years, the management of contaminated land has been incorporating sustainable practices in its various segments. The most recent development is sustainable remediation. According to SuRF-UK, sustainable remediation is defined as "*the practice of demonstrating, in terms of environmental, economic and social indicators, that the benefit of undertaking remediation is greater than its impact, and that the optimum remediation solution is selected through the use of a balanced decision-making process*" (SuRF-UK, 2009). It is "*a remedy or combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources*" (USSRF, 2009). Sustainable development has been defined as development which "*meets the needs of the present without compromising the ability of future generations to meet their own needs*" (Brundtland, 1987) (see Section 2.4).

1.2.1 Phytoremediation

Phytoremediation according to Cunningham *et al.,* (1996) is the application of plants to extract, degrade, contain, remove, sequester or immobilize contaminants in soil, water and other contaminated media. This plant technology is applicable to both organic (such as crude oil) and inorganic (such as heavy metal) pollutants present in the ecosystems including soil, water or air (Salt *et al.,* 1998; Raskin *et al.,* 1994). Phytoremediation is relatively cost effective compared to others especially engineering base. The mechanisms of action occurring in plants to combat contaminants present in polluted soil, especially hydrocarbon contaminated land, include: phytodegradation, rhizodegradation, phytovolatilization and phytostabilization. These mechanisms can treat a wide range of contaminants in low and moderate levels of concentration

including petroleum hydrocarbons (Aprill and Sims, 1990), volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), heavy metals (Brown *et al.,* 1994; Diez *et al.*, 2016; Futughe, 2012; Futughe *et al.*, 2020), radionuclides, and munitions (Dushenkov *et al.,* 1999; Huang *et al.,* 1998). However, these mechanisms might be contaminants specific (see Section 2.5).

1.2.2 Biosurfactants

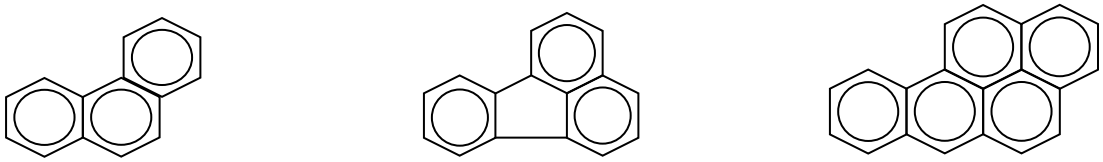
Biosurfactants such as rhamnolipids synthesized by microbes (e.g. *Pseudomonas aeruginosa*) are natural surface-active agents with the ability to reduce surface and interfacial tensions between two immiscible liquids (Banat, 1995; Rahman *et al.*, 2002), thereby enabling the uptake of hydrophobic substrates by plants and/or microorganisms particularly rhizosphere microbes. The main implication of this is to facilitate the degradation of pollutants principally by microorganisms at the rhizosphere level (rhizodegradation) and potentially by plants that could take up and metabolize moderately hydrophobic organic contaminants (phytotransformation) (Dietz and Schnoor, 2001). The *in situ* use of biosurfactants in contaminated sites bioremediation appears to be compatible environmentally and more cost-effective than using modified clay complexes or metal chelators (Kosaric, 1992; Kosaric, 2001; Rahman *et al.,* 2003; Das and Mukherjee, 2008) (see Section 2.6.)

1.2.3 Soil solarization

Soil solarization is a non-chemical soil treatment that uses radiation from the sun and a thin transparent film (normally made of polyethylene) to heat the soil to temperature range of 38 to 50ºC to a depth of about 10 to 20 cm for soil pasteurization (Gamliel and Katan, 2012). This process was initially intended as a treatment method to control soil-borne pathogens (Katan *et al.,* 1976); however, research has shown that it has other effects on soil characteristics that can influence the performance of crops, such as nutrient concentration (Chen *et al*., 1991) and soluble organic matter content (Chen *et al*., 2000). According to Emoghene and Futughe (2011), *Amaranthus viridis* grown on solarized plots performed better in all growth parameters compared to their non-solarized counterparts. In addition, the beneficial microbial population also increased post-solarization. During solarization, transparent polyethylene film is used to cover soil surface in order to reduce heat losses significantly without interfering with the absorption of solar energy, resulting to increased soil temperatures (see Section 2.7).

1.3 Pollutants of concern

Crude oil is made up of very complex chemical mixture of hydrocarbons containing more than 17,000 compounds (Marshall and Rodgers, 2004) and polycyclic aromatic hydrocarbons (PAHs) are one of the constituents of crude oil. PAHs were chosen as the pollutants of concern because they are the persistent organic pollutants (POPs) with two or more fused benzene rings (Oluseyi, *et al*., 2011) and are highly lipophilic and ubiquitous in the environment (Sun, *et al*., 2009, Wang, *et al*., 2012). In nature, more than a hundred PAHs can be identified (Sun, *et al*., 2009) however, sixteen have been identified by the USEPA as priority pollutants (USEPA, 2002) and seven of them are considered probable carcinogens (Wang, *et al*., 2012, Cai, *et al*., 2007). Phenanthrene, fluoranthene and benzo[a]pyrene as shown in Figure 1.1 below were the targeted PAH contaminants in this study because they are good monitoring indicators as PAHs environmental occurrence are highly dependent on their molecular weight. Low molecular weight PAHs with 2-3 fused rings such as phenanthrene (3 fused rings), occur in the atmosphere in the vapour phase whereas multi ringed PAHs (5 rings or more) such as benzo[a]pyrene are bound to particles, while PAHs with 4 rings such as fluoranthene are partitioned between vapour and particulate phases depending on temperature (Harner and Bidleman, 1998; Howsam *et al.*, 2000). Another rationale is that PAHs with 3 rings or more tend to be very strongly adsorbed to the soil matrices (Knox *et al.* 1993) and preferentially adsorb to small aggregate (<50µm), that also contains the most humified organic matter (Quantin *et al.*, 2005).



Phenanthrene Fluoranthene Benzo[a]pyrene

Figure 1.1: Structures of PAHs of concern and selected for study

1.4 Rationale for the research

Research into the development of alternative *in-situ* and *ex-situ* treatments for soil and water remediation has increased significantly in the past decades (Cundy *et al*., 2008; Azubuike *et al.*, 2016). The large area of land affected in the Niger Delta region precludes *ex-situ* treatment as a result of economic constraints, it requires the use of relatively inexpensive

remediation techniques, such as phytoremediation, biosurfactant and soil solarization which arguably meet most if not all the requirements for sustainable remediation. Phytoremediation is a sustainable remediation option; much of the work on this technique was undertaken in the 90's with preliminary investigation showing that it may have more advantage than utilizing microorganisms alone. Many greenhouses, growth chambers and field reports revealed that vegetative hydrocarbon contaminated soil increased the rate of hydrocarbon degradation compared to un-vegetative contaminated soil. Biosurfactants in comparison to their chemically synthesized counterparts are environmentally friendly, biodegradable, less toxic and non-hazardous with better forming qualities and increased selectivity (Smyth *et al.,* 2010b). They are also active at extreme temperatures, pH and salinity and can be synthesized from industrial wastes and from by-products making their production cheaper thereby reducing their pollution effect simultaneously (Kosaric, 1992; Kosaric, 2001; Rahman *et al.,* 2003; Das and Mukherjee, 2007). Due to their overwhelming potentials, biosurfactants have been employed in many industries including agriculture, food production, pharmaceutics, chemistry, cosmetics and most importantly in environmental biotechnology for both organic and inorganic contaminants remediation (Pacwa-Płociniczak *et al.,* 2011). A number of studies have shown that rhamnolipid biosurfactants can facilitate the degradation of aliphatic and aromatic organic compounds sorbed onto soil constituents by stimulating mass transport (Zhang and Miller, 1992, 1995; Maslin and Maier, 2000; Christofi and Ivshina, 2002; Zeng *et al*., 2007). Soil solarization on the other hand is beneficial to environmental sustainability as it leaves no toxic residues in the environment. It was first reported and developed in Israel and was later adopted in the United States and it is been utilized and studied in over sixty countries (Schreiner *et al.,* 2001). However there is very little research, if any, on the combination of soil solarization and phytoremediation as a remediation technique anywhere in the world.

1.5 Research novelty

The main purpose of remediation of contaminated land is to reduce negative human and environment impact, but remediation could also have other negative effects such as high cost and environmental footprints which are sometimes significant compared to the reduction of environmental risks. These contradicting effects have received increased attention globally, in this context, the combination of phytoremediation, biosurfactants and soil solarization is an environmentally friendly alternative to conventional remediation technologies, it also provides a sustainable, cost effective and feasible strategy for the remediation of contaminated land,

especially the large area of land impacted in the Niger Delta region. A number of studies on phytoremediation, biosurfactants and soil solarization had been carried out especially in areas with high solar radiation, but there was no research on the effect of soil solarization on phytoremediation of contaminated sites and hydrocarbon contaminated soil. There is a dearth of information on the impacts of soil solarization on biosurfactant enhanced phyremediation, soil/rhizosphere heterotrophic microorganisms and soil enzymatic activities. Thus, this novel sustainable approach contributes to original knowledge. Through an active interaction with relevant stakeholders, this study further acts as a catalyst to evaluate sustainable remediation feasibility, challenges and prospects in the oil rich Niger Delta region, as well as promote sustainability and this sustainable remediation technology.

1.6 Research aims and objectives

1.6.1 Aims

The aims of this thesis were to study soil solarization integration with phytoremediation enhanced with biosurfactant as a sustainable technique to remediate hydrocarbon contaminated land and to evaluate sustainability feasibility in the Niger Delta contaminated land clean-up.

1.6.2 Objectives

The following specific objectives were used to achieve the set out aims:

i. To survey and collect indigenous plant species growing on contaminated land in the Niger Delta region (Chapter 3);

ii. To compare the performance of the selected indigenous plant against a well-established phytoremediating non-indigenous plant; and to examine their respective associated soil/rhizosphere heterotrophic microorganisms with or without biosurfactant treatment for phytoremediation potentials in PAHs contaminated soil (Chapter 3);

iii. To investigate the effect of biosurfactant treatment on both indigenous and non-indigenous reference plants' potentials in phytoremediation of PAHs contaminated soil (Chapter 3);

iv. To conduct a laboratory study of selected plant using a bespoke microcosm designed to accommodate plant growth as well as soil and leachate collection, simulating the subtropical conditions in the Niger Delta region with or without solarization and/or biosurfactant treatments (Chapter 4);

v. To empirically investigate soil solarization and/or biosurfactant impact on PAHs removal in a simulated weathered PAHs contaminated soil (Chapter 4);

vi. To investigate the effects of these treatment factors (solarization and/or biosurfactant) on plant growth, soil/rhizosphere total heterotrophic microorganisms and soil/rhizosphere enzymatic activity of dehydrogenase and urease in simulated weathered PAHs contaminated soil (Chapter 4);

vii. To analyzed data using a general linear model (GLM) that summarize and aid in the interpretation of this new sustainable approaches (Chapter 4);

viii. To evaluate by questionnaires the sustainability awareness using sustainable development environmental milestones with concerned stakeholders in the region (Chapter 5);

ix. To assess the sustainability of applied/applicable remediation techniques using a six macro-criteria evaluation matrix with relevant stakeholders in the region (Chapter 5) and;

x. To identify the current environmental, social and economic challenges to sustainable remediation in the region by interviewing stakeholders from the region (Chapter 5).

1.7 Structure of the thesis

The thesis overall structure takes a form of six chapters and twenty appendixes. Chapter one lays the research context by given a brief introduction and background of the research in relation to contaminated land with a special focus on the Niger Delta region. A brief introduction on sustainable remediation, phytoremediation, biosurfactants and soil solarization, in addition to the rationale of the research, pollutants of concern, and research novelty. The research aims and objectives were also highlighted.

Chapter two presents a literature reviews on the Niger Delta region, crude oil production, spillages and pollution in the region. The review establishes crude oil as a source of polycyclic aromatic hydrocarbons (PAHs) which are then considered in relation to atmospheric, water, sediment, and soil pollution coupled with its exposure, toxicity and carcinogenicity. Current remediation techniques especially *in situ* remediation techniques with their merits and demerits were identified. An overview of sustainability considerations in remediation was summarized in view of sustainable remediation as an emerging concept in contaminated land particularly in Europe and the USA. This chapter also presents phytoremediation, biosurfactants and soil solarization as a potential novel sustainable

remediation approach to contaminated land clean-up especially in the Niger Delta region. An originality of the research in relations to the gaps in knowledge as identified from literatures was clearly summarized in this chapter.

The following three chapters of the thesis comprise detailed findings of the research through laboratory experiments and a qualitative field study:

Chapter three examines the potential/screening of native *Chromolaena odorata* for phytoremediation of PAHs contaminated soil enhanced with biosurfactant in relative comparison with an already established non-indigenous reference plant, *Medicago sativa* (alfalfa). These experiments showed that the native *C. odorata* plant tolerated and degraded PAHs equally well, if not better, than *M. sativa.*

Chapter four describes the novel approach using experiments on solarized soil amended with biosurfactant in conjunction with phytoremediation, undertaken alongside soil/rhizosphere heterotrophic microorganisms and soil enzymatic activity investigation. A laboratory microcosm was constructed to simulate the Niger Delta region's subtropical conditions.

Chapter five contains the qualitative findings aimed at evaluating sustainability feasibility, awareness, understanding and measurement through an active interaction with relevant stakeholders ranging from multinational oil companies with their host communities, regulatory agencies, environmental consultants, academics/researchers and technology providers/contractors in contaminated land management in the Niger Delta, with a view of promoting sustainable remediation technologies.

Chapter six which is the final chapter, draws upon the entire thesis, principally overviewing and comparing the findings obtained from chapter three to five. The implications of such findings are discussed and an overall conclusion is presented. This chapter concludes with final considerations in view of promoting and advancing phytoremediation using soil solarization with or without biosurfactants as novel sustainable remediation approach to the large hydrocarbons impacted land in the Niger Delta. Challenges, prospects and recommendations were discussed as well.

Chapter 2

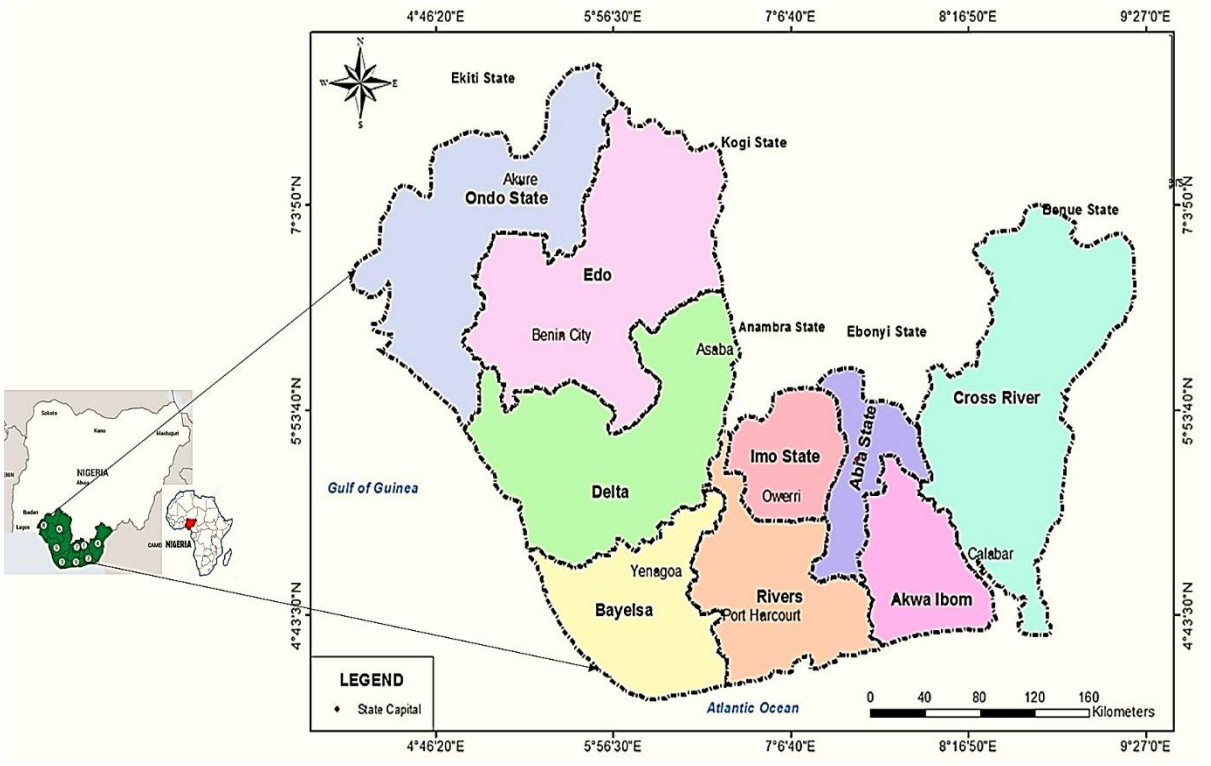
Literature Review

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 The Niger Delta region of Nigeria

The Nigerian costal line lies between latitude 4°15' to 4°50' and longitude 5°25' to 7°37' towards the Atlantic Ocean with a length of approximately 85 km. About 28,000 km^2 surface area lies within the coastal region with 46,300 km^2 surface area of continental shelf. The coastal areas are made up of freshwater swamp, mangrove swamp, beach ridges, sand bars, lagoons marshes and tidal channels. Nigeria has a total land mass of 923,768 km^2 of which 918,768 km^2 is terrestrial land and 13,000 km^2 aquatic (CIA, 2005) with an estimated population of 170 million people (OPEC, 2015). The coastal area is humid with a mean temperature of 24-32°C and average annual rainfall ranging between 1,500-4,000 mm (Kuruk, 2004). The Niger-Benue and Chad River are the two largest rivers in Nigeria. Several rivers channel into the Atlantic Ocean directly while others flow into the Chad basin or into the lower Niger and thence to the sea (Kuruk, 2004). The Niger Delta region is located in the Atlantic coast of Southern Nigeria and is the world's second largest delta with a coastline of about 450 km which ends at Imo river entrance (Awosika, 1995). The region with a surface area of about 112,000 km^2 i.e. 12 % of the total surface area in Nigeria has a population of about 31 million in nearly 3000 communities (NDDC, 2014) making it one of the most densely populated Africa regions (Steiner, 2010). The delta region has the largest wetland and mangrove in Africa and respectively the third and fourth largest in the world (Powell, *et al*., 1985; CLO, 2002; Anifowose, 2008; Chinweze and Abiola-Oloke, 2009; Spalding *et al.* 2010; Könnet, 2014). The delta mangrove swamp spans about 1,900 km^2 and is home to extraordinary biodiversity with some endemic species. The region is endowed with several mineral deposits including marble, barites, limestone, sand and gravel with fertile alluvial soils that support extensive agriculture (Zebbey, 2009; Adelana and Adeosun, 2011; Pegg and Zabbey 2013). The Niger Delta is classified as a tropical rainforest with ecosystems comprising of diverse species of flora and fauna both aquatic and terrestrial species. The region can be categoriesd into four ecological zones: coastal inland zone, freshwater zone, lowland rainforest zone and mangrove swamp zone. This region is considered one of the ten most important wetlands and marine ecosystems in the world (FME, *et al.*, 2006; ANEEJ, 2004) with the following states Abia, Akwa Ibom, Bayelsa, Cross River, Delta, Edo, Ondo, Imo and Rivers respectively (Figure 2.1).



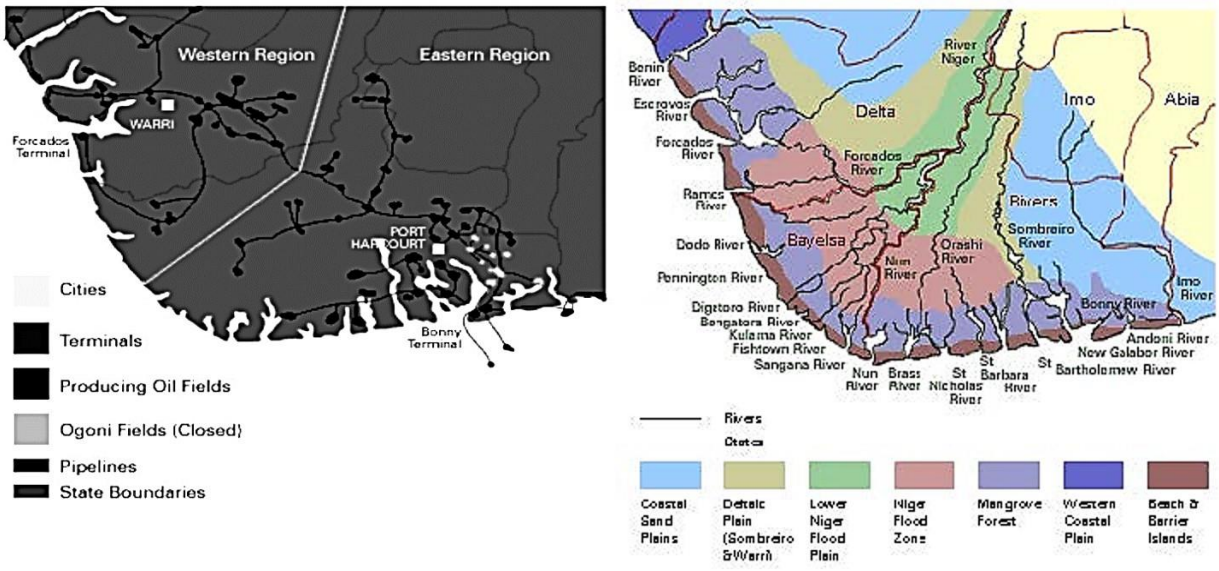
Source: Modified from Shaibu and Weli (2017)

Figure 2.1: Map of Nigeria showing the 9 States considered to be part of the Niger Delta region.

2.1.1 Crude oil production in Nigeria's Niger Delta

The Niger Delta region covers a land mass of more than 70,000 km^2, cutting across over 800 oil producing communities with extensive network of over 900 oil wells, more than 100 flow stations and gas plants, over 1,500 km trunk lines in addition to some 45,000 km of oil and gas flow lines (Figure 2.2) (Osuji, 2001). As a member of Organization of Petroleum Exporting Countries (OPEC) since 1971, Nigeria has Africa's largest natural gas reserve and second largest oil reserve making it the primary oil producer in the continent. Since the 1980s, 90% of Nigerian foreign exchange and 85% of the government earnings come from oil revenue (Odeyemi and Ogunseitan 1985) with extended 20-30 years estimated reserves (NNPC, 1984). Recently, Nigeria's oil reverse was estimated as having an export value of $89 billion per year (Könnet, 2014; OPEC 2015) with more than $600 billion revenue generated from crude oil production since 1960 (Ite *et al.* 2013).

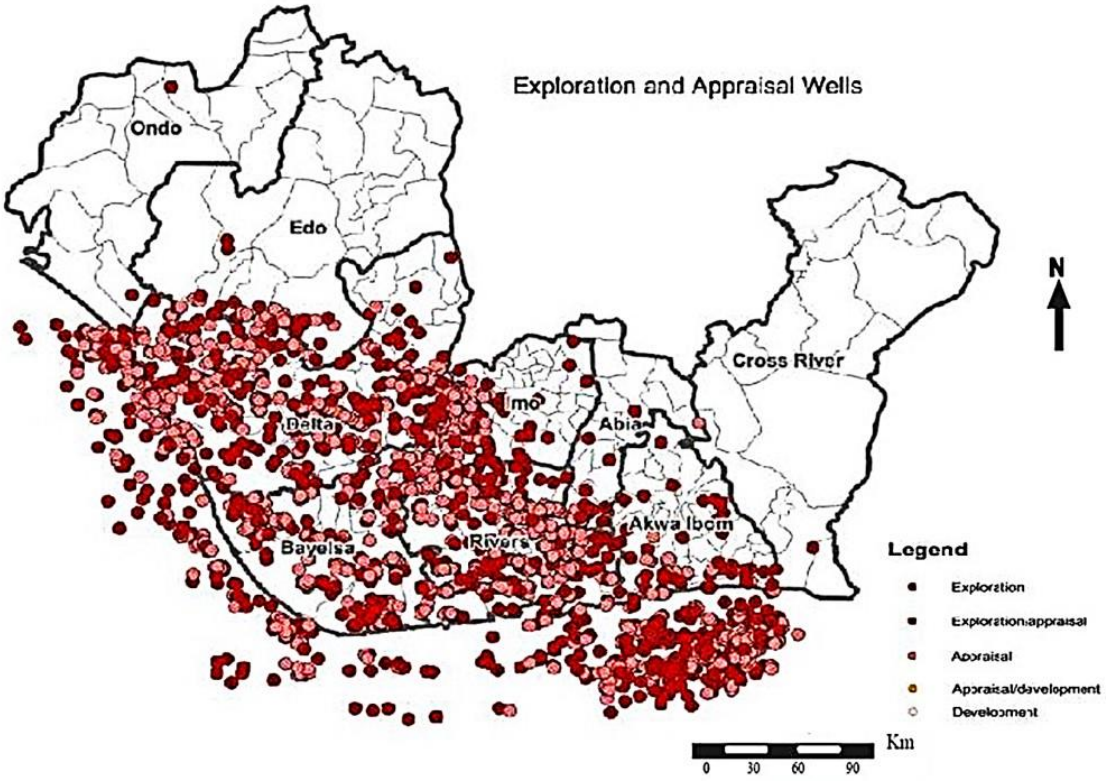
The pioneer oil company in Nigeria, Shell D'Arcy, commenced commercial production in 1958 with 5,100 barrels per day production rate which peaked at 2.44 million barrels per day within the next few year (Amu, 1982); however, production rate dropped to 1.5 million barrels per day in 1984 through OPEC from the activities carried out by 10 multinational companies exploring 122 fields with over 970 wells (NNPC 1984).



Source: Collins and Ertel (2008)

Figure 2.2: Niger Delta map showing oil fields, pipelines, rivers, states and ecological zones

There are four oil refineries in Nigeria with an estimated total refining capacity of 445,000 barrels per day (Onuoha, 2008; Anifowose, 2008), the Port Harcourt refinery being the first and oldest was commissioned in 1965 with an initial capacity of 35,000 barrels per day and was later expanded to 60,000 barrels per day and a second refinery with a capacity of 150,000 barrels per day is also located in Port Harcourt (Odeyemi and Ogunseitan 1985; Ukoli 2005). According to Anifowose (2008) and Onuoha (2008) the region has about 606 oil fields with 355 and 251 situated onshore and offshore respectively (Figure 2.3) with 5,284 drilled oil wells and 7,000 km of oil and gas pipelines.



Source: Niger Delta Regional Development Master Plan (2006)

Figure 2.3: Distribution of Onshore and Offshore Oilfields in the Niger Delta Region.

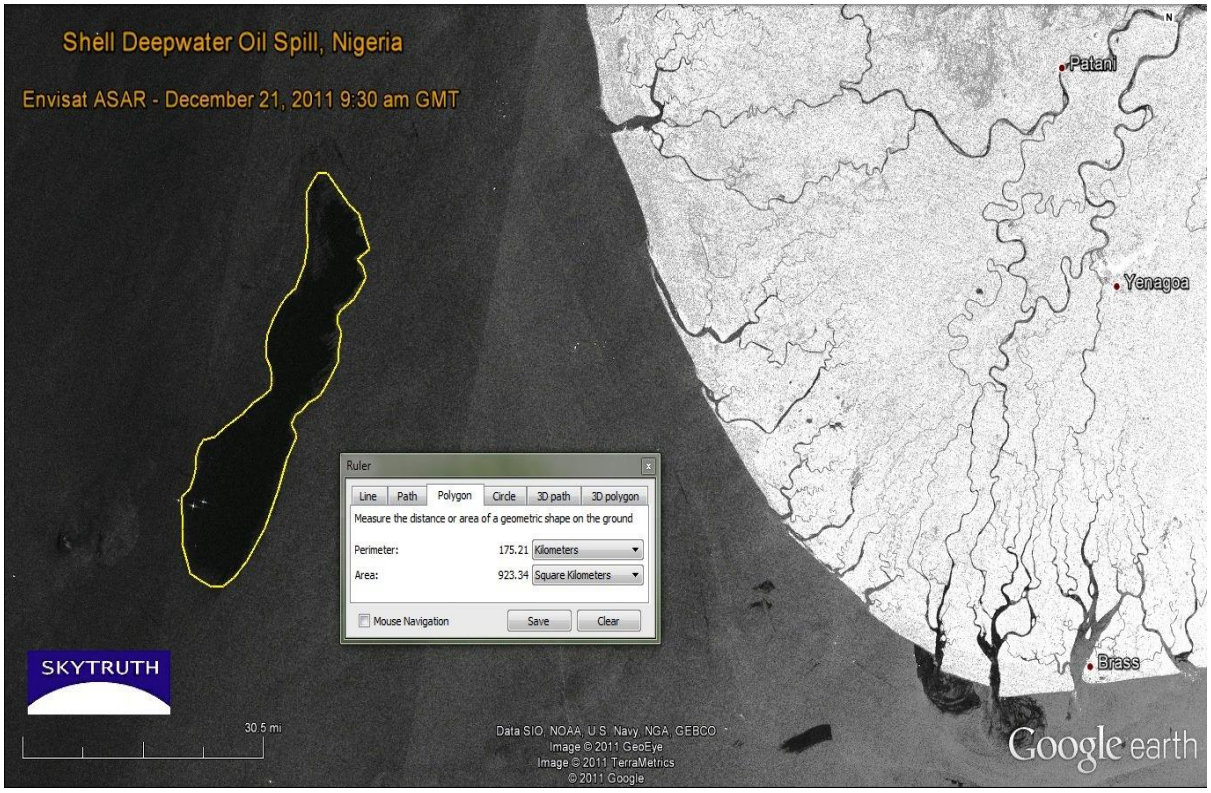
The Warri refinery commissioned in 1978 with an initial capacity of 100,000 barrels per day was later upgraded to a capacity of 125,000 barrels per day of light crude oil in 1986 (Odeyemi and Ogunseitan 1985). The Kaduna refinery was the largest inland built refinery which began operation in 1985 with an initial capacity of 100,000 barrels per day and later expended to a capacity of 110,000 barrels per day in 1986 (Odeyemi and Ogunseitan 1985) where crude oil was distributed through a 600 km pipeline from the Niger Delta oil fields (NNPC, 1984).

It was estimated that Nigeria has 30 million barrels of proven oil reserve in 2001 and 36.2 billion barrels of oil reserve in 2009 in the Niger Delta basin and continental shelf (Ukoli, 2005). One billion barrels of crude oil was recently discovered in 2016 offshore in Bayelsa state (Asu, 2016) in addition to substantial oil discoveries in hitherto non-oil producing Lagos and drier far northern Borno states. Nigeria's Gross Domestic Products (GDP) was reported to be at 35 % and represents over 90% of its foreign exchange wealth (Akpabio and Akpan, 2010; OPEC, 2015; Export, 2019). Oil exploration and production activities take place in the onshore dry or swamp lands of the Niger Delta basin and deep offshore locations of the Dahomey basin (Ukoli, 2005). Nigeria crude oil production is characterized by small fields producing between 500 – 5,000 barrels per day with 65% being light sweet crude with an API –gravity of 35^{o}C and above which is a very high quality. Over 50 % of Nigeria crude is produced by Shell from over 100 fields with oil reserve of more than 11 billion barrels per day followed by Chevron and Mobil combined. Chevron's operational base offshore is at Escravos located in Delta state, while Mobil operates offshore from Eket in Akwa Ibom state (Kadafa, 2012).

2.1.2 Crude oil spillages in the Niger Delta region

An estimated 9-13 million barrels of crude oil spillages have taken place in the Niger Delta ecosystems over the past 50 years and its equivalent to 1.5 million tons of oil and approximately 50 times the volume of the Exxon Valdez oil spill in Alaska 1989 (Leschine *et al*., 1993; Weiner *et al*., 1997; FME, 2006). A brief history of major oil spillages in the region include Forcados tank 6 Terminal in Delta State that spilled 570,000 barrels of oil polluting the Forcado estuary including the aquatic environment and surrounding in 1979 (Ukoli, 2005; Tolulope, 2004), followed by an estimated 421,000 barrels of crude oil spill from the Funiwa No. 5 Well in Funiwa Field blow out into the ocean in 1980 where 836 acres of mangrove forest within 6 miles off shore was destroyed (Ukoli, 2005; Gabriel, 2004; Tolulope, 2004). In the same year, 30,000 barrels of crude oil was spilled from Oyakama pipeline and in 1983 a

small village in River State experienced the devastating effect of a 5,000 barrel oil spill from Ebocha-Brass pipeline that flooded the lake and swamp forest with high mortality in crabs, fish and shrimp, and high mortality in embryonic shrimp and reduced reproduction eight months later due to oil in the lake's sediment (Gabriel, 2004). In 1995 about 24,000 barrels of oil was spilled from Ogada-Brass pipeline near Etiama Nembe which spread over freshwater, swamp forest, brackish water and mangrove swamp. The most recent was a 40,000 barrels Bonga oil spillage in 2011 at Bonga oil facility located 120 Km offshore the Niger Delta belonging to Shell/SNEPCo. According to the European Space Agency (2011) it was about 70 km (45 miles) long, 17 km (10 miles) wide at its widest, and covers 923sq/km (356 square miles) of Atlantic Ocean (Figure 2.4). This impacted on the host communities fishing grounds and contaminated their fishing gears, shorelines, vegetation, aquatic lives amongst others.



Source: European Space Agency (2011)

Figure 2.4: Satellite image of Bonga oil spill at the Atlantic Ocean. The extent of the spillage can be seen in the darker area highlighted in yellow.

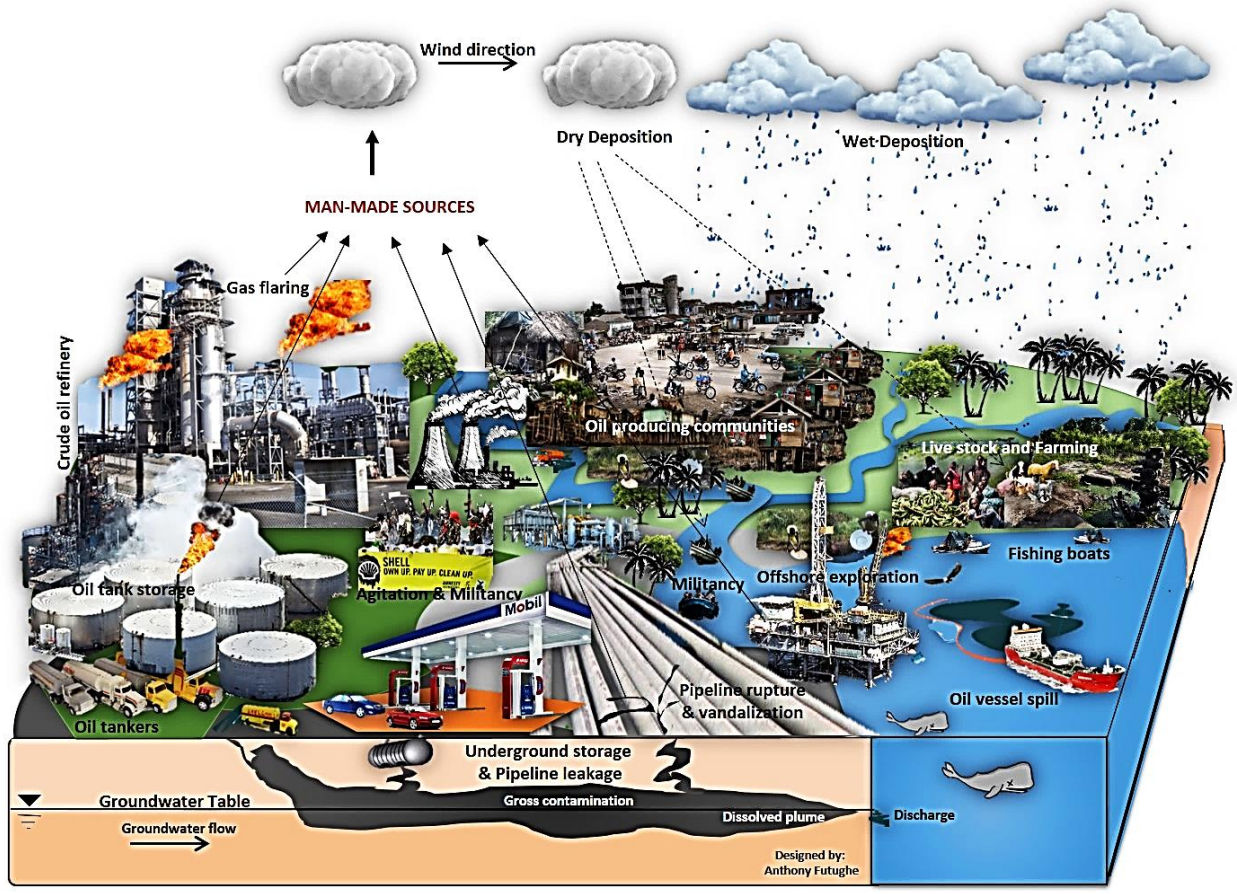
Since 1989, the Shell Petroleum Development Company (SPDC) recorded an average of 221 spills every year in its operational facility accounting for over 7,000 barrels annually (SPDC, 1995). It has been reported that a total of 4,647 oil spill incidences with about 2,369,470 barrels of crude oil were spilled into the environment from 1976-1996 in which 1,820,410.5 (77 %) were not recovered; while NNPC reported about 300 separate incidences occur annually between 1976-1996 accounting for 2,300 cubic meters of spilled oil into the environment (Twumasi and Merem, 2006). The UNDP (2006) reported that 3 million barrels of oil were spilled in the region from 6,817 oil spill incidences between 1976-2001 period of which 70 % of the spilt oil was unrecovered. The western operations of SPDC in 2001 recorded a total of 115 oil spill incidences where 5,187.14 barrels of oil were spilled and 734,053 barrels of the spilt oil (14.2 %) were recovered (SPDC, 1995). Approximately 40,000 barrels of crude oil was spilled by Mobil in Eket in 1998 but the largest crude oil spill in the Niger Delta, Nigeria was the offshore well blowout in 1980 with about 200,000 barrels of oil spilled into the Atlantic Ocean damaging 340 hectares of mangrove forest (Nwilo and Badejo 2005b). The majority of the oil spill incidences take place on land, swamp and the offshore environment (Nwilo and Badejo 2005a, 2005b, 2004; Twumasi and Merem, 2006; Uyigue and Agho 2007).

There is a complex and extensive system of pipelines criss crossing the Niger Delta region and substantial amounts of crude oil spill incidences have taken place from the pipelines and storage facility failures which may be caused by defect in material, corrosion of pipelines, ground erosion amongst others. However, multinational oil companies claim most spills are caused by sabotage. According to the Department of Petroleum Resources (DPR) 88 % of the oil spill incidences are as a result of equipment failure, while vandalism, oil blowouts from flow stations, accidental and deliberate releases in addition to tankers at sea are the main causes of oil spills in the region (Nwilo and Badejo 2004, 2005a).

2.2 Crude oil pollution of the environment

The volume of crude oil being transported across the high sea greatly increased especially after World War II, shifting the economic base of coal to crude oil and petroleum products (Onwurah *et al.,* 2007). Petroleum hydrocarbon pollution of the environment from crude oil may be as a result of oil well drilling production operations, upstream transportation and storage, downstream refining, transportation and at the sales point as shown in Figure 2.5. During gas flaring, some non-combustible hydrocarbons are released into the environment and until recently, the bulk of the associated gas generated during drilling in the Niger Delta was

flared. Other sources of petroleum hydrocarbon and its associated products are accidental spills and from ruptured oil pipelines (Figure 2.5) (Onwurah *et al.*, 2007) including vandalization of oil pipelines by local inhabitants; corrosion due to ageing pipelines; oil blow out from flow station; sabotage coupled with oil theft and illegal bunkering; inadequate care in loading and offloading of oil vessel. Petroleum hydrocarbon spilled in the environment tend to penetrate into the soil as a result of gravity until an impervious horizon such as bedrock, watertight clay or an aquifer is met (Oberdorster and Cheek, 2000). The accumulation of free oil on the surface of groundwater which tend to migrate laterally covering a wide distance is due to poor miscibility of crude oil. This pollutes other zones (e.g. vadose zones) very far away from the pollution source. Urban run-off, atmospheric deposition, natural seeps as well as industrial and municipal discharges account for hydrocarbon pollution of crude oil (Baker, 1983). Groundwater is one of the main sources of human, plants and animals exposures to petroleum hydrocarbon pollution. Extensive farm land in the Niger Delta has been lost as a result of crude oil contamination in addition to sources of drinking water and traditional occupation especially fishing and water transportation (Onwurah *et al.*, 2007).



Source: Modified from Futughe *et al.* (2020)

Figure 2.5: A conceptual site model of sources and transport of crude oil pollution in the Niger Delta environment.

2.2.1 Crude oil as a source of polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a component of the more than 17,000 compound mixture of hydrocarbon compounds contained in crude oil (Marshal and Rodger, 2004). Although some PAHs are released into the environment through natural sources such as combustion of forest fires and volcanic activities along with some minor biogenic sources, releases from anthropogenic activities (Baek *et al.*, 1991a; Harvey, 1998; Finalyson-Pitts and Pitts, 1986). Generally, pyrogenic and petrogenic sources are considered the two main sources of PAHs in the environment. Pyrogenic PAHs arise from a process known as pyrolysis formed whenever organic materials burn or decompose in high temperatures ranging from 350^{o}C to over 1,200^{o}C under limited oxygen concentrations. Examples of pyrolytic processes that are carried out intentionally include the destructive distillation of coal into coke and coal tar or the thermal cracking of crude oil into lighter hydrocarbons while unintentional examples include

incomplete combustion of fuels in cars and trucks, incomplete combustion of wood in forest fires and fireplaces, including incomplete combustion of fuel in oil heating systems. Higher concentrations of pyrogenic PAHs are commonly found in urban areas and around places close to PAHs sources. On the other hand, petrogenic sources of PAHs formed during crude oil maturation are common as a result of the widespread transportation, storage, crude oil usage and associated products. Major sources of petrogenic PAHs include oil spills in aquatic environment, leakages from underground and above ground storage tanks (see Figure 2.5) and the incremental accumulation of large amount of gasoline, motor oil and related substances associated with transportation. PAHs are also found in petroleum products (Tolosa *et al.* 1996; WHO, 2003; Masih and Taneja, 2006; Seo *et al.* 2007). In the coastal zones such as Niger Delta, PAHs are released into the environment primarily from crude oil spills (Mascarelli, 2010; Redondo and Platonov, 2009), sewage and runoff from roads (Durand *et al.* 2004) while oil seep (Tedesco, 1985), oil spills (Mascarelli, 2010; Redondo and Platonov, 2009) and produced water discharge from oil installations offshore (Roe, 1999) are the major sources of offshore PAHs in aquatic environment. According to Srogi (2007) other possible sources of PAHs include tire wear debris, automobiles, asphalt particles, re-suspended soils, sedimentary rocks and petroleum. The wide ranging sources of PAHs has led to their ubiquity in the environment (Baklanov *et al.* 2007; Latimer and Zheng, 2003) and are therefore commonly detected in air, water and soil.

2.2.1.1 General overview of PAHs

Environmental contamination by PAHs poses a major threat to public health (Skupinska *et al.,* 2004) as they are one of the most notorious semi-volatile organic pollutants and are considered as hazardous air pollutants (HAP) in the non-halogenated organic compounds group along with benzene, phenols, aldehyde among others (IARC, 1983). PAHs either as natural components (such as products of humus conversion by microbes) or as pollutants (such as in dust from petrochemical industries, in cigarette smoke, as a product of incomplete combustion) are ubiquitous in the environment (Bojakowska and Sokolowska, 2001). The term "PAH" refers to a compound consisting of only carbon and hydrogen atoms, forming two or more fused benzene rings in linear, cluster, or angular pattern as shown in Figure 2.6 (Arey and Atkinson, 2003; Di-Toro *et al.* 2000). These fused rings may contain a range of substances such as alkyl, nitro, and amino group (Fieser and Fieser, 1956) in addition to nitrogen, sulfur and oxygen atoms in their structure (Fieser and Fieser, 1956; McElroy *et al.*

1985). PAHs are commonly classified based on their molecular structures as low molecular weight (LMW) PAHs with two or three benzene rings and high molecular weight (HMW) PAHs with four or more benzene rings. Sixteen unsubstituted PAHs have been classified by USEPA as the most priority compounds to be detected in different environmental matrices (USEPA 1977) among which benzo[a]anthracene (B[a]A), benzo[a]pyrene (B[a]P), benzo(b)fluoranthene (B[b]F), benzo(k)fluoranthene (B[k]F), chrysene (Chry), dibenzo(a)anthracene (DBA), and indeno (1,2,3-c,d)pyrene (IP) have been classified as possible or probable human carcinogens (USEPA, 1993). The surrogate representative often used for the whole group of PAHs is B[a]P because of its recognition as being carcinogenic (IARC, 1987) (Figure 2.6). Their physico-chemical properties as shown in Table 2, non-polarity, hydrophobicity and, in particular stable aromatic bond structure, form their fate in the environment by determining their persistent nature in diverse environmental matrices (Srogi, 2007).

PAHs coupled with long range transport are subject to bioaccumulation and biomagnification in the environment (Liu *et al.,* 2017). They have been identified as contaminants requiring monitoring as a result of their potential carcinogenicity, mutagenicity, and toxicity (Liu *et al.*, 2017; Balcioglu *et al.,* 2014; Wu *et al*., 2008). Typical features of PAHs include: high melting and boiling points (i.e. solids), low vapour pressure and very low aqueous solubility (Masih *et al*., 2012). PAHs vapour pressure and aqueous solubility tend to decrease with increasing molecular weight while on the other hand, they are resistant to oxidation and their reduction increases with increasing molecular weight (US EPA, 2002) and PAHs aqueous solubility reduces for every additional ring (Masih *et al*., 2012). They often dissolve effectively in organic solvents as they are lipophilic in nature as measured by octanol-water partition coefficients (K_{ow}). PAHs with high melting and boiling points are all solid and bond easily to particulate matter even though they are inactive chemically. PAHs adsorbed on dust surface become highly thermo- and photosensitive and degraded at high temperature (50^{o}C) as well as on exposure to light especially ultraviolet and visible light (Zakrzewski, 1995). PAHs, depending on their volatility and molecular weight, can adsorb on soot surface as well as remaining in the gaseous phase (Sánchez *et al.,* 2013) making PAHs appear in different environmental matrices including ambient air, water, soil, street dust, sediment among others and can be inhaled or consumed with food by humans resulting to major health problems such has tumors, defects in birth, and variety of pulmonary diseases.

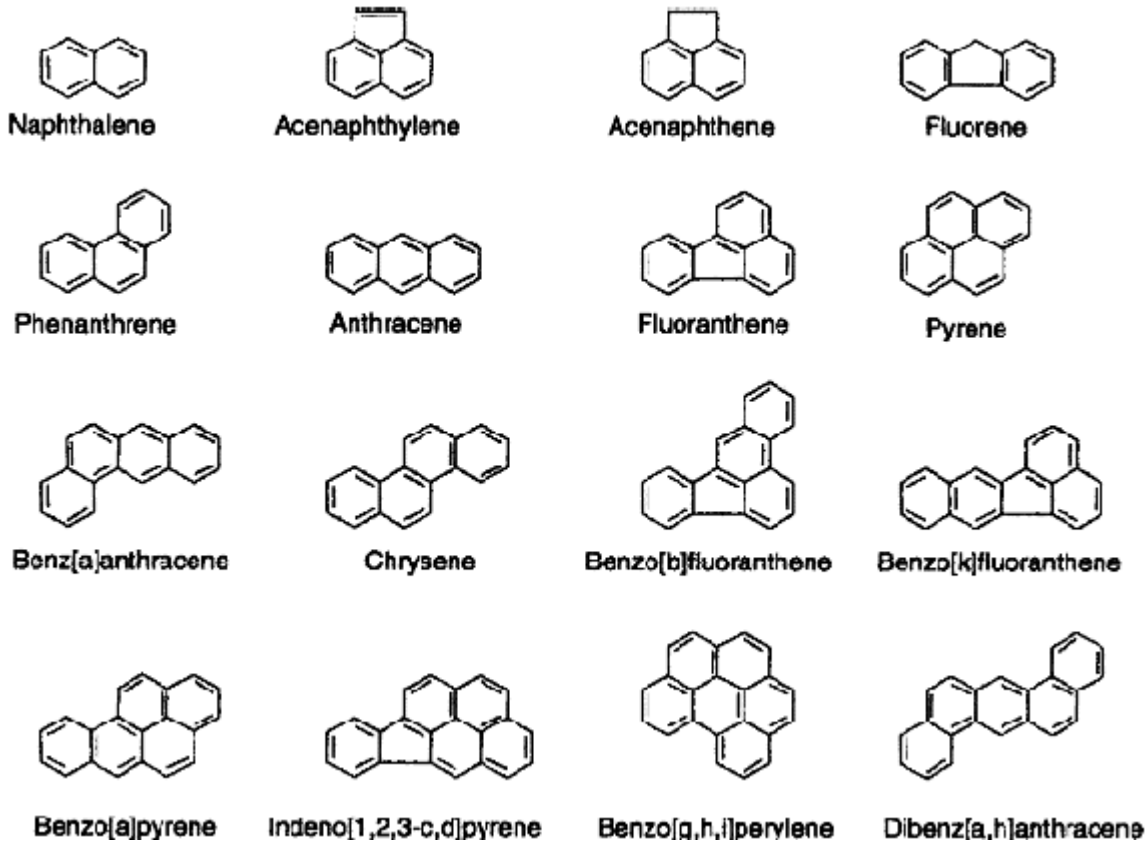


Figure 2.6: Molecular structure of the 16 PAHs selected as priority pollutants by the United State Environmental Protection Agency (EPA).

Table 2 Physical properties of the 16 PAHs

Compound	Molecular weight (g)	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa)	Solubility in water (mg/l)
napthalene	128.18	80.2	218	1.1×10^{-2}	3.93
acenaphthylene	152.20	92-93	265-280	3.9×10^{-3}	3.93
acenaphthene	154.20	90-93	265-280	2.1×10^{-3}	1.93
fluorene	166.23	116-118	293-295	8.7×10^{-5}	1.68-1.98
phenanthrene	178.24	96-101	339-340	2.3×10^{-5}	1.2
anthracene	178.24	216-219	340	36×10^{-6}	0.076
fluoranthene	202.26	107-111	375-393	6.5×10^{-7}	0.2-2.6
pyrene	202.26	150-156	360-404	3.1×10^{-6}	0.077
benzo[a]anthracene	228.30	157-167	435	1.5×10^{-8}	0.01
chrysene	228.30	252-256	441-448	5.7×10^{-10}	0.0012
benzo[b]fluoranthene	252.32	167-168	481	6.7×10^{-8}	0.0012
benzo[k]fluoranthene	252.32	198-217	471-480	2.1×10^{-8}	0.00076
benzo[a]pyrene	252.32	177-179	493-496	7.3×10^{-10}	0.0023
dibenzo[a,h]anthracene	278.35	266-270	524	1.3×10^{-11}	0.0005
benzo[g,h,i]perylene	276.34	275-278	525	1.3×10^{-11}	0.00026
indono[1,2,3-cd]pyrene	276.34	162-163	530	Ca. 10^{-11}	0.062

Source: WHO (1998a)

2.2.1.1.1 Atmospheric pollution of PAHs

It has been well established that atmospheric transfer is the principal pathway of PAHs global distribution (Birgül *et al*. 2011). Once in the atmosphere, PAHs are dispersed between gas, particle, and droplet phase depending on their physical and chemical properties (i.e. vapour pressure, Henry's law constant, and solubility) (Junge,1977; Bidleman, 1988; Larsen III and Baker, 2003; Gocht *et al*., 2007). It has been reported in most studies that PAHs containing two to three rings are mainly found in the vapour phase, while PAHs with four to six rings occur in the particulate phase at ambient temperature (Zhang *et al*., 2009; Teixeira *et al*., 2013; Delgado-Saborit *et al*., 2013; Alam *et al*., 2013). Oxidative and photolytic reactions and atmospheric depositions are the two major pathways through which PAHs are removed from the atmosphere (Garban *et al*., 2002; Manoli *et al*., 2000). According to Bidleman *et al.* (1988) vapour phase as well as particle-bound PAHs can also be removed by atmospheric bulk (dry + wet) deposition mechanism. Meteorological factors and particle-phase concentration have been found to play crucial role in PAHs deposition (Liu *et al.*, 2013). Pankow *et al*. (1993) and Chetwittayachan *et al*. (2002) documented remarkable relationship between PAHs concentration and relative humidity while Sofuoglu *et al*. (2001) observed that temperature variation has more impact on gaseous phase low molecular weight PAHs dispersion than particulate phase high molecular weight PAHs. In general, PAHs concentrations were observed in lower values during summer (dry season) or monsoon than in winter (rainy season) as a result of increase in the mean inversion height, decrease in the number of inversion days at winter and the lack of a major PAH source and residential fuel combustion for heating (Baek *et al*. 1991b; Hussain *et al*. 2016a). Fang *et al*. (2005) reported that PAHs concentrations were higher during spring and winter compared to summer and autumn in Taiwan for either PM 2.5 and PM 2.5-10. The total 17 PAHs concentration ranges between 0.84 and 152 ng/m^3 with an average of 116 ng/m^3 in urban area which were 1.1–6.6 times higher than those measured in suburban area of Beijing (China). Baek *et al*. (1991b) reveled that maximum PAHs concentration associated with particulate phase was found during winter while vapour phase PAHs concentrations were maximum during summer.

Ana *et al.* (2012) investigated the burden of PAHs in ambient air in selected Niger Delta communities and reported an average of 648 ng/m^3 which was comparable to point sources, in tunnels, and toll stations from other parts of the world as reported by ATSDR (1995). The absence of detectable quantity of B[a]P in selected communities in the region according to the report does not preclude it from being in the atmosphere as large portions of particles released

by combustion sources including automobiles and woods smoke are impregnated with PAHs rich in B[a]P (Ana *et al.*, 2012; Anittila *et al*., 2005; Glasius *et al*., 2008; Rehwagen *et al*., 2005; Spezzano *et al*., 2008). Generally, the atmospheric pollution of PAHs with risk to human exposure is highest in cities due to high population density, increasing vehicular traffic and relatively scarce atmospheric pollutants dispersion (Rockens *et al.,* 2000). The prescribed or mandatory level of concentration of B[a]P in the air is 1 or 10 ng/m^3 in Italy or Germany, respectively (Jacob and Seidel, 2002).

The common practices of slash and burn cultivation, widespread combustion of biomass for energy and waste disposal, upstream and downstream industrial oil activities in Nigeria, especially the Niger Delta, make PAHs a common constituent of atmospheric pollutant (Ana *et al.* 2012). According to Liu *et al*. (2007) and Zhu *et al*. (1997) the major source of PAHs exposure in the atmosphere was from vehicle exhaust based on calculated PAH diagnostic ratios. According to Fang *et al*. (2004a, b, c) the average total PAHs detected in central Taiwan region at industrial, urban, and rural areas ranged from 1,232 to 1,650, 700 to 1,740, and 610 to 831 ng/m^3 respectively. While particulate matter (PM) 2.5 (fine particulate) and PM 2.5-10 (coarse particulate) total concentrations of PAHs were found to be 180.62 and 164.98 ng/m^3 at the Tunghai University Pastureland (Taiwan) sampling sites respectively.

2.2.1.1.2 Water and sediments pollution of PAHs

PAHs typically enter surface water body through atmospheric fallout such as wet and dry deposition of particles and vapors, urban run-off, municipal effluents, industrial effluents and oil spillage or leakage etc. (Marsalek *et al.,* 1999; Van Metre *et al*., 2000; Manoli and Samara, 1999). Pyrogenic and petrogenic sources have been the most predominant anthropogenic sources of PAHs in aquatic environment. Combustion of organic materials such as petroleum fuel, coal, and biomass are examples of pyrogenic sources of PAH in the aquatic environment while petrogenic PAHs from crude oil and refines petroleum products are released through accidental oil spills, oil spills from tanker, used engine oils, natural seeps, and offshore drilling (Singare, 2015). It has been estimated that atmospheric sources alone contribute 10-80 % of PAHs entering the world's oceans and urban run-off carries PAHs deposited on surfaces, mobile associated PAHs from gasoline, oil drips or spills as well as vehicle exhaust products, tyre particles, and bitumen form road surfaces (Manoli and Samara, 1999). Higher levels of PAHs were reported during autumn and winter during urban run-off as a result of the high incidence of vehicles in the street in addition to use of heating systems (Manoli and

Samara, 1999). An important route of PAHs into receiving water bodies is storm or rain water irrespective of the types of PAHs sources in urban area, making it difficult to control and remediate due to their diffuse source (O'Reilly *et al.,* 2010). Individual PAHs concentration in surface and coastal waters is generally in the neighborhood of 0.05 µg/L and anything above this indicates some contamination according to a WHO report in 1997. It was reported by WHO that a concentration of 0.7 µg/L benzo[a]pyrene corresponds to an excess lifetime cancer risk of 10-5 (Hussain *et al.,* 2018). A total PAHs concentrations ranging between 4.7 and 600 µg/L was found in drinking water in four major USA cities (ASTDR, 1995). The lower water solubility attributes of high molecular weight mass PAHs such as benzo[g,h,i]perylene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene make them less unlikely for detection in water samples.

Upon the introduction of PAHs in receiving water body, they are dispersed by currents and become integrated with the sediment at some point (EPRI, 2000; Tehrani *et al*., 2012). Typically, PAHs tend to settle, partition, or adsorb onto non-aqueous phase such as soil or sediment due to their hydrophobicity (Cornelissen *et al*., 2006) and high octanol/water partition coefficients. Several researchers have investigated this trait by exploring the history of deposition in sediment cores to determine trends of PAH contribution into the environment (EPRI, 2000; Tehrani *et al*., 2012). According to Guzzella and Depaolis (1994) PAHs tend to be less susceptible to degradation upon adsorption to solid particles yet, they are not entirely insoluble especially the low molecular weights PAHs. Accordingly, pore water can dissolve and incorporate small amount of PAHs making them bioavailable, however, the existence of pore water organic colloids raise the levels of PAHs beyond their aqueous solubility since they will be sorbed onto these organic colloids. They are then transferred sequentially through the pore spaces of the sediment increasing the mobility and bioavailability of PAHs in sediments with the sorption of PAHs to colloids (Dong *et al*., 2012).

The mutagenic and carcinogenic effects of PAHs to land and water organisms (Connel *et al.,* 1997) have attracted global attention, studies have been carried out on their distribution, and source identification in water bodies close to urban centres. The lipophilic nature of PAHs and high stability in the environment enables them to be biomagnified in the food chains with humans as the final recipients (IARC, 1983; Okay *et al*., 2000; Vagi *et al*., 2005).

PAHs presence in drinking water may be a result of the surface or groundwater being used as raw water sources or due to the use of coal tar-coated pipes for public water supply systems and accordingly, the European Union directive 98/83/EC states a limit of 0.10 µg/L

for the sum concentration of B[b]F, B[k]F, B[g]P, and IP and 0.010 µg/L for B[a]P (European Communities (Drinking Water) Regulations 2007). The low permitted concentrations emphasise the need to control as well as mitigate against PAH contamination in all environmental compartments e.g. soils where migration to aqueous compartments is possible. The monitoring of these PAHs in surface water bodies is invaluable for potential toxic effect assessment as well as decision-making process for concerned authorities (Nikolaou *et al.*, 2009).

2.2.1.1.3 Soil pollution of PAHs

One of the most important pathways for PAHs introduction into soil surfaces is atmosphere to surface precipitation by dry or wet deposition (Wang *et al*., 2002; Tao *et al*., 2003), making soil a major sink of atmospheric PAHs (Morillo *et al*., 2008). Other viable PAHs dispersal mechanisms include volatilization, irreversible sorption, leaching, accumulation by plants, and biodegradation (Reilley *et al*., 1996). Surface run-off and dust re-suspension from soil are also potential sources of air and sediment contamination (Mai *et al*., 2003). Studies have shown that PAH concentration in soil has a significant relationship with corresponding levels in air (Vogt *et al*., 1987), house dust (Chuang *et al*., 1995), and urban street dust (Takada *et al*., 1990; Essumang, 2006), thus making soil a good index for PAH pollution and environmental risk (Liang *et al*., 2011). Soil serves as an important sink for products released into the atmosphere during combustion, making it the major channel for build-up in addition to assimilation of many pollutants (Wild and Jones, 1995). PAH contamination of soil is an emerging problem especially in urban areas with growing energy consumption (Dai *et al.*, 2008) which may become heightened over time resulting from the intensification of emission rates associated typically with industrialization, urbanization, and motor vehicles. Emissions from motor vehicles are mainly contributed from a mix of tailpipe emission, wear and tear of brakes and tires, and street dust re-suspension (Rogge *et al*., 1993; Thorpe and Harrison, 2008). According to Agarwal (2009) much of the PAH associated-combustion are found to be present on the top layer of the soil. It has also been reported that human exposure of PAHs through soil is more intense than that of air and water (Menzie *et al*., 1992) as highlighted by Smith *et al.* (1995) with a significantly higher PAHs level of 95 % in soil compared to 0.2 % in the air. Hence, PAHs have been transported either from close sources such as automotive exhausts from adjacent roadways, or from more distant sources such as industry to various distances via the atmosphere (Hussain *et al*., 2018). PAHs can accumulate in soil over a period of time, if

atmospheric particules contain PAHs and become mobile upon deposition on the earth's surface. The sorbent particle size and the soil's pore throat size are important in the determination of PAH mobility of particulates (Hussein *et al*., 2016) as the soil PAHs most often bound to soil particles (Masih and Taneja, 2006; Cachada *et al*., 2012). Three or more benzene rings PAHs tend to be very strongly adsorbed unto soil matrices (Knox *et al.*, 1993), especially to small aggregates (<50 µm) that contains also the most humified organic matter (Quantin *et al*., 2005). According to Riccardi (2013) the smallest opening found between each individual grain of soil is the pore throat and if PAHs movement is restricted through the soil as a result of PAH-bound particles, they will most likely remain sorbed to the particles. One of the factors determining the PAH affinity to sorbed to soil are the PAH individual properties as well as the soil's, making PAH sorption an important mechanism in dictating the soil mobility of individual PAH. Another important factor that influences the sorption of PAHs to soil is the PAHs octanol-water partitioning coefficient (K_{ow}) which is linked to the solubility of an organic compound in water (Schwarzenbach *et al.*, 1993). An increase in K_{ow}, leads to a decrease in the aqueous solubility resulting to an increase in the affinity for PAH sorption to a particular soil, thus making K_{ow} and solubility pivotal in influencing soil mobility of PAH. PAH loss by leaching is rendered insignificant due to strong adsorption coupled with very low water solubility. Soil conductivity is also considered as a factor that can also enhance PAH mobility (Shang *et al*., 2014).

The hydrophobic nature of PAHs and stable chemical structure that support adsorption onto soil particles creates a sustaining capacity for PAHs in the soil matrix to become more persistent (Means *et al*., 1980; Wilcke *et al*., 2000). Consequently, PAHs are referred to as persistent organic pollutants of the soil and they are poorly degraded. Significant correlation of PAHs concentration and soil organic carbon content has been reported (Liang *et al*., 2011) and increase of organic matter content in soil makes PAHs more resistant to degradation (Man *et al*., 2013). Some reports have identified black carbon (soot) playing an important role in PAHs distribution in the soil as a result of their co-emission and high PAHs sorption capacity (Agarwal and Bucheli, 2011; Liu *et al*., 2011; Hussain and Hoque, 2015). Black carbon is widely viewed as a strong adsorbent for hydrophobic organic compounds and also diminish toxicity and biodegradability of organic contaminant in the soil (Semple *et al*., 2013), hence, the risk estimation and remediation of contaminants are largely due to their fate and behaviour in soil (Riding *et al*., 2013).

Substantial literature on PAHs in soil have been reported in many countries (Wild *et al*., 1990; Weiss *et al*., 1994; Nam *et al*., 2003). Edward (1983) reported a typical endogenous PAHs in soils are in the range of 1-10 µg/kg which are mostly derived from oil seeps, bitumens, coal, plant debris, forest and prairie fires (Yunker *et al*., 2002). It was reported that PAHs in concentrations from 50 to 619 µg/kg dw were present in the 0 -10 cm soil from Swiss soil monitoring network observation sites (Bucheli *et al.,* 2004) with the highest recorded in urban areas (400 – 619 µg/kg dw) irrespective of land utilization in city, park, forest and arable land. Ipeaiyeda *et al.* (2015) reported a total PAHs concentrations range of 56.8 mg/kg to 112 mg/kg in crude oil contaminated soil from Ekpan town near Warri refinery in Delta State, Nigeria. This concentration range from the Niger Delta region is over a 1000 times higer than the Swiss site above and underscores the fact that some form of remediaition is urgently needed in the region to mitigate potential adverse public health effects.

2.2.1.1.4 PAHs exposure, toxicity and carcinogenicity

Exposure to PAHs by humans takes place through three possible routes, namely respiratory tract, gastrointestinal tract and skin contact. About 70 % of PAHs exposure can be associated with diet from a non-smoking individual and the main PAHs source in diet includes cereals, oils, and vegetables. However, cooked food especially over open flame has been recognized as the major contributor of PAH intake in humans, in barbecued meat for example, PAH can be as high as 10-20 µg/kg (Philips, 1999). Another importance source of exposure is water and the highest acceptable concentration of B[a]P in water as recommended by WHO is 0.7 µg/L. It has been estimated that the average PAH intake with water is 1 % of the total acceptable level (WHO, 1998a). According to UNEP (2011) some communities in the Niger Delta region are drinking water from wells contaminated with known carcinogens at levels over 900 times the WHO guideline. This heightens again the seriousness of the situation in the Niger Delta region and the need to improve matters.

Smoking habit carries risk of PAHs exposure and it's been reported that smoking one cigarette can cause 20-40 ng intake of B[a]P (Philips 1996 and O'Neill, 1997). The human exposure risk to atmospheric PAHs is maximum in the cities due to the population density and exposure concentrations (Caricchia *et al.,* 1999). The shift in the usage of coal to oil and gas in particular, for domestic heating has resulted in a drastic reduction of urban particulate pollution in cities however, particles generated by automobiles are much smaller and mostly confined in the breathable size fraction than that of coal (Manoli *et al.,* 2002). Unlike HMW PAHs, there

are relatively few studies on the vapour-phase LMW PAH components, even though they are thought to be weaker carcinogens/mutagens, they are the most abundant in the atmosphere and can react with other pollutants to form more toxic derivatives i.e. secondary pollutants in the urban atmosphere (Park *et al.*, 2002). Consequently, human exposure to PAHs mixtures, instead of individual substances is inferred to be more important (Hussain *et al.*, 2018).

High exposure to PAHs is common in industrial workplaces including coke plants; coal tar and pitch producing and manufacturing industries; aluminium plants; iron and steel foundries; and creosote, rubber, mineral oil, soot, and carbon black producing or manufacturing companies. These unusually high occupational exposures to PAHs became known after a significant increase of certain cancer diseases was reported among the workers (Hussain *et al.*, 2018). Correspondingly, chimney sweeps, roadmen (pavement tarring) and roofers (roof tarring) are subjected to increased risk and have been listed among the highly exposed occupational group to PAHs (Jacob and Seidel, 2002).

Skin cancer was reported in higher rates during the eighteenth century among roofers who were exposed to soot and in 1947, lung cancer was found to be linked with occupational condition of workers in the gas and coal tar industries (Kennaway, 1995). Studies then showed that the PAHs present in coal tar and soot were responsible for induction of cancer and the International Agency for Research on Cancer in 1983 recognized 30 PAHs as carcinogenic to people. PAHs have been given considerable attention among researchers as a result of the continuous increase in death toll caused by cancer leading to about 13 % of all human deaths globally as at 2007 (Jemal *et al.*, 2011). Researchers have successfully established the carcinogenic and mutagenic properties of a few PAH members in human and animal experiments (Grimmer, 1983; Ramdahl and Bjorseth, 1985; Dias, 1987; US EPA, 1993; Clement Associates, 1990; Department of Health and Human Services, Public Health Service, National Toxicology Program 2011; ATSDR, 1995; IARC, 1996; IPCS/WHO, 1998; Boström *et al*., 2002; Larsen and Larsen, 1998; Bartoszek, 2002; Baek *et al*., 1991a; Harvey, 1998; Howsam and Jones, 1998; NRC, 1983). Studies have also shown that PAHs may trigger various health effects including cytotoxicity, immunotoxicity, genotoxicity, carcinogenicity, reproductive toxicity, etc. on experimental animals (IARC, 1983). Table 3 shows selected PAHs carcinogenic classification by diverse agencies.

The toxicity of a PAH depends upon the structure of its particle and substituted groups. PAHs containing nitrate, methyl, and carboxylic group belong to the carcinogenic group (Skupinska *et al.*, 2004) and as a result B[a]P has high carcinogenic potency, making it termed

as the "gold standard" or index for the whole PAHs group (US EPA, 1993). B[a]P carcinogenicity was tested through inhalation only in hamsters (Thyssen *et al.*, 1981 and WHO, 2000) and studies show that about 9 in 100,000 individual spending their lifetime in ambient air exposed to an average concentration of B[a]P of 1 ng/m^3 are at risk of dying from respiratory tract cancer (Larsen and Larsen, 1998 and WHO, 2000).

Table 3: PAHs carcinogenic classifications by various agencies

Carcinogenic classification	PAH compounds	Agency
Known animal carcinogens	benzo[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, Indeno[1,2,3-cd]pyrene	US Department of Health and Human Services (HHS)
Probably carcinogenic to humans	benzo[a]anthracene, benzo[a]pyrene,	International Agency for Research on Cancer (IARC)
Possibly carcinogenic to human	benzo[a]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene	
Not classifiable as to their carcinogenicity to humans	anthracene, benzo[g,h,i]perylene, benzo[e]pyrene, chrysene, fluoranthene fluorene, phenanthrene, pyrene	
Probable human carcinogens	benzo[a]anthracene	US Environmental Protection Agency (EPA)
Not classifiable as to their carcinogenicity to humans	benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, acenaphthylene, Anthracene, benzo[g,h,I]perylene, fluoranthene, fluorene, phenanathrene and pyrene	

Source: Hussain *et al.* (2018)

According to Pott and Heinrich (1990) smoke released from both petrol and diesel car exhausts, domestic coal stove-emissions as well as tobacco contain mainly four- to seven-ring PAHs that have been found to exhibit almost all the carcinogenic potentials. PAHs exposure has also been implicated in elevated levels of DNA adduct, mutations, reproductive effects, and cancers of lung, respiratory tract, and urinary bladder (Bosetti *et al*., 2007 and Gaspari *et al*., 2003). Carcinogenic risk of inhaled PAHs as reported by Pankow *et al.* (1993) depends upon the form (gas or particulate) in which it enters the lungs, PAH carcinogenicity may prevail for a longer period of time if it entered in a particulate form compared to gaseous form.

Durant (1996) studied the mutagenic activities of 67 PAHs in human lymphoblastoid where lymphoblastoids were cultured in the presence of different PAHs concentrations. The study shows PAHs mutagenic activities as follows: dibenzo[a,l]pyrene > benzo[a]pyrene > indeno[1,2,3-c,d]pyrene > dibenzo[a,h]anthracene > benxo[b]fluoranthene > benzo[g,h,i]perylene > antraquinone >9-nitroanthracene > ben[e]pyrene >>phenanthrene and pyrene. The change in rings number in the case of benzo[a]pyrene and dibenzo[a,l]pyrene result into difference in toxicity of the PAHs. Biological activities were also observed not to be only controlled by the ring numbers but also the shape, the particles dimension, and the presence of functional groups.

It becomes pivotal to establish a safe level of PAHs for human due to its toxicity and carcinogenicity. Table 4 shows the maximal PAHs acceptable levels of concentrations from various countries. Since 2001, in Poland, workplace acceptability level of PAHs has been set to be 2 $\mu g/m^3$ (Corpus of Polish Law (Dziennik Ustaw) 2001). While in the UK, it has been ascertained that it is not possible to estimate the absolutely safe level of carcinogens exposure, PAH in particular (UK Department for Environment, Food, and Rural Affairs 1999). There is no safe concentration for carcinogenic and mutagenic substance in reality as such substance can increase the risk of neoplastic diseases by accumulating continuously for years after entering the living organism even in small quantity (Skupinska *et al*. 2004).

Table 4: Maximal permissible concentration (MPC) of PAHs in selected countries

PAH Compound	Occurrence	MPC	Selected Countries	Reference
benzo[a]pyrene	Ambient air	1 ng/m^3	Italy 1999	Kjaerheim, 1999
benzo[a]pyrene	Ambient air	1 ng/m^3	Former USSR 1985	Khesina, 1994
sum of fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, bezo[g,h,i]perylene, indeno[1,2,3-cd]pyrene	Ambient water	1.2 µ/L	EEC 1980	Slooff *et al.*, 1989
benzo[a]pyrene	Drinking water	0.7 µ/L	WHO 1995	WHO, 1998b
sum of fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, bezo[g,h,i]perylene, indeno[1,2,3-cd]pyrene	Drinking water	0.2 µ/L	EEC 1980	EEC, 1980
benzo[a]pyrene	Oven area	2 µ/m^3	Germany 1989	Disposition of German Federal Department for worker safety, 1989
benzo[a]pyrene	Workplaces	2 µ/m^3	Sweden 1993	Disposition of Swedish National Board of Occupational Safety and Health, 1994
pyrene	Workplaces	0.1mg/m^3	USA 1993	American Conference of Governmental Industrial Hygienists 1995
PAHs	Agricultural soil	0.1 mg/kg	Canada	CCME, 2007

2.3 Current remediation techniques of contaminated sites

Many remediation techniques have been developed to clean up soil, leachate, wastewater, and groundwater contaminated by various pollutants, including *in situ* (in the subsurface on site) and *ex situ* (to excavated soil, abstracted groundwater, or gaseous emissions) methods (Riser-Roberts, 1998). A combination of techniques may be required to treat a particular contaminated site for optimum remediation for the prevailing conditions. A summary of the current remediation techniques is presented in Table 5; the techniques are classified based on whether they are treatments that are applied *in situ* or *ex situ* and may be further grouped into biological, physical, chemical and thermal techniques. The focus is on individual techniques or groups of similar techniques as many remediation techniques may belong in more than one classification and/or group. Various techniques are readily available, but their selection is dependent on contaminant and site characteristics, regulatory requirements, costs, and time constraints (Riser-Roberts, 1998 and Reddy *et al*., 1999). The selection of suitable techniques is often challenging since most are site-specific but the selection step is extremely important in the successful remediation of a contaminated site. Biological, physical, chemical and thermal techniques may be applied in conjunction with one another to reduce the contamination to a safe and acceptable level (Reddy *et al*., 1999; RAAG, 2000). Only *in-situ* biological, physical, chemical and thermal techniques are currently available for remediating contaminated soil by crude oil/petroleum and related products in addition to their process, applicability, advantages, limitations and concerns, site-specific parameters, and costs of each remediation alternative (Defra 2010) is evaluated and discussed.

Table 5: Classification of remediation techniques by process

***In situ* Remediation Techniques**			
Biological	**Physical**	**Chemical**	**Thermal**
Permeable reactive barriers			Thermal desorption
Flushing			Incineration
Enhanced bioremediation		Chemical oxidation and reduction	
Phytoremediation	Electro-remediation		
Monitored natural attenuation	Stabilization/solidification		
Sparging			
Venting			
	Vitrification		

***Ex situ* Remediation Techniques**			
Biological	**Physical**	**Chemical**	**Thermal**
Biological treatment	Soil washing and separation process		Thermal desorption
	Stabilization/solidification		Incineration
	Venting		
		Chemical oxidation and reduction	
	Vitrification		

Source: Defra (2010)

2.3.1 *In situ* remediation techniques

In situ remediation methods normally take place on site, in the subsurface, without excavation of the contaminated soil or abstraction of groundwater. One of the main advantages is that *in situ* methods often avoid excessive environmental impacts and costs associated with excavation and abstraction and they can typically be applied on operational sites (Defra, 2010). A major constraint is making sure the remediation technique makes effective contact with the contaminants in the subsurface (e.g. facilitating and optimising the mixing of reagents and contaminants or installing a permeable reactive barrier in the correct place). Contact enhancement may be possible using pressure injection of reagents, or hydrofracturing techniques to improve penetration in clay (Defra, 2010). A detailed understanding of the characteristics of the site vis-à-vis contaminant properties (types, concentration, distribution etc.) and physical properties (e.g. soil matrix, heterogeneity, presence of buried structures, hydrogeology etc.) is required to overcoming this constraint (CIRIA, 1995). Pilot and treatability studies may be required in other to fully comprehend whether a particular technique will be effective on site (Defra, 2010).

However, as a result of the subsurface complex nature coupled with the required level of understanding, it becomes somewhat difficult to validate and verify performance of *in situ* remediation techniques. Consequently, a "lines of evidence" approach has been supported by the Environment Agency in order to verify the sets of data collected as key parameters to demonstrate the performance of *in situ* remediation (Environment Agency, 2010). Table 5.1 described some of the more commonly employed lines of evidence for each *in situ* remediation techniques in relation to their timescales which are generally longer than *ex situ* remediation techniques. Generally, a reduction in contaminant concentration, using accredited laboratory data will suffice as primary evidence, however, other additional lines of evidence are usually required to give more certainty in the treatment outcome. Moreover, extended time periods of monitoring and sampling may be pivotal in demonstrating successful remediation (Defra, 2010).

Most of the currently applicable *in situ* remediation techniques of contaminated soil such as venting, soil vapour extraction, bioventing, sparging, air sparging, biosparging, flushing, chemical oxidation and reduction, electro-remediation, stabilization and solidification, thermal treatment, monitored natural attenuation, enhanced bioremediation and phytoremediation are summarized below with a full scale cost comparison provided in Table 5.12.

Table 5.1: *In situ* remediation technique lines of evidence and typical timescales for verification

Techniques	Lines of evidence	Remediation timescale (year)
Venting	Remediation process conditions	1-3
Sparging	Geochemical indicators Biodegradation indicators Remediation process conditions Geophysical properties	0.5-3
Flushing	Remediation process conditions Tracer tests	1-3
Electro-remediation	Geochemical indicators Remediation process conditions	1-3
Stabilization and Solidification	Geochemical indicators Remediation process conditions Geotechnical properties	<1
Thermal Treatment	Remediation process conditions	<1
Chemical oxidation and reduction	Geochemical indicators Remediation process conditions Geophysical properties	<1
Monitored natural attenuation	Geochemical indicators Biodegradation indicators Geophysical properties Other biotransformation changes	1-30 Highly dependent on specific contaminant and remediation design
Enhanced bioremediation	Geochemical indicators Biodegradation indicators Remediation process conditions Other biotransformation changes	0.5-3
Phytoremediation	Bioassays Geotechnical properties Other biotransformation changes	>10

Source: Adapted from FRTR, 2007; CIRIA, 2004; Nathanail *et al*., 2007)

2.3.1.1 Venting

In situ venting which involves physical and biological techniques includes soil vapour extraction, bioventing, bioslurping, dual vapour extraction, dual phase extraction, multi-phase extraction in which air is moved through the unsaturated zone to encourage contaminants volatilization and/or biodegradation from soil and the vapour phase (Defra, 2010).

2.3.1.1.1 Soil vapour extraction (SVE)

Soil vapour extraction (SVE) which may also be referred to as soil venting or vacuum extraction is a recognized, acceptable and cost effective remediation techniques for unsaturated soils with volatile organic compounds (VOCs) and semi volatile organic compounds (SVOCs) contaminants (Suthersan, 1997; Zhan and Park, 2002; Halmemies *et al*., 2003). This technique normally involves vertical and/or horizontal wells installation in the area of soil contaminated which is often aided by air blower to facilitate the evaporation process (Khan *et al.*, 2004). Application of vacuums are usually through the wells close to contamination source in other to evaporate the volatile contaminated mass constituents that are withdrawn subsequently through an extraction well and treated often with carbon adsorption prior to being released into the atmosphere (USEPA, 1995a). SVE also stimulates the biodegradation of contaminants particularly the less volatile compounds by the increasing airflow through the subsurface (USEPA, 1996b, 1998a; Halmemies *et al*., 2003; Harper *et al*., 2003). This technique is also applicable in groundwater pumping and air stripping for contaminated groundwater treatment.

SVE is usually ideal in cases in which the contaminated unsaturated zone is relatively permeable and homogeneous otherwise an impermeable surface layer is most appropriate in other to minimize airflow and infiltration short-circuiting (Suthersan, 1997; Zhan and Park, 2002; Halmemies *et al*., 2003; Barnes *et al.*, 2002; Barnes, 2003). This technique is mostly successful when employed to lighter, and more volatile petroleum products such as gasoline while heavier petroleum products such as diesel fuel, heating oils, and kerosene may be difficult to treat using SVE. However, heated air injection may enhance the heavier products to be volatilized but the large quantity of energy required makes it somewhat unsustainable (USEPA, 1995a, 1998a; Zhan and Park, 2002). SVE technique effectively remediate contaminants such as benzene, toluene, xylene, naphthalene, biphenyl, perchloroethylene, trichloroethylene, trichloroethane, and gasoline from contaminated soils (see Table 5.2) and a simplified sketch of the process is depicted in Figure 2.7 (USEPA, 1996b; RAAG, 2000; Barnes *et al*., 2002).

2.3.1.1.2 Bioventing

Bioventing is a process in which air is injected at a maximum rate designed to biodegrade contaminants *in situ* from impacted media and minimize or eliminate the off gassing of volatilized contaminants into the atmosphere. The difference between bioventing and biosparging is that the latter pumps air and nutrients into the saturated zone while the former, bioventing only pumps air into the unsaturated or vadose zone (USEPA, 1998d; Mihopoulos *et al*., 2001) (see Figure 2.7). Degradation of less volatile organic contaminants also takes place during bioventing and the remediation of less permeable soil is allowed due to a reduced volume of air required (FRTR, 1999k). Generally, bioventing can be used to clean up any aerobically degradable contaminants and has been successful with a variety of petroleum products ranging from mid-weight such as diesel to light weight such as gasoline which tend to volatilize quickly and better treated with SVE. While the heavier weight takes longer to be treated with bioventing (Khan *et al.*, 2004). However, a pilot study may be required if the level of contaminants has to be remediated to lower than 0.1 ppm or if total petroleum hydrocarbon (TPH) reduction has to be greater than 95 % to ascertain the appropriateness of bioventing or consider other treatment option (USEPA, 1998d; Kao *et al*., 2001). There are potential advantages and disadvantages that should be assessed when considering the application of this technology as contained in Table 5.2.

Table 5.2: Venting applicability, potential advantage and limitations

Organic		**Inorganic**		**Materials**	
Halogenated VOCs	Y	Metals	N	Gravel >2mm	Y
Halogenated SVOCs	?	Radionuclides	N	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	N	Silt 2-60µm	?
Non-halogenated SVOCs	Y	Cyanides	N	Clay <2 µm	?
Organic corrosiveness	N	Asbestos	N	Peat	N
Organic cyanides	N	**Miscellaneous**			
PCBs	N	Explosives	N		
Pesticides/herbicides	N				
Dioxins/furans	N				

Potential advantages	**limitations**
Can be cost effective;	Limited by the structure of the soil, degree of saturation, pore connectivity and porosity;
Can treat many organic compounds, free product and dissolved phase;	Effectiveness can be hindered by a shallow water table unless water is pumped out;
Can induce physical and biological processes;	Limited by depth of contamination;
Minimal site disturbance;	Verification of treatment can be difficult;
It is easy to combine with other technologies;	
It requires short treatment times, from 6 months to 2 years;	Not applicable to inorganic compounds due to their low volatility.
Equipment is readily available and easy to install.	It cannot be applied to certain site conditions (low permeability, high clay content, etc.).
It is easy to combine with other technologies.	High concentrations of contaminants may be toxic to organisms.
It is effective at reducing VOCs in the vadose zone, thereby reducing the potential for further migration	It cannot always reach low clean-up limits.

Source: Nathanail *et al*. (2007); FRTR (2007); CL:AIRE TDP16 (2007); (USEPA, 1995a; 1996b; FRTR, 1999k).

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

2.3.1.2 Sparging

Sparging is an *in situ* physical and/or biological remediation technique which includes air sparging and biosparging that involves the injection of air or other gases below the water table to encourage volatilization and/or biodegradation of contaminants from soil, groundwatrer and the vapour phase (Defra, 2010).

2.3.1.2.1 Air sparging

Air sparging has since been used as an *in situ* remediation for VOCs dissolved in groundwater, sorbed to soils in the saturated zone, and trapped in the saturated zone pores (Suthersan, 1997; Benner *et al*., 2002; Adams and Reddy, 2003). During air sparging, atmospheric air is injected under pressure into the saturated zone to initiate the volatilization of contaminants in groundwater and to actively encourage biodegradation through increase subsurface oxygen levels (GWRTAC, 1996a; Biorem, 1998; Benner *et al*., 2002). Channels are formed by the injected air flowing upward through the contaminated plume from the saturated zone and into the vadose zone. The contaminants are volatilized by the injected air in the flow channels and subsequently transported to the vadose zone where they are biodegraded or removed by SVE system (Kirtland and Aelion, 2000) as shown in Figure 2.7. There are basically three contaminant removal mechanisms involved in air sparging and they include: (i) dissolved VOCs *in situ* stripping, (ii) trapped and sorbed contaminants volatilization below the water table in the capillary fringe, and (iii) aerobic biodegradation (Nyer, 1996). According to Bass *et al.* (2000) there is no need for active groundwater pumping when air sparging is employed as the remediation technique for contaminated soils and groundwater. As it addresses a broad range of VOCs and SVOCs contaminants in soil and groundwater including gasoline, other petroleum products and chlorinated solvents as shown in Table 5.3 (GWRTAC, 1996a). It has been reported that air sparging may be most suited to sites with relatively permeable and homogeneous soil conditions as a result of greater effective contact between injected air and soil or groundwater being treated, in addition to the effective volatilized vapour migration and/or extraction (GWRTAC, 1996a; Bass *et al*., 2000; Benner *et al*., 2002; Adams and Reddy, 2003; Tomlinson *et al.*, 2003).

Other site factors that may influence the use of air sparging are the saturated zone thickness and groundwater depth. According to Suthersan (1997), Adams and Reddy (2003) and Tomlinson *et al*. (2003) a small saturated zone thickness and shallow groundwater depth

will make the number of wells needed for adequate coverage using air sparging a more expensive treatment option.

2.3.1.2.2 Biosparging

Biosparging which is also an *in situ* technique is a process whereby air and nutrients are injected into the subsoil below the water table where it enhances the biodegradation of contaminants by indigenous microorganisms (USEPA, 1995a; Muehlberger *et al*., 1997; Brown *et al*., 1999). It can be employed to remediate petroleum products dissolved in groundwater, or absorbed to subsoil below the water table and within the capillary fringe. Biosparging is commonly used in conjunction with SVE particularly when volatiles are present (USEPA, 1998c; Muehlberger *et al*., 1997; RAAG, 2000) as demonstrated in Figure 2.7.

It can generally be used on most types of petroleum contaminated sites, even though it is least effective on heavy petroleum due to the lengthy duration needed for its treatment (USEPA, 1995a). Biosparging is often applied at sites with mid-weight and lighter petroleum products (USEPA, 1998c; Muehlberger *et al*., 1997; Brown *et al*., 1999). There are potential advantages and disadvantages that should be assessed when considering the application of this technology as contained in Table 5.3.

Table 5.3: Sparging applicability, potential advantage and limitations

Organic		**Inorganic**		**Materials**	
Halogenated VOCs	Y	Metals	N	Gravel >2mm	Y
Halogenated SVOCs	?	Radionuclides	N	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	N	Silt 2-60µm	?
Non-halogenated SVOCs	Y	Cyanides	N	Clay <2 µm	N
Organic corrosiveness	N	Asbestos	N	Peat	N
Organic cyanides	N	**Miscellaneous**			
PCBs	N	Explosives	N		
Pesticides/herbicides	?				
Dioxins/furans	N				

Potential advantages	**limitations**
Offers enhanced clean-up rates relative to groundwater pump and treat techniques;	Should only be applied to unconfined aquifers where injected air can freely reach the unsaturated zones and be subsequently collected;
Can be highly cost-effective;	Should not be applied where significant free phase hydrocarbons are present due to risk of contaminant mobilisation;
Minimal site disturbance;	Need to ensure a uniform air flow to avoid spreading the contaminant plume;
The equipment is readily available and easy to install;	Low injection rates reduce the need for vapour capture and treatment;
Treatment times are short, often from 6 months to 2 years;	There is some potential for the migration of contaminants.
Biosparging often enhances the effectiveness of air sparging;	Not suitable for treatment of inorganic contaminants.
It requires no removal, treatment, storage or discharge of groundwater;	

Source: Nathanail *et al*. (2007); FRTR (2007); CL:AIRE TDP9 (2004); Khan *et al.* (2004)

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

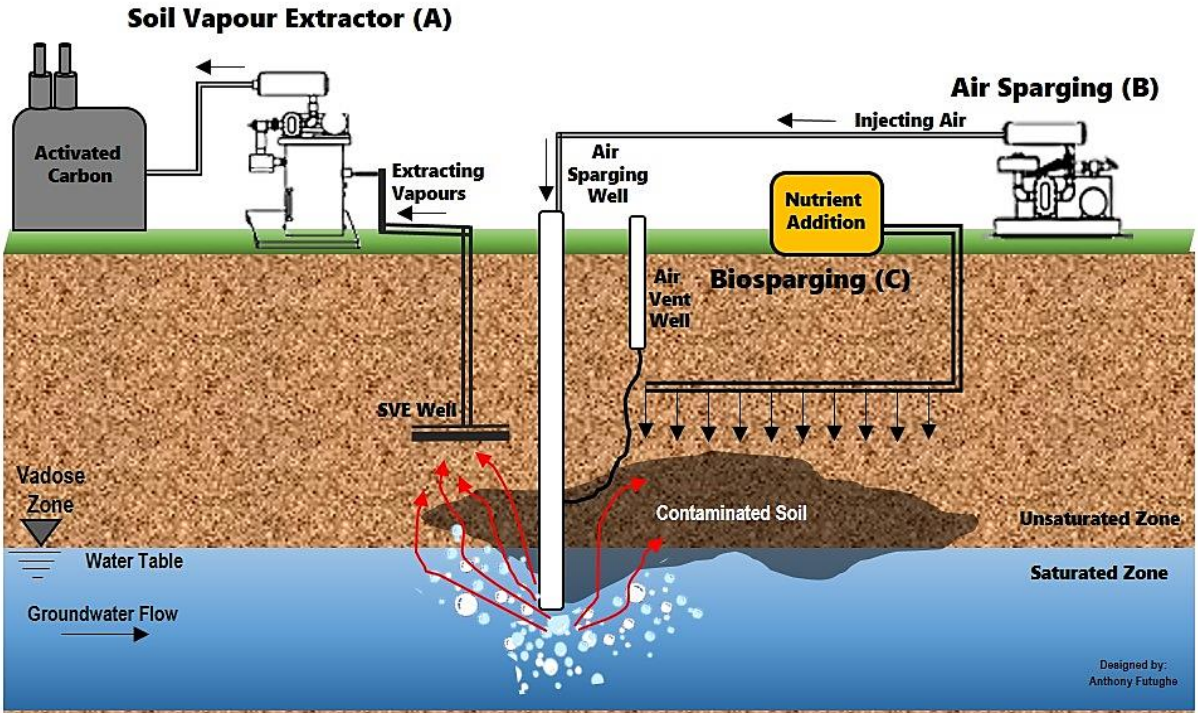


Figure 2.7: An illustration of a combination of *in situ* remediation of contaminated soil using **(A)** soil vapour extraction (SVE) in which air or steam is pumped into the contaminated soil to volatilze the organic contaminants and then extracted through SVE well for secondary treatment in the activated carbon chamber. **(B)** Air sparging injects clean air into the saturated zone or aquifer, with the air bubles traversing horizontally and vertically through the soil column, creating a subsurface stripper which removes the contaminant by volatilization. Contaminated air undergoes secondary treatment in the activated carbon chamber after extraction. **(C)** Biosparging introduces nutrients in addition to air into the subsoil below the water table where it enhances the biodegradation of contaminants by aerobic indigenous microorganisms.

2.3.1.3 Soil flushing

In situ flushing is an innovative remediation technique involving physical, biological and/or chemical processes that use aqueous solution to dissolve and recover contaminants from the ground by moving it to an area where it can be removed or recovered (USEPA, 1996e; Otterpohl, 2002; Logsdon *et al*., 2002; Di Palma *et al*., 2003; Defra, 2010). Soil flushing is accomplished by injecting an aqueous solution such as treated groundwater into the ground or sprayed over the ground and allowed to infiltrate in other to solubilise or mobilise contaminants into aqueous solution so as to stimulate *in situ* biodegradation and/or *in situ* redox reactions. After flushing, the groundwater solution or extraction fluids with the adsorbed contaminants are recovered using wells or trenches and may be treated at the surface to meet the appropriate discharge standards before being recycled or introduced into local, publicly owned, wastewater treatment plants or receiving water bodies (FRTR, 1999h; RAAG, 2000; Otterpohl, 2002; Son *et al*., 2003; Defra, 2010). A simplified sketch of the process is depicted in Figure 2.8.

In situ flushing is known to be used for both saturated and unsaturated zones treatment and also applies to all kinds of soil contaminants and is commonly used in conjunction with other remediation techniques such as activated carbon, biodegradation, and pump-and-treat (Boulding, 1996 and Defra, 2010). Additives such as acids (soil leachates), alkalis, chelating agents, surfactants and organic solvents (solvent flushing) are commonly used in soil flushing (Defra, 2010). A two-phase co-olvent flushing fungal biosorption process has been used to remediate DDT contaminated soil *in situ* as reported by Juhasz *et al.* (2003).

In situ flushing techniques can be used for remediation of inorganic, organic and radioactive contaminants including VOCs, SVOCs, fuels etc. as shown in Table 5.4 but may be relatively cheaper than alternative treatment techniques (FRTR, 1999h; Logsdon *et al*., 2002; Alter *et al*., 2003).

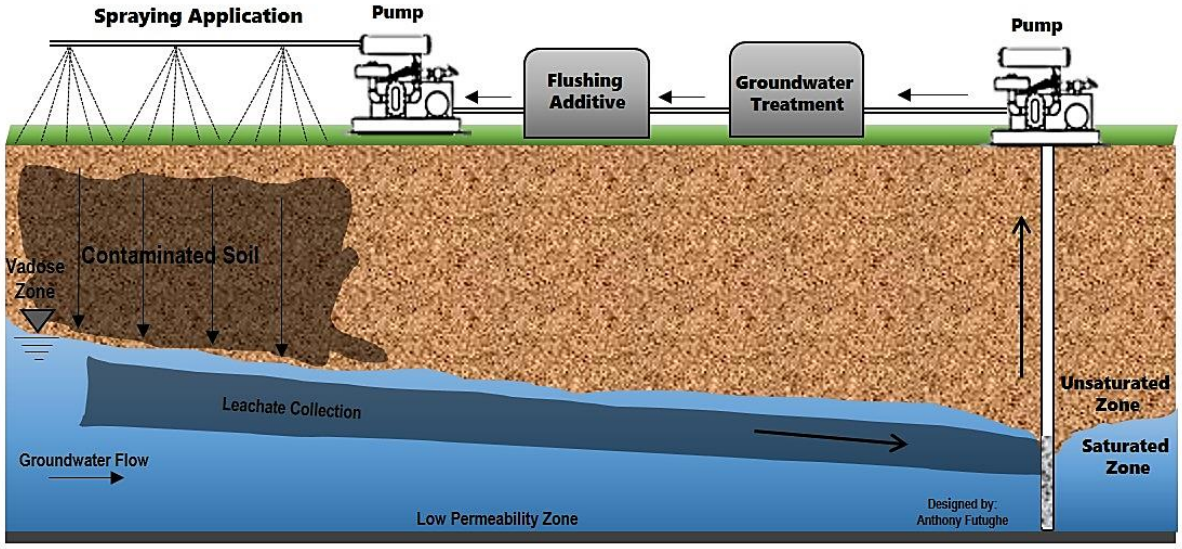


Figure 2.8: An illustration of a soil flushing *in situ* remediation of contaminated soil. Chemical solvents and solutions are injected into soil through injection wells and infiltration galleries. Extractant is removed, treated and may be recycled.

Table 5.4: Flushing applicability, potential advantage and limitations

Organic		**Inorganic**		**Materials**	
Halogenated VOCs	Y	Metals	Y	Gravel >2mm	Y
Halogenated SVOCs	Y	Radionuclides	?	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	?	Silt 2-60µm	?
Non-halogenated SVOCs	Y	Cyanides	?	Clay <2 µm	N
Organic corrosiveness	?	Asbestos	N	Peat	N
Organic cyanides	?	**Miscellaneous**			
PCBs	N	Explosives	?		
Pesticides/herbicides	N				
Dioxins/furans	N				

Potential advantages	**limitations**
Process can be designed to treat specific contaminants, including both organic and inorganic compounds; Can be used in both pathway management and source control; May prevent the need for excavation	Low permeability or heterogeneous soils are difficult to treat; Risk of worsening situation by producing more toxic or mobile compounds; Effectiveness can be hindered by a shallow water table; Good understanding of site geology and hydrogeology is required to prevent loss of contaminant and soil flushing solution beyond the capture zone and allay regulatory concerns; Above ground separation and treatment can be expensive; Remediation times are usually lengthy because of the slowness of diffusion processes in the liquid phase; This technology requires hydraulic control to avoid the movement of contaminants off-site; Hydrophobic contaminants require surfactants or organic solvents for their removal from the soil.

Source: Nathanail *et al*. (2007); FRTR (2007); Environmantal Agency (2006); CIRIA C622 (2004); Johnston *et al*. (2002); Boulding (1996); Juhasz *et al*. (2003)

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

2.3.1.4 Chemical oxidation and reduction

In situ chemical oxidation involves the introduction of liquid or gaseous oxidising agents (or oxidants) to the subsurface to bring about the rapid degradation or transformation of many organic and inorganic contaminants into less harmful chemical species (Figure 2.9). Several different forms of oxidants including Fenton's reagent (hydrogen peroxide, H_2O_2 and iron, Fe), ozone (O_3), permanganate (MnO_4^-), persulphate ($S_2O_8^{2-}$), etc. have been used for chemical oxidation. Partial degradation of some organic compounds usually occurs which can further be treated by other methods including bioremediation. Although, Arsenic (As)V may be the oxidized form of As III which becomes more toxic, requiring additional techniques in completing the remediation. Typical oxidants such as Fenton's reagent catalyst generates highly reactive free radical species. While permanganate (MnO_4^-) and ozone (O_3) by direct electron transfer or free radical species can oxidizes contaminants (Defra, 2010).

Chemical reduction on other hand involves reducing agents (reductants) addition to degrade chlorinated solvents and metals toxicity. Examples of typical reductants include zero valent iron (commonly used as the reactive material in permeable reactive barriers), zero valent iron can be added to soil by mixing or injected as nanoparticles (still at demonstration stage); Polysulphides: used in the reduction of metals to less lower toxicity forms (e.g. chromium (VI) to chromium (III)) (Defra, 2010).

Parameters including site specific condition coupled with oxidant-specific characteristics must be considered carefully in other to determine if chemical oxidation is a viable technique compared to other treatment options, and it is also equally important to determine which oxidants is most suitable (Scott and Bruce, 2006). There are potential advantages and disadvantage that should be assessed when considering the application of this technology as contained in Table 5.5.

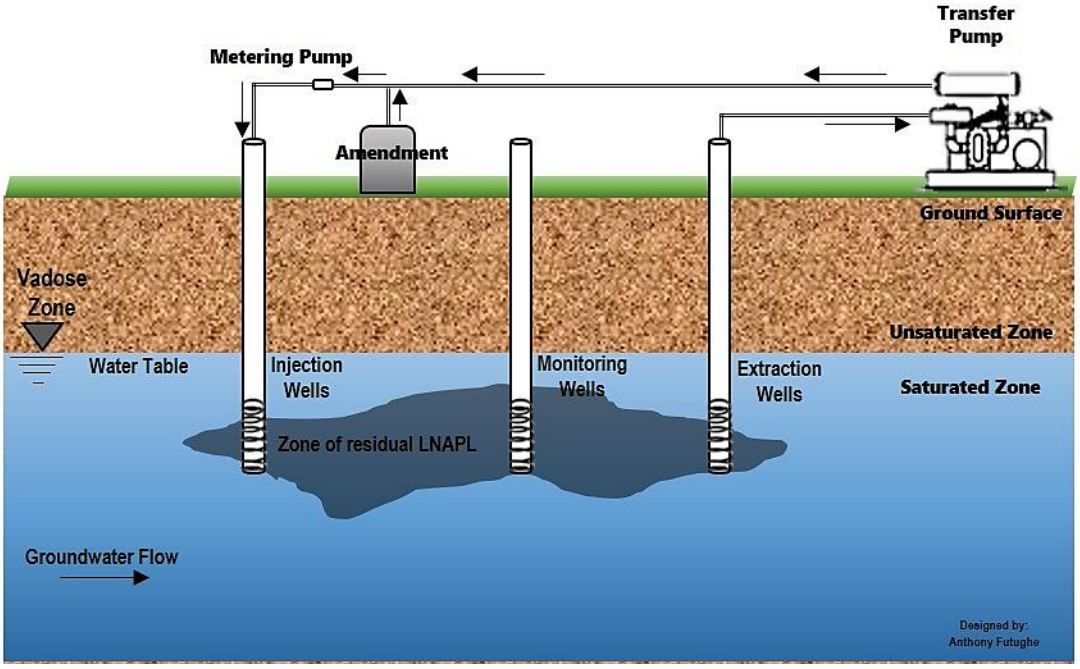


Figure 2.9: A schematic of oxidant injection process of *in situ* chemical oxidation in which the injected oxidant into the subsurface result to the target contaminants oxidation in soil and/or groundwater into relatively non-toxic products including water and carbon dioxide.

Table 5.5: Chemical oxidation and reduction applicability, potential advantage and limitations

Organic		Inorganic		Materials	
Halogenated VOCs	Y	Metals	Y	Gravel >2mm	Y
Halogenated SVOCs	Y	Radionuclides	N	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	?	Silt 2-60µm	Y
Non-halogenated SVOCs	Y	Cyanides	?	Clay <2 µm	?
Organic corrosiveness	N	Asbestos	N	Peat	N
Organic cyanides	N	Miscellaneous			
PCBs	Y	Explosives	?		
Pesticides/herbicides	?				
Dioxins/furans	N				

Potential advantages	limitations
Fast reactions can result in complete degradation and relatively fast treatment;	May require large volume of reagent;
Applicable to a wide range of organic contaminants;	Environmental considerations as using aggressive reagents;
Uses reagents that are considered low cost and easily delivered to the subsurface;	Toxic intermediate breakdown products may be formed;
Aqueous, sorbed, and non-aqueous phases of contaminants are transferred;	Groundwater may be coloured by reagents (e.g. permanganate is purple in solution);
Heat from H_2O_2 reactions enhances mass transfer, reaction rates and activity of microbes	Precipitation reactions may be reversible with changes in redox conditions over time;
Potentially enhances post-oxidation microbial activity and natural attenuation.	May be difficult to facilitate contact between contaminants and reagents in the treatment zone;
	Application limitation at heavily contaminated sites;
	Potential contaminant mobilization;
	Oxidative delivery challenges due to reactive transport and aquifer heterogeneities.

Source: Nathanail *et al*. (2007); Environmental Agency (2006); FRTR (2007); Princeton Chemistry and Environment (2003); Scott and Bruce (2006).

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

2.3.1.5 Electro-remediation

Electro-remediation which may also be referred to as electro-kinetic techniques, electrochemical techniques, electric current methods and electro-migration is the application of electro-chemical and -kinetic processes in saturated or unsaturated clay-rich soils, sediments, or sludge to remove metals, radionuclides and organic contaminants. Basically, is a separation and removal techniques that uses a low intensity direct current across a pair of electrodes already implanted in each side of a contaminated soil in the ground. Thereby mobilizing charged species such as ions and water towards the electrode and metal ions, ammonium ions and positively charged organic contaminants move towards the cathode. While anions like chloride and negatively charged contaminants move towards the anode (Defra, 2010) as demonstrated in Figure 2.10.

Electro-migration, electro-osmosis and electro-phoresis are the three mechanisms involved in the transportation of contaminants through the soil across each side of the paired electrode. Ions and ion complexes move towards an electrode in electro-migration, liquid particularly water containing ions is transported relative to a stationary charged surface in electro-osmosis, while electro-phores is involved in the movement of charged particles across the electrode. Upon migration of contaminants especially metals by electro-migration in the direction of their respective electrodes, removal and treatment usually by electroplating at the electrode; precipitation or co-precipitation at the electrode; pumping of water near the electrode above ground for *ex situ* treatment or capture on ion exchange resins which are emplaced in the ground can then take place (Defra, 2010).

The charge on an ionic species will determine the direction and transportation rate, both in polarity and in magnitude coupled with the electro-osmosis induced flow velocity. Non-ionic species including organic and inorganic contaminant will only be carried along by the electro-osmosis induced water flow. The transportation of organic contaminants back and forth through zones of treatment placed between electrodes can also be achieved using electro-osmosis. The contaminants change in direction is also reversible periodically due to the polarity of the electrodes (Defra, 2010). Some other applications of electro-remediation are the use of ion-rich precipitation band as asorptive barrier which promote chemical reactions; the use of an electro-kinetic fence for capturing ongoing contaminations from groundwater and facilitation by moving reagents and nutrients through the soil for other treatment processes (such as nutrients enhanced bioremediation). Electro-remediation technique can also be applied

ex situ on piled soil, or soils within larger containers (Defra, 2010). Table 5.6 show its applicability, advantages and limitations.

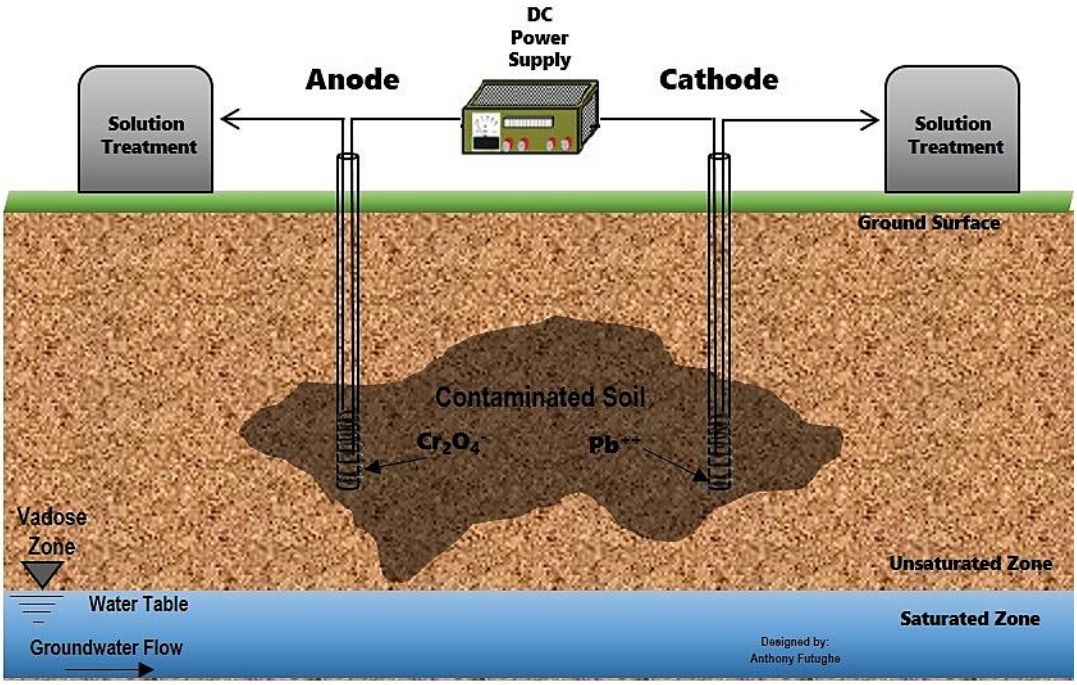


Figure 2.10: An illustration of *in situ* electro-remediation of contaminated soil. Application of a direct current voltage between a pair of electrodes placed in soil. Dissolved particles moved to respective electrodes under the influence of the electric field.

Table 5.6: Electro-remediation applicability, potential advantage and limitations

Organic		Inorganic		Materials	
Halogenated VOCs	?	Metals	Y	Gravel >2mm	N
Halogenated SVOCs	?	Radionuclides	?	Sand 0.06-2mm	?
Non-halogenated VOCs	?	Corrosives	?	Silt 2-60µm	Y
Non-halogenated SVOCs	?	Cyanides	?	Clay <2 µm	Y
Organic corrosiveness	N	Asbestos	N	Peat	?
Organic cyanides	N	Miscellaneous			
PCBs	N	Explosives	?		
Pesticides/herbicides	N				
Dioxins/furans	N				

Potential advantages	Limitations
Works best with fine grained materials such as clays; Applicable to metal contaminants, including some radionuclides; May be used to create *in situ* treatment zones by controlling water movement.	Need a soil water content of soil >10% to be effective; Buried services, metallic objects or ore deposits can cause problems; Production of hydroxide ions has to be controlled at the cathode to avoid unpredictable metal hydroxide precipitation; It is possible for the soil to heat up to temperatures that may cause damage to soil flora and fauna; Carbonate-rich materials limit application.

Source: Nathanail *et al*. (2007); CIRIA (1995); CL:AIRE RB2 (2003); FRTR (2007).

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

2.3.1.6 Stabilization and Solidification

This remediation technique also known as waste fixation, uses both physical and chemical processes in reducing hazardous substance mobility and contaminants in the environment (FRTR, 1999e; Sherwood and Qualls, 2001). The process in which the risk posed by hazardous waste is reduced by converting it into a less soluble, immobile, and less toxic form is generally referred to as stabilization. While solidification involves the process encapsulating waste materials in a monolithic solid of high structural integrity (Suthersan, 1997; Anderson and Mitchell, 2003) as illustrated in Figure 2.11. There are three main components involved in *in situ* stabilization and solidification which are: (i) mixing the contaminated soil; (ii) storage of reagent, preparation and feed system; and (iii) delivering the reagent to the soil mixing zone (Nyer, 1996). Binding refers to the mixture of reagents and additive employed in stabilization and solidification and ranges from a single to a multi-component reagent system. The addition of reagents to a contaminated material such as soil or sludge to produce more chemically stable constituents is generally referred to as stabilization while solidification impacts the physical/dimensional stability of a contaminated material upon reagents addition so that the contaminants will be contained and permeability to air and water reduced. Examples of reagents used include cements, pozzolans, ground granulated blastfurnace slag, lime-based binders (calcium oxide or hydroxide) and organophilic clays (Defra, 2010).

Soil contaminated by heavy metals, metalloids and other inorganic compounds as shown in Table 5.7 are commonly treated with either *in situ* or *ex situ* stabilization and solidification techniques. Although, stabilization may also be feasible in soil contaminated with low levels of organic constituents, even for volatile organic compounds (Riser-Roberts, 1998; Druss, 2003). However, most stabilization and solidification techniques are limited in terms of their effectiveness against organics and pesticides, except for asphalt and vitrification where most organics contaminants are destroyed (FRTR, 1999f; RAAG, 2000; Abbott *et al*., 2002; Wilk, 2003).

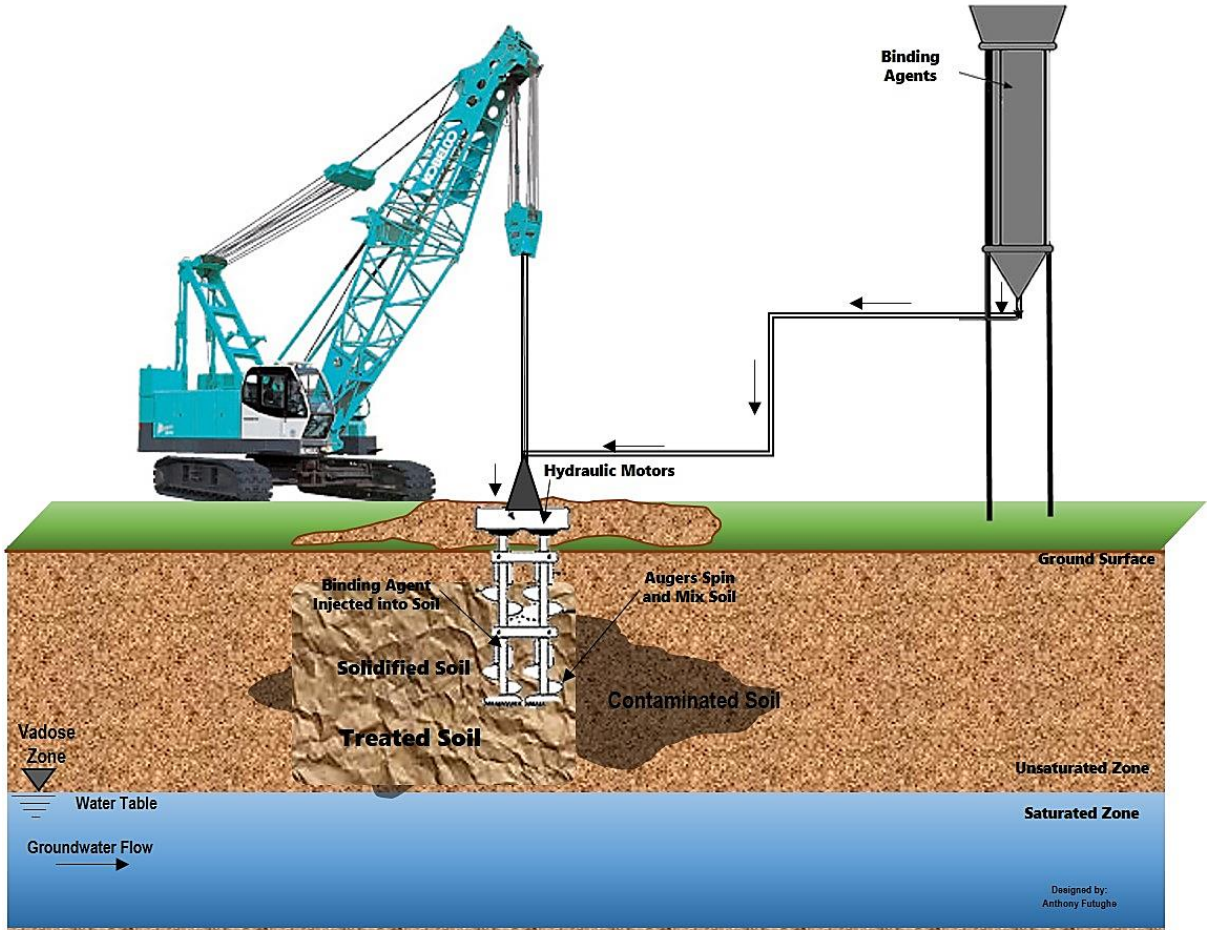


Figure 2.11: An illustration of *in situ* stabilization and solidification of contaminated soil, in which contaminants are transformed in the soil by encapsulation and fixation into environmentally inert materials of considerably reduced mobility.

Table 5.7: Stabilization and solidification applicability, potential advantage and limitations

Organic		Inorganic		Materials	
Halogenated VOCs	N	Metals	Y	Gravel >2mm	Y
Halogenated SVOCs	?	Radionuclides	Y	Sand 0.06-2mm	Y
Non-halogenated VOCs	N	Corrosives	Y	Silt 2-60µm	Y
Non-halogenated SVOCs	?	Cyanides	Y	Clay <2 µm	Y
Organic corrosiveness	?	Asbestos	Y	Peat	N
Organic cyanides	?	Miscellaneous			
PCBs	?	Explosives	?		
Pesticides/herbicides	?				
Dioxins/furans	?				

Potential advantages	Limitations
Can be used to treat recalcitrant contaminants such as heavy metals, PCBs, dioxin etc.;	Does not destroy or remove the contaminant;
Process equipment occupies a relatively small footprint;	May be difficult to predict long-term behaviour;
The physical properties of the soil are often improved by treatment such as increased strength, lower permeability.	May result in an overall increase in volume of material;
	May require long-term maintenance of protection systems and/or long-term monitoring;
	Reagent delivery and effective mixing can be difficult to achieve.

Source: Nathanail *et al*. (2007); FRTR (2007); CL:AIRE TB9 (2004); CL:AIRE GB1 (2005)

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

2.3.1.7 Thermal treatments

In situ thermal treatment is the application of electric energy or radiation to enhanced organic contaminants mobility in both the saturated and unsaturated zones in other to facilitate their recovery and treatment (Defra, 2010) as shown in Figure 2.12(a-c). The thermal treatment methods such as steam injection, hot air injection, electrical resistance heating, microwave heating, radiofrequency heating, electromagnetic heating, thermal conductive heating, thermally-enhanced soil vapour extraction increase the ground temperature and subsequently results in enhanced contaminant removal using either one or more of the following techniques: increased volatilisation; reduced viscosity; increased solubility in water; decreased adsorption; drying of the soil which can increase air permeability, hence may improve extraction; and direct application of heat that can accelerate chemical reactions resulting to the destruction of contaminants. Subsequently, upon the heating process application, subsurface conditions may encourage biodegradation acceleration of the residual contaminants (Defra, 2010).

In situ thermal treatment basically have four main methods which include:

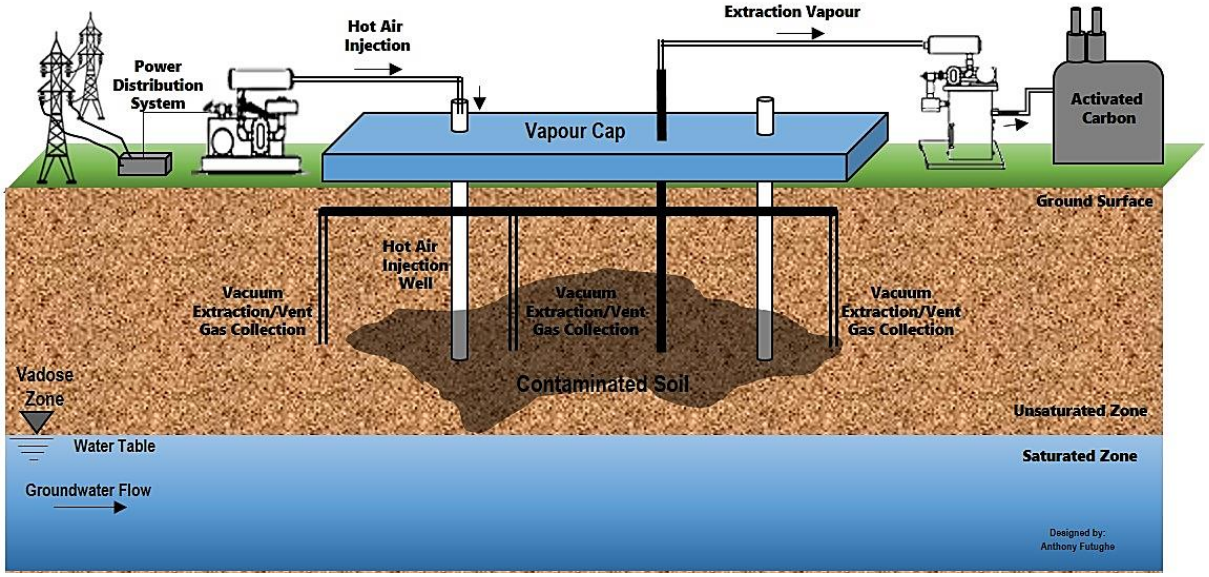
Steam or hot air injection which can generate temperatures up to 170^{o}C *in situ* on the surface and subsequently injected through a series of injection wells into the treatment zones. The contaminants are pushed towards the extraction wells as a result of both the heat and pressure exerted into the treatment zones (Defra, 2010) (see Figure 2.12a).

Electrical resistance heating passes an electric current between electrodes through the soil/aquifer within the treatment zone. Heat is generated due to soil resistance as the current flows through the moisture in between soil pores. This can generate temperatures *in situ* of about 100^{o}C (Defra, 2010).

Electromagnetic heating molecular motion and soil heating increase as a result of radiofrequency or microwaves emitted from electrodes or antennae within the treatment zone. Although radiofrequency waves are lower in energy but have greater penetration which can also heat dry soil. While microwave with greater energy have low penetration, however, the presence of free water in the matrix to be heated strongly influence the heating process as electromagnetic heating can generate temperature over 300^{o}C in the soil (Defra, 2010) (see Figure 2.12b).

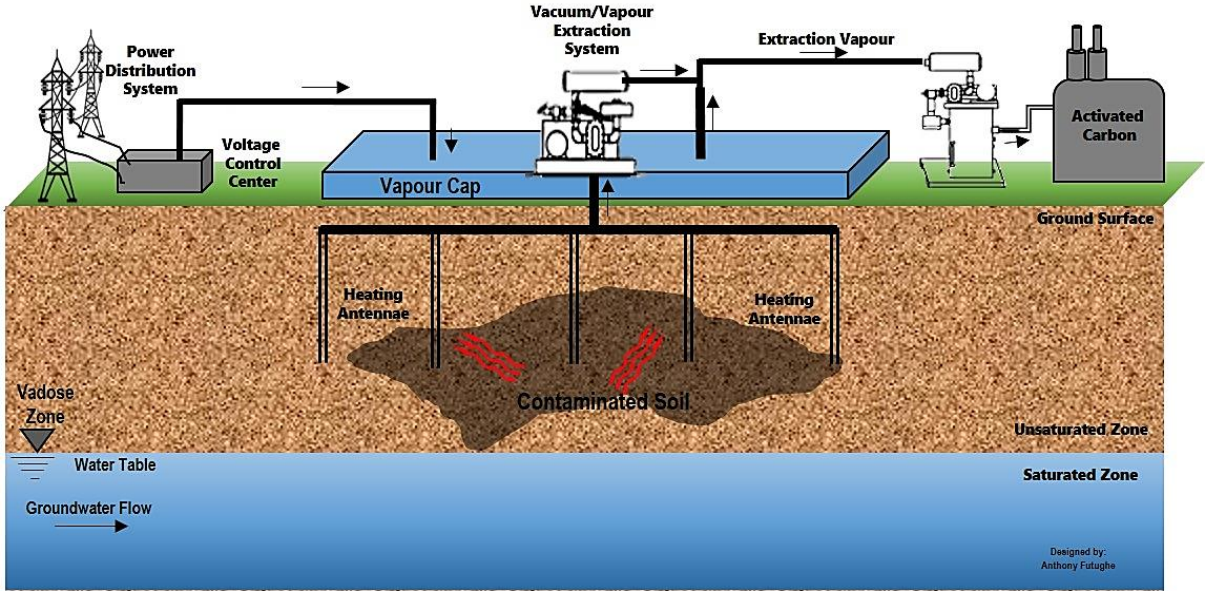
Thermal conductive heating is the application of heat via conductive transfer by utilizing installed metal rods within cased wells. This can generate approximately 800^{o}C with diverse ranges of applicability for contaminants (see Table 5.8) and soil and groundwater conditions, treatment efficiencies, and cost (Defra, 2010) (see Figure 2.12c).

Some form of recovery and treatment operations such as venting and/or pumping, activated carbon, thermal or catalytic oxidation are needed in all the heating techniques above. Thermal treatment should be employed based on their efficiency under a given conditions and not necessarily on their specific temperature attainment (Defra, 2010).



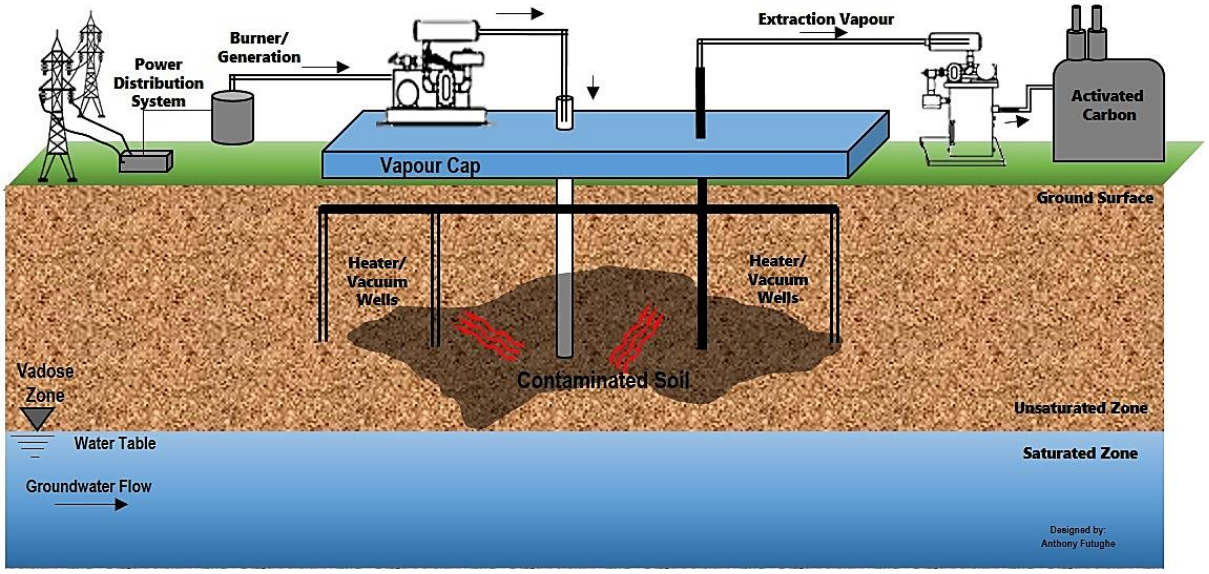
(a):

Figure 2.12a: *In situ* thermal treatments of contaminated soil. (a) *in situ* hot air injection in which injection/vacuum wells are used to introduce the hot air that heat the subsurface in order to increase contaminant mobility and extraction efficiency with off-gases extracted and treated.



(b):

Figure 2.12b: *In situ* thermal treatments of contaminated soil. (b) *in situ* electromagnetic heating with microwave emmited from antennae within the subsurface. Extracted vapours/gases may undergo further secondary treatment using activated carbon.



(c):

Figure 2.12c: *In situ* thermal treatments of contaminated soil. (c) *in situ* thermal conductive heating utilizing dual heater/vacuum wells to heat soils and displace contaminants which are collected and treated.

Table 5.8: Thermal treatment applicability, potential advantage and limitations

Organic		Inorganic		Materials	
Halogenated VOCs	?	Metals	?	Gravel >2mm	Y
Halogenated SVOCs	Y	Radionuclides	N	Sand 0.06-2mm	Y
Non-halogenated VOCs	?	Corrosives	N	Silt 2-60µm	Y
Non-halogenated SVOCs	Y	Cyanides	N	Clay <2 µm	Y
Organic corrosiveness	N	Asbestos	N	Peat	?
Organic cyanides	N	Miscellaneous			
PCBs	?	Explosives	?		
Pesticides/herbicides	?				
Dioxins/furans	?				

Potential advantages	Limitations
Applicable to a wide range of soil types; Applicable to difficult dense non-aqueous phase (DNAPL) contaminants; Minimal site disturbance.	Buried objects or utilities may cause operating problems; Potential for damage to soil structure, fauna and flora and impacts on groundwater quality; Enhanced mobility of contaminants might lead to migration outside the treatment zone.

Source: Nathanail *et al*. (2007); FRTR (2007); CL:AIRE TDP26 (2008); CL:AIRE TDP28 (2009); CL:AIRE TDP24 (2010); Unified Facilities Criteria (2006); USEPA (2006).

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

2.3.1.8 Monitored natural attenuation

Natural attenuation is an *in situ* treatment technique which is also known as passive remediation, *in situ* bioremediation, intrinsic remediation, bio-attenuation, and intrinsic bioremediation depends on the physical, chemical and biological processes for the reduction of contaminant concentration levels, flux or toxicity within a specific timeframe (Defra, 2010 and Khan *et al.*, 2004). The rate at which these processes occur can be used as a risk management method. These natural processes include biodegradation, chemical degradation, sorption, immobilisation, dispersion and dilution, or combination of all resulting to a reduction in the toxicity, mobility or concentration of the contaminant. In other words, the contaminated environment is undisturbed while these natural processes act on it. Although this remediation technique is usually seen as the 'do nothing' or 'walk away' technique to site remediation, it requires a proactive verification and monitoring approach including but not limited to extensive site characterization and collecting lines of evidence to demonstrate that natural attenuation is ongoing to meet the site remedial objectives within the specific timescale rather than totally rely on 'engineered' processes (DENIX, 1995; Wiedemeier *et al*., 1999; Khan and Husain, 2002; 2003 and Defra, 2010).

Fundamentally, natural attenuation through biodegradation processes, reduce the mass of contaminants; through dilution and/or dispersion, reduce contaminant concentrations; or prevent migration of contaminants by binding them (adsorption) to soil particles (USEPA, 1996c; Khan and Husain, 2003). The mixing of contaminants with soil and groundwater through dispersion/dilution, over time results to their concentration reduction and not their destruction (DENIX, 1995). While adsorption is the attachment or sorbtion of contaminants to soil particles underground thereby preventing contaminants migration into potential areas that might threatened public health (USEPA, 1996c). The process involving the break down or degradation of contaminants especially of organic origin such as PAHs by microorganisms e.g. bacteria, fungi and/or yeast into less toxic or non-toxic forms is referred to as biodegradation or bioremediation (USEPA, 1996c). Indigenous microorganisms use the organic contaminants in the soil or groundwater as their primary energy source, thereby resulting to the contaminants' biodegradation (DENIX, 1995). The microbial degradation of organic contaminants such as hydrocarbons, normally takes place through aerobic respiration, anaerobic respiration and fermentation (Canter and Knox, 1985). In aerobic respiration, available oxygen is employed by microorganisms to initiate the breakdown process (USEPA, 1996h) of carbon-the energy source by series of enzyme-mediated reactions where oxygen acts as an external electron

acceptor (Riser-Roberts, 1992). While in anaerobic respiration, microbial activity takes place in the absence of oxygen to break down contaminants in the soil through a series of enzyme-mediated reactions in other to release the energy it needs such as nitrates, sulfates, carbon dioxide, and other oxidized compounds (excluding oxygen) acting as electron acceptors (USEPA, 1996h; Riser-Roberts, 1992; Wiedemeier *et al*., 1999; Khan and Husain, 2002; 2003). Fermentation is the breakdown of organic contaminants (carbons) by a series of enzyme-mediated reactions without the involvement of an electron transport chain except that initiated by the organic compound acting as both electron donors and acceptors (Riser-Roberts, 1992).

Natural attenuation has been recognized by US EPA as a viable remediation technique for soil and groundwater treatment and its selection is usually based on its ability to meet remediation targets within a reasonable time scale (DENIX, 1995). Underground storage tank (UST) programs in the United States, now accept the use of natural attenuation method as a valid option to remediating petroleum hydrocarbon contaminated sites. It can effectively remediate hydrocarbon fuels, such as gasoline and BTEX compounds (benzene, toluene, ethylbenzene, and xylene) in soil and groundwater (USEPA, 1996c; Hejazi, 2002). Table 5.9 shows its applicability, advantages and limitations.

Table 5.9: Monitored natural attenuation applicability, potential advantage and limitations

Organic		Inorganic		Materials	
Halogenated VOCs	Y	Metals	?	Gravel >2mm	Y
Halogenated SVOCs	Y	Radionuclides	?	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	?	Silt 2-60µm	?
Non-halogenated SVOCs	?	Cyanides	?	Clay <2 µm	?
Organic corrosiveness	?	Asbestos	N	Peat	?
Organic cyanides	?	Miscellaneous			
PCBs	?	Explosives	Y		
Pesticides/herbicides	?				
Dioxins/furans	N				

Potential advantages	Limitations
It is a relatively simple technology compared to other remediation technologies;	Requires a long term commitment to monitoring and a contingency plan (and funds) if the contaminants or groundwater do not behave as predicted;
Less generation or transfer of remediation wastes;	Requires significant depth of understanding of local geology and hydrogeology;
Less intrusive as few surface structures are required;	Subsurface conditions may change over time and may result in renewed mobility of previously stabilised contaminants.
Can be used in conjunction with, or after, other remediation methods;	
Overall cost likely to be lower than many active remediation technologies.	

Source: Nathanail *et al*. (2007); FRTR (2007); Environmental Agency (2006); CL:AIRE RB3 (2005).

Key:
Y = usually or potentially applicable
? = may be applicable
N = not applicable

2.3.1.9 Enhanced bioremediation

Bioremediation is the use of microbes especially bacteria and/or fungi to transform or degrade contaminants to its non-toxic by-products. The introduction of reagents such as calcium peroxide, magnesium peroxide, hydrogen peroxide, proprietary oxygen release compounds which creates aerobic conditions by releasing oxygen, or stimulating oxygen removal by generating hydrogen through hydrogen-releasing reagents (e.g. molasses, vegetable oil, proprietary hydrogen release compounds), thereby creating anaerobic conditions is an enhanced form of bioremediation. These reagents are usually added in solutions, slurry or as powder by direct emplacement or by injection. Microbes can carry out biodegradation of organic contaminants under aerobic conditions to carbon dioxide and water in addition to mass of microbial cells while they biodegrade organic contaminants to methane with little quantity of carbon dioxide and traces of hydrogen gas under anaerobic conditions (Defra, 2010).

Although, inorganic contaminants such as heavy metals and metalloids cannot be degraded by bioremediation, it can however, be used to change the valence state of the inorganic contaminant species resulting to adsorption, immobilisation onto soil particles and consequently precipitation. Enhanced bioremediation can also be used in conjunction with other remediation techniques such as soil flushing. (Defra, 2010). Table 5.10 presents its applicability, advantages and limitations.

Table 5.10: Enhanced bioremediation applicability, potential advantage and limitations

Organic		Inorganic		Materials	
Halogenated VOCs	Y	Metals	?	Gravel >2mm	Y
Halogenated SVOCs	Y	Radionuclides	?	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	?	Silt 2-60µm	Y
Non-halogenated SVOCs	Y	Cyanides	?	Clay <2 µm	?
Organic corrosiveness	?	Asbestos	N	Peat	?
Organic cyanides	?	Miscellaneous			
PCBs	?	Explosives	?		
Pesticides/herbicides	?				
Dioxins/furans	?				

Potential advantages	Limitations
Can be used to treat soil and groundwater;	Difficult to apply to a heterogeneous subsurface;
Minimal site disturbance;	Uncertain supply of quantity of amendments;
Lower monitoring costs in comparison with monitored natural attenuation due to accelerated remediation;	Toxic intermediate breakdown products may be formed.
Relatively simple technique.	

Source: Nathanail *et al*. (2007); FRTR (2007); Environmental Agency (2006); CL:AIRE TDP4 (2004).

Key:

Y = usually or potentially applicable

? = may be applicable

N = not applicable

2.3.1.10 **Phytoremediation** (see Section 2.5)

Phytoremediation according to Cunningham *et al.,* (1996) is the application of plants to extract, degrade, contain, remove, sequester or immobilize contaminants in soil, water and other contaminated media. The generic term phytoremediation consists of the Greek prefix "phyto" (plant) which is attached to the Latin root "remedium" (to correct or remove an evil). This plant technology is applicable to both organic such as crude oil and inorganic such as heavy metal pollutants present in the ecosystems including soil, water or air (see Table 5.11) (Salt *et al.,* 1998; Raskin *et al.,* 1994). The use of phytoremediation is best to treat large surface areas with shallow contamination due to the toxicity of high levels of contaminants to plants and inhibition of its growth. The plant mechanisms of action employed in treating contaminated soil especially crude oil (hydrocarbons) contaminated land *in situ* are phytodegradation, phytovolatilization, phytostabilization, rhizodegradation, and phytoextraction (see Section 2.5 for detailed review). A simplified general overview of the above mechanism is presented in Figure 2.13. These various mechanisms of action can treat a wide range of contaminants at low and moderate levels of concentration including petroleum hydrocarbons (Aprill and Sims, 1990), volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), heavy metals (Brown *et al.*, 1994; Diez *et al.*, 2016; Futughe, 2012), radionuclides, and munitions Dushenkov *et al.,* 1999; Huang *et al.,* 1998), however, not all mechanisms of action are applicable to all contaminants.

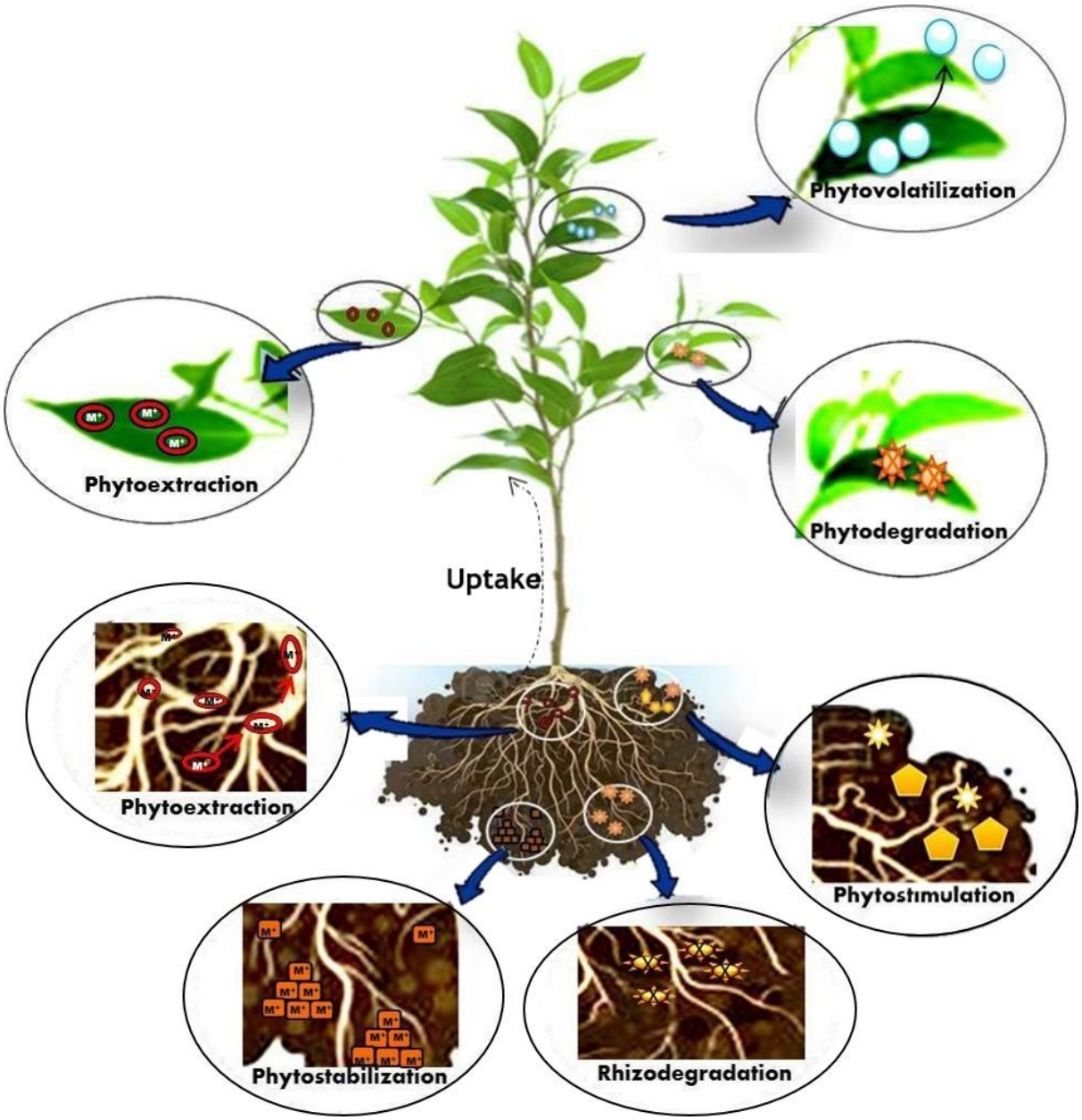
Table 5.11: Phytoremediation applicability, potential advantage and limitations

Organic		Inorganic		Materials	
Halogenated VOCs	Y	Metals	Y	Gravel >2mm	Y
Halogenated SVOCs	Y	Radionuclides	Y	Sand 0.06-2mm	Y
Non-halogenated VOCs	Y	Corrosives	Y	Silt 2-60µm	Y
Non-halogenated SVOCs	Y	Cyanides	Y	Clay <2 µm	Y
Organic corrosiveness	N	Asbestos	Y	Peat	Y
Organic cyanides	N	Miscellaneous			
PCBs	Y	Explosives	Y		
Pesticides/herbicides	Y				
Dioxins/furans	Y				

Potential advantages	Limitations
It is cost-effective for large contaminated sites (with a low concentration of contaminants);	Usually requires more than one growing season;
The soil can remain at a site after the removal of the contaminant rather than being disposed of or isolated;	Treatment is limited to soils less than one meter from the surface and groundwater less than 3 m from the surface;
Organic pollutants may be converted to CO2 and H2O instead of transferring toxicity;	Climate and hydrologic conditions such as flooding and drought may restrict plant growth and the type of plants that can be utilized;
Accomplished with minimal environmental disturbance;	Contaminants may enter the food chain through animals which eat the plants used in these projects;
It is an aesthetically pleasing and passive, solar energy driven technology;	Extraction moves the contaminants to biomass which may create ahazardous waste, which may be expensive to dispose;
	high concentrations of contaminants can be toxic to plants;
It can be used on a large range of contaminants;	Transfer of contamination across media, e.g., from soil to air; or mobilised into groundwater or bioaccumulated in animals.
The generation of secondary wastes is minimal;	
Provided vegetative cover;	
May enhance biodiversity;	
The topsoil is left in a usable condition and may be used in agriculture;	
The uptake of contaminated groundwater can prevent the migration of contaminants.	

Source: Nathanail *et al*. (2007); FRTR (2007); CL:AIRE (2001); Faisal *et al.* (2004).

Key: Y = usually or potentially applicable; ? = may be applicable; N = not applicable



Source: Futughe *et al.* (2020)

Figure 2.13: Phytoremediation mechanisms of action

Table 5.12: Cost estimate for full-scale *in situ* remediation techniques for contaminated land

Technique	Contaminants treated	Costs	Reference
Soil vapour extraction	Volatile organic contaminants (VOCs) and semi volatiles organic contaminants (SVOCs), fuels etc.	15-160 €/ton	FRTR (2005); EPA (2005a)
Bioventing	Petroleum hydrocarbons, nonchlorinated solvents	25-120 €/ton	FRTR (2005); EPA (2005a)
Biosparging	Organic contaminants	50-110 €/ton	Doelman and Breedveld (1999); EPA (2005a)
Flushing	Volatile organic contaminants (VOCs) and semi volatiles organic contaminants (SVOCs)	19-190 $/ m^3	FRTR (2005); EPA (2005a)
Chemical oxidation and reduction	Toxic organic chemicals, chlorinated solvents and metals	70-400 €/ton	FRTR (2005); EPA (2005a)
Electro-remediation	Metals and polar organics	50-170 $/$m^3$	FRTR (2005); EPA (2005a; 2005b)
Stabilization and Solidification	Inorganic and some organic contaminants	50-130 €/ton	FRTR (2005); EPA (2005a)
Thermal treatment	Volatile organic contaminants (VOCs) and semi volatiles organic contaminants (SVOCs), fuels, some pesticides etc.	30-130 $/ m^3	FRTR (2005)

Monitored natural attenuation	Benzene, toluene, ethyl benzene and xylene (BTEX), chlorinated and petroleum hydrocarbons	Depends on monitoring duration/period	Renner (1998); Mulligan and Yong (2004); Salminen *et al.* (2004)
Enhanced bioremediation	Petroleum hydrocarbons, solvents, pesticides, wood preservatives, munitions etc.	15-160 €/ton	Doelman and Breedveld (1999); EPA (2005a); FRTR (2005)
Phytoremediation	Organic and inorganic contaminants	Depends on methods	FRTR (2005); Adams *et al.* (2000)

2.4 Overview of sustainability considerations in remediation

Sustainability in relation to remediation is a complex and multi-faceted issue with a general classification of sustainability into three dimensions: environmental impacts, social effects and economic viability. These three dimensions of sustainability are often expresses under two models such as the Venn diagram and the 'bull's eye' models as shown in Figure 2.14. The Venn diagram model depicts that all three dimensions are equally important and overlapping while the bull's eye model suggests that the economy is a portion of the human society which in turn is a portion of the environment. The core mission of environmental sustainability of remediation is to reduce the risk of harm from contamination in addition to minimizing secondary adverse impacts related with remediation techniques. Two spectrums have been linked to the economic sustainability which include: (i) the cost of remediation operations; and (ii) the consequential effect of restored site in relation to the broader economy. Although, the formal is usually included in conventional remediation decision making, the latter is barely studied in literature or considered in practice (Hou and Abir, 2014). In the social aspects, impacts of remediation on worker safety, community and the general public are important and often includes stakeholder engagement and public participation, environmental justice and social inclusion. There is general consensus that social sustainability lacks developmental tools such as quantitative indicators in addressing its issues (Ellis and Hadley, 2009; ITRC, 2011). And this may be as a result of institutional barrier as remediation experts focused more on technology with little attention and knowledge on social implications. Environmental remediation processes may also be accelerated by the inclusion of social consideration (Hou and Abir, 2014).

According to the Brundtland report published in 1987 by the World Commission on Environment and Development, sustainable development has been defined as the '*development which meets the needs of the present without comprising the ability of future generations to meet their own needs'* (Brundtland, 1987) which is the most generally accepted definition.

World leaders in 2015 at a historic United Nations summit in New York, adopted sustainable development goals (SDGs) also known as 2030 Agenda for Sustainable Development with outlines of 17 SDGs and 169 accompanying targets. The following was stated about the goals:

"While the SDGs are not legally binding, governments are expected to take ownership and establish national frameworks for the achievement of the 17 Goals. Countries have the primary responsibility for follow-up and review of the progress made in implementing the Goals, which

will require quality, accessible and timely data collection. Regional follow-up and review will be based on national-level analyses and contribute to follow-up and review at the global level." (United Nations, 2017).

Globally, attempts have been made over the years to incorporate sustainability concepts in various segments of contaminated sites remediation and the most recent is sustainable remediation. Various initiatives as shown in Table 6 including sustainable remediation forum-UK (SURF-UK) and United States sustainable remediation forum (SURF-US) developed framework for sustainability assessment of contaminated land clean up in view of incorporating criteria of sustainable development in contaminated land management.

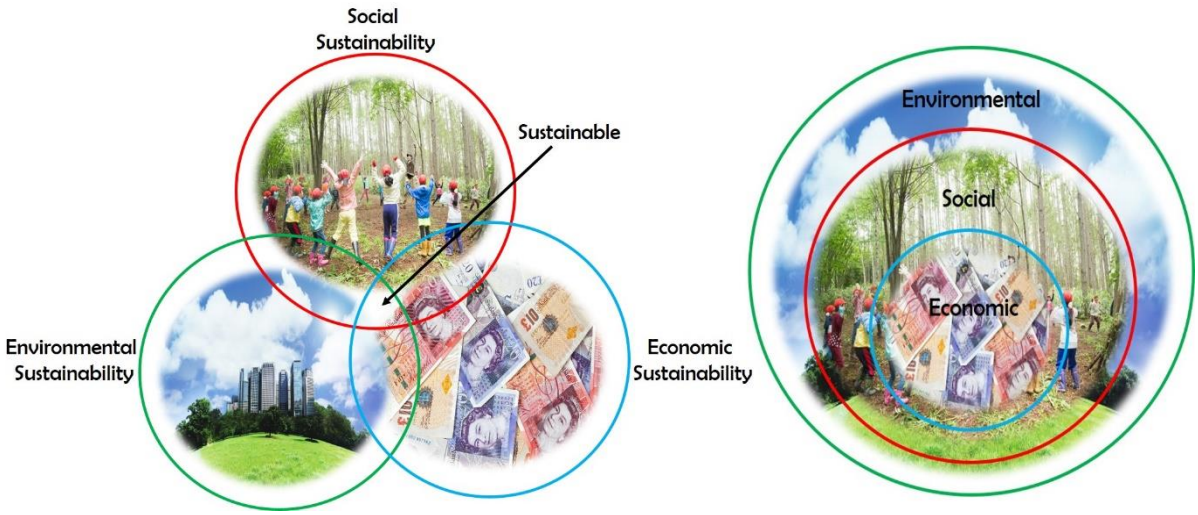


Figure 2.14: The two often used sustainable models: Venn diagram (left) and the Bull's eye (right).

Table 6: Major networks and forums involved in sustainability remediation globally

Network/Forum	Description
Sustainable Remediation Forum (SURF) (United States)	Initiated in 2006 to "promote the use of sustainable practices during cleanup activities" (SURF, 2017). Published white paper (USSRF, 2009) and framework (Holland *et al*., 2011).
Sustainable Remediation Forum – UK (SuRF-UK)	Initiative set up in 2007 to "progress the UK understanding of sustainable remediation". Published Framework, Indicator Set, and Management Practices amongst others. (CL:AIRE, 2017). Published framework and indicator set (SuRF-UK, 2010; SuRF-UK, 2011).
Common Forum (EU)	Initiated in 1994. Mission includes being a platform for knowledge exchange as well as for discussion on policy, research, technical and managerial concepts of contaminated land in Europe. (Common Forum, 2017)
Network for Industrially Co-ordinated Sustainable Land Management in Europe (NICOLE)	"The overall objective of NICOLE is to pro-actively enable European industry to identify, assess and manage industrially contaminated land efficiently, cost-effectively, and within a framework of sustainability." (NICOLE, 2017)
Interstate Technology and Regulatory Council (ITRC) (United States)	"A public-private coalition working to reduce barriers to the use of innovative air, water, waste, and remediation environmental technologies and processes." (ITRC, 2017)

Source: adapted from Anderson (2017)

2.4.1 Sustainable remediation: an emerging concept to contaminated land

Application of sustainable remediation is becoming increasingly important all over the world coupled with policy and guidance reflecting sustainable practices globally. Sustainable practices generally are those that include recognition of the economic and natural resources, ecology, human health and safety, and quality of life (NAVFAC, 2014). Consequently, an integrated assessment approach of the environmental, economic, and social impacts of remediation activities is referred to as sustainable remediation. A number of definitions have been given for sustainable remediation which include:

"The practice of demonstrating, in terms of environmental, economic and social indicators, that the benefit of undertaking remediation is greater than its impact, and that the optimum remediation solution is selected through the use of a balanced decision-making process" (SuRF-UK 2009); *"A remedy or combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources"* (USSRF, 2009); *"Sustainable practices result in cleanups minimizing the environmental and energy 'footprints' of all actions taken during a project life"* (EPA 2008b).

Sustainable remediation takes into consideration a range of environmental factors and impacts on community and integrates economic, ecological, and social implications when carrying out investigation and implementing remediation activities. Sustainable remediation may also consider the following (ITRC, 2011):

- ✓ *Impacts of site remediation on the surrounding community/region that are both economic and social (e.g., job loss/creation, tax revenue from redevelopment of brownfield sites);*
- ✓ *Effects on public health associated with remediation activities;*
- ✓ *Improved public health and safety through environmental remediation;*
- ✓ *Social benefits of site restoration activities (e.g., environmental justice and other equity issues, increased adaptability);*
- ✓ *Improved education, skills, values, and leadership capacity of individuals and/or the community;*
- ✓ *Economic incentives for various remedial options/activities;*
- ✓ *Economic implications of carbon emissions/sequestration as a result of site remediation;*
- ✓ *Economic implications of changes in resource value as a result of site remediation (e.g., habitat loss/creation); and*

- ✓ *Social implications of end land use (e.g., increased social inclusion and interaction, security, and adaptability).*

The normal rationale for remediation is the reduction of negative effects on humans and the environment. However, sustainable remediation goes beyond environmental stewardship through site restoration and revitalization (ITRC, 2011) typically associated with high cost and environmental footprints, which may be significant in comparison to the reduction risk. According to Bardos *et al*. (2011) the contradicting effects associated with remediation have not gone unnoticed among decision-makers and many stakeholders over the last decade. A more holistic view with a number of strategies and programmes on remediation has been developed so as to provide for a more sustainable remediation approach. For example, relevant metrics and methods were established by the US EPA Green Remediation programme for evaluating the environmental footprint of remediation operations (US EPA, 2012). While a framework and indicators for a comprehensive sustainable assessment has been suggested by SuRF UK on remediation actions in view of environmental, economic and social effects positively or negatively (SuRF UK, 2010; 2011). The Network for Industrially Contaminated Land in Europe (NICOLE) has also suggested a sustainability assessment framework (NICOLE, 2012). Currently, the International Standard Organization (ISO) develops an informative standard for sustainable remediation of contaminated land.

2.4.2 Sustainable remediation movement in Europe

Policy makers and industrial stakeholders in Europe started advocating since the early 2000s for a risk-based approach in contaminated land management (CLARINET, 2002a,b; NICOLE, 2002). CLARINET which is made up of a network of basically contaminated land policy makers and advisors across national ministries and environmental agencies in Europe, developed the risk-based land management (RBLM) framework with sustainability its key objective that embodies the evaluation and optimization of environmental, economic, and social factors (NICOLE, 2005). In Europe, coupled with the risk management, the concept of sustainable remediation is commonly considered in the context of sustainable land redevelopment (NICOLE, 2008). A desire for "demonstrating the need not to implement unnecessary or unsustainable remediation measures" (SuRF-UK, 2010), in addition to regulatory demand in remediation approaches that are "suitable for use" (Defra, 2006). Several regulatory and financial incentives have been reported by Thornton *et al*. (2007) to encourage brownfield regeneration of contaminated land. In England for example, 79% of new

accommodation was built on previously developed land in 2008 as a result of a public policy which mandated the development of new dwellings preferably on brownfield land (DCLG, 2009). One of the main policy objectives in the UK's statutory guidance for contaminated land was to ensure that remediation burdens are ''compatible with the principles of sustainable development'' (Defra, 2012). Generally in Europe, there are more development components in sustainable remediation which differs from the US green remediation movement as summarized below.

2.4.3 Green remediation movement in the United States of America

Until recently, the concept of green remediation or sustainable remediation was not very popular in the US (Hou and Abir, 2014). The presidential executive orders 13423 (2007) and 13514 (2009) have driven significantly sustainable remediation initiatives in the US federal agencies (AFCEE, 2010; USACE, 2010; NAVFAC, 2011) as both executive orders encourage sustainability considerations in the operations of all federal agencies. Consequently, the US EPA in 2008, incorporated sustainability practices in contaminated site remediation as a technology primer on green remediation (USEPA, 2008). This lead to several government agencies sustainable remediation initiatives on policies, regulatory guidance, and technology toolkits to encourage and promote sustainability practices in contaminated site remediation (DTSC, 2009; USEPA, 2009; Illinois EPA, 2012; Minnesota PCA, 2012; Oregon DEQ, 2012; USEPA Region 10, 2012; USEPA Region 2, 2012; USEPA Region 9, 2012) which corroborated with the advocacy from industrial associations especially the Sustainable Remediation Forum (SURF, an organization founded in 2006) (Ellis and Hadley, 2009; Favara *et al*., 2011; Holland, 2011; Holland *et al*., 2011; ITRC, 2011).

2.4.4 Theoretical framework for sustainability assessment in remediation

Contaminated land remediation is usually considered to be sustainable in practice as it often leads to the reuse and redevelopment of hitherto developed land. Most remediation techniques, however, comprise a wide range of activities with environmental, social and economic impacts. Cost and duration in particular which is the largest and most striking impact will normally be accounted for when choosing an appropriate remediation technique while overlooking other potentially significant impacts such as the use of raw materials or emission. Generally, process-based techniques are often regarded as sustainable compared to dig and dump (Harbottle *et al.,* 2008a). Currently, there are a range of frameworks and guidance

documents on sustainable remediation published all over the world, parallel with a rapidly increasing peer-reviewed journal literature. The ASTM (2013) published sustainable remediation standards, and recently ISO (2017) consolidating international state of practice on sustainability assessment and approaches in the context of optional appraisal of remediation techniques (Nathanail *et al.,* 2017). The broad concept of sustainability is generally understood as comprehensive information about individual indicators (Sing *et al.,* 2009 and World Resources Institute, 2018). Sustainability assessment usually requires all stakeholders including those executing the assessment to agree on a set of individual criteria (Bardos *et al.,* 2018). The sustainable remediation forum for the UK (SuRF-UK) in 2011 published guidance on sustainable criteria also known as "indicators" by SuRF-UK to be considered when drawing up assessment-acting as a checklist. These criteria were organized across 15 "headline" categories with each of environment, social and economic indicators having five as shown in Table 7. This indicator checklist by SuRF-UK remains the most comprehensive and detailed guidance for the selection of sustainability assessment criteria in sustainable remediation planning and appraisal option worldwide (Rizzo *et al.,* 2016) with its headline categories replicated in the ISO Standard (ISO, 2017) and its approach based on the Brundtland definition of 'sustainable development' (Brundtland, 1987).

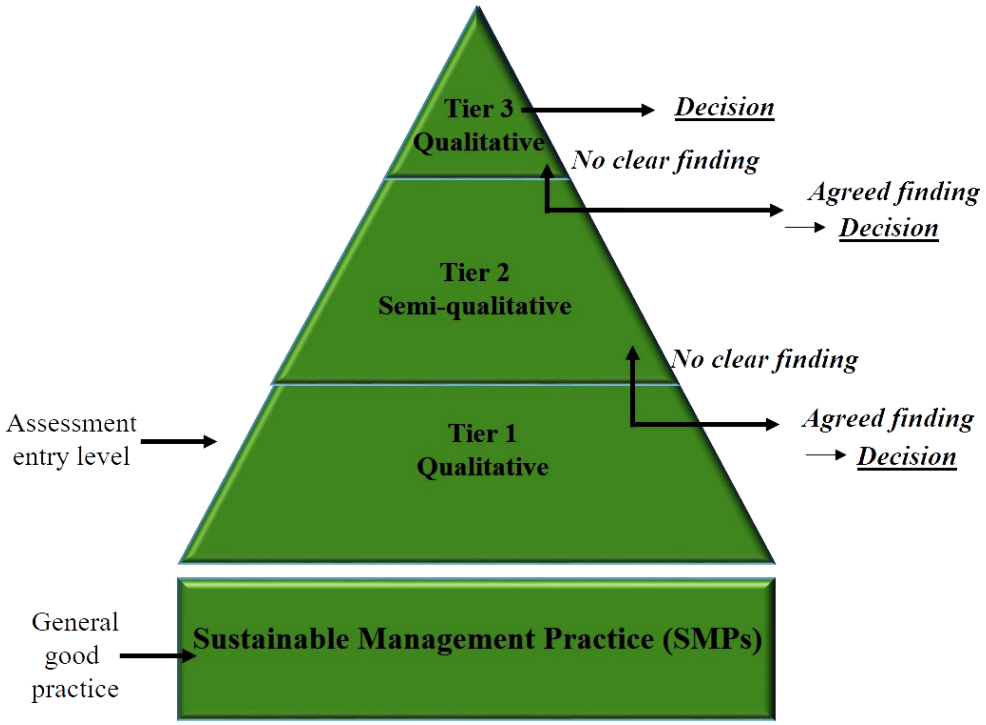
Table 7: SuRF-UK Indicators headline categories for sustainability assessment of remediation options.

Environmental	Social	Economic
✓ Emission to air (including climate change);	✓ Human health impacts and safety;	✓ Direct economic costs and benefits;
✓ Impacts on soil and ground conditions;	✓ Ethical and equity considerations;	✓ Indirect economic costs and benefits;
✓ Groundwater and surface water impacts;	✓ Impacts on neighborhoods and locality;	✓ Employment and employment capital gain;
✓ Ecology impacts;	✓ Communities and community involvement;	✓ Induced economic costs and benefits;
✓ Use of natural resources and waste generation.	✓ Uncertainty and evidence.	✓ Project lifespan and flexibility.

Source: CL:AIRE (2011); SuRF (2010).

2.4.4.1 Sustainable remediation assessment methods

In order to compare and select the optimal remediation solutions and further show how performance is verified, some form of sustainability assessment is needed. These approaches as suggested by SuRF-UK should be based on the simplest form of sustainability assessment which produces a reliable management decision which in most cases is a qualitative assessment (Bardos *et al.,* 2016). However, if there is no clear preferred option of remediation after qualitative assessment, or if one or more stakeholders questioned the option, then it becomes necessary to go for a semi-quantitative approach as shown in Figure 2.15 which is based on scorings and weightings. A fully quantitative approach would only be undertaken if the semi-quantitative assessment also failed to reach a resolution such as a monetised cost benefit assessment (Bardos *et al.,* 2018). However, transparency and reduced scope may be lost as sustainability assessment progresses through these tiers (Bardos *et al.,* 2011). A number of difficulties associated with transparency, scope, and reliability of the valuation process, may impact on the cost-benefit analysis, in particular, and may not be able to persuade all stakeholders (Ackermann, 2008). A good working practice on site as its explicitly recognised in Figure 2.15, is another important facet of achieving sustainability for which detail guidance has been developed by SuRF-UK (Cl:AIRE, 2014).



Source: CL:AIRE (2014)

Figure 2.15: A tiered approach to sustainability assessment

According to SuRF-UK (2010), sustainable remediation assessment by the applied specific tool is less important than the process and thought that goes into the assessment. Any assessment in view of environmental, social and economic factors from diverse stakeholder perspectives and that supports a management decision centred on a clear and documented process may be more accepted than the one that uses a 'black box' as sustainable assessment tool which may fail to justify properly input data and assumptions. There are a range of tools and methods available for undertaking a sustainability assessment or its component as shown in Table 8. Essentially, all tools and methods seek to achieve the same outcome: assessing the environment, social and economic benefits and costs for a range of suitable options achieving a project goal (SuRF-UK, 2010). The benefits and costs of the assessment method are measured in some way and seek to identify:

- ✓ Whether the overall benefit of remediation exceed the overall costs of doing the work; and
- ✓ Where benefit exceeds cost, for some methods, the method or methods which provides the greatest overall net-benefit.

Table 8 shows coverage of the environmental, economic and social indicators of sustainable development considered in the different tools; be it quantitative or qualitative techniques; whether or not contaminated land management applications are known to exist at the present. The scope of analysis was also shown be it limited (narrow) or not (wide) for each aspect relating to its typical coverage of any particular aspects of sustainability. As an example, an appraisal on carbon footprint focuses on a 'narrow' segment of environmental sustainability issues while ignoring soil functionality, biodiversity and landscape impact, whereas a 'wide' cost-benefit analysis could consider all of these aspects, as long as it was suitably specified (SuRF-UK, 2010).

Table 8: Sustainable remediation assessments selected relevant decision support techniques

Technique	Environment	Society	Economic	Type	CLM Application
Scoring/ranking systems (including multi-criteria analysis)	Narrow to Wide	Narrow to Wide	Narrow to Wide	Both	Yes
Best Available Technique (BAT)	Narrow to Wide	Narrow	-	Qualitative	Yes
Carbon footprint (‘area’)	Narrow	-	-	Quantitative	Yes
Carbon balance (flows)	Narrow	-	-	Quantitative	-
Cost benefit analysis (CBA)	Narrow to Wide	Narrow to Wide	Narrow to Wide	Quantitative	Yes
Cost effectiveness analysis (CEA)	Narrow to Wide	Narrow to Wide	Narrow to Wide	Both	Yes
Eco-efficiency	Narrow	-	-	Quantitative	-
Ecological footprint	Narrow	-	-	Quantitative	-
Energy/intensity efficiency	Narrow	-	-	Quantitative	-
Environmental risk assessment (ERA)	Narrow to Wide	-	-	Both	Yes
Human health risk assessment (HHRA)	-	-	Narrow	Both	Yes
Environmental impact assessment/Strategic environmental assessment (EIA/SEA)	Narrow to Wide	-	-	Qualitative	Yes
Financial risk assessment	-	Narrow	-	Quantitative	-
Industrial ecology	Narrow to Wide	Narrow to Wide	-	Quantitative	-
Life Cycle Assessment (based)	Narrow to Wide	-	-	Quantitative	Yes
Quality of life assessment	Wide	Wide	Wide	Qualitative	-

Source: SuRF-UK (2010).

Key:
Both = Qualitative and/or quantitative
CLM = Contaminated Land Management
- = Technique has no known coverage

2.4.4.2 Stakeholder's involvement

One of the important aspects of a sustainability assessment is stakeholders' engagement due to the following three reasons as stated by SuRF-UK (2010):

i. Stakeholder opinions can act as a vital source of information about specific sustainability aspects. Stakeholders may also be involved in decision-making directly such as the owner and regulator of the site; while other may still be influential even though they are not directly involved such as the local community interest;
ii. The robustness of the decision may be improved through consultative processes;
iii. Stakeholder consultation is part of good governance.

Other key issues information on contaminated land risk management have been described by SNIFFER (2010) and CL:AIRE (2007a, 2008). At the centre of decision-making, the stakeholders are generally the project team, which includes the owner of the site, those being affected by the contaminated site, the service provider, the regulator(s) and planners. Other stakeholders, nonetheless, may be influential such as:

- ✓ Those making using of the site (i.e. workers, unions, and other visitors);
- ✓ Those with financial involvement associated with the ownership of the sites (e.g. bankers, founders, lenders, insurers);
- ✓ Neighbours close to the sites (e.g. adjacent owners and tenants, local councils and communities); and
- ✓ Other technical specialist such as researchers, non-governmental organization (NGOs) and pressure groups, especially for more complicated problems (SuRF-UK, 2010).

2.5 Phytoremediation

Currently, numerous studies abound to show that energy intensive techniques burn fossil fuels and release CO_2 into the atmosphere contributing substantially to global warming (Zecca and Chiari, 2010) and remediation experts are aware of this problem (Ellis and Hadley, 2009). Phytoremediation as an emerging sustainable remediation technique does not have any negative significant effect on soil functions, structure and other environmental compartments and have received increased attention globally. The large area of land affected in the Niger Delta region precludes *ex-situ* treatment as a result of economic constraints and requires the use of a relatively inexpensive remediation techniques, such as phytoremediation. Generally, a range of different mechanisms are associated with phytoremediation which include phytosequentration/phytostabilization, phytoextraction, phytovolatilization, phytodegradation, rhizodegradation and phytostimulation. Basically, these mechanisms utilize plant physiological processes such as translocation, root exudation, uptake of water and nutrient and transpiration in relation to contaminant properties.

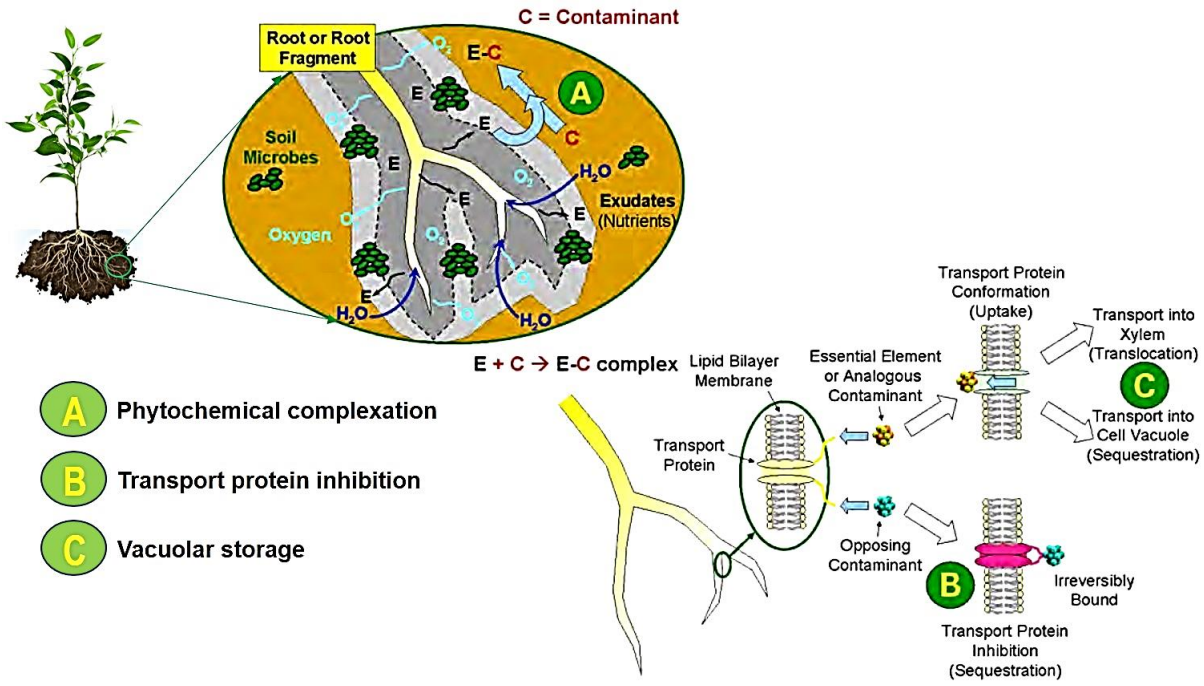
2.5.1 Phytosequestration/Phytostabilization

Phytosequestration/phytostabilization is a process whereby exudates such as phytochemicals from plant roots eliminate or reduce the mobility of contaminants in the rhizosphere through demobilization, stabilization and subsequently bind them on the roots or substrate through transport proteins and cellular process. This process can make metals and metalloids in the soil to become less toxic by transforming them and not getting rid of them from the soil (Adams *et al*., 2000; Chaney *et al*., 1997; Cunningham and Berti, 2000; Prasad, 2004). Adsorption and accumulation are usually employed by roots of some plant species in which organic and/or inorganic contaminants are adsorbed onto roots or precipitated within the root zone in other to immobilize them in the soil, sediment or groundwater (USEPA, 2000; Prasad and Freitas, 2003). There are three mechanisms of phytosequestration in contaminant mobility reduction and in the mitigation of contaminant migration to soil, water, and air as shown in Figure 2.16a. These are:

- ✓ Phytochemical complexation in the root zone: Immobilization or precipitation of contaminants of interest in the rhizosphere by exuded phytochemicals thereby reducing the fraction of the contaminant that is bioavailable (ITRC, 2009);
- ✓ Root membrane transport protein inhibition: Contaminants can bind irreversibly and stabilize on the root surface by transport proteins associated with the exterior membrane

of the root, thereby preventing them (contaminants) from entering the plant (ITRC, 2009);

- ✓ Root cells containing vacuolar storage: Transfer of contaminants between cells can also be facilitated by transport proteins in such a way that contaminants are stored or sequestered into the vacuoles of root cell thereby preventing further translocation to the xylem (ITRC, 2009).

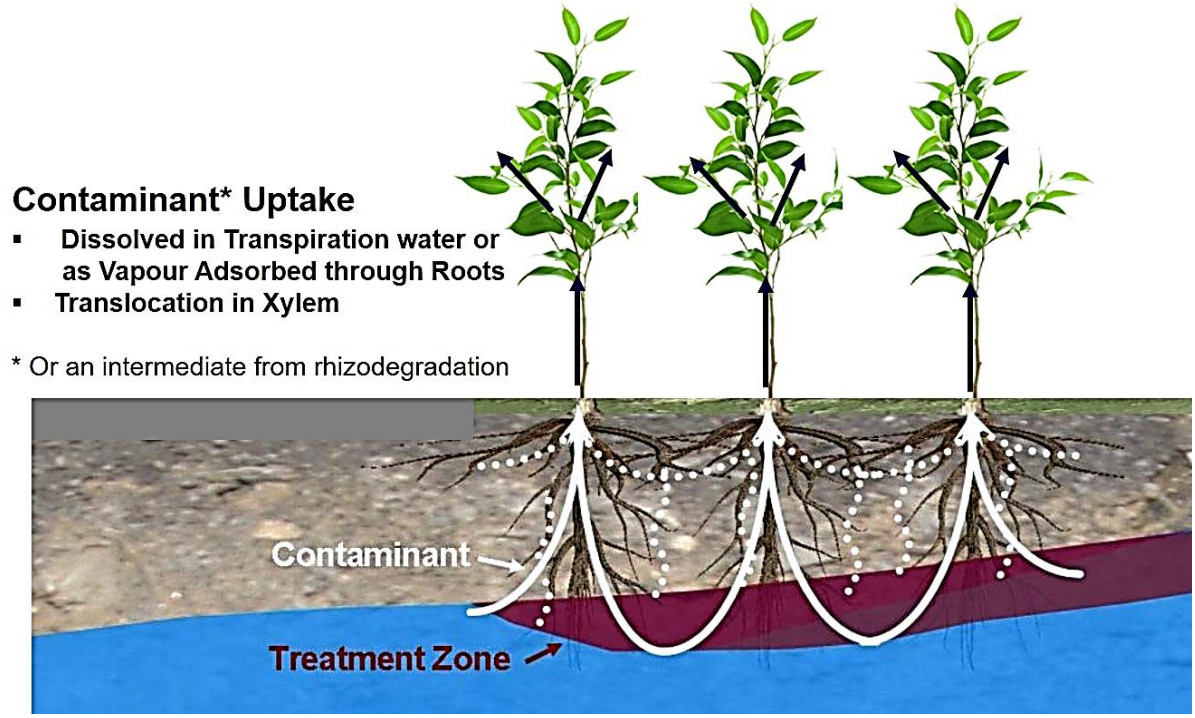


Source: Adapted and modified from ITRC (2009)

Figure 2.16a: Phytosequestration/phytostabilization mechanisms showing A: phytochemical complexation, B: transport protein inhibitor, C: vacuolar storage.

2.5.2 Phytoextraction

Phytoextraction is a process in which plants absorb and/or remove metals, metalloids, radionuclides and organic contaminants present in soils, sediments, or sludge by uptake with the transpiration stream and translocate them to the aboveground shoots or leaves which are harvested and destroyed or recycled (USEPA, 2000; Prasad and Freitas, 2003; Cunningham *et al*., 1995; Vassilev *et al*., 2004; ITRC, 2009). Contaminants must be dissolved in the soil water and make contact with the roots of the plant before it can be extracted through the transpiration stream or through vapour adsorption onto the organic root membrane in the vadose zone. Upon adsorption, the contaminants may be dissolved into the transpiration water or taken up through the active transport mechanism of the plant as depicted in Figure 2.16b (ITRC, 2009).

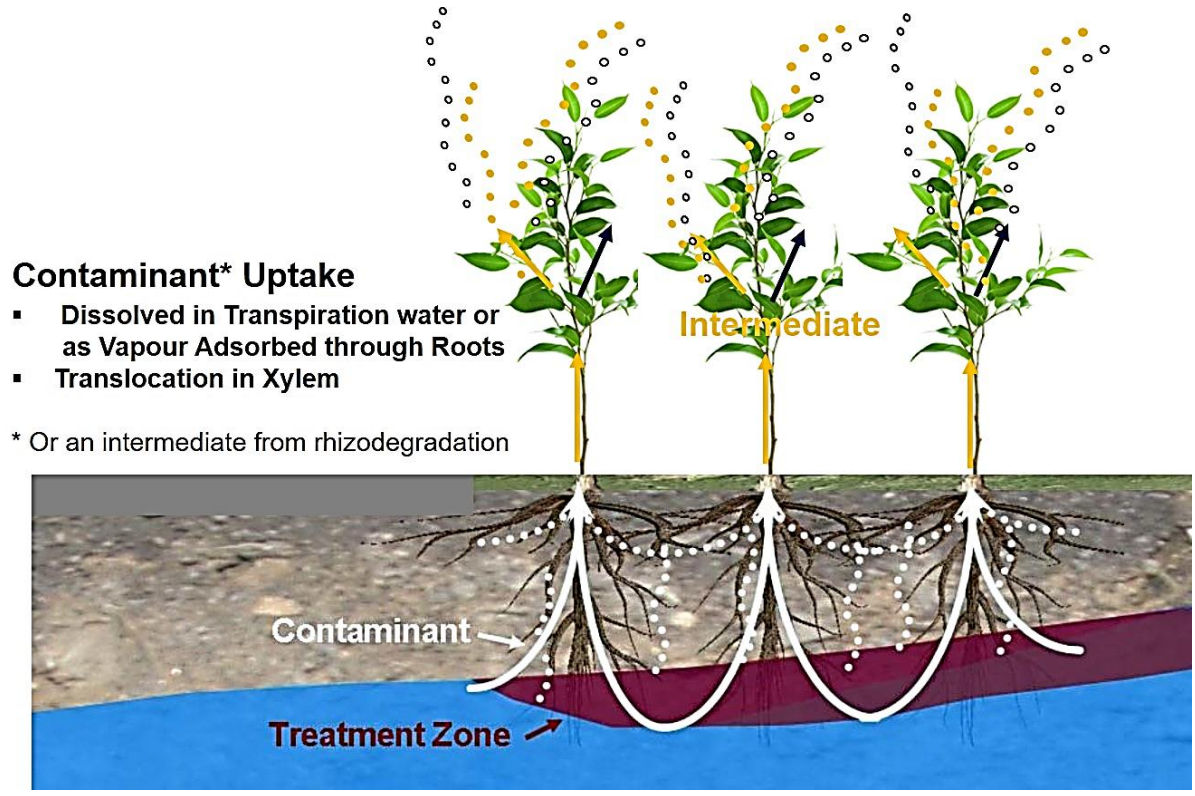


Source: Adapted and modified from ITRC (2009)

Figure 2.16b: Phytoextraction mechanisms in which specific plant species absorb and remove heavy metals, metalloids, radionuclides and organic contaminants from soils, sediments and sludge media and "uptake" them into harvestable root and shoot tissue.

2.5.3 Phytovolatilization

Phytovolatilization is the process whereby contaminants from soil, groundwater, sediment or sludge are taken up, translocated and subsequently transpired in their original or less toxic forms in the transpiration stream from the plant either from the leaf stomata or from plant stems (Ma and Burken, 2002) as shown in Figure 2.16c. The ability of organic contaminants to volatilize is dictated by their chemical properties such as the Henry's constant and vapour pressure. In some cases, rhizodegradation and/or phytodegradation breakdown products of the parent contaminant along transpiration pathway may be the phytovolatilized constituent (ITRC, 2009).

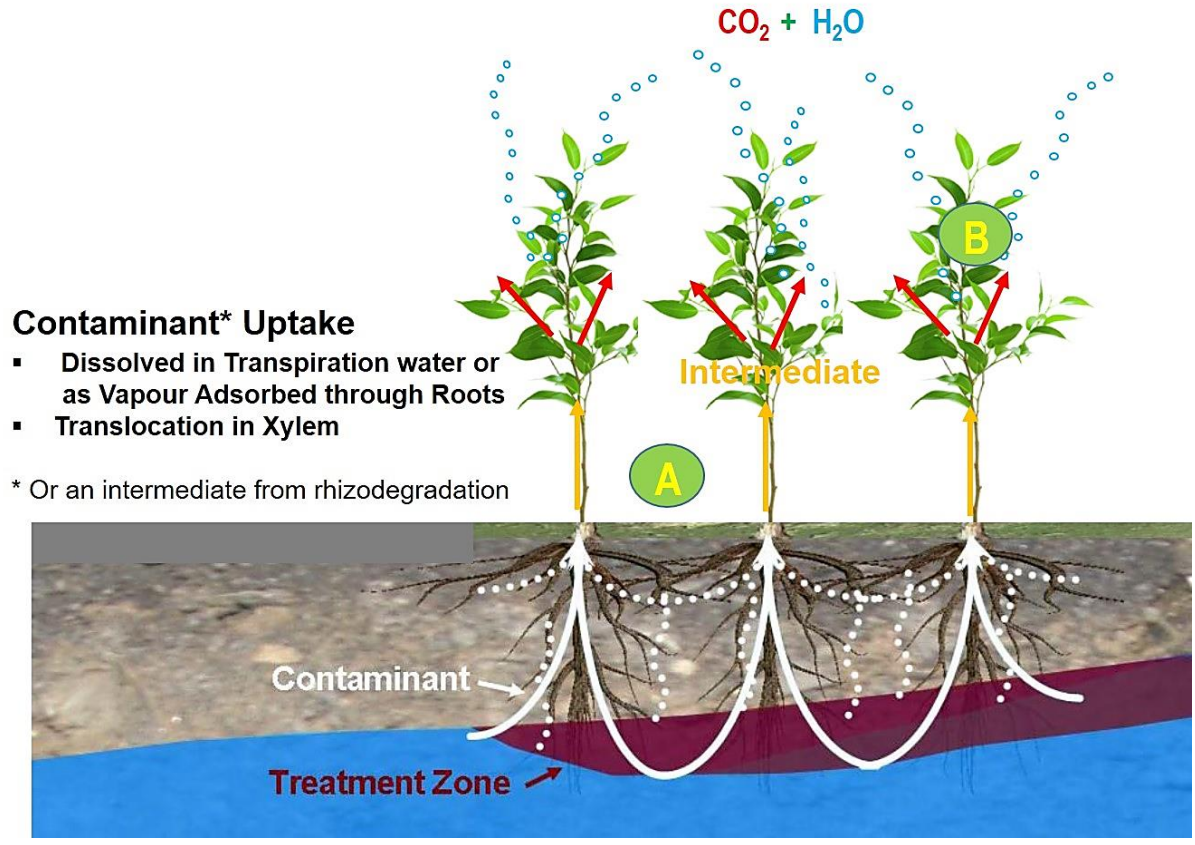


Source: Adapted and modified from ITRC (2009)

Figure 2.16c: Phytovolatilization mechanisms. Plants absorb contaminants from soil, groundwater, sediment or sludge and subsequently volatilize the contaminants or its less harmful modified forms into the atmosphere.

2.5.4 Phytodegradation

Phytodegradation is the ability of plants to breakdown contaminants upon uptake in the transpiration stream through internal enzymatic activity and photosynthetic oxidation/reduction. Factors such as concentration and composition, plant species, and the conditions of the soil may affect the passage of the contaminants from the rhizosphere into the plants with only partially or negligible phytosequestration and/or rhizodegradation. The contaminant is then subjected to the biological processes taking place within the plant itself. Phytodegradation also known as phytotransformation generally is the subsequent breakdown, mineralization, or metabolization of contaminants upon uptake by the plant itself through various internal enzymatic reactions and metabolic processes as shown in Figure 2.16d (ITRC, 2009). This mechanism is important in the degradation of complex organic compounds including hydrocarbons, PCBs, PAHs, pesticides, organic solvents, dioxins, furans etc. into simpler or mineralized forms such as CO_2 and H_2O (Adams *et al*., 2000).

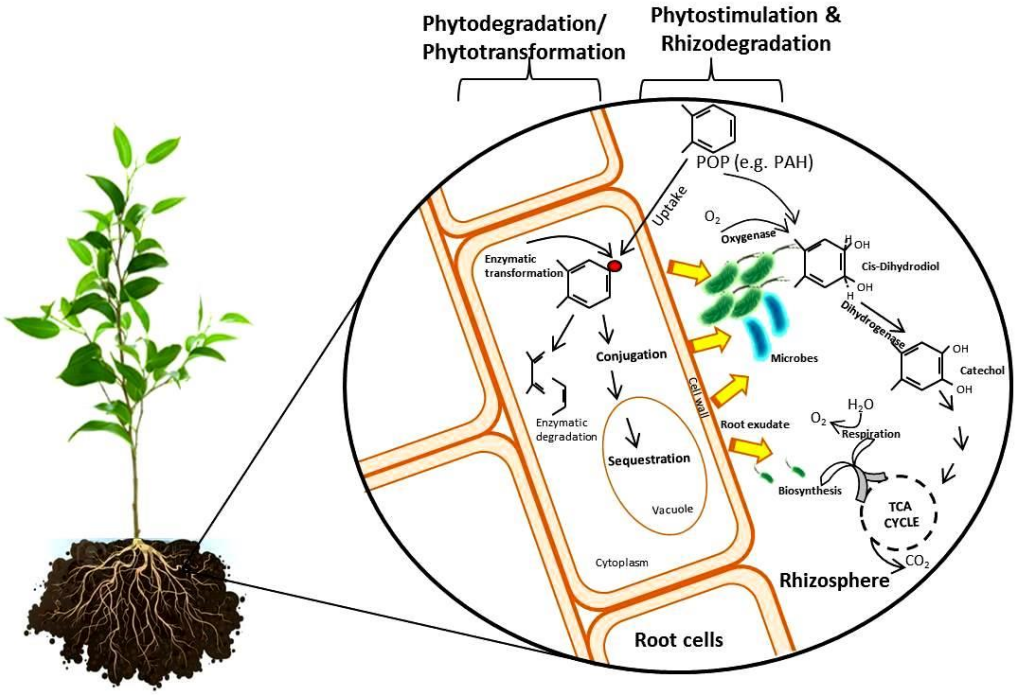


Source: Adapted and modified from ITRC (2009)

Figure 2.16d: Phytodegradation mechanisms. A: plant enzymatic activity, B: photosynthetic oxidation.

2.5.5 Rhizodegradation

Rhizodegradation also referred to as phytostimulation, rhizosphere biodegradation, or plant-assisted bioremediation/degradation is the breakdown of contaminants through microbial activity stimulated by the presence of root zone exuded phytochemicals. The enhanced or stimulated bioactivity is the primary means through organic contaminants can be cleaned up into harmless products which may serves as substrate for the plants or soil microorganism (Donnelly and Fletcher, 1994). Rhizodegradation and/or phytostimulation is the main pathway of phytoremediation of organic contaminants such as PAHs due to the catabolic activities of proliferated microbes as a result of the presence of plant roots within the dynamic region of the rhizosphere (Wild *et al.*, 2005; Siciliano *et al.*, 2003) (see Figure 2.16e).



Source: Futughe *et al.* (2020)

Figure 2.16e: Rhizodegradation/phytostimulation mechanisms: a typical plant-microbial organic contaminant degradation mechanism.

There is extensive body of literature reviews on the capability of plants especially non indigenous to remediate contaminated sites (e.g. Reilley *et al*., 1996; Jordahl *et al*., 1997; Nedunuri *et al*., 2000; Chen *et al*., 2003; Chekol *et al*., 2004; Rentz *et al*., 2005a) however, a significant factor in establishing an effective phytoremediation is to search for indigenous plants that thrived well in contaminated sites. One important advantage of employing indigenous plants for phytoremediation is the avoidance of non-indigenous and potentially invasive plants that may threatened the regional plant diversity. Table 9 shows examples of indigenous plants used for phytoremediation of persistent organic pollutants (POPs) as they can serve the dual purpose of remediation and native habitat restoration.

Phytoremediation may require lengthy periods compared with other technologies to treat contaminated sites; however, it is potentially less expensive and may be used in conjunction with others or applied as a final polishing step in remediation of sites (US EPA. 2000). Basically, three mechanisms of action are carried out by plant in the phytoremediation of organic contaminants such as the weathered crude oil contaminated land in the Niger Delta region. And they are phytodegradation, phytostabilization and phytovolatilization (Sims and Overcash, 1983; Cunningham *et al*., 1996; Siciliano and Germida, 1998b) with phytostabilization or phytovolatilization acceptable in some situations, phytodegradation into nontoxic compounds is the most desirable outcome. Generally, phytoremediation-based application benefit from the relative cost effectiveness, labour requirements, safer operations, potential income generation from biomass generation, economic viability, effectiveness and environmentally friendly (ITRC, 2009; Witter *et al.* 2012). Table 10 shows its cost estimate associated with its different mechanisms.

Table 9: Examples of indigenous plants employed in phytoremediation of persistent organic pollutants (POP)

Native Plant Species	Global Distribution	Country of Cited Publication	POPs	Mechanism and Media (substrate)	Removal Efficiency	Benefit/Comment	References
Family: Asteraceae *Chromolaena odorata*	Americas, Caribbean, Nigeria and other African countries.	Nigeria	PCBs	Phytoextraction and Phytodegradation (soil)	BCF and TF <1 for PCBs BCF>1 for hydrocarbons	Native *C. odorata* was able to phytoextract PCBs into its root comparable to other known plants. *C. odorata* thrived at highest concentration > 8000 mg/kg	Anyasi and Atagana (2014). Atagana and Anyasi (2017)
Family: Cyperaceae *Fimbristylis littoralis*	Africa, Europe, Asia	Nigeria	PAH	Phytodegradation (soil)	Up to 92% of total PAHs were removed after 90 day from 42.4 mg/kg at day 0	Potential phytoremediation for crude oil contaminated site.	White (2001); Nwaichi et al. (2015)
Family: Fabaceae *Lathyrus syvestris* (flat pea)	Africa, Europe and Asia	USA	PCBs	Rhizodegradation and Phytodegradation (soil)	Highest amount, 32.7 (+/- .3)% was recovered by flat pea; recovery levels in amended soil ranged from 20.5% to 39.2%	Highest PCB dissipation was in planted and amended soils	Dzantor and Woolston (2001)
Medicago polymorpha (burr medic**)**	Mediterranean, West and Central Asia	USA		Rhizodegradation and Phytodegradation (soil)			

Table 9: Continued

Native Plant Species	Global Distribution	Country of Cited Publication	Type of Pollutants	Mechanism and Media (substrate)	Removal Efficiency	Benefit/Comment	References
Family: Euphorbiaceae *Ricinus communis*	Tropical east Africa especially Ethiopia	Brazil	DDTs, DDE, HCHs, Heptachlors, Aldrin, Chlorpyrifoes, Transchlordane, Diclofopmethyl, Methoxychlor	Phytoextraction (soil)	25-70%	The highest BCR values were found when *Ricinus communis* was used for the uptake of diclofopmethyl, methoxychlor, trans-chlordane, aldrin, p,p' -DDT, and o,p' –DDT	Rissato et al. (2015)
Family: Plantaginaceae *Plantago major*.	Most European countries, including UK, Egypt	Egypt	Cyanophos	Phytodegradation/ Rhizodegradatiom (water)	Over 90%	*Plantago major* L. significantly reduced cyanophos in water by 11.0% & 94.7% during 2 hours & 9 days of exposure as compared with 0.8% & 36.9% in water without the plantain.	Romeh (2014)
Family: Poaceae ***Phalaris arundinacea*** **(**reed canary grass**)**	Europe, Asia, North Africa and North America	USA	PCB	Rhizodegradation and Phytodegradation (soil)	Highest amount, 32.7 (+/- .3)% was recovered by flat pea; recovery levels in amended soil ranged from 20.5% to 39.2%	Highest PCB dissipation was in planted and amended soils	Dzantor and Woolston (2001)
		Czech	PCBs	Phytodegradation	After four months, up to	Findings suggest that remediation by	

Family: Urticaceae *Urtica dioica*	USA, Canada, Europe, Asia, Africa and South America,			33% of the less chlorinated biphenyls had been removed.	stinging nettle could have a much wider range of applications than previously thought.	Viktorova et al. (2017)

Key:
BCF = Bioconcentration Factor
TF = Translocation Factor

Source: adapted from Futughe *et al.* (2020)

Table 10: Cost estimate associated with different phytoremediation mechanisms

Mechanism	Description	Details	Effective soil depth	Cost estimate	Scale	Target group	Reference
Phytosequestration/ Phytostabilization	Contaminants mobility and bioavailability were reduced by plant vegetation.	Absorption/adsorbtion to roots or organic compounds synthesized by plants in addition to mitigating groundwater leaching.	Native plants to contaminated site usually employed	0.02-1 $/ton	Field scale	Heavy metals and hydrophobic organic chemicals	Vangronsveld *et al.* (1995); Salt *et al.* (1998); Pulford and Watson (2003); Wenzel *et al.* (1999); Kremer (2003); Cunningham *et al.* (1995); Blaylock *et al.* (1997); Adams *et al.* (2000)
Phytoextraction	Extraction of heavy metals and metalloids from soil by plant into harvestable plant tissue.	Most heavy metals are found as plant nutrients or analogs depending on their metal solubility that can be enhance with chelating.	30 cm (Indian mustard), root depth limitation	29-50 $/ton	Full scale	Heavy metal	Cunningham and Berti (1993); Black (1995); Salt *et al.* (1995); Cunningham and Ow (1996); Reeves and Baker (2000); Baylock *et al.* (1997); Adams *et al.* (2000); FRTR (2005)
Phytovolatilization	Contaminants or their metabolites are released into the atmosphere upon uptake by plant.	Metabolism is more important mechanism than transpiration, 9 %	4 to 5 m (poplar)	38 % of the costs of pump and treat + revese osmosis.	Field scale		Wenzel *et al.* (1999); Schnoor *et al.* (1995); Newman *et al.* (1999); Gatliff (1996), cited in Schnoor (1997);Adams *et al.* (2000)
Phytodegradation	Contaminants are metabolize within the plants or are biodegraded by plants synthesize exudates	Plant enzymes such as cytochrome p450, peroxidases and laccases.	4 to 5 m (poplar)	3 $/ton with deep rooted plants	Field scale	Highly polar and non-polar pollutants	Baylock *et al.* (1997); Adams *et al.* (2000); Aderson *et al.* (1993); Gramms *et al.* (1999); Tsao (1999), cited in Frick *et al.* (1999); Schaffner *et al.* 2002);

							Newman and Reynold (2004)
Rhizodegradation	Microbial biomass and the rate of biodegradation are higher in the rhizosphere, mechanisms include improved aeration, substrate addition such as plant debris and root exudates	Exudates from root, small molecular weight organic compounds including amino acids, sugars, organic acids, and salt act as soil microbial substrates and stimulate cometabolic transformations of organic pollutant. Nitrogen-fixing bacteria and mycorrhiza found in many plant roots providing nutrients to the plants and improve drought resistance.	120 cm (grasses), 4 to 5 m (polar)	3 $/ton with deep rooted plants. Normal cropping practices 0.02-1$/ton 10-35 $/ton	Field scale	Organic contaminant	Schnoor (1997); Romantschuk *et al.* (2000); Aderson *et al.* (1993);Schnoor *et al.* (1995); Shann and Boyle (1994); Schwab *et al.* (1995); Tsao (1999); Baylock *et al.* (1997); Adams *et al.* (2000); Cunningham *et al.* (1995); Schnoor (1997)

2.6 Biosurfactants

Biosurfactants are natural surface-active products from a variety of microorganisms and can be classified as glycolipids, lipopeptides, fatty acids, polysaccharide-protein complexes, peptides, phospholipids, and neutral lipids that reduce the surface and interfacial tensions between two liquid phases, enabling the uptake of hydrophobic substrates by plants and microorganisms (Saharan *et al.* 2012; Pacwa-Płociniczak *et al.* 2011; Smyth *et al.* 2010a; 2010b). Biosurfactants increase the surface area of hydrophobic water insoluble substances and their water bioavailability as a result of biosurfactants amphiphilic structure which also change the properties of the bacterial cell surface making surfactant perfect emulsifiers, forming and dispersing agents (Smyth *et al.* 2010b). Biosurfactants in comparison to their chemically synthesized counterparts are environmentally friendly, biodegradable, less toxic and non-hazardous with better forming qualities and increased selectivity. Biosurfactants are also active at extreme temperatures, pH and salinity and can be synthesized from industrial wastes and from by-products-a feature that makes the production of biosurfactants cheaper by allowing the utilization of waste substrates thereby reducing their pollution effect simultaneously (Kosaric, 1992; Kosaric, 2001; Rahman *et al.*, 2003; Das and Mukherjee, 2008). Due to their overwhelming potentials, biosurfactants have been employed in many industries including agriculture, food production, pharmaceutics, chemistry and cosmetics. Applications of biosurfactants with examples abound in many literature reviews (Muthusamy *et al.*, 2008; Banat *et al.*, 2010; Soberón-Chávez and Maier, 2011) especially in environmental biotechnology (Pacwa-Płociniczak *et al.* 2011).

In physico-chemical and biological remediation techniques, the numerous properties of biosurfactants including emulsification/de-emulsification, dispersion, forming, wetting and coating become very useful in remediating both organic and inorganic contaminants (Pacwa-Płociniczak *et al.* 2011). The increase bioavailability of hydrocarbons by biosurfactants results in enhanced growth and contaminants biodegradation by hydrocarbon-degrading bacteria in the contaminated soil. While biosurfactants form complexes with heavy metals at the soil interface of heavy metal contaminated soil, thereby adding heavy metal desorption and removal (Pacwa-Płociniczak *et al.* 2011).

2.6.1 Biosurfactants classification and properties

Biosurfactants are classified by their chemical composition, molecular weight, physico-chemical properties and mode of action unlike their chemically synthesized counterparts which are categorized by their dissociation pattern in water (Pacwa-Płociniczak *et al.* 2011). Biosurfactants are divided based on their molecular weight into low-molecular-weight biosurfactants including glycolipids, phospholipids and lipopeptides and into high-molecular-weight biosurfactants with amphipathic polysaccharides, proteins, lipopolysaccharides, lipoproteins or complex mixtures of these biopolymers as examples (see Table 11). In reducing surface and interfacial tensions, low-molecular-weight biosurfactants are more efficient whereas high-molecular-weight biosurfactants are better at stabilizing oil-in-water emulsion (Rosenberg and Ron, 1999; Calvo *et al.,* 2009).

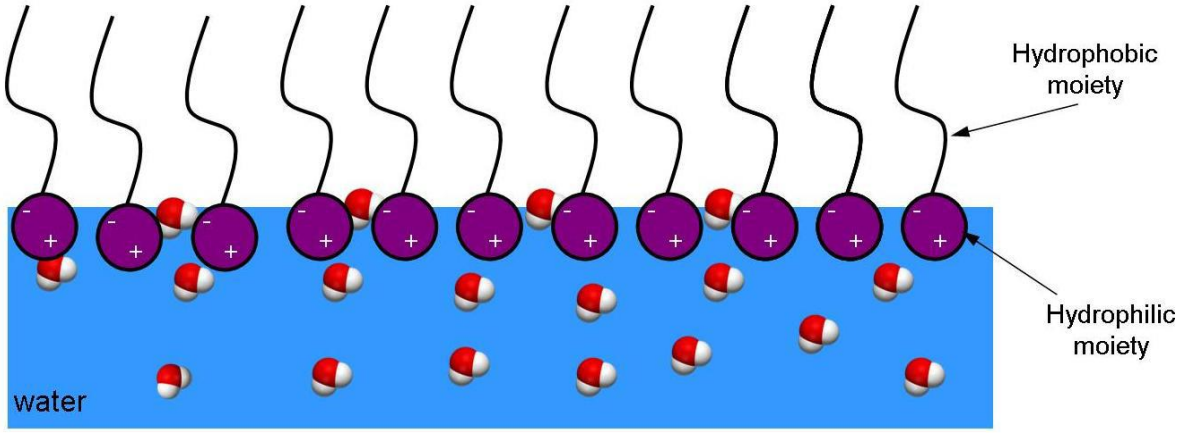
The reduction in the surface (liquid-air) and interfacial (liquid-liquid) tension between two immiscible fluids or between a fluid and a soil is as a result of the accumulation of biosurfactants at the interface thereby decreasing the repulsive forces between the two dissimilar phases in other for them to mix and interact more easily as shown in Figure 2.17a (Soberón-Chávez and Maier, 2011). According to Smyth (2010b) and Soberón-Chávez and Maier (2011) surface tension of water can be reduced by the most active biosurfactants from 72 to 30 mN/m in which the concentration of the surface-active compounds depends on the biosurfactant activities until the critical micelle concentration (CMC) is reached. Biosurfactant molecules begin to form micelles, bilayers and vesicles at concentration above the CMC as shown in Figure 2.17b. Formation of micelles by biosurfactants enable the reduction of the surface and interfacial tension thereby increasing the hydrophobic organic contaminants solubility and bioavailability (Wang *et al.,* 2008). The efficiency of surfactant is usually determined by measuring the CMC. A more efficient biosurfactant usually have a low CMC that is less amount of biosurfactant is needed to reduce the surface and interfacial tension (Smyth *et al.* 2010b).

Table 11 Biosurfactants classification and remediation application examples

Biosurfactant				
Group	**Class**	**Microorganisms**	**Applications in Environmental Biotechnology**	**References**
Glycolipids	Rhamnolipids	*Pseudomonas aeruginosa*, *Pseudomonas* sp.	Enhancement of the degradation and dispersion of different classes of hydrocarbons; emulsification of hydrocarbons and vegetable oils; removal of metals from soil	Sifour *et al.* (2007); Whang *et al.*, (2008); Herman *et al.*, (1995); Maier and Soberón-Chávez, (2000)
	Trehalolipids	*Mycobacterium tuberculosis*, *Rhodococcus erythropolis*, *Arthrobacter* sp., *Nocardia* sp., *Corynebacterium* sp		Franzeth *et al.* (2010)
	Sophorolipids	*Torulopsis bombicola*, *Torulopsis petrophilum*, *Torulopsis apicola*	Enhancement of the bioavailability of hydrocarbons; Recovery of hydrocarbons from dregs and muds; removal of heavy metals from sediments; enhancement of oil recovery	Whang *et al.* (2008); Pesce (2002): Baviere (1994)
Fatty acids, phospholipids and neutral lipids	Corynomycolic acid	*Corynebacterium lepus*	Enhancement of bitumen recovery	Gerson and Zajic (1978)
	Spiculisporic acid	*Penicillium spiculisporum*	Removal of metal ions from aqueous solution; dispersion action for hydrophilic pigments; preparation of new emulsion-type organogels, superfine microcapsules (vesicles or liposomes), heavy metal sequestrants	Ishigami *et al.* (1983);(2000); Hong *et al.* (1998)
	Phosphati-dylethanolamine	*Acinetobacter* sp., *Rhodococcus erythropolis*		Appanna (1995)

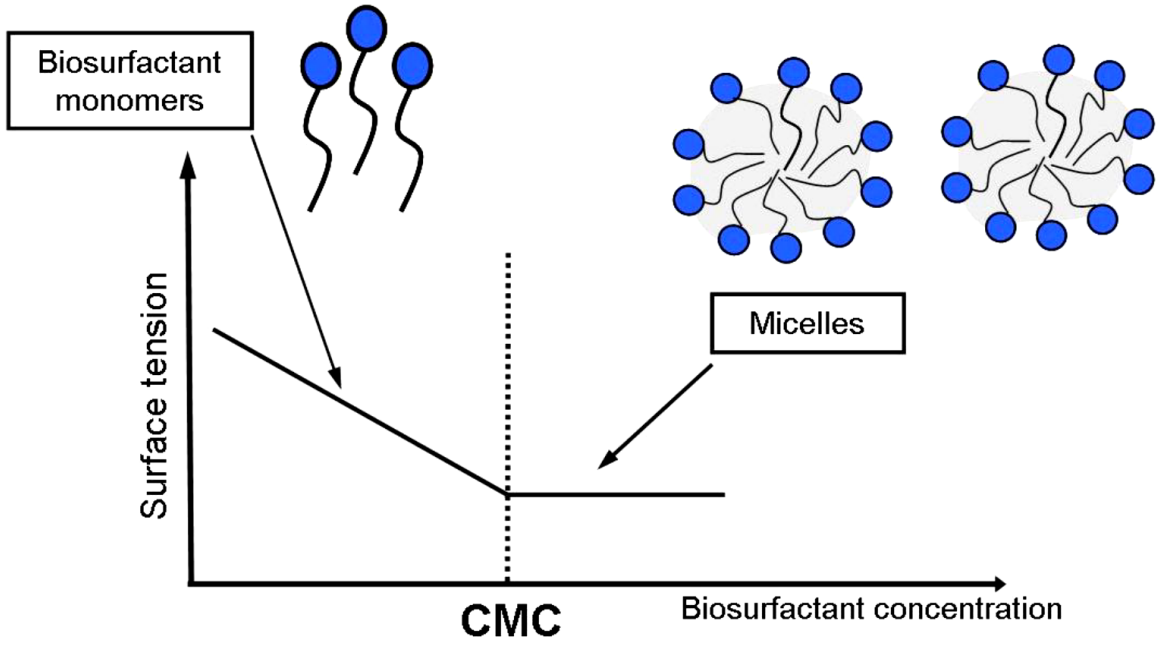
			Increasing the tolerance of bacteria to heavy metals	
Lipopeptides	Surfactin	*Bacillus subtilis*	Enhancement of the biodegradation of hydrocarbons and chlorinated pesticides; removal of heavy metals from a contaminated soil, sediment and water; increasing the effectiveness of phytoextraction Enhancement of oil recovery	Jennema *et al.* (1983); Awashti *et al.* (1999): Arima *et al.* (1968) Thoma *et al.* (1993)
	Lichenysin	*Bacillus licheniformis*		
Polymeric biosurfactants	Emulsan	*Acinetobacter calcoaceticus* RAG-1	Stabilization of the hydrocarbon-in-water emulsions	Zosim *et al.* (1982)
	Alasan	*Acinetobacter radioresistens* KA-53	Dispersion of limestone in water	Toren *et al.* (2001)
	Biodispersan			
	Liposan	*Acinetobacter calcoaceticus* A2	Stabilization of hydrocarbon-in-water emulsions	Rosenberg *et al.* (1988)
	Mannoprotein	*Candida lipolytica* *Saccharomyces cerevisiae*		Cirigliano (1984) Cameron *et al.* (1988)

Source: Pacwa-Płociniczak *et al*. (2011)



Source: Adapted from Pacwa-Płociniczak *et al.* (2011)

Figure 2.17a: Biosurfactants accumulation at the interface (liquid and air)



Source: Adapted from Pacwa-Płociniczak *et al.* (2011) and Whang *et al.* (2007)

Figure 2.17b: Biosurfactant relationship between surface tension and micelles formation

2.6.2 Biosurfactants enhanced hydrocarbon remediation

Crude oil hydrocarbons tend to partition on soil matrices as a result of solubility limitation due to their hydrophobic characteristics accounting for up to 95 % or more of total contaminant mass (Pacwa-Płociniczak *et al.,* 2011). Consequently, moderate to poor recovery of hydrocarbon contaminants is exhibited by physico-chemical treatments**;** reduced bioavailability to microbes; and reduced availability for some *in situ* and/or *ex situ* remediation applications. However, the use of biosurfactants can improve the effectiveness of bioremediation of hydrocarbon contaminated sites by enhancing its bioavailability and interactions with both plants and/or microbes in the soil as shown in Figure 2.17c. Biosurfactants increase PAH contaminants bioavailability to rhizosphere microbes and also increase the cell surface interactions with the contaminants by allowing hydrophobic substrates (hydrocarbons) associate more easily with bacteria cells (Figure 2.17c) (Mulligan and Gibbs, 2004). The reduction in the surface and interfacial tension by biosurfactants, increases the surface areas of insoluble hydrocarbon compounds resulting to increased mobility and bioavailability. This also increases the contact angle of soil-oil system thereby reducing the capillary force binding oil and soil together. Hydrocarbons are easily susceptible to biodegradation due to biosurfactants enhancement as a result to mobilization, solubilization or emulsification (Nguyen *et al.,* 2008; Déziel *et al.,* 1996; Bai *et al.,* 1997; Rahman *et al.,* 2003; Urum and Pekdemir, 2004; Nievas *et al.,* 2008).

The ability of biosurfactants and bacteria strains producing biosurfactant in enhancing hydrocarbon contaminants' availability and subsequent biodegradation has been reported by many authors (Rosenberg *et al.,* 1998; Rahman *et al.,* 2003; Inakollu *et al.,* 2004; Gao *et al*., 2007; Liao *et al*., 2015; Shah *et al*., 2016; Liang *et al*., 2017; Cheng *et al*., 2018).

2.6.2.1 Rhamnolipids

Rhamnolipids belong to the glycolipid biosurfactants class (Table 11) synthesized by various bacterial species and were initial discovered as an exoproducts of opportunistic *Pseudomonas aeruginosa* pathogen and is the best studied biosurfactant in the glycolipids containing mono- or disaccharides linked to long chain aliphatic acids or hydroxyaliphatic acids class (Figure 2.17d) (Eric *et al.,* 2010). They have been described as a mixture of four congeners: α-L-rhamnopyranosyl-α-L-rhamnopyranosyl- β-hydroxydecanoyl-β-hydroxydecanoate (Rha-Rha-C10-C10), α-L-rhamnopyranosyl-α-L-rhamnopyranosyl-β-hydroxydecanoate (Rha-Rha-C10), as well as their mono-rhamnolipid congeners Rha-C10-

C10 and Rha-C10 due to the strain of bacterium and medium components, providing rhamnolipids specific properties (Eric *et al.,* 2010; Das *et al.,* 2008).

Glycolipid biosurfactants especially rhmanolipids have been used in several potential applications including bioremediation, food industries, cosmetics and as antimicrobial agents. There is substantial evidence that rhamnolipids are efficient in chelating and removing heavy metals probably as a result of the interaction between the polar glycosidic group with metal ions (Eric *et al.,* 2010). Their interaction with organic contaminants such as petroleum hydrocarbons on the other hand increase the bioavailability of the organic contaminants or aids their mobilization and removal. Rhamnolipids have been reported to be effective in reducing oil concentration in contaminated sandy soil (Ishigami *et al.,* 2000) and substantially increase biomass growth when added at a relatively low concentration (80 mg/L) to diesel-water system as well as diesel biodegradation (Hong *et al.,* 1998).

Rhamnolipids have been shown to be effective in PAHs removal and pentachlorophenol from soil with 60-80 % removal efficiency depending on contact time and concentration of biosurfactant (Appanna, 1995; Jennema *et al.,* 198). Phenanthrene was mineralized upon introduction of rhamnolipids in high phenanthrene-sorption capacity sandy loam. Enhanced phenanthrene recovery was achieved from soil when biosurfactant was added at a concentration above the CMC (Awashti *et al.,* 1999). Rhamnolipids also enhanced the partitioning rate of PAHs including fluorine, phenanthrene and pyrene (Appanna, 1995). To date, many studies have shown that rhamnolipid can facilitate the degradation of aliphatic and aromatic organic compounds sorbed onto soil constituents by stimulating mass transport (Zhang and Miller, 1992, 1995; Maslin and Maier, 2000; Christofi and Ivshina, 2002; Zeng *et al*., 2007). According to Gerson (1993) biosurfactants can improve the bioavailability of hydrocarbons to the microbial cells by increasing the area at the aqueous-hydrocarbon interface. This increases the rate of hydrocarbon dissolution and their utilization by microorganisms.

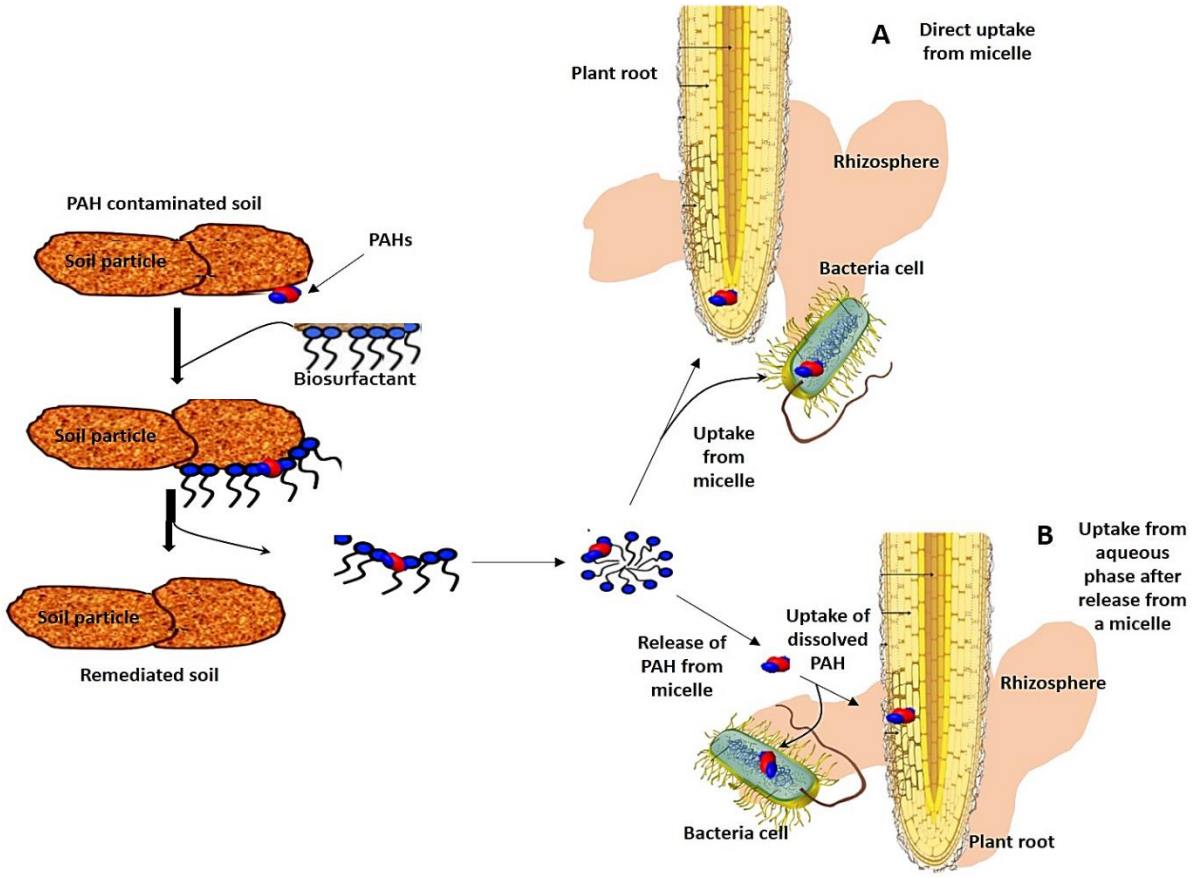
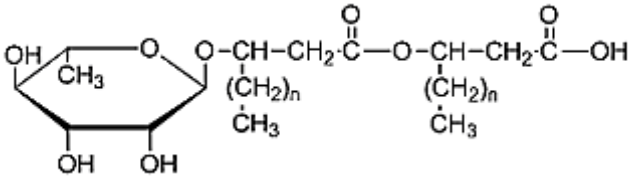
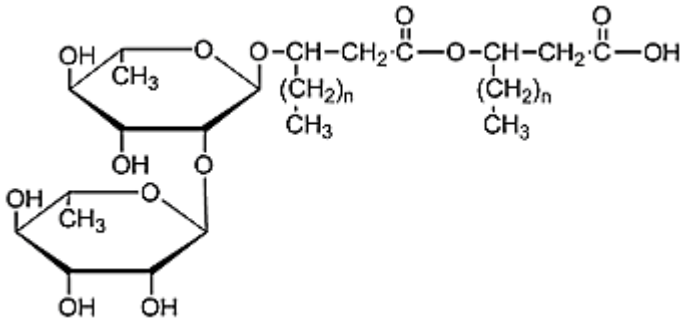


Figure 2.17c: Mechanisms for polycyclic aromatic hydrocarbon (PAH) bioavailability enhancement with biosurfactants. (A) shows direct uptake of PAH from micelle, (B) shows uptake for PAH from aqueous phase upon release from a micelle



(i)



(ii)

Figure 2.17d(i-ii): Structure of Rhamnolipids representatives: (i) mono-rhamnolipids: Rha-C_{10}-C_{10} (n=6) and (ii) di-rhamnolipids Rha-Rha-C_{10}-C_{10} (n=6)

2.7 Soil solarization

Soil solarization also known as solar heating, plastic mulching, or soil trapping is a pre-plant hydrothermal technique for soil treatment by inducing chemical, biological and physical changes into a sufficiently irrigated soil covered by a transparent polyethylene film using trapped solar radiation from the sun to heat the soil surface to temperature range of 38 to 50^{o}C to a depth of about 10 to 20 cm for pasteurization (Katan *et al*., 1976; Katan, 1981; Katan and De Vay, 1991; Stapleton, 1996; FAO, 2003; Gamliel and Katan, 2012). This technique increases soil temperature by solar radiation from the sun was initially intended for soil-borne pathogen control (Katan *et al.,* 1976). Most of the pioneering research took place in Hawaii (Hagan, 1933) but became less popular soon after World War II when soil fumigants were introduced. However, increasing concern of environmental hazards imposed by soil fumigation and rising restrictions and bans on several soil fumigants coupled with the need for organic farming have resulted in the revisiting of soil solarization (Marquez and Wang, 2014). Soil solarization became a ground breaking alternative treatment technique when Grooshevoy (1939) demonstrated that soil-borne pathogens can be controlled by simply exposing soil to solar heat. Polyethylene mulch was first introduced to control a soil-borne pathogen, black root rot (*Thielaviopsis basicola*) by Adams (1971) and as a result, the standard mulch applied for soil solarization today is polyethylene film. Pullman and DeVay (1977) reported research that utilized a wide application of soil solarization and in 1981 coined the term "soil solarization" (Pullman *et al*., 1981). Currently, over 74 countries are applying or researching on soil solarization for management of weeds and soil sterilization/pasteurization. Emoghene and Futughe (2011) reported the effect of soil solarization on *Amaranthus viridis* shoot diseases caused by *Choanephora cucurbitarium* and solarization impact on the growth of *Amaranthus viridis* as well as microbial population in Nigeria (Emoghene and Futughe, 2011).

2.7.1 Soil solarization principles

Soil solarization basically has to do with increasing the temperature in a moist pre-plant soil to a lethal level that affects the survival of soil-borne pathogens directly. However, studies have shown that soil solarization has other positive effects on soil characteristics which enhance crops performance such as nutrient concentration (Chan *et al*., 1991) and soluble organic matter content (Chen *et al*., 2000) that encourage the survival and proliferation of beneficial organisms (Katan, 1981). During soil solarization, transparent polyethylene film/sheet covering soil and acting as mulch reduces heat losses significantly without

interfering with the absorption of solar energy, thereby increasing soil temperatures as shown in Figure 2.18. The potential thermal lethal effect on soil-borne pathogens (Katan, 1987) and weed seeds (Stapleton *et al*., 2000) is determined by the level and accumulation of maximum soil temperature.

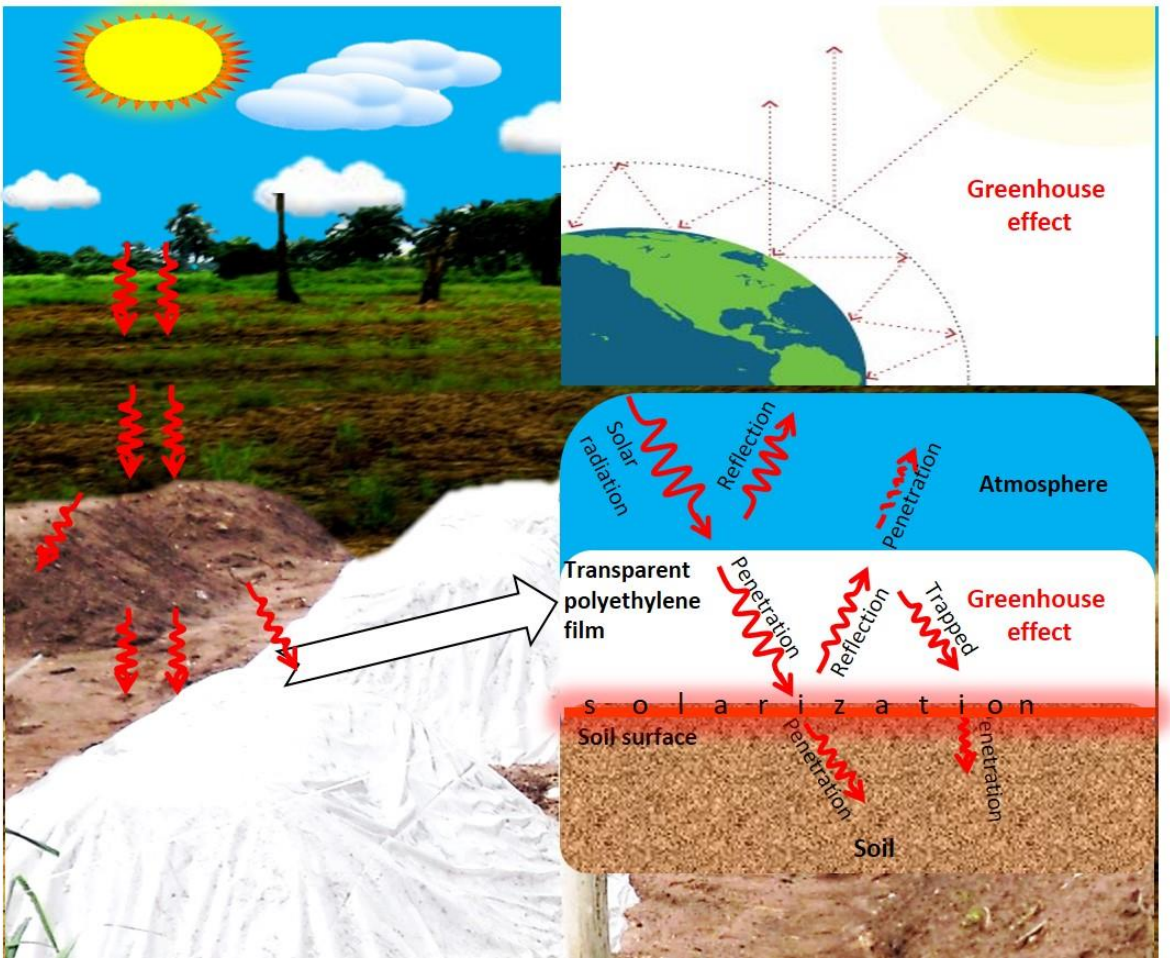


Figure 2.18: Soil solarization principle showing transparent polyethylene sheet allowing short-wavelengths of light penetration during soil solarization with some energy being lose and convert to longer-wavelengths of infrared radiation which generate heat that is trapped beneath the plastic tarp, thereby heating up the soil and mimicking the 'greenhouse effect'.

2.7.2 Factors affecting soil solarization

Soil solarization impacts are mostly determined by soil temperature, types of mulching material, soil moisture and weather and climate (Dai *et al.*, 2016).

2.7.2.1 Soil temperature

This is the most important factor in determining a successful solarization process as about 85-95 % of solar radiation penetrates polyethylene sheet resulting to heated soil (Lamont, 2005). Polyethylene sheet's colour and thickness coupled with the soil texture and moisture content also have influences on the soil temperature (Pullman *et al*., 1979, Katan, 1981). These factors may increase the soil temperature from 2 to 10°C (Dai *et al.,* 2016). According to Ham *et al*. (1993) the average soil temperature under polyethylene sheet was 6°C higher than their non-covered counterparts and this difference differed across soil depth. An increase of 10°C and 7°C at 5 cm soil depth has been reported for solarized dry and wet soils respectively (Bohra *et al*., 1996) while Pinkerton *et al*. (2000) reported soil maximum temperatures to be 8-16°C higher at 5 and 30 cm depth in solarized soils when compared to its non-solarized counterpart. Emoghene and Futughe (2011) reported a maximum soil temperature means of 48 and 41°C at 5 and 10 cm depths respectively in solarized-manure amended soil compared to a meanm maximum soil temperature of 40 and 38°C for similar depths in non-solarized-manure amended counterparts. A soil temperature of about 8°C higher at 5 cm depth. However, the difference in soil temperature at night between polyethylene covered and uncovered soil is less between 2 and 4°C (Dai *et al.*, 2016).

2.7.2.2 Soil mulching material

Solarizing plastic sheets play an important role in soil solarization effectiveness especially weed control. Polyethylene as an important plastic material in agriculture was introduced in 1939 on a commercial scale (Byrdson, 1970) and was reported for increasing soil temperature in 1950s (Emmert, 1957). Only polyethylene films were recognized as a mulching material in previous work on soil solarization, through which part of the solar energy was transmitted, absorbed by the soil surface and conserved heat transformed with the water vapour accumulating on the inner polyethylene film simultaneously which further improves the greenhouse effect with subsequent higher rise in soil temperature (Stevens *et al*., 1990).

Several types of plastic materials have been used for soil solarization in the past and the low-density polyethylene (LDPE) and ethylene-vinyl acetate (EVA) were found to be

generally perfect for solarizing properties (D'Addabbo *et al*., 2010). EVA sheets were reported to improve soil temperature during solarization then with polyethylene sheets (Gutkowski and Terranova, 1991). However, due to the difficulty and costly disposal of traditional plastic wastes, biodegradable plastic materials are gradually be used as they could be biodegraded by soil microbes gradually over time. (Al-Kayssi and Al-Karaghouli, 2002; Zheng *et al*., 2005). In addition, paraffin-wax emulsion mulch had been reported to increase soil temperature better than polyethylene and this was as a result of the excellent paraffin wax coverage of the soil surface without any air gaps formed thereby acting as an insulator (Dai *et al.,* 2016). Thinner polyethylene sheets were generally reported to be more effective in generating higher temperatures in soil than thicker polyethylene in addition to being more cost effect (Stapleton and DeVay, 1986; Abu-Irmaileh, 1991a,b). However, thinner plastic during solarization are less durable and susceptible to wind and animal damage (Rubin, 2012) and are also subjected to punctures by certain types of weeds (Chase *et al.*, 1998).

Generally, transparent, 25 µm thick, UV stabilized, low density polyethylene sheet are preferred as mulching for over 6-8 weeks soil solarazation duration. It is important that very thin (25-50 µm) transparent polyethylene sheet be used to trap solar radiation due to its permeability to short-wavelength solar radiation and its inability to transmit longer-wavelength radiation (heat) from the soil surface back into the atmosphere (McGovern and McSorley, 2004) as illustrated in Figure 2.18. Short-wavelengths solar radiation of approximately 120-400 nm have higher amounts of energy compared to longer-wavelength radiation i.e. infrared radiation of > 750 nm. During solarization, the short-wavelengths of light penetrate the plastic film with some energy being lose and convert to longer-wavelengths of infrared radiation which generate heat that is trapped beneath the plastic tarp, thereby heating up the soil (Krueger and McSorley, 2009) mimicking the greenhouse effect.

The colour of plastic films have been report to influence soil solarization due to the effect on microclimate around the vegetable plants through changes in root temperature, intensity of light and the quality of light above the plastic surface due to energy radiating properties of the plastic films (Csizinszky *et al*., 1995; Streck *et al*., 1995). Consequently, plastic film colours are considered an important parameter for effective solarization especially in its ability to retain the long-wave radiation. Thus, black, opaque, or translucent plastic films are not ideal for soil solarization due to their inability to retain the heat absorbed from solar radiation as they often tend to radiate the heat back into the atmosphere leaving the surface of the soil just slightly warm. Contrary to thin, transparent plastic films which achieve the best outcome (Dai *et al.,* 2016). Soil temperature during solarization has been affected by the colour

of plastic films in the following order: transparent plastic > black plastic > white plastic (Haynes, 1987). While Al-Karaghouli *et al.* (1990) reported the following order in the transmittance of the coloured polyethylene films to global solar radiation: black < blue < yellow < green < red < transparent.

2.7.2.3 Soil moisture

The moisture content of the soil is crucial for effective solarization as most reports have shown that wet or moist soil improves the conduction of heat and are efficient for eliminating soil borne disease and pest in deeper soil layers during soil solarization (Dai *et al.,* 2016). A sufficiently moist soil does not only make organisms more susceptible to heat but also responsible for faster heat conduction deeper into the soil. Soil moisture favours cellular activities of weed seeds and the proliferation of soil borne microbes which make them more susceptible to the lethal effects of increasing soil temperature during soil solarization. A lot of studies have reported that increasing soil moisture content leads to increasing heat capacity and apparent thermal conductivity (Nakshabandi and Kohnke, 1965; Sepaskhah and Boersma, 1979; Boulard and Baille, 1986). However, Al-Karaghouli and Al-Kayssi (2001) reported that maximum soil temperatures and soil solarization efficiency decreases with increase in moisture content of the soil during their investigation on how different soil moisture contents influenced soil temperature. Although, an increase in soil moisture content by many modelling studies has been shown to record the highest soil temperature (Mahrer *et al*., 1983 and Naot *et al*., 1987) and other reporters have suggested that a linear relationship exists between heat capacity and soil moisture content (De Vries 1963, Sesveren *et al*., 2006).

DeVay and Katan (1991) has reported that the soil should be watered to about 70 % of field capacity in the upper sub soil and moist to a depth of at least 60 cm to obtain the best effect of soil solarization. While Nakamura *et al*. (2011) suggested the conduction of irrigation before solarization commencement if volumetric moisture content is within the range of 0.15-0.35 as the moisture content do not fall significantly during this process and change of soil thermal properties value is negligible. However, this may place more demand on the scarce water resources for irrigation (Dai, 2016).

2.7.2.4 Weather and climate

A high level of solar energy is required for soil solarization which is mainly dependent on both weather and climate and as a consequence, solarization is often carried out in an

industrial scale mainly in regions with Mediterranean, desert, and tropical climates that are characterized by high summer air temperatures. It has been reported that cloud cover, cool air temperatures and precipitation during soil solarization period reduce its efficiency and effectiveness (Chellemi *et al*., 1997). Dai *et al*. (2014) also observed that there was gradual rise in daily average air temperature during solarization commencement but this reduced upon precipitation and cloudy weather in a glasshouse and suggested the extension of solarization duration when this occurs.

Soil type, soil colour and texture, organic matter content, treatment duration, sunlight intensity, heating extent, soil borne pathogens and pest species heat susceptibility, cropping history, and other soil ecology components also influenced soil solarization efficiency (Stapleton and Devay, 1986; Katan, 1987). The exposure length and intensity of sunlight also determine soil solarization effectiveness (Ben-Yephet *et al*., 1988) and Dai *et al*. (2014) has suggested 18-33 days (average of 24 days) solarization duration as beneficial microorganisms may be eliminated from absence of oxygen if soil is heated longer than required.

2.7.3 Impacts of soil solarization

2.7.3.1 Impacts on soil properties

Complex changes can take place in the physical, chemical and biological properties of a solarized soil during soil solarization which includes soil structure improvement (Chen *et al*., 1991), increase in mineral nutrient availability due to the quick decomposition of organic matter by the heat under the transparent polyethylene sheet in addition to soluble organic matter which affects microflora and microfauna population in the soil with high influence on the enzymes systems associated with the respiratory process (DeVay and Katan, 1991; Stapleton, 1994). It has been established that polyethylene sheets through solarization affects some of the soil chemical and biological properties such as an increase in the NH_4-N and NO_3-N concentration in the top 15 cm soil (Stapleton and DeVay, 1995; Grünzweig *et al*., 1999; Gelsomino *et al*., 2006) which suggested enhanced soil organic N mineralization as a result of the high soil temperature. Increases in soluble mineral nutrients concentration such as Ca, Mg, P, K etc., that may be inconsistent sometimes (Chen *et al*., 1991 and Grünzweig *et al*., 1999) with increased soil pH values, soil base saturation, exchangeable K^+ and Mg^{2+} (Chen *et al*., 1991) has also been reported.

2.7.3.2 Impacts on soil borne diseases, pest and nematodes

In regions with high solar energy, soil solarization has been effectively employed for soil borne pathogens and pests management (Eshel *et al*., 2000 and McGovern *et al*., 2002). It was reported that pathogenic fungi were reduced in population due to soil solarization in sugarcane cultivation (Dwivedi, 1998) while a significant decrease in nematophauna has been documented in solarized rice fields (Culman *et al.,* 2006). Soil solarization has been reported to have long term effectiveness in several reports in controlling soil borne diseases and soil borne pests in different crops (Katan *et al*., 1976; Ashworth *et al*., 1983; Horiuchi, 1991; Chet *et al*., 1982; Keinath, 1995; Katan, 1996; Elmer, 1997; Stevens *et al*., 2003 and Scopa *et al*., 2009; Emoghene and Futughe, 2011; Dai *et al.,* 2014) as well as nematodes (McSorley and Parrado, 1986; Chellemi *et al*., 1997; McSorley and McGovern, 2000; McGovern *et al*., 2002; Ozores-Hampton *et al*., 2004) which may quickly recolonize the soil from deeper soil layer population pools (Dai *et al.,* 2016). A significant decrease in nematophauna has been documented in solarized rice fields (Culman *et al.,* 2006).

2.7.3.3 Impacts on weeds

According to Gamliel and Katan (2012) weed management by soil solarization dated to the ancient Indian civilization were solar radiation is utilized in treating weed seeds. Soil solarization has been found to be very effective on weeds control including selective herbicides unsusceptible species (Elmore, 1991). Solarization can cause thermal elimination to seeds of weeds thereby reducing weeds emergence (Lalitha *et al*., 2003). Since soil temperature decreases with the soil depth (Shukla *et al*., 2000) germination of weed seeds decrease much more in the soil top layer but increase in the deep soil layer (Horowitz *et al*., 1983). Several studies have shown the impact of soil solarization in controlling weeds effectively (Egley, 1983; Al-Masoomet *et al*., 1993 and Patricio *et al*., 2006; Elmore, 1991 and Singla *et al*., 1997; Jacobsohn *et al*., 1980; Haidar and Sidahmed, 2000; Ashrafi *et al*., 2008). Other studies showed that annual weeds are effectively controlled more than perennial weeds using soil solarization (Egley, 1983; Rubin and Benjamin, 1983; Stevens *et al*., 1990; Kumar *et al*., 1993; Linke, 1994; Chase *et al*., 1998) while reported effective control of both (Chauhan *et al*., 1988).

2.7.3.4 Impacts on plant growth and yield

Soil solarization technique has since been reported to improve plant growth and yields through soil borne control by biological means, soil structure improvement and increase

availability of N and other vital plant nutrients in addition to the greenhouse effect (DeVay and Katan, 1991; Elmore *et al*., 1997; Stapleton, 2000). Increased yields to varying degrees has been reported with the use of soil solarization including 123, 35 and 215 % yield of peanut, potato, and eggplant respectively (Grinstein *et al*., 1979 and Katan *et al*., 1976) which also showed similar increase to cotton, onion, tomato, and carrot (Dai *et al.,* 2016). Ashrafi *et al*. (2008) reported 133 to 258 % increase in cucumber fruit yield as well as improved plant growth in the solarized treatment compared to the non-solarized treatment. In the Niger Delta region of Nigeria, Emoghene and Futughe also reported that soil solarization had significant impacts on the growth and yield of *Amarathus viridis* even at higher probability level of $p < 0.0005$ compared to their non-solarized counterparts as shown in Plate 1.0 below (Emoghene and Futughe, 2011). Generally, plant growth, yield and quality have been enhanced by soil solarization (Elmore *et al*., 1997). A number of physiological changes, increased photosynthetic activity and level of protein, tissue development acceleration etc. have been reported to increase plant growth response due to solarization (Gruenzweig *et al*., 1993). Increased gibberellins concentrations had been reported to be linearly associated to leaf dry weight increase in tomato plants from solarized soil (Grunzweig *et al.,* 2000). Generally, most authors agreed that the increased growth response of solarization is rather due to numerous effects on soil and plants including the increase of soluble mineral nutrient and mineralized organic matter (Chen and Katan, 1980; Stapleton *et al.,* 1984; Chen *et al*., 1991; Chen *et al.,* 2000) and not just strictly disease dependent as seen in pathogen free soil (Abd El-Megid *et al.,* 1998). Increases of growth regulatory factors (Grünzweig *et al.,* 2000), soil biological activities and the minor control of pathogen by soil solarization also contribute to growth and crop yield (Gruenzweig *et al.,* 1993; Gamliel and Stapleton, 1997; Tjamos and Fravel, 1995; Le Bihan, 1997).

Source: Emoghene and Futughe (2011)

Plate 1.0: Front view showing growth responses of 9 weeks old *Amaranthus viridis* between Solarized (C_2) plot with 85.20±14.25 cm and Non-solarized (D_2) plot with 31.13±5.69 cm in *Amaranthus viridis* height.

2.7.4 Soil solarization challenges and limitation

Soil solarization has considerable merit such as its simplicity, non-chemical, non-hazardous approach without the use of any toxic substances, its leaves site uncontaminated, and highly suitable for organic farming or small scale agriculture. However, it does not consistently control high tolerant soil borne pathogens as a result of solarization being most effective close to the soil surface under high air temperature dependent on climatic and weather conditions. Long days of heating soil (solarization period) may require that land be out of production usage for 3 to 6 weeks during summer months which may interfere with planting schedules, in addition to disposal of used plastic films especially if they are non-biodegradable (Katan, 1987; Stapleton and DeVay, 1995). Soil solarization unfortunately has been reported in some cases to negatively affect many beneficial microbes especially the bacterivores and fungivores which feed on bacteria and fungi and consequently aid soil organic matter decomposition (Dai *et al.*, 2016).

2.8 Soil enzymatic activity

Soil enzymes are basically derived from soil bacteria, fungi, plant roots, microbial cells, plant and animal residues, etc. (Brown, 1973; Cao *et al.,* 2003; Tarafdar and Marschner, 1994) and play a significant role in biochemical transformations mediation involving organic residue decomposition and nutrient cycling in soil (Marten *et al.,* 1992; McLatchey and Reddy, 1998). Management of land and utilization methods can affect soil enzymatic activity and as such can be used as a sensitive index to reveal changes of soil quality. The quality of soil and its degradation are largely determined by a number of physical, chemical, biological, microbiological and biochemical properties, with the last two being the most sensitive owing to their rapid response to changes. The ecosystem stability and fertility of a soil is directly influenced by the microbiological activity and it is generally accepted that a good level microbiological activity is crucial for soil quality maintenance. The enzymatic activities play a vital role in soil nutrient cycling through the soil microbiological activity and its activity is pivotal in both the mineralization and transformation of organic matters as well as plant nutrients in soil ecosystem (Dick and Tabatabai, 1993). Soil enzymes are generally very sensitive to both natural and anthropogenic stresses and are quick to respond to the induced changes (Dick, 1997). Soil enzymes analysis could als be useful in identifying positive or negative effects of residue management, soil compaction, tillage, crop rotation and soil contamination at reasoning time duration.

Consequently, enzyme activities can be considered as effective indicators of soil quality especially for changes due to environmental disturbance or management practices (Kumar *et al.,* 2013). These enzymes are very important in catalysing most vital reactions needed for the survival of microorganisms in soils in addition to soil structure stabilization, organic waste decomposition, formation of organic matter and cycling of nutrients which are all pivotal role in agricultural (Dick *et al.,* 1994 and Dick, 1997).

Soil metabolic processes are determined by a group of enzymes contained in all soils (McLaren, 1975) depending on its physical, chemical, microbiological, and biochemical properties. The amount of enzymes in soil depends on the soil type especially in its organic matter content, composition, and its living organisms' activity and biological intensity. Enzyme activity in soil is due to the accumulated activity of enzymes and from enzymatic activity of proliferating microorganisms (Kiss *et al.,* 1975). Although they are usually associated with proliferating viable cells, they can also be excreted from living cells or released from dead cells into the soil solution. Information about nutrients release in soil can be determined by studying

soil enzymes by means of organic matter degradation and microbial activity. Correlation with the degree of pollution (PAHs), soil fertility, microbiological activity, biochemical cycling of different substances in soil can be established with the help of soil enzymes analysis and also in assessing the succession stages of an ecosystem. Therefore, soil enzyme activity measurement in degraded (contaminated) soils can be used to examine the impacts of environmental changes or management on soil enzyme activities (Kumar *et al.,* 2013). A lot of studies have reported the potential use of enzyme activity as an index of soil productivity or microbial activity (Alef *et al.,* 1995 and Dick *et al.,* 1996). Generally, the biochemical reactions are usually carried out through the catalytic contribution of enzymes and various substrates that are used as energy sources for microorganisms (Kiss *et al.,* 1978). These enzymes may include amylase, arylsulphatases, β-glucosidase, cellulase, chitinase, dehydrogenase, phosphatase, protease, and urease released from plants (Miwa *et al.,* 1937), animals (Kanfer *et al.,* 1974), organic compounds and microorganisms (James *et al.,* 1991; Richmond, 1991; Shawale and Sadana, 1981) and soils (Gupta *et al.,* 1993 and Ganeshamurthy *et al.,* 1995). In addition, soil enzymatic activities can be used as microbial activity measurement, productivity of soil and inhibiting impacts of pollutants (Tate, 1995). Table 12 prsents some examples of soil enzymatic activities. Dehydrogenase and urease were chosen in this study to determine the effects of soil solarization and/or biosurfactants on soil/rhizosphere enzymatic activities as well as the soil/rhizosphere total heterotrophic microorganisms because they are commonly studied in soil samples; their level of activity characterize the potential of obtaining C for energy by soil microorganism for growth; dehydrogenase and ureas are importance in C- and N-cycling respectively; they help to determine microbial activity and biochemical reaction within the soil; and they are relatively rapid, easy and affordable to determine.

Table 12: Soil enzymes indicators of soil quality

Soil enzyme	Enzyme reaction	Indicator of microbial activity
β-glucosidase	Cellobiose hydrolysis	C-cycling
Cellulase	Cellobiose hydrolysis	C-cycling
Dehydrogenase	Electron transport system	C-cycling
Phenol oxidase	Lignin hydrolysis	C-cycling
Amidase	N-mineralization	N-cycling
Urease	Urea hydrolysis	N-cycling
Phosphatase	Release of PO_4^-	P-cycling
Arylsulphatase	Release of SO_4^-	S-cycling
Soil enzymes	Hydrolysis	General organic matter degradative enzyme activities

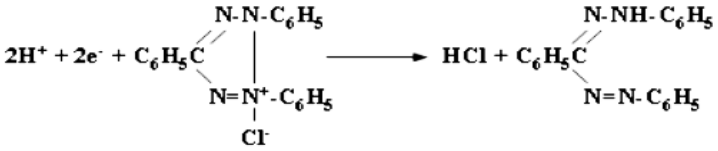
Source: Das and Varma (2011)

2.8.1 Dehydrogenase enzyme activity

Dehydrogenase enzymes are intracellular enzymes which belong to the oxidoreductases and catalyse the oxidation of organic compounds by separating two-hydrogen atoms. The separated hydrogen acted upon by many specific dehydrogenases is then transferred to either nicotinamide adenine dinucleotide or nicotinamide adenine dinucleotide phosphate. Hydrogen atoms through these co-enzymes participate in the reductive processes of biosynthesis. Consequently, the activities of various dehydrogenases depend on the overall dehydrogenase activity of a soil which is a fundamental part of the enzyme system of every microorganism (enzymes of the respiratory metabolism, the citrate cycle and N metabolism). Dehydrogenase there acts as an indicator of the microbiological redox systems and can be considered a good measure of microbial oxidative activities in soil (Tabatabai, 1982). The measurement of dehydrogenase activity can determine microbial growth and metabolism (Friedel *et al.,* 1994) as dehydrogenase enzymes are produced by every living cells. The number of living cells during growth phase is associated with the extent to which their enzymes oxidize organic matter and their activity during the production stage (Xie *et al.,* 2008). Dehydrogenase is measured using a colourless triphenyl tetrazolium chloride (TTC) as a hydrogen acceptor (Yin

et al., 2001 and Beloti *et al.,* 1998) which turns to red colour triphenyl formazan (TF) dye as soon as it accepts hydrogen atom as described in equations (1) and (2) (Burdock, 2009) of Figure 2.19.

$$RH_2 \xrightarrow{\text{Dehydrogenase}} R + 2H^+ + 2e^- \qquad (1)$$



(2)

Triphenyl Tetrazolium Chloride (TTC) (colourless)

Triphenyl Formazan (TF) (Red dye)

Figure 2.19: Equations (1) Biological oxidation of organic compounds and (2) Chemical reaction of tetrazolium salts.

2.8.2 Urease enzyme activity

Urease enzyme is usually common in nature and is present in animals, plants and microorganism. Most of the urease enzymes in soil come from syntheses by microorganism and plant materials (Bremner and Mulvaney, 1978; Frankenberger and Tabatabai, 1982). It's been estimated that 79-89% of urease activity in soil is derived from extracellular enzymes adsorbed to soil colloids (Paulson and Kurtz, 1969) and the activity of urease enzyme is higher in plant materials than in soil, and as a result, areas with crop residues such as no-till, tend to show higher enzymatic activity (Cantarella *et al.,* 2018). A threefold increase was observed by Barreto and Westerman (1989) in urease activity in no-till system compared with that in the soil of a conventional tillage area. The hydrolysis of urea fertilizers introduced to soil is carried out by urease enzyme into NH_3 and CO_2 with the concomitant rise in soil pH (Andrews *et al*. 1989; Byrnes and Amberger 1989) which leads to the rapid loss of Nitrogen to the atmosphere through volatilization of NH_3 (Simpson *et al*. 1984; Simpson and Freney, 1988). Consequently, as a result of this volatilization, urease activities in soil have received considerable attention since it was first reported by Rotini (1935).

2.9 Summary and research originality

This chapter reviews the unpleasant environmental consequences associated with crude oil development since its discovery in the Niger Delta region, Nigeria. As the country's economic power house, the Niger Delta oil pollution continues unabated with increasing environmental contamination. Crude oil is established as a source of PAHs contamination in water, sediment, soil and air pollution and were considered in this chapter as a major threat to public health due to its toxicity, carcinogenicity and recalcitrant nature. Current *in situ* remediation techniques were highlighted, their merits and demerits evaluated, and their environmental, social and economic impacts compared. An overview of sustainability considerations in remediation was summarized in view of sustainable remediation as an emerging concept in contaminated land. This chapter also presents comprehensive reviews on phytoremediation, biosurfactants and soil solarization as a potential novel sustainable remediation approach to contaminated land clean-up especially in the Niger Delta region with large area of impacted land. Phytoremediation is applicable to both organic and inorganic contaminants and is considered a sustainable remediation option with added advantages of utilizing microorganisms to increase the rate of remediation. The environmental friendliness, biodegradability, less toxicity, non-hazardous attributes and cost effectiveness of biosurfactants, makes them sustainable compared to their chemically synthesized counterparts. Soil solarization on the other hand is beneficial to environmental sustainability as it leaves no toxic residues in the environment while inducing complex physical, chemical and biological changes which includes soil structure improvement, increase in mineral nutrient availability and soluble organic matter that favourably impacts on plant growth and yields, microflora and microfauna population in the soil with high influence on the enzymes systems.

The integration of soil solarization and phytoremediation enhanced with biosurfactant in this study is first of its kind. And there is a huge gap in knowledge on the application of soil solarization in combined form with phytoremediation to treat contaminated land. Although, biosurfactants have been reported to enhance phytoremediation, it's application with soil solarization has never been carried out anywhere in the world. There are several important areas where this study makes an original contribution to knowledge such as in the effects of soil solarization on PAHs removal; biosurfactant; plant growth; soil/rhizosphere total heterotrophic microorganisms; and soil/rhizosphere enzymatic activities. The advancement of phytoremediation by integrating soil solarization is novel and most suitable to the sub-tropical Niger Delta climate and can be carried out at an industrial scale to treat the large area of

contaminated land in the region. The study also contributed to the gap in sustainability awareness and sustainable remediation assessment of applied/applicable techniques using sustainable development environmental milestones and a six macro-criteria evaluation matrix respectively with relevant stakeholders in the region. This research will shed light in the current environmental, social and economic challenges to sustainable remediation in the region by stakeholders.

Chapter 3

Biosurfactant Enhanced Phytoremediation of PAH Contaminated Soil: Comparison of the Native *Chromolaena odorata* and Non-indigenous *Medicago sativa*

3.0 Biosurfactant enhanced Phytoremediation of PAH Contaminated Soil: comparison of the native *Chromolaena odorata* and non-indigenous *Medicago sativa*

3.1 INTRODUCTION

Across the globe, petroleum hydrocarbon contamination of soil is becoming prevalent probably due to over reliance on it as a major energy source worldwide, rapid industrialization, population explosion and complete disregard for environmental and public health. Mankind has continuously introduced numerous hazardous materials into the environment since the dawn of the Industrial Revolution at an exponential rate (Jeanna, 2000). These hazardous contaminants consist of a variety of polycyclic aromatic hydrocarbons (PAHs) and heavy metals, which pose serious risks to public health. In the oil rich Niger Delta, Nigeria present day industrial activities release substantial amounts of crude oil and refined products into the natural environment as a result of events such as storage tank leakage, sabotage or oil spills during routine transporting and shipping operations. Introduction of hydrocarbons into the environment whether accidentally or due to human activities is a main cause of soil and water pollution (Holliger *et al.,* 1997). Das and Chandran (2010) reported that hydrocarbon components have been known to belong to the family of carcinogens and neurotoxic organic pollutant and they contaminate air, soil, freshwater (surface water and groundwater) especially by PAHs generating public concerns as a result of PAHs being toxic, mutagenic, and carcinogenic (Bumpus 1989; Clemente *et al.,* 2001; Cerniglia and Sutherland 2001). Hydrocarbons especially PAHs are persistent in nature with the tendency to spread into ground and surface waters, thereby constitute nuisance to the environment (Husaini, *et. al.,* 2008).

Bioremediation is one of several useful remediation techniques used for contaminant removal due to its effectiveness, costs and safety. It utilizes plants or microorganisms to degrade organic contaminants to form carbon dioxide, water and other inorganic compounds (Robert, 1998). For nearly 300 years, the ability of plant to remove pollutants from contaminated area has been recognized (McCutcheon and Schnoor, 2003). Plant use over time has evolved in treatment of waste, wetlands or even to mitigating air pollution by tree planting. The search for sustainable solutions such as phytoremediation that could clean up residual pollutants as increased in more recent years as the damaging effects after decades of chemical usage and industrial economies grew (McCutcheon and Schnoor, 2003). Phytoremediation is one of the sustainable biological remedial methods, it uses green plants to remove, contain, or render harmless environmental contaminants (Cunningham *et al.* 1996). Therefore, cleaning

up hydrocarbon contaminated soils especially PAHs with the fewest environmental side effects is of great interest and practical methods are needed.

Biosurfactants such as rhamnolipids synthesized by microbes are natural surface-active agents with the ability to reduce surface and interfacial tensions between two immiscible liquids (Banat, 1995; Rahman *et al.*, 2002), thereby enabling the uptake of hydrophobic substrates by plants and/or microorganisms particularly rhizosphere microbes. The enhancement of phytoremediation with biosurfactant is a sustainable remediation strategy for improving the mobility and biodegradability of pollutants especially PAHs. The main implication of this is to facilitate the degradation of pollutants principally by microorganisms at the rhizosphere level (rhizodegradation) and potentially by plants that could take up and metabolize moderately hydrophobic organic contaminants (phytotransformation) (Dietz and Schnoor, 2001). The use of biosurfactants in *in situ* contaminated sites bioremediation appears to be compatible environmentally and more cost-effective than using modified clay complexes or metal chelators. The present study was carried out to assess the potential of *C. odorata*-a native plant commonly found in the Niger Delta region against a well-established widely used non-indigenous plant, *Medicago sativa* (Alfalfa) for its enhanced phytoremediation potential of PAH-contaminated soil using biosurfactant for sustainable remediation in the region.

The findings from this study (Chapter 3) have been published as an original chapter titled “Phytoremediation using native plants” by Springer Nature, Switzerland AG 2020 and can be cited as: Futughe A.E., Purchase D., Jones H. (2020). Phytoremediation Using Native Plants. In: Shmaefsky B. (eds) Phytoremediation. Concepts and Strategies in Plant Sciences. Springer, Cham https://doi.org/10.1007/978-3-030-00099-8_9. Anthony E. Futughe wrote this chapter and is the corresponding author. He planned, carried out the experimental work and interpreted all the results. He also took the initiative to publish this work after consulting with his supervisory team who contributed to the final manuscript and are co-authors.

3.2 MATERIALS AND METHODS

3.2.1 Description of the sampling sites

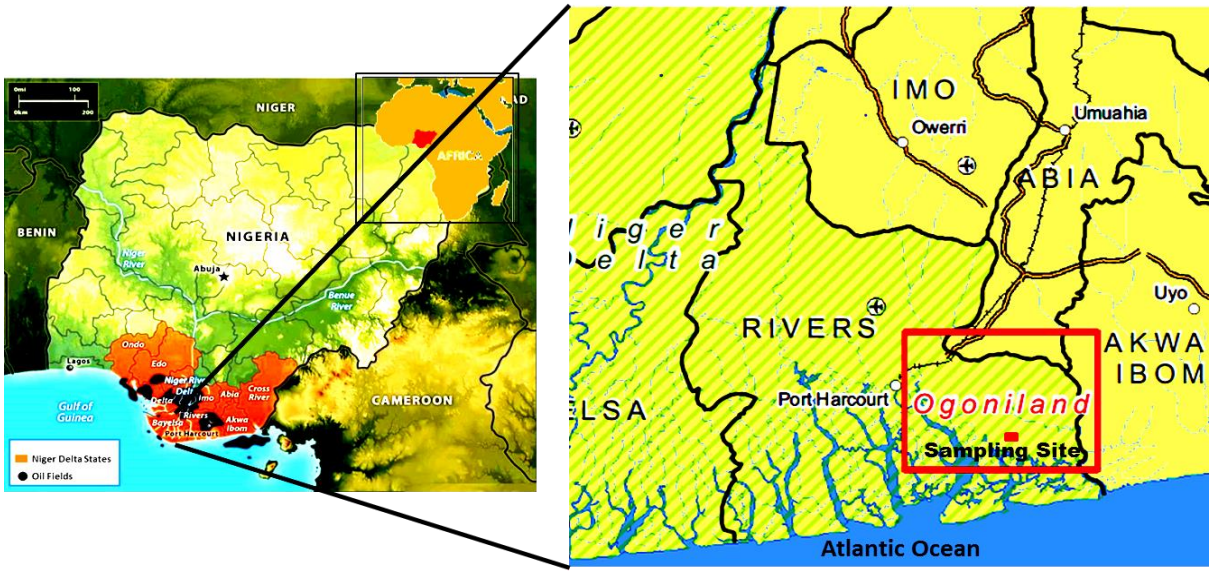
Two different types of soils were sampled: at Bomu Manifold, K-Dere, Gokana Local Government Area (Ogoniland), River State, Nigeria (Figure 3.1a) and the University of Reading Sonning Farm, Berkshire, United Kingdom respectively. Sonning farm soil was used due to the difficulty in bringing bulk quantity of contaminated soil from the Niger Delta region into the UK. And considering the fact that most contaminated soils in the region are agricultural soils with similar properties with the Sonning farm soil prior to contamination.

The Bomu Manifold was selected as the case study site in this research because it was one of the few sites that is heavily polluted in Ogoniland according to the findings of the UNEP in 2011. A summary of the findings by UNEP is presented in Table 24 (see appendix 0). The Bomu Manifold covers an area of 5,000 m^2 with two distinct gates large enough to provide heavy machinery access and it is surrounded by a 3 m high wire mesh fenced and guarded by armed army personnel and Shell Petroleum Development Company (SPDC) (Figure 3.1b). Majority of the pipes and manifold infrastructure are above ground while pipes run below ground outside the manifold area. Visible heavy polluted crude oil was found inside the fence which was seeping through the fence and contaminating additional 19,000 m^2 of land outside the manifold as there was no trench or perimeter drainage system around the manifold. Off this, some 9,000 m^2 are highly polluted with concentration of crude oil overwhelming the soil surface resulting in a strong oily smell. An old flow station, reportedly blown during the Biafran war and later decommissioned, is located 150 m to the east. At the time of sampling (September, 2015) there was a heavy down pour of rain. Contaminated soil sample for baseline study was collected close to a waterlogged area with visible oily sheen (GPS coordinates of 4º39’44.6’’N 7º16’40.1’’E) (Plate 1.1a). A total of 1 kg of contaminated soil at 20 cm depth was sampled at two spots along a transect due to the site ruggedness and remoteness. Once the samples were collected, they (soil and plant) were properly stored and preserved at 4ºC to maintain the chemical, physical and biological properties that they possessed at the time of collection.

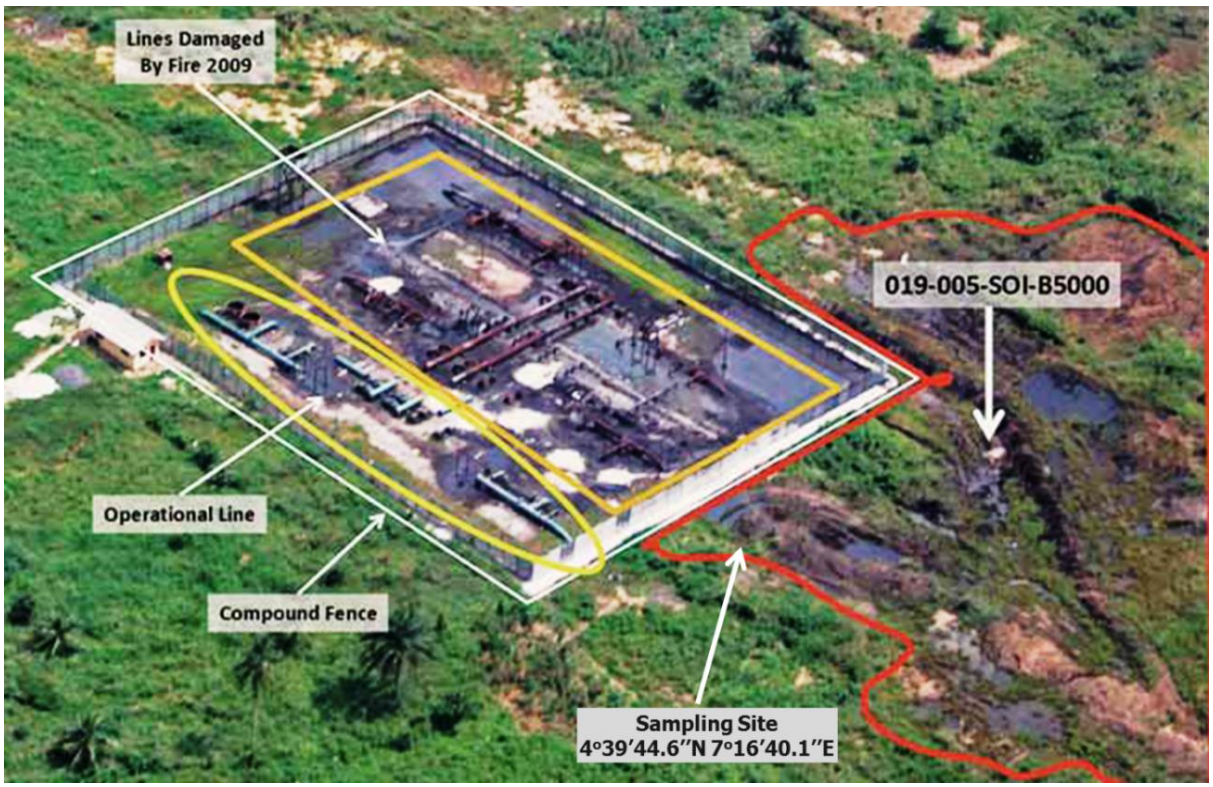
The Sonning Farm soil is a dark yellowish brown arable soil type located on an alluvial plain of the River Thames with crops growing on the surface. 20 bags filled with 50 kg each of bulked and layered soil was collected up to a depth of 25 cm with a spade at the Sonning Farm site with GPS coordinates N51’28.898 W00’53.844 (Figure 3.1c and Plate 1.1d). At the time of sampling (January, 2016) the weather was very cold and windy. Samples were transported to the laboratory for further analysis.

3.2.2 Plant sampling at contaminated site

The most thriving indigenous plant with their seeds were sampled from the Bomu Manifold contaminated land into sterile plastic bag and was identified by the Department of Plant Biology and Biotechnology, University of Benin, Nigeria (Plate 1.1(a-c)).



(a): Sources: Modified from UNEP (2011) and Stratfor (2016)



(b): Source: Modified from UNEP (2011).

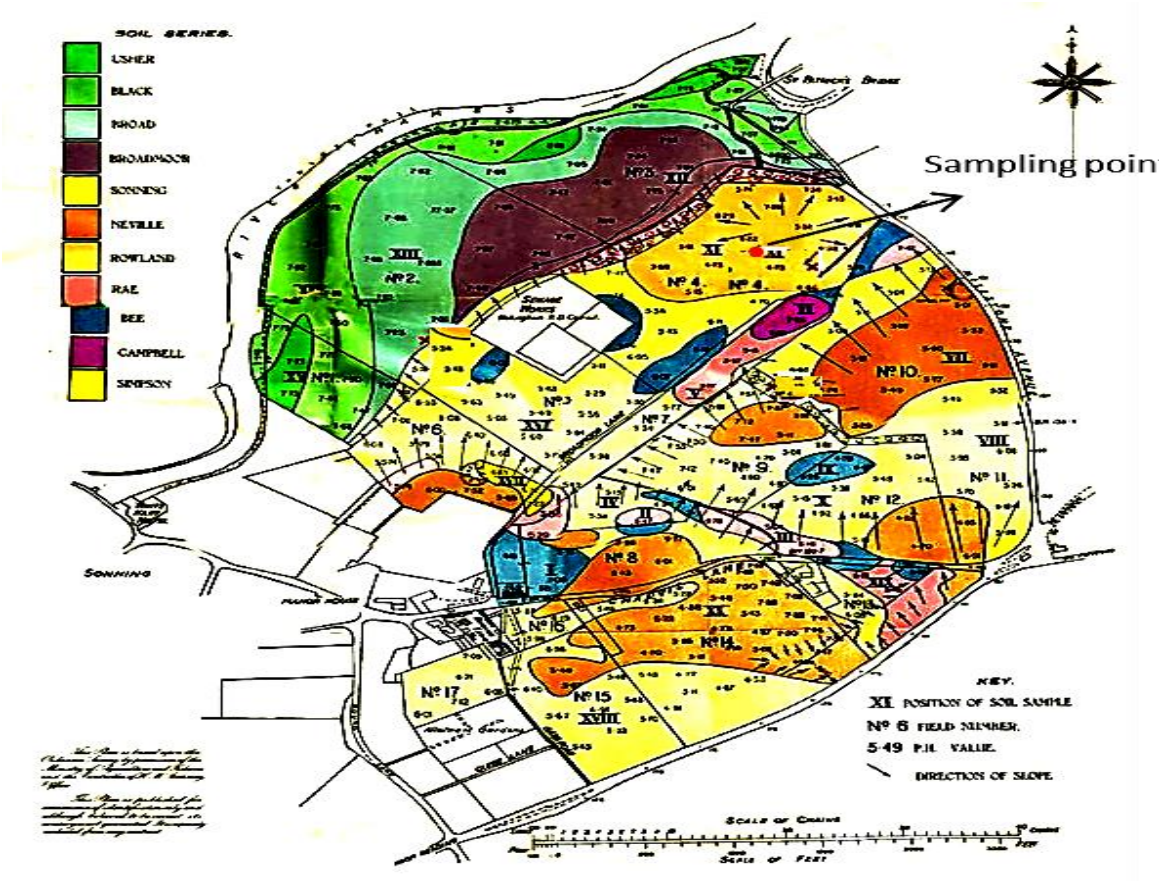
Figure 3.1(a-b): (a) Niger Delta, Nigeria, showing Ogoniland where Bomu Manifold is located. (b) Soil and Plant sampling site near Bomu Manifold, K-Dere, Rivers State, Nigeria.

(a):

(b):

(c):

Plate 1.1(a-c): (a) Sampled point closed to a visible oil waterlogged area. (b) Thriving indigenous plants at the 3 m high perimeter fence. (c) Achene seeds of *C. odorata*.



(a): Source: Modified from Kay (1936)

Figure 3.1c: (c) Uncontaminated soil sampling location at the University of Reading Sonning Farm, Berkshire, United Kingdom.

(b):

Plate 1.1d: (d) Sampling soils into clean bags with the aid of GPS.

3.2.3 Laboratory study

Formation of soil is mostly from rocks weathering of the earth crust, decaying organic matter from plants, animal waste and microorganism (Harrison, 2007). Soil serves as a natural medium to grow plants with distribution of nutrients and pollutants having effects on plants, animal and human because they are greatly influenced by soil pH, Nitrate level, cation exchange capacity (CEC) and other abiotic factors (Harrison, 2007). Soil samples collected from the various sites were thoroughly homogenized by mixing the soils respectively and air dried at room temperature ($28^oC \pm 2^oC$) for 6 days in other to retain the viable microorganisms before passed through a <2 mm sieve, as experimental observations have shown that it is very difficult to obtain reproducible subsamples from field moist soils because it does not homogenize easily. Air dried, ground soils on the other hand, homogenized better and yield little subsampling error (<1%) even on 0.5 g sample, however, loss of volatiles is a potential limitation. Sterile sample bags were used in packaging and storing air dried soils at 4^oC to maintain their individual integrity prior to analysis.

3.2.4 Soil texture

About 25 g of air dried soil sample with all particles less than 2 mm was used to form a ball of about 2 cm. Deionized water (DI) ($18M\Omega m^{-2}$) was gradually added to the soil until it adhered to itself and not to the hand. The 'key for finger assessment of soil texture guideline' by Thien (1979) was followed to determine the soil texture because texture indicates the relative content of particles of various sizes, such as sand, silt and clay in the soil and the finger assessment is quicker and reliable.

3.2.5 Soil pH

This was determined using pH meter with combined electrode. Air-dried soil (10 g) was weighed (<2 mm) into a 100 ml glass beaker, then 10 ml of DI water was added and the mixture was stirred. It was allowed to stand for 30 minutes. Suspension was stirred every 10 minutes during this period. After 1 hour, the suspension was stirred and the combined electrode was placed in the suspension (about 3 cm deep) and the pH readings were recorded after being calibrated with buffer solutions at pH4, 7 and 10 respectively.

3.2.6 Soil moisture contents

All analysis in the laboratory was related to an air dried basis and therefore must consider the actual soil moisture content (Hesse, 1971). An empty crucible was put into the muffle furnace and left over night at 105^{o}C. The crucible was then removed from the furnace and allowed to cool in the desiccators and weighed. Moist soil sample [25g (± 0.001)] was introduced into the crucible and the weight was recorded. The crucible and its content were placed in the muffle furnace and left over night at 105^{o}C after which its weight was determined when cooled. The water contents of the soil samples were determined using the following formula:

$$\text{Water Content, W (\%)} = \frac{W_2 - W_3}{W_3 - W_1} \times 100\%$$

Where W_1 = Weight of empty crucible container

W_2 = Weight of crucible container + moist soil

W_3 = Weight of crucible container + oven dried soil

3.2.7 Soil organic matter contents

The loss by ignition method procedure according to Schulte and Hopkins (1996) was used to carry out this analysis. It does not involve the use of any chemical, only the use of a muffle furnace. Its principle is based on comparing the weight of a sample before and after the soil is ignited. Before ignition, sample contains organic matter, but after ignition, only the mineral portion of the soil remains. An empty crucible was put into the muffle furnace and left over night at 105^{o}C. The crucible was then removed from the furnace and allowed to cool in the desiccators and weighed. 25g (± 0.001) air dried soil sample was introduced into the crucible and the weight was recorded. The crucible and its content were placed in the muffle furnace and left over night at 105^{o}C after which its weight was determined when cooled. After which it was then placed into a muffle furnace at 440^{o}C overnight and cooled in a desiccator again after removal. For this process, the soil was analysed in triplicate. The organic matter contents of soil samples were determined using the following formulae:

$$\text{Organic matter content (\%)} = \frac{\text{Mass of oven dried soil} - \text{Mass of ignited (burnt) soil}}{\text{Mass of oven dried soil}} \times 100\%$$

3.2.8 Nitrate (NO_3^- – N) extraction

25 ml of DI water was added into soil bottle containing 3.5 g of air dried soil and 1 shot Nitrate Extraction Powder was added to the bottle, capped and shook for 30 sec. The soil coagulated in the bottom of the bottle leaving a clear extract. 1.0 ml of the aqueous soil extract was pipette into a sample cell and filled up with DI water to the 25 ml mark. One NitriVer 6 Powder Pillow content was added to the cell, swirl stoppered and shake continuously for 2 min after which it was allowed to settle for 2 min. Sample (25 ml) was poured into another clean sample cell and the content of 1 NitriVer 3 Reagent Powder Pillow was added, stoppered and shook for 30 sec thereafter allowed to settle for 10 min with a pink colouration. The same process was used for the blank but without the soil sample. The Hash Spectrophotometer at 500 nm was used to take the readings.

3.2.9 Available phosphorus

The available phosphorus was determined using a modified procedures of Murphy and Riley (1962); Watanabe and Olsen (1965); Olsen and Sommers (1982). In the modified method, a single solution reagent containing ammonium molybdate, ascorbic acid and a small amount of antimony was used, for colour development in the soil extract. Air-dried soil sample (5 g) was weighed into a 250 ml Erlenmeyer flask and 100 ml of 0.5 M sodium bicarbonate ($NaHCO_3$) solution was added. The flask was closed with a stopper and shaken for 30 minutes on a shaker at 200 rmp. The blank comprises one flask containing all reagents but no soil. The solution was filtered through a Whatman No. 40 filter paper and 10 ml of clear filtrate was pipette into 50 ml volumetric flask and acidified with 5 N sulphuric acid (H_2SO_4) to pH 5.0. DI water was added to about 40 ml volumes and 8 ml of the single reagent was added and brought to 50 ml volume. Standard curve solution and blank were also determined using the above procedure without soil sample. The absorbance of the blank, standards, and samples were read after 10 minutes at 882 nm wavelength using spectrophotometer. Phosphorus concentration in the sample was read from the calibration curve.

3.2.10 Cation exchange capacity (CEC) using Sodium as index ion

Sodium acetate method was used to determine CEC according to Chapman (1965) protocol. Well ground air-dried soil sample (5 g) was weighed into 50ml centrifuge tube. 30 ml of 1M sodium acetate reagent was added and mixture was placed into ultrasonic bath for 5 min and centrifuge at about 1000 rpm for 3 min until the supernatant was clear, decanted and discarded. 30 ml of ethanol was then added to the soil residue and agitated to remove any excess

sodium acetate and placed into the ultrasonic bath for 5 min and centrifuge. The resultant supernatant was decanted and discarded, and the washing was repeated once more. The soil residue was then extracted thrice with 20 ml portions of ammonium acetate using the same above method except that all the supernatants were filtered into 100 ml volumetric flask and made up to the mark. Previously calibrated flame photometer was used to determine the sodium content of the combined extract (which was diluted) and ascertained from the standard calibration curve. The concentration of sodium present in 100 g of soil was determined by multiplying the sodium concentration obtained by the appropriate dilution factor and by 20. The outcome is divided by 23.0 (Relative Atomic Mass of Na) to give the CEC of the soil.

3.2.11 Background heavy metals determination

Background heavy metals especially, Pb, Cd, Cr and Cu due to their well-established toxicity in soil sample were determined in the laboratory. Air dried soil sample (0.2 g) was accurately weighed to the nearest mg in triplicates into a pressure resistance 50 ml quartz or TFM vessel and avoiding contact with the inside of the vessel. Concentrated nitric acid (3 ml) was added with the vessel lid closed and digested in microwave digestion system (CEM, Model MARS Xpress) at 120^{o}C for 10 min according to the EPA method 3015-8 (USEPA, 2007; Sosinski and Sze 1991). After cooling to room temperature, 20 ml of DI water was added to the digested solution with the inner wall and lid thoroughly rinsed and transferred into centrifuge tube where centrifugation was carried out using Eppendorf centrifuge 5702 for 5 minutes at 3000rpm before filtering through Whatman filter paper No. 42 into 50 ml volumetric flask and diluted with DI water to the mark. Reagent blank was also prepared like the sample but without adding soil solution in triplicates. The total concentrations of heavy metals were determined by Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Thermo Scientific iCAP 6000 series). The ICP was calibrated with a mixture of standard solutions of the metals of interest.

3.2.12 Background PAHs determination

PAHs originate from both natural and anthropogenic sources. The anthropogenic sources include release of petroleum products such as crude oil (petrogenic) (Oluseyi, *et al*., 2011, Kowalewska & Konat, 1997) and from combustion and pyrolysis of fossil fuels or wood (pyrolytic). An extraction of PAHs from soil samples especially the contaminated soil sample to establish a baseline study was achieved ultrasonically using modified methods of Fan *et al.* (2008) and Song *et al.* (2006). Air dried soil (5 g) was weighed and mixed with 25 ml of DCM

and extracted for 3 successive times for 1 h sonication using the ultrasonic bath (Clifton sw30H) in which the water temperature was kept at 35^{o}C in other to optimize the PAHs extraction efficiency. The mixture was centrifuged using Eppendorf centrifuge 5702 at 2,414,880 x g for 5 min to separate the supernatant from the soil and filtered into 20 ml vials where it was stored in the refrigerator at 4^{o}C in preparation for clean-up and analysis. Solid phase extraction (SPE) clean-up was carried out with a 12 port vacuum manifold from SUPELCO with 1 g/6 ml ENVI^{TM}-Florisil glass cartridges. After conditioning the sorbent of the SPE cartridges, 3 ml of the supernatant was filtered through the column and was consecutively eluted with 6 ml hexane and dichloromethane mixture of 1:1. The combined eluate was completely dried under the gentle stream of nitrogen, and then re-constituted in hexane with a final volume of 2 ml for GC- FID analysis. Samples extracts (1 µl) were analyzed by a Shimadzu GCMS–QP 2010 and a DB-5 capillary column (30 mm x 0.25 mm x 0.25 µm). Separation was achieved according to the following program: the initial oven temperature was 80^{o}C (held time for 1 min), and increased to 275^{o}C at 15^{o}C/min, held for 1 min: and then to 285^{o}C at 10^{o}C/min, held for 1 min: after that increased to 295^{o}C at 5 ^{o}C/min, held for 1 min. Helium was used as the carrier gas (1.5 ml/min) and make up gas (35 ml/min). A 1.0 µl aliquot of the extract was injected in the splitless mode. The injector was held at 250^{o}C and the detector at 300^{o}C.

3.2.13 Quality control and quality assurance

All chemical extractions were done with two blank samples per analysis and minimum of one blank per set of samples was extracted. Samples were duplicated except otherwise stated. Standard aseptic technique was strictly followed and experiments on PAHs recovery were carried out by spiking a known concentration (1 mg/kg) of phenanthrene, fluoranthene and benzo[a]pyrene standards to uncontaminated soil. The results showed satisfactory recovery of greater than 90, 80 and 70 % respectively for phenanthrene, fluoranthene and benzo[a]pyrene with a detection limit of 0.001 mg/g of soil.

3.2.14 Enumeration of total heterogeneous soil microorganisms

3.2.14.1 Serial dilution technique

Thoroughly mixed air dried soil samples (1g) was weighed onto sterile filter paper and was used to prepare the serial dilution. This soil was placed in bottle containing 99 ml of sterile water, the cap was replaced and the aliquot was mixed by shaking for 1 minute. Care was taken

not to produce aerosols. Waited for one minute to allow the soil particles to settle down and the supernatant were used as stock sample. From the stock sample suspension, 1 ml of the 10^{-2} (1:100) dilution was transferred to second bottle of sterile water and mixed which gave 10^{-4} dilution. One ml of the 10^{-4} dilution was transferred to the final bottle of sterile water and mixed resulting to 10^{-6} dilution.

3.2.14.2 Pour plate technique

In the serial dilution, 1 ml of each diluent was transfer to each of the Petri dishes under aseptic conditions. Pour plates of each of the serial dilution were prepared using approximately 20 ml of molten Tryptic Soya Agar (TSA) for bacteria, Glycerol Yeast Extract Agar (GYEA) for actinomycetes and Sabouraud Dextrose Agar (SDA) for fungi respectively, mixed thoroughly by swirling and allowed to set (solidify). Three replicate pour plates and their controls for each dilution were inverted and incubated at 25^{o}C for 3 to 7 days for the isolation of bacteria, actinomycetes and fungi. Distinct bacterial, actinomycetes and fungal colonies that appeared on each Petri dish after incubation at 25^{o}C for 3 to 7 days were counted and the colony forming units per gram (cfu/g) was determined.

3.2.15 Biosurfactant analysis

A commercially available rhamnolipid (R90 Rhamnolipid biosurfactant) produced by separation and purification processes using *Pseudomonas aeruginosa* in Canola Oil substrate was purchased from AGAE Technologies, USA.

3.2.15.1 Rhamnolipid toxicity test using Microtox

The test for rhamnolipid toxicity was carried out using the Microtox 500 Analyser which uses the bacterium *Vibrio fischeri* a luminescent marine bacterium. The dry luminescent bacterium which was constituted at about 10^{8} cfu/ml suspensions was placed in a vial as control and the photometer was used to measure the amount of florescence emitted. Nine sample dilutions were made up and put into vials with the bacterium and exposed to the test for 5 minutes and then 15 minutes intervals. The luminescence was measured with the 95 % Microtox method and the toxicity was determined in terms of EC_{50} (which is the concentration of the sample that causes a 50 % decrease in the light emitted by the bacteria).

3.2.15.2 Rhamnolipid critical micelle concentration (CMC) from surface tension

Biosurfactant activities depend on the concentration of the surface-active compounds until the critical micelle concentration (CMC) is obtained which is the minimum concentration of a monomer at which micelles form. Determination of the commercial rhamnolipid surface tension for its CMC was carried out using a Tensiometer. The Tensiometer used is a SITA Dyno Tester portable equipment that measures the surface tension as well as the surfactant concentration easily and quickly as shown in Plate 1.2 below.

Five concentrations of the ramnolipids from 50 to 250 g/l were employed to investigate the CMC which is commonly used to measure the efficiency of the surfactant.

Plate 1.2: Determination of surface tension of commercial rhamnolipid biosurfactant in increasing concentration from left to right with the highest being analyzed using SITA DynoTester portable equipment.

3.2.16 Screening of plants

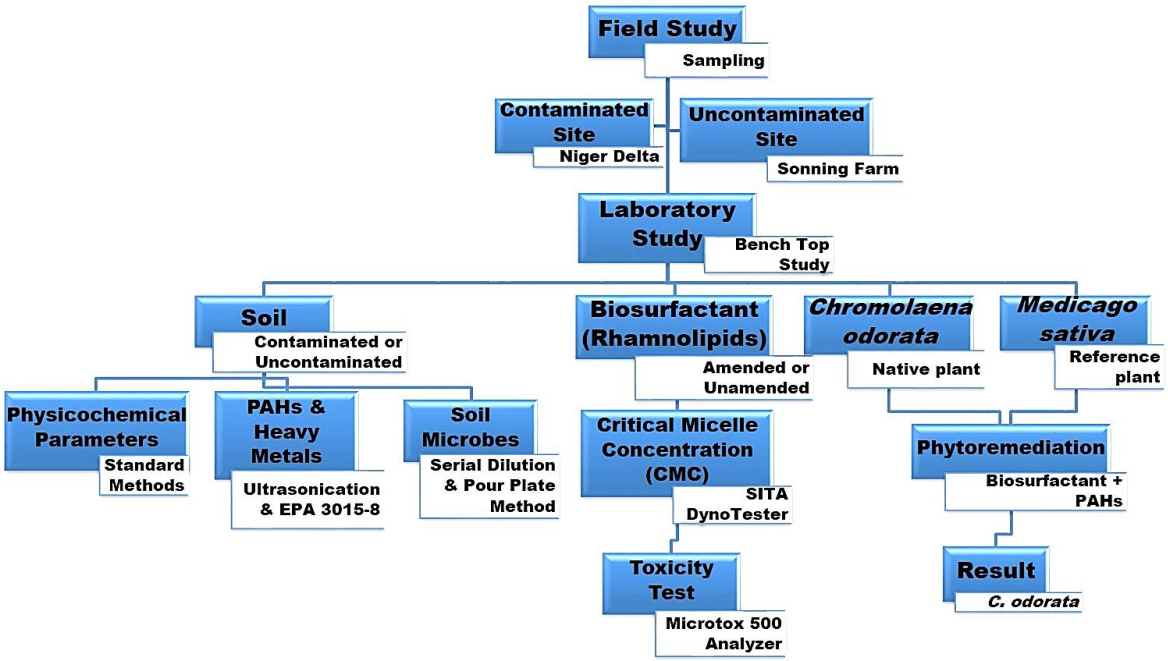


Figure 3.2: Flow chart diagram showing general overview of research methodology. The boxes in blue and white highlight key methodology themes and their sub methods or conditions respectively.

An indigenous plant, *Chromolaena odorata* as shown in Plate 1.3(a-b) was collected from a Niger Delta contaminated soil and screened against a commercially available plant, *Medicago sativa* (Alfalfa) for the most PAHs tolerant (see Table 9 for basic characteristics of plants). *C. odorata* is colloquially known in the Niger Delta as "Shell-copy"-a corrupt version of Shell Petroleum Development Company (SPDC) due to oil relating activities that coincided with the appearance of *C. odorata* (Uyi *et al.* 2014). According to Uyi *et al.* (2014) *C. odorata* thrives abundantly in the entire south-eastern, south-western, Niger Delta and parts of north-central region (see map of *C. odorata* distribution in Nigeria in Figure 6 in appendix 0). *C odorata* was selected based on its seed availability and ease of establishment in addition to its proliferation on the contaminated site over other indigenous plants species such as *Amaranthus* spp. Its suppressing capacity through light competition (Kushwaha *et al*., 1981 and Honu and Dang, 2000), high reproductivity, high growth and net assimilation rates (Ramakrishnan and Vitousek, 1999) as well as its ability to grow on many soil types and in many climatic zones (Timbilla and Braimah 1996; Goodall and Erasmus 1996; Robertson *et al*. 2008) makes *C. odorata* more suitable for this experiment. A preliminary screening of *C. odorata* with *Amaranthus* spp. both from the same contaminated site, demonstrated the superiority of *C.*

odorata especially in its thriving ability and high growth rate over petroleum-resistant *Amaranthus* spp (Mohsenzadeh and Chehregani, 2015; Mohsenzadeh *et al.*, 2009) in crude oil contaminated soil (see plate 1.15 in appendix 0).

Alfalfa was chosen as a reference plant as reports have shown its phytoremediation potentials (Fan *et al.*, 2008; Bonfranceschi *et al*., 2009; Peralta-Videa *et al*., 2004; Li and Yang, 2013; Ding and Luo, 2005; Ouvrard *et al*., 2011; Zhang *et al*., 2013). Sonning farm soil was artificially contaminated with a PAH mixtures of 60 mg/kg and 120 mg/kg as a baseline from literature reviews (Ayodele *et al.*, 2015) since background PAHs concentrations from Bomu Manifold, Niger Delta contaminated soil was relatively too low to establish a baseline.

Air-dried soil from Sonning farm was artificially contaminated with a mixture of PAHs (phenanthrene, fluoranthene and benzo[a]pyrene) using partial spiking protocol according to Jacobsen *et al.* (2002) but was not oven treated i.e. weathered (see Section 4.2.5.1). PAHs 60 mg (20 mg each) and 120 mg (40 mg each) were dissolved in 25.00 ml of acetone and were used to spike a 25% fraction (250 g) of the soil sample and the flask was closed for 5 min to let the solvent disperse. The solvent was evaporated overnight and the remaining 75% (750 g) of the soil subsample was mixed thoroughly and amended with 16.7% (dry weight) of air-dried screened (<2 mm) commercially prepared compost to give a solvent concentration of 10% (v/w) in the treated fraction. The amended compost soil mixtures were thoroughly mixed and passed 3 times through a 2 mm steel gauge sieve to ensure a uniform distribution/homogeneity of the soil-PAHs-compost amendment. The soil-PAHs-compost amendment was randomly sampled in duplicate to test for homogeneity and a satisfactory result showed 18.18±4.27, 21.82±2.18 and 29.88±10.5 mg/kg; and 38.94±1.08, 40.17±1.10 and 42.04±3.14 mg/kg for spiked 20 and 40 mg/kg each of phenanthrene, fluoranthene and benzo[a]pyrene respectively.

The plant screening experimental design as shown in Table 14 was further treated with ramnolipid biosurfactant in appropriate pots (500 or 1000 mg/kg). Control soil was treated with acetone only. Seeds of both plants were surface sterilized by immersion in 2% (v/v) hydrogen peroxide for 8 min to avoid cross contamination, thoroughly rinsed 3 x with DI water and used for the pot experiment (Qu *et al.*, 2011). Seed trays containing a 1:1 mixture of Sonning soil and organic compost were used as seed beds for growing the seeds for 4 weeks before transplanting 2 seedlings per pot into duplicate experimental plastic pots (7.5 x 7.5 x 7 cm) filled with 200 g of treated soil (Plate 1.3b). Evidence for significant difference between the two groups of plants (see Table 13) in terms of their initial height was determined using a two sample t-test. The benchtop experiment was carried out inside a Stewarts electric heated propagator at average temperature of 20^{o}C with 2 short lengths of white florescent tubes hung

above it, supplying a photoperiod of 10 h light as shown in Figure 10a. Plants received water daily by gently spraying with artificial rainwater water to prevent leaching. The location of the pots was randomly changed daily within propagator chamber. Plant mortality rates over the 4 weeks experimental time were recorded by counting live and dead plants differentiated by visual inspection. Plants were considered dead when it withered with old leaves dried out. At the harvested time, plant height, taking into account change in growth difference, root length from the base of the stem to the longest root tip of plant was measured. Shoots and roots were removed from pots and washed with DI water to remove soil particle and blotted with tissue paper. The plant material was oven dried at 70^{o}C over night (Campbell and Plank, 1998) and dry weights recorded. Soil was sampled at the same harvesting time and kept refrigerated at 4^{o}C until ready for analysis.

Both plants and contaminated soils were treated as hazardous waste as extraction moves the contaminants to plant biomass and as such were safely disposed of as clinical waste without getting into the environment.

Table 13: Tested plants and their basic characteristics

General name	Scientific name	Family and genera	Basic characteristics
Siam weed, Christmas bush, Awolowo	*Chromolaena odorata*	*Asteraceae*	A scrambling perennial shrub, with straight, pithy, brittle stems which branch readily, bear three-veined, ovate-triangular leaves placed oppositely, and with a shallow, fibrous root system (Holm *et al*., 1977; Henderson, 2001). However, it grows rapidly with a multi-stemmed shrub to 2.5 m (100 inches) tall in open areas. It has soft stems but the base of the shrub is woody. In shady areas it becomes etiolated and behaves as a creeper, growing on other vegetation. It can then become up to 10 m (33 feet) tall. It can produce large quantities of seeds estimated between 93,000 (Weerakoon, 1972) to 1,6000,000 (Wilson, 1995) per plant which may be responsible for its most aggressive nature as indigenous sub-tropical invader (Liggitt, 1983; Macdonald and Jarman, 1985; McFadyen, 1991; Wilson, 1995).
Alfalfa	*Medicago sativa*	*Leguminosae*	A cool season perennial legume, with height up to 1 m and a deep root system sometimes stretching to more than 15 m

Table 14: Experimental design of plant screening with codifies treatments.

Treatment (n=2)	Vegetated		Un-vegetated
	C. odorata	***M. sativa***	**Control**
Vegetated Control	A	H	O
Biosurfactant (500mg/kg)	B	I	P
PAHs (60 mg/kg)	C	J	Q
Biosurfactant (500 mg/kg) + PAHs (60 mg/kg)	D	K	R
Biosurfactant (1000 mg/kg)	E	L	S
PAHs (120 mg/kg)	F	M	T
Biosurfactant (1000 mg/kg) + PAHs (120 mg/kg)	G	N	U

(a):

(b):

Plate 1.3(a-b): (a) Bench top experimental design of plants (b) 4 weeks old seedlings transplanted into experimental pots with black and red coloured pots containing *C. odorata* and *M. sativa* respectively.

3.2.17 Soil PAHs analysis

An extraction of PAHs from soil samples was achieved ultrasonically using modified methods of Fan *et al.* (2008) and Song *et al.* (2006). Soils sampled at harvest time were air dried and 5 g was weighed and mixed with 25 ml of DCM and extracted for 3 successive times for 1 h sonication using the ultrasonic bath (Clifton sw30H) in which the water temperature was kept at 35ºC in other to optimize the PAHs extraction efficiency. The mixture was centrifuged using Eppendorf centrifuge 5702 at 4000 rpm for 5 min to separate the supernatant from the soil and filtered into 20 ml vials where it was stored in the refrigerator at 4ºC in preparation for clean-up and analysis. Solid phase extraction (SPE) clean-up was carried out with a 12-port vacuum manifold from SUPELCO with 1 g/6 ml ENVI^{TM}-Florisil glass cartridges. After conditioning the sorbent of the SPE cartridges, 3 ml of the supernatant was filtered through the column and was consecutively eluted with 6 ml hexane and dichloromethane mixture of 1:1. Following filtration, the volume of solvent was reduced to approximately 1 ml using a rotary evaporator with maximum water bath temperature at 30ºC. After which the concentrated sample was transferred to a small tube wrapped with foil paper to prevent photo degradation and allowed to evaporate to dryness and then re-constituted in hexane (HPLC grade with 95% purity) with a final volume of 2 ml for GC-FID analysis. All solvents used were of HPLC grade with over 95% purity from Fisher Scientific, UK. Samples extracts (1 µl) were analyzed by a Shimadzu GCFID–QP 2010 and a DB-5 capillary column (30 mm x 0.25 mm x 0.25 µm). Separation was achieved according to the following program: the initial oven temperature was 80ºC (held time for 1 min), and increased to 275ºC at 15ºC/min, held for 1 min: and then to 285ºC at 10ºC/min, held for 1 min: after that increased to 295ºC at 5 ºC/min, held for 1 min. Helium was used as the carrier gas (1.5 ml/min) and make up gas (35 ml/min). A 1.0 µl aliquot of the extract was injected in the splitless mode. The injector was held at 250ºC and the detector at 300ºC.

3.2.18 Statistical analysis

All treatments were in duplicate in this experiment except where it was otherwise stated. The mean and standard deviation (SD) of the sample were calculated with the degree of freedom (*n*-1) compensating for the small sample size. Normality and equal variance assumption tests were carried out on all experiments. An analysis of differences was carried out using either two Sample t-tests or Mann-Whitney together with its associated 95% Confidence Interval to determine any statistical difference. Differences between

means/medians were considered to be statistically significant using Tukey Pairwise Comparison at $p \leq 0.05$. Mintitab version 17 was the statically software employed.

3.3 RESULTS AND DISCUSSION

3.3.1. Soil analysis

Classification of the soil samples were sandy loam with acidic pH 4.95 for Niger Delta case study contaminated soil which is in line with very to moderately acidic pH range of 4.1-6.5 reported by Kamalu *et al.* (2002) and clay loam with neutral pH 7.14 for Sonning farm soil which agrees with a reported pH of 7.22 by Revitt *et al.* (2015) (Table 15). Although the clay loam Sonning farm soil is a dark yellowish brown arable soil type located on an alluvial plain of the River Thames and belonging to the Rowland Series with a long term historical record of soil types (Kay *et al.,* 1936), a very wide range in soil textures from sandy clay loam to sand in the levees to finer clay in the terrace and backswamp, with mostly sandy loam to clay loam in levee crest pedons have been reported in the Niger Delta region by Kamalu *et al.* (2002) (see Table 25 and Figure 7 in appendix 0). The general morphology of the Niger Delta soils showed a narrow range in morphological characteristics within the various physiographic units of the Meander Belt from dark brown to grey at the surface, and pale brown to grey at the subsurface (Kamalu *et al.*, 2002). Yellowish brown (similar to the Sonning farm soil) has been reported at the Niger Delta soil surface (Kamalu *et al.,* 2002). The irregular morphological distribution in the Niger Delta soils is due to their several cycles of deposition and limited pedogenetic development (Kamalu *et al.,* 2002). The chemical properties of both soils (case study and Sonning farm) were similar (Table 15), consequently, the results obtained with the Sonning farm soil is applicable to other soil types found in the Niger Delta region.

It has been reported that soil pH affects significantly the solubility, mobility and ionized forms of both heavy metals and petroleum hydrocarbons and the optimum pH for biodegradation lies between 6 and 8 (Roberts, 1998; Parr *et al.,* 1983). The slightly acidic nature of the contaminated soil (case study) may have impacted soil microbial content with a mean of 7,890 CFU/g as against the neutral Sonning farm soil with a mean of 42,900 CFU/g and the general trend was bacteria>actinomycetes>fungi (Figures 3.3 and 3.4). Clay loam normally supports most types of plants and crops as it contains a good deal of plant nutrient and will be suitable for used in this experiment. With a very high CEC, in combination with other soil fertility indicators like nitrate and available phosphorous, the Sonning soil is a good plant and microbial growth medium. Background study of contaminated soil sample (case study) from the region showed PAHs ranging from 0.08 to11.30 mg/kg while it was undetected in soil sample from Sonning farm, UK.

Background heavy metals and PAHs as shown in Table 15 appear to be very low in contaminated soil (case study) from the Niger Delta while PAHs were not found in Sonning

soil, making it ideal for artificial contamination. The background concentration of PAHs range of the contaminated soil was 0.08 to 11.30 mg/kg which was too low to establish a baseline for the plant screening exercise, hence, a higher concentration was used as a baseline concentration from literature (see Section 3.2.16). Ultrasonication method was the extraction method employed in determining the PAHs concentrations. It's an efficient technique when compared to others. It provides comparable or even greater quantities of hydrocarbons (Song *et al*., 2002) than other extraction methods. Sonication can have the advantage of faster extraction times depending on the type of contaminants and matrix. It provides a relatively low-cost method, using small volumes of organic solvent without the need of elaborate glassware and instrumentation, however, Berset *et al.,* (1999) reported lower recoveries in some studies. An extraction technique that should be considered efficient should produce good results within a short time with minimum operator involvement and should be cheap, and safe for both the analyst and the environment (Dean, 1998). However, each technique has its own advantages and the choice of extraction depends on several factors including capital cost, operating cost, sample matrix, simplicity of operation, sample throughput and the availability of a standardized method (Banjoo and Nelson, 2005).

Table 15: Physico-chemical properties of soil samples

Parameter	Baseline Contaminated Soil Sample	Sonning Farm Soil Sample
pH	4.95 ± 0.05	7.14 ± 0.11
Classification	Sandy Loam	Clay Loam
Moisture Content	17.83 ± 2.91%	13.72 ± 1.24%
Organic Matter Content	4.07 ± 1.34%	2.48 ± 0.24%
NO_3^- – N	5 mg/L	18 mg/L
Available P	0.01±0.00 mg/g	0.32±0.00 mg/g
Cation Exchange Capacity (CEC)	6.25 meg/100 g	17.8 meg/100 g
Background Heavy Metals		
Cd	0.00± 0.00 mg/g	BDL
Cr	0.02 ± 0.00 mg/g	0.03 ± 0.00 mg/g
Cu	0.04 ± 0.02 mg/g	0.06 ± 0.00 mg/g
Fe	6.84 ± 0.16 mg/g	9.76 ± 0.91 mg/g
Mn	0.01 ± 0.00 mg/g	0.21 ± 0.01 mg/g
Ni	0.00 ± 0.00 mg/g	0.01 ± 0.00 mg/g
Pb	0.00 ± 0.00 mg/g	0.01 ± 0.00 mg/g
Zn	0.01 ± 0.00 mg/g	0.02 ± 0.00 mg/g
Background PAHs		
naphtalene	1.99 ± 1.61 mg/kg	BDL
acenaphtalene	6.87 ± 4.26 mg/kg	BDL
acenaphtene	9.04 ± 9.09 mg/kg	BDL
fluorene	4.31 ± 4.68 mg/kg	BDL
phenantrene	11.30 ± 9.55 mg/kg	BDL
anthracene	6.65 ± 4.11 mg/kg	BDL
fluoranthene	4.08 ± 2.53 mg/kg	BDL
pyrene	4.40 ± 3.41 mg/kg	BDL
benzo[a]pyrene	0.08 mg/kg	BDL

Key:
BDL = Below Detection Limit (see Section 3.2.13).

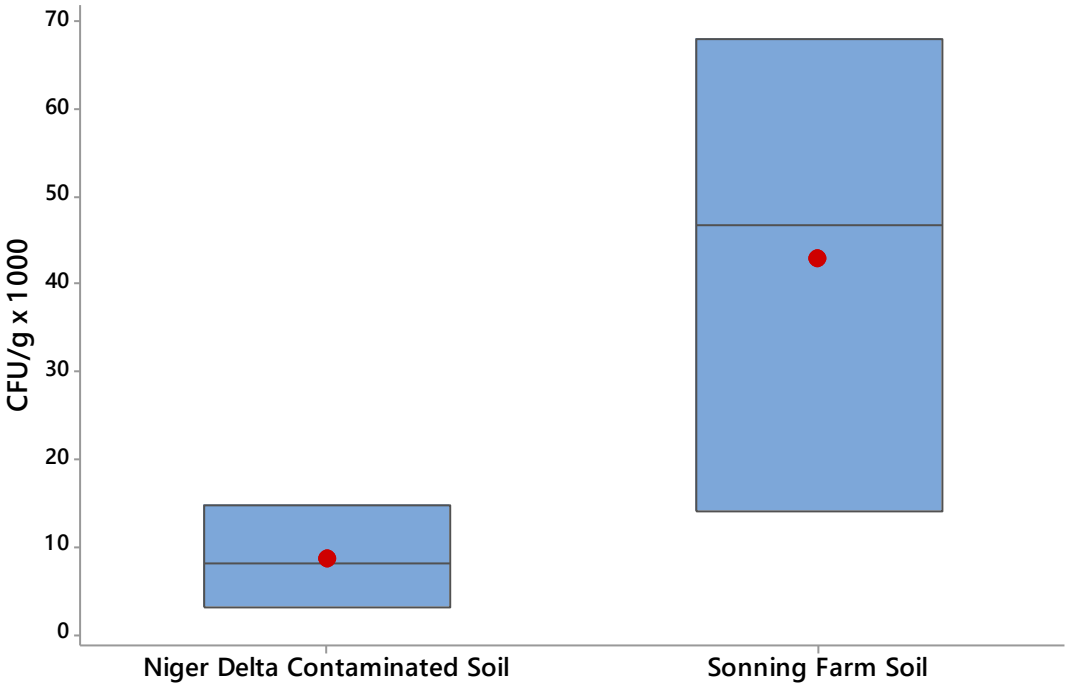


Figure 3.3: Box plot of total viable soil microorganisms. (Average microbes in Contaminated soil = 8.58±5.86 and Sonning soil = 42.9±27.2 (CFU/g x10^3)

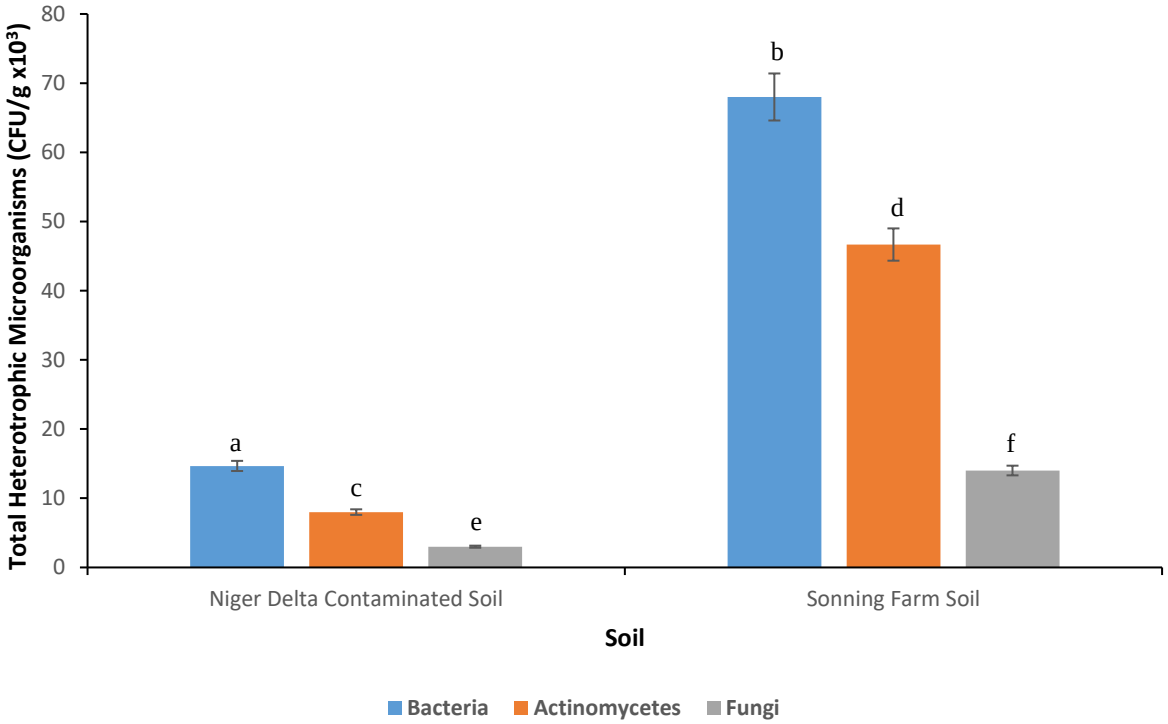


Figure 3.4: Total viable heterotrophic microbial groups isolated from soil samples. Error bars represent the standard deviation of two sampled pots. Means with different letters are significantly different (Tukey analysis $p \leq 0.05$).

3.3.2 Bench top study

A commercially synthesized rhamnolipid biosurfactant has a critical micelle concentration (CMC) and half maximal effective concentration (EC_{50}) of 105 g/l (Figure 3.5) and 0.1g/l respectively. The EC_{50} refers to the concentration of the rhamnolipid biosurfactant which induces a response halfway between the baseline and maximum after specific exposure time (see Section 3.2.15.1). It shows that 50 % of *Vibrio fischeri,* which is a light-emitting bacterium had maximal effect at 0.1g/l rhamnolipid biosurfactant concentration thereby reduced half the amount of light it emitted by inhibiting its normal metabolism. However, rhamnolipid biosurfactant was optimized using 0.5 g/kg and 1.0 g/kg (i.e. 500 mg/kg and 1000 mg/kg) respectively for soil treatments amendment during plants screening experiment due to a higher CMC of 105 g/l. This was because biosurfactant exist as monomers at low concentration in solutions while aggregate occurs with increasing concentration and results in the formation of micelles. The formation of micelles depends on the concentration of the biosurfactant. However, above a certain concentration i.e. CMC, the thermodynamics of the system enables the formation of micelles (McNaught and Wilkinson, 1997). The CMC is a characteristic of each biosurfactant and depends on the chemical structure, i.e. the hydrophilic and hydrophobic parts of the molecule. Formation of aggregate micelles in aqueous solution when the CMC has been exceeded is one of the pivotal characteristics of biosurfactant (McNaught and Wilkinson, 1997). This particular arrangement is important in phytoremediation as it creates a spherical structure in which the hydrophilic part of the biosurfactant is in contact with the polar solvent in the case soil solution, while the hydrophobic region of the molecule remains sequestered in the centre avoiding the contact with the hydrophilic medium. A peculiar property of biosurfactant when arranged in these clusters enables the non-polar central part of the micelle to interact with the hydrophobic organic compounds such as PAHs, thereby increasing their water solubility for both plant and/or microbial interactions (see Figure 2.17c) (Gao *et al.,* 2007).

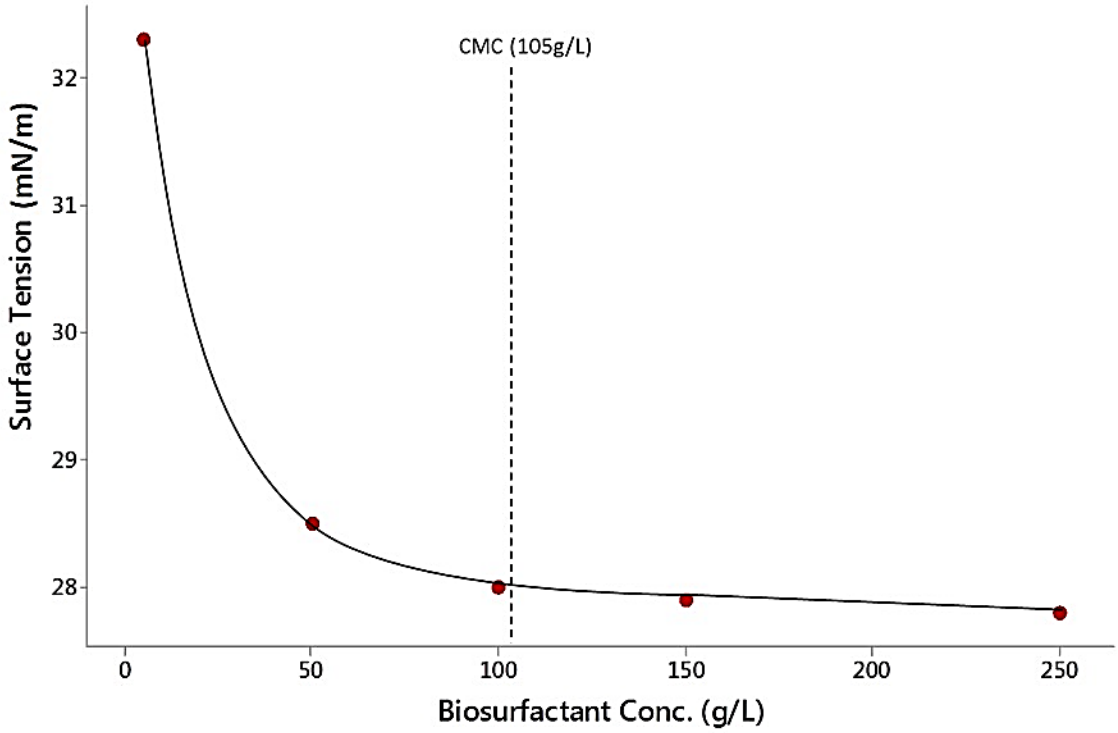


Figure 3.5: Determination of critical micelle concentration (CMC) from surface tension

The result of the plants screening bench top study shows that there was insufficient evidence of any genuine difference against the H_o which states that there was no genuine evidence of difference in the transplanting heights between *C. odorata* and *M. sativa* plants (i.e. samples come from populations with same mean, $\mu_1 = \mu_2$) ($p \geq 0.05$) with a *p*-value of 0.16. The H_o was accepted suggesting that plants randomization was done properly (Appendix i) and no one plant group had any advantage over the other before the screening commenced (see Plate 1.3(a-b). During the first two weeks (6 weeks old) after transplanting, most *C. odorata* showed healthy growth with no phytotoxicity symptoms regardless of the treatments but its counterpart, *M. sativa* has started to show signs of phytotoxicity with some yellow coloration on some of its leaves. Plants in the vegetated control soil with only acetone treatment appeared to grow better than all plants in the treatment pots (see page 149). By the 4th week, most *M. sativa* plants in biosurfactant and/or PAHs treatment pots showed more yellow leaves which may be indicative of phytotoxicity as a result of a negative synergistic effect of biosurfactant and PAHs combined treatment. At the end of the planting period of 28 days, in the *C. odorata* treatment group, plants grew to a mean height range of 5.83±3.01 to 13.00±0.91 cm from an original mean height range of 3.50±0.58 to 4.75±1.50 cm before transplanting (4 weeks old)

while *M. sativa* group has a mean height range of 5.50±0.71 to 10.13±1.38 cm at 28 day (harvest) from an original mean height range of 4.00±0.00 to 5.00±1.73 cm before transplanting as shown in Figure 3.6 and Plate 1.4(a-b). Statistically, there was a significant increase with some evidence against H_o which states that there was no significant evidence of difference in the harvesting heights between *C. odorata* and *M. sativa* plants (i.e. samples come from populations with same mean, $\mu_1 = \mu_2$) ($p \leq 0.05$) with a 3.15 cm as the best estimate of difference with *p*-value of 0.02 (Appendix ii). The H_o was rejected in favour of the H_1 (there was significant evidence of difference in the harvesting heights between *C. odorata* and *M. sativa* plants, $\mu_1 \neq \mu_2$) suggesting that *C. odorata* grew better in all the treatment soils than *M. sativa*. In terms of both plants biomasses, the shoot and root could not be determined separately due to the relatively short growth periods resulting to development of tender plants, however, the dry biomass of the whole plants (combination of shoot and root) from both groups were determined as shown in Figure 3.7 with statistically significant decrease with some evidence against the H_o which states that there was no significant evidence of difference in the dry biomass between *C. odorata* and *M. sativa* plants (i.e. samples come from populations with same mean, $\mu_1 = \mu_2$) ($p \leq 0.05$) which was rejected for the H_1 (stating that there was significant evidence of difference in the dry biomass between *C. odorata* and *M. sativa* plants, $\mu_1 \neq \mu_2$) with *p*-value of 0.04 and a *t*-value of 2.26 suggesting that there is very likely a genuine difference in the dry biomass means of the two plant groups (Appendix iii). This also shows that *C. odorata* performed significantly well than *M. sativa* under similar conditions. However, *M. sativa* has increase root lengths with statistical difference ($p \leq 0.01$) in relative comparison to *C. odorata* with very strong evidence against the H_o (states that there was no significant evidence of difference in the root lengths between *C. odorata* and *M. sativa* plants (i.e. samples come from populations with same median, $\eta_1 = \eta_2$)) which was rejected for the H_1 meaning that there was significant evidence of difference in the root lengths between *C. odorata* and *M. sativa* plants ($\eta_1 \neq \eta_2$) ($p \leq 0.01$) as shown in Figure 3.8 (Appendix iv).

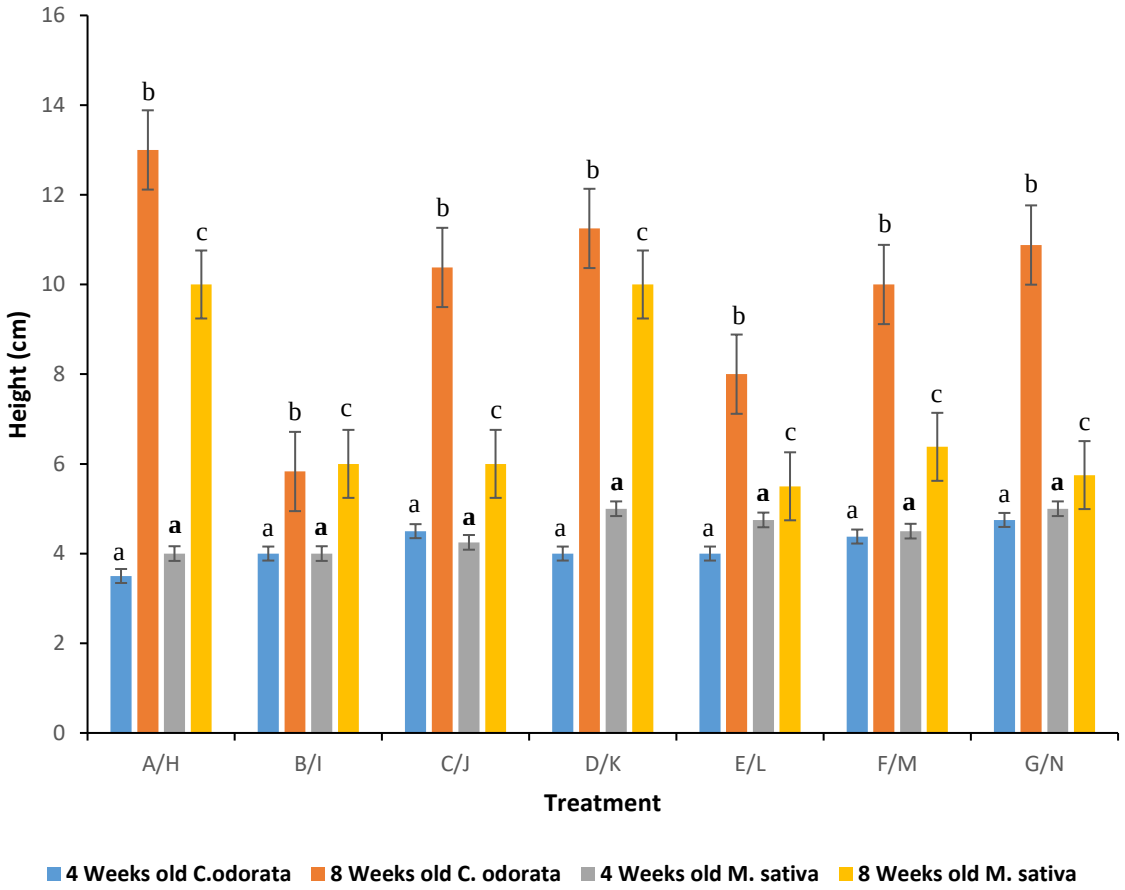


Figure 3.6: Mean growth of *Chromolaena odorata* and *Medicago sativa* from seedlings (4 weeks old) to harvest (8 weeks old). Error bars represent the standard deviation of two sampled pots. Means with different letters are significantly different (Tukey analysis $p \leq 0.05$).

Key:
A/H = Vegetated Control
B/I = Biosurfactant (500 mg/Kg)
C/J = PAHs (60 mg/Kg)
D/K = Biosurfactant (500 mg/Kg) + PAHs (60 mg/Kg)
E/L = Biosurfactant (1000 mg/Kg)
F/M = PAHs (120 mg/Kg)
G/N = Biosurfactant (1000 mg/Kg) + PAHs (120 mg/Kg)

(a):

(b):

Plate 1.4(a-b): (a) Arial and (b) lateral view displays of bench top plants before harvest. *C. odorata* and *M. sativa* in black and red pots respectively.

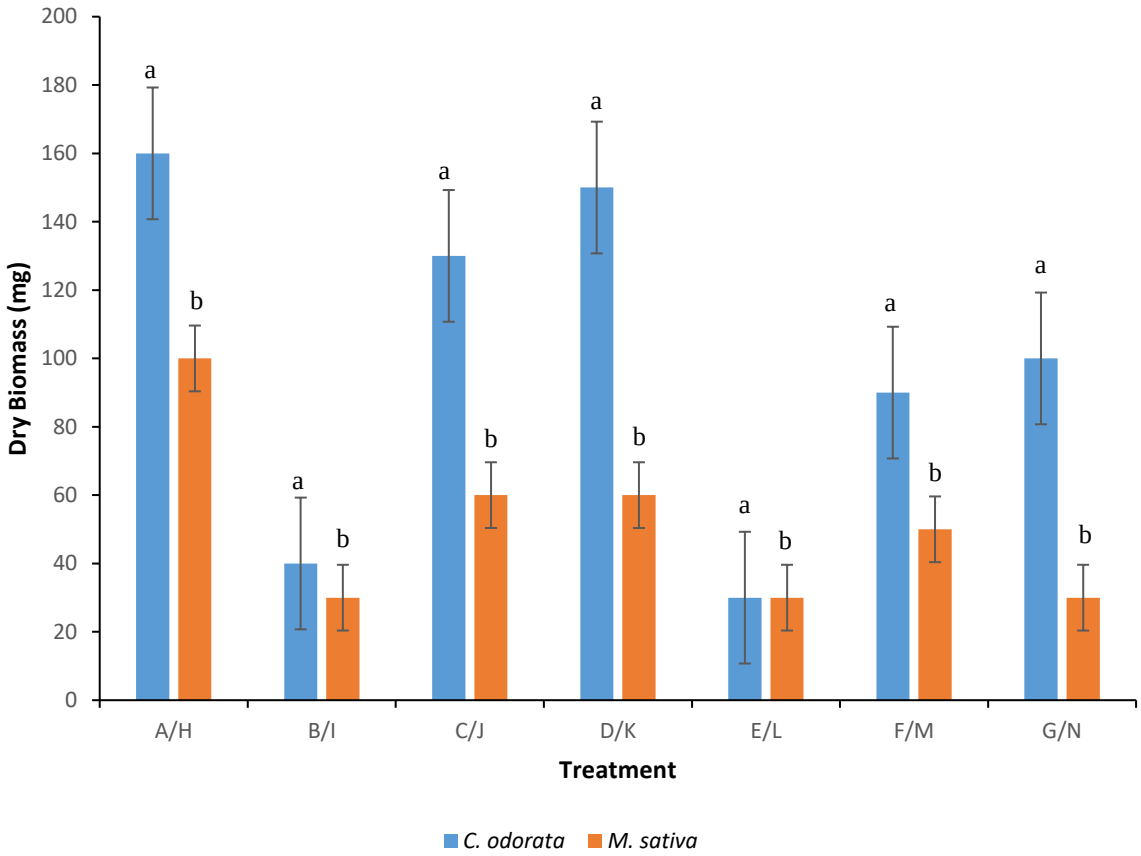


Figure 3.7: Dry biomass of *Chromolaena odorata* and *Medicago sativa* after 8 weeks of growth. Error bars represent the standard deviation of two sampled pots. Means with different letters are significantly different ($p \leq 0.05$).

Key:
A/H = Vegetated Control
B/I = Biosurfactant (500 mg/Kg)
C/J = PAHs (60 mg/Kg)
D/K = Biosurfactant (500 mg/Kg) + PAHs (60 mg/Kg)
E/L = Biosurfactant (1000 mg/Kg)
F/M = PAHs (120 mg/Kg)
G/N = Biosurfactant (1000 mg/Kg) + PAHs (120 mg/Kg)

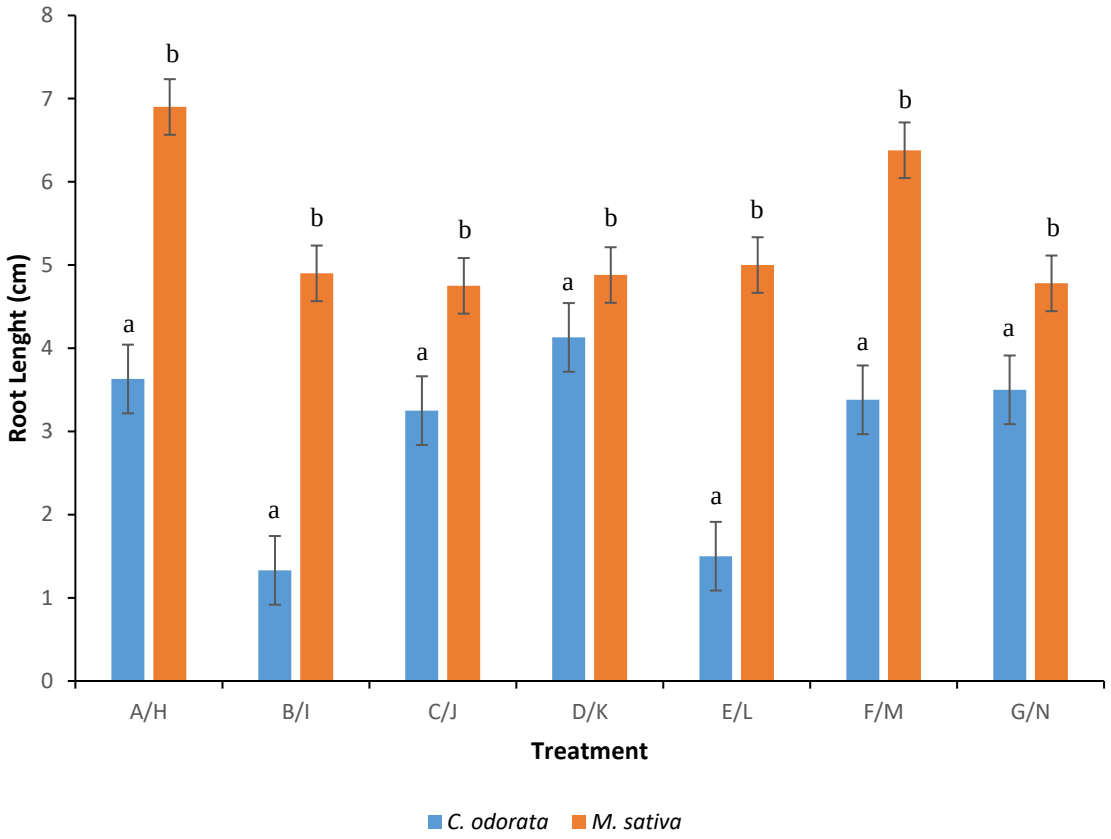


Figure 3.8: Root length of *Chromolaena odorata* and *Medicago sativa* after 8 weeks of growth. Error bars represent the standard deviation of two sampled pots. Means with different letters are significantly different ($p \leq 0.01$).

Key:
A/H = Vegetated Control
B/I = Biosurfactant (500 mg/Kg)
C/J = PAHs (60 mg/Kg)
D/K = Biosurfactant (500 mg/Kg) + PAHs (60 mg/Kg)
E/L = Biosurfactant (1000 mg/Kg)
F/M = PAHs (120 mg/Kg)
G/N = Biosurfactant (1000 mg/Kg) + PAHs (120 mg/Kg)

The significant differences in the root growth of both plants make them potential phytoremediation candidate. Plant root systems can be grouped into two main categories; tap root as seen in *M. sativa* and fibrous root systems as seen *C. odorata* (Holm *et al*., 1977 and Henderson, 2001). Tap root systems are characterized by an enlarged central root that penetrates down into the soil, with lateral roots branching off this central axis. Fibrous root systems, being finer and more profuse, offer a superior means of increasing the total rhizoplane surface area m^{-3} of soil when compared to a tap root system. The larger rhizoplane surface area of a fibrous root system would be advantageous in the establishment of an active microbial population (Aprill and Sims, 1990) and may penetrate the soil deeply. The fibrous root structure of *C. odorata* may be an added advantage over *M. sativa* despite its short root length as shown in Figure 3.8 for phytoremediation particularly in stimulating rhizosphere microorganisms to enhance degradation of PAHs. The presence of growing root systems in the soil environment can be viewed as an effective means of increasing and distributing soil organic matter throughout the soil. The proliferation of plant roots also serves as a means of distributing soil microorganisms through the soil as they are carried with growing root tips. Therefore, the probability of contact between microbes and a toxic compound is enhanced (Aprill and Sims, 1990). This was corroborated by the total mean viable count of bacteria, actinomycetes, and fungi during the plant screening as shown in Figure 3.9 and agrees with the report of Bowen and Rovira (1976) that the growth of fungi and actinomycetes are also enhanced by the presence of a root system. Both plants especially *C. odorata* had more microorganisms especially bacteria in its rhizosphere soil thriving than other treatments with or without plants. Bacteria population was the most dominant microorganism in all treatment groups with a highest mean count of $107.70\pm17.68 \times 10^3$ cfu/g dry soil in the *C. odorata* post-plant treatment group (rhizosphere soils) while the lowest was found in the pre-plant treatment group with a mean count of $49.50\pm2.12 \times 10^3$ cfu/g dry soil. The fungi population was the least dominant microorganism and was found to be almost evenly distributed between the *C. odorata* and *M. sativa* treatment groups with a total mean count range of 49.00 ± 1.41 to $66.50\pm4.95 \times 10^3$ cfu/g dry soil and 44.00 ± 5.66 to $58.50\pm2.12 \times 10^3$ cfu/g dry soil respectively (Figure 3.9). The general trend shows that there was an increased microbial activity in the post-planting period compared to the pre-planting as well as in the unvegetated treatments as shown in Figure 3.9. There was also a negligible increase in plant heights (*C. odorata* in particular) and microbial counts (bacteria especially) in biosurfactant amended treatment (500 mg/Kg).

These increases in viable count of bacteria in the plant rhizosphere especially *C. odorata* may be as a result of the direct influence of the fibrous root system. Plants supply

root exudates of carbon, energy, nutrients, enzymes and sometimes oxygen to microbial populations in the rhizosphere (Cunningham *et al*., 1996). Root exudates of sugars, alcohol and acids can amount to 10-20% of plant photosynthesis annually (Schnoor *et al*., 1995) and provide sufficient carbon and energy to support large numbers of microbes (e.g., approximately 10^8-10^9 vegetative microbes per gram of soil in the rhizosphere; Erickson *et al.*, 1995). Due to these exudates, microbial populations and activities are 5 to 100 times greater in the rhizosphere than in bulk soil (i.e., soil not in contact with plant roots) (Atlas and Bartha, 1998; Gunther *et al*., 1996). This plant-induced enhancement of the microbial population is referred to as the rhizosphere effect (Atlas and Bartha. 1998) and is believed to result in enhanced degradation of organic containment in the rhizosphere.

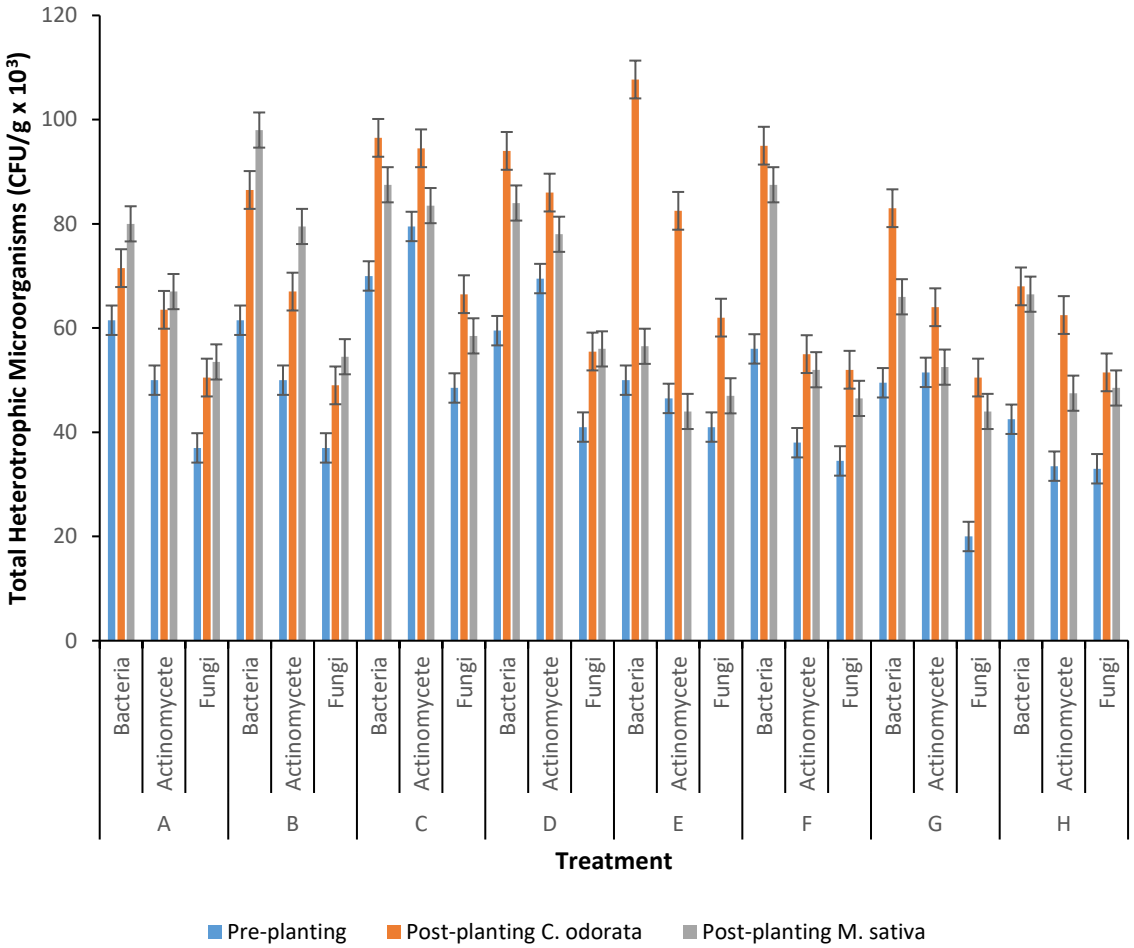


Figure 3.9: Mean total heterotrophic rhizosphere microbial groups isolated from greenhouse screened post treatment soils of *Chromolaena odorata* and *Medicago sativa* after 28 days. Error bars represent the standard deviation of two sampled pots.

Key:
A = Un-vegetated Control
B = Vegetated Control
C = Biosurfactant (500 mg/Kg)
D = PAHs (60 mg/Kg)
E = Biosurfactant (500 mg/Kg) + PAHs (60 mg/Kg)
F = Biosurfactant (1000 mg/Kg)
G = PAHs (120 mg/Kg)
H = Biosurfactant (1000 mg/Kg) + PAHs (120 mg/Kg

Biosurfactant amended soil treatments significantly enhanced the uptake of all the PAH mixtures by both plants with the most effective being 500 mg/kg biosurfactant codified PAHs treatment (Table 3) as shown in Figure 3.10. PAHs were reduced in *C. odorata* biosurfactant amended treatment soils with statistical significant reduction mean of 1.17±0.79 mg/kg compared to un-amended *C. odorata* counterparts with a mean of 6.97±3.96 mg/kg (Appendix

v) with some evidence against H_o which was rejected in favour to the H_1 stating that ***'there was a genuine difference in phytoremediation between biosurfactant-amended and un-amended treatments in PAHs reduction of contaminated soil'*** which answered the research second hypothesis. There was also a statistical significant PAHs reduction in *M. sativa* biosurfactant amended treatments with a mean reduction of 0.78±0.37 mg/kg in contrast to a mean of 7.58±4.87 mg/kg un-amended *M. sativa* treatments with some evidence of genuine reduction against H_o which was subsequently reject for the H_1 stating ***'there was a genuine difference in phytoremediation between biosurfactant-amended and un-amended treatments in PAHs reduction of contaminated soil'*** (see Section 1.7.1) (i.e. samples do not come from populations with mean) ($p \leq 0.01$) as shown in Figure 3.11 (Appendix vi). Biosurfactant also seems to have reduced PAHs in un-vegetated amended control with 28.2±7.12 than its un-amended counterpart with 19.2±9.49 but with no significant difference as shown in Figures 3.10 and 3.11 respectively (Appendix vii). However, there was a significant difference between the un-vegetated control group, *C. odorata* and *M. sativa* (the vegetated treatment groups) (see Table 13) with a very strong evidence against the H_o which states that there is no significant difference in the three groups with or without biosurfactant amendment (i.e. all samples come from populations with the same mean, $\mu_1 = \mu_2 = \mu_3$). The H_1 was accepted as the H_o could not be retained i.e. all samples do not come from population with the same means $\mu_1 \neq \mu_2 = \mu_3$ with a *p*-value of 0.00 (Appendix viii) as shown in Figure 3.12 using a Turkey simultaneous 95% confidence interval where *M. sativa* and *C. odorata* do not contain zero meaning their corresponding means are significantly different from the unvegetated control which contained zero. But in terms of phytoremediation potentials, the reference plant, *M. sativa* (Alfalfa) was not better than the fibrous root indigenous plant, *C. odorata* as there was no significant difference between them. This demonstrates that both plants especially *C. odorata* enhanced with biosurfactant were responsible for the significant reduction of PAHs in the bench top study. Consequently, *C. odorata* was preferred to the non-indigenous plant, *M. sativa* in this study. The general attributes of *C. odorata* as a ubiquitous species with the ability to proliferate in different soil types across Nigeria especially in the Niger Delta region (Uyi *et al.*, 2014) (see Figure 6 in appendix 0), makes the findings from this study applicable across Nigeria. Although, this study did not aim or attempt to measure the variability of *C. odorata* in the sense of describing its phenotypic variation which is stated as one of the limitations of this work (see Chapter 7). *C. odorata*, however, was used as a model plant and any attempt to generalise the behaviour of the model plant species to the full range of the natural species variation would not be possible without the aforementioned field survey. It is therefore acknowledged that this is

an aspect of knowledge that the thesis (purposefully) did not address but would be of great interest should a wide scale use of the plant species be implemented in future remediation efforts.

In general, according to US EPA (2000b) and Hutchinson (2003) uptake of hydrocarbons into plants, although possible, is not expected in great quantities given the compounds' chemical properties, including high molecular weights, relatively low solubilities in water, and hydrophobic nature. The use of biosurfactants to enhance the apparent aqueous solubility and bioavailability of organic compounds such as PAHs in soil had been reported. The above result shows that rhamnolipid biosurfactants have the potential for enhancing phytoremediation of PAHs contaminated soil through desorption or biodegradation processes.

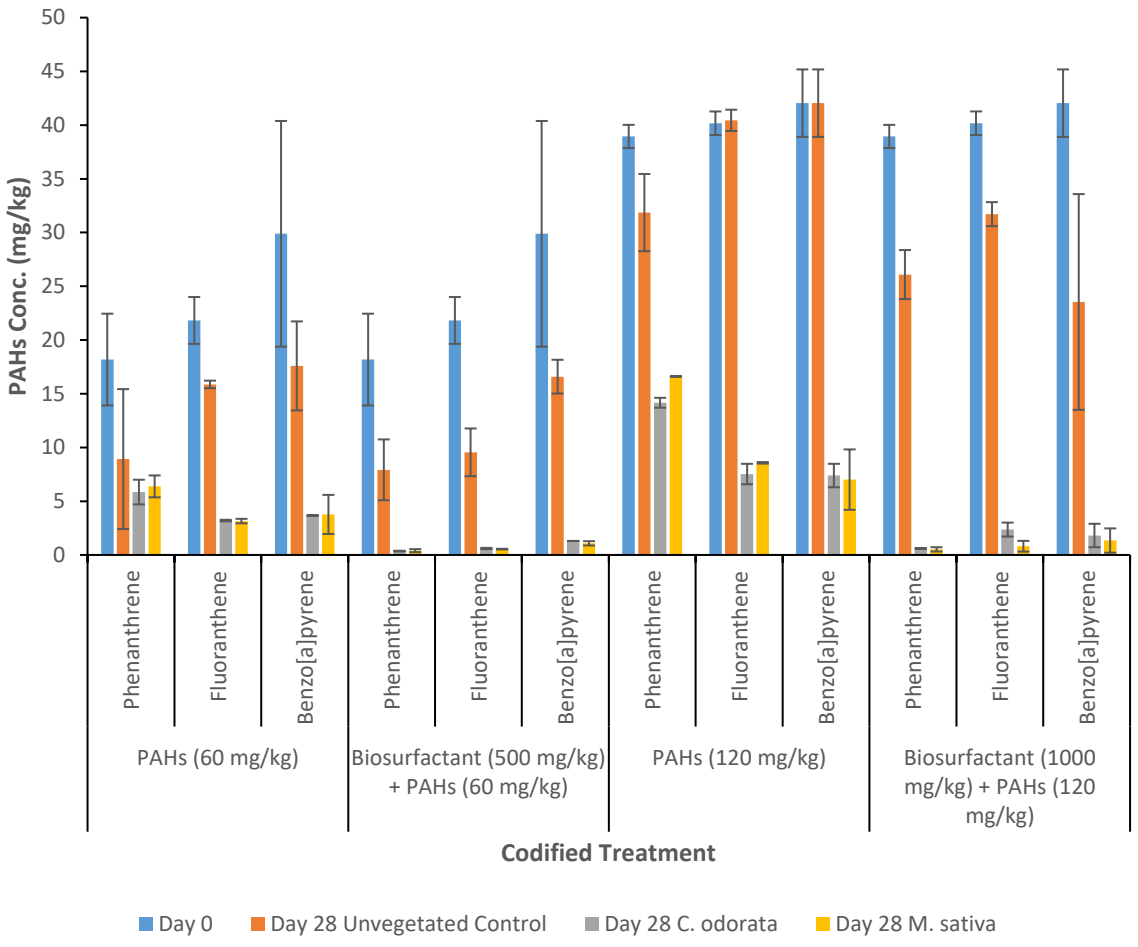


Figure 3.10: Mean concentrations of PAH mixtures in screened soil treatments of un-vegetated soil control, *Chromolaena odorata* and *Medicago sativa* after 28 days. Error bars represent the standard deviation of two sampled pots.

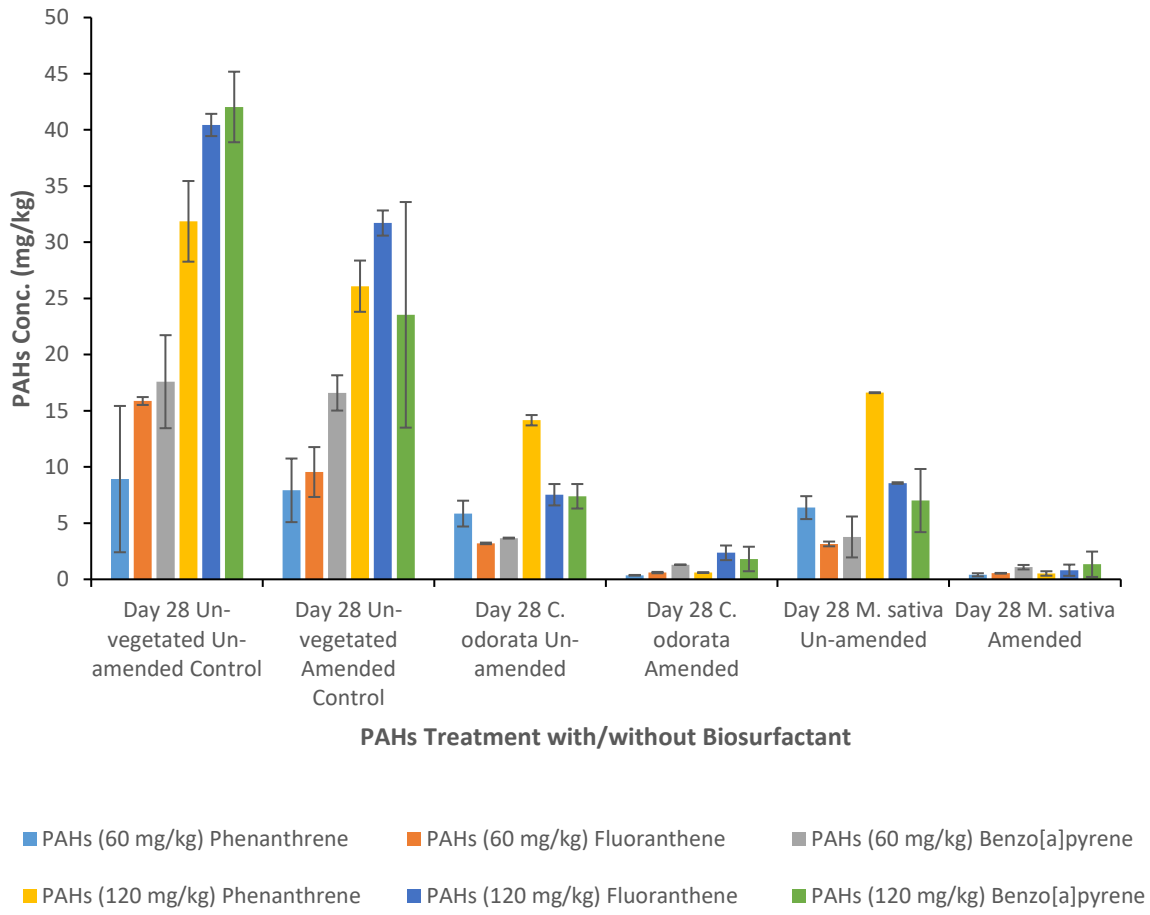


Figure 3.11: Effect of Biosurfactant on PAH mixtures reduction in screened soil treatments of *Chromolaena odorata* and *Medicago sativa* after 28 days. Error bars represent the standard deviation of two sampled pots.

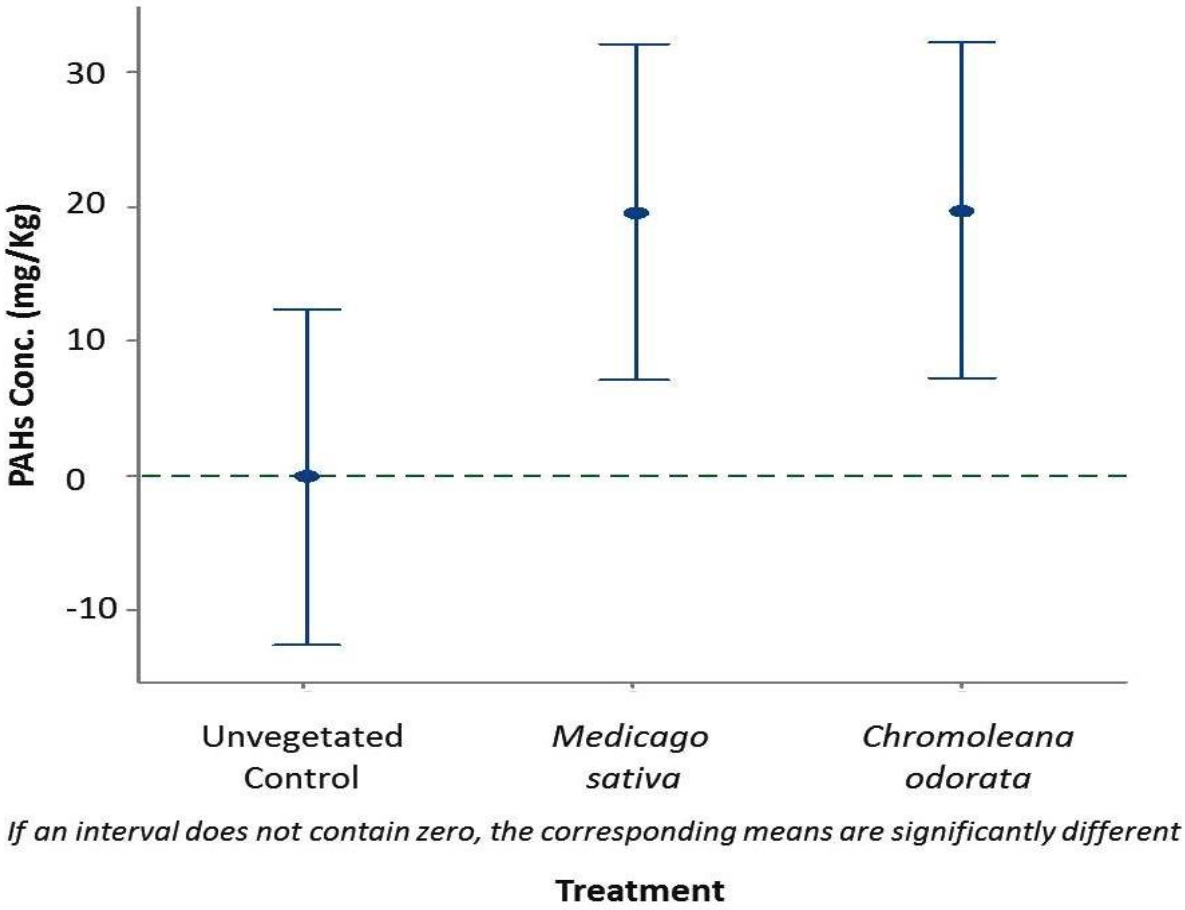


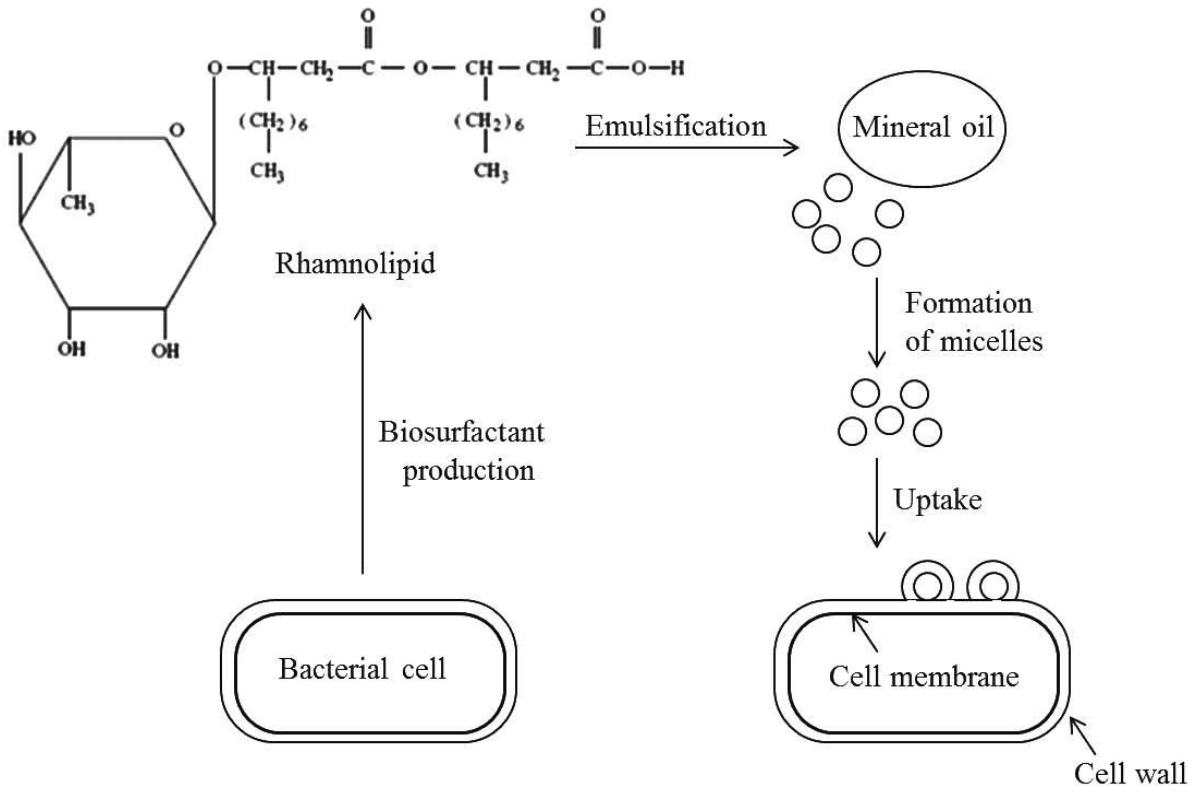
Figure 3.12: Tukey simultaneous 95% Confidence Interval plot comparing treatment differences of Day 0 & 28 of Un-vegetated control, *M. sativa* and *C. odorata* with 9.16, 27.7 and 27.8 mg/kg means respectively.

Both plants might have reduced the mass of PAHs in their respective soils through indirect degradation as numerous researchers have established that the primary mechanism for the disappearance of both petroleum hydrocarbons and PAHs is rhizodegradation (USEPA, 2000b; Hutchinson, 2003) as many times more microorganisms are generally found in the plant rhizosphere than in unplanted soil, which suggests that hydrocarbon degradation could be enhanced by the presence of vegetation (Hutchinson, 2003). There is some indication that the presence of hydrocarbons may even encourage the proliferation of hydrocarbon-degrading microorganisms (Hutchinson, 2003).

Although the biodegradation of both petroleum hydrocarbons and PAHs can proceed under either aerobic or anaerobic conditions, the degradation rates will be faster in the presence of oxygen. The presence of plants can help with oxygen availability either by transporting oxygen or by creating void spaces in the subsurface that allow for greater oxygen diffusion from the atmosphere (Tsao, 2003).

Similarly, while low-molecular-weight PAHs are known to biodegrade under aerobic conditions, larger PAHs tend to be less amenable to biodegradation, making them more persistent in soil and groundwater (Olson, 2003). Some researchers also believe that high-molecular-weight PAHs can degrade only co-metabolically, that is, when lower-molecular-weight PAHs are present and can induce the production of enzymes required for PAH degradation (McCutcheon and Schnoor 2003; Olson, 2003), which would become less likely as smaller PAHs degrade and are no longer present to participate in the co-metabolic process. The persistence of larger (three rings or more) PAHs is also of concern because they may be more toxic or carcinogenic (Olson, 2003) than the lighter PAHs.

According to Nikolopoulou and Kalogerakis (2009) biosurfactants increase the oil surface area and that amount of oil is actually available for bacteria to utilize it. Biosurfactants can act as emulsifying agents by decreasing the surface tension and forming micelles. The microdroplets encapsulated in the hydrophobic microbial cell surface are taken inside and degraded as shown in Figure 3.13 which demonstrates the involvement of rhamnolipid biosurfactant and the mechanism of formation of micelles in the uptake of hydrocarbons (Fritsche and M. Hofrichter, 2000).



Source: Das and Chandran (2011)

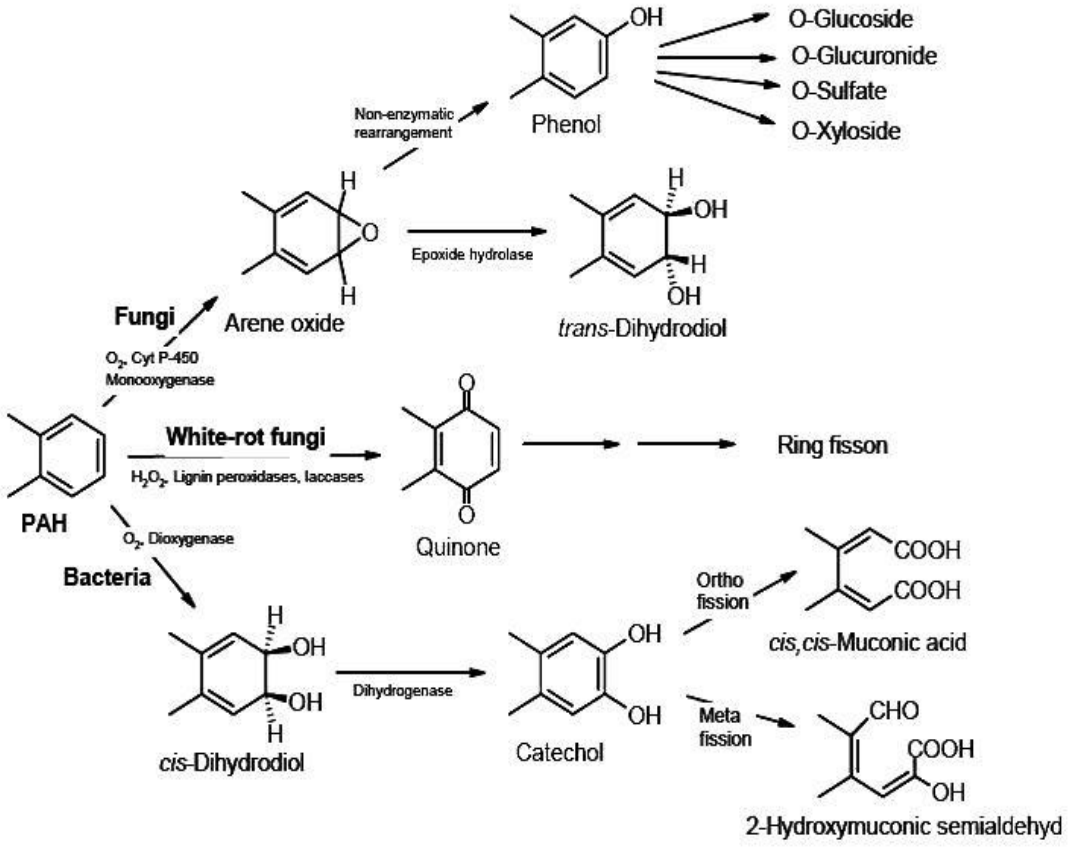
Figure 3.13: Rhamnolipid biosurfactant involvement in the uptake of hydrocarbons e.g. PAHs

The rhamnolipid biosurfactants seem to enhance phytodegradation and biodegradation by influencing the bioavailability of the PAHs mixtures in all the amended treatment soils. This report is consistent with Smith (2005) that rhamnolipids released by some bacteria make hydrophobic substances more water soluble and that organic pollutants can be directly degraded by root-released plant enzymes or indirectly by phytostimulation of microbial degradation in rhizosphere of both PAHs, and petroleum hydrocarbons. Keck *et al.* (1989) and Cunningham *et al.* (1993) reported that diesel compounds may act both as carbon sources and co-metabolites (i.e. compounds that do not support microbial growth on their own but can be modified or degraded when another growth-supporting substrate is present) and Kanaly *et al.* (2000) observed that the mineralization of [^{14}C] B[a]P in soil was 40% after 100 day incubation period with 0.2 (wt/wt) diesel fuels. According to Chaudhry *et al.* (2005), the removal rate of aliphatic hydrocarbons in the presence of ryegrass (*Lolium perenne*) was higher and was associated with an increase in microbial numbers and activities in the rhizosphere as compared to the non-planted treatment.

Frick *et al.* (1999) reported that a vast number of bacteria, fungi and algae are able to metabolize PAHs. The biochemical pathways of benzo[a]pyrene, naphthalene, phenanthrene, anthracene and acenaphthene by microbial degradation have been shown and elucidated (Cerniglia, 1992). According to Robert (1998), bacteria generally use the PAHs as a carbon and energy source and play a role in the first step of aerobic catabolism of a PAH molecular via oxidation of the PAH by dihydroxylation with the company of a multi-component enzyme system. The dihydroxylated intermediates are processed by either an *ortho* or a *meta* cleavage type of pathway, coming to central intermediates e.g., protocatechuates and catechols. Those compounds are further changed to tricarboxylic acid cycle intermediates. Microorganisms also use dioxygenase enzymes to incorporate both atoms of molecular oxygen into the aromatic nucleus to form *cis*-dihydrodiols, then these forms are stereoselectively dehydrogenated by *cis*-dihydrodiol dehydrogenases, which rearomatize the benzene nucleus to form dihydroxylated intermediates (Cerniglia, 1992). Besides, the need of methane monooxygenases and lignin peroxidases is also important in the processes of PAH catabolism.

Filamentous fungi can also prelude to detoxificate PAHs by a process of hydroxylation. They also mono-oxygenate PAH molecules by using the multifunctional oxidase (MFO) system whose membrane-bound variant includes cytochrome P-450, NADPA-cytochrome P-450 reductase and the phospholipid of endoplasmic reticulum membrane of the eukaryotic cell. Then phenols that may be transformed to the less toxic and more water-soluble, O-glucoside, -glucuronide, sulphate, -xyloside, and –methyl conjugates by transferases will be formed from

the result of disproportionation of arene oxides. They may also be metabolized to trans-dihydrodiols by fungal epoxide hydrolase in the presence of H_2O (Roberts, 1998). However, to achieve success of bioremediation technology for the decontamination of PAH contaminated sites, we need to know and understand more about the microorganisms, enzymatic processes and the environmental conditions to optimize the degradation of PAH contaminants (Cerniglia, 1992). The pathways for microbial catabolism of PAHs are expressed in Figure 3.14.



Source: Bamforth and Singleton (2005).

Figure 3.14: General pathways for the microbial degradation of polycyclic aromatic hydrocarbons (PAHs).

3.4 CONCLUSION

The preliminary investigation in Chapter 3 revealed thriving perennial shrub identified as *Chromolaena odorata* on most of the Niger Delta contaminated lands. Physico-chemical parameters of the different soils were determined and classified as Sandy clay and Clay loam with slightly acidic pH 4.95 and neutral pH 7.14 for Niger Delta contaminated soil and Sonning Farm soil respectively. Due to the low background PAHs from the contaminated soil sample (0.08 to 11.30 mg/kg), a baseline study of 60 mg/kg and 120 mg/kg of PAHs mixtures (phenanthrene, fluoranthene and benzo[a]pyrene) were used from literature for plant screening. A pilot study showed that the indigenous *C. odorata* showed a more thriving and tolerant nature in PAHs contaminated soil in almost all parameters measured compared to *M. sativa* which is a proven and well-established phytoremediation plant during the plant screening. PAHs were drastically reduced especially in biosurfactant amended treatment soils of both plants. There were significant reductions with means of 1.17±0.79 and 0.78±0.37 amended treatments against means of 6.97±3.96 and 7.58±4.87 un-amended treatments of *C. odorata* and *M. sativa* respectively suggesting '*there was a genuine difference in phytoremediation between biosurfactant-amended and un-amended treatments in PAHs reduction of contaminated soil.'* However, no difference in phytoremediation potential was observed in both plants with or without biosurfactant. The fibrous root structure of *C. odorata* may be an added advantage over *M. sativa* despite its short root length for phytoremediation particularly in stimulating rhizosphere microorganisms to enhance degradation of PAHs and as such *C. odorata* was preferred to the non-indigenous plant, *M. sativa* in this study coupled with the fact that native plant is ecologically safer, cheaper, aesthetically pleasing, socially acceptable and easier to cultivate. The total means viable count of bacteria, actinomycetes, and fungi from pre- and post-planting treatment soils showed that there was an increased microbial activity in the post-planting period compared to the pre-planting period. Results of this pilot study also indicated the need to further investigate the role and mechanisms of plants in the ability to extend PAH disappearance in soil systems via different possible mechanisms such as increased microbial interaction with PAH mixtures due to rhizosphere effects.

Chapter 4

A Novel Technology of Solarization and Phytoremediation enhanced with Biosurfactant for Sustainable Treatment of weathered PAH-Contaminated Soil

4.0 A Novel Technology of Solarization and Phytoremediation enhanced with Biosurfactant for Sustainable Treatment of weathered PAH-Contaminated Soil.

4.1 INTRODUCTION

Anthropogenic environmental pollution with persistent organic pollutants such as PAHs is well documented (see Chapter two). These recalcitrant compounds persist in soil and are ubiquitous in the environment throughout the world. Their effects and fate in nature are of considerable concern to both the environment and public health owing to their widespread occurrence, persistence in terrestrial ecosystems, and suspected carcinogenic and mutagenic properties (Sung *et al.*, 2002; Gao *et al.*, 2006a; Gao *et al.*, 2007). Various remediation approaches have been introduced during the last 30 years to remediate PAHs-contaminated soils, including physical, chemical, and biological methods. Physical methods such as soil washing with solvents to remove contaminants is relatively fast but it consumes energy and is highly expensive while chemical oxidation have a significant influence on soil physical, chemical and biological properties (Chen *et al.* 2009). Phytoremediation including microbial remediation provide an alternative approach to treat contaminated soils. However, their efficiency in aged PAHs-contaminated soils is often limited due to the residual components of PAHs in aged soil such as their water insolubility and high adsorption to soil particles which limits biodegradation (Johnson *et al.* 2002; Leonardi *et al.* 2007; Hwang and Cutright, 2002). The use of surfactant facilitates the desorption and bioavailability of PAHs, thereby enhancing their biodegradation especially in aged PAHs soil. Rhamnolipid biosurfactants due to its environmental compatibility has attracted more attention than its chemical counterparts. Numerous studies have successfully shown the treatment of aged PAHs-contaminated soil using phytoremediation enhanced with biosurfactant. Jing *et al.* (2010) reported the improvement of phytoremediation efficiency of PAHs using rhamnolipid biosurfactant that increased the bioavailability of PAHs in soils. Liduino *et al.* (2018) evaluated the use of commercially available rhamnolipid biosurfactant in phytoremediation enhancement using sunflower (*Helianthus annuus)* for 90 days and reported 48 % reduction in PAH concentration. Liao *et al.* (2016) investigated the use of rhamnolipid biosurfactant in facilitating phytoremediation of crude oil contaminated soil by maize (*Zea mays*) and reported enhanced soil microbial population, increased removal of total petroleum hydrocarbons from soil and enhanced accumulation of PAHs in maize root. Surfactants have been reported to improve pollutants solubility in the aqueous phase and consequently enhanced bioavailability of

hydrophobic organic compounds in soil (Calvo *et al*., 2009; Zhu and Aitken, 2010). Others have shown the ability of environmentally friendly biosurfactant to effectively solubilize and mobilize organic compounds adsorbed on soil particle (Mulligan, 2005; Whang *et al*., 2008) in addition to remediation of petroleum hydrocarbon-contaminated soil by various surfactants (Lai *et al*., 2009; Zhu and Aitken, 2010; Von Lau *et al*., 2014). However, there is no study on the combined effects of phytoremediation and soil solarization enhanced with biosurfactant for contaminated soil treatment in any part of the world. Thus, the impacts of soil solarization on simulated weathered PAH removal; biosurfactant enhanced phytoremediation, soil/rhizosphere heterotrophic microorganisms and soil/rhizosphere enzymatic activities of dehydrogenase and urease were evaluated in this study (see Section 1.6).

4.2 MATERIALS AND METHODS

4.2.1 Reagents and chemicals

All reagents and chemicals used in this work were of minimum analytical grade quality and were purchased from Fisher Scientific and Sigma Aldrich, UK. Phenanthrene, fluoranthene and benzo[a]pyrene were chromatography grade while dichloromethane (DCM), acetone, hexane. ethanol were high performance liquid chromatography (HPLC) grade.

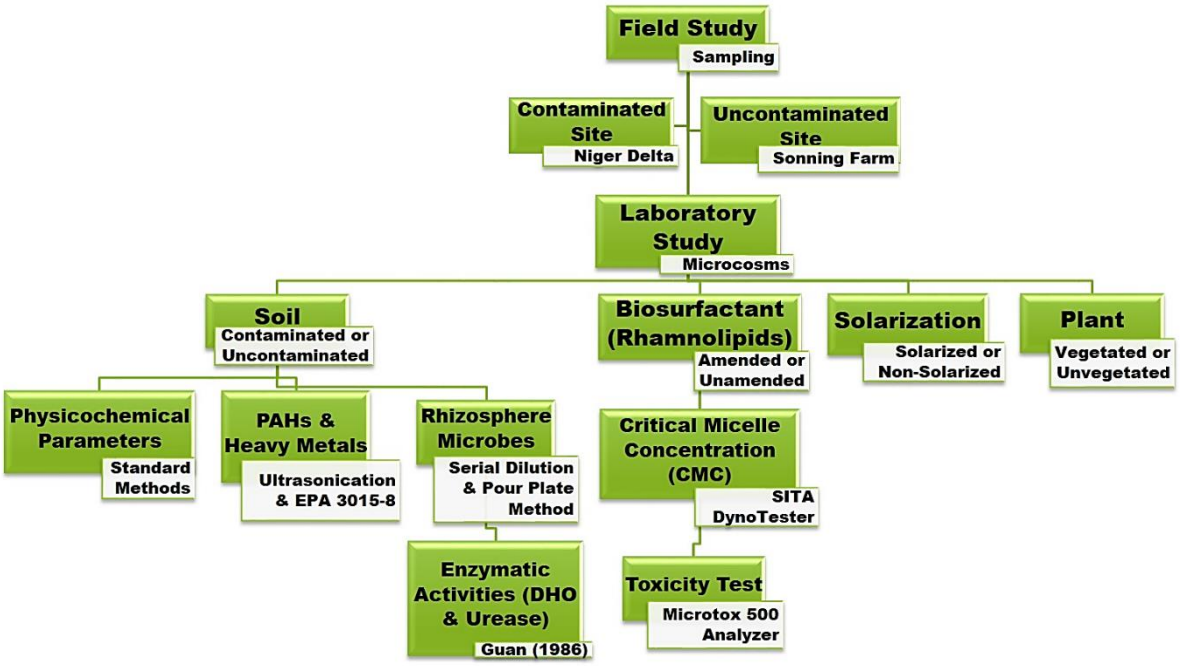


Figure 4.1: Flow chart diagram showing general overview of research methodology. The boxes in green and white highlight key methodology themes and their sub methods or conditions respectively.

4.2.2 Biosurfactant analysis

A commercially available rhamnolipid (R90 Rhamnolipid biosurfactant) with a critical micelle concentration (CMC) and half maximal effective concentration (EC_{50}) of 105 and 0. 1 g/l respectively, produced by separation and purification processes using *Pseudomonas aeruginosa* in Canola oil substrate was purchase from AGAE Technologies, USA. (see Sections 3.2.15.1-2 and 3.4.2).

4.2.3 Soil sampling

A dark yellowish brown arable soil type previously characterized by Revitt *et al* (2014) and Kay (1936) located on an alluvial plain of the River Thames with crops growing on the surface was collected from the surface to a depth of 25 cm with a spade at Sonning Farm (University of Reading, Berkshire, UK) with GPS coordinates N51'28.898 W00'53.844 (see Section 3.2.1; Figure 3.1c and Plate 1.1d). Samples were transported to a laboratory where it was thoroughly homogenized by mixing and air dried at room temperature ($28^oC \pm 2^oC$) for 6 days in other to retain the viable microorganisms before passing it through a <2 mm sieve as experimental observations have shown that it is very difficult to obtain reproducible subsamples from field moist soils if it does not homogenize easily.

4.2.4 Soil physico-chemical analysis

Soil analysis using standard methods were used to determine the following physico-chemical properties: soil texture (Thien, 1979) (see Section 3.2.4); soil pH (see Section 3.2.5); soil moisture content (Hesse, 1971) (see Section 3.2.6); soil organic matter content (Schulte and Hopkins, 1996) (see Section 3.2.7); soil nitrate (NH_3^--N) extraction (see Section 3.2.8); available P (modified procedures of Murphy and Riley, 1962; Watanabe and Olsen, 1965; Olsen and Sommers, 1982) (see Section 3.2.9); soil cation exchange capacity (CEC) using Sodium as index ion (Chapman, 1965) (see Section 3.2.10); soil background heavy metals and PAHs (see Sections 3.2.11 and 3.2.12 respectively) as shown in Table 16.

Table 16: Sonning farm soil physico-chemical properties

Parameter	Sonning Farm Soil
Classification	Clay Loam
pH	7.14 ± 0.11
Moisture Content	13.72 ± 1.24%
Organic Matter Content	2.48 ± 0.24%
NO_3^- – N	18 mg/L
Available P	0.32±0.00 mg/g
Cation Exchange Capacity (CEC)	17.8 meg/100 g
Background Heavy Metals	
Cd	BDL
Cr	0.03 ± 0.00 mg/g
Cu	0.06 ± 0.00 mg/g
Fe	9.76 ± 0.91 mg/g
Mn	0.21 ± 0.01 mg/g
Ni	0.01 ± 0.00 mg/g
Pb	0.01 ± 0.00 mg/g
Zn	0.02 ± 0.00 mg/g
Background PAHs	
naphtalene	BDL
acenaphtalene	BDL
acenaphtene	BDL
Fluorine	BDL
phenantrene	BDL
anthracene	BDL
fluoranthene	BDL
Pyrene	BDL
benzo[a]pyrene	BDL

Key:
BDL = Below Detection Limit (see Section 4.2.7.2)

4.2.5 Contaminated soil weathering procedure

Sonning farm soil was used due to the difficulty in bringing in contaminated soil from the Niger Delta region into the UK and considering the fact that most contaminated soils in the region are agricultural soils with similar properties with the Sonning farm soil prior to contamination. However, the artificially PAHs contaminated Sonning farm soil was oven treated at 30^{o}C for 14 days in other to simulate the effect of exposure of contaminated land (modified from Urum *et al.,* 2004) in the region's subtropical environmental conditions for a period of time such as during oil spill incidents or for cases when aged crude oil contaminated land needs remediation which is typical of the Niger Delta.

4.2.5.1 Experimental design

In this study, *Chromolaena odorata*-a plant commonly found in Nigeria was collected with its seeds from a contaminated site at Bomu Manifold, K-Dere, Gokana Local Government Area (Ogoniland), River State, Nigeria (see Section 3.2.2 and Plate 1.1(a-c)). Air dried soil from Sonning farm was artificially contaminated with a mixture of PAHs (phenanthrene, fluoranthene and benzo[a]pyrene) (see Section 1.3 and Figure 1.1). A partial spiking protocol according to Jacobsen *et al.* (2002) was employed. A total of 240 mg (80 mg each) of PAHs were dissolved in 25 ml of acetone and were used to spike a 25% fraction (250 g) of the soil sample and the flask was closed for 5 min to let the solvent disperse. The solvent was evaporated overnight and the remaining 75% (750 g) of the soil subsample was mixed thoroughly and amended with 16.7% (dry weight) of air dried screened (< 2 mm) commercially prepared compost. The amended compost soil mixtures were thoroughly mixed and passed 3 times through a 2 mm steel gauge sieve to ensure a uniform distribution of the soil-PAHs-compost amendment. The soil-PAHs-compost amendment was randomly sampled in duplicate to test for homogeneity and a satisfactory result showed 73.35±7.11, 74.94±10.39 and 78.44±0.93 mg/kg for spiked 80 mg/kg each of phenanthrene, fluoranthene and benzo[a]pyrene respectively. The experimental design as shown in Table 17 was further treated with or without a commercially synthesize rhamnolipid biosurfactant (500 mg/kg) with a critical micelle concentration (CMC) and half maximal effective concentration (EC_{50}) of 105 g/l and 0.1g/l respectively.

Table 17: Experimental design of treatment groups.

	Vegetated Treatment Group with *C. odorata* (240mg/kg PAHs) (*n*=4)			
Sample	Solarized and Amended	Solarized and Un-amended	Non-solarized and Amended	Non-solarized and Un-amended
A	+	-	-	-
B	-	+	-	-
C	-	-	+	-
D	-	-	-	+
	Un-vegetated Treatment Group (Control) (240mg/kg PAHs) (*n*=2)			
E	+	-	-	-
F	-	+	-	-
G	-	-	+	-
H	-	-	-	+

Key:
+ = Presence of treatment
- = Absence of treatment

4.2.6 Microcosm design and rationale

A microcosm was designed to simulate the subtropical conditions with rainfall and sunshine that contaminated land are subjected to in the Niger Delta region. The region is characterized by a humid tropical climate with high rainfall and warm temperatures. There are two seasons, wet season from April to October and dry season, November to March with yearly mean minimum and maximum temperatures of 22.5 and 31.0^{o}C respectively, mean rainfall of over 2000 mm per year, relative humidity of over 90 % per year and a mean monthly and yearly solar radiation of 10.55 and 9.25 mJm^{-2} per day respectively (Uko and Tamunobereton-Ari, 2013). A radiation balance that the contaminated land in the region receive is suggested to be as much as 8-10 mJm^{-2} per day during dry and wet seasons. Humidity all year round is about 95 to 100 % with an average range from 70 to 80 % which gets higher nearer the coast and decreases towards the interior of the delta (Niger, 2012). The microcosm was designed to accommodate plant growth, soil and leachate collection as shown in Figure 4.2. Solar radiation and visible light sources were simulated by 50W infrared and 5W LED bulbs respectively in addition to fluorescent light in line with studies that have shown that over 90 % of incoming solar radiation is formed of infrared and visible wavelength (Zhu *et al.,* 2003). The light was controlled automatically to simulate day and night and the temperature was regulated by a Biogreen Digital Thermostat. The experimental frequency was set at 24 h (day and night). Solar radiation period was 10 h (daylight) while the non-solar radiation period lasted 14 h (night). Nevertheless, light gradient was simulated during the first 3 h of the solar radiation period, the 'off' time was more than the 'on' time to simulate increase solar radiation while the reverse was the case during the last 3 h to simulate a gradually disappearing solar radiation. The light was on continually during the middle 4 h of the daylight simulation to replicate a comparable sunshine (heat level) in the region. The microcosm was watered to field capacity with artificial rainwater (0.01M of $CaCl_2$) maintaining between 80 and 100 % of the water holding capacity periodically whenever the soil dried during solarization periods and at least three times a week during growth period to compensate for loss due to transpiration. At the base of each pot in the microcosm chamber, provision was made for leachate collection. The above conditions were chosen to approximate optimal environmental/weather conditions in the Niger Delta, Nigeria.

Soil solarization was carried out with transparent polyethylene sheet for 28 days before transplanting *C. odorata* seedlings of the same age for a 84 day phytoremediation period (Plate 1.5(a and c)). Soil temperatures were measured thrice a week at 1 and 4 cm depths respectively by piercing the soil with mercury in glass thermometer (Plate 1.5b). Vegetative and their un-

vegetative counterparts consisted of randomly arranged 4 x 4 and 2 x 4 cells microcosm design respectively (Plate 1.6(a-b)) with pots locations randomly changed thrice weekly within the same microcosm chamber. Leachates were also collected from each pot and stored in amber bottles at 4^{o}C until ready for analysis.

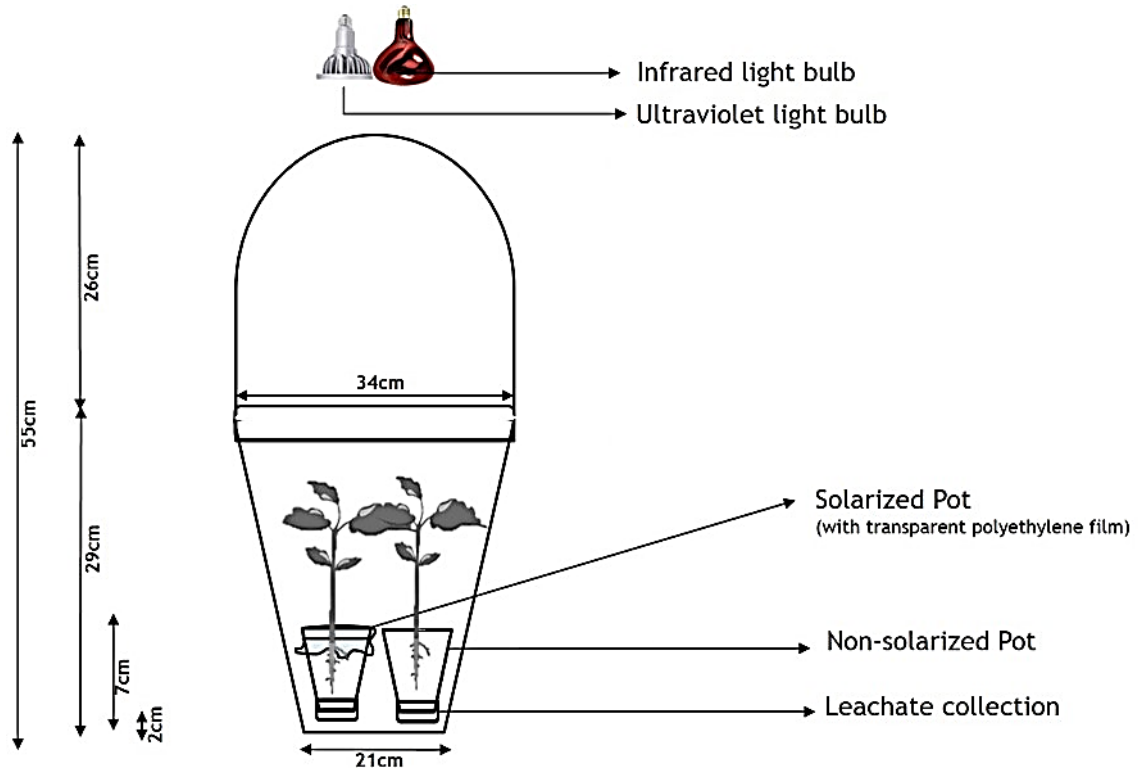
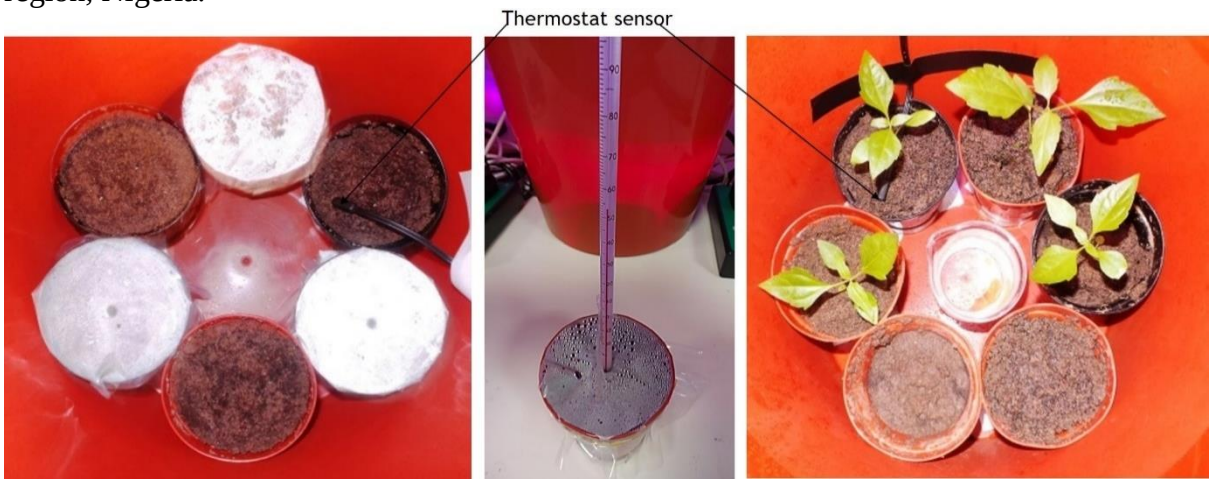


Figure 4.2: Laboratory microcosms simulating the subtropical conditions in the Niger Delta region, Nigeria.



(a) (b) (c)

Plate 1.5: (a) Treatment pots covered with transparent polyethylene sheets during 28 days solarization. (b) Piercing soil with mercury in glass thermometer for soil temperature readings at 1cm dept. (c) Transplanting of seedlings of the same aged after solarization. With vegetative and un-vegetative treatments consisting of randomly arranged 4 x 4 and 2 x 4 cells microcosm design respectively.

(a)

(b)

Plate 1.6(a-b): Laboratory microcosms experimental set up: (a) Solarization periods and (b) Post-solarization period (phytoremediation).

4.2.7 Soil PAHs extraction and analysis

An extraction of PAHs from soil samples was achieved ultrasonically using modified methods of Fan *et al.* (2008) and Song *et al.* (2006). Air-dried soil (5 g) was weighed and mixed with 25 ml of DCM and extracted for 3 successive times for 1 h sonication using the ultrasonic bath (Clifton sw30H) in which the water temperature was kept at 35ºC in other to maximize evaporative losses. The mixture was centrifuged using Eppendorf centrifuge 5702 at 2,414,880 x g for 5 min to separate the supernatant from the soil and filtered into 20 ml vials where it was stored in the refrigerator at 4ºC in preparation for clean-up and analysis. Solid phase extraction (SPE) clean-up was carried out with a 12-port vacuum manifold from SUPELCO with 1 g/6 ml ENVI^{TM}-Florisil glass cartridges. After conditioning the sorbent of the SPE cartridges, 3 ml of the supernatant was filtered through the column and was consecutively eluted with 6 ml hexane and dichloromethane mixture of 1:1. The combined eluate was completely dried under the gentle stream of nitrogen, and then re-constituted in hexane with a final volume of 2 ml for GC- FID analysis (Plate 1.7). Samples extracts (1 µl) were analyzed by a Thermo Scientific Trace 1300 Gas Chromatograph and a DB-5 capillary column (30 mm x 0.25 mm x 0.25 µm). Separation was achieved according to the following program: the initial oven temperature was 80 ºC (held time for 1 min), and increased to 275 ºC at 15ºC/min, held for 1 min: and then to 285 ºC at 10 ºC/min, held for 1 min: after that increased to 295 ºC at 5 ºC/min, held for 1 min. Helium was used as the carrier gas (1.5 ml/min) and make up gas (35 ml/min). A 1.0 µl aliquot of the extract was injected in the splitless mode. The injector was held at 250 ºC and the detector at 300 ºC.

The percentage of PAH degradation on each sampling day was determined by dividing the difference of the current PAH values with the initial PAH value, as in the following equation:

$$\text{PAH \% Removal} = \frac{PAH_0 - PAH_{SD}}{PAH_0} \times 100$$

Where PAH_0 = total polycyclic aromatic hydrocarbon on sampling day 0 and

PAH_{SD} = total polycyclic aromatic hydrocarbon on each sampling day

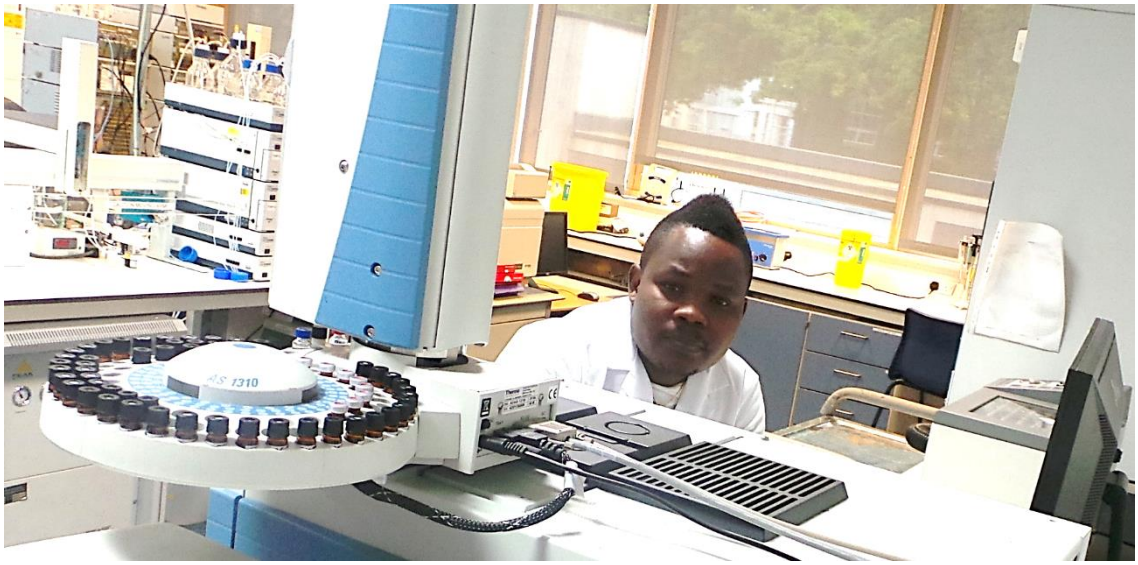


Plate 1.7: GC-FID analysis of samples using Thermo Scientific Trace 1300 GC

4.2.7.1 Leachate PAHs extraction and analysis

PAHs determination from leachate samples were subjected to a modified solvent extraction method of Jefimova *et al.* (2014). The total leachate (water) sample ~20 ml at the end of the experiment, was transferred into glass separatory funnels and shaken for 5 min with 4 ml of dichloromethane (DCM) and vent after shaken for 20 times (Plate 1.8). The DCM phase was collected into amber bottle and the extraction step was repeated twice and the solvent extracts were combined. Anhydrous Na_2SO_4 was added to remove residual water from the extracts. The samples were then evaporated under gentle stream of nitrogen flow using multi-channel evaporator at room temperature (20^{o}C). Samples were reconstituted with 2 ml of hexane into injection vial for final determination by GC-FID analysis (see Section 4.2.7. for GC-FID program).

Plate 1.8: Solvent extraction PAHs leachate in separating funnels

4.2.7.2 Quality control and quality assurance

All chemical extractions were done with two blank samples per analysis and minimum of one blank per set of samples was extracted. Samples had four replicates except otherwise stated. Standard aseptic technique was strictly followed and experiments on PAHs recovery were carried out by spiking a known concentration (1 mg/kg) of phenanthrene, fluoranthene and benzo[a]pyrene standards to uncontaminated soil. The results showed satisfactory recovery of greater than 90, 80 and 70 % respectively for phenanthrene, fluoranthene and benzo[a]pyrene with a detection limit of 0.001 mg/g of soil.

4.2.7.3 Leachate toxicity analysis

Microtox^{TM} toxicity test was carried out on leachates collected by Microtox 500 Analyzer that uses freeze-dried luminescent marine bacteria *Vibrio fischeri*. The bacterium which was constituted at about 10^8 cfu/ml suspensions was placed in a vial as control and the photometer was used to measure the florescence emitted. Nine sample dilutions were made up and put into vials with the bacterium and exposed to the test for 5 minutes and then 15 minutes intervals. The luminescence was measured with the 95% Microtox method and the toxicity was determined in terms of EC_{50} (which is the concentration of the sample that causes a 50 % decrease in the light emitted by the bacteria). The amount of light loss indicates the degree of toxicity in the leachate sample (Beckman, 1982).

4.2.8 Enumeration of soil/rhizosphere total heterotrophic microorganisms

Serial dilution and pour plate techniques were used to enumerate soil/rhizosphere total heterotrophic microorganisms. Aqueous suspension of the microbial population of 1 g rhizosphere soil sample (Plate 1.9a) was serially diluted. Pour plates of each of the serial dilution were prepared using approximately 20 ml molten Tryptic Soya Agar (TSA) for bacteria, Glycerol Yeast Extract Agar (GYEA) for actinomycetes and Sabouraud dextrose agar (SDA) for fungi respectively, mixed thoroughly by swirling and allowed to set (solidify). Three replicate pour plates and their controls for each dilution were inverted and incubated at 25^{o}C for 3 to 7 days for the isolation of bacteria, actinomycetes and fungi. Distinct bacterial, actinomycetes and fungal colonies that appeared on each Petri dish after incubation at 25^{o}C for 3 to 7 days were counted and the colony forming units per gram (cfu/g) was determined (Plate 1.9b).

Plate 1.9: (a) Rhizosphere soil attached to fibrous roots of plant and (b) Microbial colonies from a cross section of Petri dishes

4.2.9 Soil enzymatic activity

4.2.9.1 Dehydrogenase

4.2.9.1.1 Standard curve determination of Triphenyl Formazan (TF).

A standard curve was developed using solutions of triphenyl formazan (TF) and ethyl alcohol with different concentrations to determine the formazan concentration produced from the reduction of triphenyl tetrazolium chloride (TTC) using the method of Burdock *et al.* (2011). A stock solution of 0.2 µmol/ml was prepared by dissolving 0.003 g TF in 500 ml ethanol and was subsequently diluted with ethyl alcohol into TF concentrations ranging from 0.004 to 0.10 µmol/ml as shown in Plate 1.10. The corresponding absorbance of each solution was measured with a FLUOstar Omega plate reader spectrophotometer at a wavelength of 484 nm. The absorbance readings (OD_{484}) were plotted against the known concentrations of TF

(µmol/ml). A blank sample was used to zero the spectrophotometer. A linear best-fit equation (R^2 = 0.99) was obtained: OD_{484} = 4.81 TF (see Appendix ix).

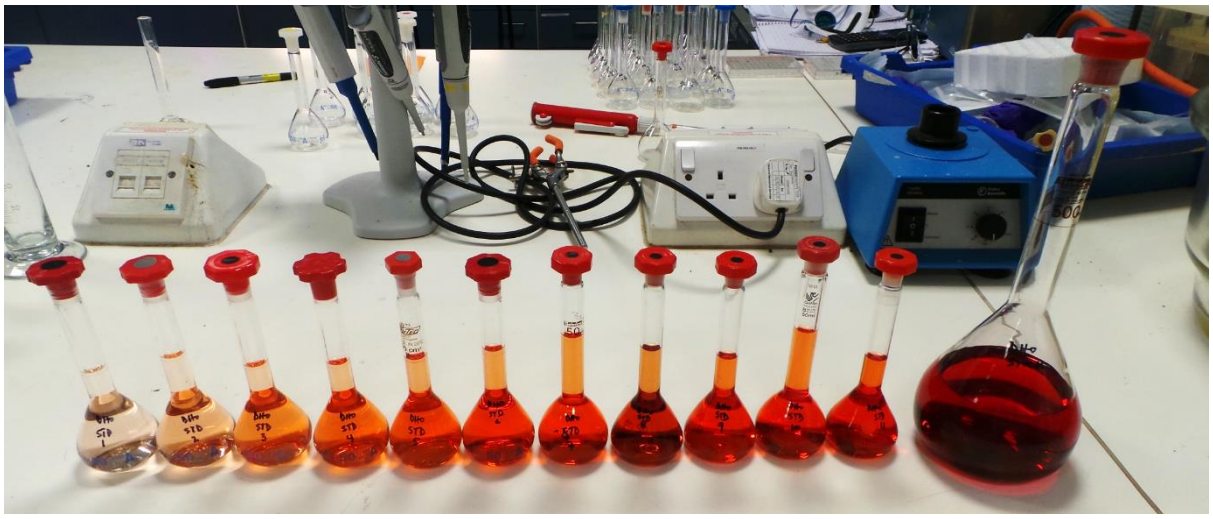


Plate 1.10 : TF solutions from stock solution in increasing concentration from left to right with the stock solution at the extreme right.

4.2.9.1.2 Dehydrogenase activity

Dehydrogenase activity was determined by monitoring the rate of reduction of 2,3,5-triphenyltetrazolium chloride (TTC) to a red, water insoluble triphenylformazan (TPF) using the protocol designed by Guan (1986). Calcium carbonate (0.03 g) and 0.5 ml of 3 % tetrazolium chloride (TTC) was added to a 3 g soil sample and the mixture was incubated at 37°C in the dark for 24 h after being mixed in the shaker. The mixture was extracted for 1 min after 5 ml of ethanol was added. Next, the solution was filtered into a 50-ml volumetric flask using glass funnels, which was plugged with adsorbent cotton at the bottom of the funnels. The soils in the tubes were washed out into the funnels using ethnol until no red colour remains on the adsorbent cotton in the funnels. The samples were then measured colorimetrically using a FLUOstar Omega plate reader spectrophotometer at 484 nm after being diluted to 50 ml using ethyl alcohol. Assays without calcium carbonate and without TTC were performed at the same time as controls. Soil dehydrogenase activity was determined by extrapolated values obtained against the standard calibration curve of TF (Appendix ix) and reported as the µg TPF/g dry soil/24/24 h.

4.2.9.2 Urease

4.2.9.2.1 Standard curve determination using Indophenol blue method.

A stock ammonium solution was prepared by dissolving 3.819 g of anhydrous ammonium chloride in 1000 ml of distilled water which is equivalent to 1000 mg NH_4-N/L. A 25 ml sample of standard ammonium solution was transferred into a 100 ml conical flask to which 1 ml of phenol solution, 1 ml of sodium nitroprusside solution and 2.5 ml of oxidizing solution were added with constant mixing. The sample was then covered with Para film and the colour was left to develop for 1 hour. A blue colour was developed ranging from dark to pale blue. The absorbance was measured at 640 nm using a FLUOstar Omega plate reader spectrophotometer. A series of five standard solutions was prepared covering concentrations of 0.01, 0.02, 0.03, 0.04 and 0.05 mg NH_4-N/ml (Plate 1.11) and were used to prepare a calibration graph (Appendix ix). The blank which was made up of distilled water was also treated as the standard. The following linear best-fit equation (R^2 = 0.97) was obtained: OD_{578} = 5.4909 NH_4-N (see Appendix ix).

Plate 1.11 : A series of five standard solutions from Indophenol blue colour method in increasing concentration from left to right.

4.2.9.2.2 Urease activity

Urease activity was determined following the method of Guan (1986) and Yang *et al.* (2007). Briefly, 5 g of air-dried soil sample was allowed to mix with 1 ml of toluene for 15 min. Then, 10 ml of 10 % urea was added to the soil followed by 20 ml of pH 6.7 citrate buffer and mixed evenly before incubating at 37 °C for 24 h. After incubation, samples were diluted with 37^{o}C distilled water and oscillated thoroughly before being filtered immediately. 3 ml filtrate was transferred into a 50 ml volumetric flask, to which 10 ml of distilled water, 4 ml of sodium phenate (1.35 M) and 3 ml sodium hypochlorite (active chlorine 0.9 %) were added. The flask was left for 20 min and then diluted to volume. The concentration of NH_4^+ ions produced from urea hydrolysis was measured calorimetrically as the blue coloured complex of urease activity and was calculated by a reference-calibrated curve determined by Indophenol Blue Method at 578 nm (Appendix ix). A control without urea was prepared with each sample. A unit of urease activity was defined as the quantity of NH_4-N produced by 1.0 g of air-dried soil at 37^{o}C/h.

4.2.10 Plant analysis

C. odorata were harvested after 84 days due to some of the plant outgrowing the microcosm chambers as shown in Plate 1.12. At harvesting time, pots were carefully removed from the *C. odorata* with the soil firmly attached to the fibrous roots of the plants (see Plate 1.9a) before separating roots and shoots. Roots were washed with DI water to remove soil particles and blotted dry with paper towel as shown in Plate 1.13. Root length from the base of the stem to the longest root tip of plant was measured. The plant material was oven dried at 70^{o}C over night (Campbell and Plank, 1998) and dry weights of shoots and roots recorded. Soil was simultaneously sampled also and kept at 4^{o}C until further analyses. Rhizosphere soil samples for vegetated pots were taken by vigorously shaking the plant roots by hand with extreme care to keep the roots intact. Soil unattached to the roots were removed while the soil closest to the roots was used for analyses including rhizosphere microorganisms and soil enzymatic activities.

Plate 1.12: Some plants in the solarized treatment had outgrown the microcosm chambers causing irritation at the tip of the shoots

Plate 1.13: A cross section of plant root length from the base of the stem to the longest root tip.

4.2.11 Statistical analysis

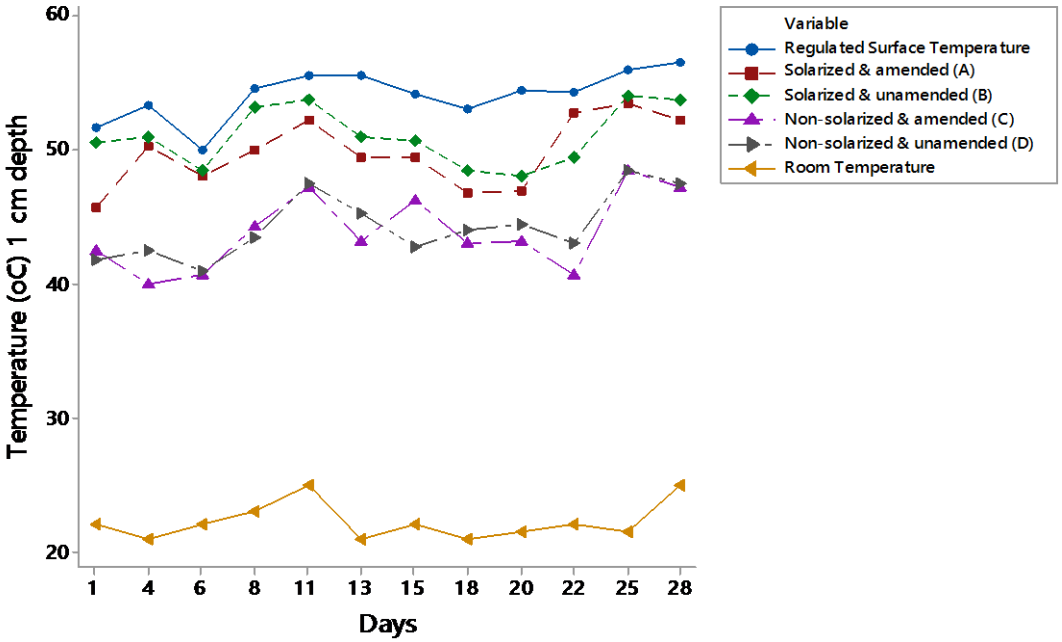
The experimental results were statistically analysed using Minitab®18 statistical software and all results were deemed significant at 95 % confidence level ($p \leq 0.05$). All treatments had four and two replicates for vegetated and un-vegetated groups respectively except where it was otherwise stated and are reported as mean ± standard deviation (SD). Differences between samples were analysed with either two sample t-tests or analysis of variance (ANOVA) with post-hoc analyses using Tukey Pairwise Comparisons with Bonferroni correction for Type 1 error inflation. Data were screened for homogeneity of variance and normality assumptions using Bonnet's variances test and Anderson-Darling normality tests respectively. Relatioships between dependent variables (% PAHs removal efficiency, plant growth parameters, total heterogeneous microorganisms and soil enzymatic activity) and the treatment independent variables (solarization, biosurfactant and/or vegetation) with time as a covariant were analysed using the general linear model (GLM) procedure. GLM predicts how the dependant or responses variables vary in response to the predictor variables. The model assumes that the variation of the dependent variable is equal to a linear combination of the explanatory variables (Akpan *et al.*, 2016; Moffat and Akpan, 2018).

4.3 RESULTS AND DISCUSSION

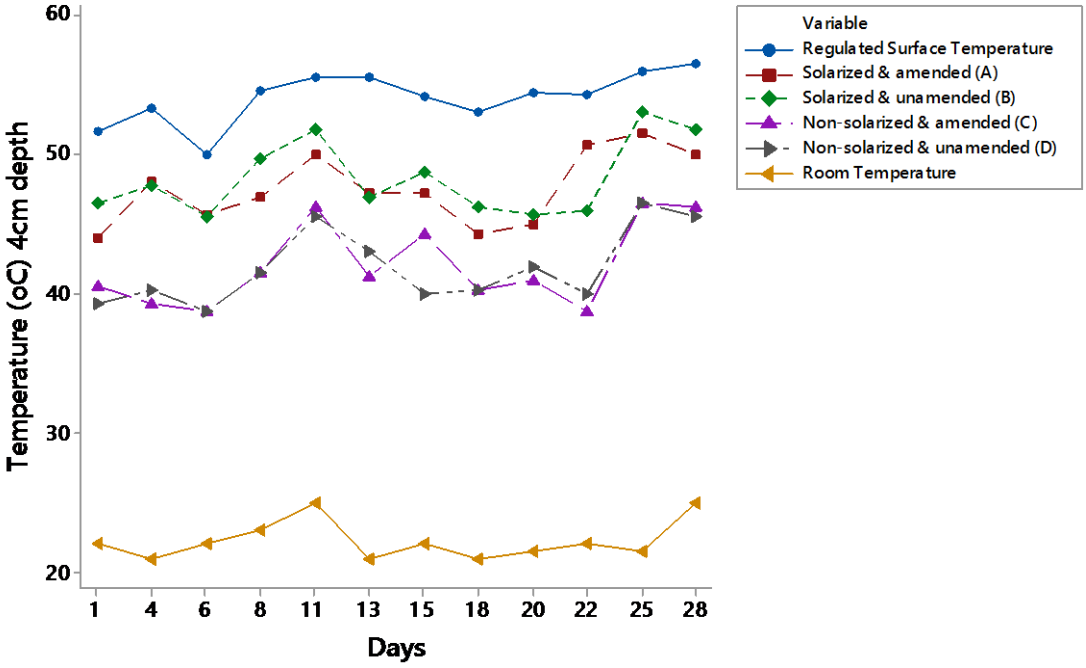
4.3.1 Soil properties and solarization effect on soil temperatures

Sonning Farm soil is an arable soil belonging to the Rowland Series with a longterm historical record of soil types and has been classified by Kay *et al.* (1936). Classification of the soil as Clay loam with neutral pH 7.14 agrees with a reported pH of 7.22 by Revitt *et al.* (2015) (see Section 3.4.1). The soil temperature results obtained with the microcosm during soil solarization by covering it with or without transparent polyethylene sheet for over 28 days (4 weeks) indicated successful simulations especially with solarized treatment. The soil temperature means for pre-vegetated solarized and biosurfactant-amended treatment (A); solarized and un-amended treatment (B); non-solarized and biosurfactant-amended treatment (C); and non-solarized and un-amended treatment (D) were 49.8, 51.0, 44.3 and 43.9^{o}C respectively at 1 cm depth and 48.3, 47.6, 42.0 and 41.9^{o}C respectively at 4 cm depth as shown in Figure 4.3(a-b) (the time series plots) and Figure 4.5(a-b) (box plots). While their un-vegetated counterparts have soil temperature means for solarized and biosurfactant-amended treatment (E); solarized and un-amended treatment (F); non-solarized and biosurfactant-amended treatment (G); and non-solarized and un-amended treatment (H) were 50.3, 49.9, 44.2 and 42.3^{o}C respectively at 1 cm depth and 48.1, 47.8, 41.9 and 40.3^{o}C respectively at 4 cm depth with mean room and regulated surface temperatures of 22.3 and 54.5^{o}C respectively as shown in Figure 4.4(a-b) (the time series plots) and Figure 4.5(a-b) (box plots). Statistically, there was a significant difference ($p \leq 0.01$) with very strong evidence against the H_0 (Appendix x(a)). This shows that the transparent polyethylene sheets were able to solarize their respective treated soils successfully from their non-polyethylene sheet counterparts at various depths despite being in the same microcosm chambers. The temperature ranges reported by various researchers especially Emoghene and Futughe (2011) who worked on *Amaranthus viridis* plants grown on solarized and un-solarized plots in the Niger Delta region is in agreement with this study. Novarro *et al.* (1992) also reported similar temperatures with maximums of 57 and 43^{o}C for solarized and non-solarized soils respectively. According to Stapleton (1997) the soil surface records the highest soil temperatures during solarization and temperatures higher than 50 ^{o}C has been reported under clear polyethylene sheet only in the top 5 cm.

However, the results did not show significant difference in soil temperatures between pre-vegetated treatments (A, B, C, and D) and their un-vegetated counterparts (E, F, G, and H) suggesting that the randomization was done properly and no treatment group had any advantage over the other prior to transplanting (phytoremediation) (Figure 4.5(a-b)).

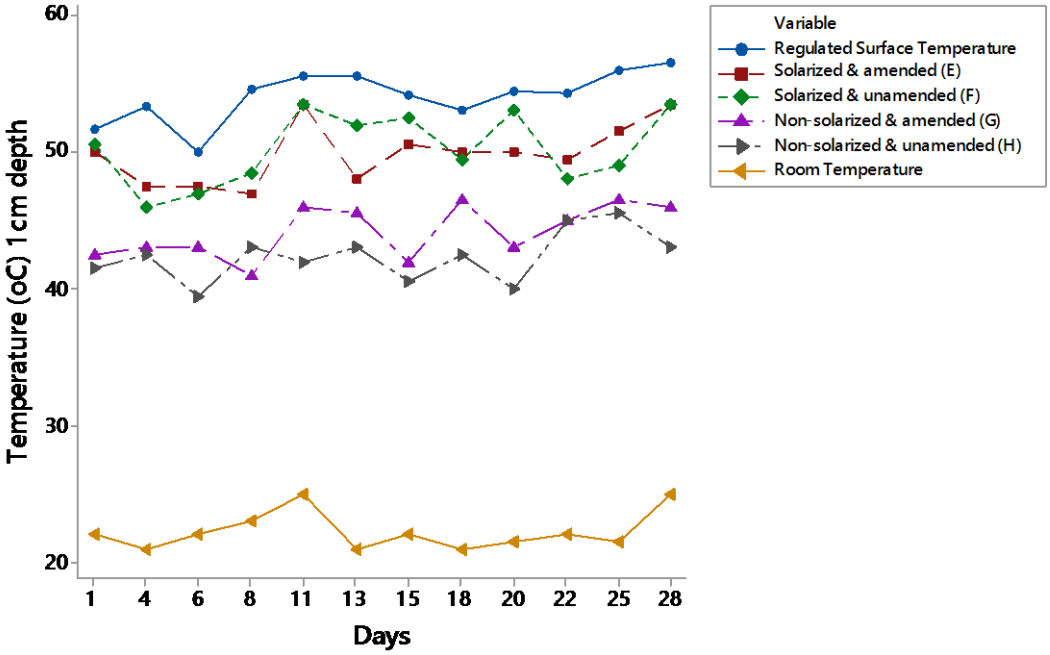


(a)

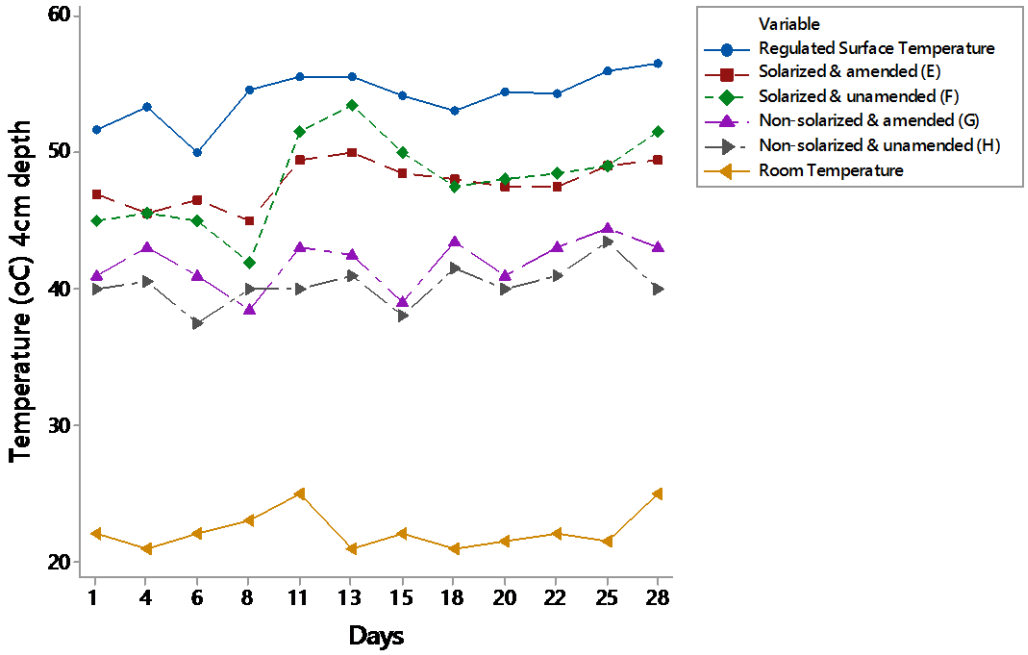


(b)

Figure 4.3(a-b): A time series plot of pre-vegetated treatments showing solarized soil temperatures with or without biosurfactant-amendment at (a) 1 and (b) 4 cm depths respectively in relations to regulated surface and room/ambient temperatures.

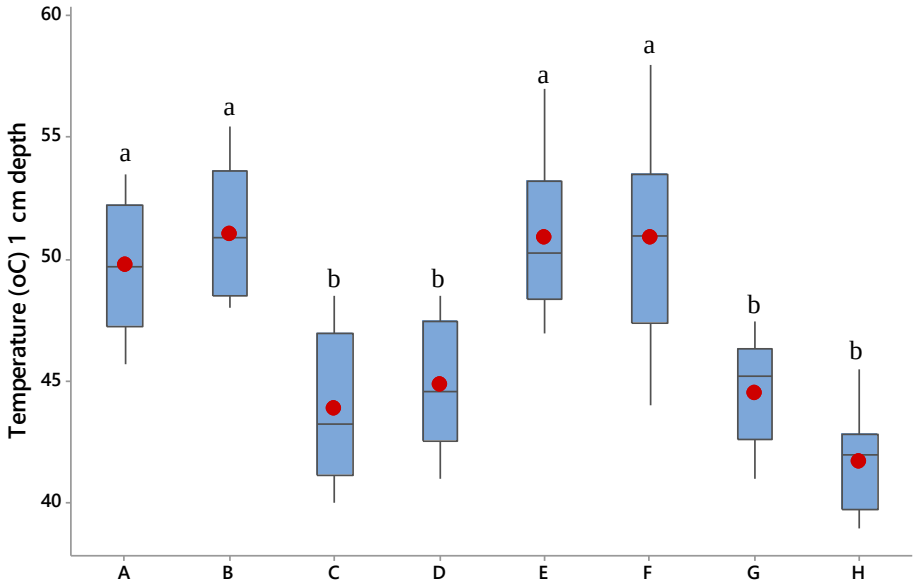


(a)

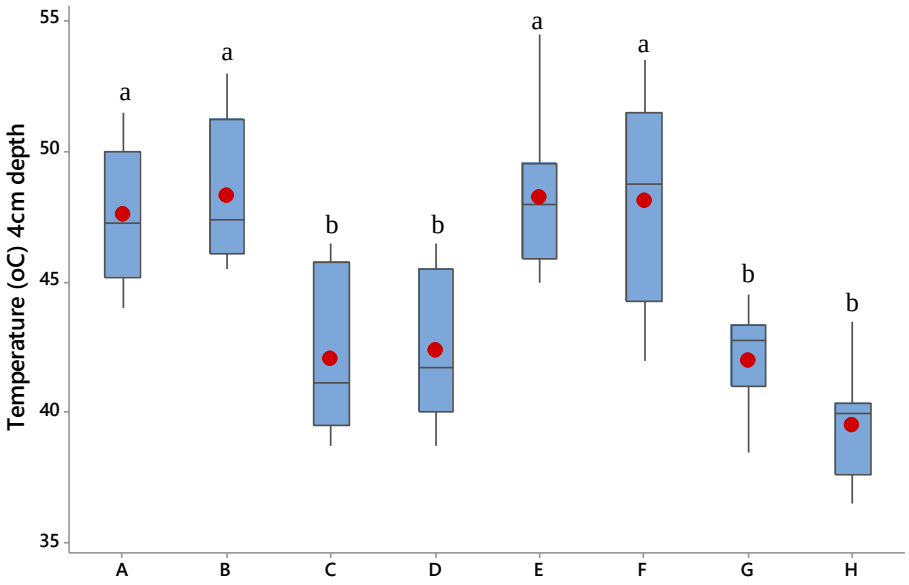


(b)

Figure 4.4(a-b): A time series plot of un-vegetated treatments showing solarized soil temperatures with or without biosurfactant-amendment at (a) 1 and (b) 4 cm depths respectively in relations to regulated surface and room/ambient temperatures.



(a)



(b)

Figure 4.5(a-b): Box plots of pre-vegetated and un-vegetated treatments showing soil temperatures for solarized and non-solarized soils with or without biosurfactant-amendment at (a) 1 cm depth and (b) 4 cm depth. Means with different letters are significantly different ($p \leq 0.01$).

Key:
A = Solarized & amended (Pre-vegetated)
B = Solarized & un-amended (Pre-vegetated)
C = Non-solarized & amended (Pre-vegetated)
D = Non-solarized & un-amended (Pre-vegetated)
E = Solarized & amended (Un-vegetated)
F = Solarized & un-amended (Un-vegetated)
G = Non-solarized & amended (Un-vegetated)
H = Non-solarized & un-amended (Un-vegetated)

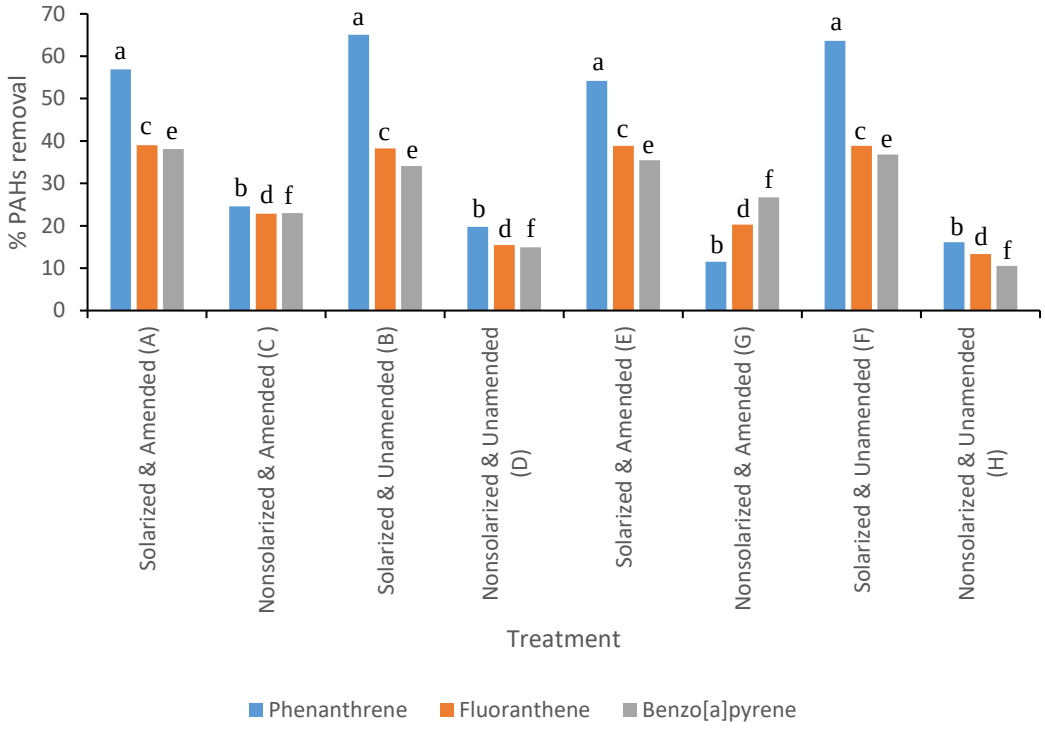
4.3.2 Treatments effects on PAHs removal

4.3.2.1 Soil solarization effects on PAHs removal

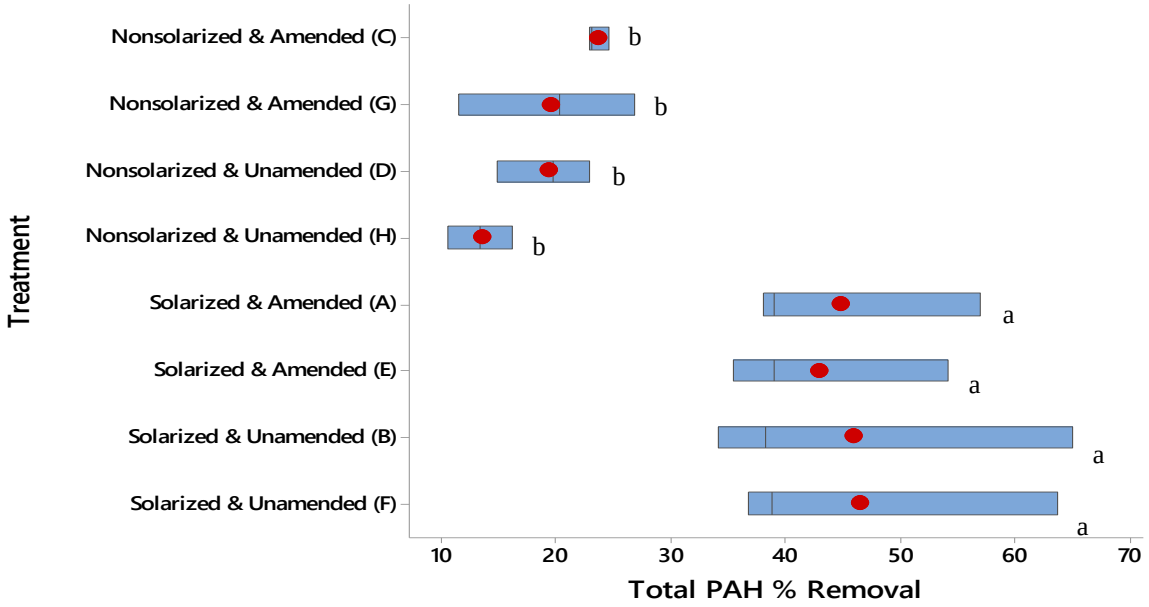
4.3.2.1.1 Effects of 28 days soil solarization on PAHs removal

The effect of soil solarization on the PAH mixtures was significant ($p \leq 0.01$) in their reduction and/or % removal after the 28 days solarization period. Phenanthrene has the highest significant reduction ($p \leq 0.01$), followed by fluoranthene and benzo[a]pyrene with means of 27.1 mg/kg or 56.9 % removal, 38.8 mg/kg or 39.0 % removal and 40.0 mg/kg or 38.1 % removal respectively in solarized and biosurfactant-amended pre-vegetated treatment (A) compared to mean reductions of 47.5 mg/kg or 24.6 % removal, 49.0 mg/kg or 22.9 % removal and 49.8 mg/kg or 23.0 % removal of phenanthrene, fluoranthene and benzo[a]pyrene respectively in non-solarized and biosurfactant-amended pre-vegetated counterpart (C) at day 28 as shown in Figure 4.6a (Appendix x(b)). Solarized and un-amended pre-vegetated treatment (B) showed significant reduction ($p \leq 0.01$) in phenanthrene, fluoranthene and benzo[a]pyrene with means of 22.0 mg/kg or 65.1 % removal, 39.3 mg/kg or 38.3 % removal and 42.6 mg/kg or 34.1 % removal compared to mean reductions of 50.5 mg/kg or 19.7 % removal, 53.8 mg/kg or 15.5 % removal and 55.0 mg/kg or 14.9 % removal in non-solarized and un-amended pre-vegetated treatment (D) for phenanthrene, fluoranthene and benzo[a]pyrene respectively (Figure 4.6a). Similar significant reduction ($p \leq 0.01$) patterns were observed in the un-vegetated treatment with 28.8 mg/kg or 54.2 % removal, 38.9 mg/kg or 38.9 % removal and 41.7 mg/kg or 35.5 % removal for phenanthrene, fluoranthene and benzo[a]pyrene respectively in solarized and biosurfactant-amended un-vegetated treatment (E) compared to mean reductions of 55.7 mg/kg or 11.5 % removal, 50.7 mg/kg or 20.3 % removal and 47.4 mg/kg or 26.7 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at day 28 for phenanthrene, fluoranthene and benzo[a]pyrene respectively. Phenanthrene, fluoranthene and benzo[a]pyrene significant reductions ($p \leq 0.01$) also occurred in solarized, un-amended and un-vegetated treatment (F) with reduction means of 22.9 mg/kg or 63.6 % removal, 38.9 mg/kg or 38.8 % removal and 40.9 mg/kg or 36.8 % removal respectively compared with its non-solarized, un-amended and un-vegetated counterpart (H) with reduced means of 52.8 mg/kg or 16.2 % removal, 55.1 mg/kg or 13.3 % removal and 57.9 mg/kg or 10.5 % removal at day 28 for phenanthrene, fluoranthene and benzo[a]pyrene respectively as shown in Figure 4.6a. A significant difference ($p \leq 0.01$) in the removal of total % PAHs was observed between solarized treatment groups with or without

biosurfactant-amendment and non-solarized treatment groups with or without biosurfactant-amendment as shown in Figure 4.6b (Appendix x(b)).



(a)



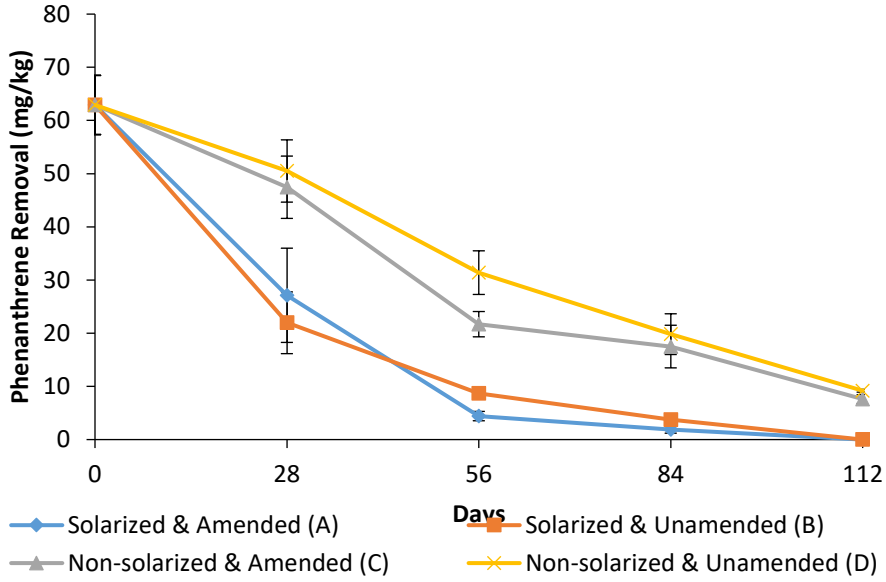
(b):

Figure 4.6(a-b): 28 days soil solarization impact on: (a) % removal of phenanthrene, fluoranthene and benzo[a]pyrene prior to planting (with or without biosurfactant-amendment) and (b) total % PAHs removal (difference of day 0 and 28) in solarized and non-solarized treatments with or without biosurfactant amendment. Means with different letters are significantly different ($p \leq 0.01$).

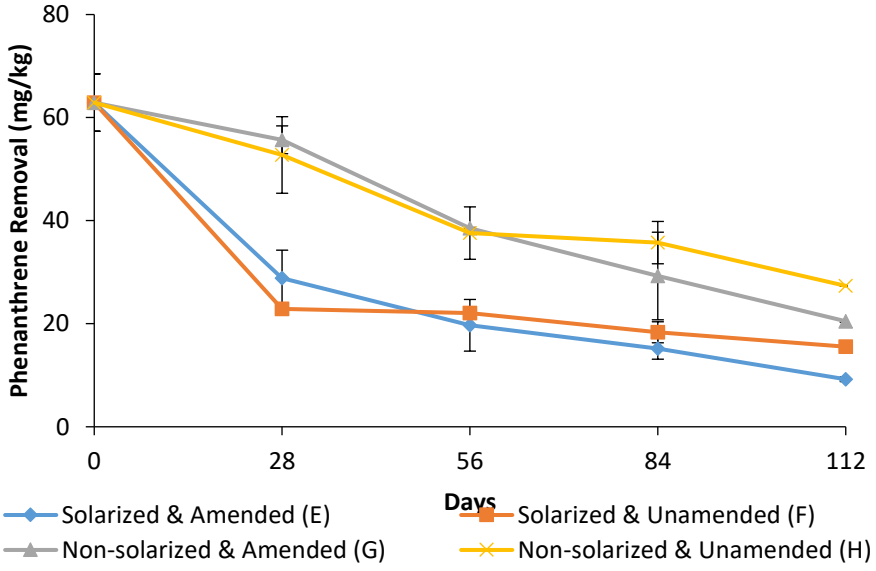
4.3.2.1.2 Effects of post-solarization on phenanthrene removal

This PAHs removal trend was sustained throughout the research duration even after transplanting seedlings of *C. odorata* of the same aged. PAHs were significantly reduced in all the treatment groups post-solarization (i.e. phytoremediation-vegetated and bioremediation-un-vegetated periods) with a significant reduction ($p \leq 0.01$) in solarized and vegetated/un-vegetated treatments compared to their non-solarized and vegetated/un-vegetated counterparts with or without biosurfactant amendment. Phenanthrene continued to be the most reduced PAH post-solarization with means of 4.42 mg/kg or 93.0 % removal, 1.89 mg/kg or 97.0 % removal and 0.00 mg/kg or 100 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to mean reductions of 21.7 mg/kg or 65.5 % removal, 17.5 mg/kg or 72.2 % removal and 7.62 mg/kg or 87.9 % removal in non-solarized and biosurfactant-amended vegetated counterpart (C) at days 56, 84 and 112 respectively as shown in Figure 4.7a. Post-solarization effect was also observed with phenanthrene in the solarized and un-amended vegetated treatment (B) with mean reductions of 8.66 mg/kg or 86.2 % removal, 3.75 mg/kg or 94.0 % removal and 0.00 mg/kg or 100 % removal compared with non-solarized and un-amended vegetated treatment (D) with 31.4 mg/kg or 50.1 % removal, 19.8 mg/kg or 68.5 % removal and 9.19 mg/kg or 85.4 % removal at days 56, 84 and 112 respectively as shown in Figure 4.7a. The un-vegetated treatment groups with or without biosurfactant-amendment showed similar trend with a relatively drastic reduction of phenanthrene with means of 19.7 mg/kg or 68.7 % removal, 15.2 mg/kg or 75.9 % removal and 9.22 mg/kg or 85.3 % removal in solarized and biosurfactant-amended un-vegetated treatment (E) compared to mean reductions of 38.5 mg/kg or 38.8 % removal, 29.3 mg/kg or 53.5 % removal and 20.48 mg/kg or 72.8 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.7b. Solarized, un-amended and un-vegetated treatment (F) has phenanthrene reduction means of 22.1 mg/kg or 64.9 % removal, 18.3 mg/kg or 70.9 % removal and 15.5 mg/kg or 75.3 % removal compared with its non-solarized, un-amended and un-vegetated counterpart (H) with 37.6 mg/kg or 40.3 % removal, 35.7 mg/kg or 43.2 % removal and 27.3 mg/kg or 64.5 % removal at days 56, 84 and 112 respectively (Figure 4.7b). A general linear model (GLM) shows that soil solarization had a statistical significance in the reduction of phenanthrene with *p*-value, *t*- and *F*- statistics of 0.00, 5.25 and 27.6 with R-square (adjustment) of 84.3 % between solarized and vegetated/un-vegetated treatments (A, B, E and F) and non-solarized and vegetated/un-vegetated treatments (C, D, G and H) with or without biosurfactant-amendment. The coefficient shows that

phenanthrene will be reduced by 11.3 % in the presence of soil solarization, while biosurfactant and plant are held constant (Appendix xi).



(a)



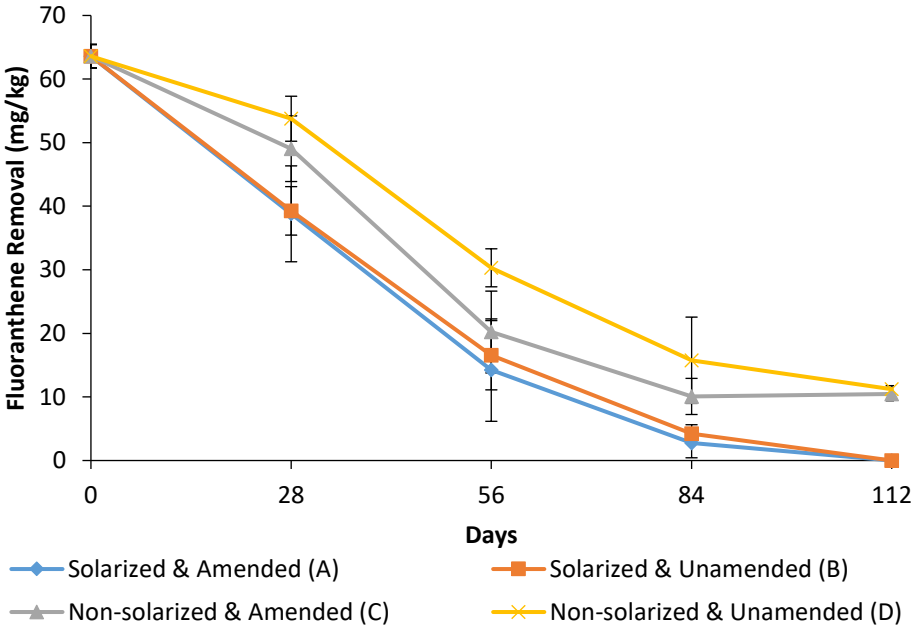
(b)

Figure 4.7(a-b): Mean reduction of phenanthrene with or without biosurfactant-amendment in (a) solarized vs non-solarized vegetated and (b) solarized vs non-solarized un-vegetated treatments respectively. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

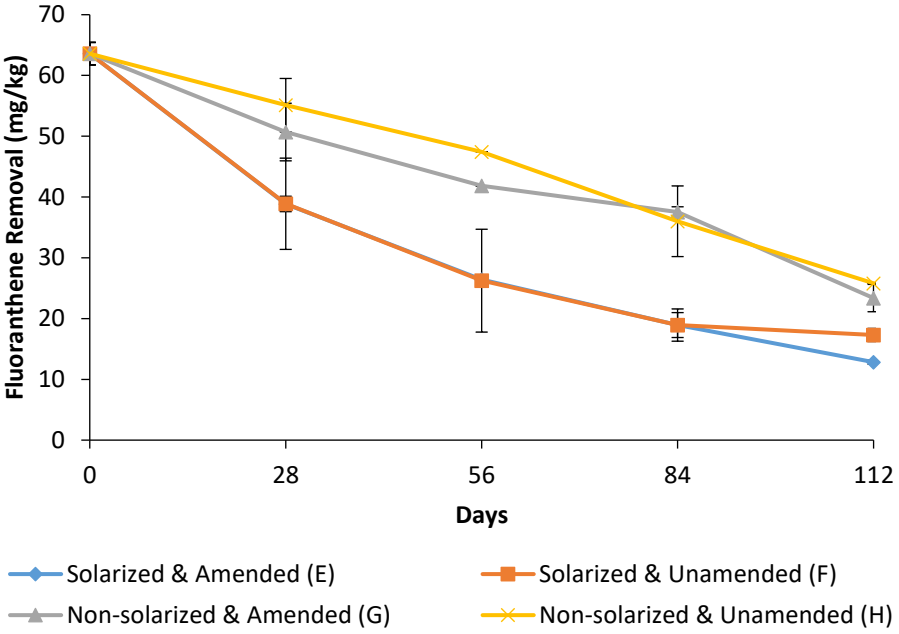
Key:
A = Solarized & amended (Vegetated)
B = Solarized & un-amended (Vegetated)
C = Non-solarized & amended (Vegetated)
D = Non-solarized & un-amended (Vegetated)
E = Solarized & amended (Un-vegetated)
F = Solarized & un-amended (Un-vegetated)
G = Non-solarized & amended (Un-vegetated)
H = Non-solarized & un-amended (Un-vegetated)

4.3.2.1.3 Effects of post-solarization on fluoranthene removal

Fluoranthene was the second most reduced PAH after phenanthrene post-solarization with means of 14.2 mg/kg or 77.6 % removal, 2.76 mg/kg or 95.7 % removal and 0.00 mg/kg or 100 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to mean reductions of 20.2 mg/kg or 68.2 % removal, 10.1 mg/kg or 84.2 % removal and 10.4 mg/kg or 83.6 % removal in non-solarized and biosurfactant-amended vegetated counterpart (C) at days 56, 84 and 112 respectively as shown in Figure 4.8a. Solarized and un-amended vegetated treatment (B) showed reduction in fluoranthene with means of 16.6 mg/kg or 74.0 % removal, 4.20 mg/kg or 93.4 % removal and 0.00 mg/kg or 100 % removal compared with mean reductions of non-solarized and un-amended vegetated treatment (D) with 30.3 mg/kg or 52.3 % removal, 15.8 mg/kg or 75.2 % removal and 11.2 mg/kg or 82.36 % removal at days 56, 84 and 112 respectively as shown in Figure 4.8a. There was a relatively reduced fluoranthene in the un-vegetated treatment groups with or without biosurfactant-amendment with means of 26.4 mg/kg or 58.4 % removal, 18.9 mg/kg or 70.2 % removal and 12.8 mg/kg or 79.8 % removal in solarized and biosurfactant-amended un-vegetated treatment (E) compared to mean reductions of 41.8 mg/kg or 34.2 % removal, 37.5 mg/kg or 41.0 % removal and 23.4 mg/kg or 63.3 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.8b. Fluoranthene reduction also occurred in solarized, un-amended and un-vegetated treatment (F) with reduction means of 26.2 mg/kg or 58.7 % removal, 19.4 mg/kg or 69.5 % removal and 17.3 mg/kg or 72.8 % removal compared with its non-solarized, un-amended and un-vegetated counterpart (H) with reduced means of 47.5 mg/kg or 25.4 % removal, 36.0 mg/kg or 43.4 % removal and 25.8 mg/kg or 55.8 % removal at days 56, 84 and 112 respectively (Figure 4.8b). Fluoranthene reduction between solarized and vegetated/un-vegetated treatments (A, B, E and F) and non-solarized and vegetated/un-vegetated treatments (C, D, G and H) with or without biosurfactant-amendment had a statistical significant reduction with *p*-value, *t*- and *F*- statistics of 0.00, 4.51 and 20.9, respectively and R-square (adjustment) of 88.5 % using a general linear model (GLM). The coefficient shows that fluoranthene will be reduced by 8.1 % in the presence of soil solarization, while biosurfactant and plant are held constant (Appendix xi).



(a)



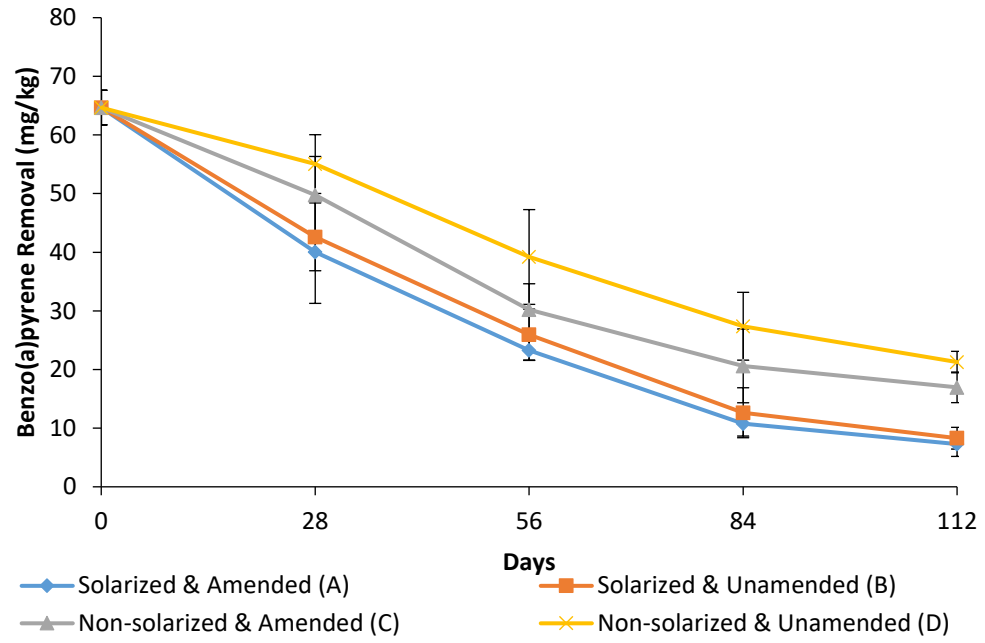
(b)

Figure 4.8(a-b): Mean reduction of fluoranthene with or without biosurfactant-amendment in (a) solarized vs non-solarized vegetated and (b) solarized vs non-solarized un-vegetated treatments respectively. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

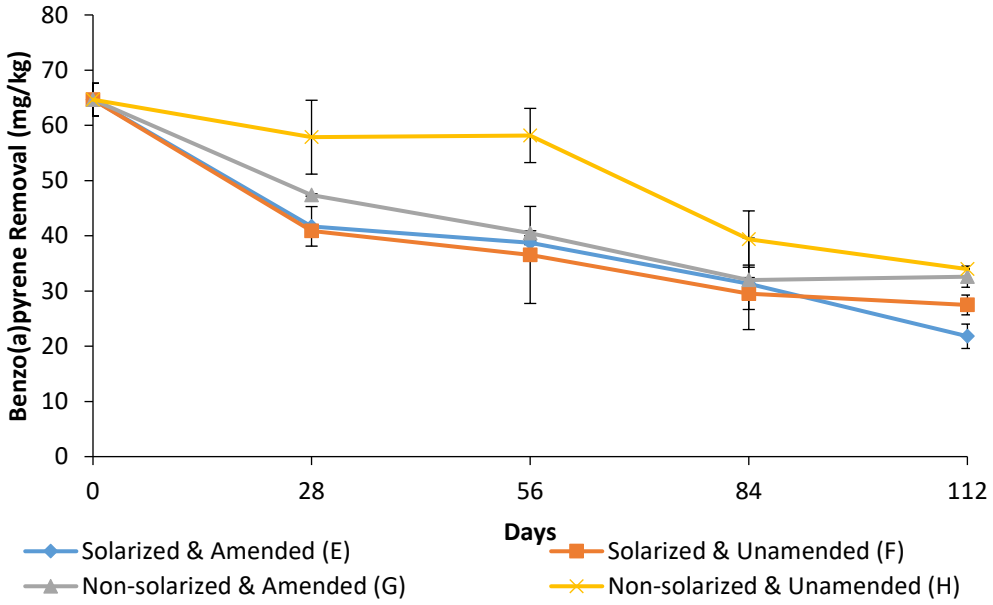
Key:
A = Solarized & amended (Vegetated)
B = Solarized & un-amended (Vegetated)
C = Non-solarized & amended (Vegetated)
D = Non-solarized & un-amended (Vegetated)
E = Solarized & amended (Un-vegetated)
F = Solarized & un-amended (Un-vegetated)
G = Non-solarized & amended (Un-vegetated)
H = Non-solarized & un-amended (Un-vegetated)

4.3.2.1.4 Effects of post-solarization on benzo[a]pyrene removal

Post solarization has the least effect on benzo[a]pyrene as the least reduced PAH with means of 23.3 mg/kg or 64.0 % removal, 10.8 mg/kg or 83.3 % removal and 7.28 mg/kg or 88.7 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to means reduction of 30.2 mg/kg or 53.3 % removal, 20.6 mg/kg or 68.1 % removal and 17.0 mg/kg or 73.8 % removal in non-solarized and biosurfactant-amended vegetated counterpart (C) at days 56, 84 and 112 respectively as shown in Figure 4.9a. Solarized and un-amended vegetated treatment (B) showed reduced benzo[a]pyrene with means of 26.0 mg/kg or 59.9 % removal, 12.6 mg/kg or 80.5 % removal and 8.29 mg/kg or 87.2 % removal compared with non-solarized and un-amended vegetated treatment (D) with 39.2 mg/kg or 39.4 % removal, 27.4 mg/kg or 57.7 % removal and 21.3 mg/kg or 67.1 % removal at days 56, 84 and 112 respectively as shown in Figure 4.9a. The un-vegetated treatment groups with or without biosurfactant amendment showed a similar trend but with a relatively least reduced benzo[a]pyrene with means of 38.7 mg/kg or 40.1 % removal, 31.3 mg/kg or 51.6 % removal and 21.8 mg/kg or 66.3 % removal in solarized and biosurfactant-amended un-vegetated treatment (E) compared to mean reductions of 40.5 mg/kg or 37.4 % removal, 32.0 mg/kg or 50.5 % removal and 32.6 mg/kg or 49.6 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.9b. Solarized, un-amended and un-vegetated treatment (F) has benzo[a]pyrene reduction means of 36.5 mg/kg or 43.5 % removal, 29.5 mg/kg or 54.3 % removal and 27.5 mg/kg or 57.5 % removal compared with its non-solarized, un-amended and un-vegetated counterpart (H) with means of 58.2 mg/kg or 10.0 % removal, 39.4 mg/kg or 39.1 % removal and 34.0 mg/kg or 47.5 % removal at days 56, 84 and 112 respectively (Figure 4.9b). The overall reduction of benzo[a]pyrene using a general linear model showed a statistical significance with *p*-value, *t*- and *F*-statistics of 0.00, 4.11 and 16.9 with R-square (adjustment) of 87.5 % between solarized and vegetated/un-vegetated treatments (A, B, E and F) and non-solarized and vegetated/un-vegetated treatments (C, D, G and H) with or without biosurfactant-amendment. The coefficient shows that benzo[a]pyrene will be reduced by 6.3 % in the presence of soil solarization, while biosurfactant and plant are held constant (Appendix xi).



(a)



(b)

Figure 4.9(a-b): Mean reduction of benzo[a]pyrene with or without biosurfactant-amendment in (a) solarized vs non-solarized vegetated and (b) solarized vs non-solarized un-vegetated treatments respectively. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

Key:
A = Solarized & amended (Vegetated)
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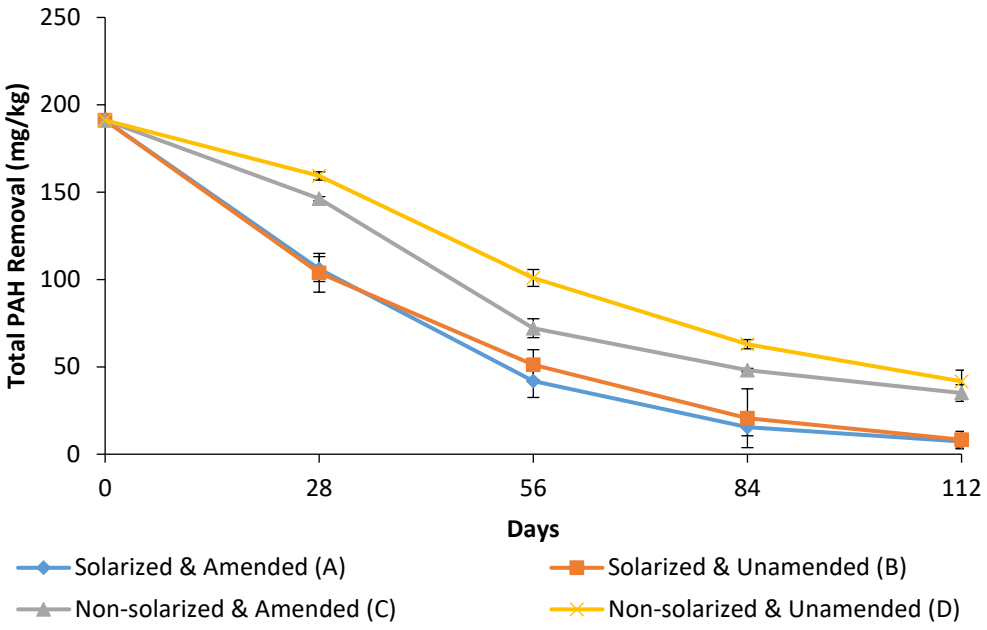
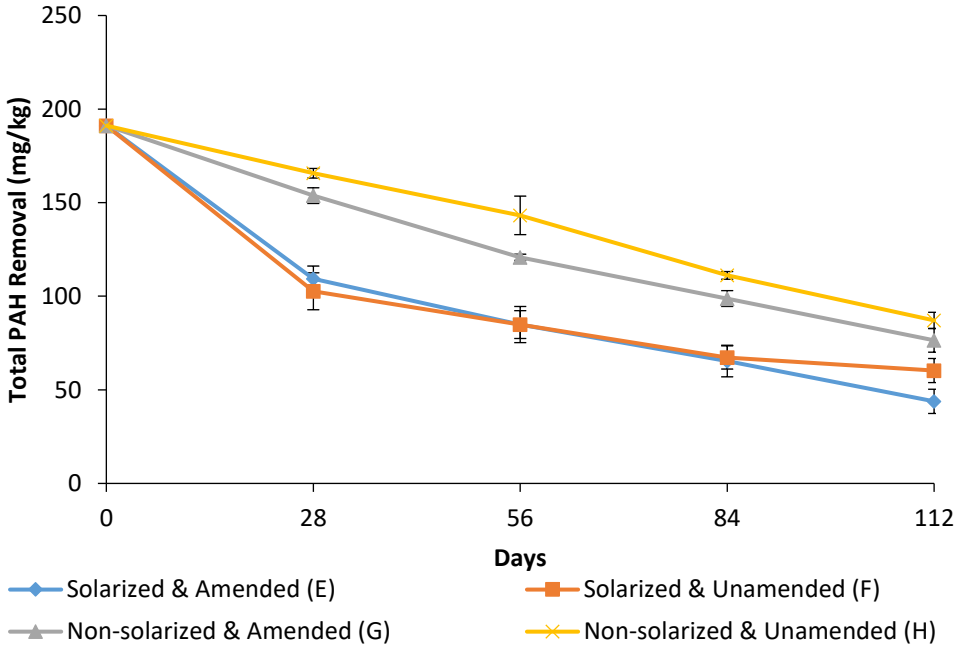
D = Non-solarized & un-amended (Vegetated)
E = Solarized & amended (Un-vegetated)
F = Solarized & un-amended (Un-vegetated)
G = Non-solarized & amended (Un-vegetated)
H = Non-solarized & un-amended (Un-vegetated)

4.3.2.1.5 Effects of post-solarization on total PAHs removal

The effect of post-solarization was observed in total PAH (phenanthrene, fluoranthene and benzo[a]pyrene) reduction with statistical significance ($p \leq 0.01$) of 41.9 mg/kg or 78.1 % removal, 15.4 mg/kg or 91.9 % removal and 7.28 mg/kg or 96.2 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to reductions of 72.1 mg/kg or 62.3 % removal, 48.2 mg/kg or 74.8 % removal and 35.0 mg/kg or 81.7 % removal in non-solarized and biosurfactant-amended vegetated counterpart (C) at days 56, 84 and 112 respectively as shown in Figure 4.10a. Solarized and un-amended vegetated treatment (B) showed significant reduction ($p \leq 0.01$) in total PAHs with 50.5 mg/kg or 73.6 % removal, 20.6 mg/kg or 89.2 % removal and 8.29 mg/kg or 95.7 % removal compared with reductions of non-solarized and un-amended vegetated treatment (D) with 100.9 mg/kg or 47.2 % removal, 63.0 mg/kg or 67.1 % removal and 41.7 mg/kg or 78.2 % removal at days 56, 84 and 112 respectively as shown in Figure 4.10a. There was also a relatively significant reduction ($p \leq 0.01$) in total PAHs in the un-vegetated treatment groups with or without biosurfactant-amendment with 84.9 mg/kg or 55.6 % removal, 65.4 mg/kg or 65.8 % removal and 43.9 mg/kg or 77.1 % removal in solarized and biosurfactant-amended un-vegetated treatment (E) compared to reductions of 120.8 mg/kg or 36.8 % removal, 98.8 mg/kg or 48.3 % removal and 76.5 mg/kg or 60.0 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.10b. Total PAH significant reduction ($p \leq 0.01$) also took place in solarized, un-amended and un-vegetated treatment (F) with reductions of 84.9 mg/kg or 55.6 % removal, 64.3 mg/kg or 66.4 % removal and 60.31 mg/kg or 68.5 % removal compared with its non-solarized, un-amended and un-vegetated counterpart (H) with reduced 143.8 mg/kg or 24.8 % removal, 111.2 mg/kg or 41.9 % removal and 87.1 mg/kg or 54.4 % removal at days 56, 84 and 112 respectively (Figure 4.10b). There was a statistical significance in the reduction of total PAH mixtures with *p*-value, *t*- and *F*- statistics of 0.00, 5.08 and 25.9 with R-square (adjustment) of 88.4 % using a general linear model between solarized and vegetated/un-vegetated treatments (A, B, E and F) and non-solarized and vegetated/un-vegetated treatments (C, D, G and H) with or without biosurfactant-amendment. The coefficient shows that total PAH will be reduced by 8.6 % in the presence of soil solarization, while biosurfactant and plant are held constant (Appendix xi).



(a)



(b)

Figure 4.10(a-b): Mean reduction of total PAH removal with or without biosurfactant-amendment in (a) solarized vs non-solarized vegetated and (b) solarized vs non-solarized un-vegetated treatments respectively. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

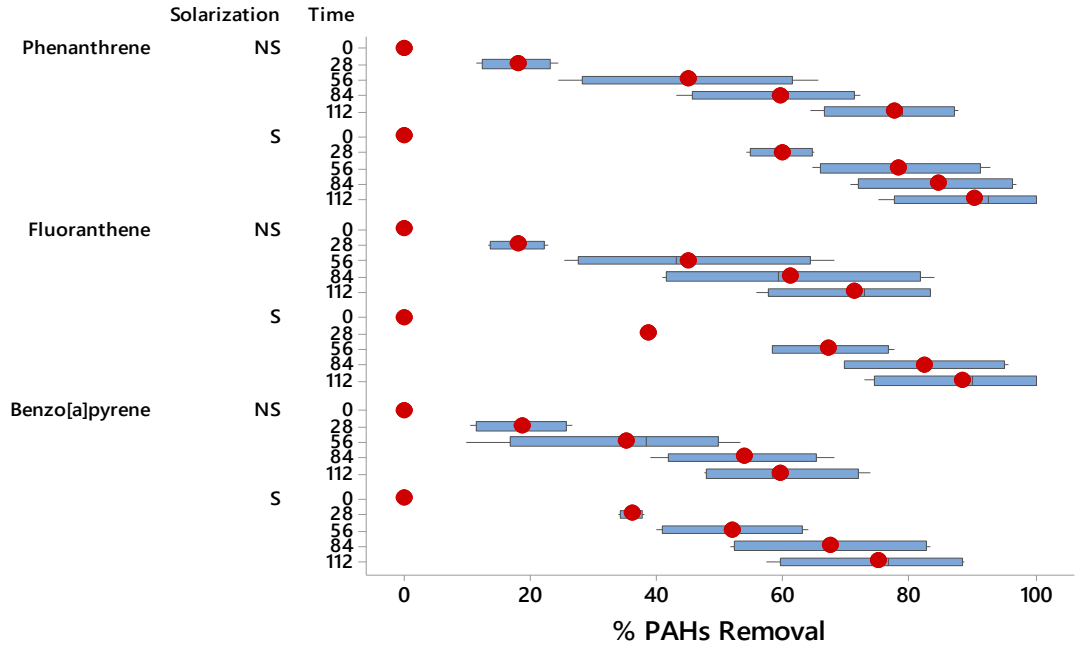
Key:
A = Solarized & amended (Vegetated)
B = Solarized & un-amended (Vegetated)
C = Non-solarized & amended (Vegetated)
D = Non-solarized & un-amended (Vegetated)
E = Solarized & amended (Un-vegetated)
F = Solarized & un-amended (Un-vegetated)
G = Non-solarized & amended (Un-vegetated)
H = Non-solarized & un-amended (Un-vegetated)

With the use of box plots, the impact of soil solarization and in combined forms with biosurfactant and phytoremediation (plant) on the % removal of phenanthrene, fluoranthene and benzo[a]pyrene over time were shown in Figure 4.11 and Figure 4.16 respectively. From the box plot (Figure 4.11), it can be seen that solarized treatments had significant ($p \leq 0.01$) % removal of the PAHs mixtures than their non-solarized counterparts both in terms of comparing their respective means and medians. The means and medians are very close to each other for the two treatments suggesting a symmetrical or normal distribution of phenanthrene, fluoranthene and benzo[a]pyrene % removal. Soil solarization showed a significant ($p \leq 0.01$) phenanthrene % removal with means of 60.0, 78.2, 84.5 and 90.0 % in solarize treatments compared to means of 18.0, 45.1, 59.4 and 77.6 % in non-solarized counterparts at days 28, 56, 84 and 112 respectively. The impact of soil solarization alone was also significant ($p \leq 0.01$) in fluoranthene % removal with 38.7, 67.2, 82.2 and 88.2 % in solarized treatments compared to their non-solarized counterparts with means of 18.1, 45.0, 60.9 and 71.2 % removal at days 28, 56, 84 and 112 respectively. Solarization was also effective on benzo[a]pyrene removal which was the least removed PAH with means of 36.1, 51.9, 67.4 and 74.9 % removal compared to means of 18.8, 35.0, 53.9 and 59.5 % removal for solarized and non-solarized treatments respectively at days 28, 56, 84 and 112 consecutively.

4.3.2.1.6 Statistical conclusion on the effects of solarization on PAHs removal

Generally, an examination of the *t*-statistics for the individual coefficients as shown in Table 18 shows that phenanthrene coefficient of -11.3 has the highest *t*-statistic of 5.25 with its associated *p*-value of 0.00, followed by fluoranthene and benzo[a]pyrene coefficients of -8.10 and -6.32 with *t*-statistics of 4.51 and 4.11 respectively and their associated *p*-values of 0.00 each. The size of the coefficient is usually a good way to assess the practical significance of the effect that solarization has on the PAHs removal. PAHs will generally be reduced by 11.3, 8.1 and 6.3 % in the presence of soil solarization while biosurfactant and plant remain constant for phenanthrene, fluoranthene and benzo[a]pyrene respectively. This suggests that soil solarization contributed the most in the removal of PAHs. The overall significance in *p*-values shows that the H_o (coefficient = 0) is rejected with very strong evidence in favour of the H_1 (coefficient $\neq$ 0) and concludes that there is very strong evidence of a linear relationship between soil solarization and the individual PAH mixtures reduction or % removal. The *F*-statistics of phenanthrene, fluoranthene and benzo[a]pyrene reductions of 27.6, 20.9 and 16.9 respectively with their corresponding *p*-values, also suggest a very strong evidence against H_o

(which states that there is no linear relationship between response (i.e. PAH mixtures) and predictor variable (i.e. soil solarization)). Therefore, H_1 is accepted i.e. there are linear relationships between phenanthrene, fluoranthene and benzo[a]pyrene reductions (response) and the soil solarization predictor variable that corresponds with the *t*-statistic of the model. The R-square (adjusted) which gives an estimate of what percentages of the total variation is explained by the general linear model (GLM) for other observation from the overall population were 84.3, 88.5 and 87.5 % for phenanthrene, fluoranthene and benzo[a]pyrene respectively also suggest the existence of a linear relationship. The remaining 15.7, 11.5 and 12.5 % unexplained variations for phenanthrene, fluoranthene and benzo[a]pyrene respectively are shown in their respective residual analysis to check the model (Appendix xi). Thus, one of the H_0 hypotheses for this research which was *'soil solarization has no effect on PAHs removal in the advance phytoremediation of PAH contaminated soil'* (see Section 1.7.1) is rejected with very strong evidence against the H_0 in favour of the H_1 stating that ***'soil solarization has effect on PAHs removal in the advance phytoremediation of PAH contaminated soil'*** (Table 18 and Appendix xi).



(a)

Figure 4.11: Impacts of soil solarization on % removal of phenanthrene, fluoranthene and benzo[a]pyrene.

Key:

S = Solarized

NS = Non-solarized

B = Biosurfactant

NB = No Biosurfactant

Table 18: Summary of coefficients and associated statistical parameters for general linear model analysis of treatment response variables and experimental conditions

Treatment	Factors	Coef.	SE Coef.	*t*-statistic	*F*- statistic	*p*-Value	R-Square (adj.)
% phenanthrene Removal	Solarization (S & NS)	-11.27	2.15	-5.25	27.55	0.00	84.28%
	Biosurfactant (B & NB)	0.89	2.15	0.41	0.17	0.68	
	Plant (V & UV)	-7.03	2.15	-3.27	10.71	0.00	
	Time	0.72	0.05	13.22	174.65	0.00	
% fluoranthene Removal	Solarization (S & NS)	-8.10	1.77	-4.51	20.93	0.00	88.49%
	Biosurfactant (B & NB)	1.72	1.77	0.97	0.95	0.34	
	Plant (V & UV)	-7.95	1.77	-4.49	20.16	0.00	
	Time	0.72	0.05	16.18	261.89	0.00	
% benzo[a]pyrene Removal	Solarization (S & NS)	-6.32	1.54	-4.11	16.90	0.00	87.54%
	Biosurfactant (B & NB)	2.75	1.54	1.79	3.21	0.08	
	Plant (V & UV)	-6.90	1.54	-4.49	20.15	0.00	
	Time	0.60	0.04	15.42	237.79	0.00	
% Total PAH Removal	Solarization (S & NS)	-8.56	1.68	-5.08	25.85	0.00	88.39%
	Biosurfactant (B & NB)	1.79	1.68	1.06	1.13	0.30	
	Plant (V & UV)	-7.29	1.68	-4.33	18.75	0.00	
	Time	0.98	0.043	15.98	255.30	0.00	
Rhizosphere Bacteria (CFU/g x 10^4)	Solarization (S & NS)	-7.50	4.67	-1.61	2.58	0.12	59.51%
	Biosurfactant (B & NB)	1.60	4.67	0.34	0.12	0.73	
	Plant (V & UV)	-23.57	4.67	-5.05	25.48	0.00	
	Time	0.68	0.12	5.76	33.14	0.00	
Rhizosphere Actinomycete (CFU/g x 10^4)	Solarization (S & NS)	-3.76	2.37	-1.59	2.52	0.12	66.21%
	Biosurfactant (B & NB)	0.14	2.37	-1.59	0.00	0.95	
	Plant (V & UV)	-12.01	2.37	-5.07	25.71	0.00	
	Time	0.43	0.06	7.22	52.17	0.00	
Rhizosphere Fungi (CFU/g x 10^4)	Solarization (S & NS)	-3.54	2.29	-1.54	2.38	0.13	67.81%
	Biosurfactant (B & NB)	0.26	2.29	0.11	0.01	0.91	
	Plant (V & UV)	-11.59	2.29	-5.05	25.53	0.00	
	Time	0.44	0.06	8.63	58.23	0.00	
Total Rhizosphere Microorganisms (CFU/g x 10^4)	Solarization (S & NS)	-14.80	9.22	-1.61	2.58	0.12	63.98%
	Biosurfactant (B & NB)	2.00	9.22	0.22	0.05	0.83	
	Plant (V & UV)	-47.17	9.22	-5.12	26.17	0.00	
	Time	1.55	0.23	6.67	44.48	0.00	

Dehydrogenase Enzymatic Activity (µg/g dry soil)	Solarization (S & NS)	-1.63	0.93	-1.76	3.09	0.09	34.32%
	Biosurfactant (B & NB)	0.81	0.93	0.88	0.77	0.39	
	Plant (V & UV)	-2.61	0.93	-2.82	7.93	0.01	
	Time	0.08	0.02	3.55	12.59	0.00	
Urease Enzymatic Activity (µg/g dry soil)	Solarization (S & NS)	-0.01	0.00	-2.86	8.16	0.01	72.61%
	Biosurfactant (B & NB)	0.00	0.00	1.50	2.24	0.14	
	Plant (V & UV)	-0.01	0.00	-3.67	13.49	0.00	
	Time	0.00	0.00	9.14	83.50	0.00	
Soil Enzymatic Activity (µg/g dry soil)	Solarization (S & NS)	-1.63	0.93	-1.76	3.10	0.09	34.46%
	Biosurfactant (B & NB)	0.81	0.93	0.88	0.77	0.39	
	Plant (V & UV)	-2.61	0.93	-2.82	7.95	0.01	
	Time	0.08	0.02	3.56	12.69	0.00	

Key:
S = Solarized B = Biosurfactant-amended V = Vegetated
NS = Non-solarized NB = No Biosurfactant amended UV = Un-vegetated

4.3.2.1.7 Discussion on the impacts of soil solarization on PAHs removal

Although the PAH mixtures may be subjected to photosensitization and photodegradation in the experiment which was conducted in a microcosm lit with both UV and IF red bulbs (see Plate 1.6(a-b)), they are still considered persistent contaminants due to their physico-chemical characteristics. According to Zhang *et al.* (2008) who carried out a comprehensive study of the photocatalytic degradation of phenanthrene, pyrene and benzo[a]pyrene on soil surface using titanium dioxide (TiO_2) under UV light. A comparable accelerated photodegradation only took place with all three PAHs in the presence of TiO_2 catalyst as against its absence and reported that variation in TiO_2 concentration had no significant effect on PAH degradation. In addition to different photocatalystic degradation rates of PAHs under distinct UV wavelengths. The possibility of photodegradation on the studied PAHs is very unlikely considering the fact that there was no catalyst used in this experiment. Consequently, this study showed that soil solarization was responsible for the significant reduction of phenanthrene, fluoranthene and benzo[a]pyrene especially in the 28 days solarization period (see objective v in Section 1.6.2).

The gradual increase in daily simulated temperatures (see Section 4.2.6) of solarized moist soil treatments as shown in this study may have impacted on the physical, chemical and biological properties of the solarized soils including increasing the mineral nutrients and

soluble organic matter content such as N mineralization, Ca, Mg, P, and K by facilitating decomposition of organic matter quickly using the heat under the transparent polyethylene sheet. This direct impact from solarization creates a favourable microenvironment for bacterial metabolic activity and ultimately, PAH biodegradation. According to Leahy and Colwell (1990); Zhang *et al.* (2005); and Okere and Semple (2012) corresponding increase in temperature up to an optimum of 30 to 40^{o}C results in corresponding increase in bacterial metabolic activity and PAH biodegradation, due to extreme temperature adaptation by PAHs degrading bacteria while maintaining their metabolic activity. According to Miller *et al.* (1989) most of the soil heterotrophic microorganisms are mesophiles with an optimum temperature of about 25-35^{o}C and a growth capacity from 10-15^{o}C to 45^{o}C but a decrease in temperature inhibits the growth and development of heterotrophic microbes and also reduced the rate of biochemical reactions. Thus, the significant removal of PAHs from solarized soils may be attributed to the physico-chemical and/or biological processes as both are affected by increase soil temperatures. Increase in soil temperature has been reported to decrease PAHs sorption by soils (Podoll *et al.,* 1980), subsequently increase their solubility and vapour pressure (Miller *et al.,* 1989) and enhance biodegradation of PAHs in contaminated sites (Ghosal *et al*., 2016) since abiotic losses of PAHs from soil depend mostly on sorption and volatilization (Bulman *et al.,* 1985; Park *et al.,* 1990). Solarization also increases soil pH values, soil base saturation and exchangeable K^{+} and Mg^{2+} (Chen *et al.,* 1991) and this abiotic condition enhance PAH biodegradation. According to Maeir *et al.* (2000) slightly alkaline soils favour PAH biodegradation because PAH degrading bacteria become less competitive with increasing acidic conditions.

The removal of PAHs especially phenanthrene and to some extent fluoranthene was greater during the interval between day 0 and 28 where soil temperatures were relatively higher due to soil solarization, but the removal rates were almost linear towards the end of the treatment period especially from day 56 to 112. Suggesting that optimum conditions enhancing the removal of PAHs early in the first 56 days particularly the 28 days solarization period may have become less favourable at the latter post-solarization/phytoremediation stage. Similar trend was reported by Mervin and Sims (1987) who observed relatively rapid loss of phenanthrene at higher temperature during the interval between 0 and 60 days when soil treatment was incubated compared to the latter stages of incubation. And attributed this loss to less favourable conditions at the latter stage. PACE (1985) also observed similar trend for the apparent removal of phenanthrene, anthracene, and fluoranthene in an agricultural soil. The increase of soil temperature by solarization impacted most significantly on the removal of low

molecular weight PAHs as seen in this study with phenanthrene and fluoranthene. This correlates with the finding of Mervin and Sims (1987) in which increasing soil temperature improved the rate and extent of apparent loss of low molecular weight PAHs but had little impact on five and six-ring PAHs.

However, there is a huge gap in literature regarding the effect of soil solarization on remediation of contaminated soil, but there is some evidence on pesticide degradation by solarization and biosolarization as reported by Fenoll *et al.* (2010). This residual dissipation could be attributed to an increase in the soil temperature or to a higher degree of accumulated duration at high temperature in the solarized soil compared to the non-solarized treatments. Studies showed that when temperature increases, PAHs solubility also increases, which in turn increases the bioavailability of PAH molecules (Ghosal *et al.*, 2016; Margesin and Schinner, 2001). Biodegradation of PAHs have been reported to take place over a wide range of temperatures, however, most studies are focused on mesophilic temperature instead of the efficiency of transformations at very high or low temperature (Bamforth and Singleton, 2005). It has been established that microorganisms have adapted to metabolize PAHs at extreme temperatures even though oxygen solubility decreases with increasing temperature which reduces their metabolic activity especially aerobic microorganisms. Siron *et al.* (1995) reported the degradation of naphthalene and phenanthrene from crude oil in sea water at very low temperature of 0^{o}C while Lau *et al.* (2003) reported to have an optimum temperatures of >50^{o}C and >75^{o}C respectively in the degradation of PAHs in spent-mushroom compost. They reported that over 90 % PAHs removal took place at these very high temperatures. Biodegradation of PAHs have also be documented at very high temperatures (60-70^{o}C) by *Thermus* and *Bacillus* spp (Feitkenhauer *et al.*, 2003)

Generally, the extent and rate of apparent removal was greater for PAHs of low molecular weight and high aqueous solubility (see Table 2). Substantial and comparative removal of phenanthrene (three-ring) and fluoranthene (four-ring) were observed respectively throughout the study period especially in solarized treatment as shown in Figures 4.7(a-b) and 4.8(a-b). While the least removed PAH was benzo[a]pyrene (five-ring) as shown in Figure 4.8(a-b). This general trend for the PAH class of compounds i.e. three-ring, four-ring and five-ring in relation to increase temperatures has been observed by other researcher (Bossert *et al.*, 1984; PACE, 1985; Sims and Overcash, 1983; Herbes and Schwall, 1978). Volatilization may have contributed significantly to the reduction of phenanthrene due to Henry's law of coefficients (vapour pressure divided by aqueous solubility) as phenanthrene falls within the range of $10^{-5} < H < 10^{-3}$ atm/mol/m^3 referred to as a region of moderate volatility by Lyman *et*

la. (1982). The petroleum association for conservation of the Canadian environment (1985) reported volatilization either as parent compound or as metabolites, as a significant mechanism of three-ring PAH removal from soil.

The effect of post-solarization of PAH mixtures' significant removal/degradation on the other hand, could be based on increased desorption, total heterogeneous microbial activity, soil/rhizosphere enzymatic activity, improved agronomic performance of plants with phytoremediation potential and/or enhanced action of catalytic substances or a combination of all of the above. Despite a very limited information of the effect of solarization on contaminant removal/degradation, a few authors have reported lower persistence of organophosphorus insecticides and benzimidazole fungicides in soils with this solarization technique (Yarden *et al.,* 1989; Gopal *et al.,* 2000). Navarro *et al.* (2009) also reported a well-established influence of the polyethylene sheet on the dissipation of some triazine and phenylurea herbicides from the soil. Fenoll *et al.* (2010) reported increased fungicide dissipation by solarization and biosolarization with regards to the control treatment and suggested the dissipation was mainly due to increased soil temperatures. The accumulation and dissipation of contaminants in soil has be demonstrated to be affected by soil solarization, resulting to either extended or shortened pesticide persistence by solarization depending on the nature and time of pesticide application (Rubin and Benjamin, 1983; Avidov *et al*., 1985; Yarden *et al*., 1989). In addition, soil organic-amendment may have an effect on soil pollutants degradation (Flores *et al*., 2008). From these findings, the novelty of integrating soil solarization as a remediation technique in treating hydrocarbon (PAHs) contaminated land has been evidently established. The demonstrated suitability and compatibility of soil solarization and phytoremediation showed the originality of this study (see Section 2.9), it can be a sustainable, environmentally friendly and cost effective treatment option for the large area of contaminated land in the Niger Delta region, Nigeria.

4.3.2.2 Biosurfactant effects on PAHs removal

4.3.2.2.1 Effects of biosurfactant after 28 days soil solarization on PAHs removal

Biosurfactant on the other hand fails to contribute significantly ($p \geq 0.05$) to the overall PAHs reductions or % removal with means of 27.1 mg/kg or 56.9 % removal, 38.8 mg/kg or 39.0 % removal and 40.0 mg/kg or 38.1 % removal for phenanthrene, fluoranthene and benzo[a]pyrene respectively in solarized and biosurfactant-amended pre-vegetated treatment (A) compared to a means of 22.0 mg/kg or 65.1 % removal, 39.3 mg/kg or 38.3 % removal and 42.6 mg/kg or 34.1 % removal in solarized and un-amended pre-vegetated counterpart (B) for phenanthrene, fluoranthene and benzo[a]pyrene respectively after 28 solarization periods as shown in Figure 4.6a (Appendix xii). Non-solarized and biosurfactant-amended pre-vegetated treatment (C) after 28 days shows insignificant ($p \geq 0.05$) PAHs reduction means of 47.5 mg/kg or 24.6 % removal, 49.0 mg/kg or 22.9 % removal and 49.8 mg/kg or 23.0 % removal of phenanthrene, fluoranthene and benzo[a]pyrene respectively compared to mean reductions of 50.5 mg/kg or 19.7 % removal, 53.8 mg/kg or 15.5 % removal and 55.0 mg/kg or 14.9 % removal in non-solarized and un-amended pre-vegetated treatment (D) for phenanthrene, fluoranthene and benzo[a]pyrene respectively (Figure 4.6a). This trend of negligible and insignificant reduction ($p \geq 0.05$) was also observed in the un-vegetated treatments with or without biosurfactant. In solarized and biosurfactant-amended un-vegetated treatment (E), the mean reductions for phenanthrene, fluoranthene and benzo[a]pyrene of 28.8 mg/kg or 54.2 % removal, 38.9 mg/kg or 38.9 % removal and 41.7 mg/kg or 35.5 % removal respectively were insignificant ($p \geq 0.05$) compared to means of 22.9 mg/kg or 63.6 % removal, 38.9 mg/kg or 38.8 % removal and 40.9 mg/kg or 36.8 % removal in solarized, un-amended and un-vegetated counterpart (F) at day 28. Phenanthrene, fluoranthene and benzo[a]pyrene insignificant reductions ($p \geq 0.05$) also occurred with means of 55.7 mg/kg or 11.5 % removal, 50.7 mg/kg or 20.3 % removal and 47.4 mg/kg or 26.7 % removal respectively in non-solarized and biosurfactant-amended un-vegetated treatment (G) compared to means of 52.8 mg/kg or 16.2 % removal, 55.1 mg/kg or 13.3 % removal and 57.9 mg/kg or 10.5 % removal in non-solarized, un-amended and un-vegetated counterpart (H) at day 28 as shown in Figure 4.6a (Appendix xii).

4.3.2.2.2 Effects of biosurfactant post-solarization on phenanthrene removal

The effect of biosurfactant on PAHs reduction continues to be insignificant ($p \geq 0.05$) although with some varied negligible reductions throughout the study period. Phenanthrene had a reduced PAH with insignificant difference ($p \geq 0.05$) between solarized and biosurfactant-amended vegetated treatment (A) with means of 4.42 mg/kg or 93.0 % removal, 1.89 mg/kg or 97.0 % removal and 0.00 mg/kg or 100 % removal and solarized and un-amended vegetated counterpart treatment (B) with means of 8.66 mg/kg or 86.2 % removal, 3.75 mg/kg or 94.0 % removal and 0.00 mg/kg or 100 % removal at days 56, 84 and 112 respectively as shown in Figure 4.7a. Mean reductions of 21.7 mg/kg or 65.5 % removal, 17.5 mg/kg or 72.2 % removal and 7.62 mg/kg or 87.9 % removal in non-solarized and biosurfactant-amended vegetated treatment (C) were not significantly impacted ($p \geq 0.05$) by biosurfactant with means of 31.4 mg/kg or 50.1 % removal, 19.8 mg/kg or 68.5 % removal and 9.19 mg/kg or 85.4 % removal in non-solarized and un-amended vegetated treatment (D) at days 56, 84 and 112 respectively as shown in Figure 4.7a. The un-vegetated treatment groups with or without biosurfactant amendment displayed identical trend with a relatively less reduced phenanthrene with means of 19.7 mg/kg or 68.7 % removal, 15.2 mg/kg or 75.9 % removal and 9.22 mg/kg or 85.3 % removal in solarized and biosurfactant-amended un-vegetated treatment (E) compared to mean reductions of 22.1 mg/kg or 64.9 % removal, 18.3 mg/kg or 70.9 % removal and 15.5 mg/kg or 75.3 % removal in solarized, un-amended and un-vegetated counterpart (F) at days 56, 84 and 112 respectively as shown in Figure 4.7b. Mean reductions in non-solarized and biosurfactant-amended un-vegetated treatment (G) of 38.5 mg/kg or 38.8 % removal, 29.3 mg/kg or 53.5 % removal and 20.48 mg/kg or 72.8 % removal were also not significant ($p \geq 0.05$) from means of 37.6 mg/kg or 40.3 % removal, 35.7 mg/kg or 43.2 % removal and 27.3 mg/kg or 64.5 % removal in non-solarized, un-amended and un-vegetated counterpart (H) at days 56, 84 and 112 respectively (Figure 4.7b). Biosurfactant shows a general linear model for phenanthrene reduction with *p*-value, *t*- and *F*- statistics of 0.68, 0.41 and 0.17 with R-square (adjustment) of 84.3 % between biosurfactant-amended, vegetated/un-vegetated treatments (A, C, E and G) and un-amended vegetated/un-vegetated treatment counterparts (B, D, F and H) with or without solarization (Appendix xi).

4.3.2.2.3 Effects of biosurfactant post-solarization on fluoranthene removal

Biosurfact also had a negligible impact on fluoranthene reduction with insignificant ($p \geq 0.05$) means of 14.2 mg/kg or 77.6 % removal, 2.76 mg/kg or 95.7 % removal and 0.00

mg/kg or 100 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to mean reductions of 16.6 mg/kg or 74.0 % removal, 4.20 mg/kg or 93.4 % removal and 0.00 mg/kg or 100 % removal in solarized and un-amended vegetated counterpart (B) at days 56, 84 and 112 respectively as shown in Figure 4.8a. Means of 20.2 mg/kg or 68.2 % removal, 10.1 mg/kg or 84.2 % removal and 10.4 mg/kg or 83.6 % removal in non-solarized and biosurfactant-amended vegetated counterpart (C) was not different significantly ($p \geq 0.05$) from means of 30.3 mg/kg or 52.3 % removal, 15.8 mg/kg or 75.2 % removal and 11.2 mg/kg or 82.36 % removal in non-solarized and un-amended vegetated treatment (D) at days 56, 84 and 112 respectively as shown in Figure 4.8a. There was a relatively reduced fluoranthene in the un-vegetated treatment groups with or without biosurfactant amendment with means of 26.4 mg/kg or 58.4 % removal, 18.9 mg/kg or 70.2 % removal and 12.8 mg/kg or 79.8 % removal in solarized and biosurfactant-amended un-vegetated treatment (E) compared to mean reductions of 26.2 mg/kg or 58.7 % removal, 19.4 mg/kg or 69.5 % removal and 17.3 mg/kg or 72.8 % removal in solarized, un-amended and un-vegetated treatment counterpart (F) at days 56, 84 and 112 respectively as shown in Figure 4.8b. This is also the case with means of 41.8 mg/kg or 34.2 % removal, 37.5 mg/kg or 41.0 % removal and 23.4 mg/kg or 63.3 % removal in non-solarized and biosurfactant-amended un-vegetated (G) compared to means of 47.5 mg/kg or 25.4 % removal, 36.0 mg/kg or 43.4 % removal and 25.8 mg/kg or 55.8 % removal in non-solarized, un-amended and un-vegetated counterpart (H) at days 56, 84 and 112 respectively as shown in Figure 4.8b. Biosurfactant did not impact on fluoranthene reduction between biosurfactant-amended, vegetated/un-vegetated treatments (A, C, E and G) and un-amended, vegetated/un-vegetated treatments (B, D, F and H) with or without solarization with *p*-value, *t*- and *F*- statistics of 0.34, 0.97 and 0.95 with R-square (adjustment) of 88.5 % using a general linear model (Appendix xi).

4.3.2.2.4 Effects of biosurfactant post-solarization on benzo[a]pyrene removal

Benzo[a]pyrene which was the least reduced PAH was not impacted at all by biosurfactant with means of 23.3 mg/kg or 64.0 % removal, 10.8 mg/kg or 83.3 % removal and 7.28 mg/kg or 88.7 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to mean reductions of 26.0 mg/kg or 59.9 % removal, 12.6 mg/kg or 80.5 % removal and 8.29 mg/kg or 87.2 % removal in solarized and un-amended vegetated counterpart (B) at days 56, 84 and 112 respectively as shown in Figure 4.9a. Non-solarized and biosurfactant-amended vegetated treatment (C) with mean reductions of 30.2 mg/kg or 53.3 % removal, 20.6

mg/kg or 68.1 % removal and 17.0 mg/kg or 73.8 % removal were not different significantly ($p \geq 0.05$) from means of 39.2 mg/kg or 39.4 % removal, 27.4 mg/kg or 57.7 % removal and 21.3 mg/kg or 67.1 % removal in non-solarized and un-amended vegetated counterpart (D) at days 56, 84 and 112 respectively as shown in Figure 4.9a. The un-vegetated treatment groups with or without biosurfactant amendment also showed no difference in benzo[a]pyrene reduction with means of 38.7 mg/kg or 40.1 % removal, 31.3 mg/kg or 51.6 % removal and 21.8 mg/kg or 66.3 % removal in solarized and biosurfactant-amended un-vegetated treatment (E) compared to means reduction of 36.5 mg/kg or 43.5 % removal, 29.5 mg/kg or 54.3 % removal and 27.5 mg/kg or 57.5 % removal in solarized, un-amended and un-vegetated treatment counterpart (F) at days 56, 84 and 112 respectively as shown in Figure 4.9b. Similarly, means of 40.5 mg/kg or 37.4 % removal, 32.0 mg/kg or 50.5 % removal and 32.6 mg/kg or 49.6 % removal in non-solarized and biosurfactant-amended un-vegetated treatment (G) were insignificant ($p \geq 0.05$) with means of 58.2 mg/kg or 10.0 % removal, 39.4 mg/kg or 39.1 % removal and 34.0 mg/kg or 47.5 % removal in non-solarized, un-amended and un-vegetated counterpart (H) at days 56, 84 and 112 respectively as shown in Figure 4.9b. Statistically, the impact of biosurfactant was not significant ($p \geq 0.05$) in the reduction of benzo[a]pyrene with *p*-value, *t*- and *F*-statistics of 0.08, 1.79 and 3.21 with R-square (adjustment) of 87.5 % between biosurfactant-amended, vegetated/un-vegetated treatments (A, C, E and G) and un-amended, vegetated/un-vegetated treatments (B, D, F and H) with or without solarization using a general linear model (Appendix xi).

4.3.2.2.5 Effects of biosurfactant post-solarization on total PAHs removal

The effect of biosurfactant was observed to be ineffective in total PAH (phenanthrene, fluoranthene and benzo[a]pyrene) reduction with 41.9 mg/kg or 78.1 % removal, 15.4 mg/kg or 91.9 % removal and 7.28 mg/kg or 96.2 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to reductions of 50.5 mg/kg or 73.6 % removal, 20.6 mg/kg or 89.2 % removal and 8.29 mg/kg or 95.7 % removal in solarized and un-amended vegetated treatment counterpart (B) at days 56, 84 and 112 respectively as shown in Figure 4.10a. The mean reductions of total PAHs with 72.1 mg/kg or 62.3 % removal, 48.2 mg/kg or 74.8 % removal and 35.0 mg/kg or 81.7 % removal in non-solarized and biosurfactant-amended vegetated counterpart (C) were insignificant ($p \geq 0.05$) in comparison to the means of 100.9 mg/kg or 47.2 % removal, 63.0 mg/kg or 67.1 % removal and 41.7 mg/kg or 78.2 % removal in non-solarized and un-amended vegetated treatment (D) at days 56, 84 and 112 respectively

as shown in Figure 4.10a. A negligible and insignificant reduction ($p \geq 0.05$) in total PAHs also occurred in solarized and biosurfactant-amended un-vegetated treatment (E) with means of 84.9 mg/kg or 55.6 % removal, 65.4 mg/kg or 65.8 % removal and 43.9 mg/kg or 77.1 % removal compared with means of 84.9 mg/kg or 55.6 % removal, 64.3 mg/kg or 66.4 % removal and 60.31 mg/kg or 68.5 % removal in solarized, un-amended and un-vegetated treatment counterpart (F) at days 56, 84 and 112 respectively as shown in Figure 4.10b. PAHs mean reductions of 120.8 mg/kg or 36.8 % removal, 98.8 mg/kg or 48.3 % removal and 76.5 mg/kg or 60.0 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) were not impacted by biosurfactant when compared with means of 143.8 mg/kg or 24.8 % removal, 111.2 mg/kg or 41.9 % removal and 87.1 mg/kg or 54.4 % removal in non-solarized, un-amended and un-vegetated counterpart (H) at days 56, 84 and 112 respectively as shown in Figure 4.10b. There was no statistical significance ($p \geq 0.05$) in the reduction of total PAH mixtures with *p*-value, *t*- and *F*- statistics of 0.30, 1.06 and 1.13 with R-square (adjustment) of 88.4 % using a general linear model between biosurfactant-amended, vegetated/un-vegetated treatments (A, C, E and G) and un-amended, vegetated/un-vegetated treatments (B, D, F and H) with or without solarization (Appendix xi). Phenanthrene, fluoranthene and benzo[a]pyrene were not impacted in their % removal by biosurfactant and in combined forms over time as shown in the box plots of Figure 4.12 and Figure 4.16 respectively.

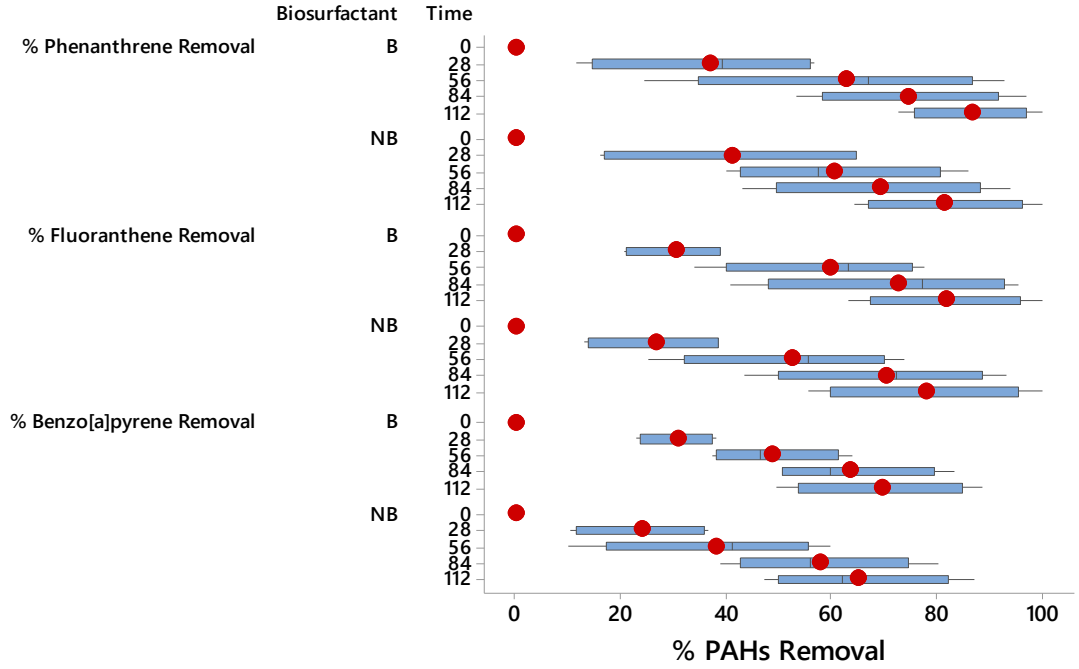


Figure 4.12: Impact of biosurfactant on % removal of phenanthrene, fluoranthene and benzo[a]pyrene.

Key:
S = Solarized
NS = Non-solarized
B = Biosurfactant
NB = No Biosurfactant

4.3.2.2.6 Statistical conclusion on the effects of biosurfactant on PAHs removal

Generally, an investigation of the *p*-value, *t*- and *F*- statistics as highlighted for the individual and combined PAHs (also see Table 18) by the general linear model show an overall insignificance ($p \geq 0.05$) in PAHs reduction by biosurfactant with insufficient evidence against the H_o. Suggesting no linear association between biosurfactant and PAHs reduction/removal i.e. biosurfactant did not impact significantly on the removal of either phenanthrene, fluoranthene, benzo[a]pyrene or total PAHs (Appendix xi). As a consequence, the second research hypothesis (H_0) which states that ***'there is no genuine difference in advance phytoremediation between biosurfactant-amended and un-amended treatments in PAHs reduction of contaminated soil'*** (see Section 1.7.1) is accepted with insufficient evidence against the H_0. (Table 18 and Appendix xi).

4.3.2.2.7 Discussion on the negligible impact of biosurfactant on PAHs removal

This result seems to be in sharp contrast with a vast body of literatures on the significant role biosurfactant plays in the removal of PAHs from contaminated soil (Cheng *et al*., 2018; Gao *et al*., 2007; Liang *et al*., 2017; Shah *et al*., 2016). Generally, low level of dissipation of PAHs in phytoremediation is as a result of low bioavailability of the PAHs. Increase in the PAHs bioavailability usually enhance the degradation efficiency of PAHs by soil microorganisms. Biosurfactants generally increase the desorption of PAHs from soils to the aqueous phase as demonstrated in Figure 2.17c thereby increasing PAHs bioavailability. Contrary to the findings of this study, it has been reported that enhanced PAHs degradation during phytoremediation can be due to biosurfactant desorption ability and microbial activity in soil (Liang *et al*., 2017; Liao *et al*., 2015). Zhang *et al.* (2010) reported that the mean removal efficiency of total PAHs was 61 % and fluoranthene, pyrene, benzo[a]pyrene removal efficiencies were 89.4, 88.4, 92.3 % respectively at 90 days of rhamnolipids surfactant enhancement, whereas in the absence of biosurfactant only 17 % PAHs was removed from an initial concentration of 12.9 g/kg. However both treatments occurred in the presence of arbuscular mycorrhizal fungal and microbial consortium of PAH degraders. Pei *et al.* (2010) reported a 99.5 % phenethrene removal within 10 days in the presence of rhamnolipid biosurfactant as against 83.6 % in biosurfactant absence from an initial concentration of 1.0 g/l, although, treatments had *Sphingomonas speices* (GF2B). In constrast, this study did not demonstrate significant impact of biosurfactant on PAHs removal in contaminated soil (see objective v in Section 1.6.2) and this may be attributed to the deactivation/denaturing of the rhamnolipid biosurfactant by the relatively high soil temperatures recorded for both solarized and non-solarized treatments especially during the 28 days solarization periods. This is in line with a report by Lamichhane *et al.* (2017) that surfactant assisted solubility of PAHs is proportional to the temperature up to a certain extent. According to Li *et al.* (2015b) the effect of rhamnolipid biosurfactant on the solubility of naphthalene, phenanthrene and pyrene increased with temperature up to 30^{o}C. A similar study was carried out by Peng *et al.* (2015) to investigate rhamnolipid biosurfactant-enhanced remediation of PAHs at a temperature range of 15 to 50^{o}C and reported an optimum temperature of 35^{o}C for PAH degradation with anthracene and pyrene degradation of 37.5 and 25.6 % respectively at 35^{o} C. However, contrary to the above findings, Peng *et al.* (2011) observed PAH removal performance not affected with the use of surfactant at temperature between 10 and 40^{o}C, and Zhou *et al.* (2019) reported that

temperature had little effect on rhamnolipid biosurfactant performance in a broad range from 20 to 80 ^{o}C.

Nonetheless, in previous experiment in this study, the impact of rhamnolipid biosurfactant was significant in the removal of PAHs from both *C. odorata* and *Medicago sativa* biosurfactant-amended treatments compared to their un-amended counterparts (see Section 3.4.2) in which the H_1 was accepted stating ***'there was a genuine difference in phytoremediation between biosurfactant-amended and un-amended treatments in PAHs reduction of contaminated soil'*** (see Section 1.7.1). Although, recent studies have also shown that bound and residual PAHs fractions can be transferred and remobilized owing to changes in the environment (Gao *et al*., 2017; Gao *et al*., 2013; Wang *et al*., 2017) and bound residues release could result to the increase of bioavailable PAHs for dissipation. This residual dissipation as demonstrated in this study is not attributed to biosurfactant but to soil solarization due to an increase in the soil temperature. According to Ghosal *et al.* (2016) and Margesin and Schinner (2001) when temperature increases, PAHs solubility also increases, resulting to increase in the bioavailability of PAH molecules for subsequent dissipation. Consequently it is important to investigate bioavailable PAHs fractions and other fractions of PAH residuals in soil to better appreciate PAHs dynamics in contaminated soil (Lu *et al.,* 2019).

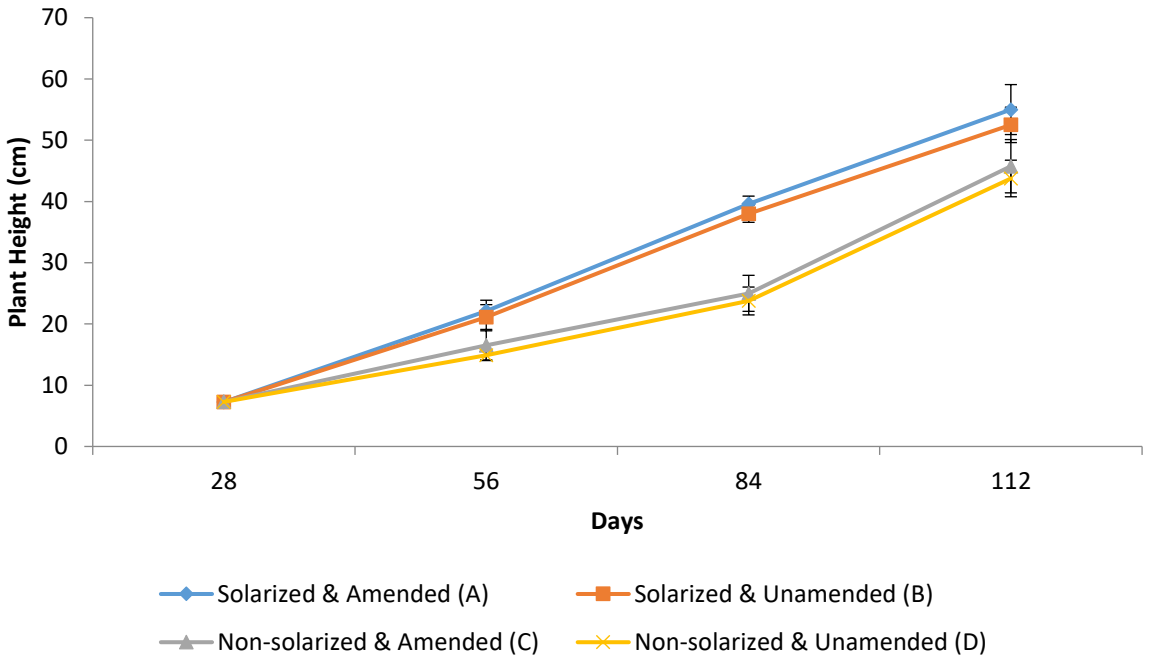
4.3.2.3 Phytoremediation (*C. odorata*) effects on PAHs removal

4.3.2.3.1 Effects of *C. odorata* on phenanthrene removal

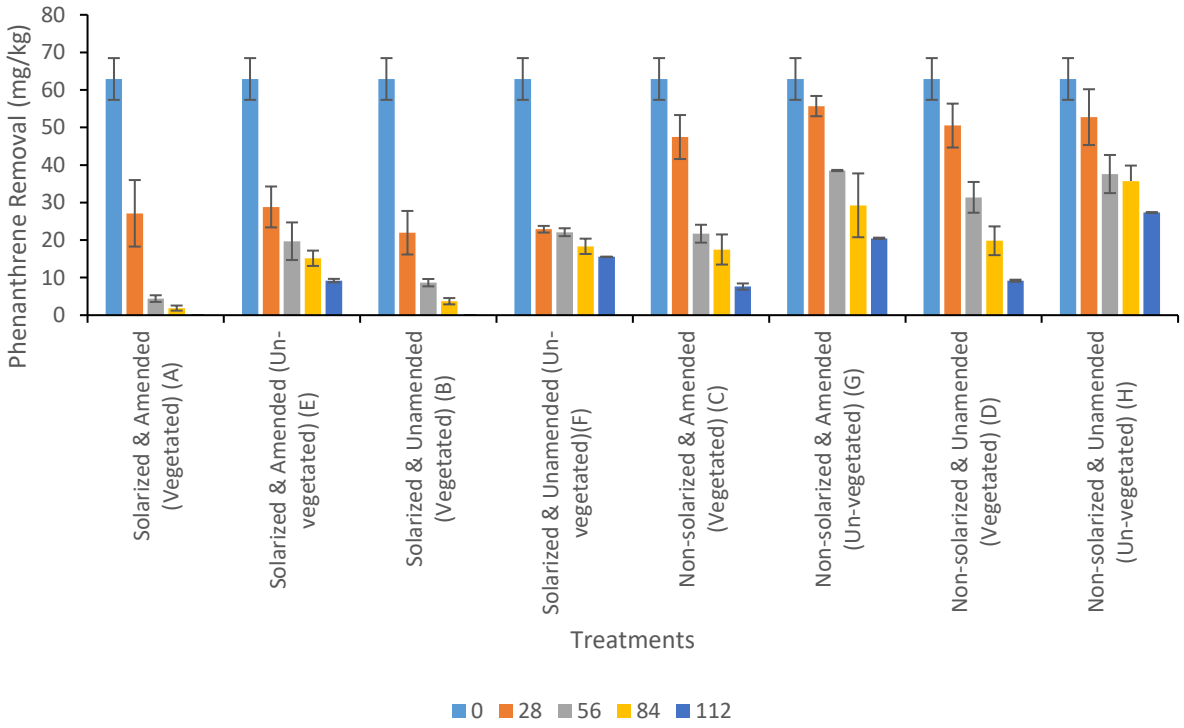
The indigenous *C. odorata* after transplanting continued to thrive without sign or symptom of phytotoxicity in respect to the various treatments throughout the phytoremediation duration. However, plants grown in the solarized treatment look healthier and outgrew the growth space provided in the microcosm faster than their non-solarized counterparts. The shoot tips of the solarized plant began to be irritated by the transparent plastic dome cover of the microcosm (see Plates 1.6b and 1.14) as there was no more room to accommodate the plant growth. This led to the termination of the phytoremediation period at day 112 and also created a short window for the non-solarized plants to catch up in height as shown in Figure 4.13a.

PAH mixtures were reduced significantly ($p \leq 0.01$) in all the vegetated treatment groups compared to their un-vegetated counterparts with or without solarization and biosurfactant-amendment. Phenanthrene was the most reduced PAH with means of 4.42 mg/kg or 93.0 % removal, 1.89 mg/kg or 97.0 % removal and 0.00 mg/kg or 100 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to mean reductions of 19.7 mg/kg or

68.7 % removal, 15.2 mg/kg or 75.9 % removal and 9.22 mg/kg or 85.3 % removal in solarized and biosurfactant-amended un-vegetated counterpart treatment (E) at days 56, 84 and 112 respectively as shown in Figure 4.13b. Significant reduction ($p \leq 0.01$) of phenanthrene also took place in solarized and un-amended vegetated treatment (B) with mean reductions of 8.66 mg/kg or 86.2 % removal, 3.75 mg/kg or 94.0 % removal and 0.00 mg/kg or 100 % removal compared with reduction means of 22.1 mg/kg or 64.9 % removal, 18.3 mg/kg or 70.9 % removal and 15.5 mg/kg or 75.3 % removal in solarized, un-amended and un-vegetated treatment counterpart (F) at days 56, 84 and 112 respectively as shown in Figure 4.12b. Mean reductions of phenanthrene in non-solarized and biosurfactant-amended vegetated treatment (C) with 21.7 mg/kg or 65.5 % removal, 17.5 mg/kg or 72.2 % removal and 7.62 mg/kg or 87.9 % removal were significantly different in reduction ($p \leq 0.01$) compared to mean reductions of 38.5 mg/kg or 38.8 % removal, 29.3 mg/kg or 53.5 % removal and 20.48 mg/kg or 72.8 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.13b. Means reduction of phenanthrene in non-solarized and un-amended vegetated treatment (D) with 31.4 mg/kg or 50.1 % removal, 19.8 mg/kg or 68.5 % removal and 9.20 mg/kg or 85.4 % removal were also significantly reduced ($p \leq 0.01$) compared to their counterpart treatment with means of 37.6 mg/kg or 40.2 % removal, 35.7 mg/kg or 43.3 % removal and 27.3 mg/kg or 56.6 % removal in non-solarized, un-amended and un-vegetated treatment (H) at days 56, 84 and 112 respectively as shown in Figure 4.13b. A general linear model (GLM) shows that *C. odorata* had a statistical significance in the reduction of phenenthrene with *p*-value, *t*- and *F*- statistics of 0.00, 3.27 and 10.71 with R-square (adjustment) of 84.3 % between vegetated (A, B, C and D) and un-vegetated (E, F, G and H) treatment groups with or without solarization and biosurfactant amendment. The coefficient shows that phenanthrene will be reduced by 7.0 % in the presence of *C. odorata*, while solarization and biosurfactant are held constant (Table 18 and Appendix xi).



(a)



(b)

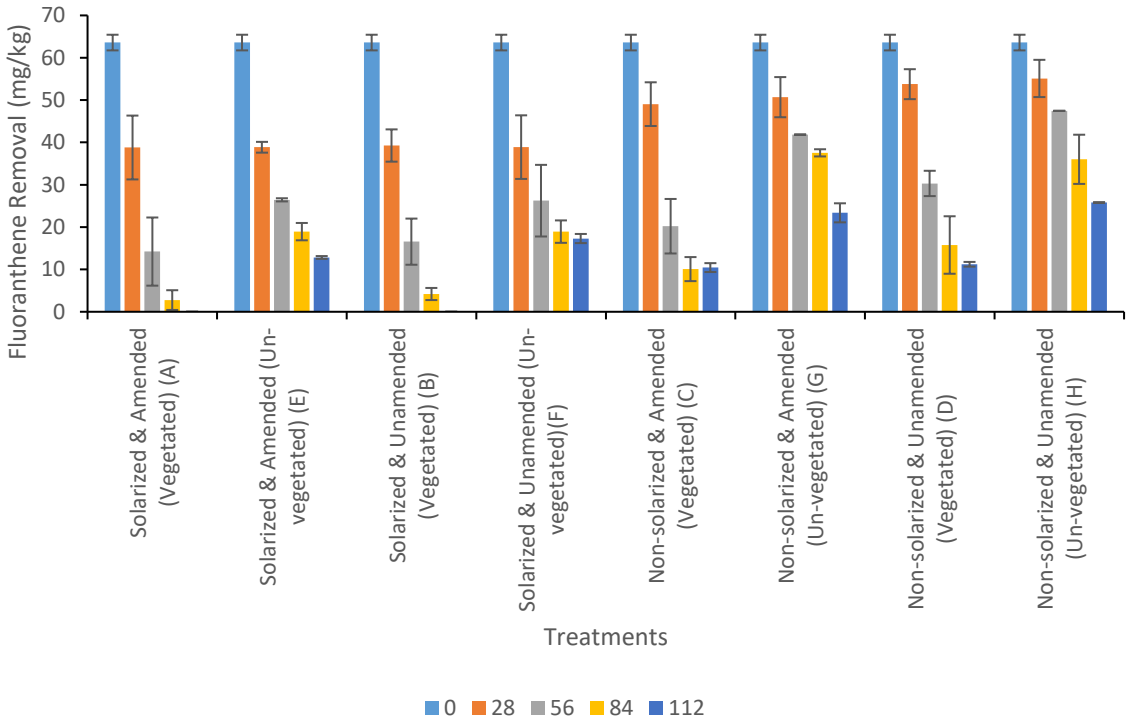
Figure 4.13(a-b): (a) Plant growth from seedlings to harvest and (b) *Chromolaena odorata* effect on phytoremediation of PAH mixtures in phenanthrene reduction with or without solarization and/or biosurfactant. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

4.3.2.3.2 Effects of *C. odorata* on fluoranthene removal

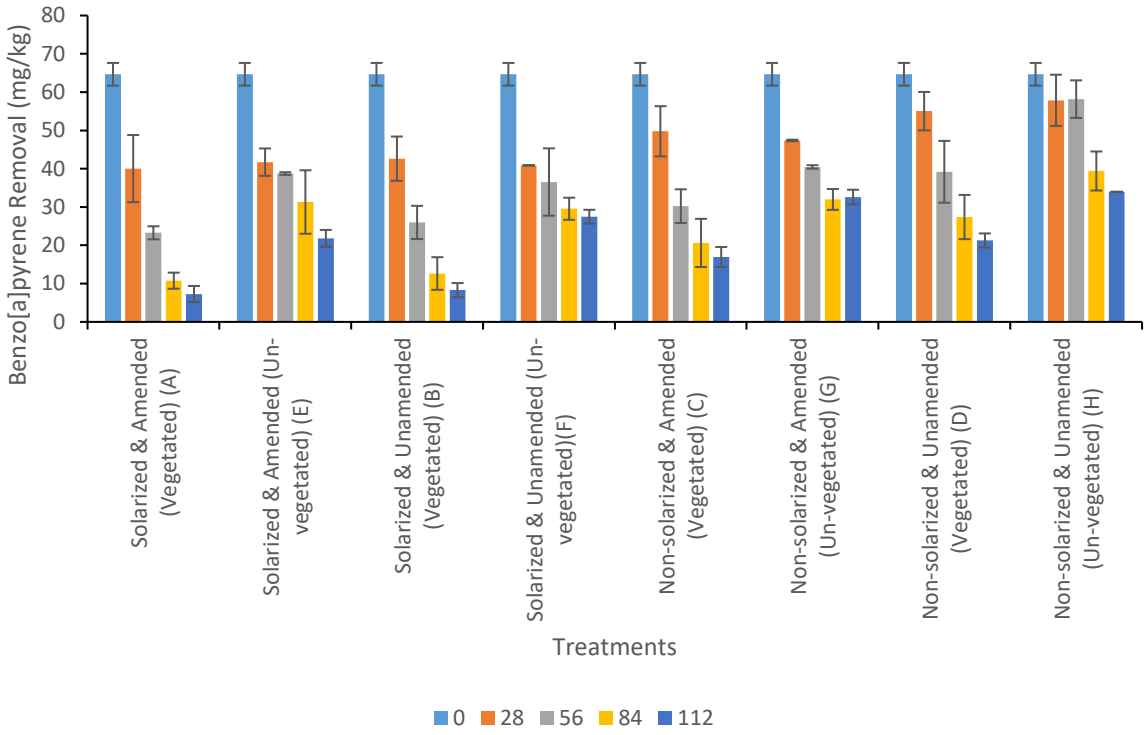
Fluoranthene removal was significantly impacted ($p \leq 0.01$) by the plant during phytoremediation with mean reductions of 14.2 mg/kg or 77.6 % removal, 2.76 mg/kg or 95.7 % removal and 0.00 mg/kg or 100 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to mean reductions of 26.4 mg/kg or 58.4 % removal, 18.9 mg/kg or 70.2 % removal and 12.8 mg/kg or 79.8 % removal in solarized and biosurfactant-amended un-vegetated counterpart (E) at days 56, 84 and 112 respectively as shown in Figure 4.14a. Solarized and un-amended vegetated treatment (B) showed significant reduction ($p \leq 0.01$) in fluoranthene with means of 16.6 mg/kg or74.0 % removal, 4.20 mg/kg or 93.4 % removal and 0.00 mg/kg or 100 % removal compared with mean reductions of 26.2 mg/kg or 58.7 % removal, 19.4 mg/kg or 69.5 % removal and 17.3 mg/kg or 72.8 % removal in solarized, un-amended and un-vegetated counterpart (F) at days 56, 84 and 112 respectively as shown in Figure 4.14a. Means of 20.2 mg/kg or 68.2 % removal, 10.1 mg/kg or 84.2 % removal and 10.4 mg/kg or 83.6 % removal in non-solarized and biosurfactant-amended vegetated counterpart (C) were significant in fluoranthene ($p \leq 0.01$) reduction compared to means of 41.8 mg/kg or 34.2 % removal, 37.5 mg/kg or 41.0 % removal and 23.4 mg/kg or 63.3 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.14a. Means reduction of fluoranthene in non-solarized and un-amended vegetated treatment (D) with 30.3 mg/kg or 52.3 % removal, 15.8 mg/kg or 75.2 % removal and 11.2 mg/kg or 82.36 % removal were also significantly reduced ($p \leq 0.01$) compared to their counterpart treatment with means of 47.5 mg/kg or 25.4 % removal, 36.0 mg/kg or 43.4 % removal and 25.8 mg/kg or 55.8 % removal in non-solarized, un-amended and un-vegetated treatment (H) at days 56, 84 and 112 respectively as shown in Figure 4.14a. Fluoranthene reduction between vegetated (A, B, C and D) and un-vegetated (E, F, G and H) treatment groups with or without solarization and biosurfactant amendment had a statistical significant reduction with *p*-value, *t*- and *F*- statistics of 0.00, 4.49 and 20.16 with R-square (adjustment) of 88.5 % using a general linear model. The coefficient shows that fluoranthene will be reduced by 8.0 % in the presence of *C. odorata,* while solarization and biosurfactant are held constant (Table 18 and Appendix xi).

4.3.2.3.3 Effects of *C. odorata* on benzo[a]pyrene removal

Phytoremediation effect by *C. odorata* was significantly observed ($p \leq 0.01$) in the reduction of benzo[a]pyrene with means of 23.3 mg/kg or 64.0 % removal, 10.8 mg/kg or 83.3 % removal and 7.28 mg/kg or 88.7 % removal in solarized and biosurfactant-amended vegetated treatment (A) compared to mean reductions of 38.7 mg/kg or 40.1 % removal, 31.3 mg/kg or 51.6 % removal and 21.8 mg/kg or 66.3 % removal in solarized and biosurfactant-amended un-vegetated counterpart treatment (E) at days 56, 84 and 112 respectively as shown in Figure 4.14b. Solarized and un-amended vegetated treatment (B) showed significant reduction ($p \leq 0.01$) in benzo[a]pyrene with means of 26.0 mg/kg or 59.9 % removal, 12.6 mg/kg or 80.5 % removal and 8.29 mg/kg or 87.2 % removal compared with means of 36.5 mg/kg or 43.5 % removal, 29.5 mg/kg or 54.3 % removal and 27.5 mg/kg or 57.5 % removal in solarized, un-amended and un-vegetated treatment (F) at days 56, 84 and 112 respectively as shown in Figure 4.14b. In non-solarized and biosurfactant-amended vegetated counterpart (C) with means of 30.2 mg/kg or 53.3 % removal, 20.6 mg/kg or 68.1 % removal and 17.0 mg/kg or 73.8 % removal, benzo[a]pyrene were significantly reduced ($p \leq 0.01$) when compared with means of 40.5 mg/kg or 37.4 % removal, 32.0 mg/kg or 50.5 % removal and 32.6 mg/kg or 49.6 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.14b. *C. odorata* was also successful in the phytoremediation of benzo[a]pyrene in non-solarized and un-amended vegetated treatment (D) with 39.2 mg/kg or 39.4 % removal, 27.4 mg/kg or 57.7 % removal and 21.3 mg/kg or 67.1 % removal compared to its non-solarized, un-amended and un-vegetated counterpart (H) with means of 58.2 mg/kg or 10.0 % removal, 39.4 mg/kg or 39.1 % removal and 34.0 mg/kg or 47.5 % removal at days 56, 84 and 112 respectively (Figure 4.14b). The reduction of benzo[a]pyrene using a general linear model showed a statistical significance with *p*-value, *t*- and *F*-statistics of 0.00, 4.49 and 20.15 with R-square (adjustment) of 87.5 % between vegetated (A, B, C and D) and un-vegetated (E, F, G and H) treatment groups with or without solarization and biosurfactant amendment. The coefficient shows that benzo[a]pyrene will be reduced by 6.9 % in the presence of *C. odorata*, while solarization and biosurfactant are held constant (Table 18 and Appendix xi).



(a)



(b)

Figure 4.14(a-b): *Chromolaena odorata* effect on phytoremediation of PAH mixtures in (a) fluoranthene reduction and (b) benzo[a]pyrene reduction with or without solarization and/or biosurfactant. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

4.3.2.3.4 Effects of *C. odorata* on total PAHs removal

The effect of vegetation also impacted on the total PAH (phenanthrene, fluoranthene and benzo[a]pyrene) with significant reduction ($p \leq 0.01$) between solarized and biosurfactant-amended vegetated treatment (A) with 41.9 mg/kg or 78.1 % removal, 15.4 mg/kg or 91.9 % removal and 7.28 mg/kg or 96.2 % removal and solarized and biosurfactant-amended un-vegetated treatment (E) with 84.9 mg/kg or 55.6 % removal, 65.4 mg/kg or 65.8 % removal and 43.9 mg/kg or 77.1 % removal at days 56, 84 and 112 respectively as shown in Figure 4.15a. Solarized and un-amended vegetated treatment (B) showed significant reduction ($p \leq 0.01$) in total PAHs with 50.5 mg/kg or 73.6 % removal, 20.6 mg/kg or 89.2 % removal and 8.29 mg/kg or 95.7 % removal compared with mean reductions of 84.9 mg/kg or 55.6 % removal, 64.3 mg/kg or 66.4 % removal and 60.31 mg/kg or 68.5 % removal in solarized, un-amended and un-vegetated treatment (F) at days 56, 84 and 112 respectively as shown in Figure 4.15a. Non-solarized and biosurfactant-amended vegetated treatment (C) with reduced means of 72.1 mg/kg or 62.3 % removal, 48.2 mg/kg or 74.8 % removal and 35.0 mg/kg or 81.7 % removal were statistically significant ($p \leq 0.01$) in total PAH reduction compare to means of 120.8 mg/kg or 36.8 % removal, 98.8 mg/kg or 48.3 % removal and 76.5 mg/kg or 60.0 % removal in non-solarized and biosurfactant-amended un-vegetated counterpart (G) at days 56, 84 and 112 respectively as shown in Figure 4.15a. Total PAH reduction by plant was observed in non-solarized and un-amended vegetated treatment (D) with 100.9 mg/kg or 47.2 % removal, 63.0 mg/kg or 67.1 % removal and 41.7 mg/kg or 78.2 % removal compared with reduced means of 143.8 mg/kg or 24.8 % removal, 111.2 mg/kg or 41.9 % removal and 87.1 mg/kg or 54.4 % removal in non-solarized, un-amended and un-vegetated counterpart (H) with statistical significance ($p \leq 0.01$) at days 56, 84 and 112 respectively as shown in Figure 4.15a. There was a statistical significance in the reduction of total PAH mixtures with *p*-value, *t*- and *F*- statistics of 0.00, 4.33 and 18.75 with R-square (adjustment) of 88.4 % using a general linear model between vegetated (A, B, C and D) and un-vegetated (E, F, G and H) treatment groups with or without solarization and biosurfactant amendment. The coefficient shows that total PAHs will be reduced by 7.3 % in the presence of *C. odorata*, while solarization and biosurfactant are held constant (Table 18 and Appendix xi).

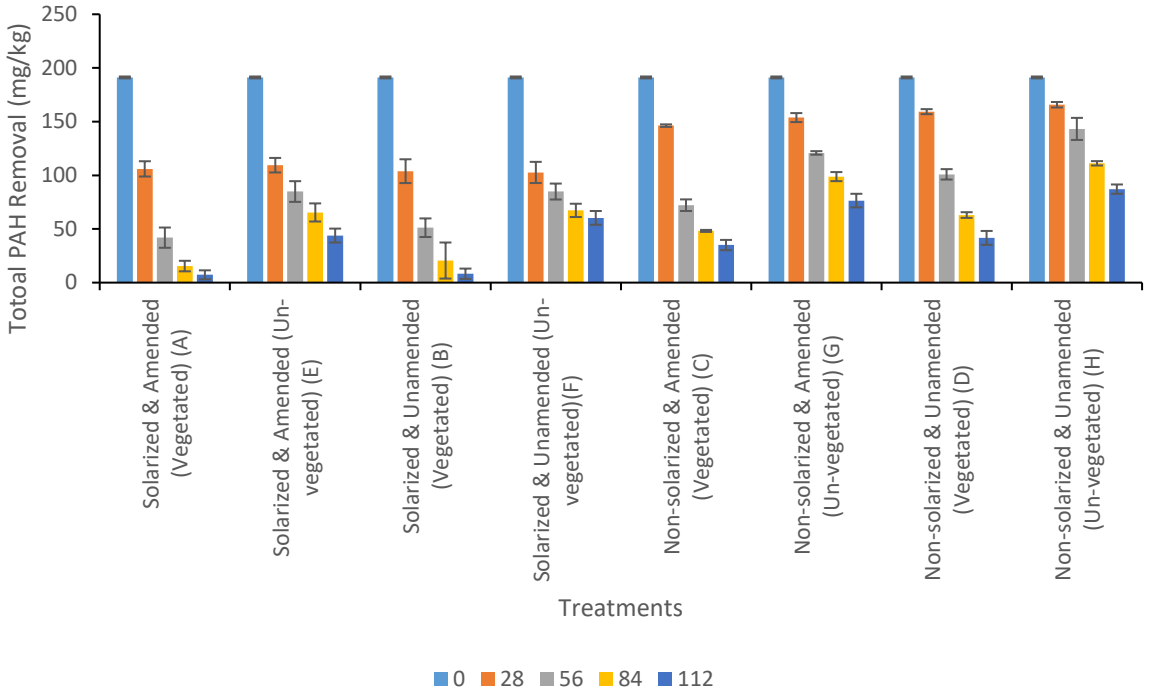
Box plots were used to show the exclusive impact of phytoremediation (plant) (Figure 4.15b) and in a combined treatment forms of solarization and biosurfactant (Figure 4.16) on the % removal of phenanthrene, fluoranthene and benzo[a]pyrene over time. From the box plot (Figure 4.15b), it can be seen that phytoremediation (vegetated treatment) had significant %

removal of the PAHs mixtures than their bioremediation (un-vegetated) counterparts both in terms of comparing their respective means and medians. The means and medians generally appear very close to each other for the two treatment groups suggesting a symmetrical or normal distribution of phenanthrene, fluoranthene and benzo[a]pyrene % removal. Phytoremediation showed a significant ($p \leq 0.01$) phenanthrene % removal with means of 77.6, 82.9 and 93.3 % in vegetated treatments compared to means of 49.6, 60.9 and 74.5 % in un-vegetated counterparts at days 56, 84 and 112 respectively. The impact of phytoremediation was also significant ($p \leq 0.01$) in fluoranthene % removal with 70.0, 87.1 and 91.5 % in vegetated treatments compared to their un-vegetated counterparts with means of 44.2, 56.0 and 67.9 % at days 56, 84 and 112 respectively. Phytoremediation was also effective on benzo[a]pyrene removal which was the least removed PAH with means of 56.1, 72.4 and 79.2 % removal compared to means of 32.8, 48.9 and 55.2 % removal for vegetated and un-vegetated treatments respectively at days 56, 84 and 112 consecutively as shown in Figure 4.14b.

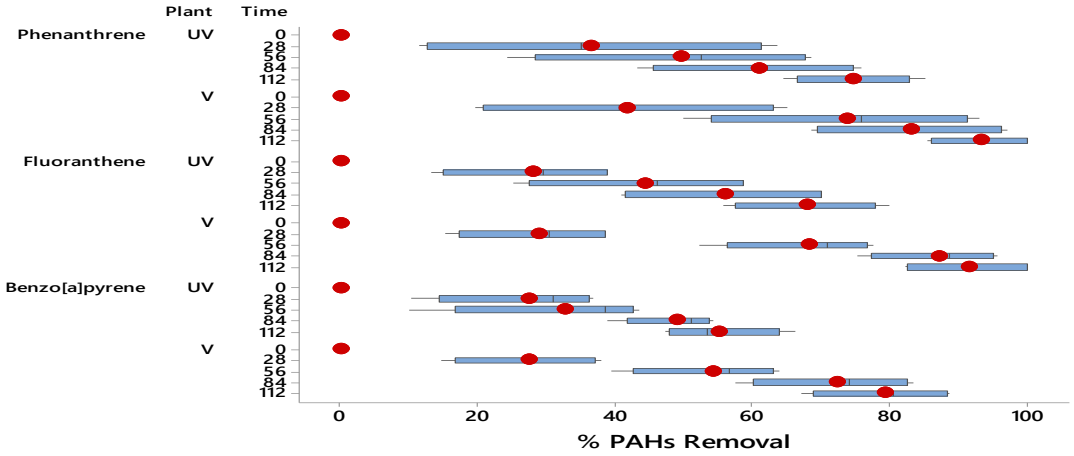
4.3.2.3.5 Statistical conclusion on the effects of phytoremediation (*C. odorata*) on PAHs removal

A general overview of the *t*-statistics for the individual coefficients as shown in Table 18 displays fluoranthene and benzo[a]pyrene with similar *t*-statistic of 4.49 and coefficient of 7.95 and 6.90 respectively with their associated *p*-value of 0.00. The overall significance in *p*-values shows that the H_o (coefficient = 0) is rejected with very strong evidence in favour of the H_1 (coefficient $\neq$ 0) and concludes that there is very strong evidence of a linear relationship between phytoremediation and the individual PAH mixtures reduction or % removal. The size of their respective coefficients also showed that *C. odorata* was the second most contributing factor to PAH removal after solarization The *F*-statistics of phenanthrene, fluoranthene and benzo[a]pyrene reductions of 10.71, 20.16 and 20.15 respectively with their corresponding *p*-values, also suggest a very strong evidence against H_o (which states that there is no linear relationship between response (i.e. PAH mixtures) and predictor variable (i.e. phytoremediation). Therefore, H_1 was accepted i.e. there is a linear relationship between phenanthrene, fluoranthene and benzo[a]pyrene reductions (response) and the phytoremedition predictor variable (*C. odorata*) which corresponded with the *t*-statistic of the model. The R-square (adjusted) which gives an estimate of what percentages of the total variation is explained by the general linear model for other observation from the overall population were 84.3, 88.5

and 87.5 % for phenanthrene, fluoranthene and benzo[a]pyrene respectively also suggest the existence of a linear relationship. The remaining 15.7, 11.5 and 12.5 % unexplained variations for phenanthrene, fluoranthene and benzo[a]pyrene respectively are shown in their respective residual analysis to check the model (Appendix xi).



(a)



(b)

Figure 4.15(a-b): (a) *Chromolaena odorata* effect on phytoremediation of total PAH reduction with or without solarization and/or biosurfactant and (b) impacts of phytoremediation (*C. odorata*) on % removal of phenanthrene, fluoranthene and benzo[a]pyrene. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

Key:
V = Vegetated
UV = Un-vegetated

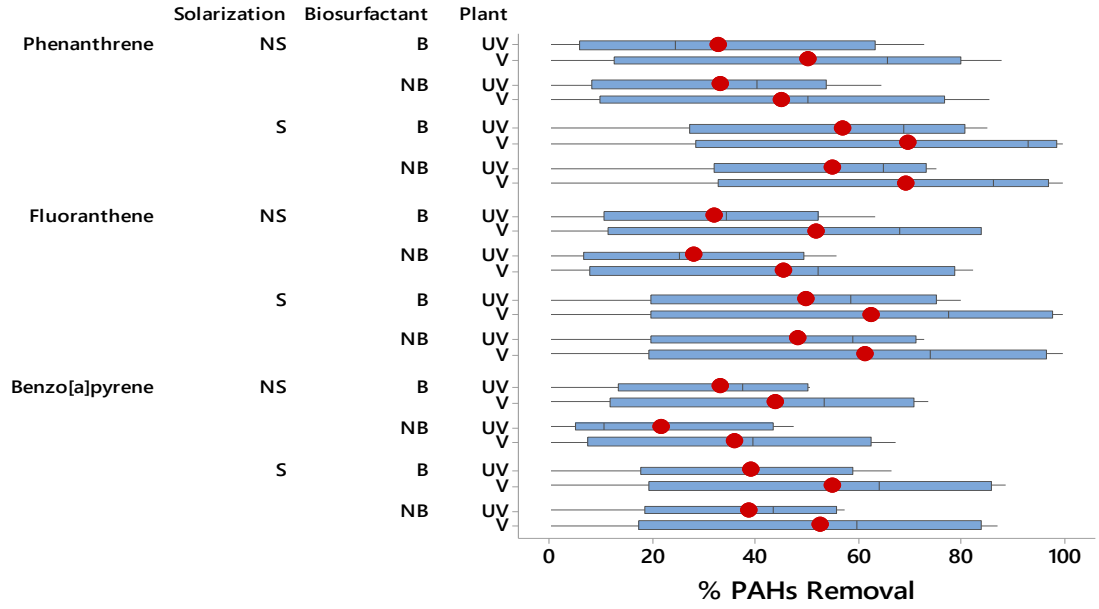


Figure 4.16: A combined impacts of solarization, biosurfactant and phytoremediation on % removal of phenanthrene, fluoranthene and benzo[a]pyrene respectively.
Key:
S = Solarized
NS= Non-solarized
B = Biosurfactant
NB = No Biosurfactant
V = Vegetated
UV = Un-vegetated

4.3.2.3.6 Discussion on the impact of phytoremediation (*C. odorata*) on PAHs removal

PAHs significant reductions in vegetated treatments against un-vegetated counterparts in this study is consistent with most studies. Huesemann *et al.* (2009) reported a 73 % reduction in total PAHs from vegetated sediments after 60 weeks but only 25 % in un-vegetated control; dissipation of benzo[a]pyrene was reported to be faster in vegetated soil than un-vegetated control (A'Ivarez-Bernal *et al.*, 2007); plant root maturity contributed to reduction in target PAH bioavailability (Parrish *et al.*, 2005); significant decrease in hydrocarbons concentration under vegetated conditions (Kaimi *et al.*, 2007) and all vegetated treatments resulted in higher remediation efficiency (Banks *et al.*, 2003).

The effect of phytoremediation on PAHs removal in this study may be attributed to the rhizosphere. There are numerous studies that have implicated rhizosphere-associated microorganisms in the remediation of PAHs contaminated soil (Khan *et al.*, 2013b; Liu *et al.*,

2015). According to Cheema *et al.* (2010) and Yu *et al.* (2011) PAHs dissipation can be significantly improved by the plant rhizosphere compared to unplanted soils and accelerated PAH removal basically attributed to the enhancement of bacterial activity; and diversity in the rhizosphere as a result of improved soil aeration, permeability, and break-up of soil aggregates that leads to increased bioavailability of PAH (Hamdi *et al.,* 2007). A large phenanthrene degrader population was observed in rhizosphere and associated to root debris and soil exudates as reported by Miya and Firestone (2001). Dzentor (2007) reported plants indirect involvement in PAHs degradation by stimulating the microbial community associated with its root. This can be achieved according to Dominguez *et al.* (2019) in multiple ways namely: (i) aeration of soil and microorganisms by plant resulting to enhance aerobic reaction (Anderson *et al*., 1993; Bisht *et al*., 2015); (ii) secretion of organic compounds such as sugar, organic acids, secondary metabolite etc. by plant that can stimulate microbial growth, select PAHs-degrading bacteria, and induce catabolic reactions of PAHs (Anderson *et al*., 1993; Balasubramaniyam, 2015; Rohrbacher and St-Arnaud, 2016); and lastly, increase in the bioavailability of PAHs by plants through physical and chemical means (Lefevre *et al*., 2013; Rohrbacher and St-Arnaud, 2016; Zhu *et al*., 2009). Thus it's not surprising that numerous PAHs rhizoremediation studies have be conducted and have been well established (Fu *et al*., 2012; Gaskin and Bentham, 2010; Khan *et al*., 2009; Kuiper *et al*., 2001 Reilley *et al*.,1996; Sivaram *et al*., 2018b; Su *et al*., 2008).

4.3.2.4 Leachate PAHs concentration and toxicity

PAHs concentrations of phenanthrene, fluoranthene and benzo[a]pyrene detected and quantified from the treatment groups at day 112 was presented in Figure 4.17. Generally, the combined leachate over the treatment period was clear and colourless. There was a reduction of PAHs concentration in vegetated treatment groups (A, B, C and D) compared to their non-vegetated counterparts irrespective of solarization and/or biosurfactant-amendment. Phenanthrene was the least detected PAHs with no significant difference ($p \geq 0.05$) between vegetated and un-vegetated treatments, followed by fluoranthene while benzo[a]pyrene was the most detected PAHs with significantly higher quantity in non-vegetated treatment range of 1.76 – 3.51 mg/l compared to vegetated range of 0.55 – 1.19 mg/l respective. The toxicity test result using MicrotoxOmni Test analyzer could not be determined probably due to the very low PAHs concentrations as the system recommended re-testing samples at higher concentrations, suggesting that the advancement of phytoremediation using solarization is eco-friendly and pose no risk to the ecosystem.

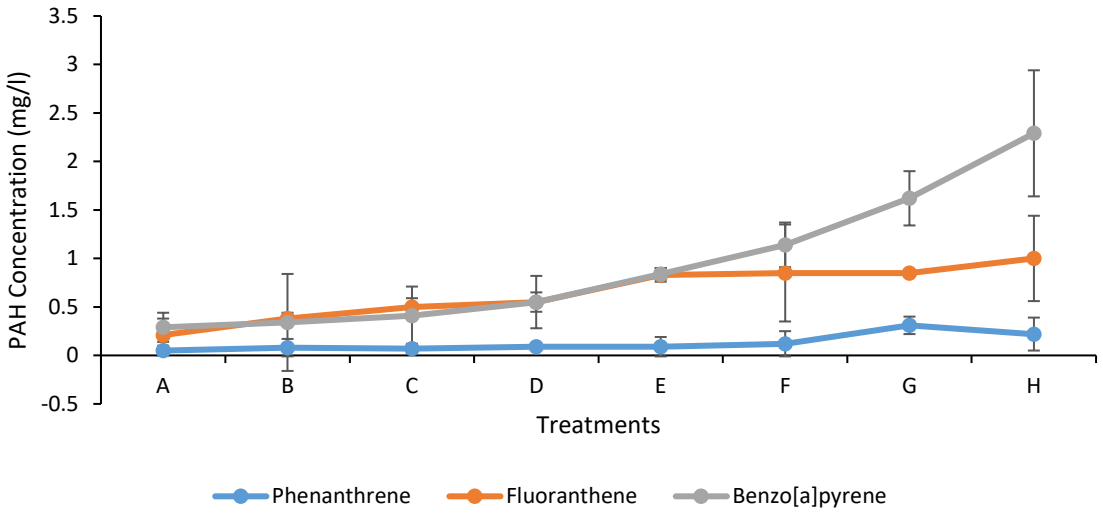


Figure 4.17: Leachate concentration of phenanthrene, fluoranthene and benzo[a]pyrene respectively. Error bars indicate mean ± S.D. of four and two sampled pots for vegetated and un-vegetated treatments respectively.

Key:
A = Solarized & amended (Vegetated)
B = Solarized & un-amended (Vegetated)
C = Non-solarized & amended (Vegetated)
D = Non-solarized & un-amended (Vegetated)
E = Solarized & amended (Un-vegetated)
F = Solarized & un-amended (Un-vegetated)
G = Non-solarized & amended (Un-vegetated)
H = Non-solarized & un-amended (Un-vegetated)

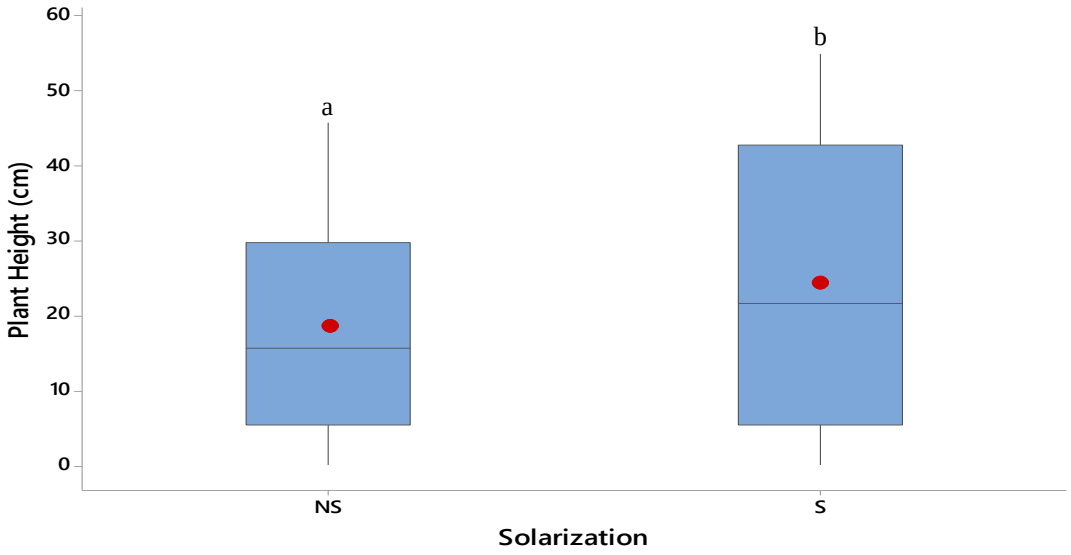
4.3.3 Treatments impacts on plant growth parameters

4.3.3.1 Soil solarization impacts on plant growth parameters

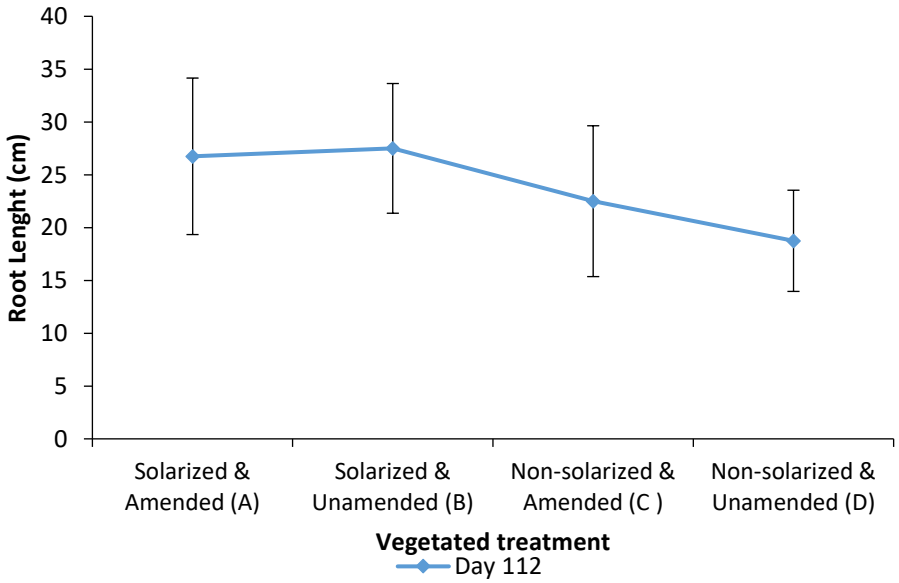
Statistically, there was insufficient evidence ($p \geq 0.05$) of any genuine difference against the H_o in the transplanting heights of *C. odorata* seedlings of the same age before transplanting at day 28 (i.e. samples come from populations with same mean, $\mu_1 = \mu_2$) with a *p*-value of 0.86 and *F*-statistic of 0.24 suggesting that *C. odorata* plants were randomly selected with no bias to their respective vegetated treatments (Appendix xiii). However, the impact of solarization significantly increased the plants growth throughout the phytoremediation period. The significant increase in heights of *C. odorata* was seen at the end of the post-solarization (phytoremediation) period in solarized and biosurfactant-amended vegetated treatment (A) with a mean height of 47.8±3.88 cm compared to a mean height of 38.45±4.23 from non-solarized and biosurfactant-amended vegetated counterpart (C) from a transplanting mean height of 7.25±0.29 and 7.38±0.15 cm respectively. Post-solarization also impacted significantly on the height of *C. odorata* in solarized and un-amended vegetated treatment (B) compared to plants' height in non-solarized and un-amended vegetated treatment (D) with mean heights of 45.3±2.90 and 36.5±2.94 cm respectively as shown in Figure 4.13a. A significant combined increase in heights of *C. odorata* was also seen at the end of the phytoremediation period in solarized treatments with a mean height of 24.9 cm compared to the combined mean height of 18.4 cm from non-solarized treatment groups as shown in Figure 4.18a (Appendix xiv). However, there was no significant ($p \geq 0.05$) post-solarization impact on plants' root lengths in both solarized and non-solarized vegetated treatment groups with or without biosurfactant amendment as shown in Figure 4.18b (Appendix xiii).

The plants' shoots and roots dry biomasses were also affected by solarization significantly ($p \leq 0.01$) upon with means of 3.10±0.10 and 2.18±0.13 g respectively in solarized and biosurfactant-amended vegetated treatment (A) compared to means of 2.63±0.44 and 1.18±0.17 g for shoot and root dry biomasses respectively in non-solarized and biosurfactant-amended vegetated counterpart (C). There was a significant ($p \leq 0.01$) post-solarization impact on solarized and un-amended vegetated treatment (B) with plants' shoot and root dry biomasses means of 2.80±0.25 and 2.03±0.05 g respectively compared to their counterpart means of 2.20±0.34 and 1.13±0.05 g respectively in non-solarized and un-amended vegetated treatment (D) as shown in Figure 4.19(a-b). Statistically, the significant increase ($p \leq 0.01$) in plants' heights, shoots and roots dry biomasses between solarized vegetated (A and C) and non-solarized vegetated (B and D) treatment groups shows a very strong evidence against the H_o

which was rejected in preference to the H_1 suggesting that ***'there was significant interaction between soil solarization and plants in advanced phytoremediation of PAHs contaminated soil'*** which is the third research hypothesis (see Section 1.7.1) (Appendix xiii).

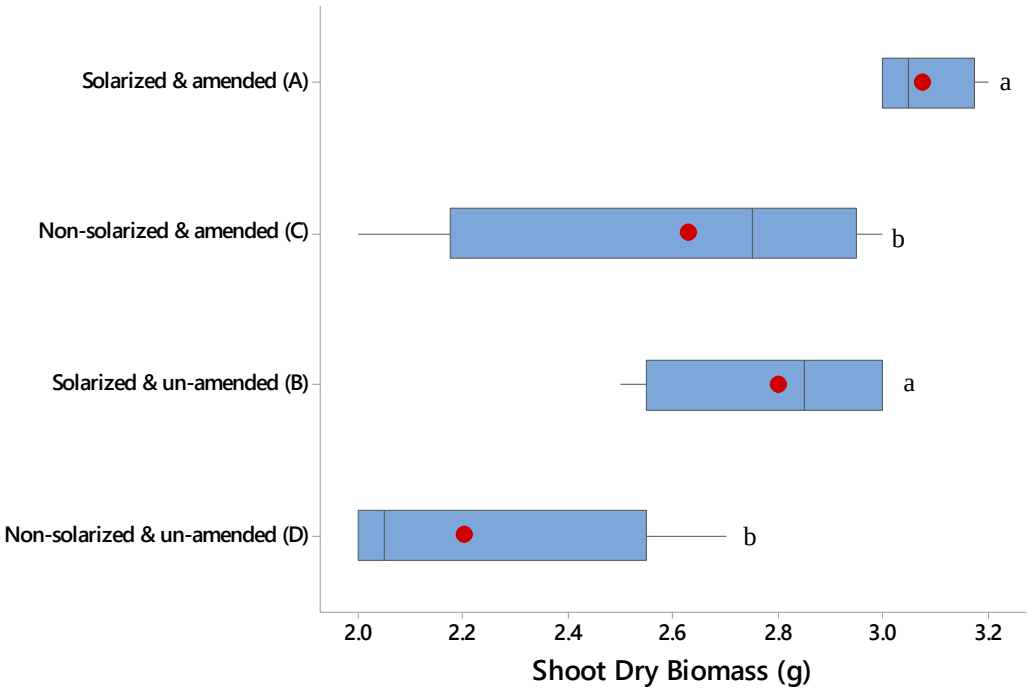


(a)

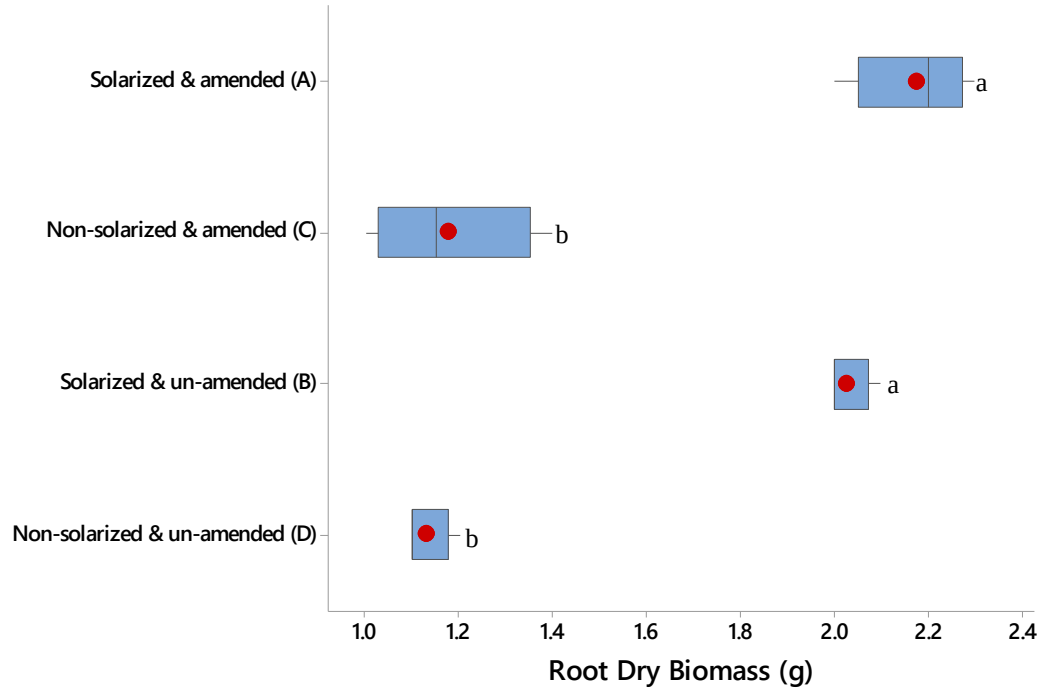


(b)Figure 4.18(a-b): (a) Impact of soil solarization on plant increase growth in height and (b) effect of soil solarization and/or bisurfactant on root length of plant. Error bars indicate mean ± S.D. of four sampled pots for vegetated treatments respectively. Means with different letters are significantly different ($p \leq 0.01$).

Key:
S = Solarized
NS = Non-solarized



(a)



(b)

Figure 4.19(a-b): Impacts of soil solarization and/or biosurfactant on vegetated treatments of (a) plant's shoot dry biomass and (b) plant's root dry biomass for solarized and non-solarized treatments with or without biosurfactant amendment. Means with different letters are significantly different ($p \leq 0.01$).

4.3.3.1.1 Discussion on soil solarization impacts on plant growth parameters

Generally, plant growth, yield and quality have been enhanced by soil solarization (Elmore *et al*., 1997) through soil borne control by biological means, soil structure improvement and increase availability of N and other vital plant nutrients in addition to the greenhouse effect (DeVay and Katan, 1991; Elmore *et al*., 1997; Stapleton, 2000). A number of physiological changes, increased photosynthetic activity and level of protein, tissue development acceleration etc. have been reported to increase plant growth response due to solarization (Gruenzweig *et al*., 1993). In this study, soil solarization had a significant impact on plant growth parameters such as heights, shoots and roots dry biomasses (see objective vi in Section 1.6.2) and this is consistent with the findings reported by Emoghene and Futughe (2011), where soil solarization was observed to affect significantly the growth parameters of *Amarathus viridis* in the Niger Delta, Nigeria. This significant growth in plants may be attributed to the chemical and physical changes caused by solarization in solarized soils such as an increase in the rate of decomposition of organic matter at high temperatures (Chen and Katan, 1980); an increase in the soluble substances which can be detected as a rise in the electrical conductivity (EC) (Chen *et al*., 1991); or liberation of soluble substances into the soil by mesophilic microorganisms killed and degraded during solarization (Stapleton, 1991). An increase in amino acids concentration has also been reported in solarized soils which was attributed to enhanced microbial synthetic activity as a result to high temperatures (Chen *et al*., 2000). It was also reported that soil solarization affects the soil ions transport to the soil surface (solute concentration) by interfering with the movement of water in the soil as a result of the evaporation of water from the soil that condenses in the mulch (polyethylene sheet) instead of escaping to the atmosphere (Chen *et al*., 1991). Several studies have reported increase in soluble mineral nutrients such as NH_4^+-N, NO_3-N, P, K^+, Ca^{+2}, Mg^{+2}, Mn^{+2}, Fe^{+3}, Cl^- and Cu^{+2} in solarized soils (Chen *et al*., 1991) however sometime inconsistently as reported by Daelemans (1989), Moura and Palminha (1994) and Coates-Beckford *et al*. (1998) and particularly for the minor elements (Stapleton, 1998; Grunzweig *et al*., 1998). Stapleton *et al.* (1985) experimented on wet soils covered with plastic mulch (polyethylene sheet) but protected from solar radiation and heating and found no difference in chemical properties from untreated control soil and came to the conclusion that heating causes the release of soluble mineral nutrients from soil organic matter. Solarization effect on soil N concentration and forms have also been studied owing to its importance as nutrient for plant growth. Linke *et al*. (1991) observed that the levels of NO_3-N in solarized soils were lower than their non-solarized

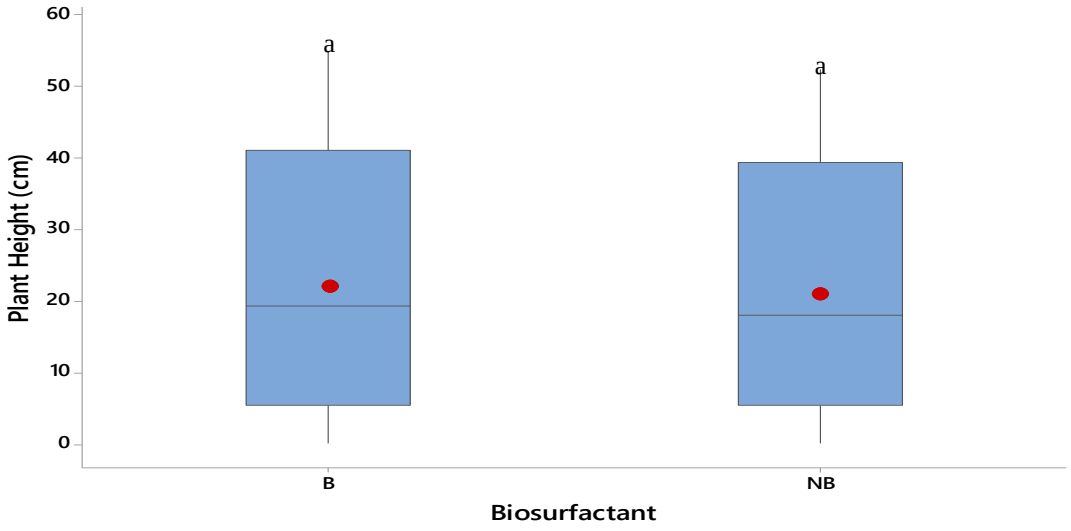
counterparts during the rapid growth stages of legumes while studying the effect of solarization in populations of nitrogen-fixing bacteria. They reported that the difference was attributed to N consumption acceleration by plants growing with enhanced vigour on solarized plots.

Although correlations between performance in agronomy and phytoremediation potential may not be fully determined, however the impact of soil solarization on phytoremediation directly and indirectly from this study is promising. As better agronomic performance of the plant has shown significant reduction in PAHs from weathered PAHs-contaminated soil as a way of advancing phytoremediation. According to Wiltse *et al*. (1998) plant that are less affected by contaminants in soils are healthier and more persistent and will yield healthier root systems and greater top growth as demonstrated in this study.

4.3.3.2 Biosurfactant impacts on plant growth parameters

The impact of biosurfactant on the growth of *C. odorata* was not significant ($p \geq 0.05$) all through the phytoremediation period with a mean height of 47.8±3.88 cm in solarized and biosurfactant-amended vegetated treatment (A) compared to a mean height of 45.3±2.90 cm in solarized and un-amended vegetated counterpart (B) from a transplanting mean heights of 7.25±0.29 and 7.25±0.29 cm respectively. This was also similar in biosurfactant insignificance ($p \geq 0.05$) in plant growth with a mean height of 38.45±4.23 cm in non-solarized and biosurfactant-amended vegetated treatment (C) compared to a mean height of 36.5±2.94 cm in non-solarized and un-amended vegetated treatment (D) from a transplanting mean height of 7.38±0.13 and 7.18±0.21 cm respectively as shown in Figure 4.13a. The combined increase in heights of *C. odorata* was seen to be almost the same at the end of the phytoremediation period in biosurfactant-amended and un-amended treatments with mean heights of 21.9 and 20.9 cm respectively as shown in Figure 4.20 and there was no significant impact of biosurfactant on the plants growth throughout the phytoremediation period with *p*-value of 0.68 (Appendix xiv). The impact of biosurfactant was also not significant ($p \geq 0.05$) in plant's shoot and root dry biomasses with means of 3.10±0.10 and 2.18±0.13 g respectively for solarized and biosurfactant-amended vegetated treatment (A) and solarized and un-amended vegetated counterpart (B) with means of 2.80±0.25 and 2.03±0.05 g for shoot and root dry biomasses respectively. Means shoot and root dry biomasses from non-solarized and biosurfactant-amended vegetated treatment (C) with 2.63±0.44 and 1.18±0.17 g respectively were not significantly different ($p \geq 0.05$) from means of non-solarized and un-amended vegetated treatment (D) with 2.20±0.34 and 1.13±0.05 g respectively as shown in Figure 4.19(a-b). In

addition, there was no significant ($p \geq 0.05$) on plants' root lengths by biosurfactant in both treatment groups with or without solarization as shown in Figure 4.18b (Appendix xiii). The overall insignificance in *p*-values on plants' heights, roots lengths, shoots and roots dry biomasses between biosurfactant-amended vegetated (A and C) and un-amended vegetated (B and D) treatment groups shows an insufficient evidence against the H_o which was accepted stating *'there was no significant interaction between biosurfactant and plants in advanced phytoremediation of PAHs contaminated soil.*' Biosurfactant did not appear to improve the plant growth parameters significantly in this study (see objective vi in Section 1.6.2), the finding agrees with a report by Liao *et al.* (2015) who investigated the effect of surfactant amendment to PAHs-contaminated soil for phytoremediation by maize, where surfactant played no significant role on the height and biomass production of maize even though plants are profoundly influenced by soil conditions. Nevertheless, Sheng *et al.* (2008) suggested a positive effect on the growth of plant in rhamnolipid-amended soil may be caused by the degradation of rhamnolipid in soil resulting to better physical soil conditions for plant nutrient uptake and increase in plant growth promoting microorganisms in the rhizosphere.



(a)

Figure 4.20: Impact of biosurfactant on plant increase growth in height. Error bars indicate mean ± S.D. of four replicates. Means with the same letters are significantly insignificant ($p \geq 0.05$).

Key: B = Biosurfactant; NB = No Biosurfactant

4.3.4 Treatments effect on soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities.

4.3.4.1 Soil solarization effect on soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities.

The 28 days soil solarization period significantly reduced ($p \leq 0.05$) the soil total heterotrophic microorganisms in solarized treatment with mean counts of 19.9, 13.5 and 9.25 x 10^4 cfu/g dry soil at day 28 from mean counts of 37.5, 23.5 and 12.5 x 10^4 cfu/g dry soil at day 0 in comparison to the insignificant difference ($p \geq 0.05$) in non-solarized treatment with mean counts of 33.9, 22.8 and 12.9 x 10^4 cfu/g dry soil at day 28 for bacteria, actinomycetes and fungi respectively. According to Stepleton (1991), soil solarization creates a partial biological vacuum in the soil. It has been reported that the rise in temperature achieved during soil solarization has a direct effect on soil ecology and many soil inhabiting microorganisms are inactivated when exposed to high temperature (Stapleton, 1991). Thermal inactivation is caused mainly due to the loss of the integrity in cellular membranes as a result of the increase in membrane lipids fluidity or the sustained inhibition of enzymatic systems particularly those involve with respiration. The proportion of saturated to unsaturated lipids in an organism' membrane determines its sensitivity to high temperature as thermotropic transition takes place at low temperature from a solid phase to a fluid-liquid crystalline phase for unsaturated lipids (Hasing, 2002). Although, tolerance to heat may varies among microorganisms, only minutes are required at temperatures above 45^{o}C to reach LD_{90} levels (Stepleton, 1991). However, thermotolerant and thermophilic microorganisms normally survive the solarization process but become weakened and vulnerable as a result of the changes in their ecosystem (DeVay and Katan, 1991).

However, post-solarization appears to have increased the density of total soil/rhizosphere heterotrophic microorganisms in all solarized treatments compared to their non-solarized counterparts but without statistical significance ($p \geq 0.05$) at days 56, 84 and 112 respectively. The highest total heterotrophic rhizosphere microorganisms were bacteria with increased density mean counts of 69.8, 113.6 and 117.0, followed by actinomycetes with increased mean density of 44.0, 70.8 and 72.3 and fungi with increased mean density of 33.8, 62.0 and 63.4 x 10^4 cfu/g dry soil in solarized treatment compared to increased mean counts of 54.9, 76.6 and 79.9 for bacteria, 36.1, 51.0 and 53.0 for actinomycetes and 33.5, 42.4 and 44.3 x 10^4 cfu/g dry soil for fungi in non-solarized treatment at days 56, 84 and 112 respectively as shown in Figure 4.21 and in combined forms with biosurfactant and phytoremediation (Figure

4.27b). Statistically, using the general linear model, *p*-values for bacteria, actinomycetes and fungi were 0.12, 0.12 and 0.13 respectively displayed an insufficient evidence against the H_0. Therefore, the H_0 is accepted, *there is no difference in total heterotrophic microorganisms between solarized and non-solarized treatments* (Table 18 and Appendix xv).

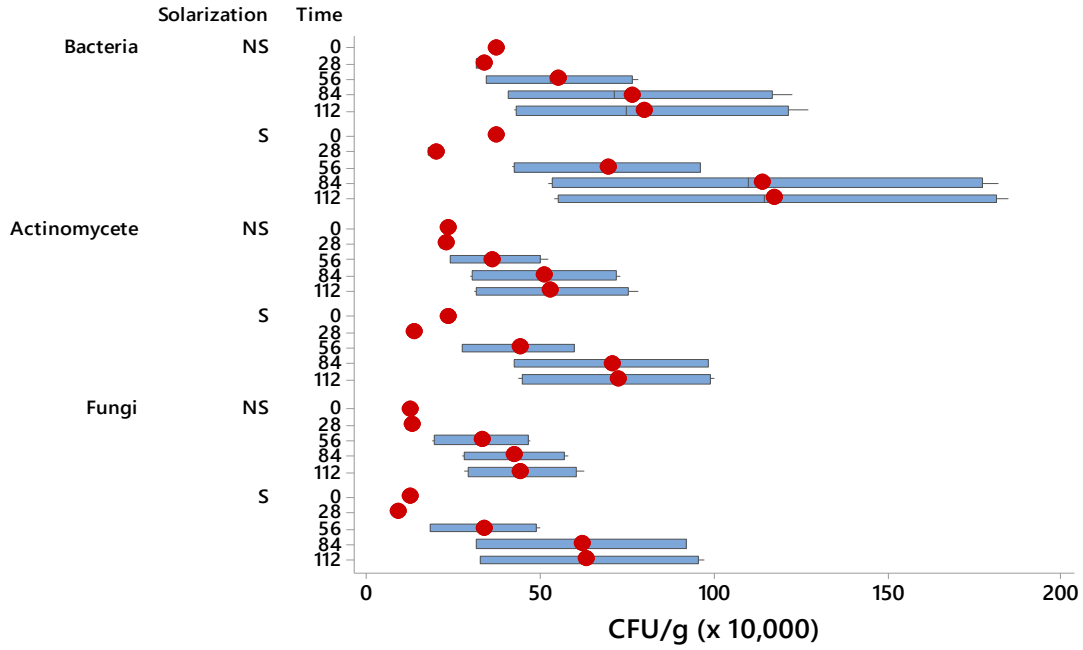


Figure 4.21: Soil solarization effects on soil/rhizosphere total heterotrophic microorganisms.

Key:
S = Solarized
NS = Non-solarized

Solarization also seems to have increased the dehydrogenase enzymatic activity in solarized treatment compared to non-solarized treatment counterpart but the increase is not statistically significant ($p \geq 0.05$). There was no significant reduction ($p \geq 0.05$) in soil dehydrogenase activity after 28 days of soil solarization in solarized treatment with a mean of 1.45 compared with a mean of 2.33 µg TF/g dry soil in non-solarized treatment from a mean of 2.13 µg TF/g dry soil at day 0. Post-solarization may have increased soil enzymatic activity of dehydrogenase in solarized treatment with means of 0.91, 16.1 and 12.5 compared to non-solarized counterparts with means of 0.33, 6.14 and 5.82 µg TF/g dry soil at day 56, 84 and 112 respectively as shown in Figure 4.22 and in combined forms with biosurfactant and phytoremediation (Figure 4.28b). But with a *p*-value of 0.09, *t*-statistic of 1.76, *F*-statistic of 3.09 and R-square (adjusted) of 34.3 %, there is insufficient evidence against the H_o. Consequently, the H_0 is accepted suggesting that *there is no difference in dehydrogenase activity between solarized and non-solarized treatments* (Table 18 and Appendix xvi).

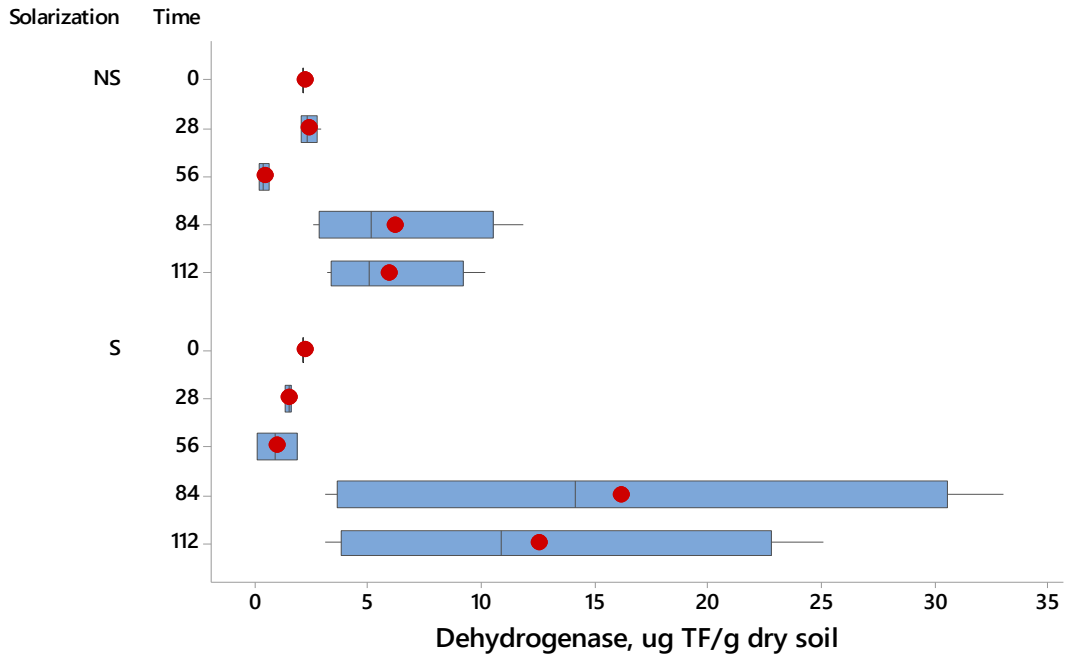


Figure 4.22: Soil solarization effects on soil enzymatic activity of dehydrogenase.

Key:
S = Solarized
NS = Non-solarized

However, post-solarization had significant ($p \leq 0.05$) effect on rhizosphere enzymatic activity of urease in solarized treatment when compared to their non-solarized counterpart with 0.04, 0.1 and 0.1 compared to means of 0.02, 0.04 and 0.04 µg NH_4-N/g dry soil at day 56, 84 and 112 respectively as shown in Figure 4.23 and in combined forms with biosurfactant and phytoremediation (Figure 4.29b). Statistically with a *p*-value of 0.01, *t*- and *F*-statistics of 2.86 and 8.16 respectively, there was a very strong evidence against the H_o which was reject in preference to the H_1 stating that *there is a difference in soil enzymatic activity of urease between solarized and non-solarized treatment i.e. solarization had impacted on the increase in urease activity* (Table 18 and Appendix xvi).

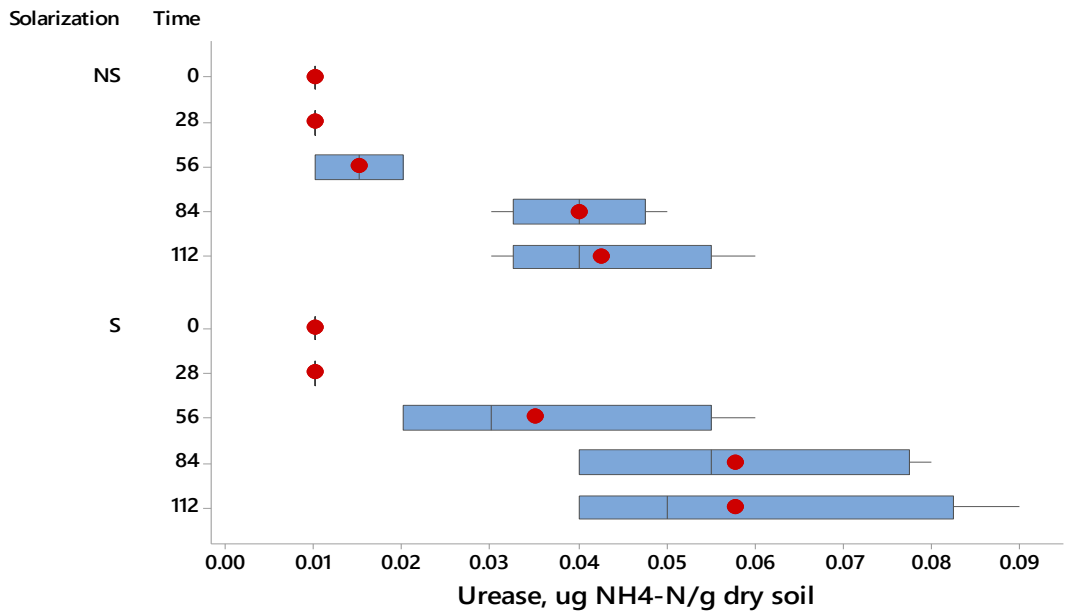


Figure 4.23: Soil solarization effects on soil enzymatic activity of urease

Key:
S = Solarized
NS = Non-solarized

4.3.4.1.1 Discussion of soil solarization effects on soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities.

It's has been reported that apart from major plant pathogens, a broad range of soil microorganisms have been impacted by soil solarization as a result of the heating treatment stimulating marked compositional shifts in richness of soil microbial communities (Chen *et al*., 1991; Schoenfeld *et al*., 2003; Palese *et al*., 2004; Culman *et al*., 2006; Gelsomino *et al*., 2006). Some studies reported a general reduction of soil total bacterial population by soil solarization (Mahmoud, 1996; Patel and Patel, 1997; Itoh *et al*., 2000; Barbour *et al*., 2002; Sharma *et al*., 2002), while others documented a decrease in soil fungal population with no impact on bacteria (Coates-Beckford *et al*., 1997; Shukla *et al*., 2000). However, other investigations showed an increase of total bacterial and actinomycetes populations in solarized soil (Kaewruang *et al*., 1989a; Khair and Bakir, 1995; Khaleeque *et al*., 1999). This study showed that soil solarization increased the total heterotrophic rhizosphere microorganisms (see objective vi in Section 1.6.2) and according to Chen *et al.* (1991) this is due to re-colonization by microorganisms soon after the end of a 28 day solarization treatment. Linke *et al.* (1991) reported reduced *Rhizobium* populations in solarized soil after soil solarization which quickly recovered after the establishment of a legume crop. Stapleton and DeVay (1984) reported an increase in the populations of beneficial gram-positive bacteria and plant growth-promoting rhizobacteria (PGPR) post-solarization probably due to their thermophilic nature. Fluorescent pseudomonads are important heat-sensitive group of PGPR, colonized soil rapidly after the initial decline of their populations due to solarization (Chen *et al.,* 1991). According to DeVay and Katan (1991) both *Bacillus spp.* and fluorescent pseudomonads are rhizosphere-competent and have been implicated in disease suppression in soil. A population increase up to 130-fold in solarized soils have been reported by Gamliel and Katan (1991). However, despite the initial development of soil solarization as a technique for soil-borne pathogens control, studies of its impact on the competitiveness of microorganisms have not been restricted to pathogen control (Katan *et al.,* 1976).

A study carried out by Brzezinska *et al.* (1998) suggested that temperature and soil water content have indirect influence on dehydrogenase activity by affecting the soil redox status. These redox transformations are closely linked with respiration activity of soil microorganisms serving as the microbiological redox indicators in soil and can be considered a possible measure of microbial oxidative activities (Tabatabai, 1982 and Trevor, 1984). Dehydrogenase enzyme is usually used as a measure of any disruption caused by pesticides, trace elements or management practices in soil (Reddy and Faza 1989; Wilke 1991; Frank and

Malkomes 1993) in addition to soil microbial activity measurement ((Trevors 1984; Garcia and Herna´ndez 1997). As shown in this study, the increased temperature during soil solarization reduced dehydrogenase activity compared to its non-solarized counterpart but gradually increases post-solarization (see objective vi in Section 1.6.2). This increase shows similar response with total heterotrophic microorganisms suggesting a positive effect of soil solarization. The dehydrogenase enzyme activity is usually used as an indicator of biological activity in soils and it is considered to exist as an integral part of intact cells but does not accumulate extracellularly in the soil. It oxidize soil organic matter by transferring protons and electrons to acceptors from substrate. The processes which are part of soil microbial respiration pathways are closely associated with the type of soil and soil air-water condition indicating the soil potential to support biochemical processes essential for maintaining the fertility of the soil and soil health. Dehydrogenase can also be used to indicate the type and significance of pollution in soils. McCarthy *et al.* (1994) reported high dehydrogenase activity in soils polluted with pulp and paper mill effluents but low in fly ash polluted soil (Pitchel and Hayes, 1990). Higher dehydrogenase activities have been reported at low doses of pesticides and lower dehydrogenase activities at higher doses of pesticide (Baruah and Mishra, 1986).

Soil urease originates basically from plants (Polacco, 1977) and microorganisms found as both intra- and extra-cellular enzymes (Burns, 1986; Mobley and Hausinger 1989). Many factors influence urease activity in soils including cropping history, organic matter content of the soil, soil depth, soil amendments, heavy metals (PAHs), and environmental factors such as temperatures (Tabatabai 1977; Yang *et al*. 2006). In this study, soil solarization significant increased the activity of urease even though there was no difference in urease activity after 28 days solarization period (see objective vi in Section 1.6.2). According to Das and Varma (2011) an increase in temperature generally results to increase in urease activity suggesting that higher temperatures increase the activity coefficient of the urease enzyme. However, urease extracted from plants and microorganisms is degraded rapidly by proteolytic enzymes in soil (Pettit *et al*. 1976; Zantua and Bremner 1977) suggesting a significant fraction of ureolytic activity in the soil is carried out by extracellular urease, stabilized by immobilization on organic and mineral soil colloids.

4.3.4.2 Biosurfactant effect on soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities.

The effect of biosurfactant on the total density of soil/rhizosphere heterotrophic microorganisms was insignificant ($p \geq 0.05$) over the treatment duration between biosurfactant-amended treatment and un-amended counterpart with or without solarization and vegetation at days 28, 56, 84 and 112 respectively. In biosurfactant-amended treatment, bacteria mean density were 25.1, 62.9, 99.9 and 102.9 compared to their counterpart mean density of 28.6, 61.8, 90.4 and 94 x 10^4 cfu/g dry soil in un-amended treatment at days 28, 56, 84 and 112 respectively. Actinomycetes mean counts were 17.5, 38.5, 61.8 and 64.6 in biosurfactant-amended treatment compared to un-amended treatment with 18.8, 41.6, 60.0 and 60.6 x 10^4 cfu/g dry soil at days 28, 56, 84 and 112 respectively. Fungi mean counts in biosurfactant-amended treatment also showed negligible increase when compared with mean counts in their un-amended counterpart with 10.4, 33.0, 52.9 and 55.8 compared to 11.8, 34.3, 51.5 and 51.5 x 10^4 cfu/g dry soil respectively at days 28, 56, 84 and 112 respectively as shown in Figure 4.24 and in combined forms with solarization and phytoremediation (Figure 4.27b). Statistically, *p*-values for bacteria, actinomycetes and fungi were 0.73, 0.95 and 0.91 respectively all displayed an insufficient evidence against the H_o using the general linear model. Therefore, the H_o is accepted, *there is no difference in total heterotrophic microorganisms between biosurfactant-amended treatment and un-amended counterparts* (Table 18 and Appendix xv).

Biosurfactant did not impact significantly ($p \geq 0.05$) on the soil enzymatic activity of dehydrogenase as shown with means of 1.92, 0.80, 12.9 and 11.3 in biosurfactant-amended treatment compared to means of 1.90, 0.50, 9.30 and 7.00 µg TF/g dry soil in un-amended treatment counterpart at days 28, 56, 84 and 112 respectively as shown in Figure 4.25 and in combined forms with solarization and phytoremediation (Figure 4.28b). Statistically, with a *p*-value, *t*- and *F*- statistics of 0.39, 0.88 and 0.77 respectively coupled with an R-square (adjusted) of 34.3 %, there is insufficient evidence against the H_o. Consequently, the H_o is accepted suggesting that *there is no difference in dehydrogenase activity between biosurfactant-amended and un-amended treatments* (Table 18 and Appendix xvi).

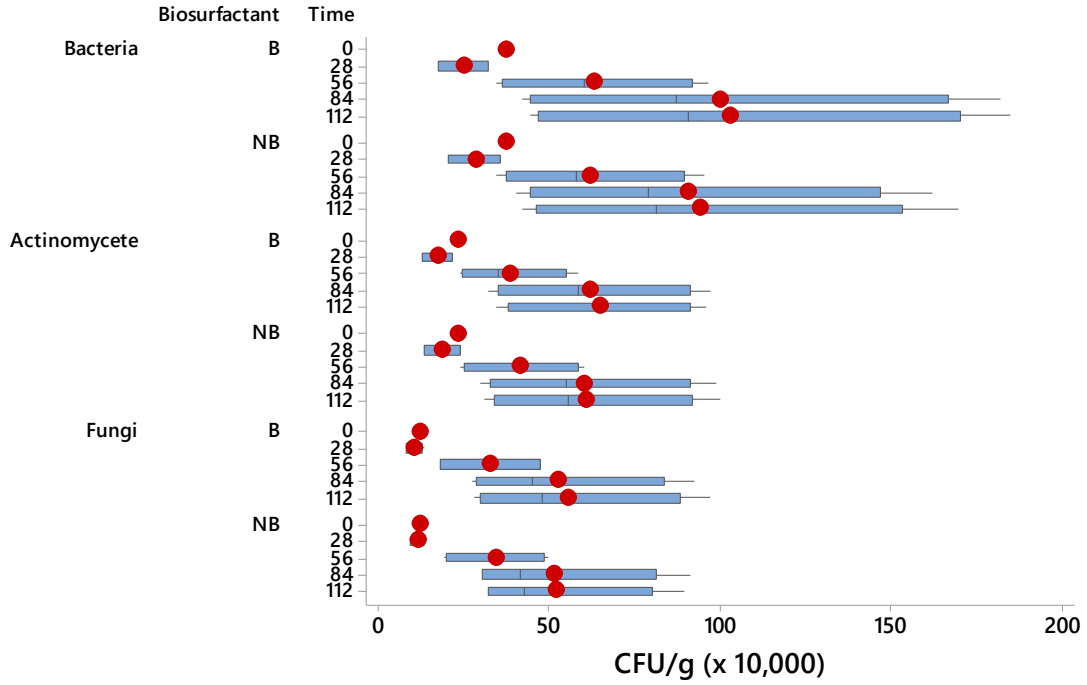


Figure 4.24: Biosurfactant impact on soil/rhizosphere total heterotrophic microorganisms
Key:
B = Biosurfactant
NB = No Biosurfactant

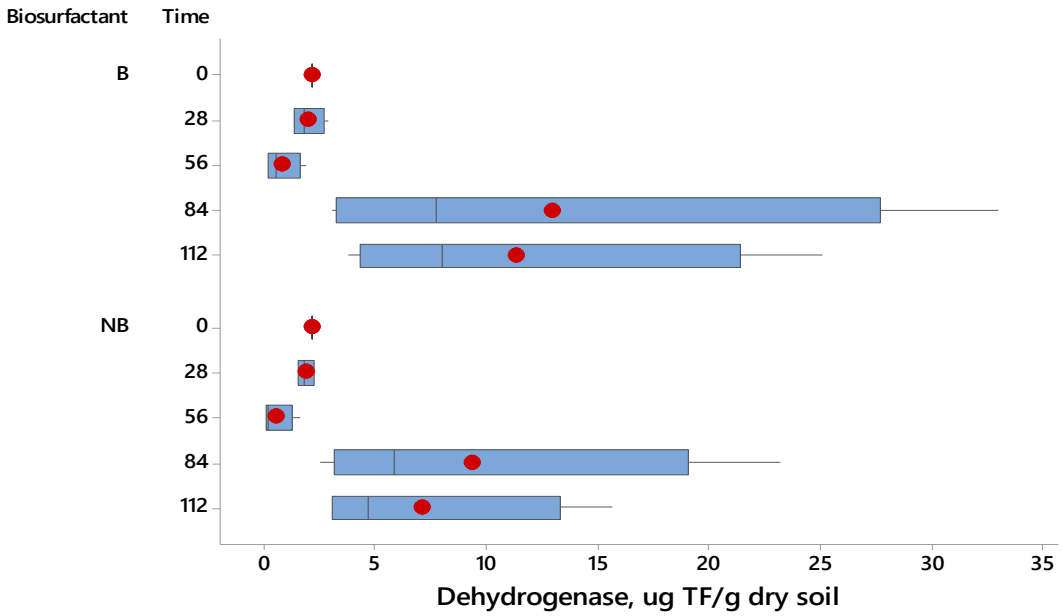


Figure 4.25: Biosurfactant effects on soil enzymatic activity of dehydrogenase
Key:
B = Biosurfactant
NB = No Biosurfactant

The effect of biosurfactant was also negligible on soil enzymatic activity of urease with means of 0.01, 0.03, 0.05 and 0.06 compared to means of 0.01, 0.02, 0.05 and 0.04 µg NH_4-N/g dry soil for biosurfactant-amended and un-amended treatments respectively at days 28, 56, 84 and 112 respectively as seen in Figure 4.26 and in combined forms with solarization and phytoremediation (Figure 4.29b). The *p*-value, *t*- and *F*- statistics of 0.14, 1.50 and 2.24 respectively despite a relatively high R-square (adjusted) of 72.6 %, shows there is insufficient evidence against the H_o. Consequently, the H_o is accepted suggesting that *there is no difference in urease activity between biosurfactant-amended and un-amended treatments* (Table 18 and Appendix xvi).

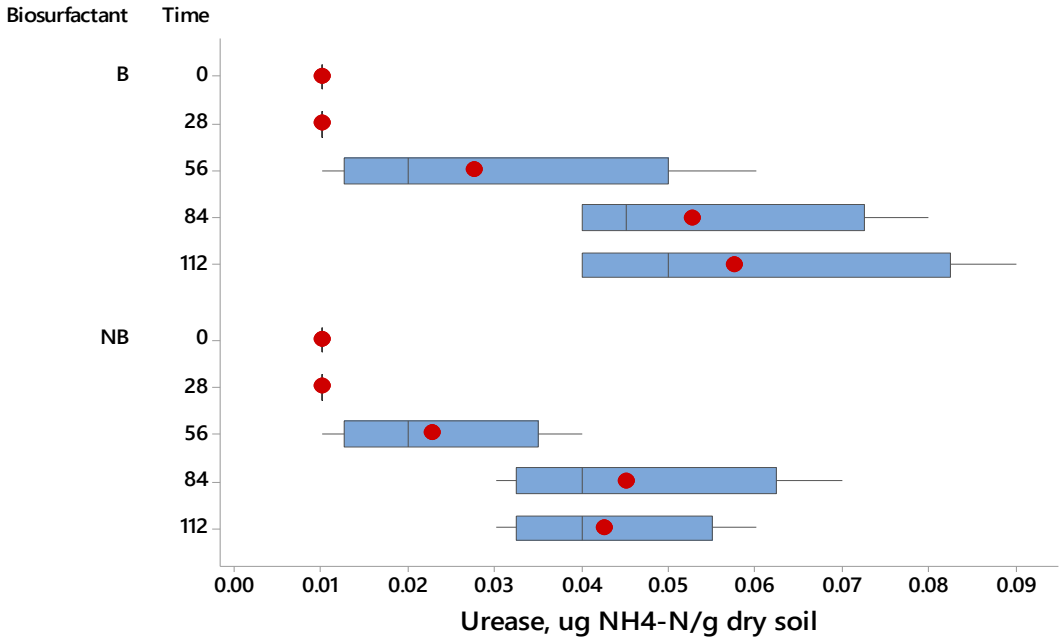


Figure 4.26: Biosurfactant effects on soil enzymatic activity of urease

Key:
B = Biosurfactant
NB = No Biosurfactant

4.3.4.2.1 Discussion of biosurfactant negligible effects on soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities.

In contrary to other reports, biosurfactant did not appear to induce significant increase in the total soil/rhizosphere heterotrophic microorganisms (see objective vi in Section 1.6.2), in this study. According to a publication by Almansoory *et al.* (2015), who investigated the potential application of a biosurfactant in phytoremediation technology for treatment of gasoline-contaminated soil, the maximum rhizosphere bacteria population was achieved with the biosurfactant additive. Liao *et al.* (2015) reported a significant increase in microbial number with increasing surfactant concentrations suggesting a promoting effect on microbial population in the soil while Mathurasa *et al.* (2012) who also reported similar increase in microbial growth suggested the significance might be due to the surfactant directly or greater levels of dissolved organic matter released by the surfactants which served as carbon sources for additional microbial growth. However, a study carried out by Whang *et al.* (2008) on rhizobacteria population in diesel-amended rhamnolipid biosurfactant treatments achieved insignificant increase but demonstrated the increasing gasoline solubility by addition of higher quantity of biosurfactant. In this study, it may be that the increase in soil temperatures during the 28 days soil solarization denatured/deactivated the rhamnolipid biosurfactant as temperature is one of the factors affecting biosurfactant. Thereby resulting to the negligible contribution of biosurfactant to soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities of dehydrogenase and urease respectively (see objective vi in Section 1.6.2). However, further study is needed to better understand the effect of solarization temperature on biosurfactant.

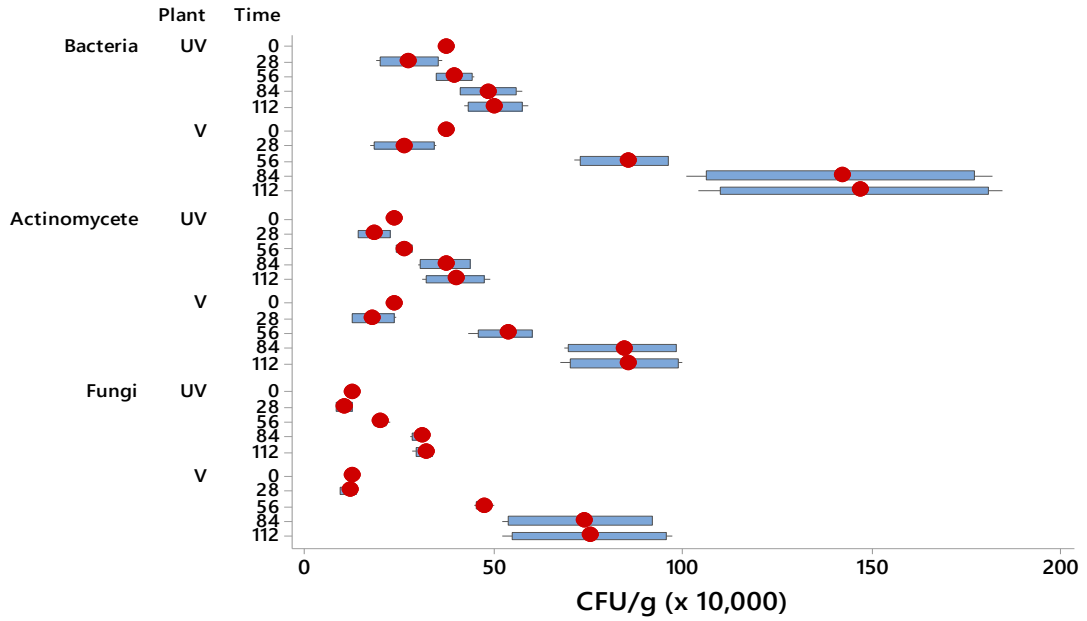
4.3.4.3 Phytoremediation (*C. odorata*) effect on soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities.

C. odorata plants significantly increased ($p \leq 0.01$) the total density of soil/rhizosphere heterotrophic microorganisms in all vegetated treatments compared to their un-vegetated counterparts at days 56, 84 and 112 respectively from their transplanting day (day 28). Bacteria were the highest heterotrophic rhizosphere microorganisms with a total mean counts of 85.5, 142.0 and 146.8 in vegetated treatment compared to 39.1, 48.3 and 50.1 x 10^4 cfu/g dry soil in un-vegetated counterpart at days 56, 84 and 112 respectively from mean counts of 28.4 and 27.4 x 10^4 cfu/g dry soil prior to transplanting in pre-vegetated and un-vegetated treatments respectively. Actinomycetes were significantly increased ($p \leq 0.01$) with mean counts of 53.9, 84.5 and 85.5 in vegetated treatment in comparison to mean counts of 26.3, 37.3 and 39.8 x

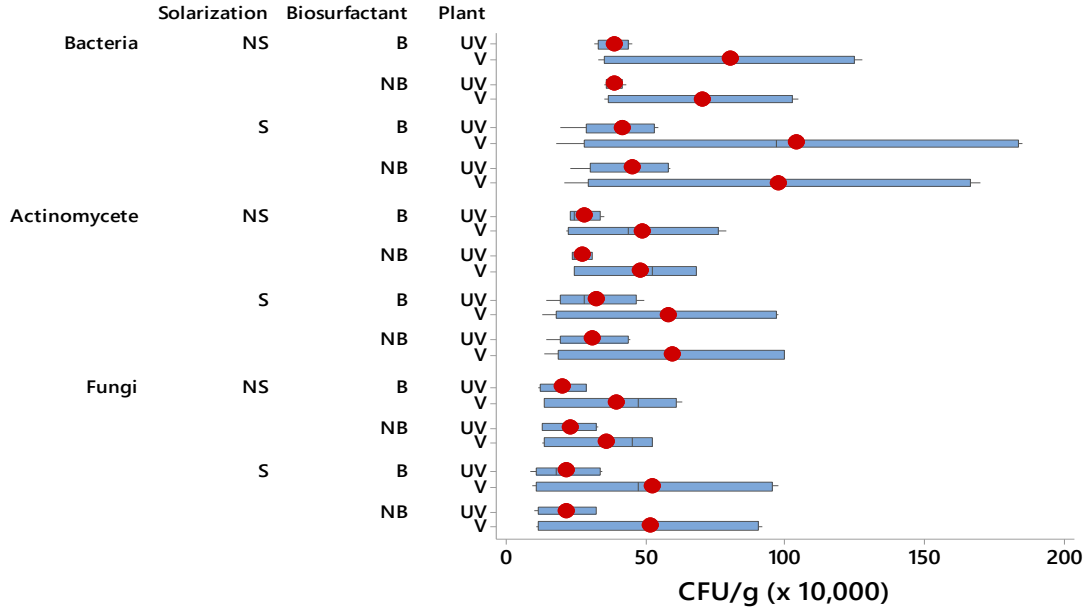
10^4 cfu/g dry soil in un-vegetated counterpart at days 56, 84 and 112 respectively from mean counts of 17.9 and 18.4 x 10^4 cfu/g dry soil prior to transplanting in pre-vegetated and un-vegetated treatments respectively. Fungi also increased significantly ($p \leq 0.01$) with mean counts of 47.5, 73.8 and 75.6 in vegetated treatment compared to mean counts of 19.8, 30.6 and 32.0 x 10^4 cfu/g dry soil in un-vegetated counterpart at days 56, 84 and 112 respectively from a mean count of 11.8 and 10.4 x 10^4 cfu/g dry soil prior to transplanting in pre-vegetated and un-vegetated treatments respectively as shown in Figure 4.27a and in combined forms with solarization and biosurfactant (Figure 4.27b). Statistically, using the general linear model, *p*-values for bacteria, actinomycetes and fungi were 0.00, 0.00 and 0.00 respectively all showed a very strong evidence against the H_o. Therefore, the H_0 stating no difference in total heterogeneous microorganisms between vegetated and un-vegetated treatments is rejected and the H_1 is accepted (i.e. *there was a significant difference in total heterotrophic microorganisms between vegetated and un-vegetated treatments*). (Table 18 and Appendix xv).

Plants also significantly increased ($p \leq 0.01$) the dehydrogenase enzymatic activity in vegetated treatment compared to their un-vegetated counterpart with means of 1.10, 18.7 and 14.3 compared to means of 0.15, 3.60 and 4.00 µg TF/g dry soil at day 56, 84 and 112 respectively as shown in Figure 4.28a and in combination forms with solarization and biosurfactant in Figure 4.28b. Statistically, with a *p*-value of 0.01, *t*-statistic of 2.82, *F*-statistic of 7.93 and despite an R-square (adjusted) of 34.3 %, there is a very strong evidence against the H_o. Consequently, the H_o is rejected in favour of the H_1 being accepted suggesting that *there is a genuine difference in dehydrogenase activity between vegetated and un-vegetated treatments* (Table 18 and Appendix xvi).

Plant had significant ($p \leq 0.01$) effect on rhizosphere enzymatic activity of urease in vegetated treatment when compared to their un-vegetated counterpart with 0.04, 0.06 and 0.06 compared to means of 0.02, 0.04 and 0.04 µg NH_4-N/g dry soil at day 56, 84 and 112 respectively as shown in Figure 4.29a and in combination forms with solarization and biosurfactant in Figure 4.29b. Statistically with a *p*-value of 0.00, *t*- and *F*-statistics of 3.67 and 13.5 respectively, there was a very strong evidence against the H_o which was reject in preference to the H_1 stating that *there is a difference in soil enzymatic activity of urease between vegetated and un-vegetated treatment* i.e. phytoremediation had impacted on the increase in urease activity (Table 18 and Appendix xvi).



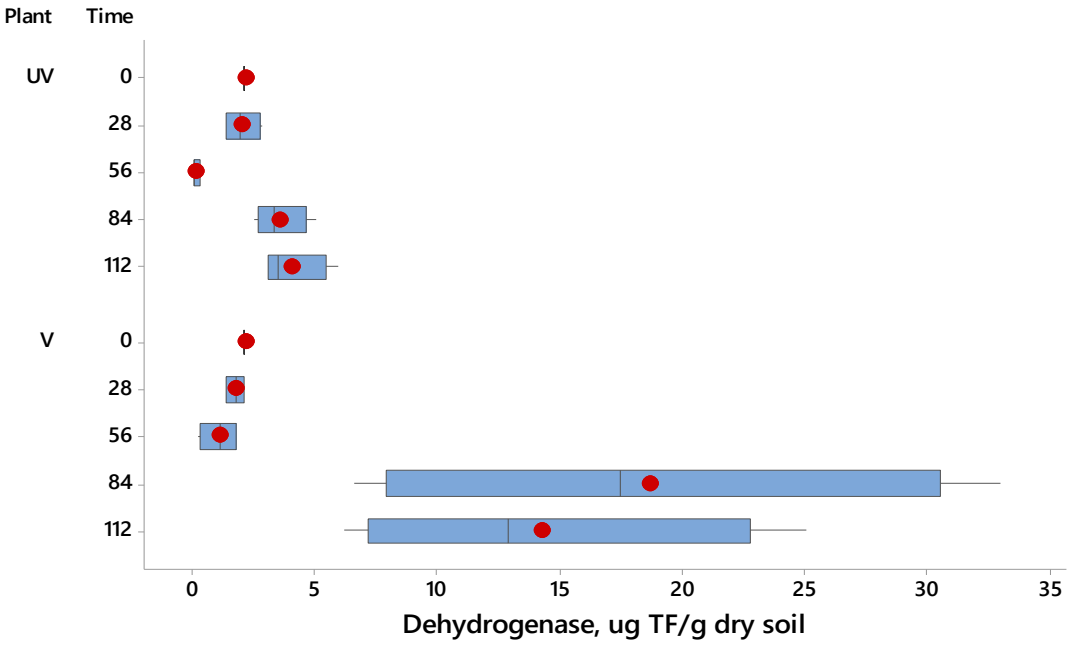
(a)



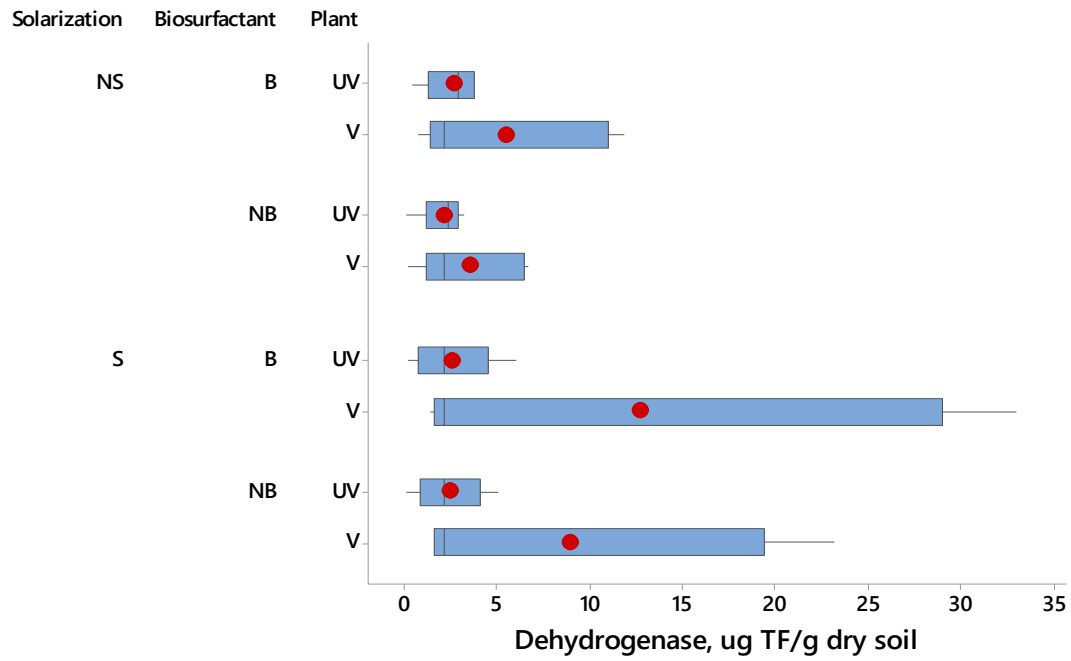
(b)

Figure 4.27(a-b): Phytoremediation (*C. odorata*) effects on (a) rhizosphere total heterotrophic microorganisms and (b) in combined forms with solarization and biosurfactant rhizosphere total heterotrophic microorganisms

Key:
V = Vegetated
UV = Un-vegetated
S = Solarized
NS = Non-solarized



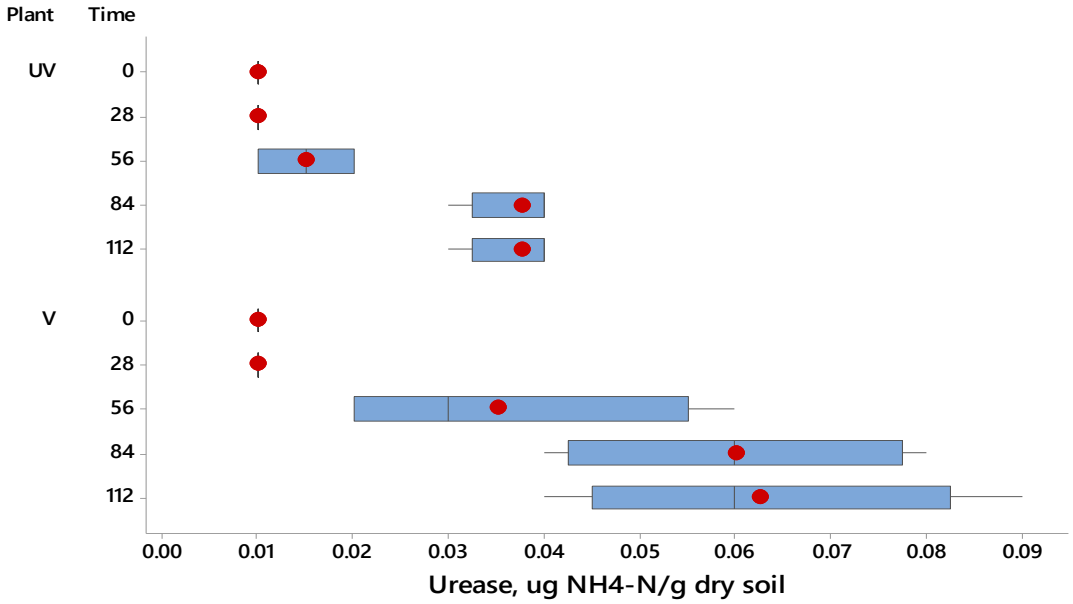
(a)



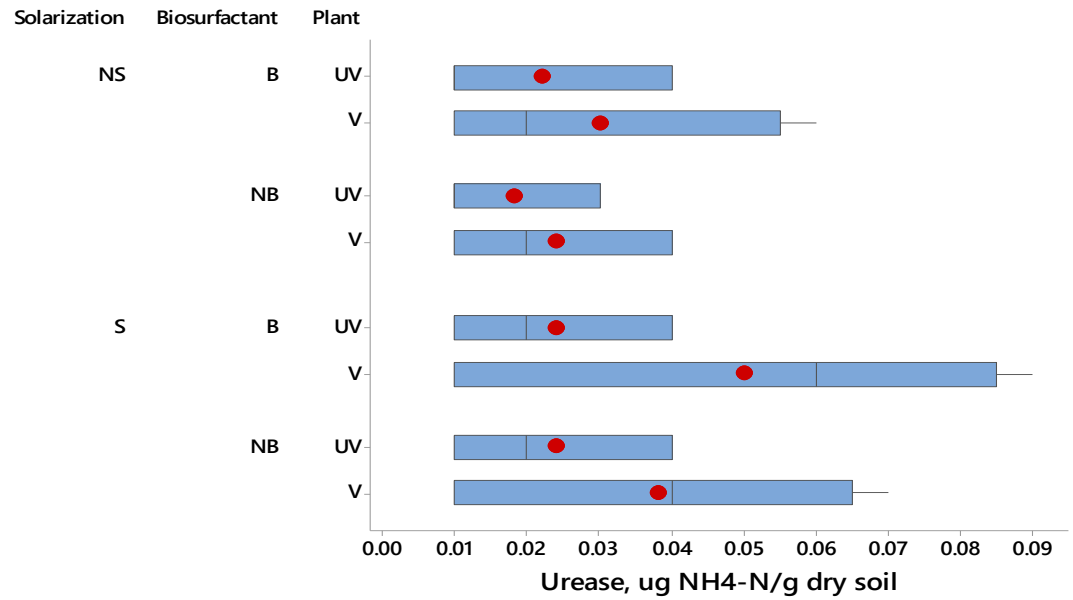
(b)

Figure 4.28(a-b): Phytoremediation (*C. odorata*) effects on (a) soil enzymatic activity of dehydrogenase and (b) in combined forms with solarization and biosurfactant on soil enzymatic activity of dehydrogenase.

Key:
V = Vegetated
UV = Un-vegetated
B = Biosurfactant
NB = No Biosurfactant



(a)



(b)

Figure 4.29(a-b): Phytoremediation (*C. odorata*) effects on (a) soil enzymatic activity of urease and (b) in combined forms with solarization and biosurfactant on soil enzymatic activity of urease.

Key:
S = Solarized
NS = Non-solarized
B = Biosurfactant
NB = No Biosurfactant
V = Vegetated
UV = Un-vegetated

4.3.4.3 Discussion of phytoremediation (*C. odorata*) effect on soil/rhizosphere total heterotrophic microorganisms and soil enzymatic activities.

These findings are consistent with numerous studies in literature such as a report by Hazaimeh *et al.* (2019) who investigated the effects of plant density on the bioremediation of soils contaminated with PAHs and reported continued increase of soil microbial contents after 1 month in contaminated soil. And that the presence of plants drastically increased the microbial growth in contaminated soil during the first month of exposure and a significant increase during the second month. He concluded that high plant density is associated with high microbial content. The significant increase in total heterotrophic microorganisms especially bacteria as observed in the vegetated treatment compared to their un-vegetated counterparts may enhance the bioremediation of PAHs in the contaminated soil given that soil microbial function supports plant phytoremediation (Tang, *et al.,* 2005). The continuous and rapidly increasing microbial density especially at days 56, 84 and 112 in vegetated treatment over their non-vegetated counterpart irrespective of solarization and/or biosurfactant could be significant in the overall % removal of PAHs in all treated soils. According to Parrish and Fike (2005), the presence of plant roots in addition to increased microbial density, result to a large increase in the bioavailability of target PAHs. Suggesting that high microbial density due to vegetation better support bioremediation than low microbial density counterpart. This was also corroborated by Ho and Banks (2006) that greater total bacterial numbers and PAH-degrading bacteria were found in the rhizosphere soil. While Olson and Fletcher (2000) reported vegetation increased total numbers of beneficial fungi and bacteria in contaminated soil.

Reports are abundant in the literature on the allocation of enzymatic activities in bulk (un-vegetated) and rhizosphere soil (Naseby and Lynch, 2002; Marinari *et al*., 2014). As nutrients are taken up by plants through the rhizosphere, the microbial community inhabiting the soil rhizosphere as well as its activity and function have a high significance for plant growth. This in turn leads to the higher enzymatic activities of rhizosphere soils than those of the bulk or un-vegetated soil as demonstrated in this study. The significant increase of rhizosphere enzymatic activity especially dehydrogenase in vegetated treatment groups compared to their un-vegetated counterparts with or without solarization and/or biosurfactant may depend not only on the stimulation of root-related microbial activity by rhizodeposition but also on the root released enzymes. A report by Gianfreda (2015) finds higher rhizosphere enzymatic activity, as a greater functional diversity of the microbial community with an interesting involvement in the possible removal of both inorganic and organic pollutants. According to Gramss *et al.* (1999), Chroma *et al.* (2002) and Harvey *et al.* (2002) these

enzymes are usually wall-associated enzymes and catalyse the formation of products which are taken up by rhizosphere microbes or plant roots. Arguably, therefore, the enzymatic activities at the plant-soil interface may be as a result of the general impacts of the combined treatments especially with soil solarization in other to improve the highly integrated plant-microorganism interactions as well as the control of plant pathogens and pests due to the long term effectiveness in controlling soil borne diseases and soil borne pests (Katan *et al*., 1976; Ashworth *et al*., 1983; Horiuchi, 1991; Chet *et al*., 1982; Keinath, 1995; Katan, 1996; Elmer, 1997; Stevens *et al*., 2003 and Scopa *et al*., 2009; Emoghene and Futughe, 2011; Dai *et al.,* 2014) as the rhizosphere may harbour pathogenic fungi, oomycetes, bacteria and nematodes that can all exert adverse effect on the growth and health of the plant (Raaijmaker *et al.,* 2009).

The significant increase in dehydrogenase as observed in this study is consistent with that of Liu *et al.* (2014) who investigated the rhizosphere effects of PAH-contaminated soil phytoremediation using fire phoenix (*Phoenix dactylifera*). They reported significant increase in dehydrogenase activity due to the presence of plant roots as against unplanted control. The dehydrogenase activity was used as an overall indication of the various microbial communities, including bacteria, fungi and algae (Sandrin *et al.,* 2009) and further suggested that they play a role in the degradation of PAHs in the soil. As shown in Figure 4.28a dehydrogenase reached its maximum activity at day 84 with 18.7 in vegetated treatment compared to 3.60 µg TF/g dry soil in un-vegetated counterparts which coincided with significant overall PAHs reduction. This may be due to increased PAH dehydrogenation effected by dehydrogenase enzyme and a relative decrease at day 112 due to the negligible residual PAHs remaining for degradation.

Soil dehydrogenase activity is considered to exist as an integral part of intact cells in soil. Measuring soil dehydrogenase activity represents immediate metabolic activities of soil microorganism at the time of the test. Its activity makes use of an oxidative degradation process such as dehydrogenation of organic matter by transferring hydrogen and electrons from substrate to acceptors (Kumar *et al.,* 2013). Soil quality can be determined by measuring changes in soil enzymatic activities as a useful index of change (Visser and Parkinson, 1992). Correlative information on the biological activity and microbial populations can also be provided by soil dehydrogenase activity in the soil. Waksman (1992) introduced the basic idea of measuring microbial indicators for soil fertility using soil enzymatic activity.

The significant increase in urease activity as reported in the vegetated treatment is almost similar to a threefold increase observed by Barreto and Westerman (1989) in urease activity in no-till system compared with that in the soil of a conventional tillage area. Urease enzymatic activity was employed due to the sensitivity to environmental changes and has been

proposed to evaluate soil sustainability and economic impact (Garcia *et al*., 1997; Tripathi *et al*., 2006) as it is closely associated with nitrogen transformation, biological turnover and bioavailability (Liang *et al*., 2003; Yuan *et al*., 1997). Urease as a hydrolase enzyme is responsible for substrate hydrolytic conversion of urea into CO_2 and ammonia. The enzyme is important in understanding mineralization process of nitrogen.

Generally, the significantly increased soil/rhizosphere total heterotrophic microbes, dehydrogenase and urease activities suggest the advancement of phytoremediation using indigenous *C. odorata* in combination with soil solarization as an eco-friendly and cost effective novel treatment. The individual and synergistic effects of this novel treatment significantly enhanced PAHs degradability with arguably reduced time frame. In addition to the above mention benefits, this innovative remediation technique enhanced soil fertility, quality as well as microbial density and diversity. Coupled with the fact that the efficiency of this treatment is highly suitable to the local environmental conditions with optimum solar radiation, high humidity and ubiquitous indigenous *C. odorata* has demonstrated phytoremediation potential in this research. This study opens up new possibilities for sustainable approach to remediate contaminated land in the oil rich Niger Delta, Nigeria.

4.4 CONCLUSION

The gradual increase in daily simulated temperatures of solarized moist soil treatments in Chapter 4 may have impacted on the physical, chemical and biological properties of the solarized soils by facilitating decomposition of organic matter quickly using the heat under the transparent polyethylene sheet. This direct impact creates a favourable microenvironment for bacterial metabolic activity and ultimately, PAH biodegradation due to extreme temperature adaptation by PAHs degrading bacteria while maintaining their metabolic activity. The enhanced removal of PAHs in this study especially in the 28 days solarization period was attributed to the increase in soil temperature through soil solarization and not to biosurfactant and photodegradation. The density of total soil/rhizosphere heterotrophic microorganisms in all solarized treatments increased during post-solarization, in comparison to their non-solarized counterparts but without statistical significance. This increase was due to re-colonization after the end of 28 days solarization treatment. Post-solarization further reduced the amount of residual phenanthrene, fluoranthene and benzo[a]pyrene throughout the phytoremediation duration significantly due to rhizodegradation and/or biodegradation. Biodegradation of PAHs have been reported to take place over a wide range of temperatures because microorganisms

have adapted to metabolize PAHs at extreme temperatures. Solarization also increased soil/rhizosphere enzymatic activity of urease and dehydrogenase in solarized treatment compared to non-solarized treatment counterpart with and without statistically significance respectively.

The contradicting findings on the impact of biosurfactant-enhanced PAH removal in this study is arguably attributed to the deactivation/denaturing of the rhamnolipid biosurfactant by the relatively high soil temperatures recorded for both solarized and non-solarized treatments especially during the 28 days solarization periods. The minimum average soil temperatures recorded in this study were 42.3 and 40.3 for non-solarized treatments at 1 and 4 cm respectively. However, reports suggest a proportional temperature up to a certain extent of 30 to 35^{o}C for biosurfactant assisted solubility of PAHs. Thus, the impact of biosurfactant in phytoremediation using soil solarization in this study was negligible compared to their non-amended counterpart treatments on PAH reduction, plant performance, total heterotrophic microbial density, soil/rhizosphere enzymatic activity of dehydrogenase and urease respectively. Nevertheless, in the pilot study, the impact of rhamnolipid biosurfactant was significant in the removal of PAHs from both *C. odorata* and *Medicago sativa* biosurfactant-amended treatments compared to their un-amended counterparts. Suggesting that soil solarization was the major factor that enhanced phytoremediation as a result of an increase in the soil temperature contributing to PAHs solubility and bioavailability. The successful integration of soil solarization and phytoremediation as a combined technique for treating contaminated land is the originality of this study.

Soil solarization on the other hand impacted significantly on plants' heights, shoots and roots dry biomasses compared to their non-solarized counterparts. This significant growth in plants was attributed to the chemical and physical changes caused by solarization in solarized soils such as an increase in the rate of decomposition of organic matter at high temperatures, an increase in the soluble substances or liberation of soluble substances into the soil by mesophilic microorganisms killed and degraded during solarization or an increase in amino acids concentration attributed to enhanced microbial synthetic activity as a result to high temperatures (Chen *et al*., 1991; Chen and Katan, 1980; Stapleton, 1991; Chen *et al*., 2000).

There was a strong association between soil solarization impact on agronomy performance and phytoremediation resulting to significant reduction in PAHs from weathered PAH-contaminated soil. *C. odorata* significantly increased the total density of rhizosphere heterotrophic microorganisms, rhizosphere enzymatic activity of dehydrogenase and urease in all vegetated treatments compared to their un-vegetated counterparts.

The significantly increased soil/rhizosphere total heterotrophic microbes, dehydrogenase and urease activities suggest the advancement of phytoremediation using indigenous *C. odorata* in combination with soil solarization as an eco-friendly and cost effective novel treatment. The significant reduction in targeted PAHs, improved agronomic performance, enhanced soil fertility, quality as well as microbial density and diversity, authenticate the integrated treatment of soil solarization and phytoremediation as a remediation technique for petroleum hydrocarbon contaminated soil. Thus this research opened up new possibilities for sustainable approach to remediate contaminated land in the oil rich Niger Delta, Nigeria with optimum solar radiation, high humidity and ubiquitous indigenous *C. odorata* with proven phytoremediation potential as demonstrated in this research.

Chapter 5

Feasibility of Sustainable Remediation to Contaminated Land Clean-up in the oil rich Niger Delta region, Nigeria.

5.0 Feasibility of Sustainable Remediation to Contaminated Land Clean-up in the oil rich Niger Delta region, Nigeria.

5.1 INTRODUCTION

The decision to globally implement the Sustainable Development Goals (SDGs) in every country starting in 2016, has further heightened the need for sustainable remediation techniques in treating contaminated sites especially in the oil rich Niger Delta region of Nigeria. The SDGs appeal to all countries, whether developed or developing (UN, 2016). Developing countries such as Nigeria, irrespective of the strength of their economy, have an opportunity and responsibility to act equally well. The report from the Brundtland Commission in 1987 has arguably the most acceptable and most recognized definition of sustainable development as *"development which meets the needs of the present without compromising the ability of future generations to meet their own needs"* (Brundtland, 1987). In spite of this definition, the concept of sustainable development has been changing in meaning depending on its users. A recent concept is Sustainable Remediation and according to SuRF-UK (2009), sustainable remediation is defined as *"the practice of demonstrating, in terms of environmental, economic and social indicators, that the benefit of undertaking remediation is greater than its impact, and that the optimum remediation solution is selected through the use of a balanced decision-making process"* and by USSRF (2009) as *'a remedy or combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources."*

The Niger Delta represents a closely woven, long-standing bond between people and the environment (see Section 2.1). The drainage basin of the Rivers Niger and Benue is its delta which deposit rich alluvial soil of 30,000 Km^2 wetland of global significance (IUCN-NDP, 2013). A large part of West Africa is drained by the River Niger which in turn discharges its waters and sediment, in addition to exotic biota, into the Niger Delta (Abam, 2001). This encourages the rich delta biodiversity spawning a variety of food and material resources (Blench and Dendo, 2007) sustaining the ecosystem balance coupled with conventional and sustainable means of livelihoods for centuries. The Niger Delta rich biodiversity is under threat from a myriad of anthropogenic activities including oil and gas exploration and exploitation especially, unsustainable deforestation activities, upstream dams and urbanization and from natural factors including erosion and rising sea levels (IUCN-NDP, 2013). The region, which is one of the most sensitive biodiversity hotspots in the continent, has lost a sizable portion of its protected land for more than the past five decades due to these pressures (Federal

Government of Nigeria, 1999 and Phil-Eze and Okoro, 2009) resulting to its environmental deterioration at an alarming rate with deepening and pervasive poverty creation despite vast oil resources (UNDP, 2006). The high level of pollution in the region as suggested by a number of oil pollution impact assessment studies, shows that the habitats, livelihoods and people are now badly impacted especially from residual/recalcitrant hydrocarbons, synthetic pollutants and ongoing pollution from anthropogenic and natural sources (UNEP, 2011 and Emoyan *et al*., 2008). It is on this premise that this study evolved in promoting sustainable remediation techniques for the clean-up of contaminated sites as the large area of land affected in the region precludes *ex-situ* treatment owing to economic constraints, thereby requiring the use of relatively inexpensive, environmentally friendly and sustainable remediation methods. The assessment of local stakeholders' wiliness to "buy-in" to remediation solutions of the kind investigated in this study is warranted and forms the central aim of this chapter.

5.1.2 Research philosophical assumptions

Generally, philosophical assumptions also referred to as epistemologies, ontologies (Crotty, 1998); paradigms (Lincoln and Guba, 2000); conceived broadly as research methodologies (Neuman, 2000); or a knowledge claim (Creswell, 2009) are beliefs or claims researchers make about the nature of reality (ontology), what counts as knowledge and how we know it (epistemology), what values go into research (axiology) and the processes for studying it (methodology) (Creswell, 1994). Broadly speaking, a philosophical approach is the lens through which the world is seen and a range of philosophical approach can be used to underpin any chosen research methods (Mesel, 2013). Basically, four schools of thoughts about philosophical assumptions have been extensively discussed in textbooks as well as literatures and they include: postpositivism (Phillips and Burbules, 2000; Creswell, 2003), social constructivism (Lincoln and Guba, 2000; Neuman, 2000 and Crotty, 1998), advocacy/participatory (Neuman, 2000), and pragmatism (Cherryholmes, 1992).

5.1.2.1 Social constructivism

Social constructivism identified assumptions that individuals seek to understand the world in which they live and work (Creswell, 2003). They develop subjective meanings of their experiences towards certain objects or things. Meanings in social constructivism varies, leading researchers to look for the complexity of views instead of narrowing meaning s into a few categories or ideals. The research usually relies as much as possible on the participants; view

of the situation being studied. The participants often construct the meaning of a situation from a broad and general questions and the meaning is usually forged in discussions or interactions with other persons. The more open-ended the questioning, the better, as the researcher carefully listens to what participants say or do in their life setting. In other words, participants express what is not merely imprinted on them but what is formed through cultural and historical norms that operate in their lives individually (Creswell, 2003). Hence, constructivist researchers often address the "processes" of the interaction among participants. Constructivists also focus on the specific contexts in which participants live and work in order to understand the historical and cultural settings of the participants (Creswell, 2003). The background of researchers also shapes their interpretation and they "position themselves" in the research to acknowledge how their interpretation flows from their own personal cultural and historical experiences. The intent of the researcher is therefore to make sense of (or interpret) the participants meanings of the world. Instead of starting with a theory as it is with postpositivism, the researcher generates or inductively develop a theory or pattern of meaning (Creswell, 2003). According to Crotty (1998) the following assumptions have being identified in constructivism discussion:

1. Human beings construct meanings as they engage with the world they are interpreting. Researchers in qualitative science tend to use open-ended questions so that participants can express their views;
2. Humans make sense of their world by engaging with it through their historical and social perspective. We all are born into a world of meaning bestowed on us by our culture, thus qualitative researchers seek to understand participants' context or setting through visiting this context and gathering information personally. They also make an interpretation of what they find which is often shaped by their own experiences and backgrounds and;
3. The fundamental generation of meaning is always social, arising in and out of interaction with a human community. The process of qualitative research is largely inductive, with the researcher generating meaning from the data collected in the field.

Hence, social constructivism with the intention to develop a theory or pattern of meaning from participants' world views is the underlining philosophical assumption in this study.

5.1.2.2 Strategies of inquiry

Strategies of inquiry or tradition of inquiry according to Crewell (1998); or methodologies (Mertens, 1998) operate at a more applied level after philosophical assumption. It provides specific direction for a research design procedures and like philosophical assumption, strategies have evolved over the years owing to advancement in computer technology with higher data analysis and ability to analyze complex models. Newer procedures have been articulated by different researchers for conducting research in social science which contribute to the overall research approach (Creswell, 2003). Strategies associated with the grounded theory approach are the only strategies discussed in this study as it forms the study's strategies of inquiry.

5.1.2.3 Grounded theory

According to *The Discovery of Grounded Theory* published by Glaser and Strauss (1967) grounded theory seeks to inductively distil issues of importance for specific groups of people, creating meaning about those issues through analysis and modelling of theory. Traditional grounded theory can be seen ontologically to be postpositivism in its intent because it is established on the premise of critical realism (Annell, 1997 and Harris, 2003) as traditional grounded theorist believe there is a "real" reality that is imperfectly perceived (Lincoln and Guba, 2000). However, over the years, many researchers have adopted and adapted grounded theory methodology to fit with a variety of ontological and epistemological positions such as constructivism (Annells, 1996 and Charmaz, 2000), feminism (Wuest and Merritt-Gray, 2001), critical thinking (MacDonald, 2001), and postmodernism (MacDonald and Schreiber, 2001). If grounded theory is seen as a spiral that begins with the traditional form, then its adaptations can be seen as a reflection of the various moments of philosophical thought that have guided qualitative researchers (Lincoln and Denzin, 2000) and that it is the researchers' ontological and epistemological position that influence the form of grounded theory undertaken (Annells, 1997). Grounded theorists acknowledge that they bring with them their underlying assumptions that can be framed ontologically and epistemologically at any point on the methodological spiral with respect to the study area (Glaser and Strauss, 1967; Charmaz, 2000; Glaser, 1978; Strauss and Corbin, 1990; Strauss and Corbin, 1998; Strauss, 1987; and Charmaz, 1995).

Constructivist grounded theorist reshapes the interaction between them and the participants during the research process and in doing so bring to the fore the notion of them being the authors. Chrmaz (2000) who is a student of Glaser and Strauss has emerged as the

leading proponent of constructivist grounded theory. A number of articles have been published on constructivist grounded theory in education (Jones, 2002; Jones and Hill, 2003), psychology (Corbet-Owen and Kruger, 2001; Dodson and Dickert, 2004; Madill *et al*., 2000; Stratton, 1997), occupational and environmental medicine (Gustafsson *et al*., 2003), and nursing (Annells, 1997c; McCann and Clark, 2003a; Norton, 1999). However, each of these researchers drew on the work of Charmaz (1995b, 2000) to strengthen their argument for assuming a constructivist approach to their studies. Since the mid-1990s, Charmaz has contended that a constructivist approach to grounded theory is both possible and desirable, because, "Data do not provide a window on reality. Rather, the 'discovered' reality arises from the interactive process and its temporal, cultural, and structural contexts" (Charmaz, 2000, p. 524).

Grounded theory as a research methodology has enormous appeal for a range of disciplines as a result of its explanatory power which illuminates common issues for people in a way that allows them to identify with theory and use it in their own life (Mills *et al.*, 2006).Qualitative researchers who first identify their ontological and epistemological position, chose a point in grounded theory methodological spiral where they felt comfortable theoretically, which, in turn, enabled them to live out their beliefs in the research process (Mills *et al.,* 2006).

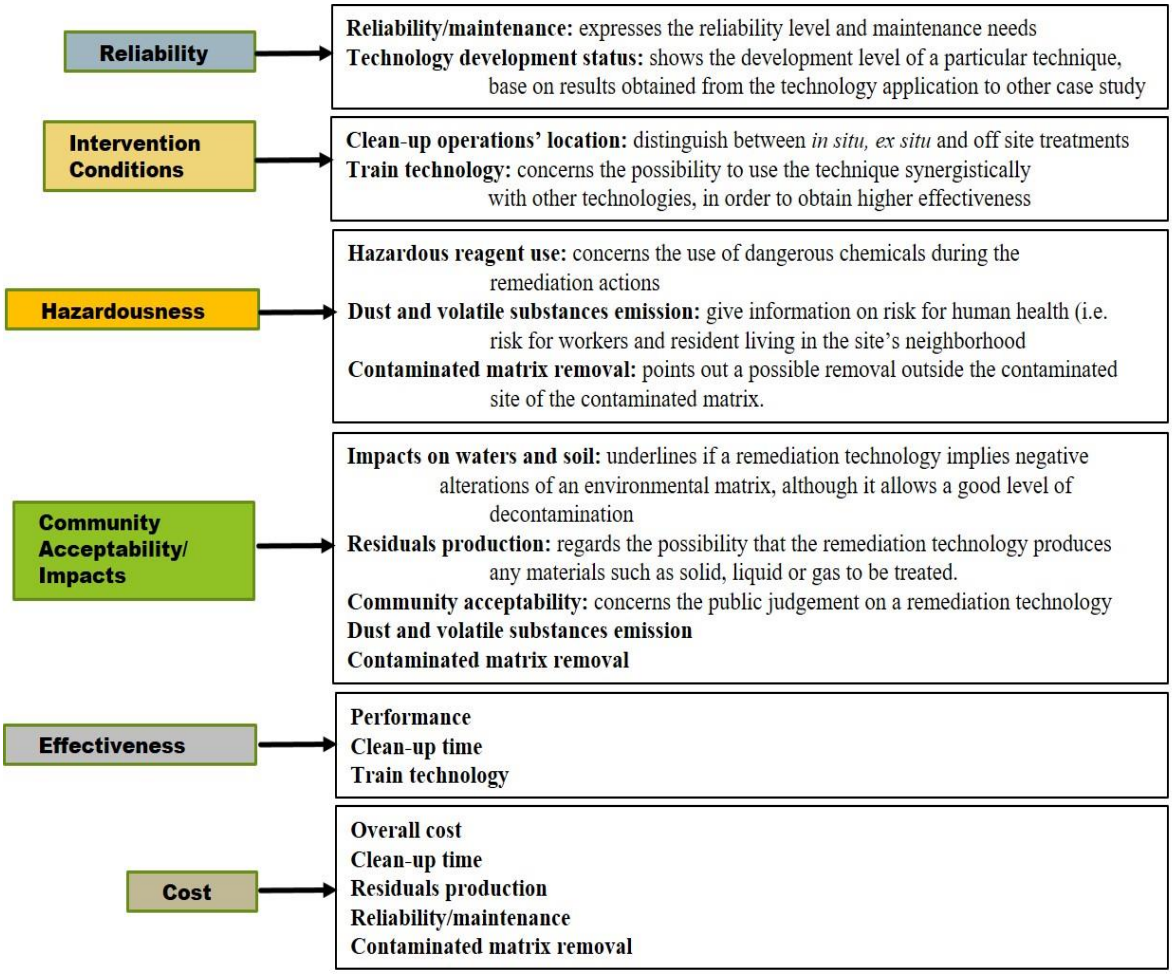
5.1.3 Macro-criteria and evaluation matrix: chosen comparative criteria

There are numerous reports in the literature on qualitative sustainability assessment, economic cost-benefit analysis (CBA), life cycle assessment (LCA), multi-criteria analysis (MCA), multi-criteria decision analysis (MCDA), decision support system for rehabilitation of contaminated sites (DESYRE) (Critto *et al.,* 2006; Bardos, 2012; Bardos *et al*., 2011; Hou *et al*., 2014b; Madejon *et al*., 2011; Witters *et al*., 2012; ASTM, 2013). But there is constraints in the adoption and implementation of sustainable remediation due to inability to quantify social and economic sustainability (Ellis and Hadley, 2009; ITRC, 2011) and the lack of sustainability assessment results transferability (Hou *et al*., 2014c) coupled with limited understanding of practitioners' (stakeholders') actual behavior (Hou *et al*., 2014a). There is also variations in research needs among stakeholders in different countries. Socio-economic and regulatory factors coupled with technical skills may influence the interest of remediation stakeholders as it is the case in the Niger Delta region.

The macro-criteria and evaluation matrix developed by Critto *et al.* (2006) was chosen because it is basic and relatively easy to apply in the study area to compare selected remediation

techniques employed. As shown in Figure 5.1, the following six comparative macro-criteria were identified as *reliability, course of action (i.e. intervention condition), hazardousness, community acceptance/impact, effectiveness, and cost* with each describing a specific aspect of remedial action as follows: ***Reliability macro-criterion*** considered as the maintenance aspects and results achieved by the applicable technique to other case study; ***Intervention condition*** *(i.e. course of action) micro-criterion* identifies the logistic and technical aspects associated to a remediation action by differentiating between *in situ, ex situ* and off-site techniques as well as considering creating a possible train technology; ***Hazardousness micro-criterion*** allows the assessment of the potential human health effects as a result of applied remediation techniques (e.g. effects such as the used of hazardous reagents or emission of dust and volatile substances); ***Community acceptability/impacts macro-criterion*** deals with the negative effects on the environment in addition to the main factors on which public judgement in evaluating a particular remediation technique depends; ***Effectiveness macro-criterion*** helps the experts to assess technology performance that depends on remediation time and removal rates; and finally ***Cost macro-criterion*** points out the parameters that determines the actual or real costs of a remediation action such as time, installation and maintenance cost, waste disposal needs etc.

However, the macro-criteria and evaluation matrix for remediation technologies comparison and risk assessment was not site specific but to reflect stakeholders perception of sustainability in contaminated land remediation from a list of potentially remediation techniques applied in the region.



Source: Critto *et al.*(2006)

Figure 5.1: The six macro-criteria and evaluation matrix employed for remediation techniques comparison in the Niger Delta region

5.1.4 Research questions

i. What is stakeholder's opinion on sustainable remediation in regards to the Niger Delta environmental, social and economic challenges?
ii. Has sustainability been considered in the clean-up of hydrocarbons contaminated land in the Niger Delta?
iii. How can sustainability be implemented in the different remediation techniques applied in the Niger Delta?
iv. Do stakeholders have a fundamental awareness and assessment approach to sustainability in remediation technology application to contaminated land in the region?
v. Will sustainability awareness and evaluation stimulate and promote sustainable remediation feasibility in contaminated land clean-up in the region?
vi. Which of the remediation techniques are considered to be most sustainable and why ?

5.2 MATERIALS AND METHODS

5.2.1 Participants (Stakeholders)

Responses that were gathered from participants through the use of survey questionnaires and one-on-one telephone interviews formed the primary data collection. Gaining access to stakeholders including host community representatives, regulatory agencies, environmental consultants, academics/researchers and technology providers/contractors formed the bulk of the participants. The participants employed in this research were not selected randomly but purposively by sampling target group of professionals as well as other stakeholders who can best and most broadly inform the research questions. According to Creswell (2009) and Kuper *et al.* (2008) participants who can best inform the research questions and enhance understanding of the phenomenon understudy should be selected. Sampling has been defined by Leary (2004) as *"the process by which a researcher selects a sample of participants for a study from the population of interest."* A total of 50 questionnaires was given out to identified stakeholders and a total of 32 stakeholder participants responded by completing the questionnaire. According to Sekaran (2003) a 30 % response rate is acceptable for most research, thus the response rate used in this study is 64 % exceeding the required minimum as proposed by Leary (2004). This was followed up by a telephone interview of five (5) stakeholder participants which represented 15.6 % of the total stakeholders and comprises of a federal/state government regulatory agency, a researcher/academic, an environmental consultant, a land user/environmentalist and a technology provider. The telephone interview was recorded using a Dictaphone and once all stakeholders' participants had finished with their interviews, thematic analysis was carried out according to Braun and Clarke (2006) six-phase guide: (i) become familiar with the data; (ii) generate initial codes; (iii) search for theme; (iv) review themes; (v) define themes; and (vi) write-up. Following this procedure, responses were read through repeatedly and relevant codes were identified, organised into patterns and later into a hierarchy of themes. Codes from across participants responses that related to a shared theme or sub-theme were clustered together. These themes became a reflection of important factors as gleaned from the data in relations to addressing specific content of this research. Themes were subsequently reviewed, refined and named in view of the research questions.

5.2.2 Participants characteristics

According to Salant and Dillman (1994) a participant selection depends on the population size, its uniformity, media, cost effectiveness and the degree of exactness needed. The characteristics of the participants selected in this study reflected a reasonable cross-section of all the stakeholders involved with contaminated land management/remediation in the Niger Delta and they were chosen purposively to ensure representation of important elements of the research questions. In other words, there was no equal opportunity for all participants to be selected due to their focused states, research institutes or organizations. This was based on the fundamental principle which is essential to participants selection that is the ability to define the target population as precisely as possible. Furthermore, participants names and recorded interviews were kept anonymous as the researcher did not disclose participants' details to any third party except researcher's supervisor for verification and authenticity purposes.

5.2.3 Data collection

5.2.3.1 Qualitative data collection

Qualitative approach according to Seale (1999) broadly reflects *'research that does not use numbers'* instead an inductive approach is employed. Morgan and Smircich (1980) has described qualitative approach as a technique having specific set of some sort with its applicability and appropriateness determined by the nature of the explored subject. However, there is no overarching definition provided due to the diversity and strategies in using qualitative approach. The use of qualitative approach in this study was to investigate and explore the current understanding and utilization of different remediation techniques in other to promote sustainability in contaminated land clean-up in the Niger Delta region. It becomes important to pre-define the philosophical assumption that forms the cardinal points of the research, prior to the choice of an appropriate qualitative approach, as research will go in the direction of the underlying assumptions (King, 2004a; Steyaert and Bouwen, 2004). Thus, pragmatism using mixed method approach is the underlining philosophical assumption in this study as it opens the door to multiple approaches with different worldviews, and diverse assumptions in addition to different form of data collection and analysis. In addition, it is applicable to the investigative stage of this study focusing on the description and testimony of participants' experience in relation to sustainability awareness, remediation techniques used, relative economic, environmental and social costs and benefits of each with a view to stimulate the clean-up of contaminated land in the Niger Delta by raising awareness of, and confidence

in, practical and sustainable remediation technologies. Special focus will be placed on their take on the feasibility of sustainable remediation practices in the region.

The following are the assumptions forming the cardinal points of this research:

i. The participants' own account reflecting their work experience in reality and their attitudes and belief towards sustainability; existing remediation techniques applied to contaminated land; and sustainable remediation implementation to impacted areas; and
ii. Insight into the subject of interest (sustainable remediation) from the participants' own account.

5.2.4 Questionnaire survey

Information gathering from respondents (stakeholders) was through the use of questionnaire survey approach. A questionnaire is usually made up of a set of questions given to a respondent for his or her possible response and the opportunity to express his or her views in writing based on the set questions. This research study employed the use of both types open and closed-ended questionnaires with more of closed-ended questions to guide respondents in achieving the set objectives (see Appendix xvii). The administered questionnaire in this study consisted of four parts: (A) the demographic characteristics; (B) awareness and understanding of current remediation techniques used in the Niger Delta; (C) sustainability understanding; and (D) sustainability measurement of contaminated land remediation techniques in the Niger Delta. The sustainability understanding questions (C), included qualitative answer categories to evaluate awareness and perception of sustainability in other to conduct sustainability measurement of contaminated land remediation techniques in section D especially by informed or enlightened stakeholders. Environmental milestones in sustainable development were used for exploring sustainability awareness due to the fact that environmental impact is one of the three pillars of sustainability. Seventeen respondents from the 32 stakeholder participants which represented 53.1 % completed section D. Respondents were asked to rate their awareness, understanding, and sustainability of different remediation techniques on different scales including a combined score expressed according to numerical scale (1= very poor, 2 = poor, 3 = average, 4 = good, and 5 = very good) that allows several judgement levels to be explained while avoiding complex computational efforts. A percentage distribution analysis was also conducted to assess the six micro-criteria and evaluation matrix for remediation techniques comparison in relation to sustainability. The questions were based on a literature review of sustainability in remediation of contaminated land context which was reviewed by

supervisory team as well as a pilot survey from fellow research students in similar discipline (see Appendix xvii). The study is based on data collected through an in-person survey carried out at the convenience of accessible and available targeted stakeholders between January and March 2019 in the Niger Delta region.

5.2.5 Reliability and validity

Reliability has been defined as *'the consistency or dependability of a measuring instrument. Validity on the other hand refers to the extent to which a measurement instrument actually measures what it is intended to measure instead of measuring something else or nothing at all"* (Leary, 2004). In the context of qualitative approach, however, validity and reliability are expressed in the forms of *'trustworthiness', 'applicability' and 'consistency'* of the result (Morse and Richard, 2002). In this study, the researcher ensured the reliability and validity by strictly adhering to the following:

i. A detailed and extensive review of literature carried out to fortified and enhanced one's understanding of the body of information relevant to the research subject and;
ii. Sticking strictly to the research aim, objectives (viii-x) and questions (see section 5.1.4) in addition to the research methods and strategies to produce and analyse the findings.

5.2.6 Data analysis technique

NVivo 12 Pro was used for the qualitative analysis to generate codes and themes. Frequency tables and graphical representations were utilized to give information on vital demographic variables in this study.

5.2.7 Ethical considerations

The research team put a number of procedures in place to protect the confidentiality of participants/respondents with allocated code used always to identify any data provide. Participants name or other personal details was not associated with data provided, for example, the signed consent form was kept separate from data provided. All paper records were stored in a locked filing cabinet, accessible only to the research team, and all electronic data was stored on a password protected computer. All information provided was treated in accordance with the UK Data Protection Act. The research team also obtained ethical approval from the

Natural Science Research Ethics Committee, Middlesex University, London using the MORE Form online, in addition to the following according to Saunders *et al* (2009):

i. Making sure that the confidentiality of data supplied and the participants details are not disclosed to a third party;
ii. Unbiased analysis of primary data collected;
iii. Attainment of the full consent of participants prior to participation;
iv. Avoids plagiarism;
v. Awareness of possible bias from respondents; and
vi. Objectivity of the researcher.

5.2.8 Research limitations

A limitation of this study was the inability to carry out randomized survey due to the important facets and perspectives related to the research questions. Consequently, the findings of the survey may not necessarily be representative of the general Niger Delta population true mean, in other words, the survey may be biased toward a group of stakeholders especially remediation experts who have more awareness of sustainable remediation. The survey response rate was also relatively low compared to others reported in the social sciences. Some of the reasons for this, were due to the country's heightened political tension during the 2019 General Elections, especially in the study area (Niger Delta) which was one of the hotspots marred with political violence at the time of the survey sampling. A group of stakeholders' from the academics/researchers institutes were on indefinite strike nationwide at the time of sampling; unavailability of some targeted groups of stakeholders in particular, federal and state regulatory agencies; and inability to access other states in the region due to safety and security reasons among others. Apart from the limitations caused by the General Elections, the issue of security has always been a persistent challenge in the region as highlighted in other reports (IUCN-NDP, 2013). The challenging prevailing circumstances impact on data collection with a relatively small sample size for most states in the region except for a few like Delta and Edo states. In other to address this impact, all the stakeholders across the region were grouped together to render aggregated results. Therefore, this study may be considered exploratory with the findings interpreted in view of the limitations, however, this study may serve as a baseline for future references.

5.3 RESULTS AND DISCUSSION

5.3.1 Questionnaire analysis

5.3.1.1 Demographic characteristics

A total of 32 stakeholder participants responded by completing the questionnaire. The demographic characteristics for the 32 participants are presented in Table 19. The gender distribution from respondents surveyed in the Niger Delta region has a majority of male participants (78.1 %) compared to female (21.9 %). However, the sex distribution of population in the Niger Delta region according to the national population census is 49.5 to 50.5 % male to female respectively (NPC, 2000). Most of the stakeholder respondents with 71.9 % (n=23) are between 31 and 40 year age group. The educational level of participants in this research, shows most of the participants have studied in universities with 84.4 % (n=27), while participants that have secondary education are 15.6 % (n=5). The high literacy rate in this study does not reflect the overall literacy rate of the population as stakeholder participants were not randomly selected. Almost half of the stakeholders with 46.9 % (n=15) have less than 5 years professional experience and close to half of the stakeholder respondents with 43.8 % (n=14) receive up to ₦1 million (US$2,752.00) income per annum. While majority of the stakeholder respondents with 81.3 % (n=26) have spent 20 years or more in the region, followed by respondents living and/or working for 10-19 years with 15.6 % (n=5).

Table 19: Demographic distribution of sample population

Demographic category	Variable	Composition of sample (%)
Gender	Male	78.1
	Female	21.9
Age	Under 30	6.3
	31 to 40	71.9
	41 to 50	9.4
	50 or more	12.5
Education level	Primary school	0
	Secondary school	15.6
	Tertiary school (university)	84.4
Professional experience	Less than 5 years	46.9
	5 to 9 years	28.1
	10 or more	25
Income per annum	Up to ₦1,000,000 (US$ 2,752.00)	43.8
	₦1,000,000 to ₦2,500,000 (US$2,752.00-6,879.99)	28.1
	₦2,500,000 to ₦5,000,000 (US$6,879.99-13,760.00)	9.4
	More than ₦5,000,000 (US$13,760.00)	18.8
Residency in the region	Less than 1 year	0
	1 to 2 years	0
	3 to 4 years	0
	5 to 9 years	3.1
	10 to 19 years	15.6
	20 or more years	81.3
Contaminated land frequency	Daily	6.3
	Once or twice weekly	6.3
	Once or twice monthly	28.1
	Once or twice yearly	59.4

5.3.1.2 Awareness and understanding of current remediation techniques used in the Niger Delta

Table 20 presents stakeholder respondents composition with majority of participants from university/research institutions with 28.1 % (n=9) and the least from environmental consultancy with 3.13 % (n=1). Over half of the stakeholder respondents with 59.4 % (n=19) come in contact with contaminated land once or twice a year while others deal with it monthly with 28.1 % (n=9); weekly and daily with 6.3 % (n=2) each (see Table 19). All stakeholders are very familiar with excavation & disposal with 100% (n=32), followed closely by bioremediation (see Section 2.3.1.9) with 96.9 % (n=31), covering with clean soil with 93.8 % (n=30), thermal treatment (see Section 2.3.1.7) with 75 % (n=24) and phytoremediation (see Sections 2.3.1.10 and 2.5) with 71.9 % (n=23). Venting (see Section 2.3.1.1) and vitrification techniques were the most unpopular with stakeholders both with 53.1% (n=17), followed closely by chemical oxidation & reduction (see Section 2.3.1.4); soil vapour extraction (SVE) (see Section 2.3.1.1.1) and nanoremediation jointly with 50 % (n=16) as shown in Figure 5.2.

Stakeholders on average displayed good understanding for both excavation & disposal and covering with clean soil with similar measurement of 43.8 % (n=14), followed by an average understanding for phytoremediation and bioremediation with 37.5 % (n=12) and 34.4 % (n=11) respectively. However, their understanding for venting, vitrification, nanoremediation, and stabilization/solidification (see Section 2.3.1.6) were very poor with 40.6 % (n=13) for both venting and vitrification; 37.5 % (n=12) and 31.3 % (n=10) for nanoremediation and stabilization/solidification respectively as shown in Figure 5.3. Almost all the stakeholders agreed that covering with clean soil is the most commonly used technique in the region with the high rating of 71.9 % (n=23), followed by bioremediation with high rating of 37.5 % (n=12) while excavation & disposal technique is moderately applied in the region with 46.9 % (n=15). Thermal treatment and phytoremediation have a low applied rating in the region with 37.5 % (n=12) and 31.3 % (n=10) respectively. But stakeholders were not sure whether or not other remediation techniques such as soil washing & separation; chemical oxidation & reduction; SVE; stabilization/solidification; venting; vitrification; and nanoremediation are applied in the region as shown in Figure 5.4.

The physical approach to contaminated land in the region especially excavation & disposal, covering with clean soil or soil replacement and thermal treatment in this case open burning appears to be the default routine to clean-up. However, the peculiarity of the Niger Delta habitat, interlinked water bodies and variable soil types has made most of these

conventional remediation techniques unsuccessful at remediating contaminated lands due to their unsuitability and inappropriate application (UNEP, 2011; Zabbey *et al.*, 2017). The use of physical remediation techniques apart from being labour intensive and expensive, are most suitable for small contaminated soil but unsuitable for large-scale contaminated land in the region (Khan *et al.*, 2004; Zabbey *et al.*, 2017).

Table 20: Respondents' composition

Stakeholder	**N**	**%**
Technology provider/Engineering contractor	2	6.25
Environmental consultant/Scientist	1	3.13
Land user/Host community	8	25
Federal/State Regulatory Agency	4	12.5
University/Research Institution	9	28.13
Oil and gas employee	5	15.63
NGOs/Activist	3	9.38
Total	32	100

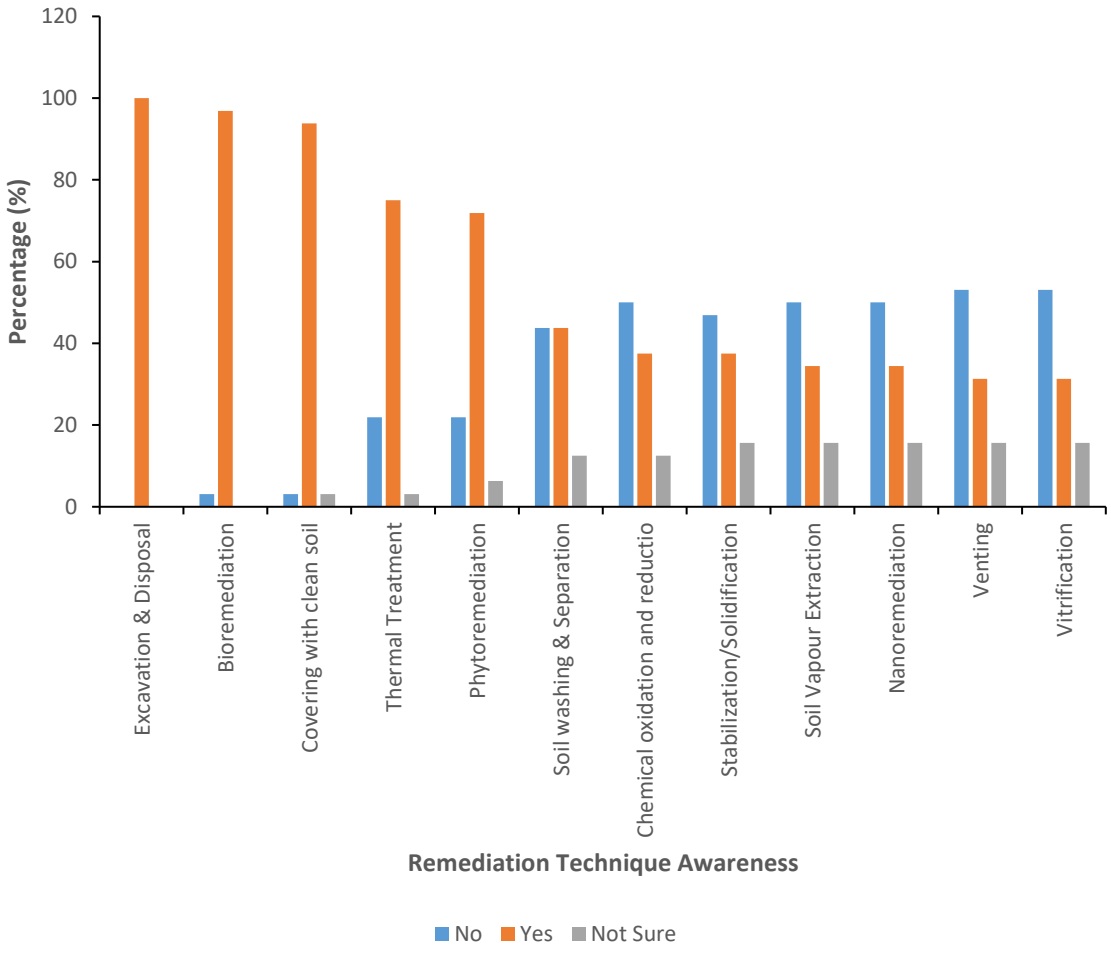


Figure 5.2: Evaluating stakeholders' remediation techniques awareness in the Niger Delta region. Awareness bars (yes) are shown in decreasing order from left to right. Scores are expressed in percentage distribution based on: not sure, no, and yes. Remediation techniques awareness = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

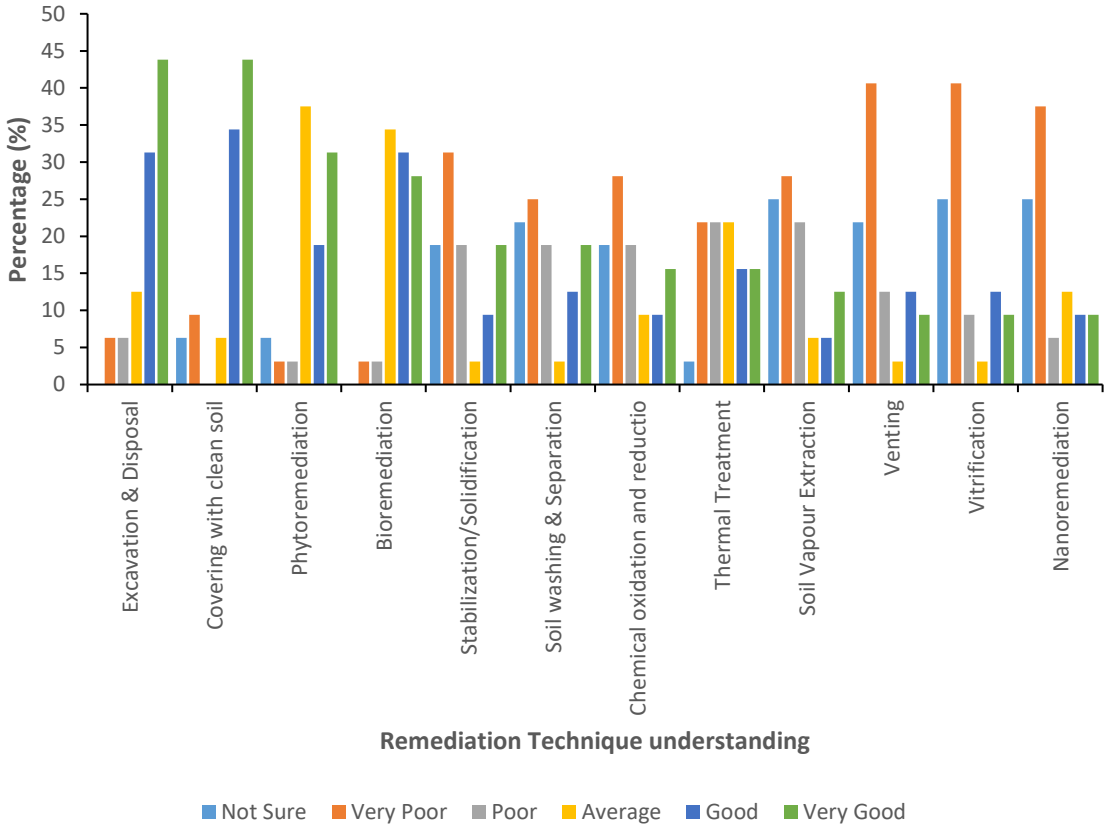


Figure 5.3: Stakeholders' self-evaluation of remediation techniques understanding in the Niger Delta region. Techniques bars with very good understanding are arranged in decreasing order from left to right. Scores are expressed in percentage distribution based on: not sure, very poor, poor, average, good, and very good. Remediation techniques understanding = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

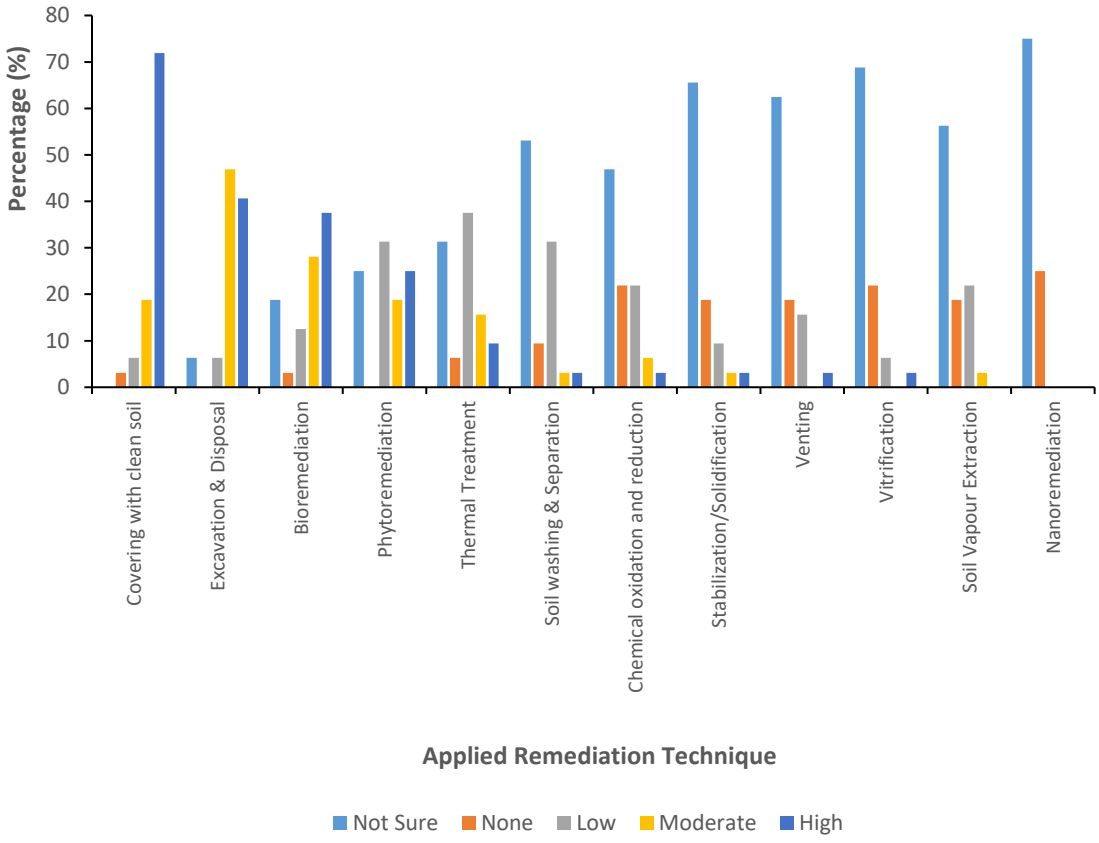


Figure 5.4: Applied remediation techniques in the Niger Delta according to Stakeholders. Bars with the high treatment applications are arranged in decreasing order from left to right. Scores are expressed in percentage distribution based on: not sure, none, low, moderate, and high. Applied remediation techniques = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

5.3.1.3 Sustainability perception

Almost all stakeholders have heard about millennium development goals/sustainable development goals (MDGs/SDGs) with 96.9 % (n=31), followed by Kyoto protocol on climate change with 81.3 % (n=26), earth summit with 59.4 % (n=19) and the least heard of are *Silent Spring* by Rachel Carson 1962 with 21.9 % (n=7) and convention on wetland with 25 % (n=8) as shown in Figure 5.5. These key global conventions on sustainability were used to assess whether stakeholder participants were abreast of sustainable development in view of sustainable remediation. The awareness especially on MDGs/SDGs and climate change have been arguably the most globally publicized issues today and in this aspect participants seem to be keeping up. While other less publicized conventions such as earth summit, convention on wetland, world conservation strategy, the Brundtland report among others were relatively less familiar to participants. This could be as a result of the time at which these conventions were held as over 70 % of the participants were below 40 years.

The general rating of stakeholders sustainability perception and application was below average as shown in Figure 5.6. Over half of the stakeholders agreed on the importance of sustainability with 56.3 % (n=18) but showed poor organizational sustainability policy with 28.1 % (n=9) based on the Likert Scale as presented in Figure 5.7. Stakeholders across board agreed that covering with clean soil is the most unsustainable technique applied in the region with very poor rating of 62.5 % (n=20), while bioremediation and phytoremediation techniques have the most sustainability approval with good rating 40.6 % (n=13) and 34.4 % (n=11) respectively, while excavation & disposal; soil washing & separation; and thermal treatment have poor sustainability rating with the same measurement 40.6 % (n=13). However, stakeholders were not sure on the sustainability of chemical oxidation & reduction; soil washing & separation; stabilization/solidification; venting; vitrification; and nanoremediation as shown in Figure 5.8. Almost all stakeholders suggested the feasibility of sustainable remediation techniques in the Niger Delta with 93.9 % (n=31) while only 3.1 % (n=1) thinks otherwise.

One of the most obvious finding in this survey is that stakeholders were able to scrutinize most of the default remediation approaches especially physical techniques such as covering with clean soil, excavation & disposal, thermal treatment among other as unsustainable. While simultaneously perceiving biological techniques such as bioremediation and phytoremediation as sustainable even though its not be largely successful in the region.

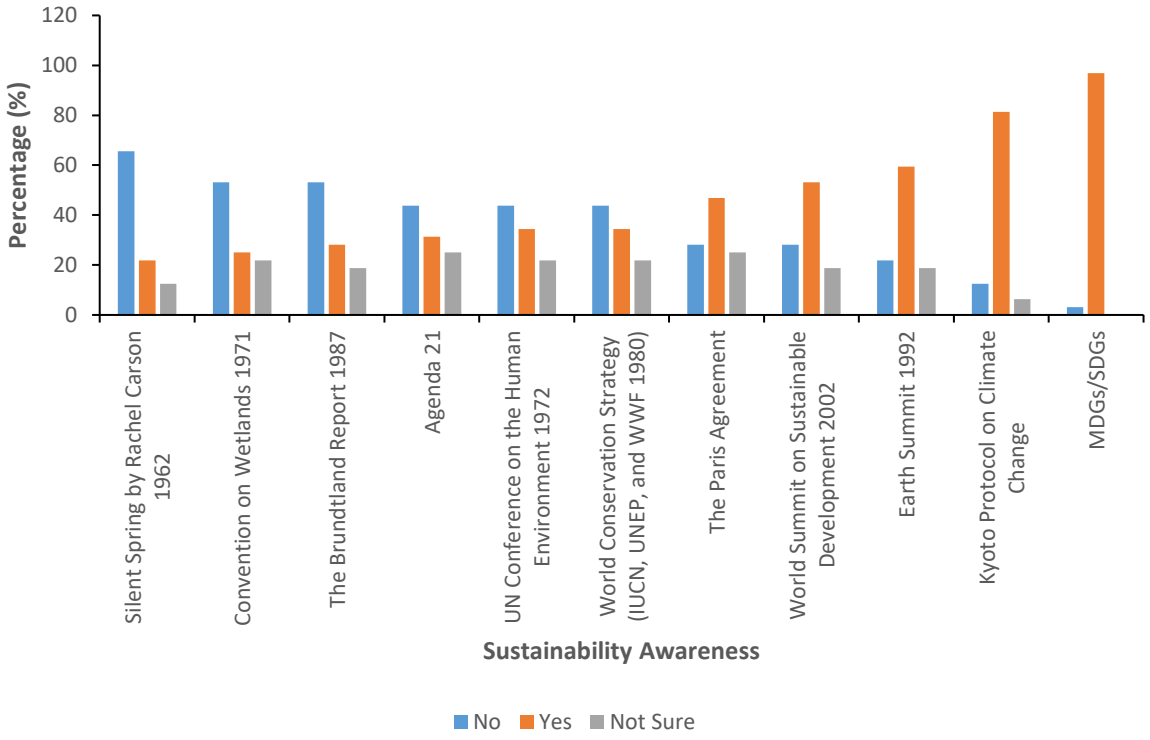


Figure 5.5: Evaluating stakeholder participants' sustainability awareness with relevant conventions and summits. Awareness bars (yes) are shown in increasing order from left to right. Scores are expressed in percentage distribution based on: not sure, no, and yes. Sustainability awareness = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

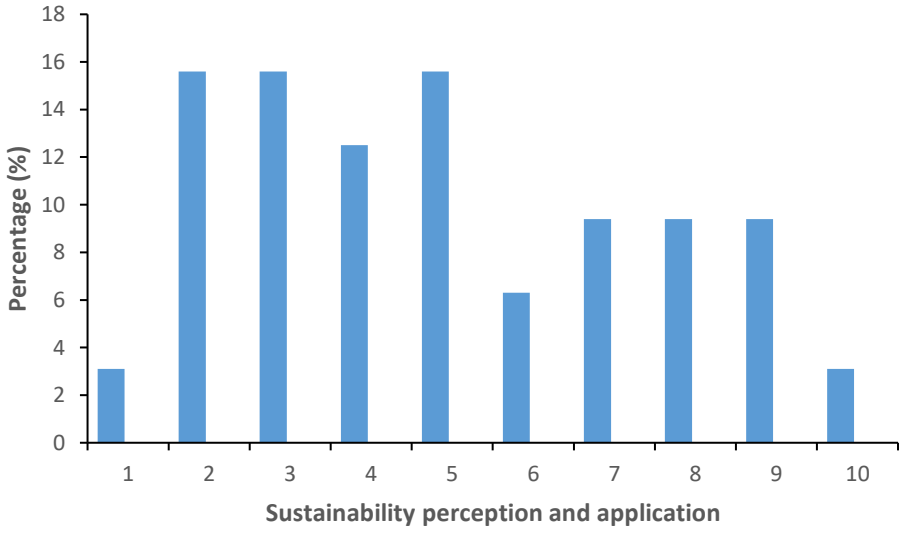


Figure 5.6: Stakeholders rating of sustainability understanding and application in the Niger Delta. Bars expressed percentage distribution based on no understanding at all (0) to very good understanding (10).

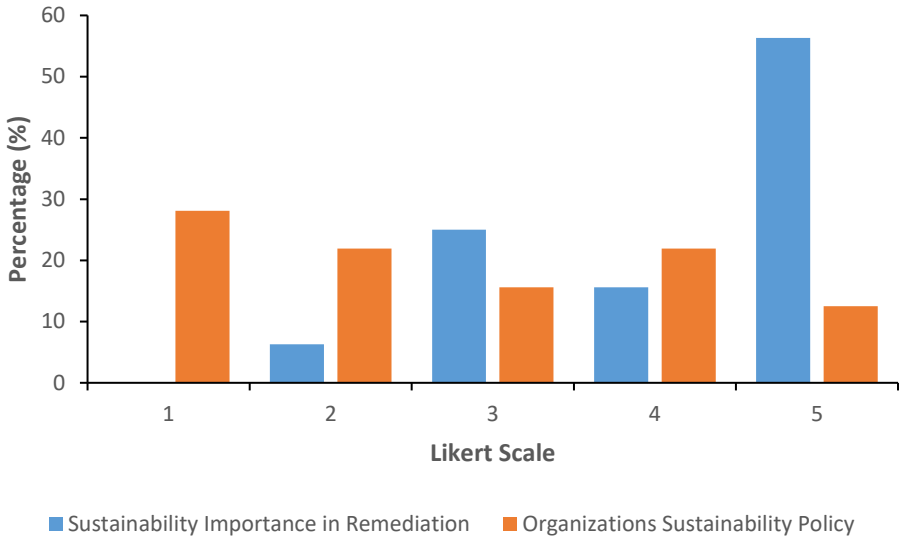


Figure 5.7: Sustainability importance and organizational policy from stakeholders' perspective.

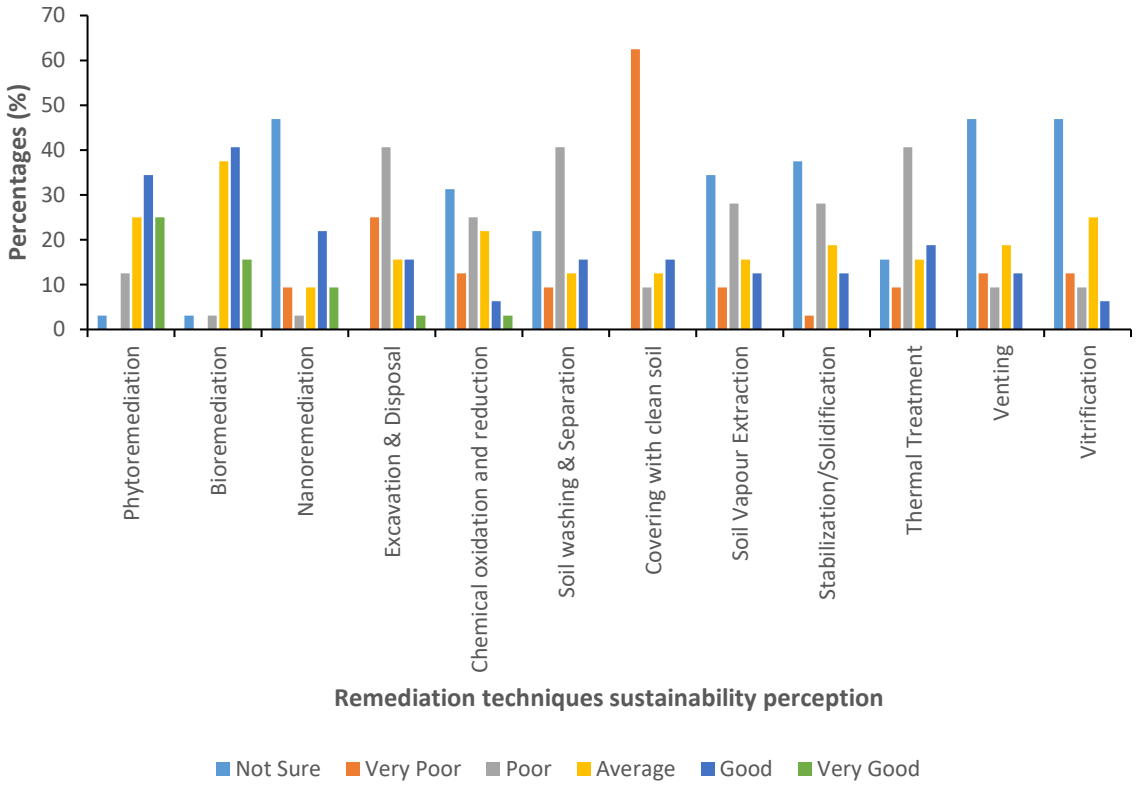


Figure 5.8: Evaluating stakeholder participants' sustainability perception of remediation techniques. Perception bars of very good are shown in increasing order from left to right, expressed in percentage distribution based on: not sure, very poor, poor, average, good, and very good. Sustainability perception of remediation techniques = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

5.3.1.4 Sustainability measurement of contaminated land remediation techniques in the Niger Delta.

These above evaluation criteria (see Section 5.1.1) were purely used for semi quantitative assessment through closed-ended question such as *"…measure the following remediation techniques for its sustainability practices in contaminated land clean-up in the Niger Delta, region"* on a scale of *"low, medium and high"* for each macro-criterion against a list of applicable remediation techniques (see Appendix xvii). The findings show a summary evaluation of stakeholders' views on remediation techniques without the use of any computerized model. Most of the remediation techniques such as soil washing and SVE with 64.7 % (n=11) each; chemical oxidation & reduction and phytoremediation with 58.8 % (n=10) each; and excavation & disposal and bioremediation with 52.9 % (n=9) each in terms of their reliability in contaminated land clean-up were rated by stakeholders participant as moderate. While covering with clean soil has a low rating with 76.5 % (n=13); thermal treatment and nanoremediation both have high rating with 47.1 % (n=8) and 41.2 % (n=7) respectively as shown in Figure 5.9.

Excavation & disposal was considered as the most clean-up operation with 41.2 % (n=7) probably due to its offsite intervention conditions while covering with clean soil was considered the least intervention conditions with 47.1 % (n=8) perhaps as a result of its *in situ* cover up. Bioremediation 70.5 % (n=12); chemical oxidation & reduction and stabilization/solidification each with 52.9 % (n=9); phytoremediation and thermal treatment with 47.1 % (n=8) each; SVE, venting and vitrification with 41.2 % (n=7) each were considered as being a moderate intervention remediation technique. Nanoremediation technique although not very popular across stakeholders with 35.3 % (n=6), was considered as one of the most favorites treatment 29.4 % (n=5) with regards to intervention criterion as shown in Figure 5.10.

Excavation & disposal; covering with clean soil; soil washing & separation and thermal treatment were generally considered to be high in terms of their hazardousness acceptance with 76.5 % (n=13); 64.7 % (n=11); 47.1 % (n=8); and 47.1 % (n=8) respectively. Interestingly, bioremediation has the least hazardousness acceptance with 47.1 % (n=8) while phytoremediation was considered to have a moderate hazardousness acceptance with 58.8 % (n=10), followed by chemical oxidation & reduction and stabilization/solidification with 52.9 % (n=9) and 47.1 % (n=8) respectively as shown in Figure 5.11. The contrasting high perception of excavation & disposal in relation to intervention conditions on one hand and hazardousness acceptance on the other hand may be due to the word 'disposal' attached with

excavation. Most stakeholders may be pleased to see that contaminated soil has been excavated from the impacted site and consider it as a good intervention technique, others may see it somewhat differently in terms of its disposal especially considering the fact that there is no government approved landfill site for contaminated soil disposal. Thus, increasing their perception of being exposed to hazardous materials from a landfill that is not built for dealing with contaminated material as this is often the case.

Phytoremediation and nanoremediation were considered the most acceptable remediation techniques with 64.7 % (n=11) and 52.9 % (n=9) respectively. Soil washing & separation and covering with clean soil were the least acceptable by communities with 64.7 % (n=11) each; followed by excavation & disposal; chemical oxidation & reduction; and thermal treatment with 58.8 % (n=10); 52.9 % (n=9); and 47.1 % (n=8) respectively while SVE and stabilization/solidification were also jointly considered unacceptable with 41.2 % (n=7) each as shown in Figure 5.12.

Nanoremediation surprisingly was considered as the most effective with 52.9 % (n=9) in spite of the fact that it was considered as one of the least popular; understood and applied remediation technique in the Niger Delta among stakeholders with 50 % (n=16), 37.5 % (n=12) and 75 % (n=24) respectively. The reason why nanoremediation is considered the most effective could be because of the word 'nano' as nanotechnology is an emerging branch of science with enormous applications in different fields. Perhaps the ideal of its application in environmental clean-up is more novel and interesting to stakeholder respondents. Bioremediation comes next to nanoremediation with 38.3 % (n=6) even though 58.8 % (n=10) considered it as moderately effective. Soil washing & separation; phytoremediation; chemical oxidation & reduction and stabilization/solidification were moderately considered effective with 76.5 % (n=13); 70 % (n=12); 64.7 % (n=11); and 58.8 % (n=10) respectively. While SVE; thermal treatment; venting; and vitrification jointly have a moderate effectiveness of 52.9 % (n=9). However, covering with clean soil was considered the least effective treatment with 64.7 % (n=11), followed by excavation & disposal with 35.3 % (n=6) which also have a 47.1 % (n=8) moderate effectiveness as shown in Figure 5.13.

Bioremediation and phytoremediation were considered to be the most cost effective remediation techniques among stakeholder with 82.4 % (n=14) and 64.7 % (11) respectively. Thermal treatment; soil washing & separation; excavation & disposal; venting; SVE; and nanoremediation were considered to be very expensive treatment techniques with 70 % (n=12); 52.9 % (n=9); 47.1 % (n=8); 47.1 % (n=8); 41.2 % (n=7); and 41.2 % (n=7) respectively. While covering with clean soil was considered alongside with chemical oxidation & reduction

treatments as moderately expensive with 58.8 % (n=10) and 47.1 % (n=8) respectively as shown in Figure 5.14.

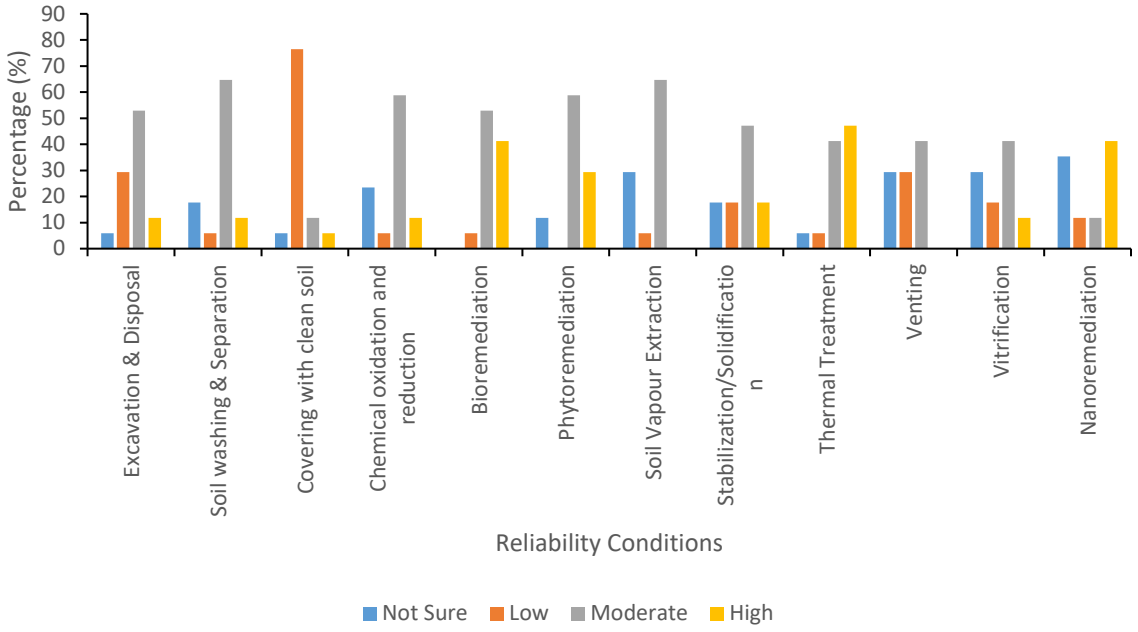


Figure 5.9: Stakeholders' perceptions on reliability conditions of remediation techniques based on results obtained from the technology application to specific sites. Scores are expressed in percentage distribution based on: not sure, low, moderate, and high. Reliability conditions = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

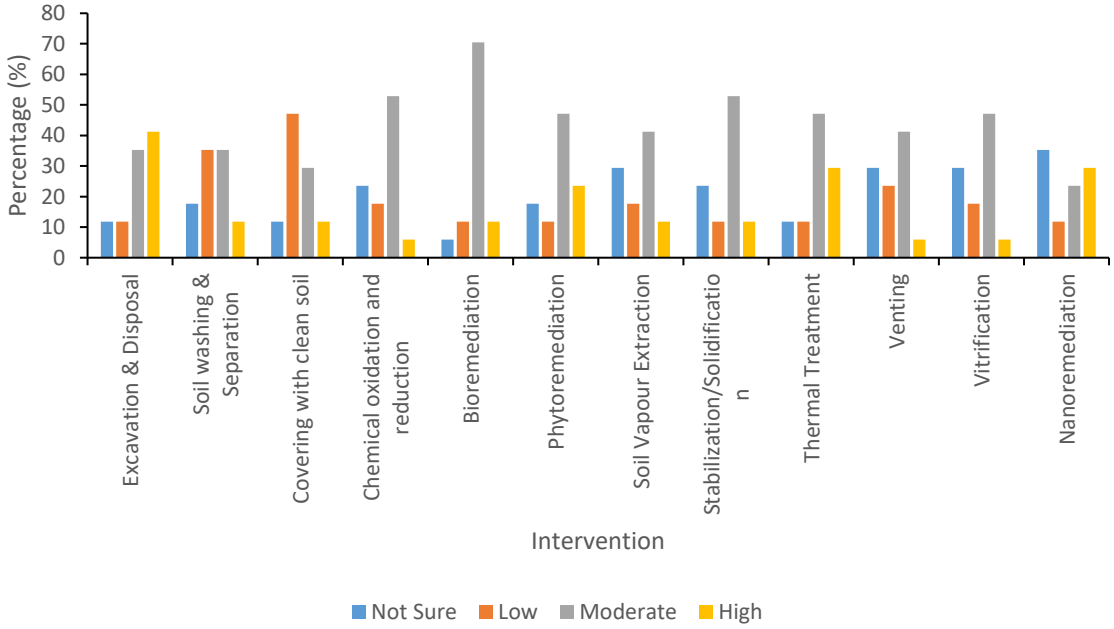


Figure 5.10: Stakeholders' perceptions on the intervention of remediation techniques based on the possibility to apply the techniques synergistically with others to obtain higher effectiveness. Scores are expressed in percentage distribution based on: not sure, low, moderate, and high. Intervention = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

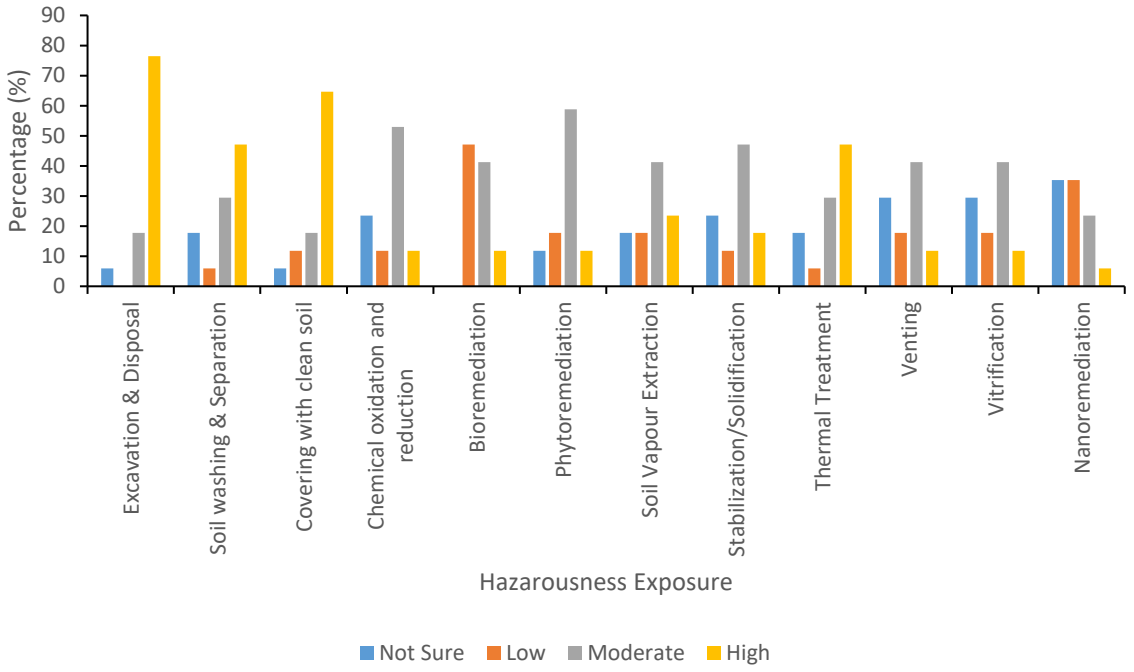


Figure 5.11: Stakeholders' perceptions on hazardousness acceptance of remediation techniques based on hazardous reagent usage, toxic volatile emission and contaminated matrix removal. Scores are expressed in percentage distribution based on: not sure, low, moderate, and high. Hazardous exposure = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

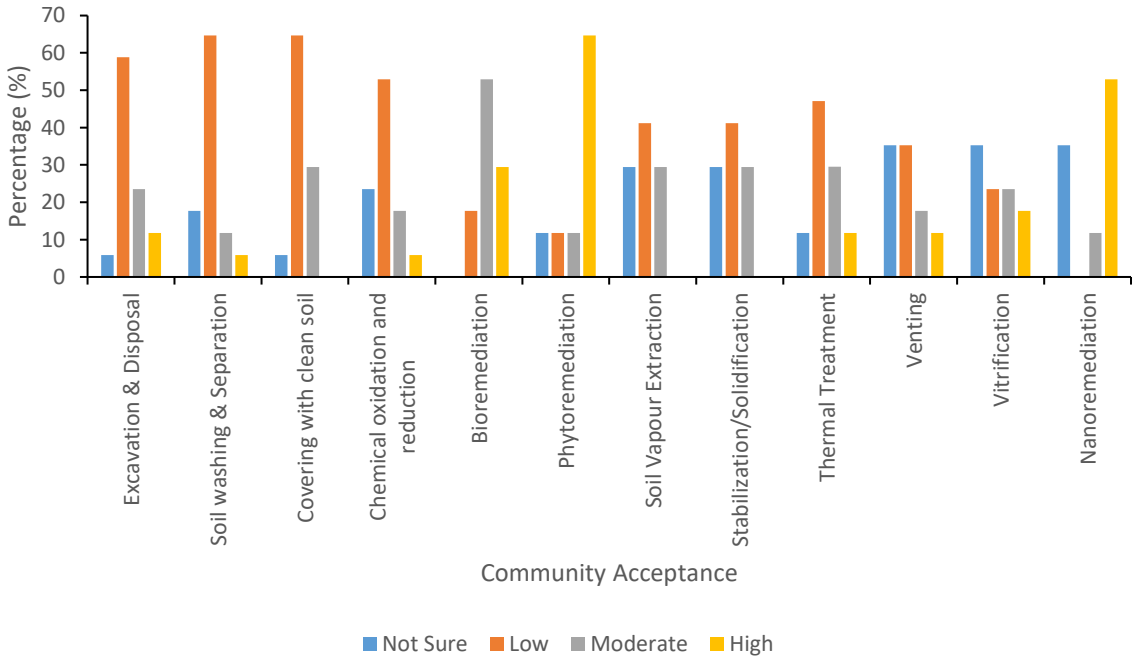


Figure 5.12: Stakeholders' perceptions on community acceptance of remediation techniques based on impacts on waters and soil, residual productions such as solid, liquid or gas to be treated. Scores are expressed in percentage distribution based on: not sure, low, moderate, and high. Community acceptance = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

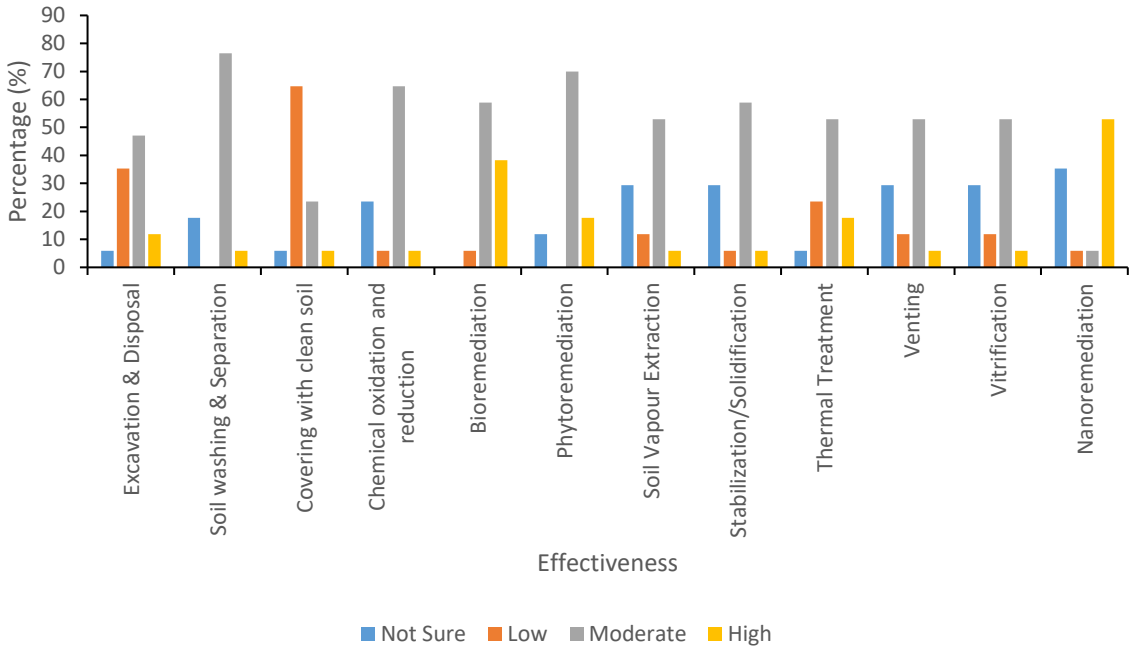


Figure 5.13: Stakeholders' perceptions on effectiveness of remediation techniques based on performance and clean-up time. Scores are expressed in percentage distribution based on: not sure, low, moderate, and high. Effectiveness = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

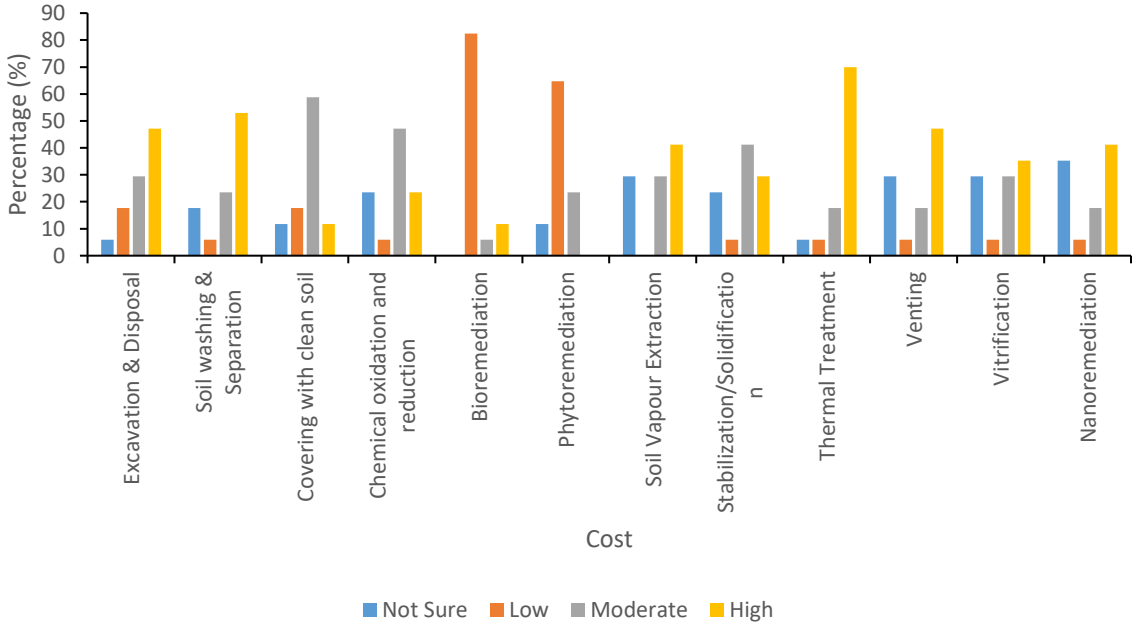


Figure 5.14: Stakeholders' perceptions on cost of remediation techniques based on overall cost. Scores are expressed in percentage distribution based on: not sure, low, moderate, and high. Cost = (stakeholder's frequency / total number of stakeholder respondents x 100 %).

Although, these macro-criteria and evaluation matrix were identified from the review of international approaches (UN 1997; UKEA. 1999; FRTR 2002) with each contributing to more than one macro-criterion for example clean-up duration may affect both effectiveness and cost. While some selected criteria may be correlated with technical aspects such as costs, duration of clean-up, performance, reliability and maintenance, technology development status, locations of clean-up operation, trained technology, reagent hazardousness, contaminated matrix removal, and residuals generation. Other criteria refer to the potential human and environmental health effects such as dust, volatile substances emitted, impacts on water as well as consequences to soil and community acceptance.

For the purpose of analyzing and evaluating sustainability measurement of contaminated land remediation techniques in the Niger Delta region, the 6 comparative macro-criteria with the highest percentage score against remediation techniques as presented in Table 21 were re-grouped into the three sustainability pillars of environmental impacts, social effects and economic viability as shown in Table 22. Each macro-criterion was grouped into one or more distinct sustainability pillars based on its suitability and assessments. Remediation techniques with a high/low percentage score based on sustainability assessment were considered the most sustainable. For example a remediation technique with high community acceptance (social impacts), low hazardous exposure (environmental impacts) and low cost (economic viability) would be considered to meet the basic requirements of sustainable remediation (Table 22). The most sustainable remediation techniques by on participants' assessment were evaluated. Among all the listed remediation techniques the most environmentally friendly with the least hazardousness exposure of 47 and 35 % were bioremediation and nanoremediation respectively. Phytoremediation and nanoremediation in terms of social impact have the most community acceptance of 65 and 53 % respectively while the most economic viable techniques were bioremediation and phytoremediation with 82 and 65 % cost effectiveness respectively. Hence, bioremediation and phytoremediation emerged as the most sustainable remediation techniques by stakeholders' assessment. Although nanoremediation has the most effective rating but was considered to be very expensive in addition to it's an 'unsure' hazardousness exposure. In terms of effectiveness, bioremediation and phytoremediation were considered to be moderate just like others. These findings evaluated sustainability measurement in remediation approaches using different techniques in the region by participants. According to Critto *et al.* (2006) performance (effectiveness), cost and clean-up time are the most important criteria in the description of a remediation technique using cost-benefit analysis (CBA).

Table 21: Remediation technique percentage rating with the highest scored based on the 6 macro-criteria evaluation.

Remediation techniques	Macro-criteria comparison (%)					
	Reliability	**Intervention**	**Hazard exposure**	**Community acceptance**	**Effectiveness**	**Cost**
Excavation & disposal	M (53)	H (41)	H (77)	L (59)	M (47)	H (47)
Soil washing & separation	M (65)	M-L (35)	H (47)	L (65)	M (77)	H (47)
Covering with clean soil	L (77)	L (47)	H (65)	L (65)	L (65)	M (59)
Chemical oxi. & red.	M (59)	M (53)	M (53)	L (53)	M (65)	M (47)
Bioremediation	M (53)	M (71)	L (47)	M (53)	M (59)	L (82)
Phytoremediation	M (59)	M (47)	M (59)	H (65)	M (70)	L (65)
Soil vapour extraction	M (65)	M (41)	M (41)	L (41)	M (53)	H (41)
Stabilization/Solidification	M (47)	M (53)	M (47)	L (41)	M (59)	M (41)
Thermal treatment	H (47)	M (47)	H (47)	L (47)	M (53)	H (70)
Venting	M (41)	M (41)	M (41)	L-N (35)	M (53)	H (47)
Vitrification	M (41)	M (47)	M (41)	N (35)	M (53)	H (35)
Nanoremediation	H (41)	N (35)	L-N (35)	H (53)	H (53)	H (41)

Key:
H = High
M = Moderate
L = Low
N = Not sure

Table 22: Evaluation of the most sustainable remediation techniques using macro-criteria grouped into the three sustainability pillars.

Sustainability dimension	Macro-criteria	Remediation techniques (sustainability evaluation)	Most sustainable
Environmental effects	Intervention (High)	Excavation & disposal	
	Hazardousness exposure (Low)	Bioremediation, Nanoremediation	
	Community acceptance (High)	Phytoremediation, Nanoremediation	Bioremediation
	Effectiveness (High)	Nanoremediation	
Social impacts	Hazardousness exposure (Low)	Bioremediation, Nanoremediation	
	Community acceptance (High)	Phytoremediation, Nanoremediation	Phytoremediation
	Effectiveness (High)	Nanoremediation	
	Reliability (High)	Thermal treatment, Nanoremediation	
Economic viability	Cost (Low)	Bioremediation, Phytoremediation	

5.3.2 Thematic analysis of qualitative data

All the five stakeholder participants interviewed were part of the initial 32 participants as presented in Table 19 and they were purposely selected due to their experience in relation to contaminated land management in the region. Analysis of the recorded telephone interview data revealed two global themes: (i) barriers to sustainable remediation feasibility in the Niger Delta region and (ii) sustainable reparation for mitigating identified barriers. Each global theme was underpinned by several sub- or organizing themes, described in detail below. Figure 5.15 presents a thematic map while Table 23 shows the breakdown of global themes, sub- or organizing themes and related initial (basic) codes. Illustrative quotes are also presented in text along with the stakeholders' participant ID code (number) in parentheses.

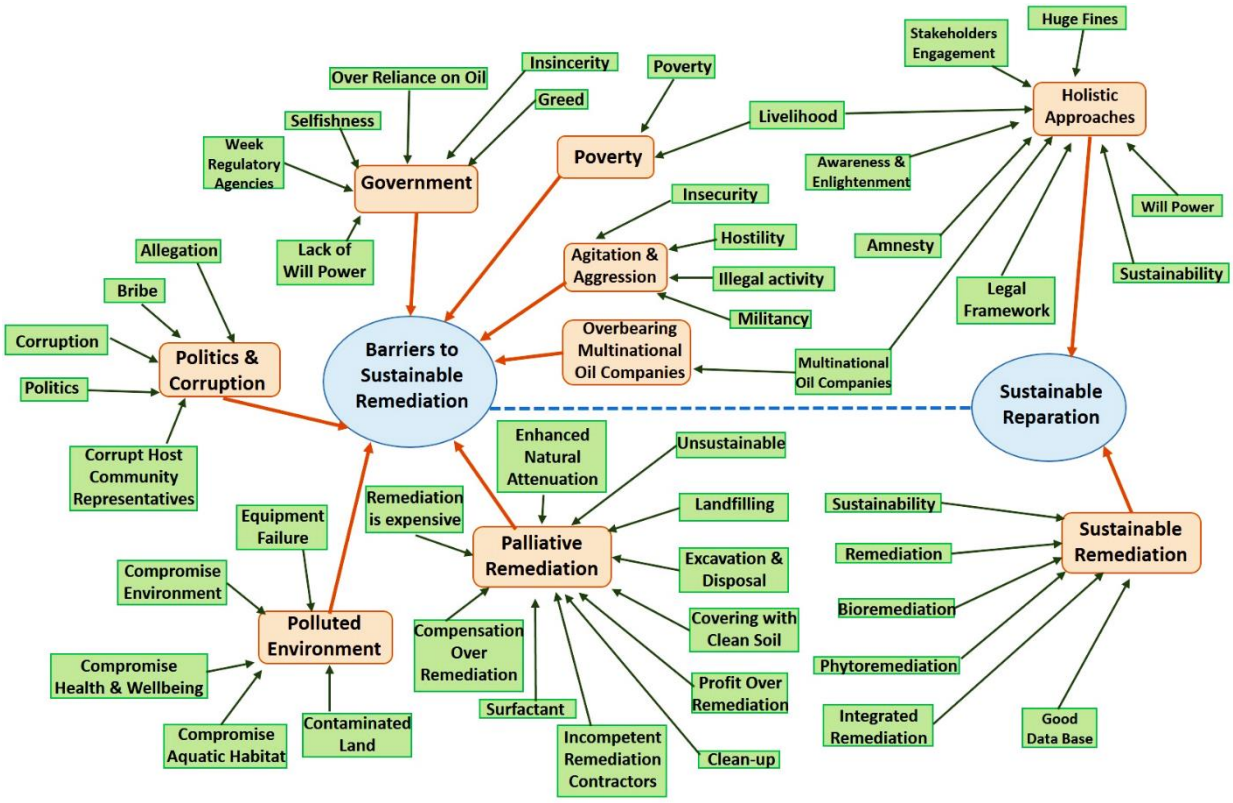


Figure 5.15: Thematic map from initial codes to global themes.
The orange boxes represent the sub- or organizing themes from a cluster of basic/initial codes represented by the green boxes. The blue boxes represent the global themes which are a cluster of the organizing boxes. Arrows represent the bottom-up relationship from initial codes to organizing themes (green arrows) and organizing themes to global themes (orange arrows). The dotted line in blue between global themes indicates sustainability approach through sustainable reparation theme required to mitigate the barriers to sustainable remediation theme in the Niger Delta region.

Table 23: Qualitative data analysis into global themes and sub-themes from initial coding

Global themes	Sub- or organizing themes	Initial or basic coding
Barriers to sustainable remediation in the Niger Delta	Polluted environment	Compromised health and wellbeing Compromised aquatic habitat Compromise environment Contaminated land Equipment failure
	Poverty	Livelihood Poverty
	Overbearing multinational oil companies	Multinationals Companies
	Agitation and aggression	Root cause Militancy Blow up of oil installations Hostility Insecurity Illegal activity
	Government	Greed Insincerity Lack of will power Over reliance on crude oil Selfishness Weak regulatory agencies
	Politics and corruption	Politics Allegation Bribe Corrupt host community representative Corruption
	Palliative remediation	Clean-up Compensation over remediation Profit over remediation Covering with clean soil Enhanced natural attenuation Excavation and disposal Landfilling Incompetent remediation contractors Remediation is expensive Remediation is time consuming Surfactant Unsustainable

Sustainable reparation	Holistic approach	Awareness and enlightenment Amnesty Livelihood Legal framework Multinational oil companies Stakeholders engagement Sustainability Will power Huge fines
	Sustainable remediation application	Sustainability Good data base Remediation Bioremediation Phytoremediation Integrated sustainable remediation

5.3.2.1 Theme 1: Barriers to sustainable remediation in the Niger Delta region

Seven sub- or organizing themes as shown in Figure 5.15 (Table 23) which are (i) polluted environment; (ii) poverty; (iii) overbearing multinational oil companies; (iv) agitation and aggression; (v) government; (vi) politics and corruption; and (vii) palliative remediation summarized the first two research questions on sustainable remediation opinion in regards to the environmental, social and economic challenges in the region and the feasibility of sustainability in the region's contaminated land clean-ups (see Section 5.1.3.1).

5.3.2.1.1 Sub-theme 1: Polluted environment

Before the advent of commercial oil exploration, the region was essentially a pristine environment that supported the substantial resources for the mostly sedentary Niger Delta populations sustainably. Accounting for a large amount of the country's commercial fisheries industry and thriving agricultural products including exotic wildlife habitat, wood for shelter and energy, medicinal herbs and barks among others. However, oil prospecting activities have been implicated with vegetation destruction, destruction of human settlements and arable lands given way for seismic cutting lines in addition to associated environmental pollution impacting negatively on aquatic life and exposure to toxic substances endangering human health and wellbeing. These impacts have compromised the Niger Delta region and there seems to be no attempt in the reparation of the polluted environment, compromised health and social well-being of the Niger Delta people. This was adequately expressed by one of the stakeholders:

> *"As a matter of fact since the oil exploration began in the region as far back as 1958 when oil was discovered, the environment has completely been compromise given the continuous exploration activities… most of the pollution in the area are actually occasion by equipment failures may be in so cases, faulty well head… most of the infrastructures began to decay and we started having corrosion… you know… leakages… most of the fishing industries that use to be viable in region is no more… and that has had some serious cost implication for livelihood… how badly the region is! As you get on the water, you could see visible seepages. So economically speaking, the compromise of the Niger Delta water…emm …region …emm regards the aquatic environment is been a major issue. I also saw first-hand that most of the arable land have also be compromised by a lot of petroleum hydrocarbon spillages."* (ED9).

Consequently, fisher-men and women were put out of jobs and gradually alienated in the society due to the impact of toxic pollutant suffocating fishes, and deteriorating the capacity of the rivers to support diverse fish species. This unemployed population resulted to take up arms

and indulge in social vices within the environment (Umukoro, 2012; Watts, 2007) as highlighted by participants:

> *"…crude oil being an oxygen demanding organic substances will cause most of the dissolved oxygen in the water to be used up and as a result of that you find some of the remaining aquatic lives having to suffocate and die."* (ED9).

> *"Their fishes are banned, oils have taken over the entire region. They can't farm. It's all over the news."* (ED11).

> *"Off course! You know that have a lot of implications to the emm… biological communities in terms of organisms in the ecosystems… so destroying a lot of… emm… in fact… altering generally the ecological balance you know in those places. The local dwellers will still depend on that land and the capacity of that land to support the growth of certain crops that he needs. And over time you just see the whole place and nothing is really happening there in terms of agricultural development. So the livelihood of people who depend on those farming activities are also seriously threatened."* (ED9).

> *"…insecurity will come into play and where ever you have insecurity, then off course… those boys (militants) came and said their environments were destroyed and secondly they were not getting good jobs on the oil…"* (ED11).

> *"There are instances where communities prevent the polluting… the polluters and the regulators from accessing these pollutant sites."* (ED5).

The greatest single environmental problem in contemporary Nigeria related to the petroleum sector is from off-shore and on-shore spillages (Eyinla and Ukpo, 2006). Host communities whose livelihood depend on farming were rendered redundant without any alternative livelihood (UNEP, 2011) as arable land for agricultural purposes were reduced due to the increase in land contamination (Orubu *et al.*, 2004; Umukoro, 2012). Migration of the farming communities into other communities for farmlands resulted to increased pressure on scarcely available fertile land and inter-communal clashes (Olawuyi, 2012; Umukoro, 2012) as this became the only viable survival option available to farmers.

5.3.2.1.2 Sub-theme 2: Poverty

The pollution and destruction of the Niger Delta environment negatively impacts livelihood following fishing grounds and gears contamination, migration of wildlife, farmlands destruction, decreased agricultural produce and yield and habitat displacement, loss of fish, crustaceans, shrimps etc. translated to hunger, grinding poverty and disease. Posing serious danger to the environmental, social and economic wellbeing of the Niger Delta people as captured by participants:

> *" The worst implication to that is the fact that most of the people who reside in this region being…emm …characteristically riverine… emm …derive their livelihood from the waters. Some of them emm… fish and they take their catfish to the market to exchange for money and other values. Most of the cash crops that use to grown in that region when I went there… it used to be a… an important hub for plantain and banana farming but no longer there… I saw skirmishes of sugar cane farm which use to be… which use to blossom much better than that."* (ED9).

> *" …that region used to be very well known for fishing and from recent report I learnt that the fishing has really reduced so if you are putting sustainability into it, it shouldn't have an impact on that… but I think why there is uprising or uproar there especially when you come in with remediation is because they are not able to fend for themselves…"* (ED10).

> *" The Niger Deltan person doesn't even get anything. So the Niger Deltan man says… make I begin dey hustle my own now. So he now start doing the illegal way. While he is doing it illegal way, he's also damaging the environment… the aspect today on ground is everybody go grab… grab your share… it's the national cake so everybody go and cut a slice… get your own slice of the national cake."* (ED11).

> *"…they (Niger Delta people) should still be able to feed and fend for their family… and for themselves."* (ED10).

"Analysis of poverty and human development paint a dismal picture, particularly when the (Niger) delta is compared with other oil-producing regions of the world… people should be able to live valued and dignified lives, in peace and free from poverty." (UNEP, 2006). The region presents itself as one of the worst degraded and most impoverished environment in the world today with untold degree of poverty and livelihood crisis to its people. In a sharp contrast, oil exploration and production instead of bringing prosperity to the region has brought aggravated poverty, rural livelihood destruction and large scale environmental degradation (Ibeanu and Luckham, 2006). According to UNEP (2006) *"the Niger Delta is a region*

suffering from administrative neglect, crumbling social infrastructure and services, high unemployment, social deprivation, abject poverty, filth and squalor, and endemic conflict."

5.3.2.1.3 Sub-theme 3: Overbearing multinational oil companies

Globally, in line with socio-economic practices particularly in more developed society, the discovery and exploration of oil in oil bearing communities was always welcome due to the perceived development for the host communities (Afinotan and Ojakorotu, 2009). The corporate social responsibility concept accepts the notion that an organization has a moral, ethical and philanthropic responsibilities coupled with its usual responsibly to earn a fair return for investors, and comply with the law (Carrol and Bucholtz, 2003). It demands corporate entities to embrace a broader view of their responsibility which takes account of not only stock holders but stakeholders also. The Niger Delta people especially the host communities have high expectation from the multinational oil companies to carry out their cooperate social responsibility including remediation of contaminated sites. But due to the prolonged denials and frustration often resulting to agitation and potentially clogging the wheel of any remediation progression be it sustainable or not. The perceived overbearing nature of multinational oil companies operating in the region have been implicated as barriers to any meaningful sustainable remediation as shown in some of the quotes below:

> *"First of all most of the companies want to abdicate responsibility for these crude oil spillages… when you contaminated an environment, its natural it follows that you sure be responsible for clean-up. And most of them want to conserve money want to make profit. …in terms of livelihood emm… the oil companies that are exploring have done very little in terms of corporate social responsibility to try to ameliorate the plight… the suffering of the host communities… emm… sometimes they build one school block… you know… it's just a mess generally."* (ED9).

> *"…the multinationals just hands off, because as far as they are concerned if you charge me 10 billion to clean the environment and I give you 10 billion, if you don't clean-up the environment, then go to hell because as far as I am concerned, I have paid."* (ED11).

> *"…maintaining the status quo which is favouring the oil companies, some key principal actors within the regulatory agencies and some government employees… sustainable management and sustainable remediation of polluted or crude oil polluted or the by-product polluted area in Nigeria will still be a mirage."* (ED5).
> *"If that is encourage (corporate social responsibility) within most of these communities, that belligerent or aggressive attitude that some of these communities*

have toward polluters and the regulators will reduce, then the communities will now see sustainable remediation to be to their own advantage." (ED5).

The multinational oil companies' activities in the region have made life unbearable by deepening the degree of impoverishment and worsening livelihood crisis aside from environmental abuse issue. This perceived attitude from the multinationals has shown glaring immiseration as revealed from all social indicators in the Niger Delta. According to Ibeanu (2002) just about 27 and 30 % of household in the region had access to safe drinking water and electricity respectively. Similarly, only 30-40 % attended primary school in some part of the region compared to 70 % of Nigerian children (Ibeanu and Luckham, 2006). This was also one of the views of the participants above (ED9). The weakness of legislative control and enforcement of regulations coupled with the callous nature of overbearing multinational oil companies operating in shrouded secrecy have amplified some of the causes of oil spillages in the region and making sustainable remediation a fantasy. Uwuigbe and Ranti (2008) reported that the activities of corporations in the region constitute a veritable threat to its environmental security, ecological balance and sustainable development (remediation). This touches on the Niger Delta people survival and livelihoods (Okoli, 2013). These corporations are perceived by the Niger Delta people as 'enemies of progress' whose operations at every levels are linked with inconvenient consequences on the land and people of the region (Okoli, 2013). Indigenous communities have ended up being frustrated both with the oil and multinational oil companies operating in the Niger Delta, and the government agencies that fail to rigorously regulate them (UNEP, 2006).

5.3.2.1.4 Sub-theme 4: Agitation and aggression

An individual's or community's level of tolerance determines aggressive response to frustration and it has been established that frustration often results to a temporary increase in motivation and subsequently more vigorous responses (Afinotan and Ojakorotu, 2009). In the Niger Delta region, the fact that frustration has led to armed insurrection against military and civilian targets by some militant groups directed against government and the multinational oil companies is view in this perspective. According to the UNEP (2006) on the Niger Delta Human Development Report (ND-HDR) unprecedented restiveness in the region often erupts into violence as a result of deep-rooted mistrust and frustration of poverty stricken communities suffering from administrative marginalization, deteriorating social infrastructure, increased

unemployment and extreme poverty in a region that is endowed with vast oil and gas deposits, good agricultural productivity, extensive forests, excellent fisheries and a large labour force.

> *"The combination of these factors (agitation and aggression) result in hostility in the region …so there is a need for agitation… and emm… the federal government wouldn't… they won't get the federal government attention until they started to blow up…emm …emm pipeline installations and then… so as it is vandalism became a major contributor to …emm …the …emm …spiraling incidence of …emm …emm petroleum and crude oil spillages in the region."* (ED9).

> *"Their soil is contaminated or polluted and then those in government says 'well na dem no na, no be dem dey bunker de oil?' ('It is their fault, after all they are carrying out illegal bunkering')… is that the issue? Up till today people keep complaining…"* (ED11).

The agitating and aggrieved communities (militants) know that the only way to get the government attention urgently is by vandalisms and blown outs because they affect oil production resulting to economic loss in terms of the needed foreign exchange to finance national development. Similarly blown oil pipelines interrupt crude oil supply to refineries and consequently leads to shortages and sudden spikes in oil prices. But most importantly, vandalism and oil blow out further worsening the pollution crisis in the region which may potentially jeopardize any sustainable remediation efforts in place.

> *"…the host communities are continually being belligerent or aggressive towards… and even there are cases of vandalism and that is why some of these companies tend to use that excuse of vandalism to justify not being able to do an adequate reclamation or remediation…there are instances where communities prevent the polluting… the polluters and the regulators from accessing these pollutant sites."* (ED5).

According to Maire (2004) *"Men who are frustrated have an innate disposition to do violence to its source in proportion to the intensity of their frustration…but it seems even less feasible to account for political violence without reference to the properties of men that dispose them to violence…"* The Niger Delta today is a place of frustrated expectations and deep-rooted mistrust (UNEP, 2006).

5.3.2.1.5 Sub-theme 5: Government

The Niger Delta region generally perceived the Nigeria government attitude of treating the region as a colonial enclave, whose natural resources the government plunder with impunity. They resent the government for using their oil resources to develop other parts of the country at the expense of the region's oil producing ethnic minorities. The peculiarities of Nigeria's federalism appear to encourage inequalities and imbalances especially in the processes of power and fiscal matters. This moral crisis of authority and serious legitimacy issue for the Nigeria government heightened the agitations for resource control and true fiscal federalism especially in the region with its deadly militant groups at large.

> *"…given the political divide, you know as regards to the administration of resources…ha…because you know the bulk of Nigeria's oil wealth is generated from that region and the region has really not got its fair share of …emm development. The Buhari (incumbent president) administration actually did something emm… okay... sign up to implement the UNEP report, and emm… we've seen skeletal implementation even though it took them very long to come to site. We are watching because you know emm… you don't do remediation on paper it's a time taken process."* (ED9).

The Nigerian government should seriously diversify its economy to provide and improve the livelihood of the people of the Niger Delta in a sustainable way that will reduce over dependence on oil and gas. This would jumpstart numerous industries and forge closer relationship linking industries, mineral products, sustainable commercial fishing and agricultural produces that would not only generate jobs for the region and Nigeria at large but also galvanize local economies through the local content initiative.

> *"…as long as Nigeria is entirely dependent on crude as source of 98% of its revenue, it will not encouraged stakeholders … to look at sustainable remediation or sustainable utilization of petroleum in Nigeria as a viable option."* (ED5)

> *"When the government feels that they are making conscious effort to clean up the environment you now begin to wonder, how long will it take? The country must first… let's be sincere with regards to who actually own the resources and who should be in charge of exploring those resources …and that's the reason why up till now, we are still talking about Ogoni for over 20 years now. When the man (Ken Saro-Wiwa) who started the whole war, I mean battle for the clean-up of Ogoni was even killed."* (ED11).

The Nigeria government seems to have connived with the perceived multinational oil companies in ruining the Niger Delta through oil exploration and production. The Niger Delta

people have been exposed to diverse socio-economic, political and ecological agitation without properly compensated. The Nigeria government amnesty programme is a sort of retribution for decades of abuse of the region and its people, however, the post-amnesty phase has left more questions than answers as capture by one of the stakeholders:

> *"Insincerity on part of government. Why do the government actually think that the amnesty program was the way out? I thought that if we were sincere… up till now we are still curing amnesty. Peoples are being paid from the oil field and when you ask them, they will tell you that emm… well it's just to guarantee that we keep having constant flow of oil into the economy...but that's not the issue. Those boys (militants) came and said their environments were destroyed and secondly they were not getting good jobs on the oil. I thought those two factors would have been tackled. But instead politician hijack the entire process and dwelled so much on the money part which is the amnesty part and refused to say anything about the remediation… up till today people keep complaining."* (ED11).

5.3.2.1.6 Sub-theme 6: Politics and corruption

Oil revenue generation in Nigeria is one of the major political attractions with massive advantages and unbridled opportunities to anyone who holds the reins of political power. The manipulation and monopoly of oil policy and revenue to the exclusion of the Niger Delta region, in particular the host communities will not only breed corruption but also inevitable compromises among and between all stakeholders which will threaten any forms of sustainable remediation. Currently, the Nigerian government led by President Muhammadu Buhari has set in motion a $1billion clean-up and restoration programme of the Ogoniland region in the Niger Delta while proclaiming that the needed financial and legislative frameworks had been put in place to commence the recommendations made by the UNEP (UNEP, 2016) but there are allegations and counter allegations of corruption from Ogoni people, concerned government agencies and remediation contractors:

> *"I think that first and foremost, the whole issue is been politicized… usually politics comes with its own negatives… Corruption and bad leadership is still enthroned in our politics today. Because government now controls the resources in a state, it means whoever is in government will always want to put his person."* (ED11).

> *"…the issue is political. Now because the federal government which is APC led (ruling political party) is in tandem with the Federal Ministry of Environment …they organized bid for the various sectors identified in the Ogoni (Ogoniland) …but the Ogonis, the*

stakeholders in the community, people within Ogoni have said that most of the consultants that were giving the green light to start the remediation processes are not competent. The clean-up of Ogoniland has been politicized… the issues of corruption and everything is engraved in so many facet of life within Nigeria …the issue of corruption has also affected some of the ways and manners some of the host communities look at remediation." (ED5).

"The driver has been the federal ministry of environment, but definitely the DPR (Department of Petroleum Resources) will play a role, probably with the permit and license …any company passing through the DPR to get things would have gone through this process and it's a scientific process. It must have been tested… So back to what you said, it's an allegation… it's one person's word against the other…" (DT1).

"The Buhari (incumbent president) administration actually did something emm… okay... sign up to implement the UNEP report, and emm… we've seen skeletal implementation even though it took them very long to come to site. We are watching because you know emm… you don't do remediation on paper it's a time taken process." (ED9).

"I think a lot of Nigerians especially the people of the Niger Delta are quite sceptical and suspicious of people when they come to their land irrespective of what the person wants to do. Even when you say you want to do remediation they are still suspicious thinking there is something you are going to benefit from them instead of them benefiting from the remediation." (ED10).

"…few of the key participants spread across the various groups you have mentioned are aware of the need to be sustainable …and also the need to undergo sustainable reclamation and restoration of polluted land but the political and economic and legal framework will not allow this… and most of these oil companies have lots of will power and way power in lobbying for certain things …issues pertaining to oil pollution has been politicised." (ED5).

"To make things worse, the oil companies are not really taking responsibility as it were. So instead what you find is a corrupt… emm… a corruption scheme whereby the JIV the joint investigation process usually consisting of the host communities, the oil company that owns the installation as well as the umpire which supposed to be the Department of Petroleum Resource (DPR) and then usually with National Oil Spill Detection and Response Agency (NOSDRA)…but finds out most time they just bribe the participants to the community and get them to sign that most of the spillages are occasion by sabotage so as to exculpate… emm… to absolve them of their responsibility of carrying out remediation. Some of these off course we know are expensive and they are eager to dodge cost and emm… without much recourse to the health, wellbeing, the livelihood of the host community." (ED9).

"…several stakeholders that are burdened or concerned with the remediation and restoration areas are not really concerned with restoring the environmental health of that particular area pertaining to sustainable use. What they are mostly concerned with is monetary benefit…and litigations issues which will now give them more monetary benefit (compensation)…" (ED5).

"…say the multinational company is fined 10 billion for some set of emm… contamination… as far as the corrupt leaders are concerned, they will always preferred that that multinational company will continue to bring 10 billion… just keep polluting the environment, as far as you give me 10 billion… no 'wahala' ('worries')… just 'dey' ('keep') pollute the environment… just keep giving me 10 billion every month." (ED11)

"…when there is a spill … they're concerned about is how to clean-up and maximized their own profit not even putting the people into consideration and their economic situation into consideration." (ED10).

"…the people (community representatives) talking are actually the big guns… the chiefs, the big boys that talk, the war lords that talk… I have never seen on the news the very people who are affected talking. If you see anybody talk may be is emm… the chief… big chief…big stomach, big 'agbada' (big native wears)… that chief obviously is looking fine from third party agents or from multinationals, so he does not want to say the truth about the whole-entire thing… these are the ones whose houses are not even in the creeks, their houses are in GRAs…" (ED11).

"…you should know that the SPDC the Shell Petroleum Development Company don't answer the laws from the region. The implications are so wide that most of these companies don't mind getting political. Just to be in bed with the political class …the wiliness of the joint venture partners the NNPC (Nigerian National Petroleum Corporation) and the federal government to hold these oil companies to account is not really …we don't find the will …so we are just in the process that is laden with compromise." (ED9).

"…we not heard of pipe burst… because the amnesty program is in place and because the war lords and some other guys are being loaded. The oil boom is still there…" (ED11).

From the various quotes above it can be inferred that the current socio-political and environmental atmosphere in the region will not encourage the optimization of sustainable remediation techniques in the clean-up of contaminated land in the Niger Delta. According to Okoli (2013) the prevailing socio-political and ecological conditions in the region has been bad enough to precipitate and sustain crises and continually put the lives of the people and wellbeing at stake, usually with reckless abandon, they are often forced to resort to desperate

tactics to redress the situation (Okoli, 2013). Political marginalization and social deprivation have worsened the impoverishment of the Niger Delta people. There was the issue relating to federal government neglect of the region which was deepened by the unbalance distribution of oil revenues often diverted into development and elite accumulation elsewhere in Nigeria (Ibeanu and Luckham, 2006). This has brought about perceived short changing of the region in terms of political representation, resource control and allocation within the Nigerian context. Although the proclamation of state amnesty on the region's militants in 2009 seemed to be a water-shed in search for a lasting solution to the crisis, 10 years of post-amnesty, it appears to be a palliative solution.

5.3.2.1.7 Sub-theme 7: Palliative remediation

Various remediation techniques have been employed over the years to clean-up contaminated sites in the Niger Delta region with little or no success (UNEP, 2011) due to the complexity of the environment and socio-political situation. Complete remediation has not been achieved (Giadom, 2015) coupled with its associated negative impact on the environment such as open dump burning consequently resulting to air pollution. The UNEP (2011) reported vast unsuccessful remediation attempts due to the application of inappropriate techniques worsen by the peculiar nature of the Niger Delta terrain such as its variable habitat, interlinked water bodies and variable soil types. The quotes below from the interviewed participants also highlighted some of the unsuccessful remediation techniques used in the region:

> *"What is being done is emm… enhanced natural attenuation or they do simple emm... landfilling… as in they excavate the top soil, the polluted top soil, they excavate that and they sort for another huge clean topsoil and fill up…for aquatic what they do is to contain …to use various equipment to contain the flow of the or use and employed dispersants. So the dispersant sort of enhance the sinking of the crude or of the refined petroleum compound down the depth of the contaminated water body. As the sleek disappears there is now an assumption by mostly the oil company and the regulators that the crude oil has been remediated."* (ED5).

> *"…they've carried out some palliative remediation. Off course they have to give contract awarded. Usually in other to gratify some of the …emm people in the community who are important, whom they have compromised, they give them remediation contract. Instead of going through certified company with proven capacity to carry crude oil remediation… I saw a situation whereby they just took shovels and they just turn the soil upside down. Once they did that they set fire on the other part… they burn the soil in other to burn off the oil in the soil. Off course you know that have a lot of implications to the emm… biological communities in terms of organisms in the*

ecosystems. So destroying a lot of …emm… in fact …altering generally the ecological balance you know in those place. I saw some of those jobs poorly done… when they carry out remediation in water they use surfactant… most of which don't really work. Instead you find the seepages now.. being roll over and because of the density now they begin to sink to the bottom, thereby causing another adverse effect on the organisms that dwell in the Benthic zones. Generally, when they say they carry out remediation the quality of remediation has been very poor, substandard, badly done and worst still, most of it are not done in a sustainable way." (ED9).

"…enhanced natural attenuation by most of the oil companies …that is not a sustainable remediation approach towards restoration or reclamation of polluted terrestrial and extreme location in the delta." (ED5).

According to the UNEP report on Ogoniland environmental assessment, the continuous use of remediation by enhanced natural attenuation (RENA) has become inappropriate for the region (Sam *et al.,* 2016; UNEP, 2011; Zabbey *et al.,* 2017). RENA colloquially referred to as the "do nothing" technique, has been traditionally employed for contaminated land clean-up in the region by key stakeholders especially the multinationals, industry operators and concerned regulatory agencies (Sam *et al.,* 2015; UNEP, 2011). RENA which is arguably a sustainable remediation technique is however unsuitable for majority of the contaminated land in the region because the spilled oil has percolated the soil beyond 5 M, hence contaminated groundwater aquifers in different locations (Ebueghi *et al.,* 2005; Orji *et al.,* 2012). According to Bierkens and Geerts (2014) soils have limited ability to absorbed, degrade and attenuate the effects of contaminants.

5.3.2.2 Theme 2: Sustainable reparation

Two sub- or organizing themes (see Figure 5.15 and Table 23) which are (i.) holistic approaches; and (ii.) sustainable remediation application summarized the last four research questions on sustainability implementation; awareness and understanding in promoting sustainable remediation in the clean-up of contaminated land in the Niger Delta (see Section 5.1.3.1).

5.3.2.2.1 Sub-theme 1: Holistic approaches

A constructive and sincere round table engagement of the Niger Delta people especially the host communities to dialogue with the Nigerian government and the multinational oil companies free of partisan politics. This will precipitate over time to pave the way for improved

livelihood, legal framework and the needed sustainability awareness and enlightenment for sustainable remediation of contaminated land. As recommended by the UNEP (2006) social inclusion promotion of deprived and impoverished communities in development planning and mainstreaming of environmental sustainability coupled with steps to reduce pollution, conserve natural resource and set adequate targets for clean air, water and soil, backed by vigorous enforcement of environmental standards and laws. All the stakeholder participants interviewed in this research were unequivocal about the way forward for sustainability and sustainable remediation in the Niger Delta region. They did not mince words and were very precise and articulate in their respective quotes below:

> *"Sustainability can be implemented if there is a holistic approach towards emm… the issue of pollution… it is feasible if the host communities are encouraged or are enlightened to see the holistic benefit of sustainable remediation."* (ED5).

> *"So before we start talking of what measures we are going to take for the sustainable environment we have to still go back to awareness and enlightenment. I don't think those people in those parastatals or agencies have a deep knowledge."* (ED10).

> *"…established the right information, let the information be… let it be in the open… let it be so open that even students in the primary and secondary school can have access to such information. So that they will be able to access the level of improvement as far as government intervention, third party intervention or multinational intervention is concerned with regards to remediation."* (ED11).

> *"…a large number of people I've interacted with who are in some of these organisations you've mentioned without me mentioning any names are oblivious of what sustainability entails… they just know the word sustainable… sustainable …sustainable. But they… they don't know … they don't really understand it… when you discuss it rather they are on the fence."* (ED10).

> *"It's a clear fora of issues that will take you a holistic process to unravelled with a view to finding lasting solutions."* (ED9).

> *"I think that all stakeholders, international communities, the third party agent, government, all stakeholders will have to come to a round table and invade the community… everybody should put hands together to ensure that the whole thing is done the right way."* (ED11).

> *"There has to be a whole screening sensitization and even may be an incentive to encourage the host communities to allow or to even participate."* (ED5).

"…when there is a collective will and the people with sincerity of purpose and genuine concern about the need for the future generation. I think it is possible to edge out mechanisms for sustainable remediation." (ED9).

"Let's move round the creeks, move round all oil installations, what level of contamination takes place every day? As it stands today what quantity of oil has contaminated our soil? As it stands today, how many years will it take to clean-up the soil? As it stands today, what methods or methodologies are available for us as a country? Or are available for us to buy from the international market? With which to clean-up our oil… I mean to clean-up our soil. For me that is the most important. No other things matter to me." (ED11).

"…we have good legislators who make very fantastic laws and will guide this country. Let's start implementing the law… great laws that will now suggest that at least 60 % of the workforce should also come from that community… monitor the remediation and put laws that will ensure that they remediate. Otherwise withdraw their licences." (ED11).

"I think we should also have an environmental court. I think that we should now begin to separate the environment from civilities, otherwise aspect of technicalities will begin to make mockery of the entire environment. So separate environment from civilities let's have an environmental courts where issues regarding the environment will be trashed. Government can be taken to the court. Laws will be set to the extent that there wouldn't be any aspect of immunity because it is immunity and breeds impunity." (ED11).

"…one of the ways in ensuring that we have a safer environment, is to place a huge fines on multinationals… pay huge fines may be you have any spills you place huge fines…and those fines should be used to eventually take of such commission, but unfortunately that doesn't happen here, if you collect huge fines from multinationals, in fact it's almost looks like those in charge are benefitting fast…" (ED11).

This holistic approaches from the above quotes reiterate the UNEP (2006) which emphasized first and foremost the use of the region's vast oil wealth to address the region's multi-faceted challenges. To create an environment in which most people can flourish, able to live valued and dignified lives, overcome poverty, enjoy a peaceful atmosphere and expect a sustainable environment (remediation). According to the UNEP (2006) report, for development (remediation) to be meaningful, people-cantered and sustainable, it has to be rooted in (i) peace promotion as the foundation for development (remediation); (ii) effective and responsive local governance to the peoples' needs; (iii) improve and diversify the economy; (iv) promote social inclusion and improved access to social services; (v) promote environmental sustainability to

preserve the means of people's sustainable livelihoods; (vi) build sustainable partnerships for the advancement of human development. From the findings of this research, an integrated approach to sustainable remediation is recommended as suggested by participant ED11:

> *"…an integrated remediation brings together all the experts. Those who have the capacity for physical remediation, those that have capacity for chemical remediation, who can use chemical surfactants you know and all that and those who have capacity for bioremediation. They will seat on a table, and then take each of the remediation technique and access it in terms of the impact of the environment… I think if we have a body of scientists coming together and then assessing each of the components, then of course by integrated remediation, we can guarantee sustainability and we can also guarantee the speed of the remediation process rather than relying only on bioremediation. I usually converse for integrated remediation."* (ED11).

5.3.2.2.2 Sub-theme 2: Sustainable remediation application

Sustainable remediation application has increasingly gained global attention in addition to policy and guidance reflecting sustainable practices worldwide. Sustainable practices generally are those that include recognition of the economic and natural resources, ecology, human health and safety, and quality of life (NAVFAC, 2014) (see Section 2.4.1). Considering the large area of land impacted by pollution, the pollutants complexity, the closeness of communities to crude oil contaminated sites and reoccurring sensitivities within the Niger Delta, new approaches are urgently required for pragmatic, safe, cost-effective, low-techniques and efficacious methods in promoting sustainable remediation within reasonable timeframe. Below are participants take on sustainable remediation in relations to the prevailing environmental, socio-political and economic challenges bedeviling the Niger Delta region:

> *"Sustainable remediation approach is still a novel idea for the participants that are involved in exploration, production… and transportation and refining of crude oil…in the Niger Delta… and as long as that is the norm now we can't really say that sustainable remediation will be utilized as far as the regulation and monitoring of the polluters (is concerned)."* (ED5).

> *"…it's difficult to established sustainability… very little is done. As a matter of facts new oil wells are still been exploited every day. Nobody cares about the future generation as far as Nigerian situation is concern right now…the concept of sustainable development is not in view at all."* (ED9).

"…sustainable remediation approaches are not been utilized by the key participants in the Niger Delta." (ED5).

"I find it very difficult to find a standard remediation technique." (ED9).

"…it goes beyond endangering the lives of the Sharks, the Whales and the large fishes as far as the environmentalist is concerned if it will endanger as little as the life of a phytoplankton, that is not environmentally sustainable." (ED11).

"One of the worst factors in remediating the activity in the region will be lack of emm... in fact should I say inadequate or total lack of baseline data… you want to restore the environment to the pristine state yet you don't … you can't tell emm… what constituted the pristine state." (ED9).

"What is the reference point with regards to oil contamination in the country? If the background information regarding that polluted environment is not correct, then there's no way you will correctly assess the levels of contamination… I mean the level of remediation that have actually taken place… poor background data to assess the level of improvement." (ED11).

"…biological mechanisms, they are more sustainable although on the down side they take time you know to achieve their set goals… you will be looking at biostimulation and basically bioaugmentation mechanisms in which case you need to ferry inorganic nutrients to the environment so that the microbial indigenous …organisms can replicate at such speed in view to using up the organic compound as carbon sources emm… but most of these processes… takes time except when you want to augment with some other process that are non-biological." (ED9).

"Bioremediation is actually sustainable because it is what is close to what we call natural attenuation… the environment will now be able to create for itself new colonies… plant colony, plant communities… I mean new communities… new communities of organisms, of plants that are now well adapted to the new environment." (ED11).

"I would like to also say bioremediation but again it depends on what … what going to be used for the bioremediation…" (ED10).

"…bioremediation is 100 % clean? Well that's not true. There is a possibility that you organism can just become the dominant organism in that community… it still doesn't mean that bioremediation would not have its own trouble particularly given the time that its always slow." (ED11).

"I would go for phytoremediation. I'm choosing phytoremediation… I think Nigeria and Niger Delta as a whole they are blessed with a lot of flora." (ED10)

"…usually the standard will be to either use a phytoremediation mechanism… that has different mechanisms… phytostabilization… you plant some trees... so that they can trap or do some conversion metabolism… trapping those crude oil deposit so that they don't seep beyond the subsurface to the water table to compromise the underground water reserves... we also have plants that have the ability to extract crude oil and some metals and translocate these … to the harvested shoots… so that such shoot can be harvested and removed continually. Otherwise you have phytovolatilization in which case most of the crude oil contaminants can be converted into gaseous forms…expelled through transpiration processes in plant… those are some of the standard phytoremediation mechanisms available." (ED9).

"…an integrated remediation brings together all the experts. Those of who have the capacity for physical remediation, those that have capacity for chemical remediation, who can use chemical surfactants you know and all that and those who have capacity for bioremediation. They will seat on a table, and then take each of the remediation technique and access it in terms of the impact of the environment." (ED11).
"I think if we have a body of scientists coming together and then assessing each of the components, then of course by integrated remediation, we can guarantee sustainability and we can also guarantee the speed of the remediation process rather than relying only on bioremediation. I usually converse for integrated remediation." (ED11).

The highlighted socio-political, socio-economic and environmental barriers to sustainable remediation (see Figure 5.16) of the Niger Delta contaminated land suggest that an effective sustainable remediation could, to a large extent, resolve the damaging effects suffered in the Niger Delta. Therefore, there is the urgent need to explore measures that would achieve sustainable reparation using holistic approaches in tandem with sustainable remediation to clean-up contaminated land and ensure concentrations of residual contaminants in soils are within acceptable limits to both human and environmental health.

5.4 CONCLUSION

The demographic characteristics for the 32 participants in Chapter 5 showed a majority of male participants (78.1 %) compared to female (21.9 %). Over 70 % of the stakeholder participants are between 31 and 40 years age group, with above 80 % tertiary educational level and more than 80 % have lived in the region for 20 year or more. 47 % of participants have less than 5 years professional experience. Gender distribution and literacy rate are not representative of the Niger Delta population due to purposive sampling. The highest composition of stakeholders were from university/research institutions (28 %) with the least from environmental consultancy (3 %). Stakeholders awareness of applied/applicable

remediation techniques were highest with excavation & disposal (100%) and lowest with vitrification (53 %). The survey showed that stakeholders demonstrated above average understanding of most of the remediation techniques in use especially in relation to their sustainability perception. Remediation techniques such as covering with clean soil, excavation & disposal, thermal treatment (open burning) were perceived by stakeholders as the most unsustainable techniques employed in the region to clean-up contaminated land. Environmental milestones in sustainable development showed that almost all stakeholders are aware of the relatively recent milestones such as MDGs/SDGs, Kyoto protocol on climate change and earth summit. Phytoremediation and bioremediation were seen as the most sustainable remediation techniques by stakeholder participants as they were perceived to pose the least hazardous exposure to the public with high community acceptance despite not being perceived as the most effective.

Polluted environment, palliative remediation, politics and corruption, government, overbearing multinational oil companies, agitation and aggression, and poverty were seen as the current environmental, social and economic challenges to sustainable remediation among the stakeholder participants in the Niger Delta. However the feasibility, implementation and optimization of sustainability from the sustainable reparation global theme perspective requires an holistic approach which includes but not limited to stakeholders engagement especially multinational oil companies and their host communities, awareness and enlightenment, amnesty, legal framework, huge fines, and will power from all parties especially from the Nigerian government. Therefore at the very least, remediation techniques of the type studied in this research would have acceptance among stakeholders and with good will, the ability to contribute to the sustainable clean-up of contaminated land such as the ongoing Ogoniland clean-up and restoration project in the Niger Delta, region.

Chapter 6

General Discussion of Experiments, Sustainable Remediation Feasibility, Challenges and Prospects in the Niger Delta region, Nigeria.

6.0 General discussion of experiments, sustainable remediation feasibility, challenges and prospects in the oil rich Niger Delta region, Nigeria.

6.1 General discussion of experiments undertaken.

This PhD research was carried out to investigate the potential of advancing phytoremediation using soil solarization enhanced with biosurfactant as a novel sustainable remediation approach to crude oil contaminated land in the Niger Delta region.

A pilot study to compare the phytoremediation potential of the indigenous *Chromolaena odorata* against a non-indigenous *Medicago sativa* as contained in the research objectives i-iii was the first quantitative experiment carried out in this study (see Chapter 3). The result showed a more resilient and thriving *C. odorata* compared to *M. sativa* in 60-120 mg/kg PAHs contaminated soil. This demonstrates that biosurfactant-amended treatments in both plants especially *C. odorata* significantly influenced the reduction of PAHs and suggests '*there was a genuine difference in phytoremediation between biosurfactant-amended and un-amended treatments in PAHs reduction of contaminated soil'* in the pilot study which addressed the research objectives (i – iii). Rhamnolipid biosurfactant with 500 mg/kg appeared the optimal treatment in enhancing the apparent aqueous solubility and bioavailability of the PAHs in the soil. The different root systems of both plants may have influenced their phytoremediation potentials. The tap root system of *M. sativa* characterized by enlarged central root have deeper penetration into the soil with lateral roots branching off the central axis while the fibrous root structure of *C. odorata*, being finer and more profuse, provides an advantage of increasing the total rhizoplane surface area in order to establishe an active microbial population (Aprill and Sims, 1990; Henderson, 2001). This fibrous root system might have influenced the slight increase in heterotrophic rhizosphere microorganisms especially bacteria in *C. odorata* treatment than *M. sativa* to establish an indirect rhizodegradation mechanism but without statistical significance. Thus, the pilot study showed indigenous *C. odorata* as a potential candidate for phytoremediation with added advantages of being ecologically safer, cheaper, aesthetically pleasing, socially acceptable, easier to cultivate and potentially more effective than its non-indigenous *M. sativa.*

C. odorata was employed to investigate the effect of soil solarization enhanced with biosurfactant on phytoremediation of weathered 240 mg/kg PAH contaminated soil. In addition, the impact of solarization and/or biosurfactant was evaluated on total heterotrophic microorganisms in the soil/rhizosphere and their soil enzymatic activity of dehydrogenase and urease as a novel integrated sustainable remediation approaches for contaminated land clean-

up in the Niger Delta region (see Chapter 4). A microcosm was designed to simulate the subtropical conditions contaminated land are subjected to in the Niger Delta region which is largely characterized by a humid tropical climate with high rainfall and warm temperatures (see Section 4.2.6). Soil solarization was conducted for 28 days before introducing seedlings of *C. odorata* for a 84 day phytoremediation period. The soil temperature results obtained with the microcosm during soil solarization by covering it with or without transparent polyethylene sheet indicated successful simulations especially with solarized treatment at both 1 and 4 cm depths respectively. The reported temperature range of highest mean for solarized treatment with 51.0 and 48.3^{o}C compared to non-solarized counterpart with 44.3 and 42.0^{o}C at 1 and 4 cm depths respectively agrees with previous reports (Emoghene and Futughe, 2011; Novarro *et al.,* 1992; Stapleton, 1997) (see Section 4.4.1). The 28 day solarization period had significant effect on PAH reduction especially phenanthrene and fluoranthene (see Section 4.3.2.1). The gradual increase in daily simulated temperatures of solarized moist soil treatments as shown in this study may have impacted on the physical, chemical and biological properties of the solarized soils including increasing the mineral nutrients and soluble organic matter such as N mineralization, Ca, Mg, P, K etc. by facilitating decomposition of organic matter quickly using the heat under the transparent polyethylene sheet. This direct impact from solarization creates a favourable microenvironment for bacterial metabolic activity and ultimately, PAH biodegradation. According to Leahy and Colwell (1990); Zhang *et al.* (2005); and Okere and Seme (2012) corresponding increase in temperature up to an optimum of 30 to 40^{o}C results in corresponding increase in bacterial metabolic activity and PAH biodegradation due to extreme temperature adaptation by PAHs degrading bacteria while maintaining their metabolic activity. Other studies have shown that an increase in the soil temperature could result in residual dissipation. According to Ghosal *et al.* (2016), Margesin and Schinner (2001) an increase in temperature leads to an increase in PAHs solubility which in turn increases the bioavailability of PAH molecules. Thus, the significant removal of PAHs from solarized soils may be attributed to the physico-chemical and/or biological processes as both are affected by increased soil temperatures. Increases in soil temperature have been reported to decrease PAHs sorption by soils (Podoll *et al.,* 1980), and subsequently increase their solubility and vapour pressure (Miller *et al.,* 1989) and profoundly enhance biodegradation of PAHs in contaminated sites (Ghosal *et al*., 2016) since abiotic removal of PAHs from soil depend mostly on sorption and volatilization (Bulman *et al.,* 1985; Park *et al.,* 1990).

According to Miller *et al.* (1989) most of the soil heterotrophic microorganisms are mesophiles with an optimum temperature of about 25-35^{o}C and a growth capacity from 10-

15^{o}C to 45^{o}C but a decrease in temperature inhibits the growth and development of these communities of heterotrophic microbes and also reduce the rate of biochemical reactions. PAHs biodegradation have also been reported to take place over a wide range of temperatures, Lau *et al.* (2003) reported to have an optimum temperatures of >50^{o}C and >75^{o}C respectively in the degradation of PAHs in spent-mushroom compost. They reported that over 90 % PAHs removal took place at these very high temperatures. Similarly PAHs biodegradation have been reported at very high temperatures (60-70^{o}C) by *Thermus* and *Bacillus* spp (Feitkenhauer *et al.*, 2003). Studies have shown that microorganisms have adapted to metabolize PAHs at extreme temperatures however with most reports focusing on mesophilic temperature instead of the efficiency of transformations at very high or low temperature (Bamforth and Singleton, 2005).

In the post-solarization or phytoremediation period, phenanthrene, fluoranthene and benzo[a]pyrene were further reduced with a significant reduction ($p \leq 0.01$) in solarized and vegetated/un-vegetated treatments compared to their non-solarized and vegetated/un-vegetated counterparts with or without biosurfactant amendment. Phenanthrene has the highest significant reduction ($p \leq 0.01$), followed by fluoranthene and benzo[a]pyrene (see Section 4.4.2.1). The size of the general linear model (GLM) coefficient was a good way to assess the practical significance of the effect that solarization has on the PAHs removal. Phenanthrene, fluoranthene and benzo[a]pyrene would be reduced by 11.3, 8.1 and 6.3 % respectively in the presence of soil solarization while biosurfactant and plant remain constant. This suggests that soil solarization contributed the most in the removal of PAHs as set out in objective v. The overall significance in this study gave a very strong evidence that *'soil solarization has effect on PAHs removal in the advancement of phytoremediation of PAH contaminated soil.'* The removal of PAHs especially phenanthrene and to some extent fluoranthene was greater during the interval between day 0 and 28 where soil temperatures were relatively higher due to soil solarization but the removal rates were almost linear towards the end of the treatment period especially from day 56 to 112. This suggests that optimum conditions enhancing the removal of PAHs early in the first 56 days particularly the 28 days solarization period may have become less favourable at the latter post-solarization/phytoremediation stage. A similar trend was reported by Mervin and Sims (1987) who observed relatively rapid loss of phenanthrene at higher temperature during the interval between 0 and 60 days when soil treatment was incubated compared to the latter stages of incubation and attributed this loss to less favourable conditions at the latter stage. PACE (1985) also observed similar trend for the apparent removal of phenanthrene, anthracene, and fluoranthene in an agricultural soil. The increase of soil

temperature by solarization impacted most significantly on the removal of low molecular weight PAHs as seen in this study with phenanthrene and fluoranthene. This correlates with the finding of Mervin and Sims (1987) in which increasing soil temperature improved the rate and extent of apparent loss of low molecular weight PAHs but had little impact on five and six-ring PAHs.

Generally, the extent and rate of apparent removal was greater for PAHs of low molecular weight and relatively high aqueous solubility (see Table 2). Substantial and comparative removals of phenanthrene (three-ring) and fluoranthene (four-ring) were observed respectively throughout the study period especially in solarized treatment as shown in Figures 4.7(a-b) and 4.8(a-b). While the least removed PAH was benzo[a]pyrene (five-ring) as shown in Figure 4.8(a-b). This general trend for the PAH class of compounds i.e. three-ring, four-ring and five-ring in relation to increase temperatures has been observed by other researchers (Bossert *et al.,* 1984; PACE, 1985; Sims and Overcash, 1983; Herbes and Schwall, 1978). Volatilization may have contributed significantly to the reduction of phenanthrene due to Henry's law of coefficients (aqueous solubility divided by vapour pressure) as phenanthrene falls within the range of $10^{-5} < H < 10^{-3}$ atm/mol/m^3 referred to as a region of moderate volatility by Lyman *et al.* (1982). PACE (1985) reported volatilization as a significant mechanism of three-ring PAH removal from soil, either as parent compound or as metabolites. Despite very limited information on the effect of solarization on contaminant removal/degradation, this study provides a rich empirical evidence demonstrating the suitability and compatibility of this novel technique, particularly soil solarization as a remediation option that is sustainable, environmentally friendly and cost effective for PAHs contaminated soils clean-up especially for the vast contaminated sites in the Niger Delta region.

The effect of biosurfactant in Chapter 4 was observed to be insignificant ($p \geq 0.05$) to the PAHs overall removal having negligible impact throughout the study period (objective v). Biosurfactant did not impact on phenanthrene fluoranthene and benzo[a]pyrene removals between biosurfactant-amended, vegetated/un-vegetated treatments and un-amended, vegetated/un-vegetated treatments with or without solarization (see Section 4.4.2.2). The highlighted *p*-values of the individual PAHs show an overall insignificance in PAHs removal by biosurfactant with insufficient evidence against the H_0 thereby contradicting the previously established effect of biosurfactant: *'there is no genuine difference in advance phytoremediation between biosurfactant-amended and un-amended treatments in PAHs reduction of contaminated soil.'* This finding initially appeared unexpected as it contradicts numerous reports on the positive impact of biosurfactants in enhancing PAHs removal as previously

established. However, considering the relatively high temperatures recorded during the 28 day soil solarization period for both solarized and non-solarized treatments, rhamnolipid biosurfactant may have been deactivated/denatured. According to Lamichhane *et al.* (2017) surfactant-assisted solubility of PAHs is proportional to the temperature up to a certain extent. It was also reported that the effect of rhamnolipid biosurfactant on the solubility of naphthalene, phenanthrene and pyrene increased with temperature up to 30 ^{o}C (Li *et al.,* 2015b). A similar study was carried out by Peng *et al.* (2015) to investigate rhamnolipid biosurfactant-enhanced remediation of PAHs at a temperature range of 15 to 50 ^{o}C and reported an optimum temperature of 35 ^{o}C for PAH degradation with anthracene and pyrene degradation of 37.5 and 25.6 % respectively at 35 ^{o}C. Interestingly, however, the increase in soil temperature caused by soil solarization, appears to have increased PAH solubility and thus bioavailability (Ghosal *et al.,* 2016; Fenoll *et al.,* 2010; Margesin and Schinner, 2001). This suggesting the possibility that soil solarization may have also played the role of biosurfactant in solubilizing and subsequently making PAHs to be bioavailable for degradation as a result of the direct impact of soil temperatures.

Indigenous *C. odorata* drastically reduced PAH mixtures significantly ($p \leq 0.01$) in all the vegetated treatment groups compared to their un-vegetated counterparts. Phytoremediation effect by *C. odorata* was significantly observed ($p \leq 0.01$) in the removal of phenanthrene, fluoranthene, benzo[a]pyrene between vegetated and un-vegetated treatment groups with or without solarization and/or biosurfactant amendment (see Section 4.4.2.3). The impact of treatment factors (solarization and/or biosurfactant) on plant growth as contained in objective vi showed that soil solarization significantly increased ($p \leq 0.01$) *C. odorata's* growth throughout the phytoremediation period. Solarization also impacted significantly ($p \leq 0.01$) upon the *C. odorata's* shoots and roots dry biomasses. Statistical significant increase ($p \leq 0.01$) in heights, shoots and roots dry biomasses of *C. odorata* between solarized vegetated and non-solarized vegetated treatment groups was observed (see Section 4.4.3.1), suggesting *'there was significant interaction between soil solarization and plants in advanced phytoremediation of PAHs contaminated soil.'* This finding on the impact of solarization on plant is consistent with a vast body of literatures on improved plant growth, yield and quality and has been attributed to soil borne control, soil structure improvement, increase availability of N and other vital plant nutrients in addition to the greenhouse effect (DeVay and Katan, 1991; Elmore *et al*., 1997; Stapleton, 2000; Emoghene and Futughe, 2011). Although correlations between performance in agronomy and phytoremediation potential may not be fully determined. However, the impact of soil solarization on phytoremediation directly and/or indirectly from this study is promising,

as better agronomic performance of the indigenous *C. odorata* has shown significant reduction in PAHs from weathered PAHs-contaminated soil as a way of advancing phytoremediation. According to Wiltse *et al*. (1998) plant that are less affected by contaminants in soils are healthier and more persistent and will yield healthier root systems and greater top growth which is demonstrated in this study. On the other hand, biosurfactant was not essential in the agronomic performance of *C. odorata* as contained in the research objectives (vi) (see Section 4.4.3.2) in this study and a similar report by Liao *et al.* (2015) also showed that surfactant played no significant role on the height and biomass production of maize even though plants are profoundly influenced by soil conditions. However, Sheng *et al.* (2008) suggested a positive effect on the growth of plant in rhamnolipid-amended soil may be caused by the degradation of rhamnolipid in soil resulting to better physical soil conditions for plant nutrient uptake and increase in plant growth promoting microorganisms in the rhizosphere. Considering the possibility that the rhamnolipid biosurfactant in this study may have been denature or deactivated by higher soil temperatures due to soil solarization, any plausible effect of the biosurfactant would have been adversely compromised. And as a consequence, *'there was no significant interaction between biosurfactant and plants in advanced phytoremediation of PAHs contaminated soil.'*

The impact of soil solarization on the soil total heterotrophic microorganisms (objective vi) shows a significant reduction ($p \leq 0.05$) after the 28 day period compared to the non-solarized treatments (see Section 4.4.4.1). However, solarization appears to have increased the density of total soil/rhizosphere heterotrophic microorganisms in all solarized treatments compared to their non-solarized counterparts but without statistical significance ($p \geq 0.05$) at days 56, 84 and 112 respectively. The highest total heterotrophic rhizosphere microorganisms were bacteria, followed by actinomycetes and fungi respectively. Reports have shown that a broad range of soil microbes in addition to major plant pathogens have been negatively impacted by soil solarization due to the heating treatment (Chen *et al*., 1991; Schoenfeld *et al*., 2003; Palese *et al*., 2004; Culman *et al*., 2006; Gelsomino *et al*., 2006). Some studies reported a general reduction of soil total bacterial population by soil solarization (Mahmoud, 1996; Patel and Patel, 1997; Itoh *et al*., 2000; Barbour *et al*., 2002; Sharma *et al*., 2002), while others documented a decrease in soil fungal population with no impact on bacteria (Coates-Beckford *et al*., 1997; Shukla *et al*., 2000). However, other investigations showed an increase of total bacterial and actinomycetes populations in solarized soil (Kaewruang *et al*., 1989a; Khair and Bakir, 1995; Khaleeque *et al*., 1999). The increase in total heterotrophic rhizosphere microorganisms in solarized treatments as demonstrated in this study according to Chen *et al.*

(1991) was due to re-colonization by beneficial microorganisms soon after the end of a solarization treatment.

Solarization also seems to have increased the dehydrogenase enzymatic activity (objective vi) in solarized treatment compared to non-solarized counterpart but the increase was not statistically significant ($p \geq 0.05$) (see Section 4.4.4.1). According to Brzezinska *et al.* (1998) temperature and soil water content have indirect influence on dehydrogenase activity by affecting the soil redox status. These redox transformations are closely linked with respiration activity of soil microorganisms serving as the microbiological redox indicators in soil and can be considered a possible measure of microbial oxidative activities (Tabatabai, 1982 and Trevor, 1984). As shown in this study, the increased temperature during soil solarization initially reduced dehydrogenase activity compared to its non-solarized counterpart but gradually increases post-solarization in relations to increasing total heterotrophic microorganisms re-colonizing the soil especially vegetated soil suggesting a positive response. The dehydrogenase enzyme activity is usually used as an indicator of biological activity in soils and it is considered to exist as an integral part of intact cells but does not accumulate extracellularly in the soil. Dehydrogenase can also be used to indicate the type and significance of pollution in soils. McCarthy *et al.* (1994) reported high dehydrogenase activity in soils polluted with pulp and paper mill effluents but low in fly ash polluted soil (Pitchel and Hayes, 1990). Higher dehydrogenase activities have been reported at low doses of pesticides and lower dehydrogenase activities at higher doses of pesticide (Baruah and Mishra, 1986). There was a solarization effect with significant ($p \leq 0.05$) on rhizosphere enzymatic activity of urease in solarized treatment when compared to their non-solarized counterpart (objective vi). Many factors influence urease activity in soils including cropping history, organic matter content of the soil, soil depth, soil amendments, heavy metals (PAHs), and environmental factors such as temperatures (Tabatabai 1982; Yang *et al*. 2006). The significant increase in urease activity as observed in this study agrees with a report by Das and Varma (2011) that an increase in temperature generally results to increase in urease activity suggesting that higher temperatures increase the activity coefficient of the urease enzyme.

However, the effect of biosurfactant on the total density of soil/rhizosphere heterotrophic microorganisms (objective vi) was insignificant ($p \geq 0.05$) over the treatment duration between biosurfactant-amended treatment and un-amended counterpart with or without solarization and vegetation at days 28, 56, 84 and 112 respectively (see Section 4.4.4.2). Although there are conflicting reports on the impact of biosurfactant on microbial density, however, the deactivation/denaturing of rhamnolipid in this study by higher soil

temperatures during soil solarization compromised the true impact of biosurfactant on the total heterotrophic soil/rhizosphere microorganisms. According to Liao *et al.* (2015) a significant increase in microbial number was observed by increasing surfactant concentrations and Mathurasa *et al.* (2012) also reported similar increase in microbial growth and suggested the significance might be due to the surfactant directly or greater levels of dissolved organic matter released by the surfactants which served as carbon sources for additional microbial growth. However, a study carried out by Whang *et al.* (2008) on rhizobacteria population in diesel-amended rhamnolipid biosurfactant treatments achieved insignificant increase. Biosurfactant in this study also have negligible impact ($p \geq 0.05$) on the soil enzymatic activity of dehydrogenase and urease respectively (objective vi) (see Section 4.4.4.2).

The Niger Delta indigenous *C. odorata* significantly increased ($p \leq 0.01$) the total density of soil/rhizosphere heterotrophic microorganisms in all vegetated treatments compared to their un-vegetated counterparts at days 56, 84 and 112 respectively from their transplanting day (day 28) (see Section 4.4.4.3). Bacteria were the highest heterotrophic rhizosphere microorganisms, followed by actinomycetes and fungi respectively. This finding is consistent with numerous studies in literature where vegetated treatment have statistically significantly higher amount of microbial population than their un-vegetated counterparts (Hazaimeh *et al.*, 2019; Tang, *et al.*, 2005; Parrish and Fike, 2005; Ho and Banks, 2006; Olson and Fletcher, 2000). The significant increase in total heterotrophic microorganisms especially bacteria as observed in the vegetated treatment may enhance the bioremediation of PAHs in the contaminated soil given that soil microbial function supports plant phytoremediation (Tang, *et al.*, 2005). The continuous and rapidly increasing microbial density especially at days 56, 84 and 112 in vegetated treatment over their non-vegetated counterpart could be significant in the overall % removal of PAHs in all treated soils. Parrish and Fike (2005) reported that the presence of plant roots in addition to increased microbial density, usually result to a large increase in the bioavailability of target PAHs. Suggesting that high microbial density due to vegetation better support bioremediation than low microbial density counterpart. This was also corroborated by Ho and Banks (2006) that greater total bacterial numbers and PAH-degrading bacteria were found in the rhizosphere soil. Olson and Fletcher (2000) also reported vegetation increased total numbers of beneficial fungi and bacteria in contaminated soil. *C. odorata* also significantly increased ($p \leq 0.01$) the soil enzymatic activity of dehydrogenase and urease in vegetated treatment compared to their un-vegetated counterpart (see Section 4.4.4.3). The overall significance in *p*-values shows *'C. odorata plant has effect on the total density of soil/rhizosphere heterotrophic microorganisms and the soil enzymatic activity of*

dehydrogenase and urease in advance phytoremediation of PAH contaminated soil.' The uptake of nutrients by plants through the rhizosphere interacts with the microbial community inhabiting the soil rhizosphere resulting to mutually benefiting significance to both plant and rhizosphere microbes. This in turn leads to the higher enzymatic activities of rhizosphere soils than those of the bulk or un-vegetated soil as demonstrated in this study. The significant increase of rhizosphere enzymatic activity especially dehydrogenase in vegetated treatment groups compared to their un-vegetated counterparts with or without solarization and/or biosurfactant may depend not only on the stimulation of root-related microbial activity by rhizodeposition but also on the root released enzymes. According to Gianfreda (2015) higher rhizosphere enzymatic activity is a reflection of a greater functional diversity of the microbial community with the possibility of removing both inorganic and organic pollutants. The significantly increased soil/rhizosphere total heterotrophic microbes, dehydrogenase and urease activities suggest the advancement of phytoremediation using indigenous *C. odorata* in combination with soil solarization as an eco-friendly and cost effective novel treatment. The enhanced soil fertility, quality as well as microbial density and diversity in addition to significant reduction in targeted PAHs, opens up new possibilities for sustainable approach to remediate contaminated land in the oil rich Niger Delta, Nigeria with optimum solar radiation, high humidity and ubiquitous indigenous plants such as *C. odorata* with proven phytoremediation potential as demonstrated in this research.

Soil solarization integrated with phytoremediation as a remediation technique is first of its kind and bridged the knowledge gap on its application especially in combined form. Biosurfactants, however, have been reported to enhance phytoremediation but it's application with soil solarization has never been carried out anywhere in the world. Consequently, this study shows that in the presence of soil solarization, biosurfactant plays a minor role to affect PAHs removal, soil/rhizosphere total heterogeneous microorganisms and enzymatic activities in contaminated soil. And this may be attributed to the deactivation/denaturing of the rhamnolipid biosurfactant by the relatively high soil temperatures recorded for both solarized and non-solarized treatments especially during the 28 days soil solarization periods. Nevertheless, PAHs were significantly removed in contaminated soil and this was attributed to the increase in the soil temperatures due to soil solarization which resulted to the PAHs increased solubility and bioavailability. Soil solarization also continued to impact on PAHs removal, soil/rhizosphere total heterogeneous microorganisms and enzymatic activities post solarization (i.e. phytoremediation and/or bioremediation) in contaminated soil when compared with their non-solarized counterparts. These are some of the key outcomes of the

research especially in Chapter 4 and its transferability is promising even at an industrial scale to treat mega crude oil contaminated land in the Niger Delta region characterized by a humid tropical climate with high rainfall and warm temperatures.

The successful laboratory scale quantitative experiments (Chapters 3 and 4), advancing phytoremediation using soil solarization in particular, as a novel and sustainable remediation technique for contaminated land clean-up in the oil rich Niger Delta was followed up with a qualitative field study (Chapter 5). The qualitative field study was designed to understand the extent of knowledge and acceptance of sustainable remediation (sustainability feasibility) to contaminated land clean-up in the region. This was achieved by interacting with relevant stakeholders in the region using both survey questionnaires with a six macro-criteria evaluation matrix (objectives viii and ix) and one-on-one telephone interviews in relation to current environmental, social and economic challenges to sustainable remediation (objective x) in the region. A total of 32 stakeholder respondents out of which five were interviewed responded by completing the questionnaires (see Section 5.3.1.1). Generally, according to stakeholder respondents assessment, most of the remediation techniques employed in the region to clean-up contaminated site are unsustainable. All stakeholders unanimously agreed on the importance of sustainability in remediation but with different views in terms of organizational sustainability policy implementation. Stakeholders perceptions of remediation techniques sustainability were generally above average. The implication of this finding shows that on average, stakeholders in the Niger Delta region are not only aware of the different remediation techniques applicable or applied in the region but also understand and able to assess them based on their perceived sustainability. Thus, providing the platform for the emergence of sustainable remediation techniques in treating the region's contaminated sites with this novel treatment as demonstrated in Chapter 3 and 4.

The result from the six macro-criteria evaluation matrix shows that stakeholders were able to measure how sustainable a technique is from a list of remediation techniques in relation to its reliability, intervention, hazardousness exposure, community acceptance, effectiveness and cost (see Section 5.3.1.4). However, the re-grouping of the six macro-criteria into the three sustainability pillars of environmental impacts, social effects and economic viability shows that bioremediation and phytoremediation were seen as the most sustainable remediation techniques. Participants viewed bioremediation and phytoremediation as sustainable because they were perceived to pose the least hazardous exposure to the public with high community acceptance even though they were not perceived to be the most effective among other techniques (see Tables 21, 22 and Section 5.3.2.2.2). This study in Chapter 5 also contributed

to the gap in sustainability awareness and sustainable remediation assessment of applied/applicable techniques with relevant stakeholders in the region. In addition to shedding more light to the current environmental, social and economic challenges to sustainable remediation in the region.

6.2 Sustainable remediation feasibility, challenges and prospects

The world today is increasingly recognizing the need and importance of sustainability especially relating to the environment as contained in no 7 of the 8 UN's Millennium Development Goals (MDGs) which has been replaced by no 15 of the 17 UN's Sustainable Development Goals (SDGs) *'to ensure environmental sustainability'* and *'protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss'* respectively. Sustainable remediation continually attracts global attention both in policy and guidance in order to reflect sustainable practices worldwide. Sustainable practices generally are those that include recognition of the economic and natural resources, ecology (environment), human health and safety, and quality of life (see Section 2.4.1). In view of the vast contaminated land impacted mostly by oil spills and other complex hydrocarbons byproducts and the closeness of communities to crude oil contaminated lands coupled with the reoccurring sensitivities within the region, new approaches are urgently required for pragmatic, safe, cost-effective, low-techniques and efficacious remediation methods that are sustainable within reasonable timeframe.

The technical feasibility of sustainable remediation in the Niger Delta region is clear but it has to contend with so many challenges/barriers identified in this study as continuous environmental pollution especially sabotage, vandalism, oil well blow out, artisanal refining, infrastructural failure; deepening poverty; overbearing multinational oil companies; agitation and aggression of host communities; government unwillingness; interference of politics and corruption; and palliative remediation (see Section 5.3.2.1). Current remediation techniques used in the region based on the responses from interviewed participants which include covering with clean soil, excavation & disposal, open burning (thermal treatment), natural attenuation among others are seen as default remediation practices that are not sustainable.

There are fundamental gaps in the policy frameworks for remediation as it relates to the oil sector in Nigeria not to even mention sustainable remediation. Although there are regulatory guidelines by several government agencies for biodiversity conservation but these are not

stringent enough and lacks the required resources. One of the draw backs is inadequate acceptable pollutant benchmarks for contaminated land clean-up and the lack of a regulatory framework for sustainable remediation assessment. Nevertheless, most stakeholder participants were optimistic about the feasibility of sustainable remediation in the Niger Delta as a sustainable reparation to improve environmental management in the region.

A holistic approach to tackle the multifaceted challenges/barriers in tandem with integrated sustainable remediation techniques appeared to be the prospect for sustainability and sustainable remediation in the Niger Delta region as the current socio-political and environmental atmosphere will not encourage the optimum utilization of sustainable remediation. Okoli (2013) viewed these prevailing socio-political and ecological conditions in the Niger Delta as the bane for the sustained crisis that put the lives and wellbeing of the people at risk forcing them to resort to desperate tactics to redress the situation. Although the State's amnesty programme appeared to have cushioned the crisis it is far from a lasting solution which is largely viewed as resource control by the people of the region. The Niger Delta people strongly perceive that the predicament from their polluted environment contributes to their socio-economic deprivation and abject poverty but a sincere attempt to restore their environment from a sustainable approach may be a welcome reparation.

There has to be an all-inclusive credible stakeholders' participation for the long-term success of sustainability and sustainable remediation. In order to achieve an enabling environment in which most of the people in the region can flourish by living dignified, quality and valued lives, overcome poverty while enjoying a peaceful atmosphere and the benefit of sustainable environment. The findings from the qualitative study (Chapter 5) agrees with many scholarly reports especially the UNEP (2006) on the Niger Delta-Human Development Report, Niger Delta Regional Master Plan by Niger Delta Development Commission (NDDC), Environmental Assessment of Ogoniland recommendations by UNEP (2011); International Union for Conservation of Nature-Niger Delta Panel (IUCN-NDP) (2013) among others. IUCN-NDP (2013) also proposed the adoption of a holistic approach such that communities become true business partners in the socio-environmental plan because often time, communities see remediation strategies as being shrouded in mystery with no genuine effort to de-mystify them resulting to criticism and outright rejection. As part of the holistic approaches, UNEP (2011) recommended a combination of remediation approaches especially for the Ogoniland clean-up which is a microcosm of the entire Niger Delta region, ranging from active intervention for cleaning the top soil and replanting mangrove to passive monitoring of natural

regeneration. As no one single remediation technique is appropriate for the entire region due to the wide extent of contamination.

The integration of soil solarization in combination with phytoremediation using indigenous *C. odorata* as demonstrated in this study seems to be a very promising remediation technique that is not only novel but also suitable, sustainable and effective in treating even the most recalcitrant form of hydrocarbons-PAHs. One of the numerous advantages of this techniques is the use of a native plant from the region's contaminated site which will allow natural restoration of the habitat by simultaneously establishing a plant community comparable to that existing in the vicinity. The outcome will be both site remediation and ecological restoration. The advancement in phytoremediation using solarization as demonstrated in this study will likely lead to enhanced soil fertility, quality as well as microbial density and diversity in addition to significant reduction in targeted hydrocarbon contaminants. IUCN-NDP (2013) also propose biological approaches as the safest, most efficacious and cost-effective ways of *in-situ* remediation of target habitats including farmlands, soil, forest, groundwater, fresh/brackish water bodies, swamps, creeks, mangrove forests, shorelines and marshes through a systematic application of techniques to support ecological restoration. According to IUCN-NDP (2013) phytoremediation as a technique will further reduce petroleum hydrocarbon concentration while initiating a rehabilitation process at the same time with emphasis on naturally-occurring, indigenous plants of high economic value in addition to other plants that stimulate rhizosphere biodegradation such as wheat grass, rye grass, fescue, vetiver and many others like *C. odorata* as shown in this study. The familiarity of these plant species to the communities will increase phytoremediation acceptance as a self-sustaining technique in the long term. Phytoremediation application as reported by the IUCN-NDP (2013) is an integrated socio-environmental approach for rehabilitation of biodiversity and habitats (sustainable remediation) with the potential to generate income through nurseries for seedlings and other related activities. It will also ensure restitution of livelihood by stimulating activities such as farm settlement and aquaculture.

The current environmental, social and economic challenges to sustainable remediation in the Niger Delta with optimum solar radiation, high humidity and ubiquitous indigenous plant species would require a holistic approach which encompasses but is not limited to stakeholders engagement, awareness and enlightenment, sustainable livelihood, strong legal framework. In addition to utilizing integrated remediation techniques including advanced phytoremediation using indigenous *C. odorata* in combination with soil solarization as an eco-friendly and cost

effective novel treatment, that opens up new possibilities for a sustainable approach in the oil rich Niger Delta, Nigeria.

6.3 Research potentials

Currently, the Nigerian government has launch US$1 billion for Ogoniland clean-up and restoration programme in the Niger Delta to begin implementing the recommendations made by the United Nations Environment Programme (UNEP) in 2011. Soil solarization in combination with phytoremediation using indigenous *C. odorata* can potentially play a key role in the clean-up and restoration of Ogoniland, considering the fact that the preliminary survey was carried out on Ogoniland where *C. odorata* was collected for this study (see Sections 3.2.1 and 3.2.2). The findings of this study showed that it is very promising with potential transferability throughout the Niger Delta region. The very wide range in the Niger Delta soil textures and morphological characteristic (see Section 3.3.1) showed that the results from this study using UK's Sonning farm soil is transferable in the region, considering the fact that some soils in the region has similar soil classification with Sonning farm soil. In addition, the chemical properties of both soils (case study soil and Sonning farm soil) were not so different (see Table 15). The fact that native *C. odorata,* a common plant in the entire south-eastern, south-western, Niger Delta and parts of north-central regions of Nigeria (see Section 3.2.16) thrived in UK's Sonning farm soil, demonstrated the transferability of the findings of this study. The region's suitable climate for soil solarization which was simulated in laboratory based microcosm (see Section 4.2.6), makes this novel remediation technique more appealing and more cost effective. The high community acceptance of phytoremediation due to least hazardous exposure perception by stakeholders, makes this new approach (soil solarization integration with phytoremediation) urgent for pragmatic, safe, cost-effective, low-techniques and efficacious industrial scale remediation treatment that meets the UNEP recommended timeframe. And opens up new possibilities for sustainable approach to remediate contaminated land.

Chapter 7

Conclusion, Limitations and Recommendations.

7.0 Conclusion

The pilot study in Chapter 3 showed that native *C. odorata*, preliminary selected from a case study site in the Niger Delta region, demonstrated a more thriving and tolerant nature in artificially contaminated PAHs Sonning farm soil compared to *M. sativa*-a proven and well established phytoremediation plant. Although the case study soil from the region was different in soil texture from the Sonning farm soil in the UK, the results is transferable in the region, considering the region in its wide range of soil textures and morphological characteristics has similar characteristics to Sonning farm soil. PAHs were significantly reduced by *C. odorata* and *M. sativa* respectively, however with no significant difference between their phytoremediation potentials. Rhamnolipid biosurfactant significantly reduced PAHs in all amended treatments compared to their un-amended counterparts. The fibrous root structure of *C. odorata* gives it the added advantage over *M. sativa* for phytoremediation particularly in stimulating rhizosphere microorganisms to enhance degradation of PAHs and as such it was preferred to the non-native *M. sativa* in this study. The general attributes of *C. odorata* as an invasive species with the ability to proliferate in different soil types across Nigeria especially in the Niger Delta region, makes the findings from this study generalizable and transferable and also a representative of the entire plant species particularly in Nigeria. Native plants such as *C. odorata* are ecologically safer, cheaper, aesthetically pleasing, socially acceptable and easier to cultivate.

A microcosm successfully simulated the sub-tropical conditions in the Niger Delta region and the impact of soil solarization significantly enhanced phytoremediation with native *C. odorata* in PAHs reduction especially in the 28 days pre-plant solarization period. This PAHs reduction was attributed to the increase in soil temperature through soil solarization and not to biosurfactant and may have impacted on the physical, chemical and biological properties of the solarized soils. This direct impact created a favourable microenvironment for bacterial metabolic activity and ultimately, PAH biodegradation due to extreme temperature adaptation by PAHs degrading bacteria while maintaining their metabolic activity. The total soil/rhizosphere heterotrophic microbial density in all solarized treatments increased during post-solarization, compared to their non-solarized counterparts but without statistical significance. This increase was due to re-colonization after the end of 28 days solarization treatment. Post-solarization further reduced significantly the amount of residual PAHs throughout the phytoremediation duration. Solarization also increased soil/rhizosphere

enzymatic activity of urease and dehydrogenase in solarized treatment compared to non-solarized treatment counterpart with and without statistically significance respectively.

Contrary to the pilot study in Chapter 3, rhamnolipid biosurfactant did not contribute to PAHs removal in Chapter 4 due to the possible deactivation/denaturing of the biosurfactant by the relatively high soil temperatures recorded for both solarized and non-solarized treatments especially during the 28 days solarization periods. Thus, the impact of biosurfactant in this study was negligible compared to their non-amended counterpart treatments on PAH reduction, plant performance, total heterotrophic microbial density, soil/rhizosphere enzymatic activity of dehydrogenase and urease respectively. Consequently, soil solarization was the major factor that enhanced phytoremediation with significant impact on *C. odorata* growth parameters resulting to PAHs removal. *C. odorata* significantly increased the total density of rhizosphere heterotrophic microorganisms, rhizosphere enzymatic activity of dehydrogenase and urease in all vegetated treatments compared to their un-vegetated counterparts.

The significant reduction in targeted PAHs, improved agronomic performance, enhanced soil fertility, quality as well as microbial density and diversity, authenticate the integrated treatment of soil solarization and phytoremediation as a remediation technique for crude oil contaminated soil. It opens up new possibilities for sustainable approach to remediate contaminated land in the oil rich Niger Delta, Nigeria.

A qualitative survey was employed to evaluate the sustainability feasibility of remediation techniques in the Niger Delta in Chapter 5. The survey shows that stakeholder participants have above average understanding of most of the remediation techniques in use. Stakeholders scrutinized most of the default remediation approaches such as covering with clean soil, excavation & disposal, thermal treatment among others, and came to the conclusion that most of the applied remediation techniques were unsustainable. Suggesting that on average, stakeholders in the Niger Delta region are not only aware of the different remediation techniques applicable or applied in the region but also understand and were able to assess them based on their perceived sustainability. Almost all stakeholders are aware of the relatively recent environmental milestones in sustainable development such as MDGs/SDGs, Kyoto protocol on climate change and earth summit. Thus, providing the platform for the emergence of sustainable remediation techniques in treating the region's contaminated sites. Phytoremediation and bioremediation were seen as the most sustainable remediation techniques by participants because they were perceived to pose the least hazardous exposure to the public with high community acceptance even though they were not perceived to be the

most effective. Consequently, setting the stage for the application of phytoremediation using soil solarization as demonstrated in Chapter 3 and 4.

The current environmental, social and economic challenges to sustainable remediation among the stakeholder participants in the Niger Delta are: polluted environment; palliative remediation; politics and corruption; government; overbearing multinational oil companies; agitation and aggression; and poverty. However, from the sustainable reparation global theme perspective, the feasibility of sustainability in the clean-up of contaminated land requires an holistic approach which encompasses but is not limited to stakeholders engagement especially multinational oil companies and their host communities; awareness and enlightenment; amnesty; legal framework; huge fines; and will power from all parties especially from the Nigerian government. Thus, at the very least, remediation techniques of the type investigated in this study (advanced phytoremediation using soil solarization) can be concluded to have acceptance among stakeholders and with good will, the ability to contribute to the sustainable clean-up of contaminated land in the Niger Delta, region.

7.1 Limitation of research

The quantitative experiments of Chapter 3 and 4 were laboratory-benchtop based with Stewart electric propagator and bespoke microcosms used as growth chambers simulating the region's sub-tropical conditions in addition to solar radiation from the sun using infra-red and LED bulbs. The inability to use case study aged-contaminated soil from the Niger Delta region as a result of the challenges encountered in bringing large quantity into the UK led to the use of artificially contaminated UK Sonning farm soil with similar physico-chemical characteristics with the region's wide range of soil types. Although the results are transferable and representative, it would be interesting to investigate these parameters in real life field conditions in the Niger Delta. The study falls short of identifying PAHs degraders/thermophiles from the soil/rhizosphere total heterotrophic microorganisms and was restricted to just two soil/rhizosphere enzymatic activities.

This study did not address the considerable heterogeneity in characteristics of the selected plant species especially *C. odorata* in their natural population, since both plant species were selected as a model. This aspect of knowledge is one of the limitations of this work and would be of great interest should a wide scale use of the plant species, *C. odorata*, in particular be used in future remediation efforts.

A key limitation for the qualitative field study is the inability to carry out randomized survey and relatively low survey response rate due to the country's heightened political tension at the time of sampling. The study area was one of the epicenters of insecurity during the 2019 general elections, and was marred by political violence at the time of the survey. A group of key stakeholders from the academic/researcher institutions at the time was on indefinite strike nationwide and this affected the sampling size as access was almost restricted. The unavailability of some targeted groups of stakeholders in particular, federal and state regulatory agencies also contributed to the limitation of this study. For safety and security reasons, the researcher could not access other targeted states in the Niger Delta region. In other to address this limitation, all the stakeholders across the region were grouped together to render aggregated results. Consequently, the findings from this PhD research despite its limitations, are not only valuable and valid but also make original contribution to knowledge, especially in the integration of soil solarization as a novel remediation technique advancing phytoremediation. The study also contributed to the gap in sustainability awareness and sustainable remediation assessment of applied/applicable techniques in the region. And shed light on the current environmental, social and economic challenges to sustainability feasibility in the region. Thus, the survey outcome may be considered exploratory and interpreted in view of its limitations as the issue of security has always been a persistent challenge in the Niger Delta region.

7.2 Recommendations for future research

Based on the findings of this PhD research, the recommended future work is divided into two categories below:

1. Quantitative future work
    i. A field study integrating soil solarization in combination with several indigenous plant species for phytoremediation of crude oil, heavy metals or co-contamination of impacted land is highly recommended to assess the true potential of this technique;
    ii. Improving the phytoremediation potential of indigenous plants with high biomass yield, increased root depth, high toxicity tolerance, more metal-metalloid accumulation, and enhanced persistent organic pollutants (POPs) degradation through genetic engineering; and

iii. Investigating soil solarization mechanism in the degradation of POPs and the effect of solarization on phytoremediation enhanced with chemical surfactant.

2. Qualitative future work
   i. The use of a site-specific approach for selecting a set of remediation techniques applicable to a contaminated site and to develop a comparative system for these techniques is required in the region due to the large area of land or mega-sites contaminated with several different sources and contaminants;
   ii. A variety of tools such as qualitative sustainability assessment, multi-criteria analysis (MCA), life cycle assessment (LCA), cost benefit analysis (CBA) in relations to the region's environmental, social and economic challenges should be developed or adopted across board by stakeholders especially federal/state government regulatory agencies including the federal/state ministry of environment, department of petroleum (DPR), national oil spill detection and response agency (NOSDRA) etc. for evaluating the sustainability of remedial alternatives in order to inform the selection and optimization of remedial action;
   iii. Stakeholders especially the Nigerian government through its concerned regulatory agencies should developing global partnership with leading sustainable remediation bodies such as sustainable remediation forum, UK (Surf-UK), United State sustainable remediation forum (USSRF), network for industrially contaminated land in Europe (NICOLE), contaminated land rehabilitation network for environmental technologies in Europe (CLARINET) among others in order to adopt, implement or develop sustainable remediation assessment in addition to the required technical skills especially for developing strong regulatory framework; and
   iv. Strong awareness and enlightenment campaign on the benefits of sustainable remediation to contaminated sites clean-up especially in the region should only be prioritized after sustainable livelihoods that hinge on job creation and good quality of life for poor and vulnerable groups in the region.

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Appendix 0

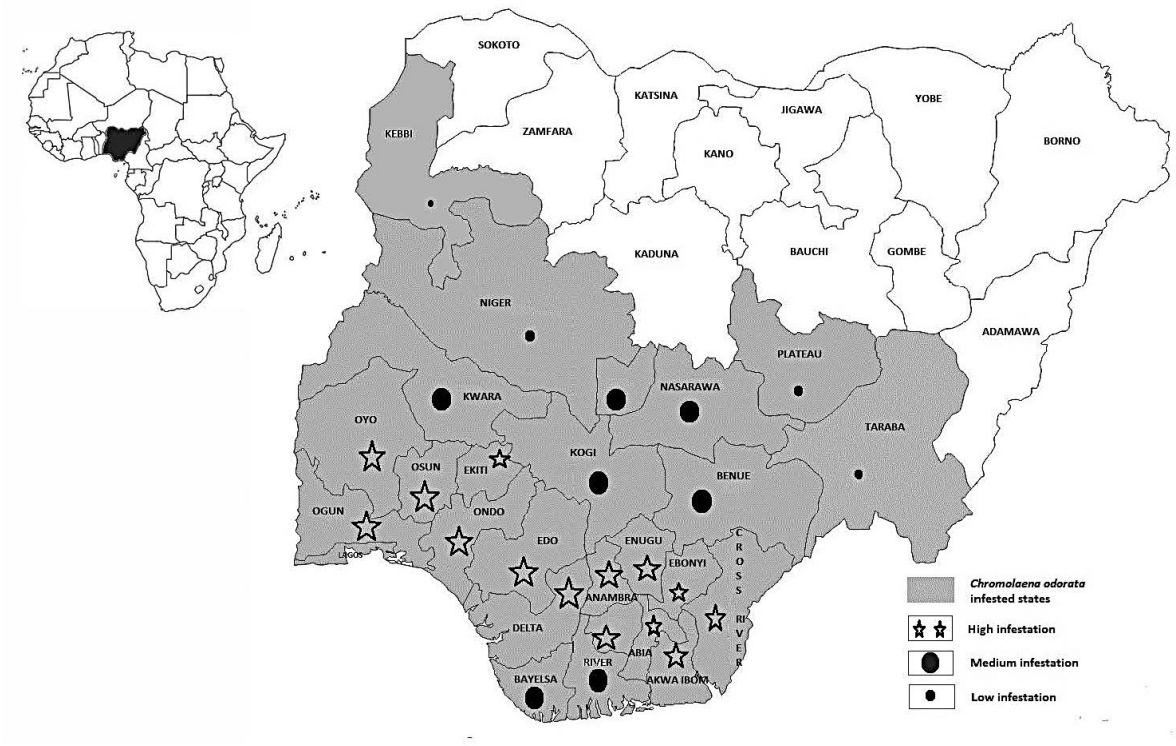


Figure 6: Map of Nigeria showing *C. odorata* distribution. Source: Uyi *et al.* (2014)

Plate 1.15: Preliminary screening of *C. odorata* with other indigenous plants (*Amaranthus* spp.) found in case study contaminated site. (a) 250 ml/kg crude oil contaminated soil; (b-c) transfer of indigenous plant seeds into treatment bags; (d-f) thriving 3 weeks old *C. odorata* with high growth rate.

Table 24: Bomu Manifold soil and groundwater result summary by UNEP

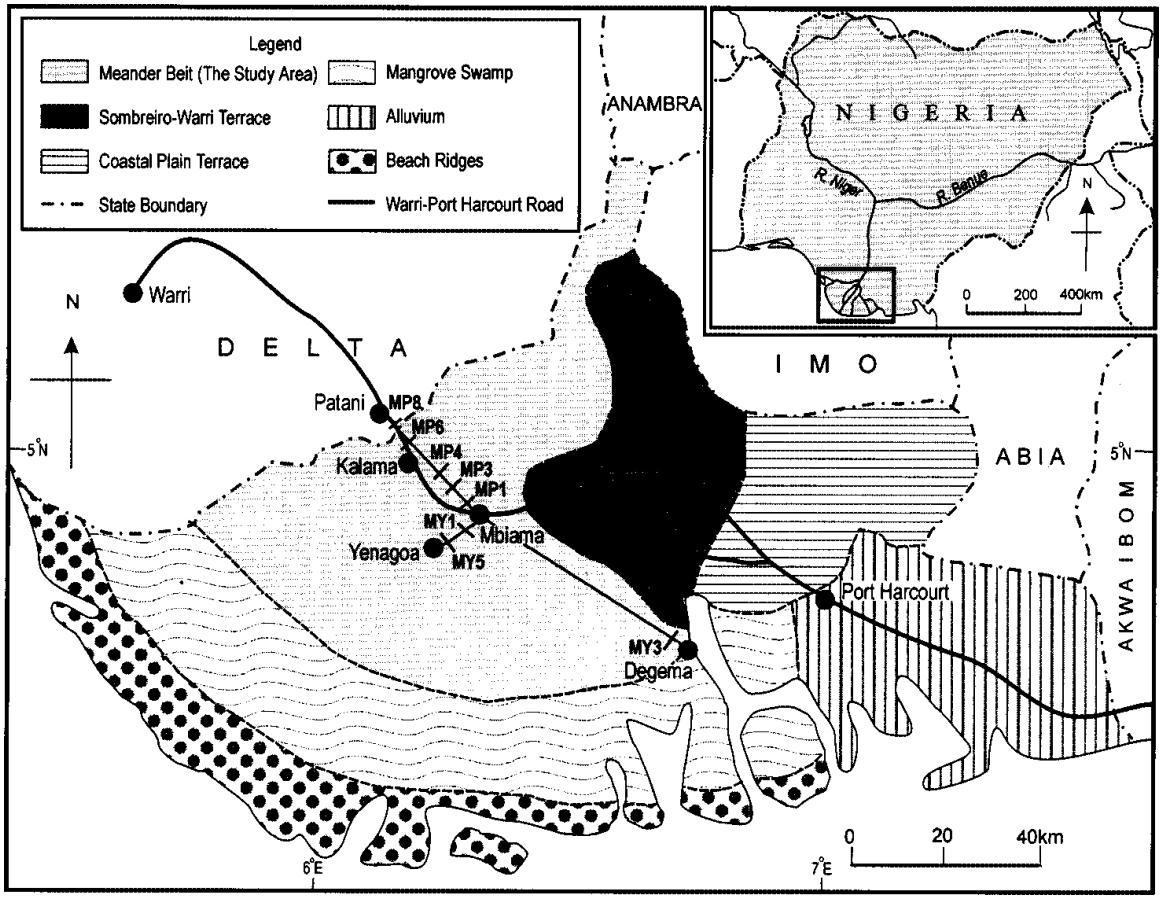
UNEP site code	**qc_019-005**
Site name	**Bomo Manifold**
LGA	Gokana
Site description	SPDC operating site
Area Investigated (m^2)	37,988
Number of soil samples	56
Number of groundwater samples	5
Deepest investigation (m)	5.00
Maximum soil TPH (mg/kg)	63,600
Number of soil measurements greater than EGASPIN intervention value	21
Deepest sample greater than EGASPIN intervention value (m)	5.00
Maximum water TPH (µg/l)	3,410
Number of water measurements greater than EGASPIN intervention value	1
Presence of hydrocarbons in surface water	yes
Number of soil measurements below 1 m	38
Number of soil measurements below 1 m greater than EGASPIN intervention value	17
Total volume of soil above intervention value (m^3)	38,257
Total volume of soil above target value (m^3)	62,775

Source: UNEP (2011)

Table 25: Soil textures of representative pedons of the Niger Delta Meander Belt

HORIZON	DEPTH (cm)	BULK DENSITY (gcm^{-3})	PARTICLE DENSITY (gcm^{-3})	TOTAL POROSITY (%)	CLAY (%)	SILT (%)	SAND (%)	TEXTURAL CLASS
Backswamp (Pedon MP1)								
AP	0-7	1.31	2.32	43.53	52.00	41.00	7.00	Clay
CI	7-18	1.35	2.43	44.44	58.00	35.00	7.00	Clay
g 21	18-52	1.41	2.45	42.45	63.00	21.00	16.00	Clay
Cg 22	52-102	1.38	2.42	42.95	77.00	9.00	14.00	Clay
Cg 3	102-180	1.43	2.43	41.15	70.00	20.00	10.00	Clay
Terrace (Pedon MP6)								
AB	0-21	1.41	2.44	42.21	59.00	18.00	23.00	Clay
Ccl	21-53	1.38	2.50	42.80	54.00	27.00	29.00	Clay
Ccm 21	53-104	1.59	2.51	36.66	27.00	60.00	13.00	Silty clay loam
Ccm 22	104-180	1.61	2.53	36.11	31.00	44.00	15.00	Loam
Levee slope (Pedon MP3)								
AC	0-10	1.38	2.43	42.98	48.00	32.00	20.00	Clay
Cg 1	10-29	1.35	2.41	43.98	53.00	28.00	19.00	Clay
Cgc 2	29-72	1.41	2.39	41.00	62.00	22.00	16.00	Clay
Cgc 3	72-102	1.50	2.46	39.02	50.00	21.00	29.00	Clay
2Cg 4	102-145	1.55	2.59	40.15	6.00	6.00	88.00	Sand
3C 5	145-200	1.69	2.64	39.01	6.00	1.00	93.00	Sand
Levee crest (Pedon MY5)								
AP	0-13	1.35	2.58	47.67	9.00	16.00	75.00	Sandy loam
AB	13-46	1.40	2.60	46.15	14.00	16.00	70.00	Sandy loam
2C2	46-65	1.41	2.66	46.99	7.00	14.00	79.00	Loamy sand
2Cc21	65-118	1.43	2.65	46.04	13.00	1.00	86.00	Loamy sand
2Cc22	118-130	1.42	2.66	46.62	10.00	2.00	88.00	Loamy sand
3Cc3	130-150	1.45	2.57	43.80	27.00	2.00	71.00	Sandy clay loam
4Cg	150-2,000	1.52	2.48	38.71	42.00	25.00	33.00	Sandy clay loam

Source: Kamalu *et al.*(2002)

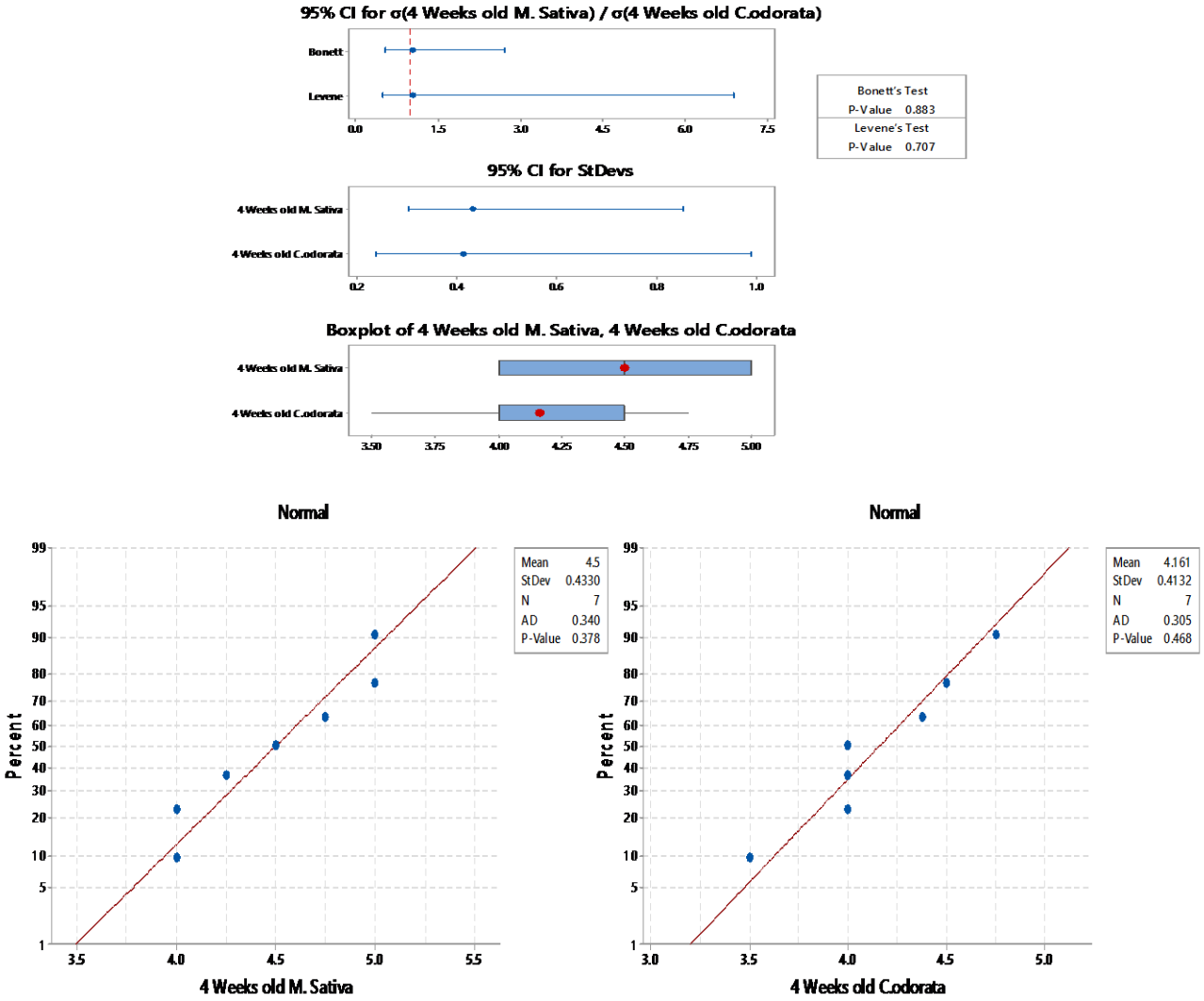


Source: Kamalu *et al.*(2002)

Figure 7: Map of the Niger Delta showing the Meader Belt study area and representative pedons of the terrace (MP8,MP6), levee slope (MP4, MP3), backswamp (MP1, MY1), and levee crest (MY3, MY5)

Appendix i

Mintab output for equal variance and normality testing for plants initial height differences at 4 weeks



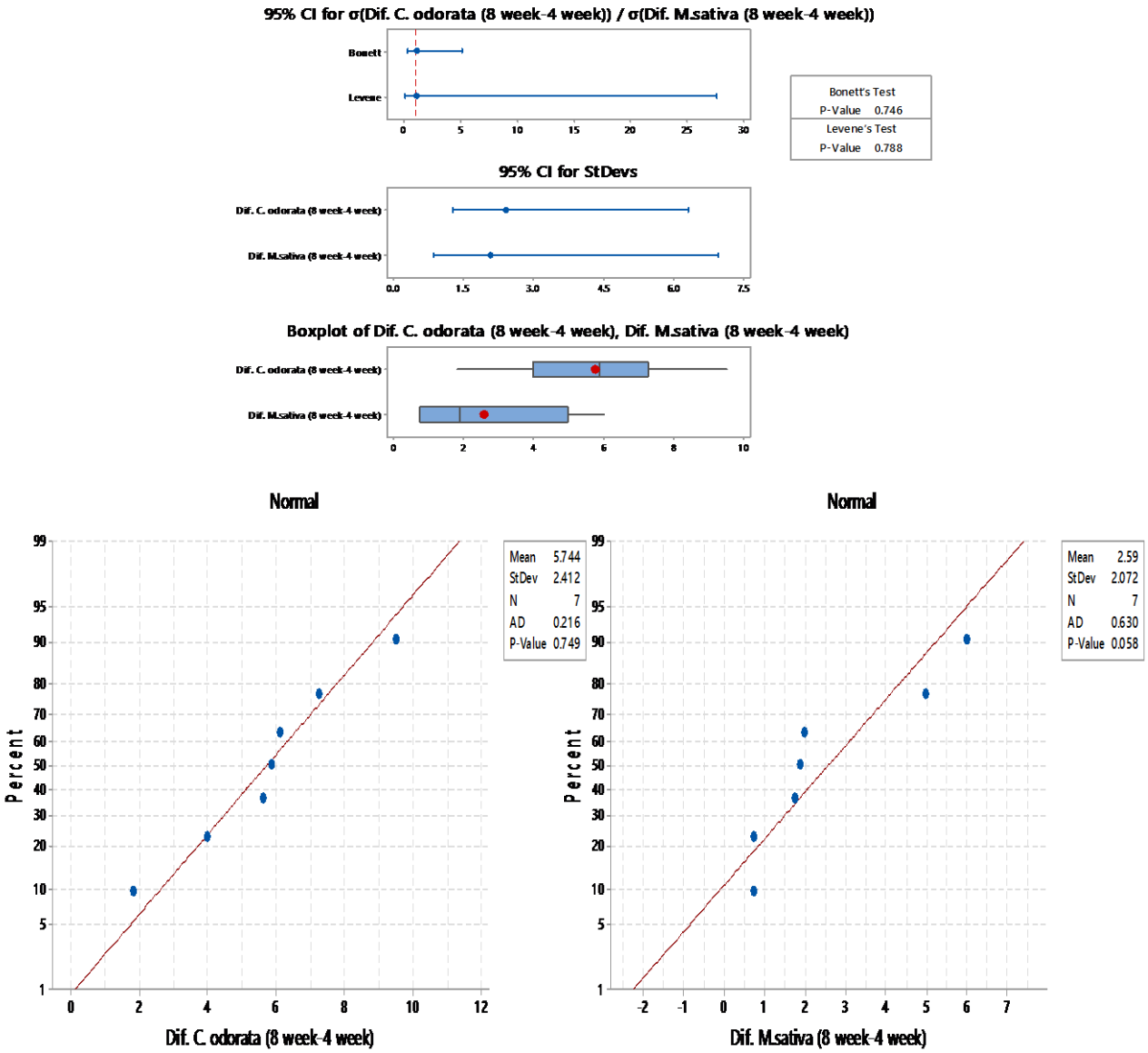
Two Sample T-Test and Confidence Interval for plants difference between 4 weeks old *M. sativa* and *C. odorata* before transplanting.

Sample	N	Mean	StDev	SE Mean	T-Value	P-Value
4 Weeks old *M. sativa*	7	4.50	0.43	0.16	1.50	0.16
4 Weeks old *C. odorata*	7	4.16	0.41	0.16		

Difference = μ (4 Weeks old *M. sativa*) - μ (4 Weeks old *C. odorata*)
Estimate for difference: 0.339
95% CI for difference: (-0.154, 0.831)
T-Test of difference = 0 (vs ≠): T-Value = 1.50 P-Value = 0.160 DF = 12
Both use Pooled StDev = 0.4232

Appendix ii

Mintab output for equal variance and normality testing for overall plants heights in *C. odorata* and *M. sativa*



Two Sample T-Test and Confidence Interval for height difference between *C. odorata* and *M. sativa* after harvest.

Sample	N	Mean	StDev	SE Mean	T-Value	P-Value
C. odorata height difference (8week- 4week)	7	5.74	2.41	0.91	2.62	0.02
M. sativa height difference (8week- 4week)	7	2.59	2.07	0.78		

Difference = μ (Dif. *C. odorata* (8 week- 4 week)) - μ (Dif. *M. sativa* (8 week- 4 week))
Estimate for difference: 3.15
95% CI for difference: (0.54, 5.77)
T-Test of difference = 0 (vs ≠): T-Value = 2.62 P-Value = 0.022 DF = 12
Both use Pooled StDev = 2.2488

One-way ANOVA: 4 Weeks old C.odorata, 4 Weeks old ... old M. sativa

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	4 Weeks old C.odorata, 4 Weeks old M. sativa, 8 Weeks old C. odorata, 8 Weeks old M. sativa

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	149.71	49.902	20.27	0.000
Error	24	59.10	2.462		
Total	27	208.80			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
1.56920	71.70%	68.16%	61.48%

Means

Factor	N	Mean	StDev	95% CI
4 Weeks old C.odorata	7	4.161	0.413	(2.937, 5.386)
4 Weeks old M. sativa	7	4.500	0.433	(3.276, 5.724)
8 Weeks old C. odorata	7	9.906	2.338	(8.682, 11.130)
8 Weeks old M. sativa	7	7.090	2.006	(5.866, 8.314)

Pooled StDev = 1.56920

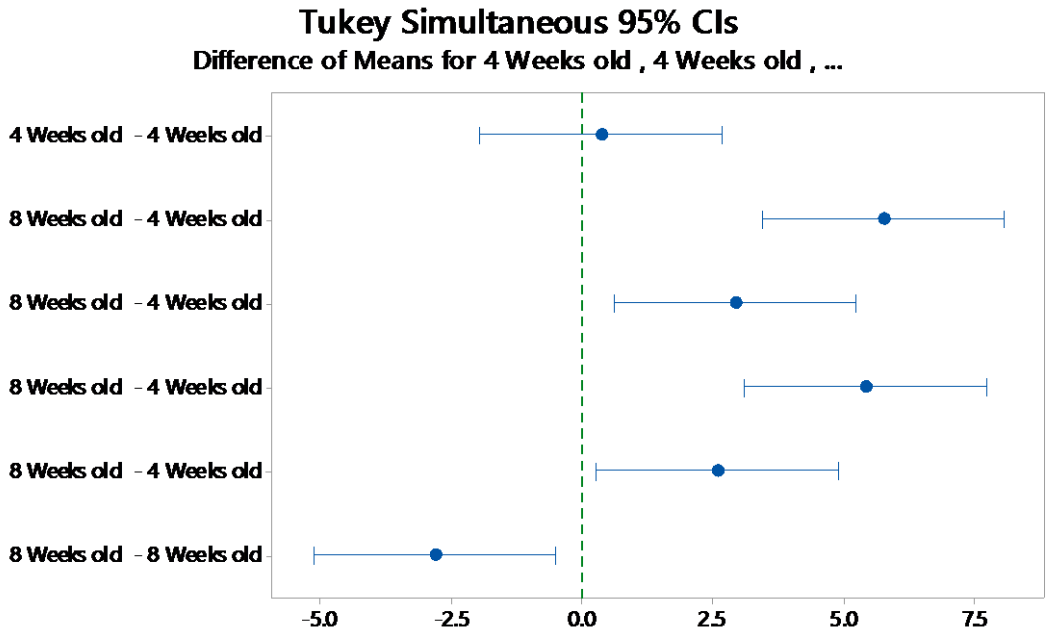
Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping		
8 Weeks old C. odorata	7	9.906	A		
8 Weeks old M. sativa	7	7.090		B	
4 Weeks old M. sativa	7	4.500			C
4 Weeks old C.odorata	7	4.161			C

Means that do not share a letter are significantly different.

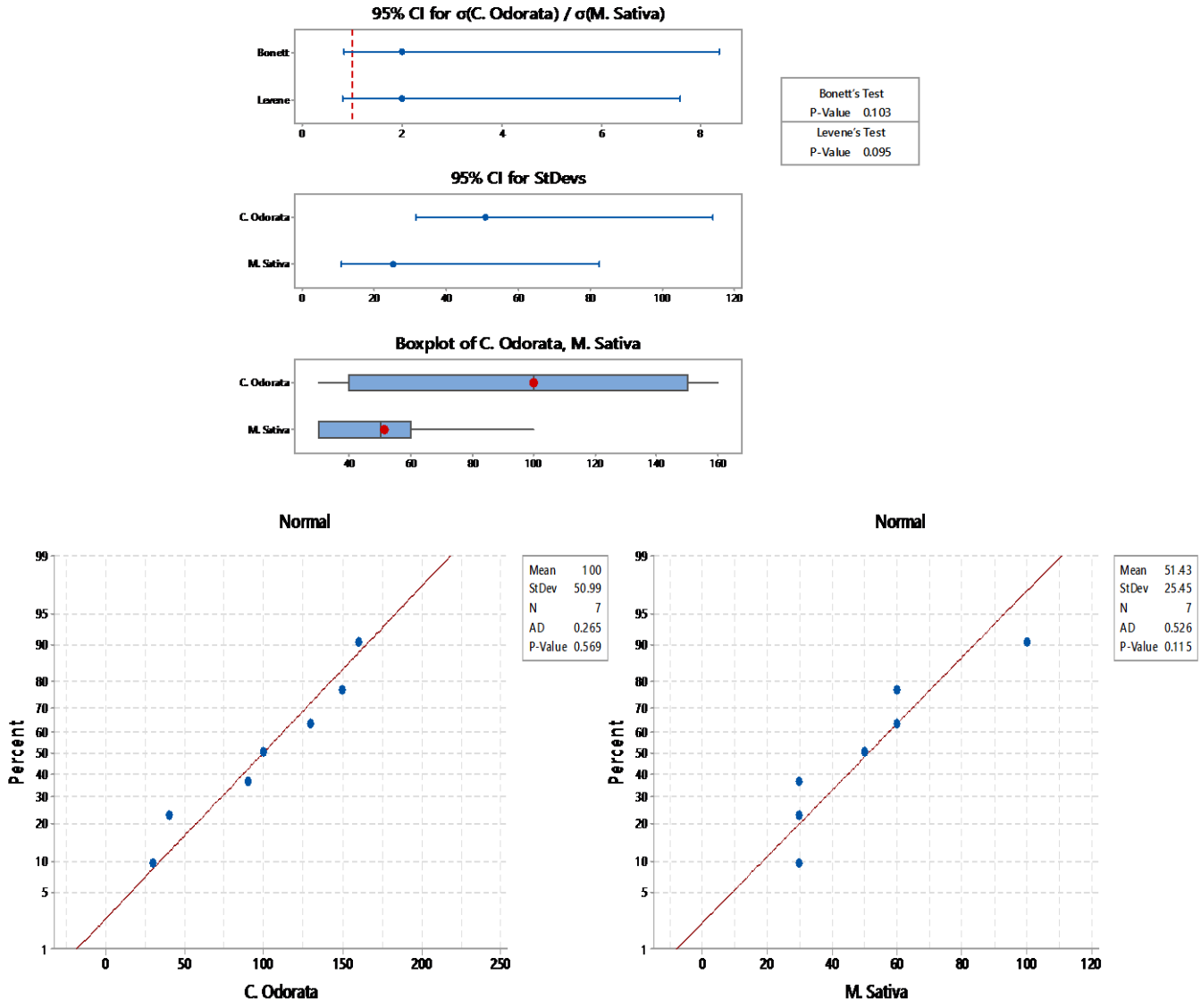
Tukey Simultaneous 95% CIs



If an interval does not contain zero, the corresponding means are significantly different.

Appendix iii

Mintab output for equal variance and normality testing for plants dry biomass in *C. odorata* and *M. sativa*



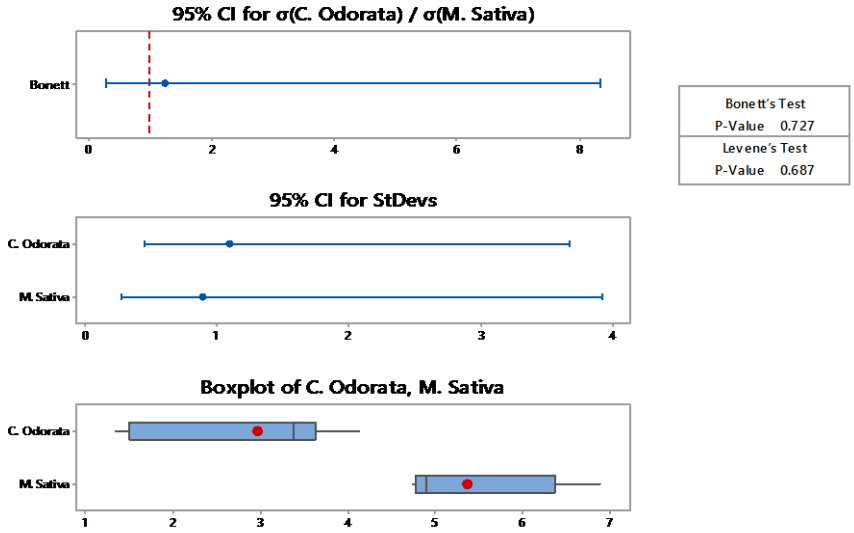
Two Sample T-Test and Confidence Interval for dry biomass difference between *C. odorata* and *M. sativa* after harvest.

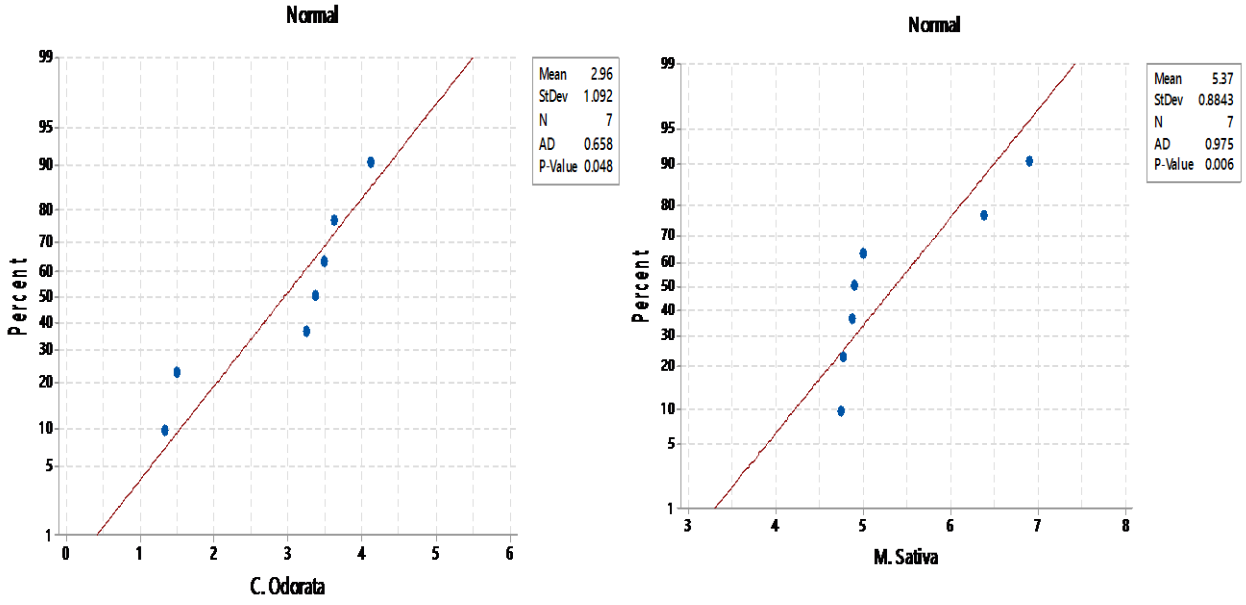
Sample	N	Mean	StDev	SE Mean	T-Value	P-Value
C. odorata dry biomass difference	7	100.0	51.0	19	2.26	0.04
M. sativa dry biomass	7	51	25.4	9.6		

Difference = μ (*C. odorata*) - μ (*M. sativa*)
Estimate for difference: 48.6
95% CI for difference: (1.6, 95.5)
T-Test of difference = 0 (vs ≠): T-Value = 2.26 P-Value = 0.044 DF = 12
Both use Pooled StDev = 2.2488

Appendix iv

Mintab output for equal variance and normality testing for plants root lengths *C. odorata* and *M. sativa*



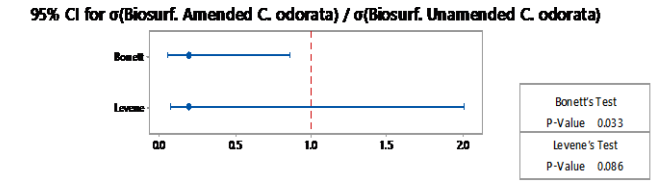


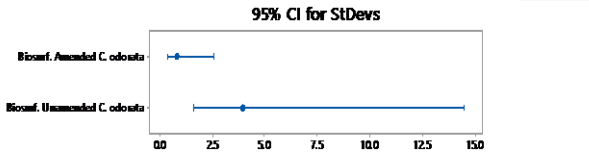
Mann-Whitney Test and Confidence Interval for root length difference between *M. sativa* and *C. odorata* after harvest.

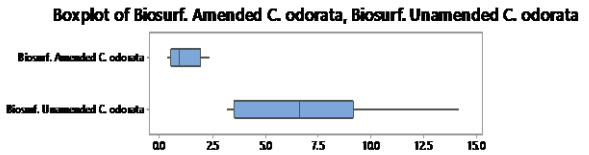
Sample	N	Median	P-Value
M. sativa root length	7	4.90	0.00
C. odorata root length	7	3.38	
Point estimate for η1 - η2 is 1.750			
95.9 Percent CI for η1 - η2 is (1.250,3.519)			
W = 77.0			
Test of η1 = η2 vs η1 ≠ η2 is significant at 0.0022			

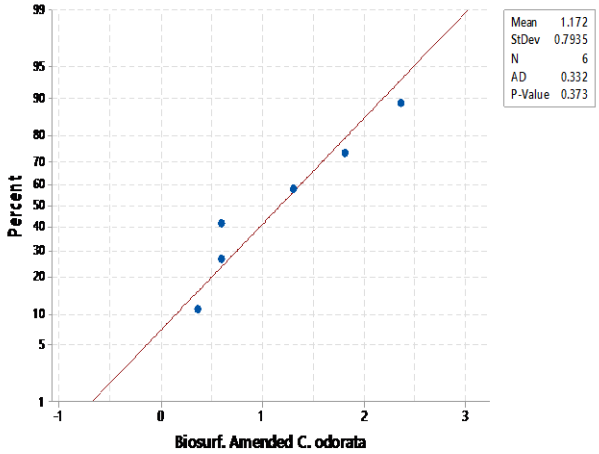
Appendix v

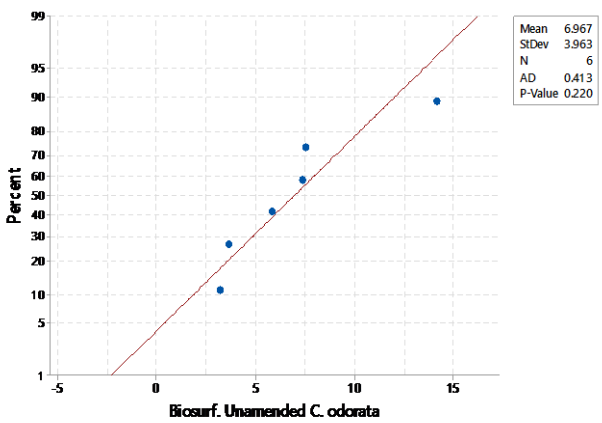
Mintab output for equal variance and normality testing for Biosurfactant effect on *Chromolaena odorata* uptake of PAHs in soil











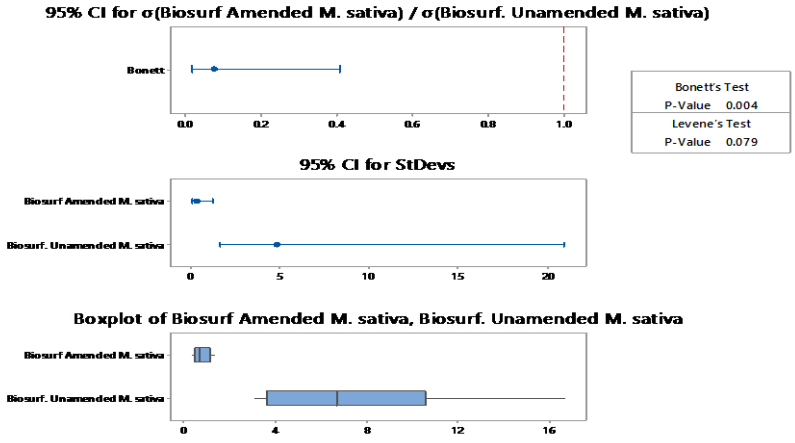
Two Sample T-Test and Confidence Interval for Biosurfactant Amended and Unamended *C. odorata*

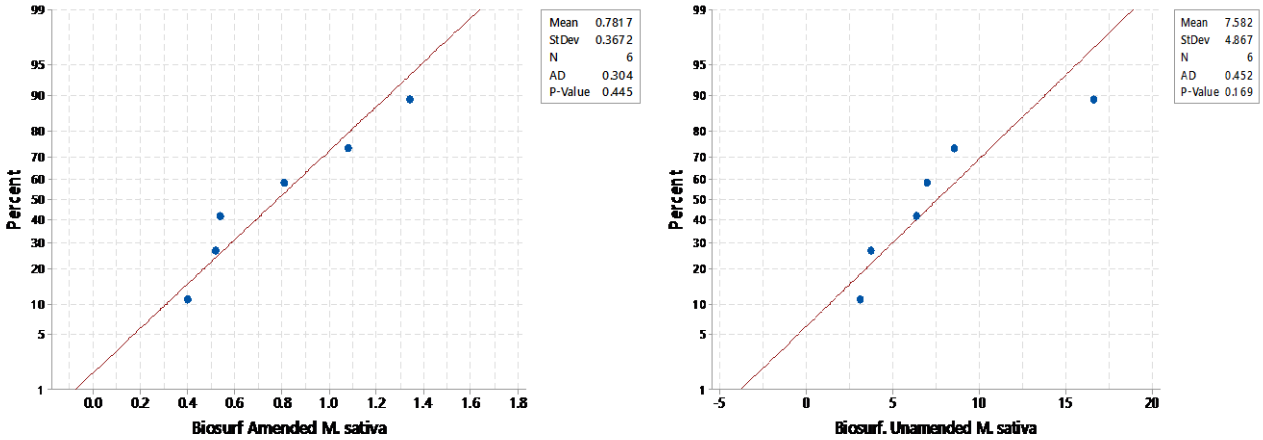
Sample	N	Mean	StDev	SE Mean	T-Value	P-Value
Biosurf. Unamended *C. odorata*	6	6.97	3.96	1.60	3.51	0.006
Biosurf. Amended *C. odorata*	6	1.17	0.79	0.32		

Difference = μ (Biosurf. Unamended C. odorata) - μ (Biosurf. Amended C. odorata)
Estimate for difference: 5.80
95% CI for difference: (9.47, 2.21)
T-Test of difference = 0 (vs ≠): T-Value = 3.51 P-Value = 0.006 DF = 10

Appendix vi

Mintab output for equal variance and normality testing for Biosurfactant effect on *Medica sativa* uptake of PAHs in soil





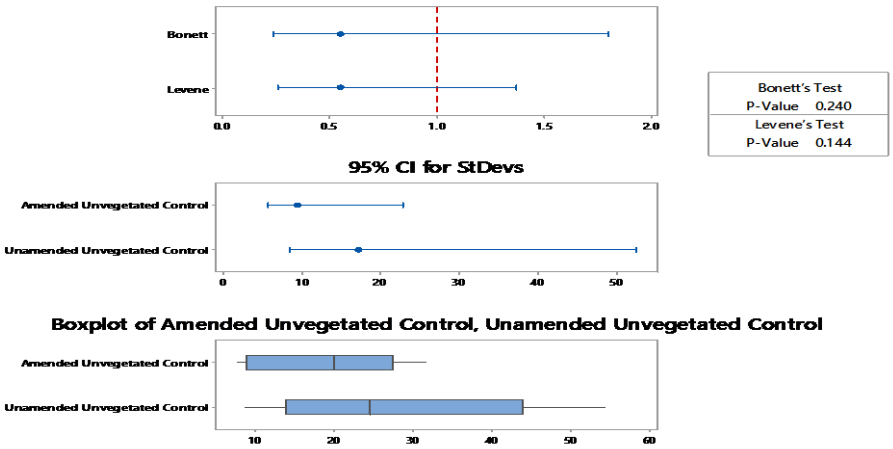
Two Sample T-Test and Confidence Interval for Biosurfactant Amended and Unamended *Medicago sativa*

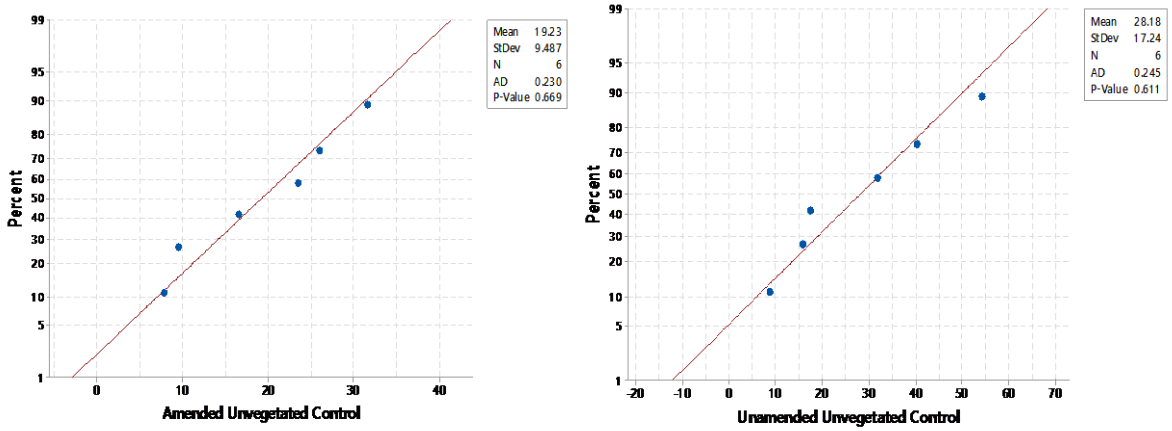
Sample	N	Mean	StDev	SE Mean	T-Value	P-Value
Biosurf. Unamended *M. sativa*	6	7.58	4.87	2.00	3.41	0.007
Biosurf. Amended *M. sativa*	6	0.78	0.37	0.15		

Difference = μ (Biosurf. Unamended M. sativa) - μ (Biosurf Amended M. sativa)
Estimate for difference: 6.80
95% CI for difference: (2.36, 11.24)
T-Test of difference = 0 (vs ≠): T-Value = 3.41 P-Value = 0.007 DF = 10

Appendix vii

Mintab output for equal variance and normality testing between Day 0 & 28 Difference of Unvegetated biosurfactant amended control and Unvegetated unamended control uptake of PAHs in soil.





Two Sample T-Test and Confidence Interval for Unvegetated biosurfactant Amended and Unvegetated Unamended Control

Sample	N	Mean	StDev	SE Mean	T-Value	P-Value
Unvegetated Amended Control	6	19.23	9.49	3.9	1.00	0.34
Unvegetated Unamended Control	6	26.1	13.9	5.7		

Difference = μ (Amended Unvegetated Control) - μ (Unamended Unvegetated Control)
Estimate for difference: 6.89
95% CI for difference: (-26.19, 8.42)
T-Test of difference = 0 (vs ≠): T-Value = 1.00 P-Value = 0.34 DF = 10

One-way ANOVA: Day 0 & 28 Differences between Un-vegetated Control, *Chromolaena sativa* and *Medicago sativa*

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	3	Day 0 & 28 Diff. Un-vegetated, Day 0 & 28 Dif. C. odorata, Day 0 & 28 Dif. M. sativa

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	2	2753	1376.63	20.31	0.000
Error	33	2237	67.78		
Total	35	4990			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
8.23291	55.18%	52.46%	46.65%

Means

Factor	N	Mean	StDev	95% CI
Day 0 & 28 Diff. Un-vegetated	12	9.16	5.45	(4.33, 14.00)
Day 0 & 28 Dif. C. odorata	12	27.77	9.12	(22.93, 32.60)
Day 0 & 28 Dif. M. sativa	12	27.66	9.51	(22.82, 32.49)

Pooled StDev = 8.23291

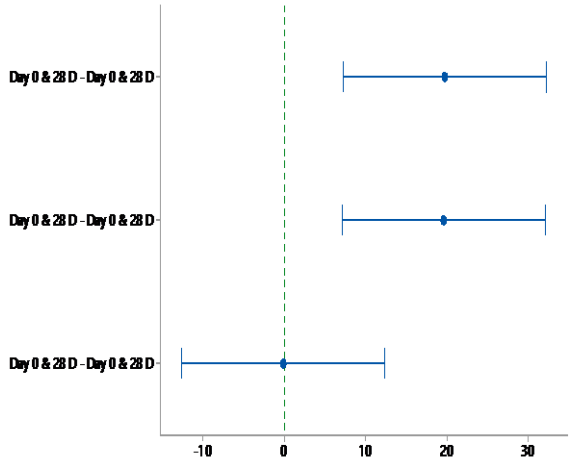
Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

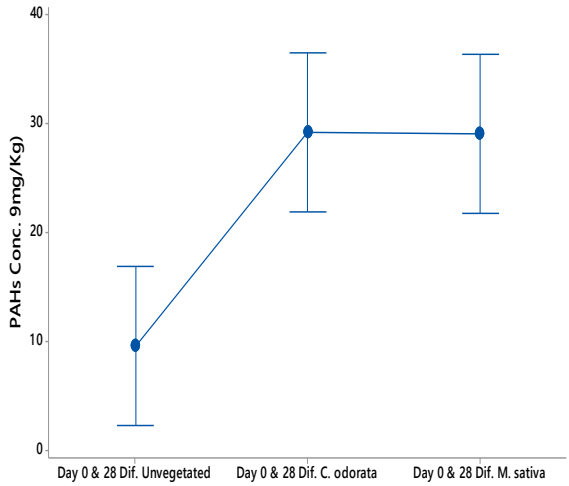
Factor	N	Mean	Grouping
Day 0 & 28 Dif. C. odorata	12	27.77	A
Day 0 & 28 Dif. M. sativa	12	27.66	A
Day 0 & 28 Diff. Un-vegetated	12	9.16	B

Means that do not share a letter are significantly different.

Turkey Simultaneous 95% Cis and Interval plot of Treatment



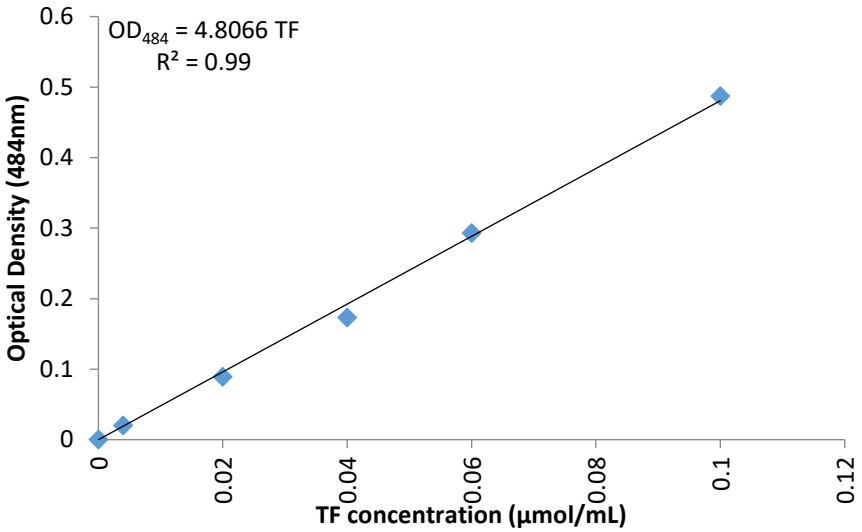
If an interval does not contain zero, the corresponding means are significantly different.



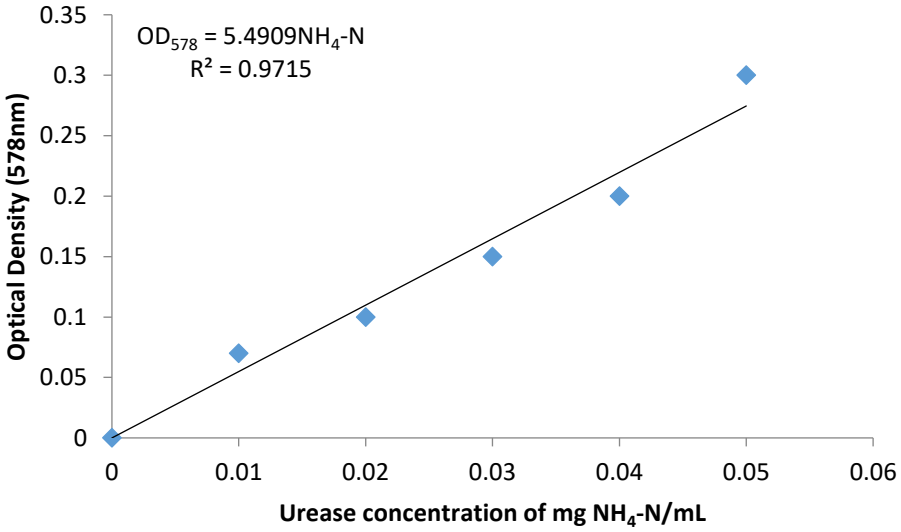
The pooled standard deviation is used to calculate the intervals.

Appendix ix

Standard curve relating TF concentration to absorbance at 484 nm (n = 4)



Standard reference-calibrated curve determined by Indophenol Blue Method at 578 nm (n = 4).



Appendix x(a)

One-way ANOVA: Solarization Soil Temperatures of Treatment A-D (1 cm depth)

Method

Null hypothesis	All means are equal
Alternative hypothesis	At least one mean is different
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (A), Solarized & unamended (B), Non-solarized & amended (C), Non-solarized & unamended (D)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	486.9	162.303	25.76	0.000
Error	44	277.3	6.301		
Total	47	764.2			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.51028	63.72%	61.24%	56.82%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (A)	12	49.792	2.551	(48.331, 51.252)
Solarized & unamended (B)	12	51.042	2.200	(49.581, 52.502)
Non-solarized & amended (C)	12	43.917	2.827	(42.456, 45.377)
Non-solarized & unamended (D)	12	44.313	2.422	(42.852, 45.773)

Pooled StDev = 2.51028

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping
Solarized & unamended (B)	12	51.042	A
Solarized & amended (A)	12	49.792	A
Non-solarized & unamended (D)	12	44.313	B
Non-solarized & amended (C)	12	43.917	B

Means that do not share a letter are significantly different.

One-way ANOVA: Solarization Soil Temperatures of Treatment A-D (4 cm depth)

One-way ANOVA: Solarized & amen, Solarized & unam, Non-solarized & , Non-solarized &

Method

Null hypothesis	All means are equal
Alternative hypothesis	At least one mean is different
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (A), Solarized & unamended (B), Non-solarized & amended (C), Non-solarized & unamended (D)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	432.5	144.182	19.56	0.000
Error	44	324.3	7.371		
Total	47	756.9			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.71495	57.15%	54.23%	49.00%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (A)	12	47.563	2.554	(45.983, 49.142)
Solarized & unamended (B)	12	48.313	2.650	(46.733, 49.892)
Non-solarized & amended (C)	12	42.042	2.973	(40.462, 43.621)
Non-solarized & unamended (D)	12	41.875	2.664	(40.295, 43.455)

Pooled StDev = 2.71495

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping
Solarized & unamended (B)	12	48.313	A
Solarized & amended (A)	12	47.563	A
Non-solarized & amended (C)	12	42.042	B
Non-solarized & unamended (D)	12	41.875	B

Means that do not share a letter are significantly different.

One-way ANOVA: Solarization Soil Temperatures of Treatment E-H (1 cm depth)

Method

Null hypothesis	All means are equal
Alternative hypothesis	At least one mean is different
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (E), Solarized & unamended (F), Non-solarized & amended (G), Non-solarized & unamended (H)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	577.9	192.644	41.12	0.000
Error	44	206.1	4.685		
Total	47	784.1			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.16452	73.71%	71.92%	68.71%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (E)	12	49.875	2.186	(48.616, 51.134)
Solarized & unamended (F)	12	50.250	2.624	(48.991, 51.509)
Non-solarized & amended (G)	12	44.167	1.946	(42.907, 45.426)
Non-solarized & unamended (H)	12	42.333	1.813	(41.074, 43.593)

Pooled StDev = 2.16452

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping
Solarized & unamended (F)	12	50.250	A
Solarized & amended (E)	12	49.875	A
Non-solarized & amended (G)	12	44.167	B
Non-solarized & unamended (H)	12	42.333	B

Means that do not share a letter are significantly different.

One-way ANOVA: Solarization Soil Temperatures of Treatment E-H (4 cm depth)

Method

Null hypothesis	All means are equal
Alternative hypothesis	At least one mean is different
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (E), Solarized & unamended (F), Non-solarized & amended (G), Non-solarized & unamended (H)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	580.9	193.644	40.23	0.000
Error	44	211.8	4.814		
Total	47	792.7			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.19406	73.28%	71.46%	68.20%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (E)	12	47.792	1.602	(46.515, 49.068)
Solarized & unamended (F)	12	48.083	3.309	(46.807, 49.360)
Non-solarized & amended (G)	12	41.917	1.832	(40.640, 43.193)
Non-solarized & unamended (H)	12	40.250	1.545	(38.974, 41.526)

Pooled StDev = 2.19406

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping
Solarized & unamended (F)	12	48.083	A
Solarized & amended (E)	12	47.792	A
Non-solarized & amended (G)	12	41.917	B
Non-solarized & unamended (H)	12	40.250	B

Means that do not share a letter are significantly different.

Appendix x(b)

Day 28 2-Sample t-test statistical analysis

Two-Sample T-Test and CI: % Phen Removal (Solarized), ... n-solarized)

Method

μ_1: mean of % Phen Removal (Solarized)

μ_2: mean of % Phen Removal (Non-solarized)

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% Phen Removal (Solarized)	4	59.95	5.23	2.6
% Phen Removal (Non-solarized)	4	17.98	5.54	2.8

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
41.97	5.39	(32.65, 51.29)

Test

Null hypothesis $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
11.01	6	0.000

Two-Sample T-Test and CI: % Fluo Removal (Solarized), ... n-solarized)

Method

μ_1: mean of % Fluo Removal (Solarized)

μ_2: mean of % Fluo Removal (Non-solarized)

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% Fluo Removal (Solarized)	4	38.740	0.332	0.17
% Fluo Removal (Non-solarized)	4	17.99	4.37	2.2

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
20.75	3.10	(15.39, 26.11)

Test

Null hypothesis $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value

9.47	6	0.000

Two-Sample T-Test and CI: % BaP Removal (Solarized), % ... -solarized)

Method

μ_1: mean of % BaP Removal (Solarized)

μ_2: mean of % BaP Removal (Non-solarized)

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% BaP Removal (Solarized)	4	36.11	1.71	0.86
% BaP Removal (Non-solarized)	4	18.79	7.40	3.7

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
17.32	5.37	(8.02, 26.62)

Test

Null hypothesis H_0: $\mu_1 - \mu_2 = 0$

Alternative hypothesis H_1: $\mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
4.56	6	0.004

Two-Sample T-Test and CI: % S.S PAH Removal_1, % N.S ... Removal_1

Method

μ_1: mean of % S.S PAH Removal_1

μ_2: mean of % N.S PAH Removal_1

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% S.S PAH Removal_1	4	44.94	1.56	0.78
% N.S PAH Removal_1	4	18.25	4.30	2.2

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
26.68	3.24	(21.08, 32.28)

Test

Null hypothesis H_0: $\mu_1 - \mu_2 = 0$

Alternative hypothesis H_1: $\mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
11.66	6	0.000

Appendix xi

General Linear Model: % Phenanthrene Removal versus ... ctant, Plant

Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	32229.6	32229.6	174.65	0.000
Solarization	1	5083.7	5083.7	27.55	0.000
Biosurfactant	1	31.5	31.5	0.17	0.682
Plant	1	1976.0	1976.0	10.71	0.002
Error	35	6458.8	184.5		
Total	39	45779.6			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
13.5844	85.89%	84.28%	81.41%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	11.13	3.72	2.99	0.005	
Time	0.7168	0.0542	13.22	0.000	1.00
Solarization					
NS	-11.27	2.15	-5.25	0.000	1.00
Biosurfactant					
B	0.89	2.15	0.41	0.682	1.00
Plant					
UV	-7.03	2.15	-3.27	0.002	1.00

Regression Equation

Solarization	Biosurfactant	Plant			
NS	B	UV	% Phenanthrene Removal	=	-6.28 + 0.7168 Time
NS	B	V	% Phenanthrene Removal	=	7.78 + 0.7168 Time
NS	NB	UV	% Phenanthrene Removal	=	-8.06 + 0.7168 Time
NS	NB	V	% Phenanthrene Removal	=	6.00 + 0.7168 Time
S	B	UV	% Phenanthrene Removal	=	16.27 + 0.7168 Time

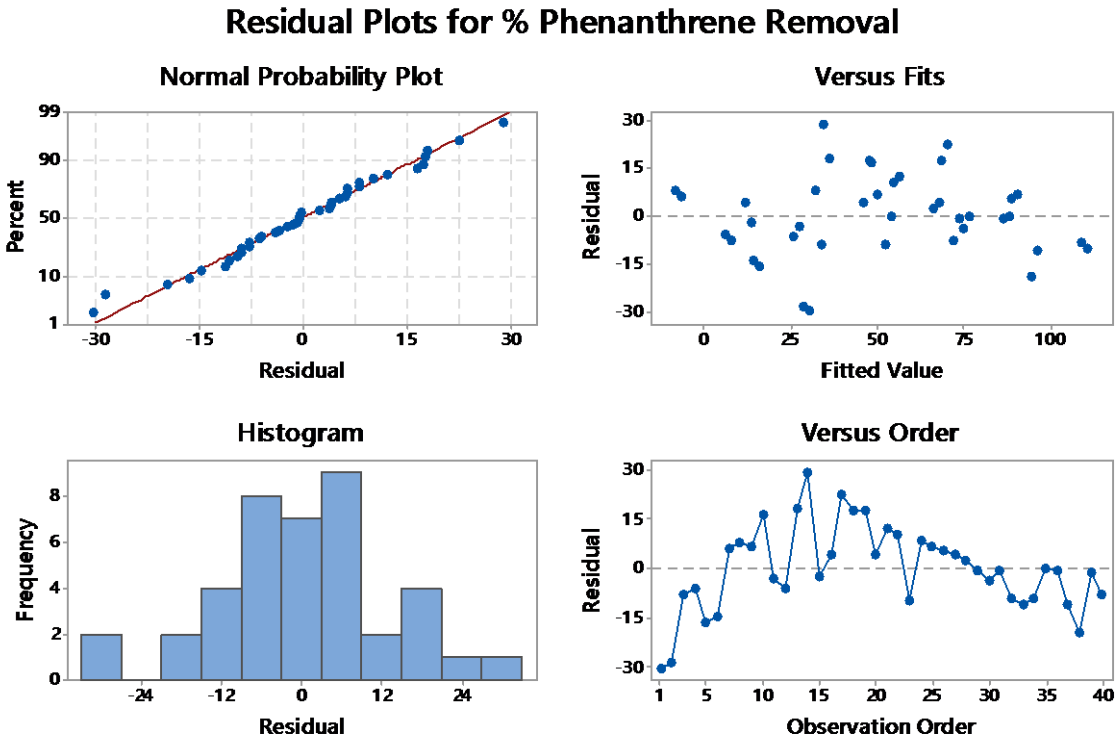
S	B	V	% Phenanthrene Removal	=	30.32 + 0.7168 Time
S	NB	UV	% Phenanthrene Removal	=	14.49 + 0.7168 Time
S	NB	V	% Phenanthrene Removal	=	28.55 + 0.7168 Time

Fits and Diagnostics for Unusual Observations

Obs	% Phenanthrene Removal	Fit	Resid	Std Resid	
1	0.00	30.32	-30.32	-2.42	R
2	0.00	28.55	-28.55	-2.28	R
14	63.62	34.56	29.06	2.27	R

R Large residual

Residual Plots for % Phenanthrene Removal



General Linear Model: % Fluoranthene Removal versus ... actant, Plant

Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	32815.1	32815.1	261.89	0.000
Solarization	1	2622.6	2622.6	20.93	0.000
Biosurfactant	1	118.9	118.9	0.95	0.337
Plant	1	2526.4	2526.4	20.16	0.000
Error	35	4385.5	125.3		
Total	39	42468.5			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
11.1938	89.67%	88.49%	86.42%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	6.65	3.07	2.17	0.037	
Time	0.7233	0.0447	16.18	0.000	1.00
Solarization					
NS	-8.10	1.77	-4.57	0.000	1.00
Biosurfactant					
B	1.72	1.77	0.97	0.337	1.00
Plant					
UV	-7.95	1.77	-4.49	0.000	1.00

Regression Equation

Solarization	Biosurfactant	Plant			
NS	B	UV	% Fluoranthene Removal	=	-7.67 + 0.7233 Time
NS	B	V	% Fluoranthene Removal	=	8.22 + 0.7233 Time
NS	NB	UV	% Fluoranthene Removal	=	-11.12 + 0.7233 Time
NS	NB	V	% Fluoranthene Removal	=	4.78 + 0.7233 Time
S	B	UV	% Fluoranthene Removal	=	8.52 + 0.7233 Time
S	B	V	% Fluoranthene Removal	=	24.42 + 0.7233 Time

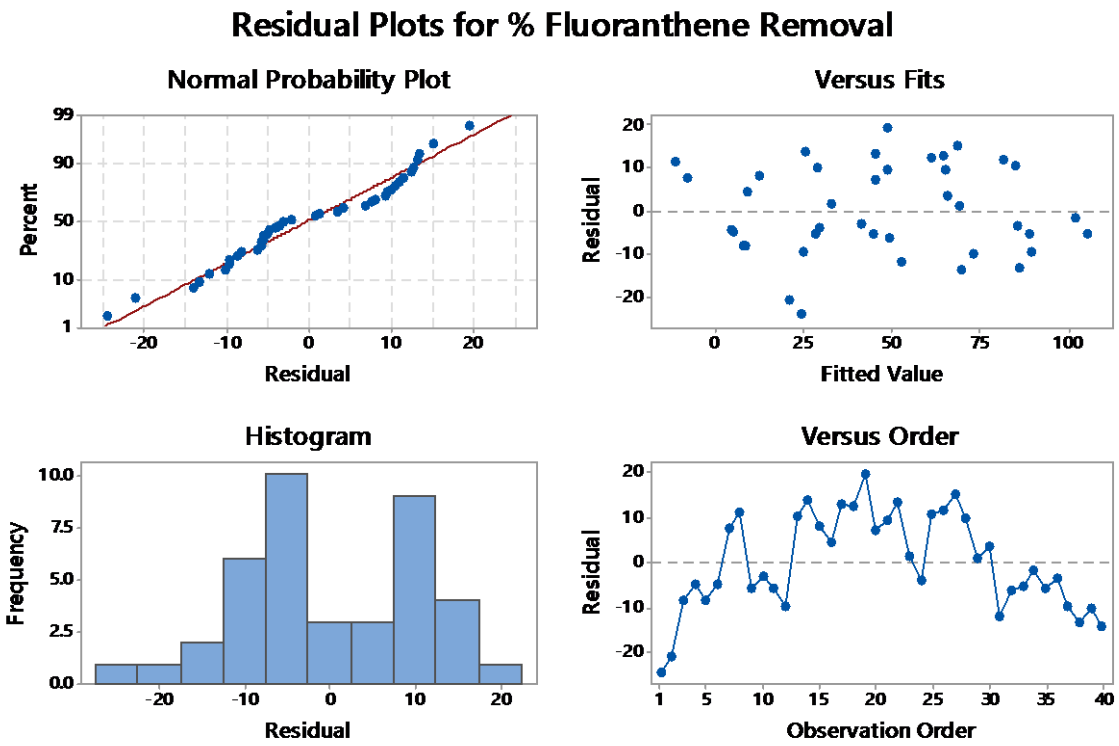
S	NB	UV	% Fluoranthene Removal	=	5.08 + 0.7233 Time
S	NB	V	% Fluoranthene Removal	=	20.97 + 0.7233 Time

Fits and Diagnostics for Unusual Observations

Obs	% Fluoranthene Removal	Fit	Resid	Std Resid	
1	0.00	24.42	-24.42	-2.37	R
2	0.00	20.97	-20.97	-2.03	R

R Large residual

Residual Plots for % Fluoranthene Removal



General Linear Model: % Benzo[a]pyrene Removal versus ... tant, Plant Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	22471.8	22471.8	237.79	0.000
Solarization	1	1597.1	1597.1	16.90	0.000
Biosurfactant	1	303.4	303.4	3.21	0.082
Plant	1	1904.3	1904.3	20.15	0.000
Error	35	3307.7	94.5		
Total	39	29584.2			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
9.72134	88.82%	87.54%	85.25%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	6.23	2.66	2.34	0.025	
Time	0.5986	0.0388	15.42	0.000	1.00
Solarization					
NS	-6.32	1.54	-4.11	0.000	1.00
Biosurfactant					
B	2.75	1.54	1.79	0.082	1.00
Plant					
UV	-6.90	1.54	-4.49	0.000	1.00

Regression Equation

Solarization	Biosurfactant	Plant			
NS	B	UV	% Benzo[a]pyrene Removal	=	-4.24 + 0.5986 Time
NS	B	V	% Benzo[a]pyrene Removal	=	9.56 + 0.5986 Time
NS	NB	UV	% Benzo[a]pyrene Removal	=	-9.74 + 0.5986 Time
NS	NB	V	% Benzo[a]pyrene Removal	=	4.05 + 0.5986 Time
S	B	UV	% Benzo[a]pyrene Removal	=	8.40 + 0.5986 Time

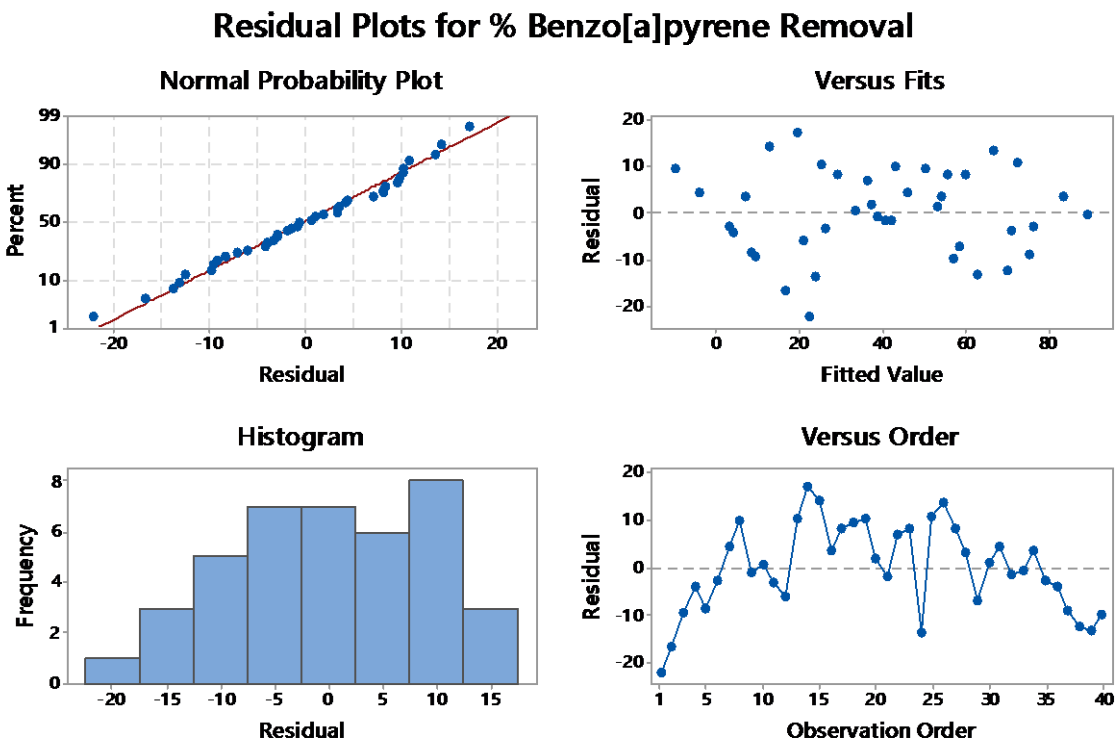
S	B	V	% Benzo[a]pyrene Removal	=	22.20 + 0.5986 Time
S	NB	UV	% Benzo[a]pyrene Removal	=	2.89 + 0.5986 Time
S	NB	V	% Benzo[a]pyrene Removal	=	16.69 + 0.5986 Time

Fits and Diagnostics for Unusual Observations

Obs	% Benzo[a]pyrene Removal	Fit	Resid	Std Resid	
1	0.00	22.20	-22.20	-2.48	R

R Large residual

Residual Plots for % Benzo[a]pyrene Removal



General Linear Model: Total % PAH Removal versus Time, ... tant, Plant

Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	28967.1	28967.1	255.30	0.000
Solarization	1	2933.0	2933.0	25.85	0.000
Biosurfactant	1	127.9	127.9	1.13	0.296
Plant	1	2126.9	2126.9	18.75	0.000
Error	35	3971.2	113.5		
Total	39	38126.2			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
10.6519	89.58%	88.39%	86.22%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	8.00	2.92	2.74	0.010	
Time	0.6796	0.0425	15.98	0.000	1.00
Solarization					
NS	-8.56	1.68	-5.08	0.000	1.00
Biosurfactant					
B	1.79	1.68	1.06	0.296	1.00
Plant					
UV	-7.29	1.68	-4.33	0.000	1.00

Regression Equation

Solarization	Biosurfactant	Plant			
NS	B	UV	Total % PAH Removal	=	-6.06 + 0.6796 Time
NS	B	V	Total % PAH Removal	=	8.52 + 0.6796 Time
NS	NB	UV	Total % PAH Removal	=	-9.64 + 0.6796 Time
NS	NB	V	Total % PAH Removal	=	4.94 + 0.6796 Time
S	B	UV	Total % PAH Removal	=	11.06 + 0.6796 Time

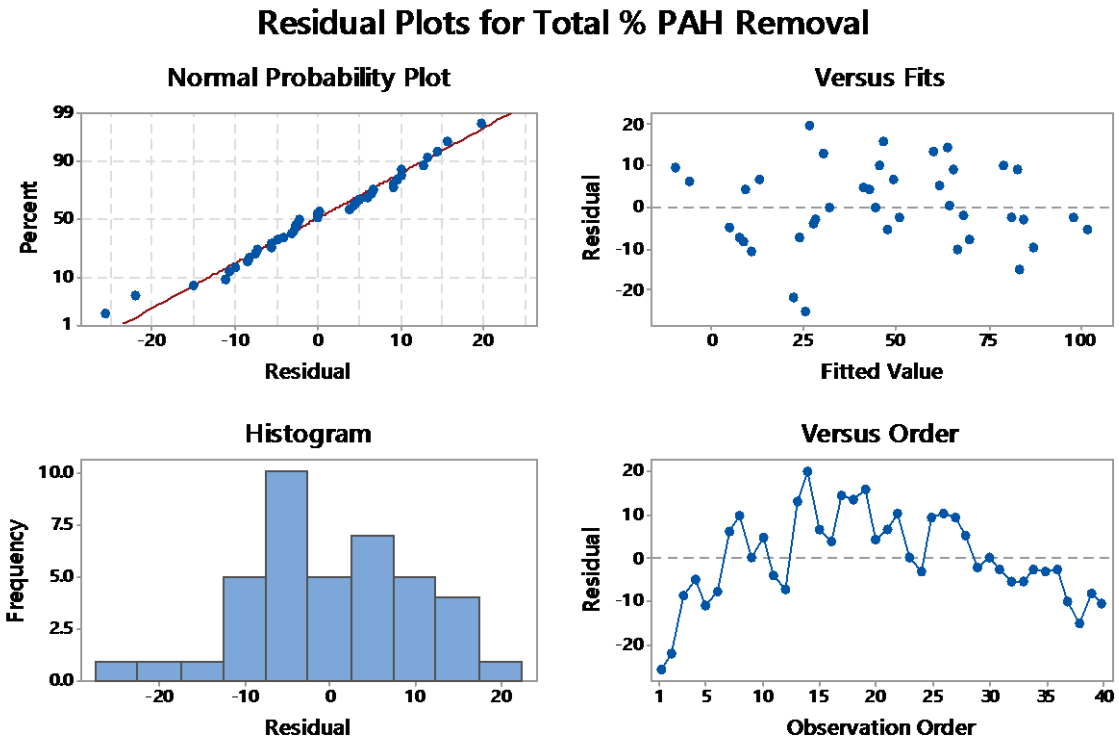
S	B	V	Total % PAH Removal	=	25.65 + 0.6796 Time
S	NB	UV	Total % PAH Removal	=	7.49 + 0.6796 Time
S	NB	V	Total % PAH Removal	=	22.07 + 0.6796 Time

Fits and Diagnostics for Unusual Observations

Obs	Total % PAH Removal	Fit	Resid	Std Resid	
1	0.00	25.65	-25.65	-2.61	R
2	0.00	22.07	-22.07	-2.25	R

R Large residual

Residual Plots for Total % PAH Removal



Appendix xii

Two-Sample T-Test and CI: % Phen Removal ... oval (No-Biosurfactan Method

μ_1: mean of % Phen Removal (Biosurfactant)

μ_2: mean of % Phen Removal (No-Biosurfactan

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% Phen Removal (Biosurfactant)	4	36.8	22.3	11
% Phen Removal (No-Biosurfactan	4	41.1	26.8	13

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
-4.4	24.7	(-47.1, 38.4)

Test

Null hypothesis $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
-0.25	6	0.811

Two-Sample T-Test and CI: % Fluo Removal ... moval (No-Biosurfacta) Method

μ_1: mean of % Fluo Removal (Biosurfactant)

μ_2: mean of % Fluo Removal (No-Biosurfacta)

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% Fluo Removal (Biosurfactant)	4	30.3	10.1	5.0
% Fluo Removal (No-Biosurfacta)	4	26.5	14.0	7.0

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
3.79	12.18	(-17.28, 24.86)

Test

Null hypothesis $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0.44	6	0.675

Two-Sample T-Test and CI: % BaP Removal ... moval (No-Biosurfactan)

Method

μ_1: mean of % BaP Removal (Biosurfactant)

μ_2: mean of % BaP Removal (No-Biosurfactan)

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% BaP Removal (Biosurfactant)	4	30.83	7.12	3.6
% BaP Removal (No-Biosurfactan)	4	24.1	13.3	6.6

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
6.76	10.66	(-11.69, 25.21)

Test

Null hypothesis H_0: $\mu_1 - \mu_2 = 0$

Alternative hypothesis H_1: $\mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0.90	6	0.405

Two-Sample T-Test and CI: % Biosurfactan PAH ... ctan PAH Removal_1

Method

μ_1: mean of % Biosurfactan PAH Removal_1

μ_2: mean of % No-Biosurfactan PAH Removal_1

Difference: $\mu_1 - \mu_2$

Equal variances are assumed for this analysis.

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
% Biosurfactan PAH Removal_1	4	32.6	13.0	6.5
% No-Biosurfactan PAH Removal_1	4	30.6	18.0	9.0

Estimation for Difference

Difference	Pooled StDev	95% CI for Difference
2.1	15.7	(-25.1, 29.2)

Test

Null hypothesis H_0: $\mu_1 - \mu_2 = 0$

Alternative hypothesis H_1: $\mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
0.19	6	0.859

Appendix xiii

Analysis for heights of seedlings prior to transplant

One-way ANOVA: Solarized & amended (A), ... ized & un-amended (D)

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (A), Non-solarized & amended (C), Solarized & un-amended (B), Non-solarized & un-amended (D)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	0.04250	0.01417	0.24	0.864
Error	12	0.69500	0.05792		
Total	15	0.73750			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.240659	5.76%	0.00%	0.00%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (A)	4	7.250	0.289	(6.988, 7.512)
Non-solarized & amended (C)	4	7.3750	0.1500	(7.1128, 7.6372)
Solarized & un-amended (B)	4	7.250	0.289	(6.988, 7.512)
Non-solarized & un-amended (D)	4	7.275	0.206	(7.013, 7.537)

Pooled StDev = 0.240659

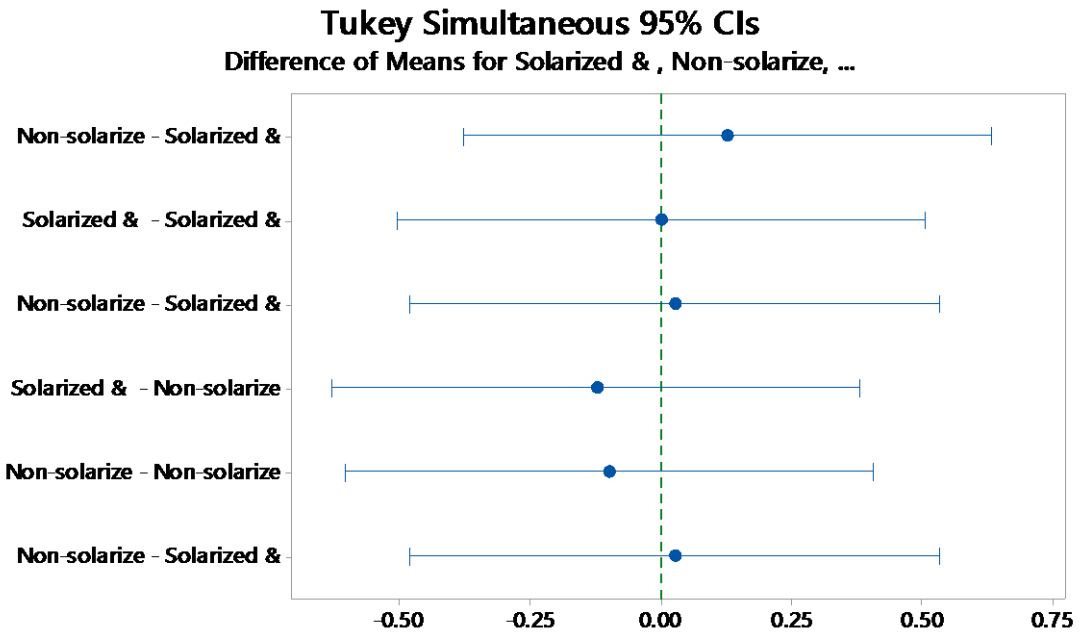
Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping
Non-solarized & amended (C)	4	7.3750	A
Non-solarized & un-amended (D)	4	7.275	A
Solarized & un-amended (B)	4	7.250	A
Solarized & amended (A)	4	7.250	A

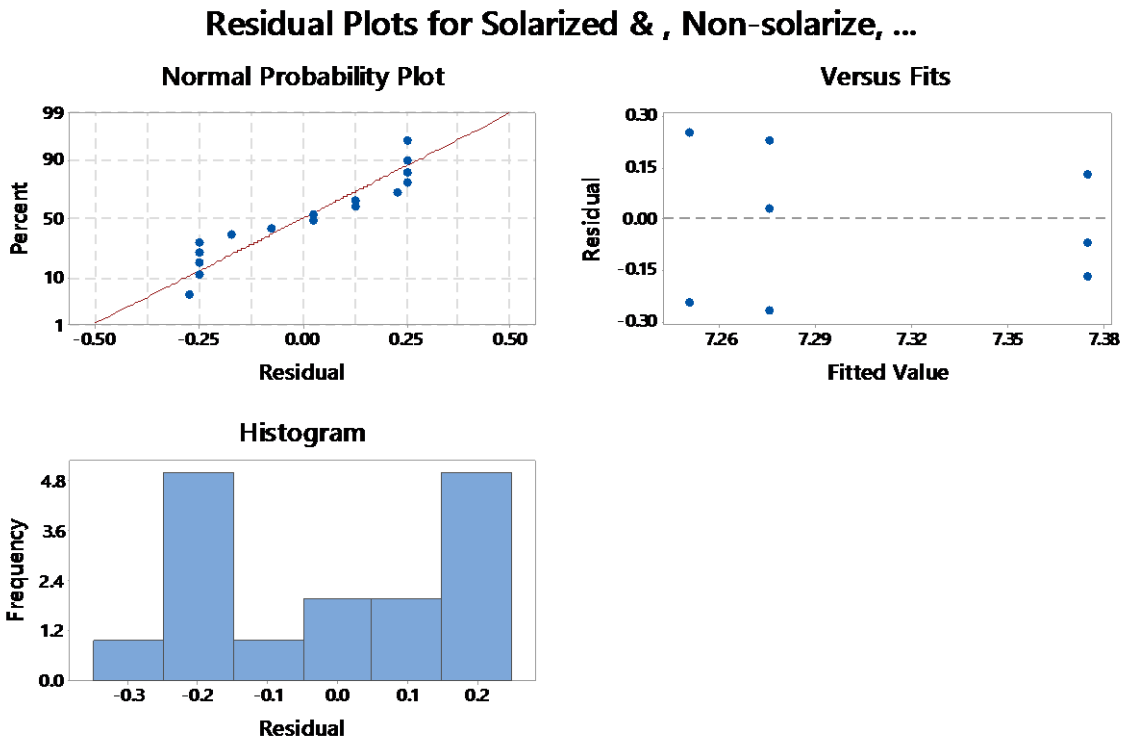
Means that do not share a letter are significantly different.

Tukey Simultaneous 95% Cis



If an interval does not contain zero, the corresponding means are significantly different.

Residual Plots for Solarized & , Non-solarize, ...



Analysis for heights of plants after harvest

One-way ANOVA: Solarized & amended (A), ... ized & un-amended (D)

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (A), Non-solarized & amended (C), Solarized & un-amended (B), Non-solarized & un-amended (D)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	347.0	115.67	9.24	0.002
Error	12	150.2	12.51		
Total	15	497.2			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
3.53739	69.80%	62.25%	46.31%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (A)	4	47.75	3.88	(43.90, 51.60)
Non-solarized & amended (C)	4	38.45	4.23	(34.60, 42.30)
Solarized & un-amended (B)	4	45.25	2.90	(41.40, 49.10)
Non-solarized & un-amended (D)	4	36.48	2.94	(32.62, 40.33)

Pooled StDev = 3.53739

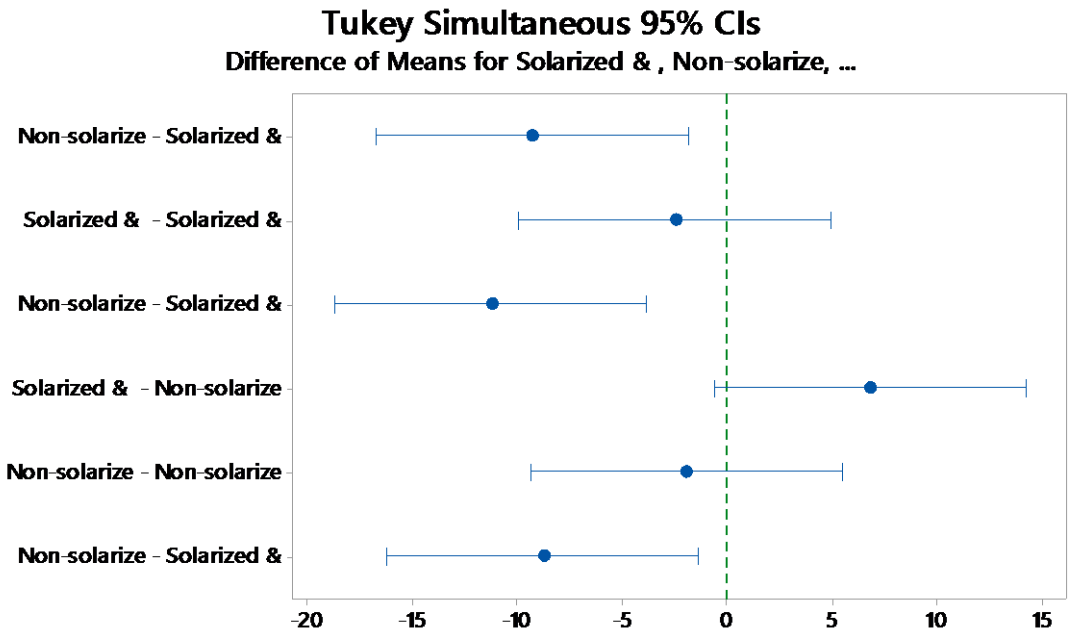
Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping		
Solarized & amended (A)	4	47.75	A		
Solarized & un-amended (B)	4	45.25	A	B	
Non-solarized & amended (C)	4	38.45		B	C
Non-solarized & un-amended (D)	4	36.48			C

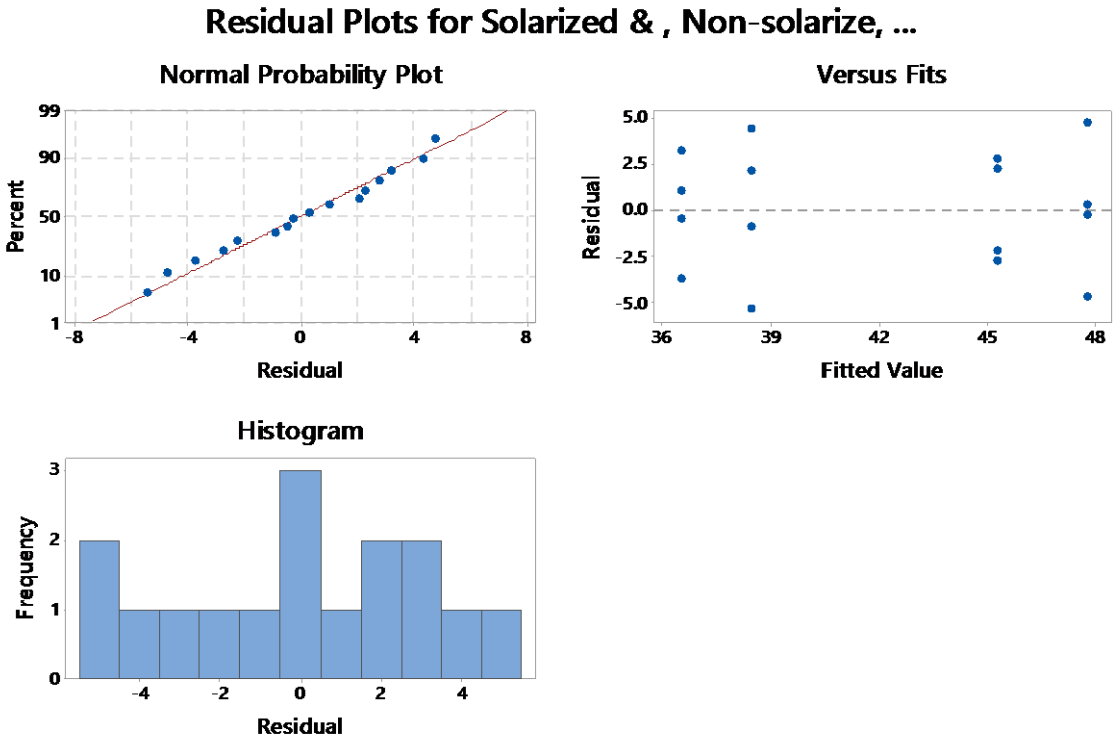
Means that do not share a letter are significantly different.

Tukey Simultaneous 95% CIs



If an interval does not contain zero, the corresponding means are significantly different.

Residual Plots for Solarized & , Non-solarize, ...



Analysis for plants (shoots) dry biomass after harvest

One-way ANOVA: Solarized & amended (A), Solarized & ... ended (D)

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (A), Solarized & un-amended (B), Non-solarized & amended (C), Non-solarized & un-amended (D)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	1.615	0.53833	5.79	0.011
Error	12	1.115	0.09292		
Total	15	2.730			

Model Summary

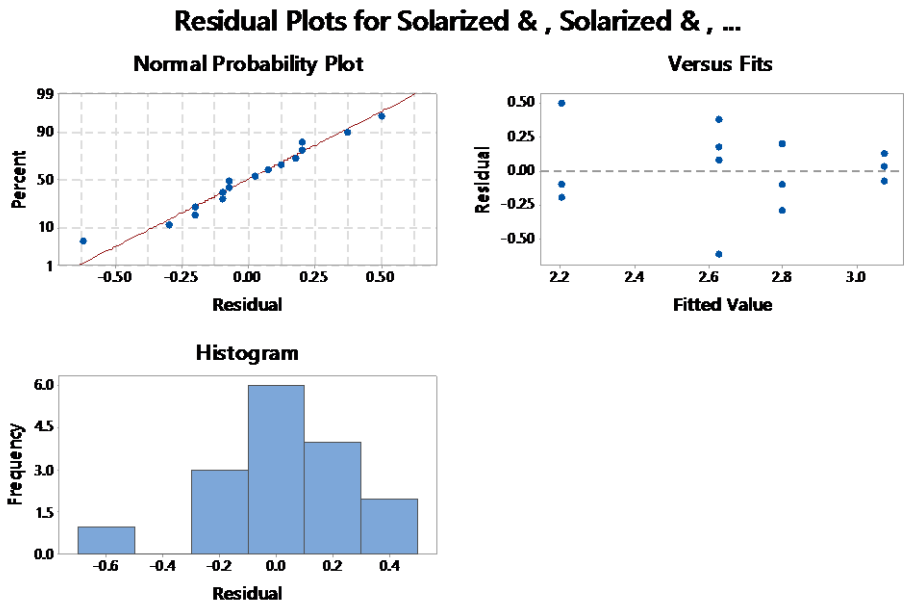
S	R-sq	R-sq(adj)	R-sq(pred)
0.304822	59.16%	48.95%	27.39%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (A)	4	3.0750	0.0957	(2.7429, 3.4071)
Solarized & un-amended (B)	4	2.800	0.245	(2.468, 3.132)
Non-solarized & amended (C)	4	2.625	0.435	(2.293, 2.957)
Non-solarized & un-amended (D)	4	2.200	0.337	(1.868, 2.532)

Pooled StDev = 0.304822

Residual Plots for Solarized & , Solarized & , ...



Analysis of roots length after harvest

One-way ANOVA: Solarized & amended (A), Solarized & ... ended (D)

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (A), Solarized & un-amended (B), Non-solarized & amended (C), Non-solarized & un-amended (D)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	198.3	66.08	1.59	0.244
Error	12	499.5	41.63		
Total	15	697.8			

Model Summary

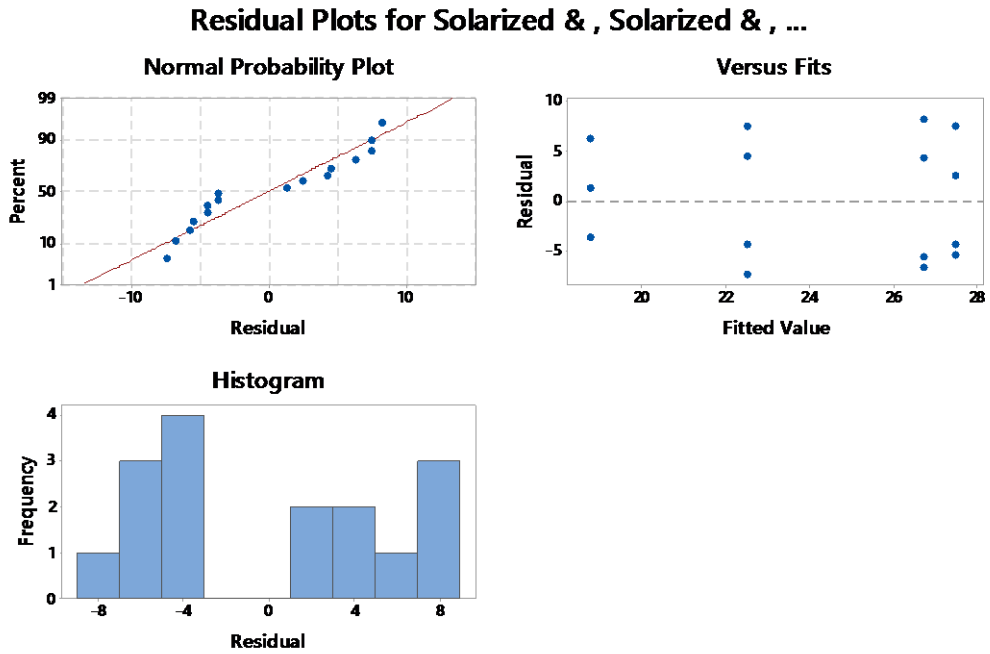
S	R-sq	R-sq(adj)	R-sq(pred)
6.45174	28.41%	10.52%	0.00%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (A)	4	26.75	7.41	(19.72, 33.78)
Solarized & un-amended (B)	4	27.50	6.14	(20.47, 34.53)
Non-solarized & amended (C)	4	22.50	7.14	(15.47, 29.53)
Non-solarized & un-amended (D)	4	18.75	4.79	(11.72, 25.78)

Pooled StDev = 6.45174

Residual Plots for Solarized & , Solarized & , ...



Analysis for roots dry biomass after harvest

One-way ANOVA: Solarized & amended (A), Solarized & ... ended (D)

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Solarized & amended (A), Solarized & un-amended (B), Non-solarized & amended (C), Non-solarized & un-amended (D)

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	3.6600	1.22000	97.60	0.000
Error	12	0.1500	0.01250		
Total	15	3.8100			

Model Summary

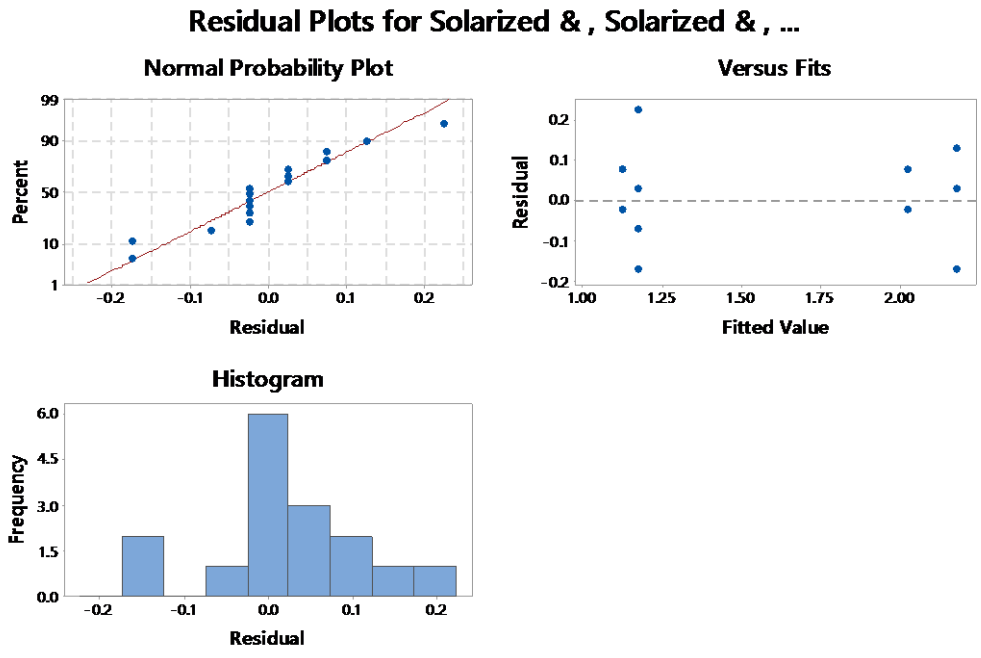
S	R-sq	R-sq(adj)	R-sq(pred)
0.111803	96.06%	95.08%	93.00%

Means

Factor	N	Mean	StDev	95% CI
Solarized & amended (A)	4	2.1750	0.1258	(2.0532, 2.2968)
Solarized & un-amended (B)	4	2.0250	0.0500	(1.9032, 2.1468)
Non-solarized & amended (C)	4	1.1750	0.1708	(1.0532, 1.2968)
Non-solarized & un-amended (D)	4	1.1250	0.0500	(1.0032, 1.2468)

Pooled StDev = 0.111803

Residual Plots for Solarized & , Solarized & , ...



Appendix xiv

General Linear Model: Plant height versus Time, Solarization Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	6034.39	6034.39	335.34	0.000
Solarization	1	172.11	172.11	9.56	0.007
Error	17	305.92	18.00		
Lack-of-Fit	7	296.88	42.41	46.96	0.000
Pure Error	10	9.03	0.90		
Total	19	6512.42			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
4.24205	95.30%	94.75%	93.37%

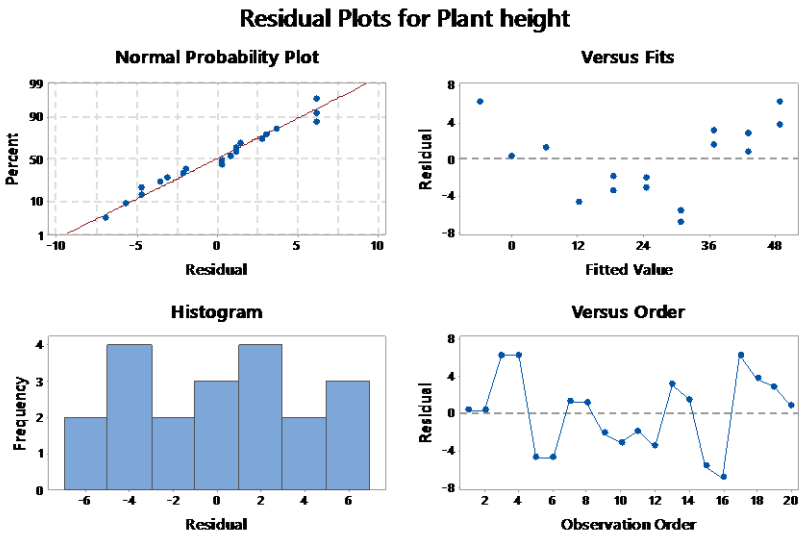
Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	-3.21	1.64	-1.95	0.067	
Time	0.4387	0.0240	18.31	0.000	1.00
Solarization					
NS	-2.933	0.949	-3.09	0.007	1.00

Regression Equation

Solarization			
NS	Plant height	=	-6.14 + 0.4387 Time
S	Plant height	=	-0.28 + 0.4387 Time

Residual Plots for Plant height



General Linear Model: Plant height versus Time, Biosurfactant Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Biosurfactant	Fixed	2	B, NB

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	6034.39	6034.39	216.87	0.000
Biosurfactant	1	5.01	5.01	0.18	0.677
Error	17	473.01	27.82		
Lack-of-Fit	7	148.08	21.15	0.65	0.708
Pure Error	10	324.93	32.49		
Total	19	6512.42			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
5.27488	92.74%	91.88%	89.92%

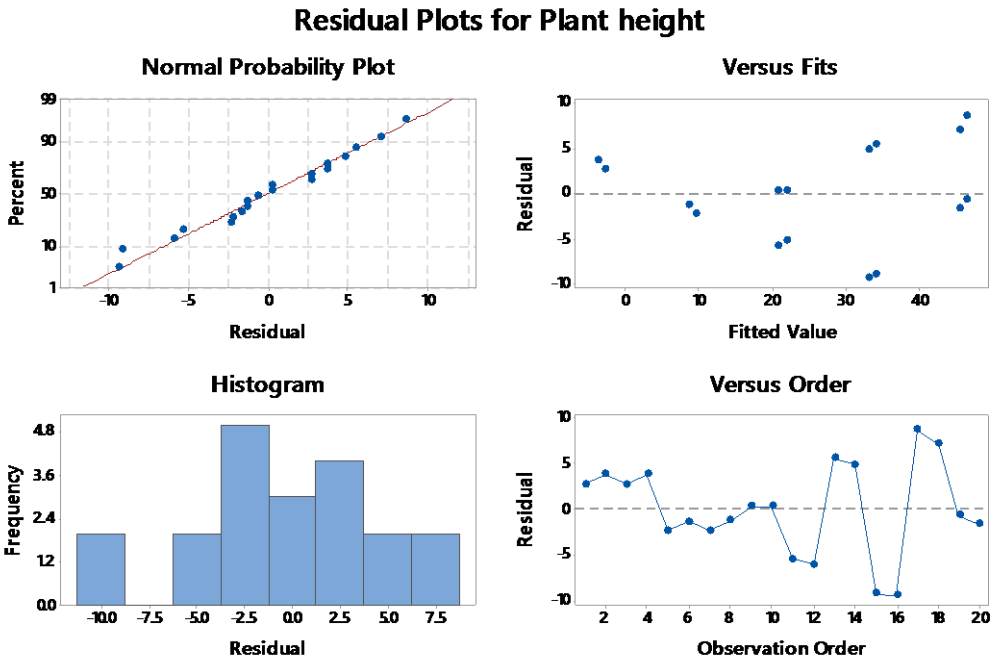
Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	-3.21	2.04	-1.57	0.135	
Time	0.4387	0.0298	14.73	0.000	1.00
Biosurfactant					
B	0.50	1.18	0.42	0.677	1.00

Regression Equation

Biosurfactant			
B	Plant height	=	-2.71 + 0.4387 Time
NB	Plant height	=	-3.71 + 0.4387 Time

Residual Plots for Plant height



Appendix xv

General Linear Model: Bacteria versus Time, Solarization, ... tant, Plant Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	28918.0	28918.0	33.14	0.000
Solarization	1	2250.0	2250.0	2.58	0.117
Biosurfactant	1	102.4	102.4	0.12	0.734
Plant	1	22231.2	22231.2	25.48	0.000
Error	35	30539.3	872.6		
Total	39	84040.9			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
29.5390	63.66%	59.51%	52.04%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	26.02	8.09	3.22	0.003	
Time	0.679	0.118	5.76	0.000	1.00
Solarization					
NS	-7.50	4.67	-1.61	0.117	1.00
Biosurfactant					
B	1.60	4.67	0.34	0.734	1.00
Plant					
UV	-23.57	4.67	-5.05	0.000	1.00

Regression Equation

Solarization	Biosurfactant	Plant			
NS	B	UV	Bacteria	=	-3.4 + 0.679 Time
NS	B	V	Bacteria	=	43.7 + 0.679 Time
NS	NB	UV	Bacteria	=	-6.6 + 0.679 Time
NS	NB	V	Bacteria	=	40.5 + 0.679 Time

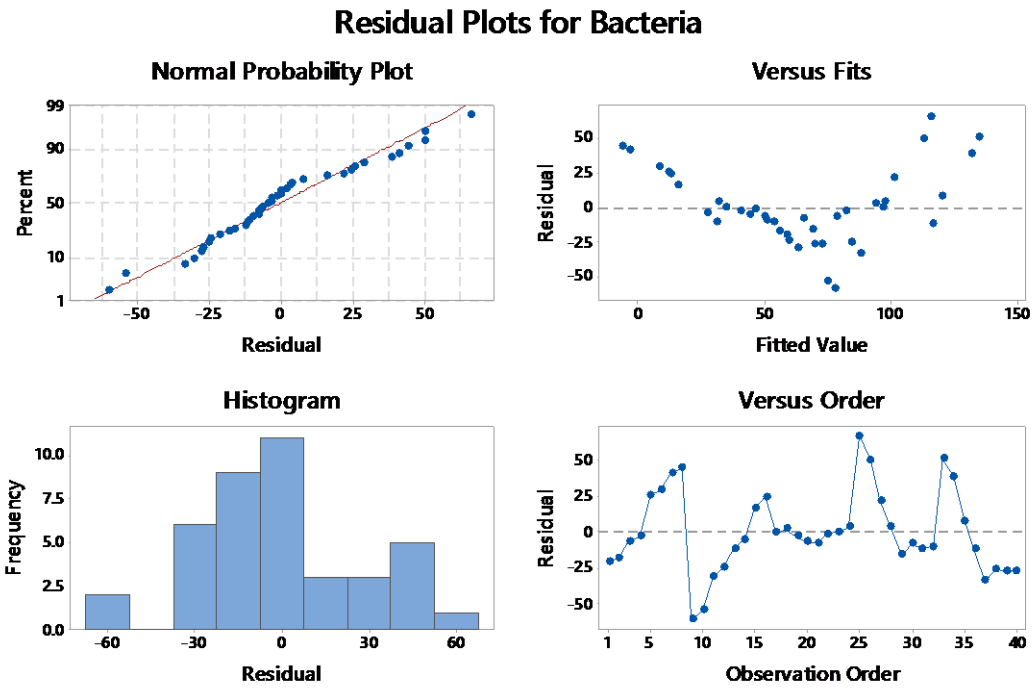
S	B	UV	Bacteria	=	11.5 + 0.679 Time
S	B	V	Bacteria	=	58.7 + 0.679 Time
S	NB	UV	Bacteria	=	8.3 + 0.679 Time
S	NB	V	Bacteria	=	55.5 + 0.679 Time

Fits and Diagnostics for Unusual Observations

Obs	Bacteria	Fit	Resid	Std Resid	
9	17.5	77.7	-60.2	-2.16	R
25	182.0	115.7	66.3	2.38	R

R Large residual

Residual Plots for Bacteria



General Linear Model: Actinomycete versus Time, ... osurfactant, Plant Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	11712.8	11712.8	52.17	0.000
Solarization	1	566.3	566.3	2.52	0.121
Biosurfactant	1	0.8	0.8	0.00	0.954
Plant	1	5772.0	5772.0	25.71	0.000
Error	35	7857.9	224.5		
Total	39	25909.7			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
14.9837	69.67%	66.21%	60.16%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	16.84	4.10	4.10	0.000	
Time	0.4321	0.0598	7.22	0.000	1.00
Solarization					
NS	-3.76	2.37	-1.59	0.121	1.00
Biosurfactant					
B	0.14	2.37	0.06	0.954	1.00
Plant					
UV	-12.01	2.37	-5.07	0.000	1.00

Regression Equation

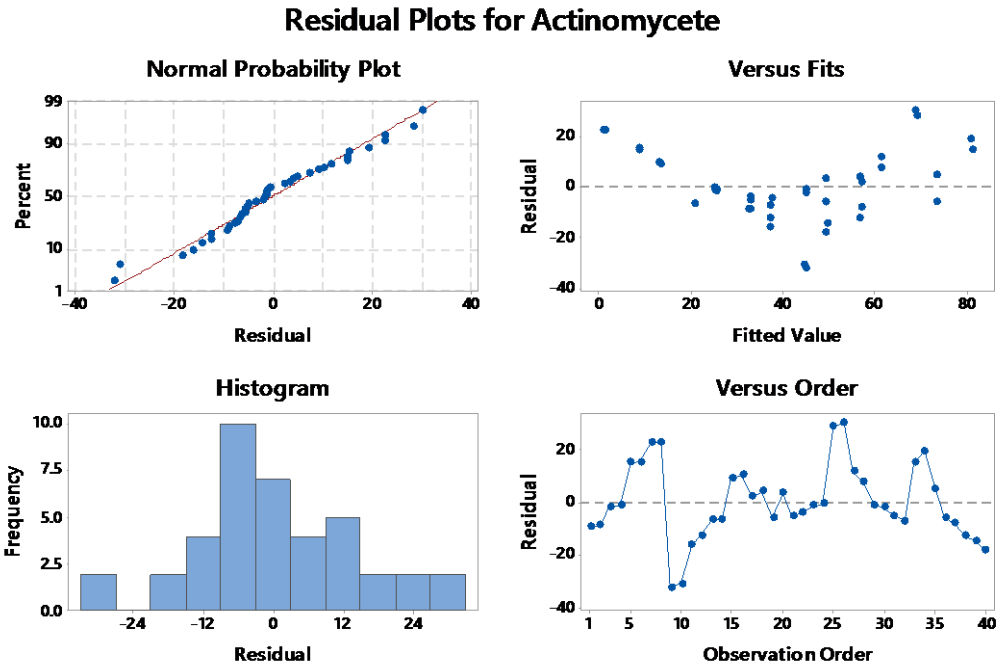
Solarization	Biosurfactant	Plant			
NS	B	UV	Actinomycete	=	1.20 + 0.4321 Time
NS	B	V	Actinomycete	=	25.22 + 0.4321 Time
NS	NB	UV	Actinomycete	=	0.93 + 0.4321 Time
NS	NB	V	Actinomycete	=	24.95 + 0.4321 Time
S	B	UV	Actinomycete	=	8.73 + 0.4321 Time
S	B	V	Actinomycete	=	32.75 + 0.4321 Time
S	NB	UV	Actinomycete	=	8.45 + 0.4321 Time
S	NB	V	Actinomycete	=	32.47 + 0.4321 Time

Fits and Diagnostics for Unusual Observations

Obs	Actinomycete	Fit	Resid	Std Resid	
9	12.50	44.85	-32.35	-2.29	R
10	13.50	44.57	-31.07	-2.20	R
25	97.50	69.05	28.45	2.02	R
26	99.00	68.77	30.23	2.14	R

R Large residual

Residual Plots for Actinomycete



General Linear Model: Fungi versus Time, Solarization, ... factant, Plant Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	12251.3	12251.3	58.23	0.000
Solarization	1	500.6	500.6	2.38	0.132
Biosurfactant	1	2.8	2.8	0.01	0.910
Plant	1	5370.8	5370.8	25.53	0.000
Error	35	7364.1	210.4		
Total	39	25489.5			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
14.5053	71.11%	67.81%	61.90%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	7.89	3.97	1.99	0.055	
Time	0.4420	0.0579	7.63	0.000	1.00
Solarization					
NS	-3.54	2.29	-1.54	0.132	1.00
Biosurfactant					
B	0.26	2.29	0.11	0.910	1.00
Plant					
UV	-11.59	2.29	-5.05	0.000	1.00

Regression Equation

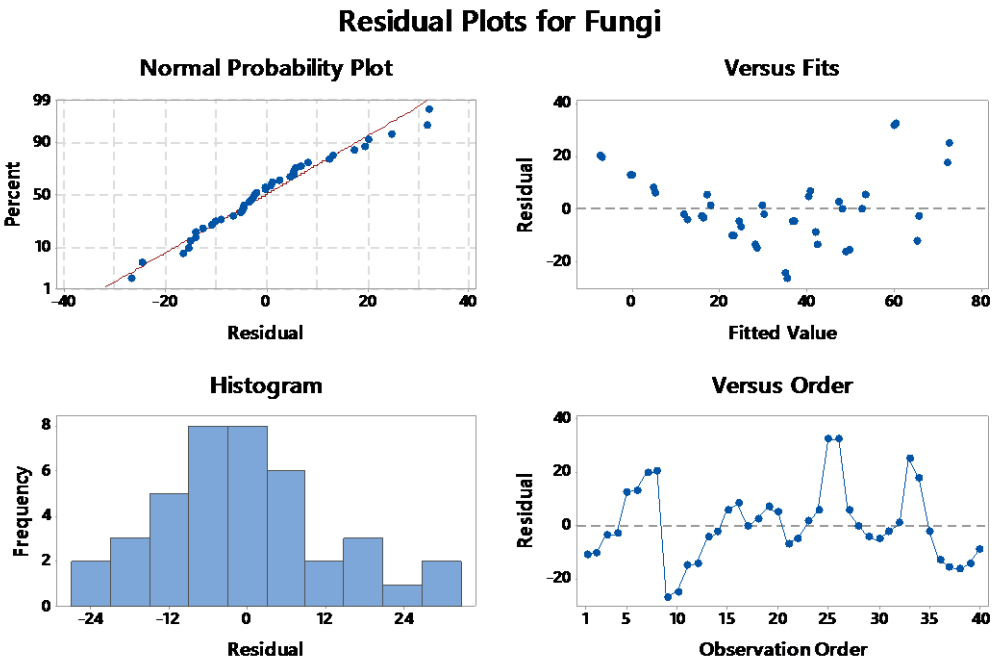
Solarization	Biosurfactant	Plant			
NS	B	UV	Fungi	=	-6.97 + 0.4420 Time
NS	B	V	Fungi	=	16.20 + 0.4420 Time
NS	NB	UV	Fungi	=	-7.50 + 0.4420 Time
NS	NB	V	Fungi	=	15.67 + 0.4420 Time
S	B	UV	Fungi	=	0.10 + 0.4420 Time
S	B	V	Fungi	=	23.27 + 0.4420 Time
S	NB	UV	Fungi	=	-0.43 + 0.4420 Time
S	NB	V	Fungi	=	22.75 + 0.4420 Time

Fits and Diagnostics for Unusual Observations

Obs	Fungi	Fit	Resid	Std Resid	
25	92.50	60.40	32.10	2.35	R
26	91.50	59.87	31.63	2.31	R

R Large residual

Residual Plots for Fungi


Residual Plots for Fungi
Normal Probability Plot
Percent
99
90
50
10
1
-40
-20
0
20
40
Residual
Versus Fits
Residual
40
20
0
-20
0
20
40
60
80
Fitted Value
Histogram
Frequency
8
6
4
2
0
-24
-12
0
12
24
Residual
Versus Order
Residual
40
20
0
-20
1
5
10
15
20
25
30
35
40
Observation Order

Appendix xvi

General Linear Model: DHO versus Time, Solarization, ... factant, Plant Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	431.38	431.38	12.59	0.001
Solarization	1	105.79	105.79	3.09	0.088
Biosurfactant	1	26.29	26.29	0.77	0.387
Plant	1	271.60	271.60	7.93	0.008
Error	35	1198.87	34.25		
Total	39	2033.93			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
5.85265	41.06%	34.32%	23.95%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.33	1.60	0.21	0.838	
Time	0.0829	0.0234	3.55	0.001	1.00
Solarization					
NS	-1.626	0.925	-1.76	0.088	1.00
Biosurfactant					
B	0.811	0.925	0.88	0.387	1.00
Plant					
UV	-2.606	0.925	-2.82	0.008	1.00

Regression Equation

Solarization	Biosurfactant	Plant			
NS	B	UV	DHO	=	-3.09 + 0.0829 Time
NS	B	V	DHO	=	2.12 + 0.0829 Time
NS	NB	UV	DHO	=	-4.71 + 0.0829 Time
NS	NB	V	DHO	=	0.50 + 0.0829 Time

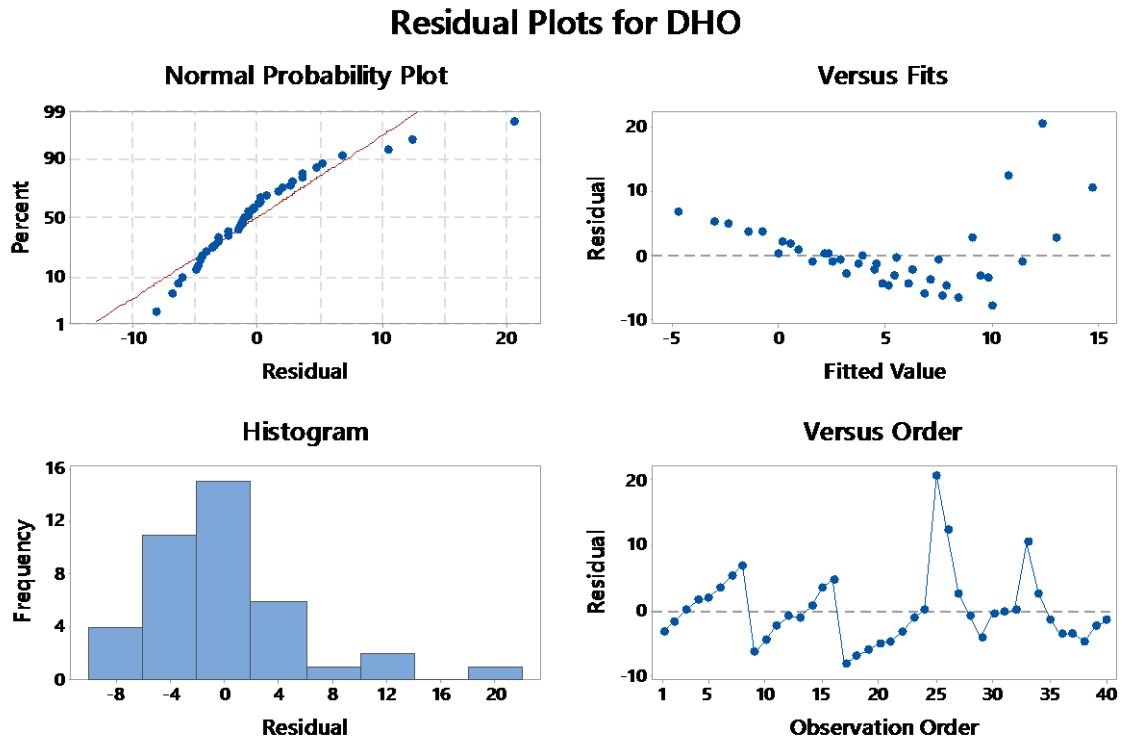
S	B	UV	DHO	=	0.16 + 0.0829 Time
S	B	V	DHO	=	5.37 + 0.0829 Time
S	NB	UV	DHO	=	-1.46 + 0.0829 Time
S	NB	V	DHO	=	3.75 + 0.0829 Time

Fits and Diagnostics for Unusual Observations

Obs	DHO	Fit	Resid	Std Resid	
25	33.02	12.34	20.68	3.75	R
26	23.17	10.72	12.45	2.26	R

R Large residual

Residual Plots for DHO



General Linear Model: URE versus Time, Solarization, ... rfactant, Plant Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
Solarization	Fixed	2	NS, S
Biosurfactant	Fixed	2	B, NB
Plant	Fixed	2	UV, V

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time	1	0.011281	0.011281	83.50	0.000
Solarization	1	0.001103	0.001103	8.16	0.007
Biosurfactant	1	0.000303	0.000303	2.24	0.144
Plant	1	0.001822	0.001822	13.49	0.001
Error	35	0.004729	0.000135		
Total	39	0.019238			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0116236	75.42%	72.61%	67.84%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.00500	0.00318	1.57	0.125	
Time	0.000424	0.000046	9.14	0.000	1.00
Solarization					
NS	-0.00525	0.00184	-2.86	0.007	1.00
Biosurfactant					
B	0.00275	0.00184	1.50	0.144	1.00
Plant					
UV	-0.00675	0.00184	-3.67	0.001	1.00

Regression Equation

Solarization	Biosurfactant	Plant			
NS	B	UV	URE	=	-0.00425 + 0.000424 Time
NS	B	V	URE	=	0.00925 + 0.000424 Time
NS	NB	UV	URE	=	-0.00975 + 0.000424 Time
NS	NB	V	URE	=	0.00375 + 0.000424 Time
S	B	UV	URE	=	0.00625 + 0.000424 Time

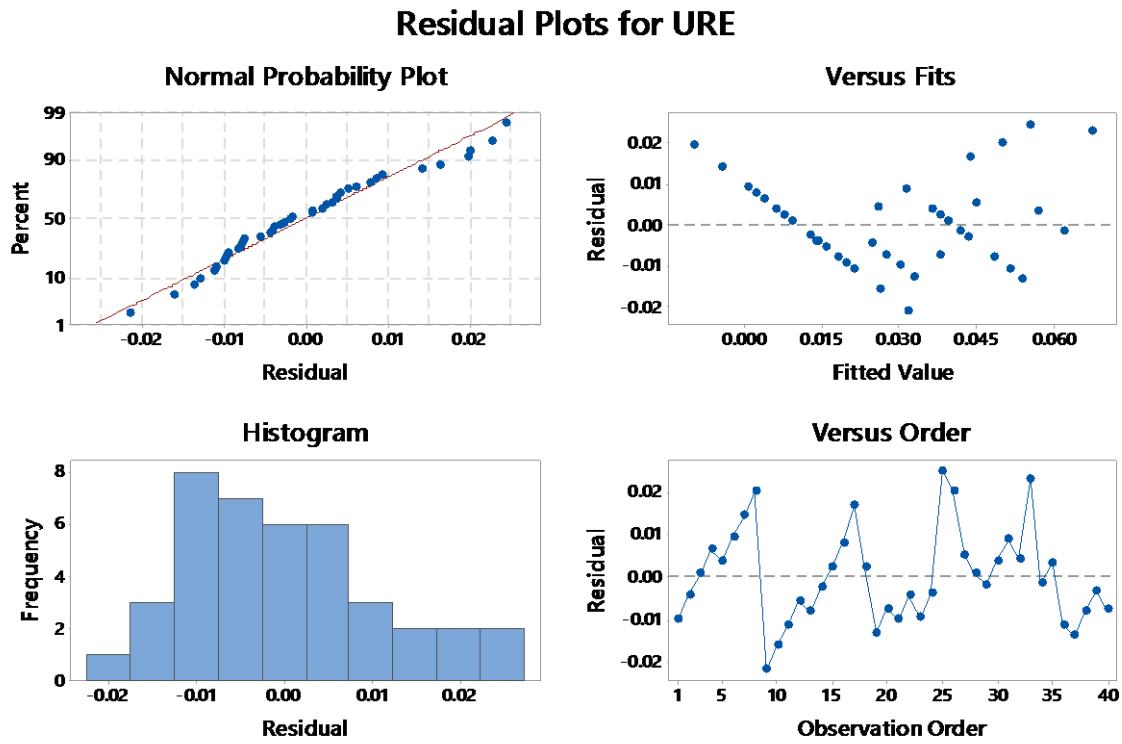
S	B	V	URE	=	0.01975 + 0.000424 Time
S	NB	UV	URE	=	0.00075 + 0.000424 Time
S	NB	V	URE	=	0.01425 + 0.000424 Time

Fits and Diagnostics for Unusual Observations

Obs	URE	Fit	Resid	Std Resid	
25	0.08000	0.05538	0.02462	2.25	R
33	0.09000	0.06725	0.02275	2.12	R

R Large residual

Residual Plots for URE



Appendix xvii

MIDDLESEX UNIVERSITY

PARTICIPANT INFORMATION SHEET (PIS)

Participant ID Code:……

1. Study title

Advanced Phytoremediation using Soil Solarization enhanced with Biosurfactant as a Novel Approach to Sustainable Remediation of Crude Oil Contaminated Land in the Niger Delta, Nigeria.

2. Invitation paragraph

You are being invited to take part in a research study. Before you decide it is important for you to understand why the research is being done and what it will involve. Please take time to read the following information carefully and discuss it with others if you wish. Ask us if there is anything that is not clear or if you would like more information. Take time to decide whether or not you wish to take part.

Thank you for reading this.

3. What is the purpose of the study?

The purpose of the study is to gauge the status of sustainability awareness, understanding and measurement through an active interaction with relevant stakeholders ranging from multinational oil companies with their host communities, regulatory agencies, environmental consultants, academics/researchers and technology providers/contractors in applied remediation techniques in the Niger Delta, with the aim of promoting sustainable remediation technologies. At the end, the research will recommend possible sustainable remediation options that will be aesthetically pleasing, environmentally friendly, relatively easy to apply and cost effective.

4. Why have I been chosen?

It is important that we assess as many participants as possible, and your professional experience, expertise and opinion from a stakeholder's point of view are crucial to achieve this purpose and in particular, how it should be promoted for a net benefit on human health and the environment through prudent use of limited resource.

5. Do I have to take part?

It is up to you to decide whether or not to take part. If you do decide to take part you will be given this information sheet to keep and be asked to sign a consent form. If you decide to take part you are still free to withdraw at any time and without giving a reason. If you do decide to withdraw from the study then please inform the researcher as soon as possible, and they will facilitate your withdrawal. If, for any reason, you wish to withdraw your data please contact the researcher within a month of your participation. After this data it may not be possible to withdraw your individual data as the results may have already been published. However, as all data are anonymised, your individual data will not be identifiable in any way. A decision to withdraw at any time, or a decision not to take part, will not affect your

6. What will I have to do?

By taking part, you will be contributing to sustainable remediation of contaminated land in the Niger Delta region by completing a questionnaire and/or interviewed which will be recorded using a Dictaphone.

Please note that in order to ensure quality assurance and equity this project may be selected for audit by a designated member of the committee. This means that the designated member can request to see signed consent forms. However, if this is the case your signed consent form will only be accessed by the designated auditor or member of the audit team.

7. Will I have to provide any bodily samples (i.e. blood/saliva/urine)?

No

8. What are the possible disadvantages and risks of taking part?

Appropriate risk assessments for all procedures have been conducted, and will be followed throughout the duration of the study. However there are no disadvantages or risks foreseen in taking part in the study.

9. What are the possible benefits of taking part?

We hope that participating in the study will help you. However, this cannot be guaranteed. The information we get from this study may help us to gauge the awareness, understanding and measurement of sustainability in remediation of contaminated land in the Niger Delta from a stakeholder's point of view.

10. Will my taking part in this study be kept confidential?

The research team has put a number of procedures in place to protect the confidentiality of participants. You will be allocated a participant code that will always be used to identify any data you provide. Your name or other personal details will not be associated with your data, for example, the consent form that you sign will be kept separate from your data. All paper records will be stored in a locked filing cabinet, accessible only to the research team, and all electronic data will be stored on a password protected computer. All information you provide will be treated in accordance with the UK Data Protection Act.

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11. What will happen to the results of the research study?

The results of the research study will be used as part of an Postgraduate dissertation. The results may also be presented at conferences or in journal articles. However, the data will only be used by members of the research team and at no point will your personal information or data be revealed.

12. Who has reviewed the study?

The study has received full ethical clearance from the Research ethics committee who reviewed the study. The committee is the Natural Science Research Ethics Committee.

13. Contact for further information

If you require further information, have any questions or would like to withdraw your data then please contact:

Anthony E. Futughe, email: a.futughe@mdx.ac.uk

Professor Diane Purchase, Department of Natural Science, Faculty of Science and Technology, Middlesex University, London NW4 4BT. Tel:+44(0)2084115262 or email her at d.purcahse@mdx.ac.uk

Thank you for taking part in this study. You should keep this participant information sheet as it contains your participant code, important information and the research teams contact details.

A. Demographic Information

These questions are included to assist in understanding responses to the questionnaire with regard to social and economic profiles of the Niger Delta participants i.e. to see if gender, age, income, level of education etc. relate to any pattern.

A.1 Please indicate your gender

(Please tick one box only)

☐ Male
☐ Female

A.2 Please mark your age group

Under 30 year ☐
31 – 40 year ☐
41 – 50 year ☐
51 or more ☐

A.3 Educational level

Primary ☐
Secondary ☐
Tertiary ☐

A.4 Professional experience

Less than 5 years ☐
5-9 years ☐
10 year or more ☐

A.5 Are you employed in paid work? **Yes** ☐ **No** ☐

A.5.1 If yes what type(s) of work do you do? *(Please list)*

_____

_____

A.5.2 Please indicate you/your family income per annum

Up to ₦ 1,000,000 ☐
₦ 1,000,000 - ₦ 2,500,000 ☐
₦ 2,500,000 - ₦ 5,000,000 ☐
More than ₦ 5,000,000 ☐

A.6 Operational State in the Niger Delta

Abia	☐	Delta	☐	Rivers	☐
Akwa-Ibom	☐	Edo	☐		
Bayelsa	☐	Imo	☐		
Cross Rivers	☐	Ondo	☐		

A.7 How long have you lived/worked in the Niger Delta? *(Please mark the appropriate box)*

Less than one year	☐	5-9 years	☐
1-2 years	☐	10-19 years	☐
3-4 years	☐	20 years or more	☐

A.8 Where do you live in the Niger Delta (City/Town/Community)?

_____

A. Awareness and Understanding of Current Remediation Techniques used in the Niger Delta

B.1 What is your position or role related to Contaminated Land Management?

(Please mark the appropriate box)

a. Technology provider/Engineering contractor ☐
b. Environmental Consultant/Scientist ☐
c. Land user/Host community (e.g. farmer, tenant, indigene etc.) ☐
d. Local Government Authority ☐
e. Federal/State Government Regulatory Agency ☐
f. University or Research Institute ☐
g. Employee of oil and gas company ☐
h. Stakeholders (NGOs, human right, environmental activist, concern citizen etc.) ☐

B.2 How often do you deal with Contaminated Land issues?

(Please mark the appropriate box)

a. Daily ☐
b. Once or twice weekly ☐
c. Once or twice monthly ☐
d. Once or twice yearly ☐

B.3 Have you heard of the following remediation techniques undertaken in any of the Niger Delta States? *(Please mark the appropriate boxes).* If 'yes' do you remember where you heard about them? (Indicate in the Heard About box e.g. TV, radio, newspaper, school, internet, work, friend, specify other source, or not sure)

#	Remediation Techniques	No	Yes	Heard About
i.	Excavation and disposal	☐	☐	----------
ii.	Soil washing and Separation processes	☐	☐	----------
iii.	Covering with clean soil	☐	☐	----------
iv.	Chemical oxidation and reduction	☐	☐	----------
v.	Bioremediation	☐	☐	----------
vi.	Phytoremediation	☐	☐	----------
vii.	Soil vapour extraction	☐	☐	----------
viii.	Stabilization/Solidification	☐	☐	----------
ix.	Thermal treatment	☐	☐	----------
x.	Venting	☐	☐	----------
xi.	Vitrification	☐	☐	----------
xii.	Nanoremediation	☐	☐	----------

B.4 Please rate your understanding of the application of each of the remediation techniques. *(Please mark the appropriate boxes. Note: Numbers correspond to the remediation techniques in the question above e.g. B.3)*

#	Very Poor	Poor	Average	Good	Very Good	Unsure
i.	☐	☐	☐	☐	☐	☐
ii.	☐	☐	☐	☐	☐	☐
iii.	☐	☐	☐	☐	☐	☐
iv.	☐	☐	☐	☐	☐	☐
v.	☐	☐	☐	☐	☐	☐
vi.	☐	☐	☐	☐	☐	☐
vii.	☐	☐	☐	☐	☐	☐
viii.	☐	☐	☐	☐	☐	☐
ix.	☐	☐	☐	☐	☐	☐
x.	☐	☐	☐	☐	☐	☐
xi.	☐	☐	☐	☐	☐	☐
xii.	☐	☐	☐	☐	☐	☐

B.5 Which remediation techniques are commonly applied to clean-up contaminated land in the Niger Delta especially in your state/host community? *(Please mark the appropriate column at the end of each row. If you don't have enough knowledge of a particular technique commonly use mark the* Unsure *box)*

		None	Low	Moderate	High	Not Sure
i.	Excavation and disposal	☐	☐	☐	☐	☐
ii.	Soil washing and Separation processes	☐	☐	☐	☐	☐
iii.	Covering with clean soil	☐	☐	☐	☐	☐
iv.	Chemical oxidation and reduction	☐	☐	☐	☐	☐
v.	Bioremediation	☐	☐	☐	☐	☐
vi.	Phytoremediation	☐	☐	☐	☐	☐
vii.	Soil vapour extraction	☐	☐	☐	☐	☐
viii.	Stabilization/Solidification	☐	☐	☐	☐	☐
ix.	Thermal treatment	☐	☐	☐	☐	☐
x.	Venting	☐	☐	☐	☐	☐
xi.	Vitrification	☐	☐	☐	☐	☐
xii.	Nanoremediation	☐	☐	☐	☐	☐

B.6 Can you identify current and likely future factors influencing their selection? *(Please list any factors you think are responsible for the various remediation techniques used in the region* from B.5 above*)*

_____
_____
_____
_____

C. Sustainability Understanding

C.1 Have you heard of the following? *(Please mark the appropriate box at the end of each row):*

	Publication – Plan – Conference etc.	No	Yes	Not sure
i.	The book – Silent Spring (by Rachel Carson, 1962)	☐	☐	☐
ii.	Convention on Wetlands (Ramsar, Iran, 1971)	☐	☐	☐
iii.	United Nation Conference on the Human Environment Stockholm, Sweden 1972	☐	☐	☐
iv.	World Conservation Strategy (IUCN, UNEP, and WWF 1980)	☐	☐	☐

v.	The Brundtland Report – Our Common Future: Report of the World Commission on Environment and Development (1987)	☐	☐	☐
vi.	United Nations Conference on Environment and Development (Earth Summit), Rio de Janeiro, Brazil 1992	☐	☐	☐
vii.	Agenda 21	☐	☐	☐
viii.	Kyoto Protocol on Climate Change	☐	☐	☐
ix.	World Summit on Sustainable Development, Johannesburg, South Africa 2002	☐	☐	☐
x.	The Paris Agreement (United Nation Framework Convention on Climate Change) 2015	☐	☐	☐
xi.	Millennium Development Goals (MDGs) and Sustainable Development Goals (SDGs)	☐	☐	☐

C.2 How would you rate your understanding of Sustainability and Sustainable Remediation application in the Niger Delta *(Please circle a point where 0 is no understanding at all and 10 is very good understanding)*

0 1 2 3 4 5 6 7 8 9 10

C.3 How sustainable do you think the following remediation techniques are?

(Please rate from very poor to very good)

		Very Poor	Poor	Average	Good	Very Good
i.	Excavation and disposal	☐	☐	☐	☐	☐
ii.	Soil washing and Separation processes	☐	☐	☐	☐	☐
iii.	Covering with clean soil	☐	☐	☐	☐	☐
iv.	Chemical oxidation and reduction	☐	☐	☐	☐	☐
v.	Bioremediation	☐	☐	☐	☐	☐
vi.	Phytoremediation	☐	☐	☐	☐	☐
vii.	Soil vapour extraction	☐	☐	☐	☐	☐
viii.	Stabilization/Solidification	☐	☐	☐	☐	☐
ix.	Thermal treatment	☐	☐	☐	☐	☐
x.	Venting	☐	☐	☐	☐	☐
xi.	Vitrification	☐	☐	☐	☐	☐
xii.	Nanoremediation	☐	☐	☐	☐	☐

C.**4** **How important do you personally consider sustainability in remediation of contaminated land?** *(Please rate from 1 (Not important) to 5 (very important))*

Not Important ☐ **1** ☐ **2** ☐ **3** ☐ **4** ☐ **5** ☐ **Very Important**

C.5 **In a scale of 1 to 5, describe your organization's sustainability policies that were applied in remediation of contaminated land that you know.**

Not Applicable ☐ **1** ☐ **2** ☐ **3** ☐ **4** ☐ **5** ☐ **Mostly Applicable**

C.6 What is your understanding of overall Sustainable Remediation process?

_____

_____

_____

_____

C.7 Do you think Sustainable Remediation techniques are feasible in contaminated land clean-up in the Niger Delta?

☐ Yes

☐ No

Why? (Please explain)_____

_____

_____

_____

C.8 What is your opinion on Sustainable Remediation in regards to environmental, social and economic indicators?

_____

_____

_____

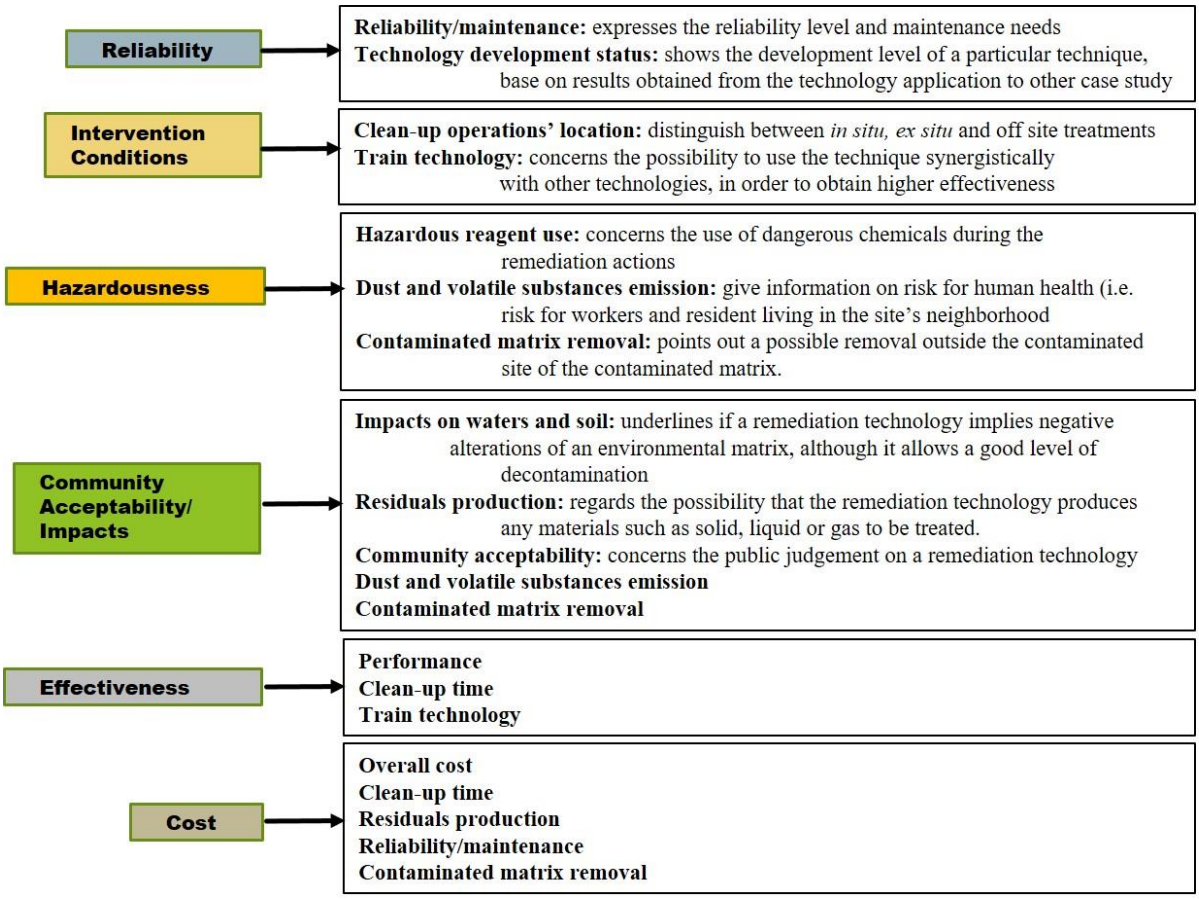
_____

Are you currently employed in the oil & gas industry, regulatory agencies, academic institutions, technology providers & contractors, environmental consultancy firms or other stakeholders with direct or indirect involvement in contaminated land management/remediation?

1. **Yes (If 'yes' Please answer the following question)**
2. **No (If 'no' You have now completed the questionnaire)**

D. Sustainability Measurement of Contaminated Land Remediation Techniques in the Niger Delta.

The figure below gives definition of 6 comparative macro-criteria to be used to compare the pool of selected remediation technologies especially those used in the Niger Delta. Please use these macro-criteria to measure sustainability and its benefit with a view to promote Sustainable Remediation in the region.



Source: [1]Critto *et al.*(2006)

[1] Critto, A., Cantarella, L., Carlon, C., Giove, S., Petruzzelli,jj, G., and Marcomini, A. (2006). Decision Support–Oriented Selection of Remediation Technologies to Rehabilitate Contaminated Sites *Integrated Environmental Assessment and Management* **2**(3): 273–285

D.1 Based on the above macro-criteria, measure the following remediation techniques for its sustainability practices in contaminated land clean-up in the Niger Delta, region. *(Please rate from low to high)*

Macro-criteria Comparison

	Remediation Techniques	Reliability Conditions			Intervention			Hazardousness Exposure			Community Acceptance			Effectiveness			Cost		
		Low	**Medium**	**High**	**Low**	**Medium**	**High**	**Low**	**Medium**	**High**	**Low**	**Medium**	**High**	**Low**	**Medium**	**High**	**Low**	**Medium**	**High**
i.	Excavation and disposal	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
ii.	Soil washing and Separation processes	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
iii.	Covering with clean soil	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
iv.	Chemical oxidation and reduction	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
v.	Bioremediation	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
vi.	Phytoremediation	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
vii.	Soil vapour extraction	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
viii.	Stabilization/Solidification	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
ix.	Thermal treatment	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
x.	Venting	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
xi.	Vitrification	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
xii.	Nanoremediation	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

D.2 From the above remediation techniques, which is the most sustainable remediation option that will be aesthetically pleasing, environmentally friendly and cost effective based on the above macro-criteria comparison?

_____

Thank You!!

Appendix xviii

From: Nicholas Nikeforou
Campus: HENDON
Ext: 6052
Email: N.Nikeforou@mdx.ac.uk

To: Anthony Futughe
Student Number: M00329892
Copies to: Diane Purchase, Huw Jones

Registration for MPhil/PhD

Title of Thesis: 'Advanced Phytormediation using Soil Solarization Enhanced with Biosurfant as a Novel Approach to Sustainable Remediation of Crude Oil Contaminated Land in the Niger Delta, Nigeria'.

I am pleased to inform you that your application to register as a candidate for the degree of MPhil/PhD with Middlesex University has been successful. Please consider the following recommendations made by the panel;

1. Clarify the overall methodology (include diagram of methodology flowchart and 5 treatments diagram).
2. Explain the soil spiking and sampling procedure, ensuring at the outset of the Experiment the homogeneity and contaminant distribution.
3. Ensure proper procedures are in place for importing plants and seeds.

The effective date of registration is: 11/06/15

Ethics approval is required before the research

can start. Kind Regards

N.Nikeforou

Nicholas Nikeforou
Senior Research Degrees Officer
School of Science & Technology
Middlesex University
London
NW4 4BT

Appendix xix

Appendix xx

NIGERIA AGRICULTURAL QUARANTINE SERVICE
PLANT HEALTH

PHYTOSANITARY CERTIFICATE **CERTIFICATE PHYTOSANITAIRE**

REG NO: A5CAF

PSC No: NAQS/FT/2015/000298

TO: NATIONAL PLANT PROTECTION ORGANIZATION OF United Kingdom
A: ORGANISATIONNATIONALE DE LA PROTECTION DES VEGETAUX

DESCRIPTION OF CONSIGNMENT	DESCRIPTION DE L'ENVOI
1. Declared Name and Address of Exporter Nom et Adresse de L'exportateur ANTHONY ESIMAJEMITE FUTUGHE 6 EHIMA LANE OFF AGHO ROAD OFF EKEHUAN ROAD BENIN CITY EDO STATE, NIGERIA	2.Declared Name and Address of Consignee Nom et Adresse du Destinataire ANTHONY ESIMAJEMITE FUTUGHE MIDDLESEX UNIVERSITY THE BOROUGHS HENDON LONDON NW4 4BT
3.Declared Name of Plant products & quantity Nom du vegetaux ou produits vegetaux et quantitie Different amaranthus species seeds and Chromolaena plants samples for research purpose 5KG	4. Botanical name of plant Nom botanique des vegetaux Amaranthus viridis, Amaranthus hybridus, Amaranthus albus and Chromolaena odorata
5.Declared Number and Description of Package Nombre et Nature des colis 4 PACKAGES Amaranthus seeds and Chromolaena plant samples stored on ice	6. Container No:
7.Distinguishing marks/marques des colis AS ADDRESSED	8. Means of conveyance Moyen de transport BY AIR
9. Place of origin / Lieu d' origine PORT HARCOURT, NIGERIA	10. Point of entry (airport,seaport,landborder) Point d'entrée (aèroport, maritime,terrestre) HENDON ,LONDON
11.CERTIFICATION	
11. This is to certify that the plants, plant products or other regulated articles described herein have been inspected and /or tested according to official procedures and are considered to be free from the quarantine pests specified by the importing contracting party, including those for the regulated non-quarantine pests.	11. est certifié que les végéetaux,produits végétaux, ou austres articles reglemnétés décrits et dessus on été inspectes et/ou testés suivant des procedures officielles appropriées et estimés exempts d'organismes de quarantine comme spécifié par la partie contractante importatrice; et qu'ils sont jugés conformes aux exigencies phytosanitaires en vigueur de la partie contractante.
12. ADDITIONAL DECLARATION	DECLARATION ADDITIONELLE
DISINFESTATION AND /OR DISINFECTION TREATMENTS TRAITMENT DE DESINFESTATION ET/OU DESINFECTION 13. Type and date of treatment/Type et date du traitment	18. Name of authorized officer Nom du fonctionnaire autorise M. Adewunmi
14. Chemical (Active Ingredients). Produit chimique (Matiere active)	
15. Concentration / Concentaition Duration and temperature / Deurée et température /	
16. Place of issue/Lieu de déliverance PIA-Portharcourt Date/Date 2015-09-17 01:21PM	19. Signature and stamp/signature et cachet NIGERIA AGRICULTURAL QUARANTINE SERVICE ZONAL COORDINATOR 17 SEP 2015 SOUTH EAST ZONE PORT HARCOURT NAQS
17. Additional information Renseignements complémentaires	

WARNING: Any alterations and/or mutilation will render this certificate invalid.
N'importer quel changement annule la fiabilit'e de cet cet certificate Phytosanitaire