An investigation into the technical feasibility and social acceptance of biochar-based remediation for crude oil polluted soils

by

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Abstract

Crude oil spills have remained a major cause of environmental devastation in Nigeria's Niger-Delta region despite efforts by government and industry professionals to remedy the situation. Over the last decade, carbonaceous sorbent-based technologies such as biochar have been advancing and employed increasingly in developed countries. Biochar remediates contaminants by making them biologically unavailable to receptors and has been proposed as a cost-effective option for organic contaminant remediation. This research therefore aims to evaluate the viability of coconut shell activated biochar as a sustainable technology solution for the remediation of petroleum contaminated soils in Nigeria from a scientific as well as social point of view. This is achieved through empirical comparison of biochar-based remediation with bioremediation, risk assessment and a critical analysis of the factors which influence biochar technology implementation in Nigeria and the USA. This combination of technical and social perspectives seeks to enable a more comprehensive understanding of the factors which influence the implementation of a new remediation technology in Nigeria. Microcosm experiments compared remediation of artificially-polluted biochar-amended soils with soils treated by biostimulation. Biostimulation which involves the use of microbes to degrade contaminants with the aid of added nutrients has been widely used in Nigeria. Laboratory results showed that biochar-amended microcosms had significantly lower volatilization flux (t-test $p < 0.05$) than those without biochar during the period of active volatilization. Relatively high amount of residual oil were observed in biochar-amended microcosms, but passive sampling experiments showed that biochar amended batches had significantly lower available concentrations of oil in the aqueous phase than unamended batches. Partition coefficient (K_d) values derived from the batch study were used as input for risk assessment modelling using the United Kingdom's CLEA (Contaminated Land Exposure Assessment) tool. Risk assessment modeling and experimental results demonstrated the importance of incorporating bioavailability assumptions into risk management decisions. The Mirror Lake restoration project in Delaware, USA was used as a case study for exploring the social acceptance of the new technology by highlighting the factors which impacted on its implementation in the USA and comparatively analysing them with those of relevance in Nigeria. Factors identified include remediation challenges, technical requirements, cost considerations, pollution typology, risk considerations & regulatory concerns. The main obstacles to the implementation of the technology in Nigeria that were identified include lack of enabling legislation, inefficiencies and corruption within the regulatory framework; as well as the prevalence of highly contaminated sites and ongoing contamination.

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Dedication

To God Almighty, for helping me begin and finish this project. I am forever grateful!

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List of Acronyms

ABSd	Dermal Absorption Fraction
AC	Activated Carbon
AF	Skin-soil adherence factor
ALARP	As Low As Reasonably Practicable
ASE	Accelerated Solvent Extraction
ASMB	Alberta Sweet Mix Blend
BC	Biochar
BSAF	Biota to Soil Accumulation Factors
BTEX	Benzene, Toluene, Ethylene and Xylene
CARACAS	Concerted Action on Risk Assessment
CF	Concentration Factor
CGs	Carbonaceous Geosorbents
CLEA	Contaminated Land Exposure Assessment
CLR	Contaminated Land Reports
CNA	Clean Nigeria Associates
DEFRA	Department for Environment, Food and Rural Affairs
DNREC	Delaware Department of Natural Resources and Environmental Control
DPR	Department of Petroleum Resources
DW	Dry Weight
EA	Environment Agency
EFCC	Economic and Financial Crimes Commission
EGASPIN	Environmental Guidelines and Standards in the Petroleum Industry in
EIA	Environmental Impact Assessment
ERA	Environmental Risk Assessment
FEPA	Federal Environmental Protection Agency
FGN	Federal Government of Nigeria
FME	Federal Ministry of Environment
GAC	Granular Activated Carbon
GCMS	Gas Chromatography Mass Spectrometry
HCV	Health Criteria values

HOC	Hydrophobic Organic Compounds
HPCD	Hydroxypropyl-β-cyclodextrin
IAD	Institutional Analysis and Development framework
IMO	International Maritime Organization
IR	Intake Rate
Kaw	Air-water partition coefficient
K_d	Biochar-water Partition coefficient
K_{sw}	Total soil-water partition coefficient
MADEP	Massachusetts Department of Environmental Protection
MNA	Monitored Natural Attenuation
MOC	Multinational Oil Companies
MoE	Margin of Exposure
NAPL	Non-Aqueous Phase Liquid
NDDC	Niger Delta Development Commission
NEEDS	National Economic Empowerment Strategy
NEMA	National Emergency Management Agency
NEPAD	New Partnership for African Development
NESREA	National Environmental Standards and Regulations Enforcement Agency
NIMASA	Nigerian Maritime Administration and Safety Agency
NNOC	Nigerian National Oil Corporation
NNPC	Nigerian National Petroleum Corporation
NOSCP	National Oil Spill Contingency Plan
NOSDRA	National Oil Spill Detection and Response Agency
NPE	National Policy on Environment
NRC	National Research Council,
ONWA	Oil in Navigable Waters Act
OPA	Oil Pollution Act
OPEC	Organisation of Petroleum Exporting Countries
OPRC	Oil Pollution Preparedness, Response and Cooperation
OSRL	Oil Spill Response Limited
PAC	Powdered Activated Carbon

PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated biphenyls
PE	Polyethylene
PEF	Particulate Emission Factor
PIB	Petroleum Industry Bill
PM	Particulate Matter
PPMC	Pipeline Product Marketing Company
PPP	Polluter Pays Principle
PR	Public Relations
PRP	Potentially Responsible Party
PTDF	Petroleum Technology Development Fund
R and D	Research and Development
RDMP	Remediation Decision Making Process
RENA	Remediation by Enhanced Natural Attenuation
SES	Socio-Ecological Systems
SGV	Soil Guideline Values
SPDC	Shell Petroleum Development Company
SVOC	Semi-Volatile Organic Compound
TBT	Tributyltin
TF	Minimum Transport Factor'
TOX	Toxicological
TPH	Total Petroleum Hydrocarbon
UNEP	United Nations Environment Programme
USA	United States of America
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons
WHO	World Health Organization

Chapter 1.   Introduction

1.1   Introduction & outline

This chapter presents the motivation, aim and objectives of this research work. It gives an overview of oil pollution remediation in Nigeria and highlights the rationale for exploring the potential of biochar as a remediation option within the Nigerian context. It also gives an introduction to the laboratory and risk assessment work that were carried out as part of the investigation.

Section 1.2 provides an overview of the problem and proposed technology solution under three major headings; which are key components of this research. First, I discuss oil spill remediation in the Nigerian environment. Second, I look at biochar as an oil spill remediation technology and third, the role of technical risk assessment and social perceptions in oil spill remediation decision-making is analysed. The section also highlights important research gaps within the field.

Section 1.3 presents the research aims and objectives of the research.

In section 1.4, boundaries and limitations of the research are discussed under the heading; 'Thesis Scope and Outline'. The section also includes a diagrammatic illustration of the research strategy to facilitate easy understanding of the interconnections that exist within this inter-disciplinary work.

Section 1.5 gives a summary of the research methodology used throughout the thesis.

1.2   Background

1.2.1   *Oil pollution remediation in Nigeria*

There is large scale oil pollution in Nigeria's oil-rich Niger Delta region. The Niger-Delta which is one of the world's largest Tertiary delta systems is situated on the West African continental margin and occupies an area of about 75,000 km^2 (Oforka, 2012). The physical and social implicatons of the pollution cannot be overstated. There have been numerous attempts to remedy the situation by governments and Nigerian researchers (both locally and in the diaspora), who continue to explore technologies that may be most suitable for remediation of oil spills in Nigeria. One of the core motivations for this particular research work is the fact that existing solutions have not been effective at causing substantial change in the situation. Although technologies like bioremediation for cleaning-up oil spills have been researched and applied extensively and are relatively well understood, bioremediation

techniques do not always guarantee cost-effective remediation of oil spills. Challenges are encountered as a result of insufficient nutrient, limited oxygen availability and poorly biodegradable pollution residuals (Nwogu *et al.*, 2015). In proposing a new and innovative technology for remediating the pollution situation in Nigeria, the author takes care to consider the technology not as an independent variable but as one which is influenced by other, including social factors. This is because acceptance and implementation of a technology is usually based, not just on its technical efficacy, but on additional factors such as risk perception and legislative restrictions.

1.2.2 *Biochar in oil spill remediation; a change in trajectory*

Over the last decade, there has been a gradual shift in the approach to pollution risk assessment that is being employed in developed countries. Carbonaceous sorbent-based technologies such as activated carbon (AC) and biochar (BC) which influence bioavailability of contaminants by immobilizing and sequestering organic contaminants in sediments and soils have been advancing rapidly (Hilber *et al.*, 2009) as efforts have been made to develop them through laboratory and field trials and more recently through full-scale implementations. The USA and a number of countries in Europe such as Norway and the Netherlands have been at the fore-front of these developments. Much greater focus has been given to research on AC for contaminant remediation than BC due to its greater efficacy and because it has been used successfully in water treatment for decades (Patmont *et al.*, 2015). Interest in BC for soil remediation has however increased in recent years (Ahmad *et al.*, 2014; Koltowski *et al.*, 2016) because of the potential soil conditioning properties and other added benefits that biochar gives to amended soil (Beesley *et al.*, 2010). Biochar is generally cheaper and more sustainable than activated carbon, especially if the activated carbon is produced from fossil biomass like coal. One of the objectives of this research is therefore to provide more knowledge that would be useful in progressing biochar from an innovative approach to a more proven one, focusing on activated biochar produced from coconut shells. Apart from its potential use in remediation, biochar has also been identified as a promising amendment for soil enhancement hence the decision to explore its use for soil remediation as opposed to sediment which has historically received greater research attention. Studies involving PAH-contaminated soil amended with biochar demonstrate the potential that biochar holds for land remediation (Beesley *et al.*, 2010; Bushnaf *et al.*, 2011; Meynet *et al.*, 2014).

Between 2004 and 2013, over 25 field-scale or full-scale projects were used to demonstrate the efficacy of using AC for remediation of sediments contaminated by hydrophobic organic compounds (HOCs) in the USA, Norway and the Netherlands. The projects typically involved placing AC directly onto the surface of the sediment or incorporating the AC into a pre-mixed blended cover of clean sand or sediment which was subsequently applied unto the sediment's surface (Patmont *et al.*, 2015). Results from the studies generally demonstrated rapid risk reductions that became more effective over time as long as there was no significant flux from the underlying sediment to the surface. Exceptions were however observed on some of the projects. For instance, AC amendment at Grenlandsfjords, Norway only produced marginal reductions in dioxin and furan flux compared to traditional technologies partially due to relatively slow sediment-to-AC transfer rates (Patmont *et al.*, 2015). This highlights the impact that specific site and sediment characteristics can have on the effectiveness of AC relative to other technologies.

Studies by (Gomez-Eyles *et al.*, 2013) showed that the sorption capacity of biochar for many HOCs is typically less than half that of AC. It is thus still uncertain, if the positive remediation results reported for AC can be replicated for biochar (Hale *et al.*, 2011). Therefore, this study focuses on an activated biochar produced from coconut shells, which combines some of the sustainability advantages of biochars produced from modern instead of fossil biomass with the high HOC sorption capacity of AC (Denyes *et al.*, 2013). Following on from the successful pilot-scale trials, carbonaceous sorbent-based remediation technologies are now being embraced in several countries, but are not without challenges; some of which have nothing to do with the efficacy of the technology itself. People's perception about the approach, nature of relevant legislation and the presence or absence of regulatory frameworks to access the technology are all issues that have been encountered. If such technology is to be considered for implementation in Nigeria, it is important that learnings from implementation in countries like the USA be translated into parameters that are workable within the Nigerian context. In attempting to do this, this research work first seeks to gain a broad understanding of the factors affecting ongoing remediation efforts in Nigeria (see Chapter Six) and how important they are for decision-making. Biostimulation is widely used in Nigeria however, conditions are not always favourable for this. Biostimulation will therefore be used as a benchmark for the discussion of the new technology. We need to find out what is preventing people from making remediation interventions and why more sites are not currently being remediated. Even if oil spillage stopped today, there would still be a great deal of remediation work required in order to restore the environment in the Delta

region of Nigeria. It is therefore expedient to find more effective and less expensive alternatives to existing remediation technologies.

1.2.3 *Risk Assessment & Social Acceptance of Carbonaceous Sorbent-based Remediation Technologies*

The laboratory investigation carried out as part of this research (See Chapter Two) compared remediation of artificially crude oil–polluted, biochar-amended soils with soils treated by biostimulation. The results were used to calibrate input parameters for risk assessment modelling using the United Kingdom's CLEA (Contaminated Land Exposure Assessment) tool (See Chapter Three). Remedial objectives are usually based primarily on reduction of risks to human receptors, ecosystems and property hence the choice of the CLEA model which is also representative of risk assessment models for contaminated land that are used globally. Site-specific assessments are necessary for determining the technical feasibility of a technology for a particular location. Of equal importance is the need to evaluate the level of acceptance and peculiar challenges that may be encountered in attempting to implement a new technology in a specific location. There has been a lot of research interest on remediation technologies in Nigeria but not much focus on exploring the suitability of these technologies based on the unique social and technical conditions in the country. The responsible party generally make decisions about choice of technology, subject to the approval of regulators who tend to be government agencies or functionaries. Factors which affect choice of remediation technology include familiarity of the decision-makers with the concepts underpinning remediation technology, how effective it is anticipated to be in achieving remedial goals/endpoints; legislative requirement, sustainability and cost. The acceptance of biochar-based soil remediation by stakeholders is explored in this work by highlighting the social factors that affected the implementation of the technology in the USA, where the technology originated. It is also explored by comparatively analysing those factors with those obtainable in Nigeria (see Chapter Six), where stakeholders are less familiar with the underpinning concepts but where there are many potential future technology applications.

1.3 Thesis Scope & outline

The research aim which is (in summary) to determine the 'viability' of the technology in a holistic manner may be described as ambitious, however, effort has been made to be as in-depth as possible in every area while staying within the designated boundaries of the work. Throughout the thesis, adequate interconnectivity is maintained among the three different aspects to make sense of the inter-disciplinarity, which is a key element of the research.

From a technical standpoint, the experimental work involved soil even though the USA case study involved application in sediment. However, in order to focus on mechanistic processes within this work, distinctions may not always be drawn between soils and sediments; rather they may be referred to generically as "geochemical matrices" or just "soil and sediments''. Literature evidence shows that remediation of oil-polluted soils is a major challenge in the Niger-Delta of Nigeria. Pipeline leakages, blowouts, sabotage and illegal crude oil refining activities all contribute to the devastation of agricultural lands which are vital for sustenance of members of the local communities (Ekundayo *et al.*, 2001; Ayotamuno and Kogbara, 2007; Asimiea and Omokhua, 2013). Even though a significant proportion of oil spills in Nigeria also occurs in sediment, this study focused on soil because contaminated soils often pose a more direct and immediate exposure risk to human life and the environment. Furthermore, contaminated soil acts as a secondary contamination source to the atmosphere, groundwater, plants, animals, and humans. Also, there are claims that RENA (Remediation by enhanced natural attenuation) which is a very commonly applied method for treating oil-contaminated soil in the Niger-Delta (Ebuehi *et al.*, 2005) is ineffective and hence the technology faces opposition from various quarters (UNEP, 2011). Bioremediation is much slower in sediment than in soil because of limited availability of oxygen (Zhu *et al.*, 2004). It is hence logical to use bioremediation as a relevant benchmark for soil remediation with biochar. The CLEA model is thus employed within this work to assess risks, which may be associated with spills which occur in residential areas or agricultural lands within the Niger Delta. Activated carbon and biochar may also be referred to as geo-sorbents or simply sorbents. Chapters four and five focus on the social components of the research and are aimed at understanding the rules that govern decision-making for the implementation of remediation technologies in Nigeria and identifying critical rules that would influence implementation of sorbent-based remediation technology. This would lead eventually to an integrated analysis taking into account the results from the experimental work in chapter two and risk modelling components analysed in chapter three. Figure 1-1 gives an overview of the structure of the thesis based on the objectives.
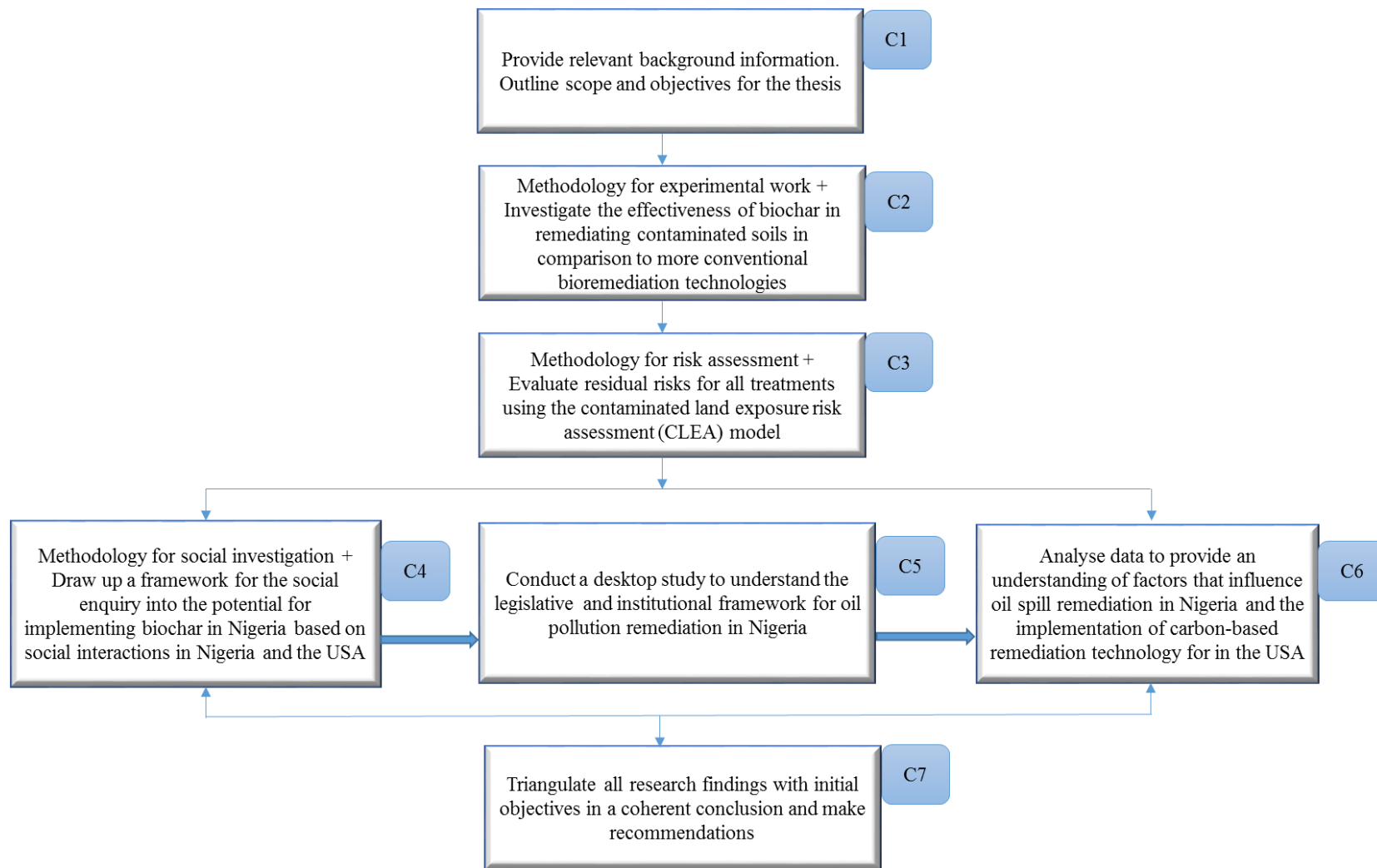
Figure 1-1 Schematic diagram of thesis structure thesis showing objectives, methods and chapters (C1-C7)

1.4 Research Aim and Objectives

The general aim of this work is to evaluate the viability of activated biochar as a sustainable technology solution for the remediation of petroleum contaminated soils in Nigeria from a scientific as well as social point of view. It will involve investigation at the science-policy interface with a view to gaining the interest of stakeholders including government and industry professionals.

The objectives, which will be achieved through further sub-objectives to be discussed within future chapters are outlined below;

1. Investigate the effectiveness of biochar in remediating contaminated soils in comparison to a more conventional bioremediation technology i.e. biostimulation based on laboratory evidence (Chapter 2).

2. Evaluate residual risks for all treatments using the Contaminated Land Exposure Assessment (CLEA) model of the UK Environment Agency (Chapter 3).

3. Draw up a framework for social enquiry into the potential for implementing biochar in Nigeria based on social interactions in Nigeria and the USA (Chapter 4).

4. Conduct a desktop study to understand the legislative and institutional framework for oil pollution remediation in Nigeria (Chapter 5).

5. Analyse data from social interactions to provide an understanding of factors that influence oil spill remediation in Nigeria and the implementation of carbon-based remediation technology in the USA (Chapter 6).

6. Triangulate all research findings with initial objectives in a coherent conclusion and make recommendations based on these (Chapter 7).

1.5 Research data and methodology

The interdisciplinary nature of the research made it pertinent that the tools & approaches for different aspects of the investigation varied greatly in nature. The author therefore adopted a mixed-method approach involving both qualitative and quantitative research methods. Experimental methods for the laboratory analysis, which involved batch experiments in soil microcosms, are contained in chapter two. Methods for determination of volatile, solid phase and bioavailable concentrations of residual compounds are explained in this context.

The basis for the choice of risk assessment modelling framework used; the UK's Contaminated Land Exposure Assessment (CLEA) model is explained in chapter three. The

chapter elucidates on how bioavailability assumptions inherent within the model are assessed, and compares model predictions against data from the experimental work.

Chapter four is dedicated to presenting the strategies for data collection and analysis of the social aspects of the investigation. It explains the pragmatic posture that was chosen for the analysis; sampling for the semi-structured interviews and surveys that were done as well as how the Institutional Analysis and Development framework (IAD) was used for analysing the interview data collected, which is presented in the subsequent chapters.

1.6   Conclusion

This introductory chapter introduced every major aspect of the thesis. It puts the challenge of oil spill remediation in Nigeria in context for the reader. The tone is set for how the thesis explores biochar as a viable technology for oil spill remediation in Nigeria. The aims and objectives outlined herein will be re-stated in the concluding chapter of this work where recommendations for implementation and future work will be made. The following chapter 2 seeks to answer the first objective of this research, which is experimental work to determine the effectiveness of biochar in remediating contaminated soils in comparison to biostimulation as a more conventional in-situ remediation technology.

Chapter 2. Experimental assessment of remediation approaches

2.1 Introduction

The present changing paradigm in pollution remediation approaches towards exploration and adoption of more risk-based options makes it expedient that there is sufficient scientific evidence to support risk assessment decision making. This chapter presents the experimental aspect of this thesis by comparing sorbent-based remediation outcomes in the form of activated biochar with a bioremediation technique (biostimulation).

2.2 Chapter scope and outline

This experimental work focuses on biochar application in soil remediation as opposed to sediments even though more research has been done overall in sediments (Ahmad *et al.*, 2014). This initial focus on sediments in the USA has been driven primarily by growing concerns over historically contaminated sediments throughout the USA in recent years (USEPA, 2005) as well as because of how relatively easy it is to amend sediments with sorbents compared to soil due to their water-saturated nature (Hilber, 2010). This chapter investigates biochar for soil remediation because of the current challenge of oil contaminated land in Nigeria and the resultant pollution risks to humans and to water bodies as well as because of the dearth of knowledge relating to the use of biochar for soil remediation globally. Section 2.3 provides relevant background information on contaminant fate and transport processes including sorption by biochar; contaminants of interest; as well as the principles for extraction and quantification of these contaminants. Afterwards, the hypothesis is outlined in section 2.4 followed by a presentation of the methodology in section 2.5. Section 2.6. is dedicated to discussing the empirical evidence from the experimental work.

2.3 Literature review

2.3.1 Crude oil contamination

The production and consumption of large quantities of crude oil and petroleum products is at the forefront of global environmental concerns today (Fingas and Charles, 2001). Crude oil spills often accompany oil exploration and exploitation. Lubeck (1998) defines crude oil as 'a highly complex combination of hydrocarbons; heterocyclic compounds of nitrogen, oxygen, and sulphur; organometallic compounds; inorganic sediment; and water'. Despite increased research and great advancement in crude oil pollution control and clean-up operations in

recent years, remediation challenges still exist, partially due to the complex nature of crude oil, the high costs of conventional remediation approaches, and the sensitive nature of many ecosystems. Crude oil contaminated soil often poses a risk to groundwater resources as well as air quality as demonstrated by Niger-Delta contamination statistics discussed in chapter five (5.3.2). The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons however this work focuses on the following contaminants, which are generally of concern to human health.

2.3.2 *Contaminants of concern*

Priority contaminants contained within crude oil include alkanes, Volatile organic compounds (VOC) and Polycyclic Aromatic Hydrocarbons (PAHs). Alkanes (C_nH_{2n+2}) are saturated hydrocarbons and major crude oil constituents. Lower molecular weight alkanes (ethane through butane) are gases at standard temperature and pressure while the remainder are water-insoluble liquids. They are more easily volatilized than mid-length alkanes, which are generally non-polar liquids with minimal water solubilities. The greatest hazard from alkanes is flammability (Cheremisinoff, 2002b). Alkanes may be more prone to evaporative losses than are the aromatics because aromatics are 100 times more soluble in water than alkanes of the same carbon number (Hilber, 2010; Turner et al., 2014).

Volatile organic compounds (VOCs) are another important group of compounds to which low molecular weight alkanes contribute. VOCs refer to compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which take part in atmospheric photochemical reactions (USEPA, 2016). VOCs are one of the pollutants typically generated from the refining of crude oil in petroleum refineries (Cheremisinoff, 2002a). In soil, VOCs occur in several phases: gas, aqueous solution, sorbed, and non-aqueous phase liquid (NAPL). Due to the volatility of VOCs, it is easy for them to move across compartments from the soil into the atmosphere or into groundwater (Abbas et al., 2012). Even though VOCs are multiphasic, they do have an affinity for the vapour phase, and VOC quantitation is impacted by the relative mobility of the vapour phase. This multiphasic nature of VOCs has led to debates over the use of soil vapour measurements vs. soil extraction techniques for the quantification of VOCs (USEPA, 1993a; Minnich *et al.*, 1997). VOCs may pose a risk to human health via vapour intrusion from the subsurface into indoor air (McAlary et al., 2014). Many VOCs found in crude oil including benzene, toluene, ethylene and xylene (BTEX) are known human toxicants and

exposure to them has been linked to adverse health effects, including cancer and birth defects (MDE, 2007; Johnson, 2011). Long-term exposure to high concentrations of benzene may cause circulatory, immunological and neurological dysfunctions (USEPA, 2012). Exposure to BTEX can occur by inhalation in addition to the ingestion and absorption routes (MDE, 2007).

Polycyclic Aromatic Hydrocarbons *(*PAHs) are a widespread class of environmental pollutants which have an organic molecular structure with multiple benzene rings (C_6H_6) as the basic units (Cheremisinoff, 2002a). Sixteen (16) of these PAHs (unsubstituted) have been classified as priority contaminants and recommended for monitoring in the framework of the environmental quality control by United States Environmental Protection Agency (USEPA) because of their carcinogenic and mutagenic properties (Gremm and Frimmel, 1994; Soclo et al., 2000; Spasojević et al., 2015). Soil contamination by PAHs is often used as an indicator of the level of environmental pollution by human activities (Placha et al., 2009). This is because PAH patterns usually possess characteristic patterns, which indicate the source from which they are generated. This source is usually the result of pyrolytic (incomplete combustion of organic matter at high temperature), petrogenic (slow maturation of organic matter) or diagenetic (degradation of biogenic precursors) processes (Soclo et al., 2000). PAHs are often grouped based on their properties and molecular masses into two classes; the low molecular-weight PAHs (2- and 3-ring) which have a significant acute toxicity; and the high molecular-weight PAHs, some of which show high carcinogenic and mutagenic potentials (Doong et al., 2000).

2.3.3 *Contaminant fate and transport*

When an oil spill occurs, the fate and transport of the oil in the environment, just like other pollutants, is impacted by physical, chemical and biological processes. Oil spills can occur either on land or on water; in which case, it spreads immediately and would usually migrate to land resulting in soil contamination. Oil can also get into sewer systems and threaten underground water sources. When a spill occurs, the gaseous and liquid components evaporate while some get dissolved in water and (or) get oxidized. Some other components undergo bacterial transformations and eventually sink to the bottom by gravitational action (Akpomuvie, 2010). Oil washed into the soil increases the possibility of groundwater contamination due to migration of the contaminant plume to groundwater. Knowledge of the phase distribution of contaminants is necessary for understanding and predicting their fate in

the environment. The form in which oil exists also impacts on its fate and behaviour in the environment (Bucheli and Gustafsson, 2000). The 'leaving' and 'gaining' of pollutants among compartments are usually controlled by the following specific partitioning relationships; volatilization, organic carbon–water partitioning and sorption (Vallero, 2008). The solubility of a compound in water is an important determinant for how easily that compound would move between compartments such as from soil to groundwater. The more hydrophobic a compound is, the less likely it is to be found in the water column in an environmental study (Vallero, 2006). Solubility is usually expressed by solubility or dissolution coefficients (Vallero, 2006). HOCs tend to sorb mainly to organic matter in soils and bottom sediments (Mackay, 2001). Organic carbon-water partition coefficient (K_{oc}) is used to depict the extent to which an organic chemical is partitioned between the soil and aqueous phases (Letcher, 2007). Other processes involves in the weathering process which includes biodegradation, photo-oxidation, dispersion, dissolution, emulsification and tar-ball formation (Jordan, 1980). The major processes of interest in this work are volatilization, sorption and biodegradation.

Volatilization is the process by which a condensed phase substance such as a liquid or solid is transformed to a more mobile vapour as a result of increase in temperature or decrease in external pressure (Rao, 2000). Evaporation is a very important process for most oil spills and it is often considered the most significant process for the removal of low molecular weight hydrocarbons from the oil (Hamoda et al., 1989). The rate of evaporation is assumed to be a function of key physical parameters; spill area, wind speed, vapour pressure, slick thickness and temperature (Fingas, 1997). The vapour pressure of specific hydrocarbons is inversely proportional to their molecular weight and volatilization generally decreases with increasing number of fused rings (Jordan, 1980; Joa, 2009). Atmospheric fate assessment is important when significant amounts of gaseous or particulate matter are released from a site into the atmosphere. In recent years, the focus of air pollution has been its linkage with harm particularly the ability of the polluted air to cause harm to humans (Vallero, 2008).

The way and rate at which contaminant molecules partition into the solid and liquid phases of a soil or sediment is influenced by the physical, chemical, and biological properties of the contaminant and the matrix (Sijm *et al.*, 2000; Vallero, 2006). The physical and chemical properties of soil are however impacted by the soil's texture and composition. These physical properties and chemical properties include the clay, organic matter, water, oxygen, salt and mineral contents as well as pH (Sijm *et al.*, 2000). The characteristics of the soil for instance,

determines whether the elevated concentrations of the contaminant (above equilibrium levels) are transferred to the soluble, bioavailable or mobile fractions (Beesley and Marmiroli, 2011). The sorption capacity of soil is directly related to its organic matter content (van Leeuwen and Hermens, 2012). The nature of organic matter in soil is also relevant, with black carbon typically binding 10-100 times HOCs more strongly than humic substances (Blume *et al.*, 2015). However, studies by (Gomez-Eyles *et al.*, 2013) showed that the sorption coefficient (K_d) of black carbon in the environment can be about one order of magnitude less than in clean water due to sediment properties such as type and relative content of organic matter as well as mass transfer kinetics. In exploring the potential for applying AC or biochar in contaminated soil remediation, it is important that the soil is able to maintain a high pollutant sorption capacity for a prolonged period irrespective of changes in environmental conditions (Hale *et al.*, 2011).

2.3.4 *Remediation approaches*

Environmental remediation can be defined as the removal of pollution or contaminants from environmental media such as soil, groundwater, sediment, or surface water for the general protection of human health and the environment or from a brownfield site intended for redevelopment (Higgins, 2010). A number of technology options exist to remedy crude oil spills and these can be grouped into three broad categories.

Mass Transfer Technologies

Here, the contaminant mass is removed from the soil matrix by physical or chemical means, and subsequently treated or destroyed in a different process step. This group includes technologies that can be applied either in-situ or ex-situ, such as soil vapour extraction, low temperature thermal desorption and solvent extraction (Elorriaga, 2003).

Transformation /Destruction technologies. These transform the contaminant mass into products of different chemical compositions by various chemical or biochemical means. The purpose is to transform the contaminant into harmless by-products or into a new form that is easier to treat or dispose. Such technologies include bioremediation and thermal destruction (Elorriaga, 2003). Bioremediation is of interest to this work and the two of the most commonly used bioremediation approaches (biostimulation and natural attenuation) are discussed below; *Stabilisation/Fixation technologies.* This involves incorporating the contaminants into a solid matrix so that leaching into the environment is reduced to levels below those required by regulatory agencies. The incorporation of the contaminant into a

monolithic structure can be accomplished by physical or chemical means or by a combination of both. Examples include cement or lime stabilisation, vitrification and other macro or microencapsulation techniques (Elorriaga, 2003). Carbon amendment is one of the remediation technologies within this category, which is currently gaining increased interest and implementation.

2.3.5 *Bioremediation*

Bioremediation is presently a very widely accepted technology for cleaning up oil-polluted sites (Onwurah, 2007). The main principle behind hydrocarbon bioremediation is that microorganisms utilize hydrocarbons as food and energy sources to develop and maintain cell mass (Hinchee *et al.*, 1995). This process commonly referred to as biodegradation, is controlled by the presence and activities of microorganisms; environmental conditions and by the amount of bioavailable contaminant. It is the most significant process by which PAHs are removed from the environment (Spasojević *et al.*, 2015). Hydrocarbons are generally ranked in the following order of decreasing susceptibility to microbial degradation: n-alkanes < branched alkanes < low molecular weight aromatics < cyclic alkanes < high molecular weight aromatics <<<< hopanes and teranes hydrocarbons (Turner *et al.*, 2014). In-situ remediation of contaminated soils such as those involving bioremediation have been embraced in recent years because of their cost-efficiency. However in order for these techniques to be successful, they need to be able to enhance the rate of release of contaminants from the soil-sorbed as well as the non-aqueous phase liquid (NAPL) phases into the aqueous or gaseous phases. This is because contaminants can be more readily bioavailable in these 'environmentally mobile' forms to the degrading bacteria. Contaminant concentrations in these phases usually decline over time, causing a reduction in economic efficiency and overall success of remediation technologies (Beck and Jones, 1995). This suggests that unless contaminant concentrations are able to reach acceptably low levels before contaminants in the free phase start to 'diminish', then alternative technique(s) may need to be employed (Beck and Jones, 1995).

Biostimulation. Biostimulation or enhanced bioremediation, as a bioremediation technique involves enhancing microbial activity by stimulation of the indigenous microbial community thus destroying target compounds at a rate that meets the clean-up objectives at the site (Suthersan, 2002). It involves addition of nutrients, either organic or inorganic, to enhance the activities of native degradative microbial population. This is the most widely used bioremediation strategy for remediation of crude oil contaminated soil. Input of large

quantities of carbon sources, as is usually the case when a crude oil spill occurs, results in rapid depletion of the available pools of major inorganic nutrients, such as N and P (Morgan and Watkinson, 1989; Suthersan, 2002) and biostimulation seeks to establish more optimal C:N:P ratios through nutrient addition. Even though PAHs may undergo volatilization, adsorption, photolysis, and chemical degradation, microbial degradation is the process by which major degradation occurs (Haritash and Kaushik, 2009), with smaller molecular weight PAHs being more readily biodegradable as compared to large molecular weight PAH compounds.

Natural attenuation

Natural attenuation, which can also be termed intrinsic bioremediation, bioattenuation or monitored natural attenuation (MNA), can be defined as ''the use of natural processes to contain the spread of the contamination from chemical spills and reduce the amount of pollutants at contaminated sites''(USEPA, 1999b; USEPA, 2005). A general definition of natural attenuation is the reduction in toxicity, mass and/or mobility of a contaminant without human intervention owing to both physical (e.g. dilution, sorption and precipitation) and biological processes (biodegradation) (Norris and Matthews, 1994). In soils and sediments, a combination of different mechanisms is usually involved in attenuating contaminants. For instance, contaminants which may be released in-situ by natural processes such as desorption or dissolution from NAPL can subsequently by degraded by microorganisms within the same system (USEPA, 1999b).

Natural attenuation is based on the concept of allowing naturally occurring microorganisms to degrade contaminants that have been released into the subsurface while minimizing risks to public health and the environment (Norris and Matthews, 1994). It is important to monitor the performance of a natural bioremediation system by what is sometimes referred to as monitored/intrinsic natural attenuation. This provides an indication of the treatment effectiveness and parameters to be monitored which typically include: individual hydrocarbon components, dissolved oxygen, nitrate, dissolved iron, redox potential, carbon dioxide, pH and total organic carbon (Norris and Matthews, 1994). It is however essential that the right conditions exist in order for sites to be cleaned up properly within acceptable periods. Regular monitoring is therefore essential for evaluating if MNA is working although it may be a challenge as it requires a rigorous understanding of complex processes (ESTCP, 2009; USEPA, 2012). For instance, the rates of contaminant volatilization and biodegradation

are key factors in evaluating the effectiveness of natural attenuation (Chaplin *et al.*, 2002). In addition to its relative slowness in reducing risks in comparison to active remedies, the fact that contaminants are generally left in place without engineered containment could also be a cause for concern to decision makers (USEPA, 2005).

2.3.6 *Biochar in land remediation - A novel approach*

A novel technology for land remediation which has gained interest in recent years is the sorption of organic pollutants by strong sorbents like charcoal. The process by which a chemical species from a gas (or liquid) is collected and concentrated onto or near the surfaces or pores of a solid surface is defined as adsorption (Cheremisinoff, 2002a). This sorption process can be classed as a solidification/stabilisation technology (Noyes, 1991). Adsorption processes or similar processes which involve organic chemicals and soil fractions are usually governed by i) the surface properties of the soil fraction ii) the chemistry of the porewater and iii) the chemical and physical—chemical properties of the pollutants (Mulligan and Yong, 2004). In-depth study of sorption kinetics in soils and sediments began in the late 1980s (Pignatello and Xing, 1996) and a variety of sorption models (Weber *et al.*, 1992; USEPA, 1999a; Jonker and Koelmans, 2002a) currently exist to explain the mechanisms by which Hydrophobic Organic Compounds (HOCs) are sorbed onto carbonaceous geosorbents. According to Ghosh *et al.* (2011), removal of harmful and persistent organic molecules in soils and sediment by physical means can be prohibitively difficult, expensive, and may not ultimately prove effective. An alternative is to locally change the geochemistry to stabilize and sequester the contaminants and make them biologically unavailable. The term bioavailability is often used to represent the accessibility of a chemical compound for biotransformation and toxicity (Spasojević *et al.*, 2015). Interactions between the contaminant and soil surfaces are important in predicting the bioavailability of the contaminant. These interaction mechanisms are in turn influenced by soil fractions, the type and size of the organic molecule as well as the presence of water (Mulligan and Yong, 2004). The sorption of organic contaminants to soils and sediments has been shown to be up to two orders of magnitude higher than expected because of the presence of carbonaceous geosorbents (CGs). CGs refer to carbon-containing matter such as coal and BC, which generally have very high sorption capacity to natural organic matter (Cornelissen *et al.*, 2005; Beesley *et al.*, 2011). Biochar as a material is defined as: "charcoal for application to soils" (Verheijen *et al.*, 2010). Biochar, just like charcoal is produced through an energy conversion process called pyrolysis, which is essentially the heating of biomass in the complete or near

absence of oxygen (Reddy *et al.*, 2011). It can be produced from a variety of local biomass feedstocks, but is generally designated as biochar only if it produces a useable co-product for soil improvement. The physicochemical properties of biochar are governed by the conditions of pyrolysis and the original feedstock (Enders *et al.*, 2012). Coconut shell activated biochar produced at a pyrolysis temperature of 800 °C was chosen for this study because research shows that pyrolysis temperatures greater than 550˚C produce biochars with high surface areas (>400m^2/g) (Gai *et al.*, 2014). Also, the activation process would have further enhanced the porosity of the coconut shell biochar resulting in potentially increased sorption ability. Surface area, pore size distribution and ion-exchange capacity all impact on the efficacy of biochar (Ahmad *et al.*, 2014). The basic difference between activated carbon and biochar is in their method of preparation and source material which ultimately results in products with varied physiochemical properties (Hale *et al.*, 2011). Although both are stable carbon-rich by-products of pyrolysis, the source material for BC is recent plant- and animal-based biomass while AC generally refers to the pyrolysed product of coal or fossil-based feedstock (Ahmad *et al.*, 2014). Some authors however refer to BC as biomass-based AC (McDougall, 1991; Amstaetter *et al.*, 2012). AC is charcoal that has been treated (activated) with oxygen usually to increase microporosity and surface area (Ahmad *et al.*, 2014). Due to the enhanced surface area that is derived from the thermal or chemical treatment (activation) of AC (Ahmad *et al.*, 2014), BC is sometimes subjected to an activation step, resulting in the production of ''activated biochar'' which is essentially AC produced from biomass (Lehmann and Joseph, 2009). In reality, there is no clear distinction between "activated biochar" and AC produced from modern biomass feedstock, if the material is used in the context of soil remediation.

A wide variety of feedstock have been shown to produce biochar with reasonable sorption ability relative to soil (Lehmann and Joseph, 2009). Among these are woody materials, poultry litter, grasses, bones and rice straw (Lehmann and Joseph, 2009; Wong *et al.*, 2016). Rice husk has been shown to possess relatively low porosity attributable to the high amount of silica which it contains (Ahiduzzaman and Sadrul Islam, 2016) even though silica contributes to the long-term stability of biochar *(Wong et al., 2016).* Affordability and availability of feedstock are usually key motivators in deciding whether biochar would be a suitable option for remediation.

Owing to its inherent properties (Lopez-Capel *et al.*, 2016), scientific consensus exists that biochar application to soil at a specific site is expected to sustainably sequester atmospheric

carbon fixed in the biochar and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health. Other applications for biochar include removal of water and air pollutants, carbon sequestration and improvement of soil quality and fertility'' (Bell and Worrall, 2011). The application of biochar for land remediation is of interest in this particular research. Biochar is proposed to reduce environmental risk by preventing the migration of pollutant molecules in a process referred to as stabilisation (Hale *et al.*, 2009). One might ask 'why bother with biochar?' There is a gap in knowledge concerning how to deal with residual contamination in-situ when bioremediation is used. According to (Hale *et al.*, 2009), ''bioremediation is a low cost solution which causes minimal environmental disturbance, but the recalcitrant nature of PAHs and suboptimal onsite conditions may limit its success''. One of the socio-economic implications of biochar is that it could be produced locally within the community and hence be potentially more acceptable to the community thereby making implementation easier. Economic and business considerations are arguably the primary driving force in the development and use of new and innovative bioremediation techniques (Ronneau and Bitchaeva, 1997). According to Yu *et al.* (2010), biochar amendment of soils can affect the fate of organic contaminants in the soil environment and their potential risks to human and ecosystem health. Their results showed that biochar produced from incomplete combustion of red gum woodchip could enhance the sorption of pesticide pyrimethanil when incorporated into soil. They stated that marked effects of biochar on the sorption capacity and desorption irreversibility is expected to have strong influences on the bioavailability of organic contaminants in terrestrial and aquatic ecosystems. Also, studies by (Chai *et al.*, 2012) showed that soil amendment with biochar and activated carbon reduced the availability of aged polychlorinated dibenzo-p-dioxin/dibenzofurans (PCDD/Fs) in two soils. Other studies by Zheng *et al.* (2010) evaluated the ability of an unmodified biochar to sorb two triazine pesticides – atrazine and simazine, and thereby explored potential environmental values of biochar on mitigating pesticide pollution in agricultural production and removing contaminants from wastewater. The study suggested that biochar may effectively remove pesticide residues from aquatic environment and thus mitigate pesticide pollution by sorption. Additional benefits and motivation for the use of biochar include its relative cost-effectiveness compared to off site remediation as well as its minimal intrusion of ecosystems and reduced likelihood of producing new amounts of pollutants as may take place while dredging or digging (Hilber, 2010). Biochar does have its

own limitations such as concerns about its stability and possible contamination (Shackley and Sohi, 2010) which are addressed in a bit more detail in chapter six. Activated carbon has been used widely for treatment of drinking water for almost three decades as well as more recently in soil and sediment management. Some types of activated carbon such as those produced from coconut shells or wood can also be classified as an activated biochar. Activation is more expensive as compared to unactivated biochar, which is produced from pyrolysis of organic matter such as wood, crop debris, sewage sludge, manure, and yard trimmings without the addition of chemicals such as acids and bases or the injection of steam at the end of pyrolysis. Research interest into the production of low-cost alternatives to activated carbons has therefore grown (Boudrahem *et al.*, 2009). For soil remediation applications, it is important to balance the enhanced sorbent properties of activated charcoal as compared to unactivated biochar, versus the increased costs. Another important phenomenon that is often considered when investigating sorption of organic contaminants to CG is ageing. The ageing process has been observed in various studies where HOCs are biodegraded only up to a certain residual concentration after which reduction in concentration slows down greatly or stops completely (Luthy *et al.*, 1997). The observed change in microbial activity is often attributed to limited availability of HOCs to the microorganisms (Geng *et al.*, 2001) and is usually referred to as bioavailability. The bioavailable portion of contaminants is often evaluated using biomimetic devices. There has recently been increased advocacy for the use of freely dissolved concentrations instead of total concentrations for determination of bioremediation endpoints and acceptable risk levels in sediment or soil (Cornelissen *et al.*, 2005). The partitioning coefficient (K_d) which is also referred to as 'distribution coefficient' is an important parameter for estimating the migration potential of contaminants present in aqueous solutions which are in contact with surface, subsurface and suspended solids, or, consequently, contaminant leaching risks from soil. It is defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of solid to the quantity of the adsorbate remaining in solution at equilibrium and is usually obtained from laboratory experiments (USEPA, 1999a).

2.3.7 *Measuring contaminant concentrations; total versus bioavailable concentrations*

Due to the potentially carcinogenic nature of some PAHs, total petroleum hydrocarbon (TPH) concentrations and PAH levels are often used as indicators of potential oil contamination at oil spill sites (Kim *et al.*, 2012). These total concentrations are usually determined by chemical methods, which typically include vigorous extractions (normally called total or exhaustive), performed by hot solvent ultrasonic or accelerated solvent extraction. These

procedures do not, however, take cognisance of the bioavailable fraction of contaminants and are thus widely considered as being over-predictive of availability to organisms by a factor that can reach 10 – 10,000 times (Cui *et al.*, 2013). Analytical methods that are more relevant have thus been developed in response. These non-exhaustive extractions and biomimetic methods not only measure different components of the matrix, but are based on the fact that the contaminants exposure to soils organisms occurs mainly through the aqueous phase (Kelsey *et al.*, 1997; Gomez-Eyles *et al.*, 2011; Cui *et al.*, 2013). Uptake of contaminants is often conceptualized as a two-step process where contaminants desorb from the solid matrix into the aqueous phase or gut fluid and are subsequently taken up into the tissue (McLeod *et al.*, 2007). The degree to which biomimetic devices or passive samplers then absorb the contaminants indicates the availability of the contaminant for mass transfer and uptake and hence its susceptibility to biodegradation, but also availability to cause toxic effects. Several studies have reported the use of passive samplers such as polyethylene (PE) devices in measuring the availability of organic contaminants in soils (Adams *et al.*, 2007; Chai *et al.*, 2011) demonstrating that biological uptake of contaminants is dependent on contaminant pore-water concentrations. Work by (Millward *et al.*, 2005) demonstrated the effect of coke and activated carbon on PCB bioavailability in contaminated sediment at Hunters point, San Francisco bay. They discovered that ''reductions in aqueous PCB concentrations in equilibrium with the sediment were similar to reductions in PCB bioaccumulation''. Also, studies by (Bucheli and Gustafsson, 2000) and (Socha and Carpenter, 1987) show that soot, which is representative of black carbon, is able to reduce the aqueous availability of PAHs.

2.4   Hypothesis

1. It is anticipated that volatilization of the volatile petroleum hydrocarbon would be reduced by the addition of biochar to crude oil contaminated soil (because biochar binds petroleum hydrocarbons, reducing their concentration in soil air).

2. Higher crude oil residuals concentrations are expected with biochar amendment due to inhibition of biodegradation (because biochar binds petroleum hydrocarbons, reducing their biodegradation).

3. Bioavailable concentrations of crude oil in soil are expected to be significantly less upon biochar amendment (because biochar binds petroleum hydrocarbon, reducing their availability for biouptake).

2.5   Methodology

Laboratory-scale remediation trials using sacrificial batches with 20g of moist soil were carried out comparing biostimulation (addition of nutrients, pH and water content optimization) with biochar amendment. Soil pollutant concentrations and the solid-water partitioning of these pollutants were determined at the end of the experiments by accelerated solvent extraction of solid and aqueous samples and clean-up by silica gel fractioning and analysis by gas chromatography – mass spectrometry. Conditions were simulated to suit tropical temperature.

2.5.1   *Soil*

Surface soil samples were obtained from the Exhibition Park in Newcastle for the experiment, as this soil was readily available. Exhibition Park is a typical urban soil and many oil spills occur in an urban environment. It was anticipated that the soil would be relatively clean as it was used for landscaping as part of the development of children's playground. It was also assumed to be fertile soil with good microbial activity due to its use to support the establishment of plants. The soil was stored in a cold room at about 5˚C for one week. The organic carbon (2.33%) and inorganic carbon (1.01%) contents were determined using a LECO carbon analyzer (LECO, 1996). Soil pH was 7.88, elemental nitrogen content 0.132% and sulphur content 0.05%. The soil was sieved to remove gravel stones resulting in a sandy soil. Soil properties such as pH, Total Kjeldahl Nitrogen, and water–holding capacity were determined prior to the experiments according to ASTM methods and these measurements will be reported later. Samples were stored in a cool and dry place.

2.5.2   *Nutrient addition*

17.25g of NH_4Cl and 2g of KH_2PO_4 was weighed using an analytical balance and dissolved in 250ml distilled water to produce a nutrient solution, which contained 0.069g/ml, NH_4Cl and 0.008g/ml KH_2PO_4. Nutrient solutions were prepared by adding sterile water to measured salts and autoclaved twice at 121˚C for 15 minutes, with a 24 hours interval at 37 ˚C to allow any spores to grow before the second autoclaving and ensure that microorganisms in the microcosms came from the soil and not nutrients. 1ml of nutrient solution was added to all batches. Nutrients are the basic building blocks of life and nutrient addition has been demonstrated to counteract nutrient limitation in crude-oil polluted soils, stimulating microbial growth and synthesis of enzymes needed necessary for break-down of petroleum hydrocarbons (Nwogu *et al.*, 2015).

2.5.3 *Biochar addition*

Activated biochar (Norit coconut shell activated carbon; mesh size: $< 212\mu L$) produced by fast pyrolysis at high temperature (800°C) was obtained and used for the experiments. This biochar was chosen because of the conditions of its productions which typically yield desirable properties including relatively high recalcitrance in the environment (Gomez-Eyles *et al.*, 2013) and larger surface area (Park *et al.*, 2013). It was also chosen because it is easy to source (readily available in large quantities with well-defined properties). The surface area of the activated biochar was $975m^2/g$, open surface area was $40m^2/g$, pore volume was $0.47cm^3/g$, micro-pore volume was $0.43cm^3/g$ and pore size was 37.1 Å. (Han *et al.*, 2015). The biochar was also stored in a cool and dry environment until use. 1g (5% w/w) of the activated biochar was added to each microcosm. This is a typical concentration for activated carbon amendment (Hilber, 2010).

2.5.4 *Crude oil and Tracer*

North Sea crude oil originally supplied by BP plc was obtained from Dr Martin Jones at Newcastle University. Saturated and aromatic hydrocarbon standards were obtained from Sigma Aldrich. In order to determine the density of crude oil, an empty 5ml volumetric flask was weighed with the lid after which 5ml of the crude oil sample was poured into it using a weighing balance. The difference in weight was obtained and this weight divided by 5ml to obtain the density (specific gravity) of the crude oil sample (0.82g/ml). The API gravity of the crude oil was 39°. 0.5ml (2% w/w) crude oil was added to each batch using volumetric pipettes ensuring that batch contents were stirred with different spatulas to avoid cross-contamination. This oil contamination level exceeds about fourfold the permissible limit i.e. EGASPIN intervention value in soil of (0.5% w/w) based on Nigerian legislation. Thus it is within the range of the actual crude oil contamination level in soils requiring remediation at various sites in the Niger Delta where levels range from 0 - 10% w/w (UNEP, 2011; Nwankwo, 2014). It is also within a concentration where biodegradation is expected to occur, i.e. below crude oil toxicity levels (Bossert and Bartha, 1984).

2.5.5 *Batch experiments design/ set-up*

Batch experiments were carried out according to the methods described in 2.5.5 at room temperature for 7 months in 60ml amber glass vials stoppered with 24mm polyurethane foam plugs (PUFP) (VWR International Ltd, Leicestershire, UK). The PUFP were cleaned before use by placing them in a beaker and soaking in hexane (Sigma Aldrich, Dorset, UK) for 48hrs

and repeating the process to ensure removal of any possible contaminants, before air-drying in the fume cupboard. PUFP were used as traps to monitor VOC volatilisation from the batches, whilst allowing oxygen to diffuse through the foam into the batches.
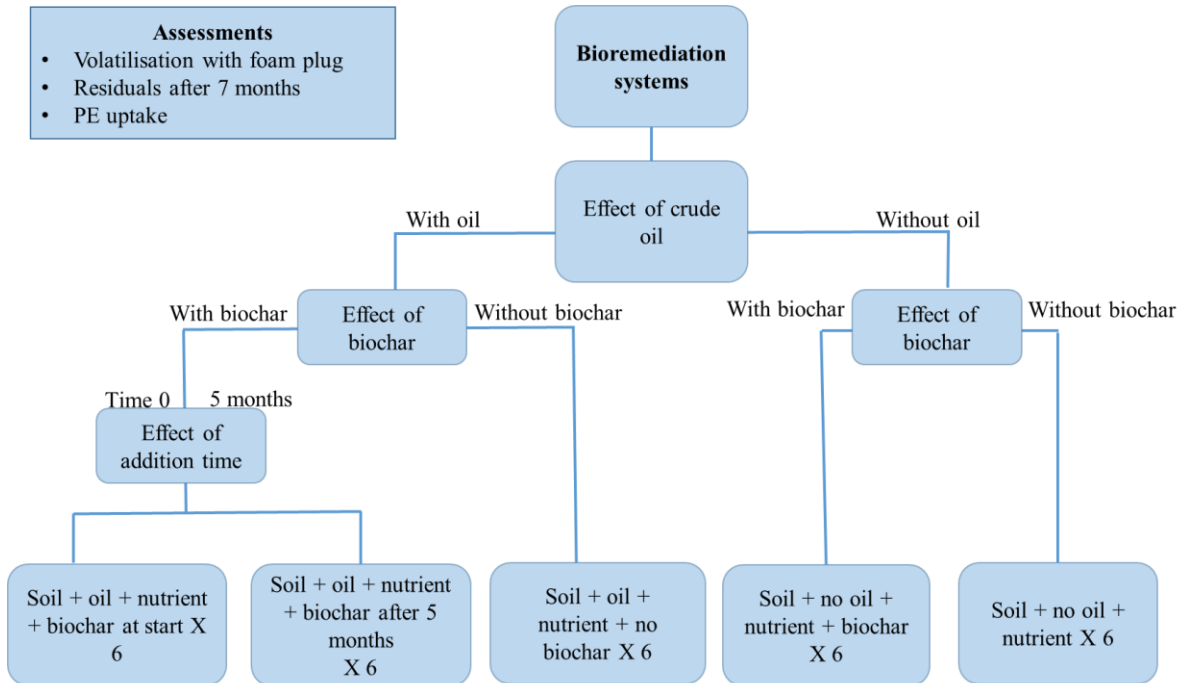
Figure 2-1 Schematic representation of sorption and biostimulation experiment

The experiment had five sets of batches (Figure 2-1). Three sets had crude oil added; to one of these, the sorbent (biochar) was added from the beginning, a second set of oil amended batches had biochar added after 5 months and a third set were not amended with biochar. The second set of oil-amended batches were amended with biochar after 5 months to study the impact of biochar addition time on sorption. It was anticipated that this would be sufficient time for significant biodegradation to occur based on typical crude oil remediation timescales, hence simulating the stabilization of poorly biodegradable crude oil residuals (Council *et al.*, 2003; Lens *et al.*, 2005). The experiment also had two sets of controls with no oil added, one with biochar addition and another without. Each treatment consisted of six replicated batches. There was no sterile control in this work as a previous trial (Ugim, 2012) had recorded a high number of cells in abiotic systems indicating regrowth even after repeated sterilization of the batches in the autoclave. The key parameters of the experimental design were the oil addition versus controls, biochar addition and biochar addition time.

Controls with and without biochar addition, but without crude oil addition, were set up to investigate pollutants, which were already present in the soil in order to see the effect of background native pollution such as PAHs in urban soil.

Microbial activity was not measured in this work however, it can be easily determined by monitoring properties such as respiration, mineralizable nitrogen and PLFA (phospholipid fatty acid) activity. For instance, batch studies carried out by (Bushnaf *et al.*, 2011) involved studying the impacts of biochar amendments on the production of biogenic gases. The experiment was set up within one week of the soil being collected to prevent the microbial activity from changing.

2.5.6 *Determination of solid phase concentration of pollutants*

Extraction of organic contaminants

Organic contaminants (alkane and PAH) were extracted from the soil after 7 months according to a modified USEPA extraction method 3540C with hexane-acetone (50:50) using accelerated solvent extraction (ASE). This was done at the end of the whole experiment and involved solid phase extraction of the contaminant. ASE is a new technique for extraction of several organic micropollutants including PAH. It is fast and easy to perform and involves minimal use of solvents and labour (Olivella, 2006). Studies by (Sun *et al.*, 2012) and (Lau *et al.*, 2010) showed that the removal efficiency of ASE is affected by temperature, pressure, solvent, matrix composition and mode of operation. A study by (Fisher *et al.*, 1997) showed that for PAH-contaminated soils, ASE recoveries were greater or equal to bath sonication/shaking giving approximately double the total PAH content for matrices which contained small stones and/or coal. The study showed that ASE recoveries would likely be increased with respect to Soxhlet extraction if 1:1 hexane/acetone had been used instead of the general screening solvent. Triplicates of each of the five treatments in the batch experiment were used for this phase of the experiment. The remaining 15 sacrificial microcosms were used for determination of the aqueous phase concentration.

Silica gel clean-up

ASE extract clean-up was done to recover only the required organic substances from the sample. It was carried out with silica gel (Sigma Aldrich, Dorset, UK) using USEPA method 3630C. The protocol used enabled the fractionation of the crude oil into aliphatic and

aromatic fractions. Alkane fractions were obtained using hexane for the elution while aromatic fractions were eluted using hexane-DCM (60:40).

2.5.7 *Determination of oil volatilization*

Extraction of polyurethane foam plugs (PUFP)

PUFP were replaced and extracted every two to three weeks over a 91 day period to determine hydrocarbon losses to the headspace. The VOC calibration standard used was 100 ug/ml. Each pre-cleaned foam plug was placed in a 40 ml glass vial along with approximately 30ml of hexane as the extraction solvent. A predetermined volume of squalane was added to the sample as surrogate spike. The vials were placed on a horizontal shaker (Bellco Biotechnology, NJ) for extraction, overnight. The extraction solvent was removed from the vial with a glass pipette and replaced with fresh solvent. The extraction process was repeated for a total of two times. The extracted hexane was pooled, concentrated by evaporation with nitrogen, and cleaned using silica gel as described above before GC-MS analysis (Baker, 2011).

2.5.8 *Determination of aqueous phase concentrations*

The aqueous phase concentrations of the pollutant was measured after 7 months for the second set of 15 sacrificial microcosms. PE passive samplers were used to determine free aqueous concentrations of alkanes and PAHs. Polyethylene Devices (PEDs) were custom-made from low-density Polyethylene (PE) sheets obtained as plastic bags (VWR International Ltd, Leicestershire, UK) by cutting them into 20 rectangles of approximately 0.15 ± 0.01g. Each PE sheet was pre-cleaned by placing it in a beaker and adding Hexane-Acetone (80:20) until the PE was covered. The beaker was covered with aluminum foil and placed in the fume cupboard overnight. The Hexane-Acetone (80:20) was drained off and the cleaned PE sheets were placed in each of the 15 sacrificial microcosms. 1ml of 10% sodium azide (NaN_3) solution (VWR International Ltd, Leicestershire, UK) was added to 50ml distilled water in each batch to make a 0.2g/L solution which was subsequently added to each of the 15 sacrificial microcosms containing soil and relevant nutrient or biochar amendment as appropriate. NaN_3 was used to act as a biocide to inhibit microbiological growth (Adams *et al.*, 2007). The microcosms were shaken by hand and subsequently tumbled at 20 rpm continuously in a shaker for 14 days at room temperature to allow adsorption equilibrium to be achieved which usually requires weeks to many months in the absence of mixing (Uchimiya *et al.*, 2012; Holm *et al.*, 2014). The PE sheets were removed from each of the 15

microcosms using a tweezer. The sheets were then rinsed with water, patted dry and then extracted with Hexane-Acetone (80:20). Internal standard was spiked to the cleaned extract at the beginning of extraction to monitor recovery during processing. 25uL of squalene to the alkane fractions and 25uL of D-phenanthrene to the aromatic fractions. Extracts were combined, concentrated and cleaned up as described in section 2.5.6. Samples were transferred into blowdown vials and blowdown to 1ml and transferred into GC vials. Aliquots of the dialysate were analysed for alkanes and PAHs.

Derivation of aqueous phase concentration from PE concentration

Free aqueous concentrations, S_w (g/cm^3) were calculated from PE concentrations using K_{pe} values according to the equation below. K_{pe} values are compound-specific PE-water partitioning coefficients which were obtained from literature (Adams *et al.*, 2007).

$$K_{PE-water} = \frac{S_{PE}}{S_w}$$

Where $K_{PE-water}$ (g/cm^3 PE)(g/cm^3 water)$^{-1}$ is the dimensionless PE-water partitioning coefficient and S_{PE} is the volumetric PE sampler concentration.

Aqueous concentrations were calculated for the PAHs as K_{pe} values were readily available for them. Alkanes are either non-polar or very weakly polar therefore aqueous solubility data does exist for the shorter chained alkanes however for the heavier ones from about C_{12} upwards, what is available is mainly experimental data for individual compounds or values predicted by modelling (Yalkowsky, 2003; Tinsley, 2004). An attempt was made to derive alkane K_{pe} values from their aqueous solubility values however the values found in literature were widely inconsistent differing by several orders of magnitude and it was therefore believed that they would be unreliable (van Oss, 2006). Consequently, free aqueous concentrations of alkanes could not be derived from the PE concentrations.

2.5.9 *Determination of solid-water partitioning coefficient (K_d)*

The affinity of a HOC for soil is symbolized by the solid-water partition coefficient, K_d (Vance, 1993). This coefficient gives for instance an indication of the tendency of the pollutant to leach into groundwater. The value of K_d is expressed by the following relationship:

$$K_d = \frac{S_S}{S_w}$$

Where K_d = The soil-water partitioning coefficient (L/kg)

S_S = The solid phase concentration of the pollutant (mg/kg)

S_w = The aqueous phase concentration of the pollutant (mg/L)

In order to determine the solid-water partitioning, the solid and PE-derived aqueous phase concentrations obtained from the experiment were used in the above equation. K_d is an important parameter for risk assessment and was fed into the CLEA model in chapter three.

2.5.10 *Analysis/Monitoring of Hydrocarbons*

Chromatographic analysis of the concentrated samples from the clean-up steps were carried out using the GCMS to determine the concentration of the different compounds in the mixtures from the foam plug experiment, ASE extraction and passive sampling experiment. This was performed on a Hewlett-Packard 6890 GC fitted with a split/splitless injector (280°C) linked to a Hewlett-Packard 5973MSD. The contaminants were monitored using the gas chromatography running conditions as defined below. GC-FID analysis was also used for extraction from the foam plug experiment prior to analysis on the GCMS.

Gas chromatography mass spectrometry (GCMS) running conditions

GCMS was carried out on a Hewlett-Packard 7890A GC fit with a split/split less injector (temperature: 280^{0}C), connected to a Hewlett-Packard 5975inertXLMSD. To enhance the sensitivity, data acquisition was in full scan and SIM (selected ion mode) (50-550 amu/sec or 30 ions 0.7cps 35ms dwell). The program was set and the compounds were separated by a built in fused silica capillary column (30m x 0.25 mm i.d) with a 0.25µm film thickness HP-5 phase coating (Agilent LTD, Wokingham, Berkshire, UK). The GC oven temperature was set at 50^{0}C-300^{0}C/min and held at 300^{0}C for 20 minutes with helium as the carrier gas. 1 µL of the sample was injected by a HP7683 automatic sampler in a split/pulse mode with an initial pressure of 150 kpa held for 1 minute, split less and thereafter the pressure was 50kpa with a split flow rate of 30ml/min. The acquired data was then stored on DVD for any further data processing, integration and printing.

GC-FID running conditions

GC-FID was also be used for analysis of aliphatic and/or aromatic compounds to reduce cost instead of using the GC-MS for all samples. This was performed on a Hewlett-Packard 7890 GC in split less mode, the injector at 280°C, FID at 310°C. The acquisition was stored on an

Atlas laboratory data system. The sample (20ul headspace) was injected manually with the split constantly open. After the solvent peak had passed the GC temperature programme and data acquisition commenced. Separation was performed on a fused silica capillary column (30m x 0.25mm i.d) coated with 0.25um dimethyl poly-siloxane (HP-5 phase). The GC was temperature programmed from 30°C-120°C at 10°C/min and held at final temperature for 6 minutes with Helium as the carrier gas (flow 1ml/min, pressure of 50kPa, split at 30 mls/min). The acquired data was stored on DVD for later data processing, integration and printing.

2.5.11 *Data analysis and Risk assessment*

Data was statistically analysed using Microsoft excel and differences were reported using t-tests ($p < 0.05$). Reported error ranges represented the experimental standard deviations.

2.6 Results and discussions

2.6.1 *Alkane profile of the oil*

Figure 2-2 below shows the distribution pattern of the normal alkanes (ranging from C_{10} – C_{28}) in the North Sea Crude oil used for this study.
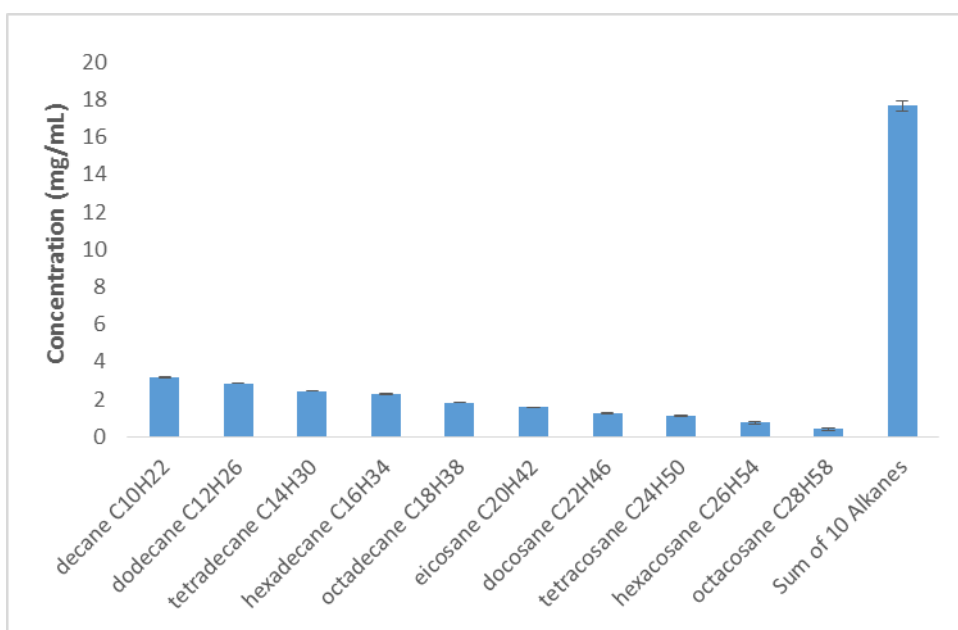
Figure 2-2 The distribution of alkanes in the North sea crude oil. Error bars represent one standard deviation from the mean of duplicate crude oil extractions

Alkane values ranged from 0.4 ± 0.04 mg/ml to 3.16 ± 0.04 mg/ml crude oil and the total concentration of n-alkanes was determined to be 17.67 mg/ml. This range is as expected, as

alkanes contribute significantly to the crude oil make-up, although the composition and relative abundance of crude oil constituents do tend to vary significantly depending on the source (NIOSH, 2010). A progressive decrease in abundance of alkane analytes was observed with increase in carbon numbers as is generally the case for most crude oils (Hester *et al.*, 2008). A similar trend was noticed in a crude oil quantitation analysis carried out by Wang *et al.* (1994) on a light crude Alberta Sweet Mix Blend (ASMB) where a gradual decrease in abundance of n-alkanes was observed as the carbon numbers increased. The study by Wang *et al.* (1994) also showed the most abundant n-alkanes to be around n-C_8 to n-C_{17}.

Figure 2-3 shows the source of the alkanes in the batches as determined by mass balance calculations (See section 2.8). It compares the amount of oil that was estimated to have been in the soil microcosm initially by considering the amount of oil that was added and the oil's alkane content. The native alkane concentrations in the soil was very low (non-detectable) compared to the high alkane concentration from the added crude oil.
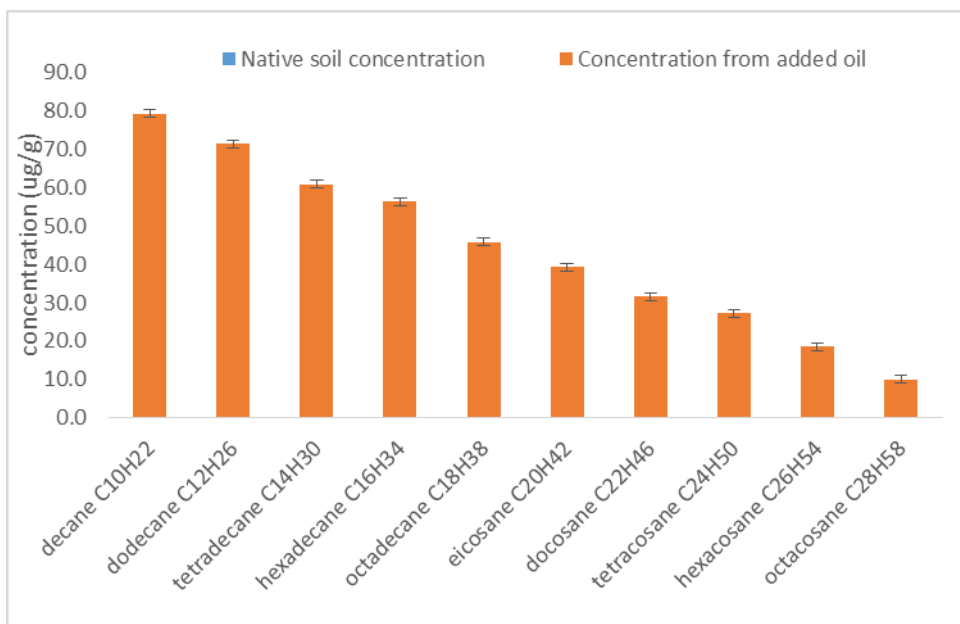
Figure 2-3 Source profile of the alkanes as determined by mass balance calculations.

2.6.2   *PAH profile of the oil*

Figure 2-4 below shows the PAH profile of the crude oil. It is dominated by 2-ringed and 3-ring compounds with naphthalene having the highest concentration (1.53 ± 0.04mg/ml) followed by phenanthrene and fluorene. These three compounds make up 89% of the total PAH mass in the crude oil. The PAH profile is comparable to the ASMB study carried out by

Wang *et al.* (1994), although the dominant aromatic hydrocarbons were alkyl homologues of benzene, naphthalene and phenanthrene, which were not quantified in this study, which focused on the 16 USEPA PAHs. Naphthalene, which is the main USEPA PAH compound in crude oil is examined independently in section 2.7 of this chapter.
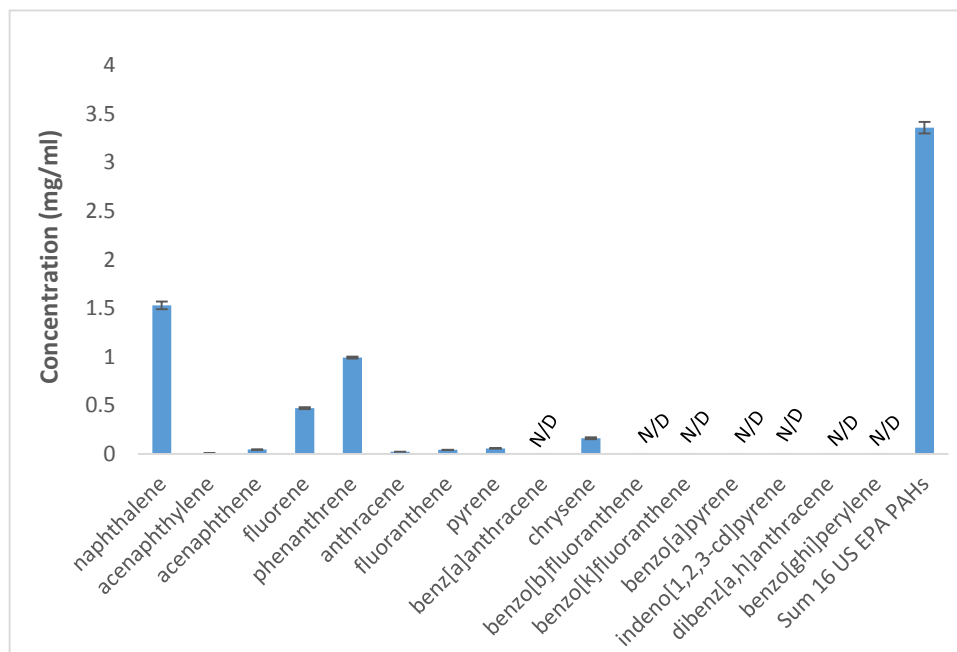
Figure 2-4 the distribution profile of the 16 EPA PAHs in the North Sea crude oil. Error bars represent one standard deviation from the mean of duplicate extractions

Ratio values such as fluoranthene/pyrene (Flu/Pyr) and phenanthrene/anthracene (Phe/Ant) have been widely used as characteristic tools in order to determine the dominant source of PAHs in samples. Pyrogenic processes usually release PAHs with Phe/Ant ratios <10, while (petrogenic process) leads to Phe/Ant ratios >10. Pyrogenic processes involve high temperature combustion while petrogenic processes usually involve the slow maturation of the organic material (Benlahcen *et al.*, 1997; Budzinski *et al.*, 1997). The relatively high Phe/Ant ratio of 47.1 of this crude oil is similar to a Phe/Ant ratio of 50 observed by (Yang *et al.*, 1991) in crude oil. Seven out of the sixteen USEPA PAHs analysed were non-detectable including benzo-a-pyrene. Figure 2-5 shows the source profile of the PAHs in the batch study as determined by mass balance calculations. The higher molecular weight PAHs (from phenanthrene onwards) have their source primarily from the soil, which was sampled in Exhibition Park in the Newcastle city centre, and are likely of pyrogenic origin (domestic and industrial coal combustion in the 20th century).
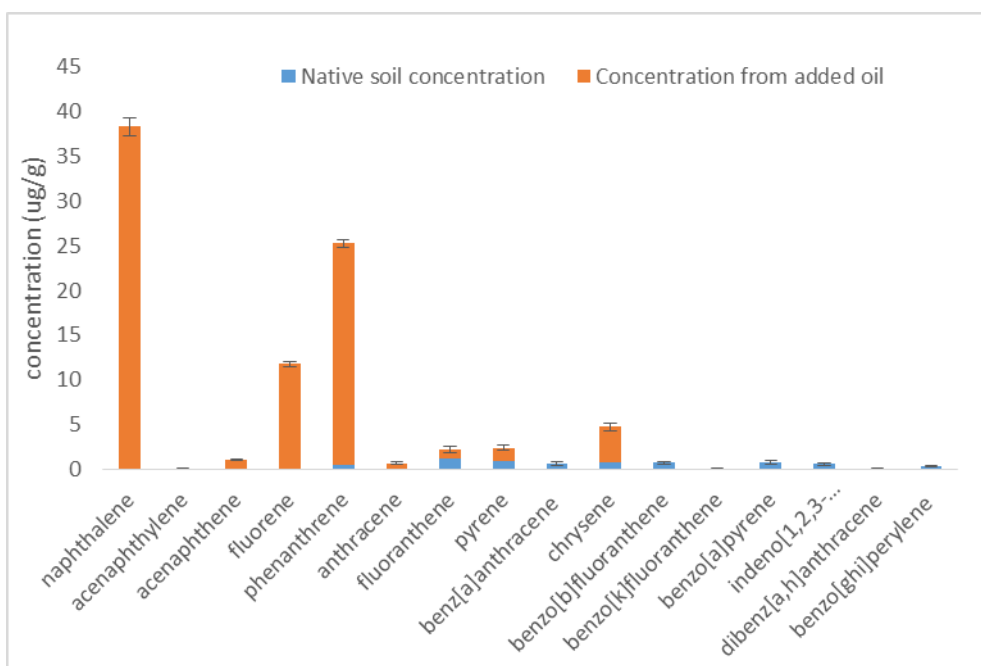
Figure 2-5 source profile of the PAHs as determined by mass balance calculations.

2.6.3 *Volatilization of aromatic hydrocarbons*

Due to their rapid evaporation, focus was placed on the identification and quantitation of eight exemplary aromatic hydrocarbons to illustrate remediation treatment effects on the volatilisation flux of VOCs. Extracts from the PUFP gave an indication of the amount of oil volatilized from the soil in each batch. GCMS analysis of the PUFP extracts identified and quantified eight aromatic hydrocarbons (toluene, ethylbenzene, m-xylene, 1,3,5-TMB, 1,2,4-TMB, P-isopropyltoluene, n-butylbenzene and naphthalene), for which quantification standards were available. Benzene was included in the standard, however, it was eluted along with the extraction solvent (hexane) hence it could not be quantified from the GC-MS chromatogram. Figure 2-6 below shows the total volatilization flux of the eight measured compounds over 91 days. Error bars represent one standard deviation of the mean of triplicate extractions. The 'oil + biochar after 5 months' batches are identical to the 'oil only' batches at this point because the biochar amendment was added after more than 91 days (after 5 months). Hence measurements are nearly identical for the 'oil + biochar after 5 months' and 'oil only' batches.
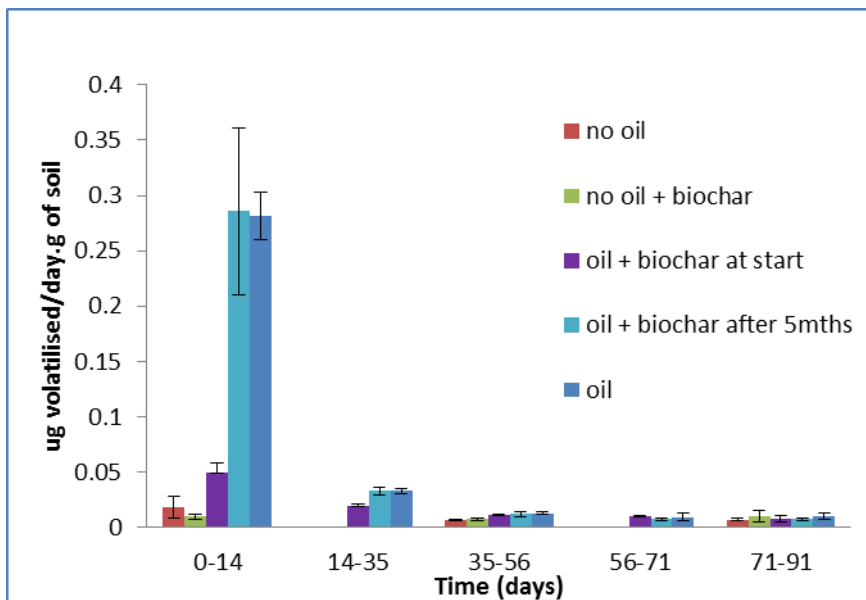
Figure 2-6 Total volatilization flux of 8 aromatic hydrocarbons over 91 days

Initially, there was a significant volatilisation flux from the oil polluted microcosms without biochar ('oil + biochar 5 after months' and 'oil'). In contrast, microcosms amended with biochar at the start showed a significant and almost immediate sequestration of VPHs reducing their mobility in the soil and preventing their volatilisation. The 'oil + biochar at start' batches had a significantly (t-test $p < 0.05$) lower volatilization flux (see appendix 10.6) in comparison to the unamended batches between day 0 and day 14. The flux from the 'Oil + biochar at start' batches was 82.67% less than from the 'oil + biochar after 5 months' and 82.39% less than 'oil' batches. This difference can be attributed to sorption and immobilization of the Volatile Petroleum Hydrocarbons (VPHs) by the biochar which prevents it from moving from the soil into the gaseous phase. These results are in line with the intended effect of sorbent-based contaminant immobilisation and corroborated by previous work which showed that organic contaminants sorb strongly to carbonaceous sorbents such as black carbon and activated carbon (Brändli *et al.*, 2008). Batch and column studies by (Bushnaf *et al.*, 2011) reported retardation in vapor migration of petroleum hydrocarbon following amendment of an aerobic sandy soil by 2% biochar. Research carried out by (Meynet *et al.*, 2014) showed that similar CO_2 fluxes emanating from soil columns with and without biochar indicated a comparable overall extent of VPH biodegradation, while the emanating VPH flux was substantially lower from the biochar amended soil over the 30 day duration of the experiments, due to VPH sorption by the biochar. This observed benefit

was, however, short-lived as a massive decrease in volatilisation is observed between day 14 and day 35 for all treatments. The average volatilization flux of the 'oil' sample decreased by 88.3% between day 14 and day 35, 60.3% between day 35 and day 56, 27.2% between day 56 and day 71 and 5.8% between day 71 and day 91. The massive decrease observed between day 14 and day 35 was expected because according to Fingas (1997), light crude oils can be reduced by up to 75% of their initial volume in a few days while reduction for medium crudes can be up to 40% of their volume. In contrast however, heavy or residual oils will only lose about 5% of their volume in the first few days following a spill (Fingas, 1997). Evaporation of compounds with molecular weights greater than n-C_{15} would usually continue for a long time however the evaporation rates greatly diminish and become insignificant after 100 hours (Jordan, 1980). Also, volatilization is usually proportional to the concentration of the contaminant in the system due to equilibrium dynamics. Between day 14 and day 35, volatilization flux from biochar-amended microcosms was approximately 67.6% less than the flux from unamended microcosms. Overall flux diminished further between day 35 and day 56 and flux from biochar-amended microcosm was 8.4% and 17.1% less than unamended microcosms (oil + biochar 5 months and oil only respectively). After 56 days, the flux from amended and unamended microcosms were at comparable levels and it appears that the biochar was no longer having a significant effect, although this is likely due to the exhaustion of the volatile fraction from the oil. The figure below shows changes in the volatilisation flux for individual aromatic hydrocarbons for the first 14 days of the volatilization experiment. Error bars represent the standard deviation among triplicates and results displayed are for the 5 different experimental treatments as outlined in the legend. It was expected that part of the reduced volatilisation from the system at later times would also be attributable to biodegradation occurring within the batches after an initial lag phase since the soil was non-sterile and had been amended with nutrient.
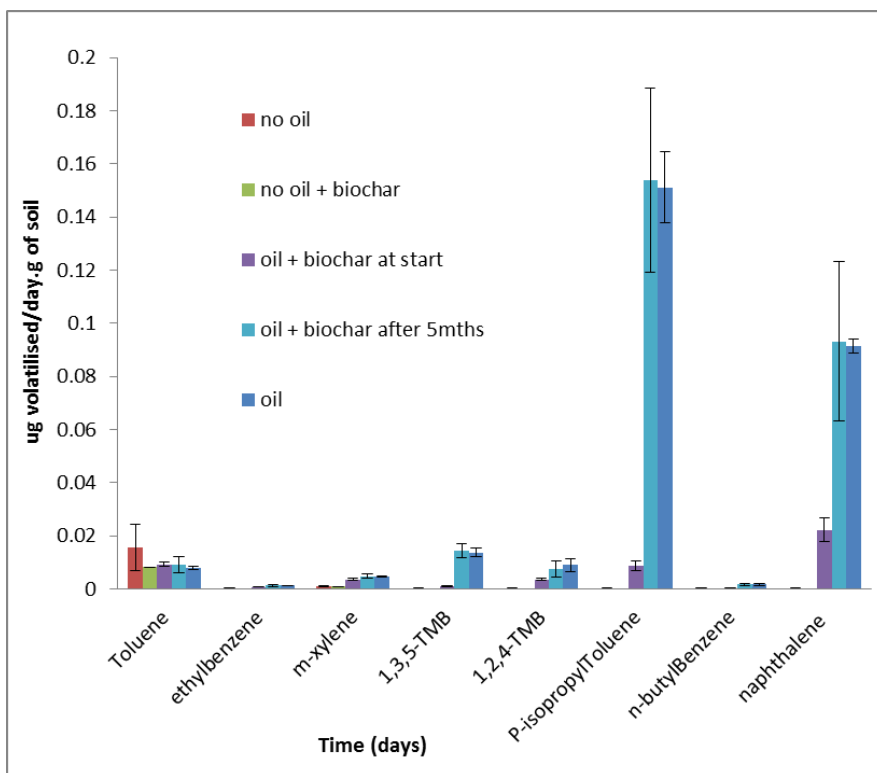
Figure 2-7 Aromatic hydrocarbon volatilization flux for day 0-14

A broadly similar trend is observed for individual compounds as was observed for the total volatilization concentrations. Significant differences (t-test $p < 0.05$) between amended ('Oil + biochar at start') and unamended ('oil + biochar after 5 months' and 'oil') batches were observed in five out of the eight aromatic hydrocarbons within the first 14 days (see Table 8-1 in Appendix A). Toluene was however different showing comparable (t-test $p = 0.927$) concentrations for amended and unamended microcosms. This is in contrast to results by (Bushnaf *et al.*, 2011) which recorded 36 fold increase in K_d value of toluene upon addition of 2% biochar due to a high due to strong π–π electron interactions between toluene and the aromatic surface of biochar, and reduced toluene volatilisation from biochar amended soil (McBeath and Smernik, 2009). Naphthalene, which had the highest abundance in the source oil, is clearly seen as having a relatively high volatilization flux compared to the other compounds, despite of its comparatively lower vapour pressure. This may be partially due to its lower biodegradability. Table 8-1 in Appendix A reports total volatilisation flux for all 8 aromatic compounds over 14 days.

2.6.4 *Alkane residuals in soil after bioremediation and BC amendment*

Less volatile oil fractions tend to remain in the soil even after significant volatilization has occurred, at which point, biodegradation and other natural processes tend to be more effective at reducing the oil residuals. Seven months after set-up of the batch experiment, residual oil concentrations were determined by Accelerated Solvent Extraction (ASE) to determine how much oil remained in the soil after volatilization and biodegradation. At this point, the 'oil + biochar at 5 months' batches had been amended with BC for approximately two months. 10 straight chained alkanes (decane $C_{10}H_{22}$, dodecane $C_{12}H_{26}$, tetradecane $C_{14}H_{30}$, hexadecane $C_{16}H_{34}$, octadecane $C_{18}H_{38}$, eicosane $C_{20}H_{42}$, docosane $C_{22}H_{46}$, tetracosane $C_{24}H_{50}$, hexacosane $C_{26}H_{54}$, octacosane $C_{28}H_{58}$) were quantified. Results (Figure 2-8) indicate a significantly higher (t-test $p < 0.05$) level of biodegradation in batches containing just oil compared to those containing oil and biochar from the start. This is evidenced by very high amounts of residual alkanes in the microcosm amended with biochar from the start due to the inhibition of biodegradation as a result of sorption, causing reduced alkane bioaccessibility. The very low abundance of alkanes in microcosms without biochar amendment or with biochar added after five months indicates a high level of biodegradation had occurred within a relatively short time period (Donaldson *et al.*, 1985). This trend was observed for all the alkanes in Table 8-2.
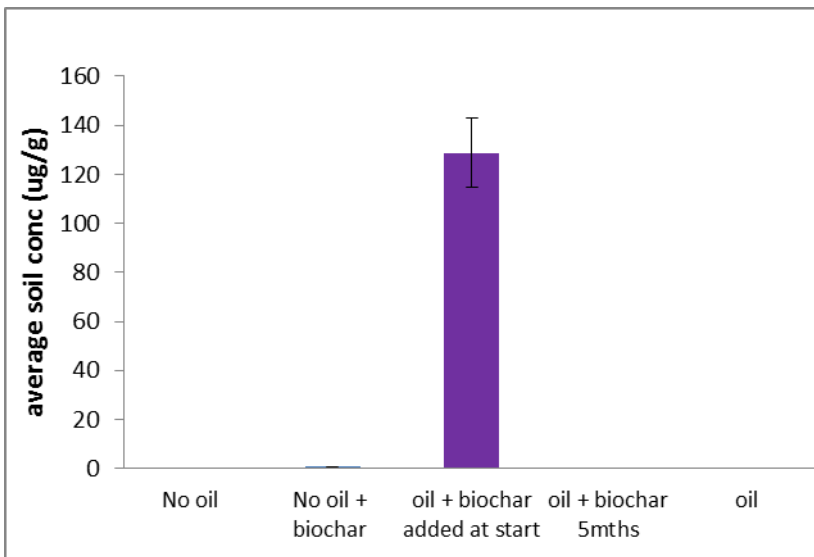
Figure 2-8 Total concentration of 10 alkanes between C_{10} and C_{28} measured after Accelerated Solvent Extraction of soil. (The initial total alkane concentration from pyrolytic (i.e. crude oil) and pyrogenic sources was 440.3 ± 7.3 ug/g).

These results are in line with many studies which have shown that carbonaceous geosorbents affect the bioavailability of organic compounds (McLeod *et al.*, 2004; Kookana, 2010; Gomez-Eyles *et al.*, 2011). Table 8-2 in Appendix A reports total concentration of 10 alkanes between C_{10} and C_{28} measured after Accelerated Solvent Extraction of soil.

2.6.5 *PAH availability after bioremediation and BC amendment*

For solid phase concentration of the aromatics, residual 16 EPA PAHs concentrations were also quantified as they are priority contaminants and usually of interest at crude oil spill sites.
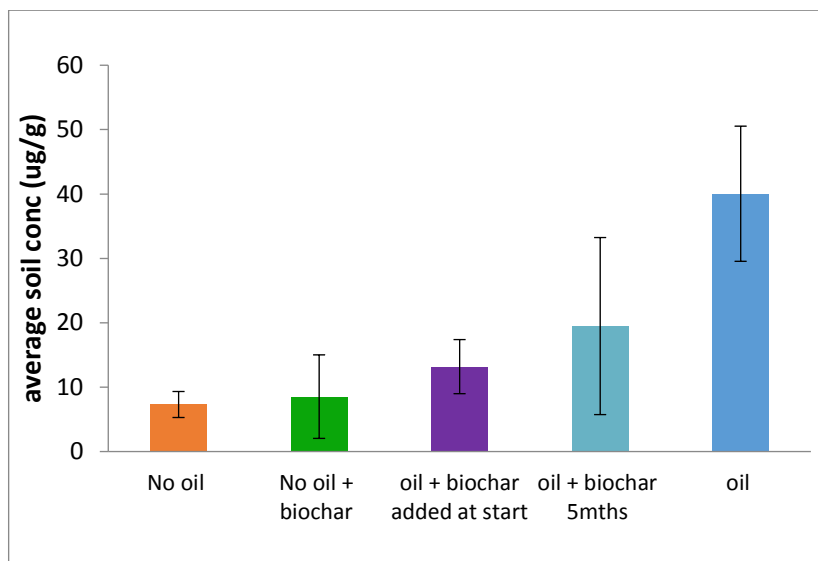
Figure 2-9 Total concentration of 16 EPA PAHs measured after Accelerated Solvent Extraction of soil. (The initial total PAH concentration from pyrolytic (i.e. crude oil) and pyrogenic sources was 89.4 ± 1.9 ug/g).

Solvent extraction results indicated a significantly higher level (t-test p = 0.015) of residual PAHs in the 'oil' batches compared to 'Oil + biochar at start' batches. This is counter-intuitive, as the relatively limited bioaccessibility of the BC-associated PAHs should have slowed down their biodegradation as compared to the unamended batches, similar to the observation for the alkane fraction. However, the activated biochar may bind the PAH contaminants so strongly that they remain associated with the biochar even after accelerated solvent extraction. This is supported by previous studies (Jonker and Koelmans, 2002b; Rhodes *et al.*, 2008) which suggest that the highly hydrophobic nature of biochar may make it difficult even for organic solvent extractants to completely desorb tem from BC matrices. This strong binding of Hydrophobic Organic Compounds (HOCs) in microporous domains of charred materials makes them become unavailable for uptake by soil organisms and plants

and this occlusion reduces HOC ecotoxicity. However, it also hinders HOC accessibility for intracellular biodegradation by soil microorganisms (Meynet *et al.*, 2014). This phenomenon which is referred to as ageing involves the movement of compounds from accessible soil compartments into less or inaccessible compartments resulting in reduced extractability (Reid *et al.*, 2000). Reduced biodegradation of the herbicide of IPU (isoproturon) was observed following biochar amendment in studies by Sopeña *et al.* (2012). Other studies by (Rhodes *et al.*, 2008) (Yang *et al.*, 2006) (Zhang *et al.*, 2004) also suggest that sorption of organic compounds to black carbon is able to reduce bioaccessibility and hence biodegradation. A 60-day field experiment by Beesley *et al.* (2010) in which total PAH concentrations as well as bioavailable concentrations were reduced by biochar showed reductions of between 40-50% relative to the untreated soil. The fact that the total PAH concentration was also reduced is postulated to be due to the fact that the acetone-hexane extraction was not exhaustive enough to extract the PAHs that were more strongly bound to the added soil amendments. In line with other authors, Beesley et al. concluded that these very strongly bound PAHs were not readily bioavailable and therefore do not pose a risk to the environment (Beesley *et al.*, 2010). They suggested that it was unlikely that biochar addition had increased PAH degradation by the stimulation of microbial activity in the soil due to previous studies (Rhodes *et al.*, 2008) using radioactive, labelled compounds, which showed that carbonaceous sorbents cause a decrease in PAH mineralization by reducing the availability of PAH microbial degradation. Literature does however show varying impact regarding the effect of biochar on biodegradation. (Anyika *et al.*, 2015; Fang *et al.*, 2016). In this work, there was however no significant difference observed between 'oil' batches and 'oil + biochar after 5 months' batches perhaps due to sorbent-contaminant contact time and/or high variations between replicate measurements among the 'oil + biochar after 5 months' batches. This is because one of the batches (See Table 8-3) had a much higher residual PAH concentration than the other two replicates and this is likely the result heterogeneity in soil-BC or PAH pollution in soil or variability in the PAH biodegradation (Ahn *et al.*, 2005; Cho *et al.*, 2012b). A shorter contact time (2 months versus 7 months) may also have limited the mass transfer of the PAHs to the biochar for subsequent sequestration in the 'oil + biochar after 5 months' versus 'oil + biochar at the start' batches. The oil in the 'oil + biochar after 5 months' sample had likely been partially degraded to more oxidized metabolites before the addition of biochar after five months. The biodegradation likely resulted in the production of surfactant-like, partially hydrophobic and partially hydrophilic, by-products (Henkel *et al.*,

2012). These by-products would have competed with PAHs for adsorption sites and thus 'fouled' the biochar and enhanced PAH solubility in water consequently resulting in more readily extractable residual concentration. Research by (Hale *et al.*, 2010) shows that the presence of natural dissolved organic matter in sediment inhibits the adsorption of PCBs by AC as compared to clean water systems. The PAH distribution of for all five treatments is reported in Table 8-3 in Appendix A.

The presence of PAH contamination in the soil without added oil is explained by its origin from the Exhibition Park in Newcastle; in the centre of a coal mining region. PAH and PCB tend to remain in soil for extended periods ranging from years to decades of time because of their comparatively long half-life (Vane *et al.*, 2014). This also explains why overall there was more PAH retained in the soil than alkanes in addition to the fact that aromatics generally do not degrade as easily as alkanes. Source diagnostics studies by Wei *et al.* (2014) showed that coal combustions and refined petroleum are the major input sources of anthropogenic PAHs. Furthermore, the 'no oil' batches are comparable in concentration to the 'oil + biochar' amended batches. This is probably due to the ability of activated biochar to reduce extractable PAH concentrations to background levels, if added from the start. Figure 2-10 compares the total residual concentrations of the alkanes and PAHs after seven months from the ASE experiment. It is interesting to note that, depending on which crude oil fraction is considered (alkanes versus PAHs), the assessment of the remediation outcomes would differ, as the 'oil and biochar added at start' batches had the highest solvent extractable residuals of total alkanes, but the 'oil' batches had the highest solvent extractable residuals of PAHs. Not the entire solvent extractable residual is, however, necessarily readily bioavailable, which is why the more readily bioavailable alkane and PAH concentrations in soil were also quantified with passive sampling methods.
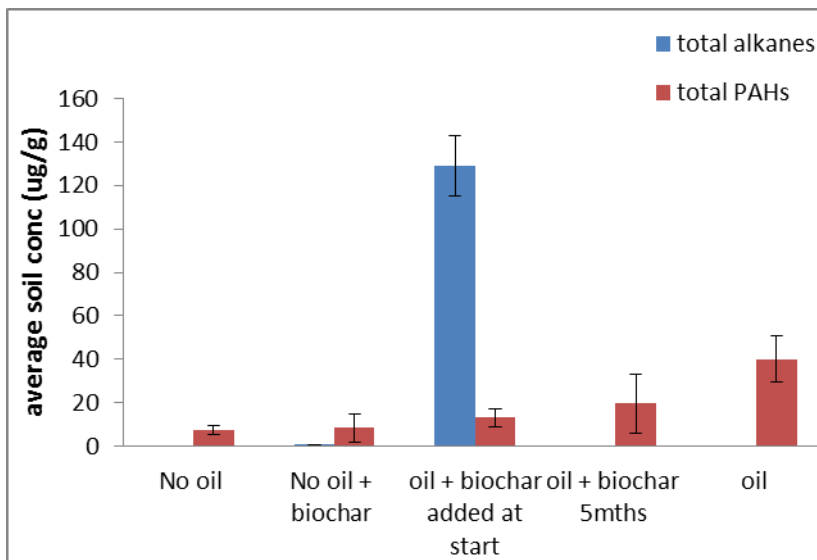
Figure 2-10 comparison of total residual 'solid' concentrations of alkanes and PAHs after seven months

2.6.6 *Alkane concentrations in PE samplers after bioremediation and BC amendment*

The sets of microcosms used for determination of the polyethylene and aqueous phase concentrations were homologous to those used for the ASE experiment. Polyethylene (PE) samplers were added to the batches to sample available alkanes, while the added biocide inhibited alkane biodegradation.
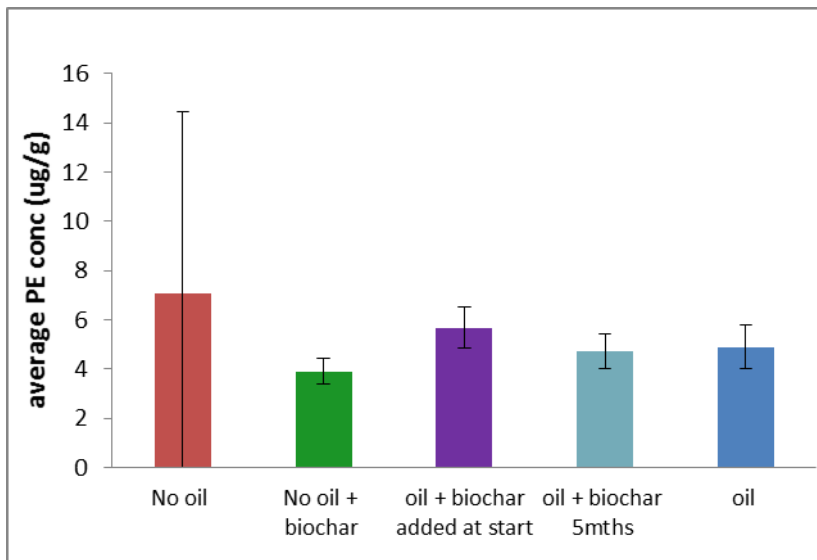
Figure 2-11 Total alkane concentration in PE experiment after 7 months

Ten straight chained alkanes (decane $C_{10}H_{22}$, dodecane $C_{12}H_{26}$, tetradecane $C_{14}H_{30}$, hexadecane $C_{16}H_{34}$, octadecane $C_{18}H_{38}$, eicosane $C_{20}H_{42}$, docosane $C_{22}H_{46}$, tetracosane $C_{24}H_{50}$, hexacosane $C_{26}H_{54}$, octacosane $C_{28}H_{58}$) were quantified as in the previous experiment.

Figure 2-11 shows all treatments to be of very low and comparable alkane concentrations. It is believed that the results cannot be relied upon to accurately assess treatment effects, as they are all very close to the detection limit levels which is evidenced by the very low and comparable levels between treatments and controls without added crude oil (range $= 4 - 7$ ug/g). It is interesting to note that even the 'oil + biochar at start' batch which showed significantly higher concentration in the ASE experiment is not significantly different from any of the other treatments within the PE experiment. This demonstrates that the alkanes were present in those soils, but were present in strong association with the biochar and therefore not readily bioavailable and not biodegradable. No noticeable trends were observed among treatment for individual alkanes. Table 8-4 (Appendix A) shows the alkane distribution for all five treatments. Overall these results demonstrates that alkane availability was very low after seven months either due to rapid alkane biodegradation (in 'oil' and 'oil + biochar after 5 months' batches) or very strong alkane sequestration by the biochar (in 'oil + biochar from start' batches).

2.6.7   *PAH concentration in PE samplers after bioremediation and BC amendment*

PAHs results from the PE experiments (Figure 2-12) showed a significantly higher uptake of total PAHs by the samplers in the 'oil' batches (94.0%) compared to the measurements obtained from all the other batches. This shows that in the absence of biochar, PAHs from crude oil are much more readily available for uptake by the PE membrane, and hence, presumably also by biotic membranes. Crude oil pollution may even have resulted in the solubilisation of pyrogenic PAHs which were already present in the soil, the availability of which was originally very low as indicated by the 'no oil' control. It is interesting to note that biochar addition to the soil in the absence of crude oil pollution further reduced the already very low availability of native PAHs in this urban soil, although not significantly ('no oil + biochar' versus 'no oil' controls; $P = 0.72$).
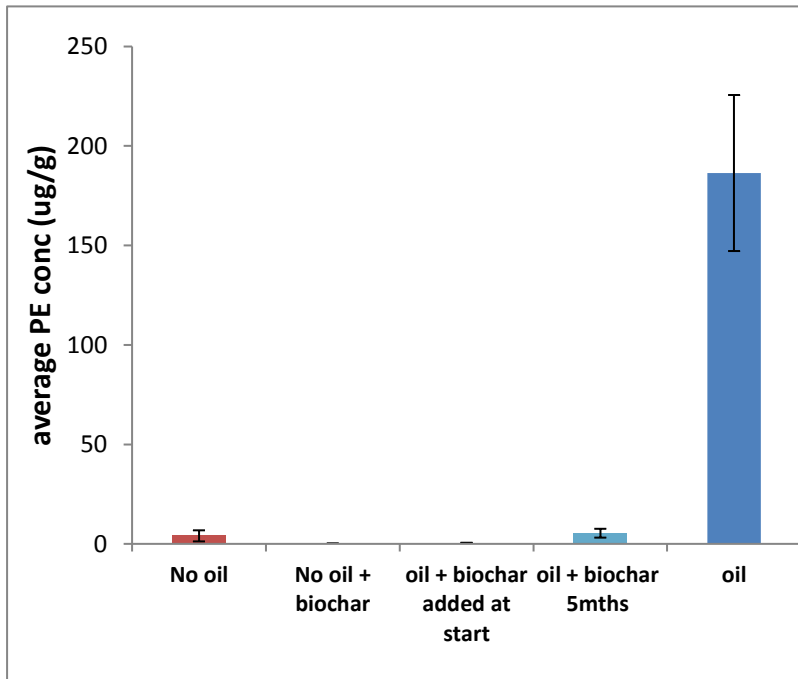
Figure 2-12 Total PAH concentration in PE after 7 months

These results are in line with several PE studies, which show that BC or AC addition is able to reduce PE, and hence, freely dissolved aqueous PAH concentrations in soil and sediments. Studies by Brändli *et al.* (2008) showed that 2% PAC addition to moderately contaminated urban soil reduced the freely dissolved aqueous concentration of native PAH in soil/water suspensions up to 99%. Field studies at Hunters' point, CA, USA showed that AC amendment caused reduction in the PCB uptake to PE samplers from sediment after five years of deployment (Cho *et al.*, 2012a). For AC-treated sediment, studies by Zimmerman *et al.* (2004) showed reductions in the total aqueous PCB concentrations by 87% and 92% for contact times of 1 and 6 months, respectively. Table 8-5 in Appendix A reports Total PAH concentration in PE after 7 months.
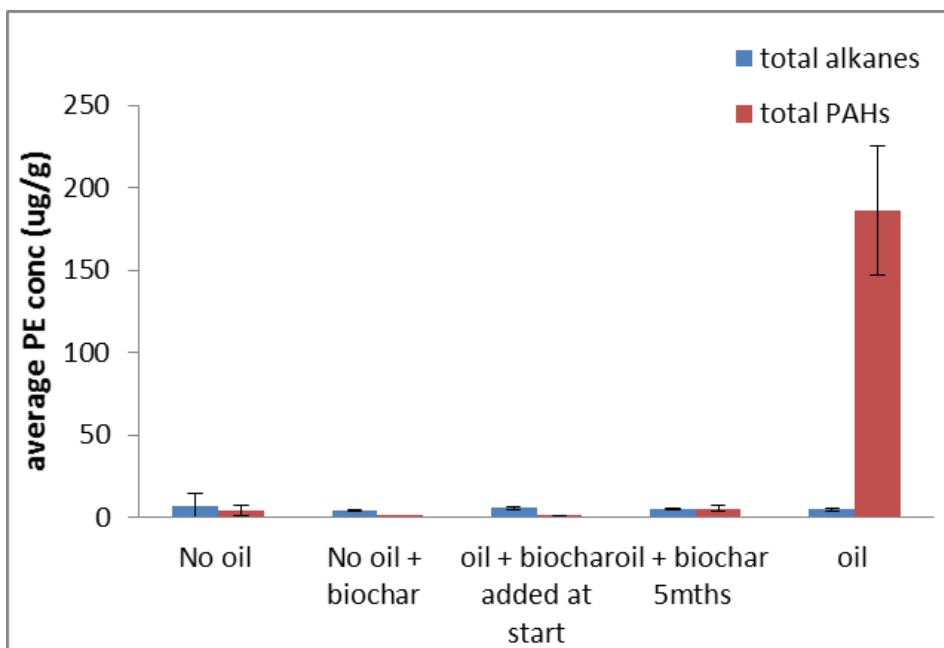
Figure 2-13 comparison of total alkane and PAH concentrations from the PE experiment.

Figure 2-13 compares available concentrations of the alkanes and PAHs after seven months from the PE passive sampler experiment. This assessment, which focused on the readily available, rather than total pollutant concentrations in soil is interesting. It suggests that the biochar amended batches ('oil + biochar added at start', 'oil + biochar added after 5 months') had risks comparable to the controls seven months after the crude oil addition, whereas the unamended 'oil' batches had much higher risks due to the greater PAH availability as compared to the 'no oil' control.

2.7   Naphthalene

Naphthalene is an important fraction of crude oil and special attention is paid to it in this work because due its unique physical and chemical properties (semi-volatile), it was detected in all of the experimental assessments, including the volatilisation experiment. It is also present in crude oil in much higher abundance than all the other 16 EPA PAHs analysed in this work; accounting for 45.5% of the total EPA PAHs concentration, and while less readily biodegradable than most alkanes, it is not as recalcitrant than some of the higher molecular weight PAHs. Naphthalene is therefore used as an example to illustrate treatment effects for an individual compound, to add further depth of understanding of treatment benefits and disadvantages.

2.7.1   *Volatilization of naphthalene*

The volatilization flux observed for naphthalene (Figure 2-14) exhibited a similar trend among treatments as the total volatilization flux of the other low molecular weight aromatic hydrocarbons discussed in section 2.7.3. Initial rapid sequestration of naphthalene was observed in the BC amended batches 'oil + BC at start' as was the case with the sum of the aromatic compounds.
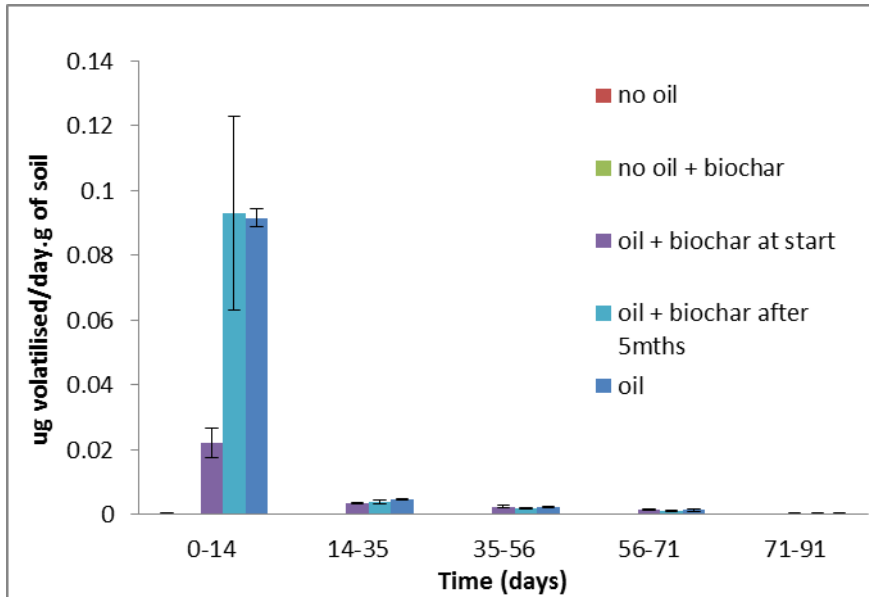
Figure 2-14: Daily volatilization flux for Naphthalene over 91 days

Naphthalene showed a significantly higher volatilization flux than all aromatic hydrocarbons in the volatilization experiment except P-isopropyltoleune (also known as Cymene) which is commonly found in aromatic oils. This can be attributed to the fact that naphthalene is one of the lowest molecular weight EPA PAHs and therefore has a relatively higher volatility (Soclo *et al.*, 2000). Naphthalene evaporates readily and is classified as a semi-volatile organic compound (SVOC) because of its vapour pressure of 0.087 mmHg at 25 °C which is just below the 0.1 mmHg cut-off often used to define VOCs (Jia and Batterman, 2010) (Booth, 2005). Naphthalene has often been listed both as a VOC and as a PAH. It has however also been excluded from many VOC and PAH studies because it is one of the least volatile VOCs and the most volatile PAH (Jia and Batterman, 2010). At contaminated sites,

where naphthalene vapour inhalation is a potential risk, this risk could be mitigated with biochar amendment.

2.7.2   *Naphthalene availability after bioremediation and BC amendment*
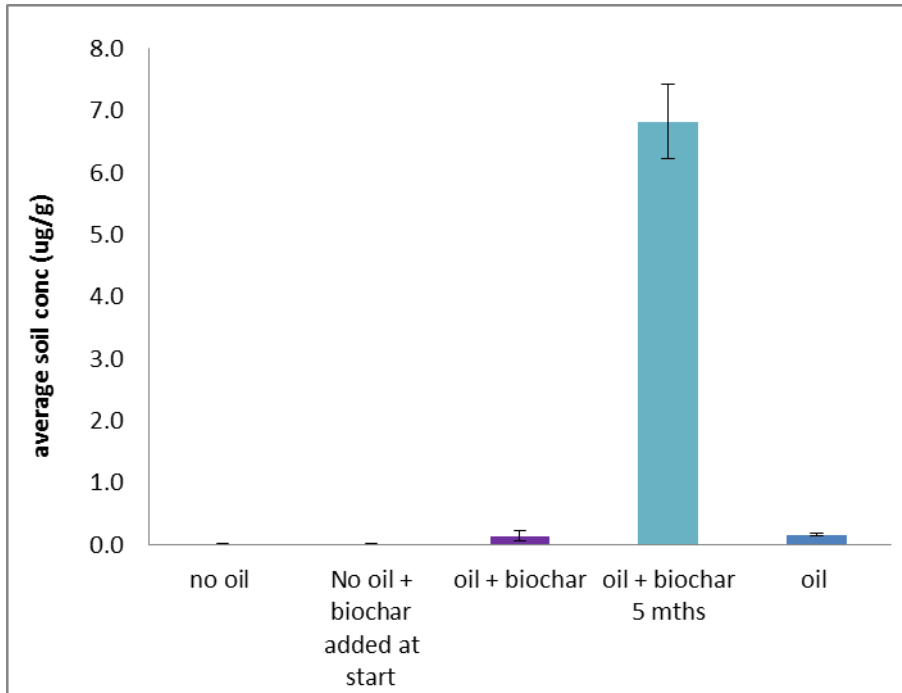
Figure 2-15 : Solid phase concentration of naphthalene after 7 months

A trend similar to the total PAHs solid phase concentration profile (presented in **Error! Reference source not found.**) is observed for all the PAHs except naphthalene for which a distinct behaviour is observed (Figure 2-15). This may be attributed to the fact that the main source of naphthalene is the added crude oil while many other PAH compounds have the soil as their main source. The ASE extraction suggests that solvent extractable naphthalene residuals were highest in the batches, where biochar was added after 5 months. The difference with the 'oil' batches could be explained by a reduced biodegradation of naphthalene in the last two months, after the addition of the biochar. The difference with the 'oil and biochar at the start' batches on the other hand, could be explained by the longer contact time with the biochar resulting in stronger association with the biochar matrix to the point where the naphthalene is no longer solvent-extractable.

It should be noted that there is a very significant apparent loss of naphthalene in all the systems by either both volatilisation and biodegradation in the absence of biochar, or very strong sorption in the presence of biochar. However, 'oil +, biochar after 5 months' had the

highest solvent extractable residual concentration relative to the initial amount in the microcosm based on the mass balance analysis presented in table 2.1. As noted above, naphthalene acted differently from the other PAHs. For the less biodegradable high molecular weight PAHs, the 'oil' microcosms had the highest extractable residuals. At 5 months, the oil was partially degraded so there were likely some metabolites present, which were in competition for sorption sites with naphthalene or helped to desorb the naphthalene during solvent extraction, hence reducing the benefit of the biochar, if added after five months. Very commonly, where only little carbon is available, organic chemicals in solution attach to the surface of clay particles through the sorption mechanism commonly referred to as adsorption (Vallero, 2006). Hence, it is in principle possible that naphthalene was trapped in clays in the soil. According to (Mackay and Boethling, 2000) however, the type and amount of clay in the soil has little effect on the sorption process of HOCs unless the organic carbon content is low or the clay content is high. With respect to potential error sources, at time 0, the volatilisation results show that the naphthalene concentration of the 'biochar + oil after 5 mths' samples and the 'oil' sample (figure. 2-14) were very similar. This would suggest that the amount of naphthalene in the batches was comparable at time 0, making it unlikely that the observation after seven months is affected by how batches were set up. Also, based on the generally good repeatability of naphthalene concentrations measurements, the naphthalene heterogeneity between batches was low. Naphthalene concentration in 'soil only' samples from Exhibition Park was measured, although not at time zero, but after 7 months; and results were almost 100 times lower than after crude oil addition, making it unlikely that heterogeneity in the urban soil matrix affected naphthalene results. Contrary to the larger molecular weight PAHs, which mainly originated from the soil matrix, naphthalene was added with the crude oil. In any case, the assessment outcome for naphthalene differs in that respect from the other PAH compounds which illustrates the complexity of designing optimal remediation strategies for complex mixtures of hundreds if not thousands of compounds such as crude oil.
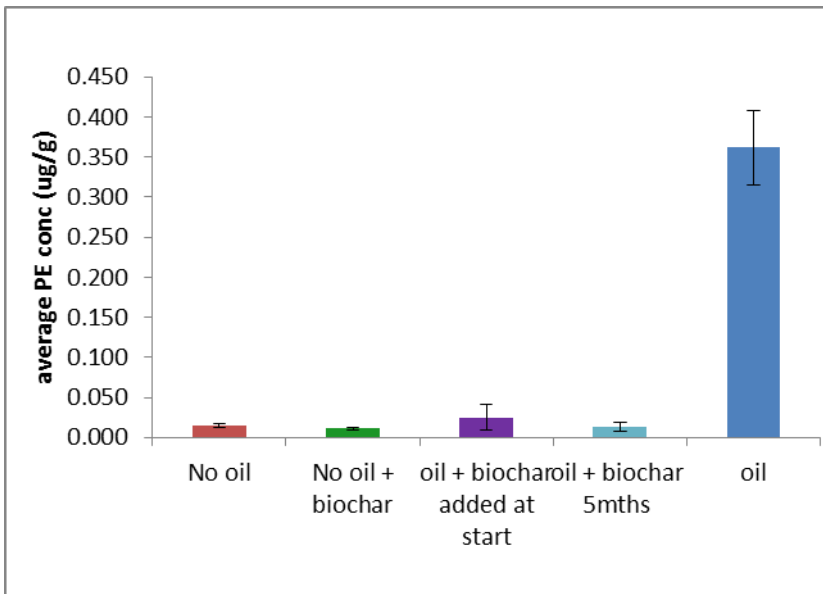
Figure 2-16 PE concentration of naphthalene after 7 months

2.7.3 *PE uptake of naphthalene after bioremediation and BC amendment*

The naphthalene PE concentration profile is similar to that of the total PAHs indicating the highest naphthalene availability in the 'oil' soil, whereas oil polluted soils with biochar amendments had a very low naphthalene availability in the range of the unpolluted controls.
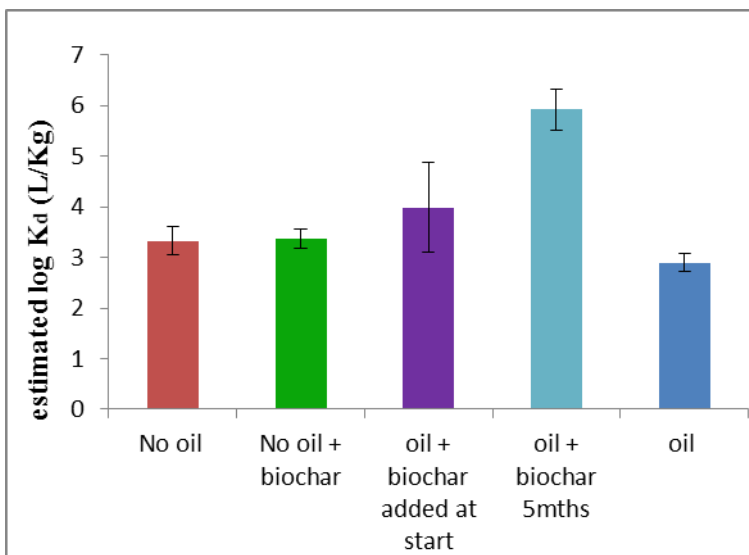
Figure 2-17 K_d of naphthalene after 7 months

Based on this criterion, biochar amendment is a promising remediation approach even for one of the less recalcitrant PAH compounds. Biochar-water partitioning coefficient (K_d)

represents the slope of the linear relationship between the contaminant concentration in the sorbent (ug/g) and the contaminant concentration in the aqueous phase (ug/ml) at equilibrium (Guerin and Boyd, 1992). It is an important parameter for assessing the strength of the pollutant association with the soil and is used in risk assessments and pollutant fate models. Aqueous concentrations were calculated from PE concentrations using K_{pe} values in section 2.5.8. K_d values were then calculated from these PE-derived aqueous concentrations and the measured soil concentrations (section 2.5.9).

The addition of 5% biochar resulted in higher sorption coefficient K_d values in the biochar amended batches compared to the unamended batches. K_d values of batches amended with biochar at start and those amended after 5 months were higher than unamended batches by a factor of 1.4 and 2.0 respectively. The addition of 2% biochar to an aerobic sandy soil was observed to have increased the K_d values for a range of alkanes by a factor of 1.1 to 4.2 and toluene by a factor of 36 (Bushnaf *et al.*, 2011). A higher K_d value implies that naphthalene is less mobile in the biochar amended soils and therefore less likely to transfer to other environmental compartments such as groundwater or the atmosphere, but also less available for biodegradation by soil microorganisms.

2.8   Mass balance analysis

Attempts to calculate mass balance after an oil spill is usually essential in order to fully understand the fate of an oil spill in a marine environment (Jordan, 1980). The mass balance of this experimental work is based on the hypothesis that hydrocarbons are being lost from the soil into the gaseous phase by volatilization and also being degraded by microorganisms already present within the soil. In this experiment, a three-phased partitioning equilibrium was assumed based on the fact that phase transfer processes are generally fast compared to the other processes such as bioremediation (Schwarzenbach *et al.*, 2016). In reality however, equilibrium is not always reached because of which overall mass transfer rate data are usually necessary for designing an adsorption system.

The compound 'naphthalene' was chosen to demonstrate the mass balance analysis because volatilization data was available for it, but not for the other PAHs. However, since the other PAHs are less volatile than naphthalene, it can be safely assumed that volatile losses would be even less significant for these other compounds. Mass balance parameters used in the analysis are; i) initial and final oil concentrations from the microcosm systems ii) amounts volatilized and capture in foam plugs, with the missing mass after 7 months then being

attributed to iii) other losses including degradation by microorganisms and irreversible sorption.

Table 2-1 Mass balance analysis for naphthalene

Test	A Initial amount in microcosm (mg)	B Solvent extractable amount in microcosm after 7 months (mg)	C Amount volatilised (mg)	D Amount biodegraded or irreversibly sorbed (mg)
Oil	0.7654	0.0033	0.0283	0.7338
Oil + biochar	0.7653	0.0028	0.0085	0.7540
Oil + biochar after 5 months	0.7653	0.1364	0.0283	0.6006

Table 2-6 above presents the data for the mass balance analysis for naphthalene, which was obtained by the calculations below.

A- Initial amount in microcosm (mg)

This is the sum of the amount of naphthalene initially present in the soil, referred to as the 'Native amount in soil (A_1)' and the amount of naphthalene added to each microcosm via the crude oil (A_2).

$$A = A_1 + A_2$$

A_1- Native naphthalene amount in soil

$$Native\ amount = concentration\ in\ control\ soil\ (mg/g)\ x\ mass\ of\ soil\ added\ (g)$$

The control sample concentration is obtained from the ASE experiment. Although it would have been best to measure the initial soil PAH concentration for this calculation, this was not

done, as the presence of native PAHs exceeding in some cases the levels in the added oil were not anticipated. However, because the soil had been weathered in the environment for many decades, it is unlikely that the PAH concentration in the soil from the Exhibition Park would have changed significantly while in the lab without any external influence within the 7 months between microcosms set up and ASE extraction. The concentration measured by the ASE extraction was therefore assumed to be a good estimate for the original amount of naphthalene present in the soil. Previous studies show that HOCs may be biodegraded to a residual concentration that becomes stable with time or which decreases only very slowly over years with continued treatment (Luthy *et al.*, 1997). In any case, naphthalene is predominantly from the added crude oil.

A_2 - Amount of naphthalene added via crude oil to each microcosm

$$Amount\ added\ (mg) = concentration\ in\ crude\ oil\ \left(\frac{mg}{ml}\right)\ x\ volume\ of\ crude\ oil\ added\ (ml)$$

B- Naphthalene mount in microcosm after 7 months (mg)

This is the residual soil concentration at the end of the ASE experiment.

$$Amount\ after\ 7\ months = Cs\ in\ 'test'\ microcosm\ (mg/g)\ x\ mass\ of\ soil\ added\ (g)$$

C- Amount of naphthalene volatilized and capture by foam plug over 91 days (mg)

$$total\ amount\ volatilized\ over\ experimental\ period$$
$$= \Sigma(amount\ volatilised\ (ug)$$
$$/day.g\ of\ soil\ x\ Number\ of\ days\ x\ mass\ in\ g\ of\ soil)$$

Even for the most volatile PAH compound, naphthalene, the amount volatilized over the 91 day period is small compared to the amount of naphthalene added via crude oil. We thus see that a large percentage has been either biodegraded or irreversibly sorbed.

D- Amount biodegraded or irreversibly sorbed (mg)

This is comprised of the amount degraded as well as the amount which is very strongly sorbed by the biochar, i.e. no longer solvent extractable.

$$losses\ from\ the\ system = A - (B + C)$$

It must be noted that it would be inaccurate to totally attribute the losses to just volatilization and biodegradation as a variety of transformation and transport processes usually contribute to the disappearance of a contaminant (Kim *et al.*, 1995). Also, errors in the procedures as well as unquantified breakdown products may affect the amounts obtained by calculations.

Furthermore, laboratory experiments do not typically replicate the field scenario and so a mass balance may be inaccurate.

2.9   Conclusion

The foam plug experiment showed that 5% biochar was effective at reducing volatilization of aromatic hydrocarbons. This retardation of VPH volatilization by biochar amendment was in line with the hypothesis however the benefit of this rapid sequestration effect of biochar was not sustained as overall concentrations dropped significantly after 14 days in all treatments, likely due to the onset of biodegradation. Biochar amendment of top soil to prevent volatilisation during periods with ineffective biodegradation may therefore be a beneficial remediation strategy for crude oil contaminated sites. The experimental results showed less degradation of aromatics than alkanes. Aromatic hydrocarbons are more difficult to break down because of their ring structure hence the alkanes are usually more easily degraded. The fact that the aromatics were not so easily biodegraded provides evidence that the sharp decrease in volatilization flux observed for the aromatic compounds was most likely due to decrease in VPH concentration within the soil as a result of volatilization that had occurred as opposed to biodegradation. Accelerated Solvent Extraction results showed that soil amendment with biochar enhanced sorption of contaminants thereby reducing their bioavailability to soil microorganisms. This would appear to be detrimental where readily biodegradable crude oil components such as alkanes are still abundantly present in soil, as their break-down by soil microorganisms, and hence, permanent removal from the system would be inhibited. The results suggest that the presence of biochar may increase the persistence of alkanes in soils as there was sequestration of alkanes which would otherwise have been biodegraded. It may thus be suggested that BC be applied only after easily biodegradable compounds have had the opportunity to be acted upon by micoorganisms. Persistence of biodegradable pollutants has been a major cause for concern at contaminated sites which involve application of strong sorbents due to the impact of these sorbents on the bioavailability and intrinsic biodegradation of organic pollutants (Oen *et al.*, 2006; Rhodes *et al.*, 2008; Beesley *et al.*, 2011; Bushnaf *et al.*, 2011).

The passive sampler results revealed that alkane availability was relatively low for all treatments due to biodegradation, which had occurred, or very strong alkane sorption by the biochar. Polyethylene uptake for PAHs indicated a reduction of readily available, and by implication also freely dissolved aqueous PAH concentrations, in BC-amended microcosms

as anticipated. Despite of the evidence for very effective alkane degradation, PAH availability in the unamended batches remained high after seven months. In some cases, the availability of native soil PAHs was even increased as compared to the control, which was postulated to be due to dissolution of native soil PAHs in crude oil, when was added to the microcosms, making them more available.

In summary, the experimental work provides evidence for the potential benefits of using biochar in crude oil polluted soil remediation. An example is the reduction in the emanation of volatile crude oil components from soil, and the very low availability of the crude oil components after 7 months, which was comparable to the controls without crude oil addition for the biochar amended systems. However, there is also clear evidence that the immediate addition of biochar to the freshly polluted soil will inhibit the removal of readily biodegradable crude oil components by soil microorganisms. Consequently, it would appear that biochar amendment could be utilized most beneficially as a stabilisation strategy for the crude oil residuals remaining after bioremediation treatments, and the optimal time for the biochar addition needs to be carefully chosen. This would be particularly useful if conditions are not favourable for bioremediation to occur (Boopathy, 2000). Ultimately, in terms of technicality and economics, the choice of remediation technology applied to a site would have to be based on considerations of parameters specific to that site (Bage *et al.*, 2003).

Selected results from this chapter will be used in risk assessment modelling in chapter three.

Chapter 3.   Risk Assessment

3.1   Introduction

According to USEPA, Environmental risk assessment (ERA) is a scientific process used to characterize the nature and magnitude of health risks to humans and ecological receptors from chemical contaminants and other stressors that may be present in the environment. Examples of human receptors are residents, workers, and recreational visitors while ecological receptors include birds, fish and wildlife (Hosford, 2009). The increased need to conserve environmental resources and reduce the burden of aftercare on future generations makes it expedient that best practices are employed when assessing the likely impacts contaminants on humans and ecological receptors. Risk management involves making decisions while risk assessment estimates the risk. However, they are often difficult to separate. In order for risk assessment to be useful for decision-making, it has to be in line with various national contaminated land policies. Current approaches do not generally consider bioavailability and bioaccessibility when determining remediation endpoints. This chapter aims to demonstrate the importance of incorporating bioavailability predictions into risk assessment and why risk assessment approaches need to be improved upon, if biochar-based soil remediation is to be implemented. It discusses current and evolving global approaches to risk assessment and management. Bearing in mind the already broad scope of this research work, this chapter focuses on assessing the suitability of current frameworks for assessing residual risk from crude oil pollution after remediation by biochar amendment using the framework of the UK's CLEA model as a case study. Particular emphasis is placed on highlighting whether or not bioavailability considerations are currently incorporated into different aspects of the framework.   This is done by incorporating results from the experimental work in chapter two into the CLEA model and highlighting the impact on current risk assessment decisions, as well as by studying the compatibility of model predictions with experimental results. From an oil spill point of view, risk assessment for land contamination is very important because contaminated land could potentially result in pollution of water resources in addition to harm caused to humans, ecosystems and property. Imposing overly restrictive guidelines may however have a counter-productive effect in the sense that techniques, which are 'imposed' on potentially responsible parties may not be affordable or technically feasible, or may even have excessive secondary environmental impacts under certain circumstances. This chapter explains the structure and basic principles

of the UK's Contaminated Land Exposure Assessment (CLEA) model and how it functions as a tool for ERA. Results from chapter two will be discussed from a risk perspective, highlighting the implications for the different exposure pathways within the CLEA model and how the effects of biochar application are currently accounted for, or not accounted for, within the model.

Asides from the CLEA framework, the UK's Environment Agency also provides guidance for assessing the risks associated with soil and groundwater contamination in order to protect the water environment. The agency published the 'Remedial Targets Methodology', which describes the recommended approach assessment of controlled water as well as for deriving site-specific remedial objectives. It is a tool that supports CLR 11. In addition to the excel worksheet that accompanies the Remedial Targets Methodology' report, the agency also developed a probabilistic modelling package known as ConSim (Carey *et al.*, 2006). As discussed in chapter two, soil contamination is a major challenge in Nigeria and so the CLEA model is used in this research as focus is placed on pathways linked to contaminated land.

Figure 3-1 An illegal crude oil refinery site in the creeks of an Ogoni community in Nigeria's Niger Delta. (Akinleye 2010)

3.2   Overview of the CLEA guidance; Historical development, structural composition & related documents

Risk Assessment approaches tend to vary from country to county although certain aspects are uniform internationally. Even though this thesis explores the implementation of remediation technologies within the Nigerian environment, this chapter will be based on UK's risk assessment framework which is similar to what is obtainable across Europe so this would in a sense be a representation of the European framework. Models are mostly used in contaminated land risk assessment to estimate the contribution from each exposure route. The formulas used in a model are sub-models and provide allowance for adjustments to be made to parameters so that they are more specific to local conditions at a contaminated site (CARACAS, 1998). There are different models that exist for measuring exposure by UK government departments and agencies. The appropriateness of the tool selected is however based on factors such as the types of exposure pathway to be considered, the environmental media for operation of the pathway and the types of receptors involved (IGHRC, 2010). The CLEA Guidance is a non-statutory tool designed by the UK's Environment Agency to help in the estimation of the risk that a child or adult may be exposed to for a pollutant concentration in soil on a given site depending on site usage over a long exposure period which may be of concern to human health. It is a generic approach for deriving clean-up guidelines which are based on estimated intakes of contaminants from a particular concentration of soil by incorporating certain assumptions about human behaviors and other factors influencing exposure into a computer model (DEFRA, 2006) (Searl, 2012). It is a suitable choice for this research because the experimental work was carried out on soil as opposed to sediments. The Environment Agency is the leading public body that is responsible for protecting and improving the Environment in England and Wales and it has produced a series of Contaminated Land Reports (CLR) which provide ''relevant, appropriate, authoritative and scientifically based information and advice on the assessment of risks arising from the presence of contamination in soils'' (DEFRA, 2006). The guidance was designed for use by suitably qualified assessors however, regulators are not under any obligation to use it (Jeffries and Martin, 2009a). It was produced following the issue of a discussion paper by DEFRA titled ''Soil Guideline values: the way forward in 2006 and another DEFRA publication; improvements to contaminated land guidance. Outcome of the 'way forward' exercise in 2008''. It is aimed at providing technical guidance for statutory regimes relating to land contamination particularly Part 2A of the Environmental Protection Act 1990. Part 2A is the

Contaminated Land Statutory Guidance which is used to define contaminated land according to whether or not it poses a significant harm to human health and the environment. It provides a regime for the identification and remediation of contaminated land (ODPM, 2004a).

3.3 Components of the CLEA guidance/framework

The CLEA guidance is based on certain principles which form the framework for its use in risk assessment. It is made up of four components; two guidance reports, one software and one software handbook as outlined below;

3.3.1 *Science Report SC050021/SR2 (Human health toxicological assessment of contaminants in soil):*

This is an update to CLR 9 (contaminants in soil: collation of toxicological data and intake values for humans). It provides technical guidance to regulators by describing a framework by which toxicological data can be collected and reviewed. It also describes how this data can be used in deriving soil contaminant intakes which would be considered protective of human health (Hosford, 2009) and is often referred to as 'TOX report'. It addresses two principal areas of risk assessment; chemical risk assessment and toxicological risk assessment as outlined below;

Basic principles of chemical risk assessment

i. Hazard identification: this involves determining the ability of a substance to produce a toxic effect. It helps to point out the specific kinds of hazards which need to be more carefully considered for instance, its ability to act as a carcinogen or a mutagen. The availability of sound data is important in hazard identification, however, limitations such as bias and lack of accurate information from epidemiological studies can limit its effectiveness (Hosford, 2009).

ii. Hazard characterization: this involves assessing the toxicity of the chemical, particularly the relationship between the dose or exposure level and the effect on the subject. Different approaches exist for characterizing an identified hazard however dose-response curves are typically used and there is usually a threshold value that must be breached before an adverse effect is generated (Hosford, 2009). The terms no-observed adverse effect level (NOAEL) and lowest-observed adverse effect level (LOAEL) are used to refer to the highest and lowest doses respectively at which adverse effects are seen in a toxicity study. One of these two parameters; preferably

the NOAEL is what is usually used to derive Health Criteria values (HCV). HCVs are health contaminant intakes that are considered to be adequately protective of human health, however, they are only available for a select number of contaminants (Searl, 2012).

iii. Exposure assessment: The driving force for pollution prevention and control is the protection of human health, hence risk cannot exist without exposure. It is therefore important to evaluate and quantify the extent to which subjects are exposed to hazards of concern. In this context, determination of the bioaccessible fraction is a very important factor that must be considered when determining exposure.

iv. Risk characterization: this usually involves evaluation of the risk that a chemical poses to humans by comparing human exposure with the estimated Health Criteria Value (HCV). When an established HCV is not available, an approach known as the Margin of Exposure (MoE) approach is used (Hosford, 2009). The MoE approach gives an indication of the level of concern posed by exposure to a specific compound (Benford *et al.*, 2010).

v. Risk management: This is usually carried out after an assessment determines that an unacceptable risk exists. It involves taking steps to eliminate or reduce the risk to an acceptable level. Contaminated land risk management usually involves removal or remediation of the soil; barriers or land use restrictions (Hosford, 2009).

Framework for toxicological risk assessment of chemical contaminants in soil

This deals with the framework for deriving Health Criteria Values (HCV) that may be used when setting Soil Guideline Values (SGVs). It involves collection, evaluation and collation of data. The CLEA guidance describes soil concentrations above which there may be concerns that warrant further investigation and risk evaluation. These concentrations would normally be subject to the opinion of the Environment Agency and are usually for both threshold and non-threshold substances. Generic or site-specific soil-quality limits are used to control or assess contamination (Beck *et al.*, 1995). SGVs usually combine both authoritative science and policy judgements.

3.3.2 *Science Report SC050021/SR3 (Updated technical background to the CLEA model):*

This is the second report within the current CLEA framework and it is an update to CLR 10 (the contaminated land exposure assessment (CLEA) model: technical basis and algorithms).

It identifies the technical approach taken in the development of the CLEA model (DEFRA, 2006). Some of the key concepts within this particular report are outlined below;

Estimating human exposure to soil contaminants

This is the first stage in assessment of a contaminated site. It involves describing the contaminants of concern, receptor pathways for the contaminants, potential receptors and people where applicable as in the case of health risk assessment (Searl, 2012). Risk indicators do vary for different contaminant phases for instance, benthic organisms are more suited for the aqueous phase. It involves exposure principles and health criteria values as well as SGVs. Due to the fact that it may not always be possible to provide a complete set of generic guideline values for all the contaminants identified in CLR8, the framework recommends that certain contaminants will always require site specific evaluation in order to predict their particular behaviour and effect (DEFRA, 2006).

Generic land use scenarios

There are three land uses scenarios that are considered within the model; residential (with or without plant uptake are two different scenarios), allotment and commercial land use. Certain generic assumptions are made for all three of the land use scenarios and these assumption values are incorporated into the CLEA model.

Chemicals, soils, receptors and buildings

Contaminant, pathway and receptor are the three essential elements for determining the existence of risk particularly as it pertains to land contamination and this pollutant linkage relationship is often referred to as the source-pathway-receptor concept (Stanger, 2004). Data relating to chemicals, soils, receptors and buildings are necessary in order to quantify exposure within the CLEA model. Information about the fate and transport of a chemical (discussed in chapter two) as well as the chemical intake/uptake rate would be required. Soil parameters considered by the model include pH, organic carbon fraction, organic matter content and porosity. Characteristics of the receptors (humans) which the model considers include weight, height, skin area, inhalation rate and consumption rate for fruits and vegetables. The model also considers characteristics of the indoor environment through building parameters such as building height, foundation thickness and volume of living space (Hosford, 2009).

Chemical partitioning

It has become increasingly important to incorporate bioavailability considerations into contaminated soil and sediment risk evaluation in recent times (Sorell and McEvoy, 2013). There are two types of bioavailability; absolute bioavailability which is the fraction of an external chemical dose that reaches systemic circulation and relative bioavailability which compares absolute bioavailabilites of different forms of a contaminant (NRC, 2003). Relative bioavailability can also be used for comparing the absolute bioavailiabilities of the different exposure media containing the contaminant. It is particularly important in risk assessment for land contamination because of the possible impact of matrix effect on the bioavailability of soil-associated contaminants (EA, 2005). Matrix refers to the components of a sample other than the analyte of interest and can usually have an impact on the quality of results obtained from a chemical analyses (Patel, 2011). A number of factors currently exist within the model that limit its ability to fully adopt bioavailability or bioaccessibility concepts. Consideration for bioavailability should be done on a site-to-site basis. A major concern with respect to bioavailability is ageing and the fact that bioavailability may change with time (CARACAS, 1998). Even though research is ongoing in this area, more work is still required. One of the major issues which impacts on bioavailability is contaminant sorption by the soil matrix.

Routes of entry & exposure fate pathways

In order for a risk to exist, there has to be a pollutant linkage, and hence exposure pathways are a core component of the model. There are up to ten different pathways from which the model can estimate intake of pollutants however the specific combination of pathways considered would depend on the conceptual model for that particular land use scenario (Jeffries and Martin, 2009a). There are three main routes of entry through which exposure is estimated in the model; ingestion, inhalation and dermal absorption with ingestion being the most common. The pathways are discussed within the results section (3.7) of this chapter. The ten different exposure pathways are listed at the bottom of figure 3.2 below. *Fig 3.3 illustrates the additional possible exposure pathways that would result from groundwater being contaminated by crude oil within the Nigerian scenario.*

Figure 3-3 shows an illustration of a house cross-section with various exposure pathways labeled.

Labels in the illustration:
- Ingesting dust
- Inhaling indoor dusts and vapours
- Ingesting soil
- Inhaling outdoor dusts and vapours
- Rising vapours
- Tracking back of soil/dust from garden into home
- Rising vapours
- Wind-blown dust
- Eating contaminated vegetables and soil adhering to vegetables
- Skin contact with dust
- Skin contact with soil
- Plant uptake

— Exposure pathways   〜〜〜 Migration of contamination

Route		Route	
1	Ingestion of soil	6	Dermal contact with household dust
2	Ingestion of household dust	7	Inhalation of fugitive soil dust
3	Ingestion of contaminated vegetables	8	Inhalation of fugitive household dust
4	Ingestion of soil attached to vegtables	9	Inhalation of vapours outside
5	Dermal contact with soil	10	Inhalation of vapours inside

Figure 3-3 Illustration of the different exposure pathways in the CLEA model (Source: (Jeffries and Martin, 2009b))

Soils are a major sink for organic contaminants in the environment. Soil and water systems are however interrelated by a complex network of processes, and the introduction of HOCs into the water cycle are of great concern (Cisneros and Rose, 2009). These interconnections between terrestrial and aquatic pollutant pathways mean that similar contaminants are often found in soils and sediments. Water quality hence impacts on sediment quality, especially in lakes where the residence time of water is long and contaminants are concentrated over time. (Stewart, 1994; Reible, 2013). Many treatment strategies proposed for the remediation of contaminated sediments therefore arise from those developed for soil management (Akcil et al., 2015). Even though this research work demonstrates the applicability of sorbent-based technologies in soil, the literature review focuses on examples of the technology's applicability in sediment because of the dearth of literature relating to soil. As stated previously, this historic research focus on sediment is because uptake of contaminants is far greater from fluid than from sorbed states (Ogram *et al*., 1985) and because of the immense challenge of contaminated sediments in the USA. Recalcitrant fractions of crude oil that are not easily degraded in soils are of concern in Nigeria and have huge impact on agriculture and livelihood of residents in affected communities. It is important to note that processes developed for the remediation of soils are not always effective to achieve adequate quality

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standards because efficiency depends on characteristics of the contaminated matrix (USEPA, 1993b; Rulkens and Bruning, 2005). Site-specific investigations involving comprehensive and detailed characterizations of subsurface geology and contaminant distribution would therefore be required prior to remedial design. (Fan et al., 2017). Soil deposition processes such as surface runoff and erosion affect water quality by enhancing the transport of dissolved chemicals and sediment-borne pollutants into natural waters. Leaching also impacts on contaminant concentration in natural waters. Runoff causes erosion and transport of soil particles through a river system and subsequent deposition in a reservoir or at sea (IAHS, 1998). Reducing contaminant bioavailability and migration ability in soil would therefore reduce release into the aquatic environment and consequently, sediments (Akcil et al., 2015). The relative distribution and occurrence of contaminants among various phases, as well as the physical relationship between the phases and the soil or sediment also impacts on a contaminant's dissolution properties and its bioavailability (NRC, 2003). Significant concentrations of HOCs may be retained within soils depending on their fate and behaviour in the soil (Semple et al., 2003; Ogbonnaya et al., 2017).
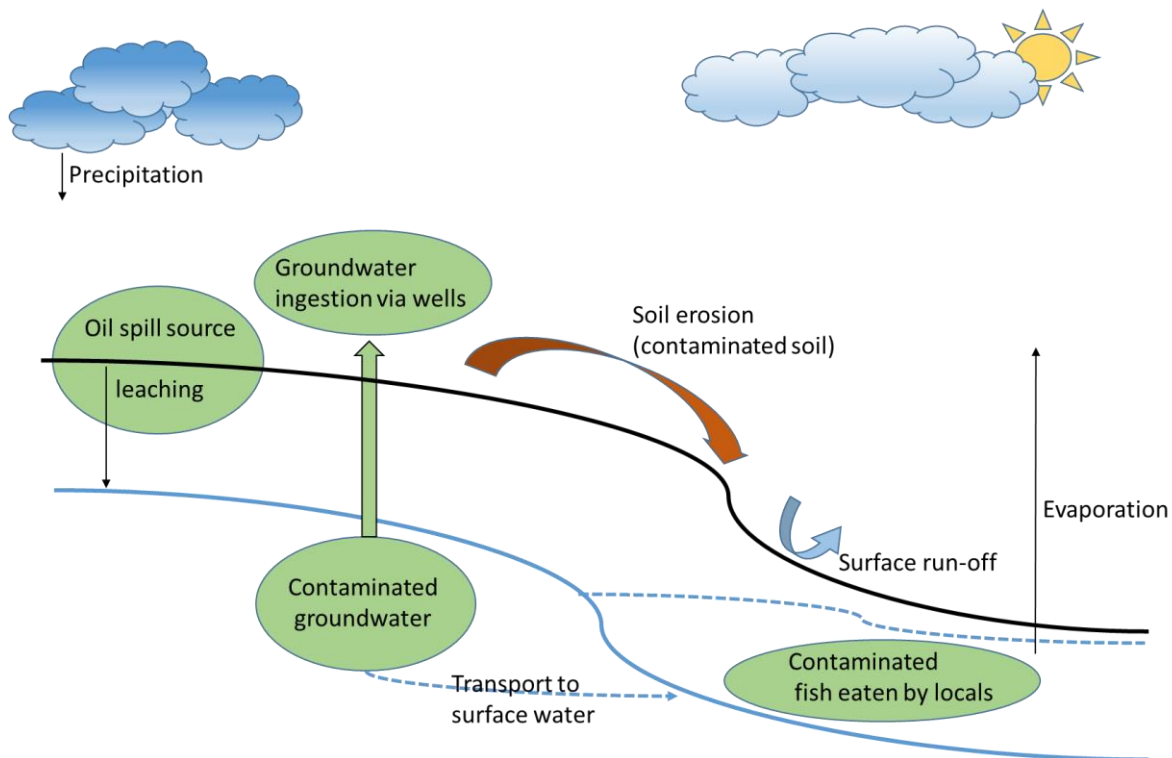
Figure 3-3 Possible exposure pathways from soil and groundwater contamination

3.3.3 *Science Report SC050021/SR4*

This is the Handbook for the CLEA software version 1.05. It however is still relevant for versions 1.06 and 1.071 of the software. It provides information on how to use the CLEA software for deriving generic or site-specific assessment criteria and ADE (Acceptable Daily Exposure)/HCV ratios (Jeffries, 2009b).

3.3.4 *CLEA software*

The CLEA software is based on the modelling approach described in the technical framework document discussed in previous section 3.3.2 of this chapter. Although the software was originally made available to show professionals how published Soil Guideline Values (SGVs) for metals were derived, it was updated to enable further SGVs to be derived for organic contaminants such as naphthalene. However, SGV reports published by the Environment Agency (EA) and DEFRA (Department for Environment Food and Rural Affairs) before 2009, which were prepared using previous framework guidance, have now been withdrawn. Current TOX reports published by the EA contain SGVs for a number of organic contaminants including the BTEX compounds and some metals. The CLEA software is based on Microsoft Excel and its functionality is supported by VBA (Visual Basic for Applications) macros (Mouchel, 2010).

3.4 Risk assessment of crude oil components under the CLEA guidance

A vast array of hazardous substances can usually be found on a contaminated land site, hence many countries have a list of selected priority contaminants (CARACAS, 1998). These priority substances would normally be selected based on factors such as mobility of the contaminant in the environment, potential for bioaccumulation, human toxicity and likelihood of the substance being present in significant concentrations on land affected by past or current industrial use (CARACAS, 1998). PAHs are of particular concern in this work as has been highlighted in chapter two, which involved analysis of 16 unsubstituted PAHs that have been identified as priority pollutants by the EPA. Simultaneous exposure to chemical mixtures is known to generally pose problems for environmental risk assessment (CARACAS, 1998), hence the fact that crude oil is a mixture of many different compounds may make it difficult to accurately assess risks associated to it.

3.5 Current approaches to contaminated land risk assessment; Total concentration

Currently, different countries have different approaches. However, worldwide, the approach predominantly used in the assessment of risk posed by contaminated land to human health is based on total pollutant concentrations (Collins *et al.*, 2013), which are typically the solvent extractable pollutant concentrations. In Nigeria, target values and intervention values are recorded as 'total oil concentrations' in mg/Kg dry weight or ug/L for groundwater. Pollutants which are monitored in Nigeria are aromatic compounds, metals, chlorinated hydrocarbons, PAHs and mineral oil (DPR, 2002)

3.6 Bioavailability and bioaccessibility considerations in risk assessment

Despite significant research efforts within the last five decades, the clean-up of PAH-contaminated soils to background level has achieved only limited success particularly with high molecular weight compounds. The approach to remediation has begun to change within the last decade where remediation interventions are prioritized on the basis of risk (Menzie *et al.*, 2000; Schoof, 2003). This approach shifts the focus away from the commonly measured total chemical concentration of PAHs as other factors also influence the exposure and environmental effects associated with PAHs (Duan *et al.*, 2015). It has been widely established that using total pollutant concentrations may significantly overestimate the amount of pollutant available for uptake by biota, including humans. Overestimating exposure can result in significant additional remediation costs and reduce the sustainability of land for development (Collins *et al.*, 2013). During digestion, only those contaminants that are mobilized by the digestive juices are available for absorption in the digestive tract, while pollutants that are strongly fixed to indigestible particles leave the body without any effect. Research conducted over the last two decades has shown that for many contaminants, the bioavailable concentration which causes a toxic effect in the receptors is usually much less than the total concentration of the contaminant in soils or sediments (Zimmerman *et al.*, 2004; Sorell and McEvoy, 2013). Based on this, it has been suggested that a non-linear relationship exists between contaminant concentration and risk from exposure (Sorell and McEvoy, 2013). According to (Schoof, 2003), adjusting risk assessments to account for lower site-specific bioavailability, would result in increased acceptable clean-up levels without necessarily endangering receptors who come in contact with the site. Remedial approaches which are based on bioavailability hold great potential for decreasing remedial costs and scope of remediation work carried out as well as providing an opportunity for less intrusive

remedial approaches (NRC, 2003). When bioavailability is used in the context of human health risk assessment, it usually refers to relative or absolute absorption of a chemical through the oral, dermal or inhalation routes of exposure (NRC, 2003).

3.7   Implications of experimental results for risk assessment & management

Section 3.3.2e of this chapter lists the three main routes of exposure, however, all 10 pathways will be discussed in this section based on results illustrated in chapter two as well as on available literature data where applicable. At least one CLEA model equation will be examined for each exposure pathway and naphthalene will be used to illustrate the impact of sorption on estimated exposures within each selected equation. This will be done by substituting relevant naphthalene values obtained in chapter two where possible and highlighting differences in results obtained between the different remedial treatment options. Where this is not possible, data from the literature will be used. It is clear that crude oil consists of many toxic compounds in addition to naphthalene, however, naphthalene is used to illustrate bioavailability effects which would equally apply for the exposure calculations of related compound such as other PAHs. Within each section, bioavailability considerations are mainly discussed to highlight the implication that biochar has for the different exposure pathways, and to what extent such effects are accounted for in current exposure assessment formulas. Naphthalene is chosen because it is a semi-volatile compound with all three main uptake modes (inhalation, ingestion, dermal uptake) having some relevance. It is however important to note that while effects may be qualitatively similar for related compounds such as other PAHs, the magnitude of the contribution each pathway makes to exposure would differ between compounds according to compound properties. The main purpose of this chapter is to discuss each pathway's consideration of bioavailability within the CLEA modelling framework by determining, whether K_d or a K_d derivative, is incorporated into the equation. This is because K_d is a measure for the strength of contaminant binding in the soil which will affect the contaminant bioaccessibility. Remediation with biochar aims to reduce exposures by increasing K_d.

Individual pathways within a conceptual model add up to give the total exposure for that scenario. Children are considered the critical receptor for residential and allotment land uses and this is usually the case in most scenarios. Children are thus assumed as the critical receptor for the purpose of this illustration and this will be reflected in parameters used in the calculations in this section. The chemical intake rate (IR) is an important parameter for

estimation of risk and exposure and will therefore be the focus in the naphthalene example. Naphthalene is used to illustrate the impact of sorption within the different pathways of the CLEA model using selected equations from the model as shown below. Empirical soil concentration and vapour concentration values for naphthalene are obtained from the experimental work which is dealt with in detail in chapter two. The results are displayed in tables below each formula.

Within each example, it will be discussed whether the CLEA model factors in bioavailability. Bioavailability can be defined as the fraction of a chemical which is accessible to an organism for absorption and is able to reach systemic circulation in the organism (Semple *et al.*, 2004).

According to (Jia and Batterman, 2010), the main exposure route of naphthalene to the public is inhalation of ambient and indoor air, followed by dietary and non-dietary ingestion.

Within the CLEA model, there used to be a naphthalene guidance value derived from health criteria, however, this has now been withdrawn. All equations used in illustrating the different pathways for naphthalene exposure are obtained from the CLEA model technical guidance document.

3.7.1 *Direct soil & household dust ingestion*

Soil ingestion is a major exposure route for many soil contaminants in humans and it can occur intentionally or unintentionally through hand-to-mouth contact, dust ingestion, or from poorly washed vegetables (Oomen *et al.*, 2002; Lorenzi *et al.*, 2012). Direct ingestion due to hand-to-mouth activity is often the most significant pathway for human exposure to PAH contaminated soils (Jeffries and Martin, 2009b). This combined pathway involves direct ingestion of contaminant through oral intake of either soil or dust. Direct soil ingestion and household dust ingestion are modelled for by a single equation within the CLEA model which uses a single combined default value for soil and dust ingestion. This is because there is currently insufficient knowledge to separate ingestion of soil from soil-derived dust (Jeffries, 2009a). Not much is known about the fate of dust-associated contaminant in the body.

Studies by USEPA (2006) stated difficulty in differentiating between soil and dust within the current recommended value for soil ingestion rate. It however admitted that indoor dust is probably an important component (USEPA, 2006). This is the position that is taken

concerning dust-associated contaminant throughout the discussions in this chapter. This is an important pathway for semi- or non-volatile contaminants such as polycyclic aromatic hydrocarbons (PAH) particularly for children (IGHRC, 2010).

Equation 1 below is used in the CLEA model for cumulative calculation of the soil and dust Intake Rate (IR). The total concentration of the chemical in soil (C_s) is the key consideration within this equation. There is currently no provision to factor in bioavailability for this pathway as the model assumes that all of the ingested contaminant is taken up by the body.

Equation 3-1

$$IR_{direct\ soil\ and\ dust\ ingestion} = C_S S_{ING}$$

Where: *IR* is the chemical intake rate from direct soil and dust ingestion, mg day^{-1}

Cs is the total concentration of the chemical in soil, mg g^{-1}

S_{ING} is the direct soil and dust ingestion rate, [default value for ages 0-16 for residential/allotment land use scenario = 0.1g/day ;] (Jeffries and Martin, 2009a).

Results in chapter two showed that soil amendment with biochar impacts on total and bioavailable PAH concentrations. This trend is again observed in the naphthalene example (Table 3-1 below) where the batch with biochar amended from the start (C) seemingly has the lowest naphthalene ingestion rate (0.00001mg/day) among the three oil-amended batches; C,D and E. In the experimental study, PAHs were extracted from soil by accelerated solvent extraction (ASE) using hexane:acetone. The results imply that the presence of biochar reduced the hexane:acetone extractable pollutant concentrations resulting in seemingly lower total concentrations in soil. It may well be that there was a biochar associated PAH residual left in the soil after ASE extraction, however, such as residual would be considered to present minimal risks, as ASE is a rigorous extraction procedure (Brockmeyer *et al.*, 2015) using high temperature, high pressure and organic solvents. In fact, it is very likely that the bioaccessible pollutant concentration in biochar amended soil is lower than the concentration measured by ASE extraction. Even though Equation 3-1 does account for the fact that non-solvent extractable pollutants are not bioaccessible, the effect of biochar sorption on the

pollutant accessibility is likely not fully seen in the estimated ingestion rate via this pathway. If this biochar sorption effect was to be taken into account, the bioaccessible concentration is likely to be less than Cs. In-vitro test systems such as gastric and gastro-intestinal models which simulate the human gastrointestinal tract have been used to determine oral bioaccessibility of PAH and metals in soil and sludge samples (Hack and Selenka, 1996; Oomen *et al.*, 2002; Lorenzi *et al.*, 2012). These physiologically-based extraction tests (PBET) help in assessing the mobilization of these contaminants from soil during digestion (Oomen *et al.*, 2002; Meyer *et al.*, 2015). Based on this literature and also earthworm studies (Gomez-Eyles *et al.*, 2011; Jakob *et al.*, 2012), it is known that there would be less uptake of the pollutant from the biochar-amended soil into the gastrointestinal system upon ingestion due to limited oral bioaccessibility. Earthworms (*Eisena fetida)* have been demonstrated to be good bioaccumulators of PCBs and other organic compounds from soil (Denyes *et al.*, 2012). Contaminants have to be mobilized by digestive juices in order to be available for absorption in the digestive tract and those which remain fixed to indigestible particles usually leave the body without any effect (Hack and Selenka, 1996). A review of data from more than 10 bioaccessibility studies involving varying experimental set-ups /models was carried out by Meyer *et al.* (2015). The study showed that PAH bioaccessibility ranges between 0% and 100% (Meyer *et al.*, 2015). Work by Meyer *et al.* (2015) involving four different geosorbents (pure quartz sand, Na-montmorillonite clay, Pahokee peat, and charcoal "Sommerhit") showed lowest bioaccessibility results for the charcoal (0.1±0.1 % for Σ10 PAH-d) indicating that black carbon is a very strong sorbent and its presence in soil samples can almost totally reduce PAH bioaccessibility in the digestive tract. Studies by (Rhodes *et al.*, 2008) showed that biochar addition led to significant reductions ($p < 0.001$) in phenanthrene extractability following a non-exhaustive aqueous-based extraction procedure known as hydroxypropyl-β-cyclodextrin (HPCD) extraction. These effects were attributed to the strong sorption of the contaminants within the microporous biochar matrices and difficulty of extractants to displace target chemicals from these sorption sites. Similarly, studies by (Sopeña *et al.*, 2012) observed that Hydroxypropyl-β-cyclodextrin (HPCD) extractability of the herbicide isoproturon (IPU) was also reduced following biochar amendment. In addition, studies by (McLeod *et al.*, 2007) involving clams (*M. balthica*) showed that activated carbon amendments of 0.34, 1.7 and 3.4% wet weight caused average reductions in PCB bioaccumulation of 22, 64 and 84% respectively relative to untreated sediment. Based on this, we can see that one should introduce an additional factor $F_{oral\ bioaccessibility}$ in Equation

3-1 with values ranging between 0 – 1, to account for the contaminant bioaccessibility in the digestive tract.

Table 3-1 Naphthalene intake rate calculation for the 'Direct soil & household dust ingestion' pathway

	A	B	C	D	E
Treatment	**No oil**	**No oil + biochar**	**Oil + biochar added at start**	**Oil + biochar 5mths**	**Oil**
Cs (mg/g)	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
$S_{ING\ (g/day)}$	0.1	0.1	0.1	0.1	0.1
IR(mg/day)	**0**	**0**	**0.00001**	**0.00068**	**0.00002**

Results in Table 3-1 show a 68 fold difference between the calculated ingestion rates of naphthalene for microcosms amended with biochar at start (C) and amended after 5 months (D) based on the total measured naphthalene concentration in soil using the ASE method. This difference shows that the effectiveness of biochar amendment is strongly dependent on the time of biochar addition. After 5 months, readily biodegradable crude oil components may have been transformed into metabolites which could have competed with naphthalene for biochar sorption sites (fouling effect), reducing the effectiveness of biochar as a naphthalene sorbent in the ASE extraction. Alternatively, naphthalene may have already associated with weaker sorption sites in the soil by month 5, when the biochar was added to microcosms D, reducing naphthalene mass transfer to the strong biochar sorption sites. In any case, these examples illustrate the complexity of contaminant binding in biochar amended soil. Risk assessors may therefore prefer to err on the side of caution, as in the above calculation, by assuming that the total contaminant concentration in soil is bioaccessible. Ideally, however, in-vitro tests or similar methods would be used to more accurately determine the bioaccessibility of the contaminants in soil from experiments. It would then be useful if the CLEA model had a factor; $F_{oral\ bioaaccessibility}$ (Jeffries and Martin, 2009a) which could account for what fraction of the total pollutant mass ingested with soil is taken up during gut passage, as this would likely cause a further reduction in the estimated exposure

risks for the biochar amended batches than is currently observed. Such in-vitro tests could then be conducted, if predicted intakes are close to thresholds. If there was an additional factor that considers bioavailability, the results obtained in the naphthalene example would be different and would correspond more with what is obtainable in literature regarding bioavailability.

3.7.2 *Ingestion of soil attached to vegetables*

This pathway is often referred to as indirect soil ingestion in the CLEA model and uptake of contaminant is usually through consumption of dirt entrained with fruit and vegetables. It is practically the same as direct soil and dust ingestion (discussed in section 3.7.1) as it looks at the contamination obtained from the 'soil attached to vegetables' rather than from 'contaminated vegetables' (discussed in section 3.7.3). The discussions on bioavailability are therefore also applicable here. In Nigeria, there is a likelihood of members of the local community ingesting vegetables with soil attached even though vegetables are traditionally washed before consumption. Contamination through this route is however not expected to be as significant as through ingestion of contaminated fruits and vegetables. Equation 3-2 below shows the complex ingestion rate formula for the six produce groups described in the CLEA model guidance documents. For the purpose of illustration of bioaccessibility issues, however, IR will represent ingestion rate for 'green vegetables only' as opposed to the summation of ingestion rates for the six produce groups, since effects will be the same for all groups. The values imputed will therefore be the CLEA model default values for green vegetables.

Equation 3-2

$$IR_{indirect\ soil\ ingestion} = \sum_{all\ produce\ groups} C_s\ SL_x\ PF_x\ CR_x\ BW\ DW_x\ HF_x$$

IR is the chemical intake rate from indirect ingestion from attached soil, mg day^{-1}

Cs is the total chemical concentration in soil, mg/g dw [measured]

SLx is the soil loading factor, [0.001 per g dw]

PFx is the food preparation correction factor, dimensionless [0.2]

CRx is the food consumption rate per unit body weight, g fw/kg bw/day [6.85 toddler aged 2-4]

BW is the body weight, kg [19.7 for a six year old female]

DWx is the fresh plant weight to dry plant weight conversion factor, [0.096g dw /g fw]

HFx is the homegrown fraction, dimensionless [1]

Equation 2 considers parameters relating to the total soil concentration, production and preparation of the food as well as receptor characteristics such as body weight. $''SL_x \, PF_x \, CR_x \, BW \, DW_x \, HF_x{}_{''}$ is an indication of how much soil is consumed along with the vegetable while Cs, just like in Equation 3-1 is the total contaminant concentration in soil. Hence, this equation also assumes that the total concentration of pollutant in the soil is absorbed as the bioaccessibility fraction is not accounted for. However, as previously mentioned, many would argue that this assumption is inherently wrong. It does not consider the extent of adsorption by human receptors which is a necessary factor in order for an adverse health effect to occur (Frankenberger, 2001). In reality, equation two should also be multiplied by a factor $F_{oral\ bioaccessibility}$ where $F_{oral\ bioaccessibility}$ = oral bioaccessibility factor in order to obtain the chemical intake rate (IR).

Table 3-2 Naphthalene intake rate calculation for the 'Ingestion of soil attached to vegetables' pathway

	A	B	C	D	E
Treatment	**No oil**	**No oil + biochar**	**Oil + biochar added at start**	**Oil + biochar 5mths**	**Oil**
Cs (mg/g)	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
SLx (per g dw)	0.0010	0.0010	0.0010	0.0010	0.0010
PFx (dimensionless)	0.2000	0.2000	0.2000	0.2000	0.2000
CRx (g fw/kg bw/day)	6.8500	6.8500	6.8500	6.8500	6.8500
BW (kg)	19.7000	19.7000	19.7000	19.7000	19.7000
DWx (096g dw /g fw)	0.0960	0.0960	0.0960	0.0960	0.0960
HFx (dimensionless)	1.0000	1.0000	1.0000	1.0000	1.0000
IR$_{\text{indirect soil ingestion for green vegetables}}$ (mg/day)	4.8544E-08	3.8957E-08	3.6681E-07	1.7674E-05	4.2736E-07

3.7.3 *Ingestion of contaminated fruits and vegetables*

PAH can contaminate plants through several pathways including absorption of volatile PAH from air, aerial deposition and penetration of soil & dust onto leaves. Root uptake, however, is considered the major pathway through which PAHs accumulation in plant tissues, particularly for high molecular weight PAHs (Fismes *et al.*, 2002; IPCS, 1998.). This pathway estimates the transfer of chemicals from soil into fruit and vegetable grown in contaminated ground. The six produce groups that are considered within the CLEA model are green vegetables, root vegetables, tuber vegetables, herbaceous fruit, shrub fruit and tree fruit (Jeffries and Martin, 2009a). An estimation of the human daily intake and uptake of PAH via this route in addition to 'Ingestion of soil attached to vegetables' will help to assess the health

risks due to consumption of food grown on contaminated sites. In addition to the ingestion rate (IR), the concentration factor (CF) is another key parameter that is considered here. Also known as the soil-to-plant concentration factor, the CF is a useful concept for predicting the relationship between the concentration of an organic chemical in soil and that in plant. Bioconcentration is the uptake and concentration of anthropogenic substances into a living organism from its environment (Bernes, 1998) and is often expressed by a Bioconcentration Factor (BF) which may also be referred to as Concentration Factor (CF). The hydrophobicity of the pollutant as well as the organic content of the soil and soil sorption are among factors which affect uptake of organic pollutants into vegetation (Hellström, 2004). Field studies carried out by Denyes *et al.* (2013) showed reduction in concentration of PCB taken up into plants (*Cucurbita pepo* root tissue) by 74%, 72% and 64% upon addition of 2.8% GAC (Granular Activated Carbon), Burt's biochar and BlueLeaf Biochar respectively. According to them, the decrease in uptake and also increase in plant growth was likely due to the strong sorption of the PCB molecules unto the carbon particles. Additionally, a field lysimeter study on PAH-contaminated soil by Jakob *et al.* (2012) investigated the impact of 2% powder and granular activated carbon (PAC and GAC) on the PAH bioaccumulation by earthworms and plants. Results showed significant reduction of biota to soil accumulation factors (BSAFs) of PAHs in earthworms and plants with reductions ranging between $72 \pm 19\%$ and $46 \pm 36\%$. Based on this, it would be expected that the difference between biochar-amended soil and non-biochar amended soil would be about a factor of 2 (50% reduction) as the CF is related to the biota to soil accumulation factor. The difference in the calculated CF values for amended and unamended microcosms in the naphthalene example (Table 3-3) is however far greater than a factor of 2. It thus appears that the effectiveness of biochar may have been overpredicted. The fact that the CF value is variable for the different soils, however, further confirms that equation 3 considers sorption effects on naphthalene bioavailability. This is because equation 3 depends on K_d values and so the sorbent strength impacts on the estimated plant uptake. Equation 3-3 below and Table 3-3 show how the CF for green vegetables is calculated.

Equation 3-3

$$CF_{green\ vegetables}$$
$$= \left(10^{0.95\ \log K_{ow}-2.05} + 0.82\right)\left(0.784\ X\ 10^{-0.434(\log K_{ow}-1.78)^2}\right)$$
$$/2.44 \left[\frac{\rho_s}{\theta_w + \rho_s\ K_{oc}\ f_{oc}}\right]$$

Where

CF is the calculated soil-to-plant concentration factor for green vegetables, mg/ g fw plant over mg /g dw soil

K_{ow} is the octanol-water partition coefficient for the chemical, dimensionless

ρs is the dry soil bulk density, g/ cm^3 [Density of naphthalene at 20°C = 1.145 g/mL (ATSDR, 2005)]

θ_w is the soil-water content by volume, cm^3/ cm^3

Residual water content of sand = 0.07cm^3/cm^3 (IGHRC, 2010)

K_{oc} is the organic carbon-water partition coefficient for the contaminant, cm^3/ g dw

f_{oc} is the fraction of organic carbon in the soil, dimensionless

$K_d = K_{oc}\ f_{oc}$ (Ryan *et al.*, 1988) = 2144.372cm^3/g dw (measured)

Log K_{ow} of naphthalene = 3.29 (USEPA, 2003)

Log K_{oc} of naphthalene = 2.97 (USEPA, 2003)

Residual water content of sand = 0.07cm^3/cm^3

F_{oc} is an index for organic carbon content that gives an idea of the amount of organic matter present in soil which is an important sorbent matrix for hydrophobic organic contaminants and some metals. It is therefore an indicator of potentially reduced bioavailability if the organic carbon content of soil is high (NRC, 2003). The CLEA model uses the estimation Kd=foc*Koc. However, Koc is different for different types of organic carbon (Karapanagioti and Sabatini, 2000). Instead of having foc*Koc in the formula, the formula should use measured K_d values to account for the effects of biochar on the pollutant accumulation by

vegetables from soil. It is important to note that the model only considers intake from fruits and vegetables. It discounts intakes from other sources (such as meat and dairy produce) as background intakes (Jeffries and Martin, 2009a). In the CLEA model, x represents the summation of the six produce groups however for the purpose of this illustrative calculation, x represents 'green vegetables' summation only. For green vegetables, CF is the ratio of stem concentration to soil concentration (Ryan *et al.*, 1988). Due to the fact that there are large variations in the reported uptake of contaminants from soil in the literature, the CLEA model employs a cautious approach which uses different models for organic and inorganic chemicals and different vegetable produce groups (IGHRC, 2010).

Although it is possible to estimate sorption coefficient from K_{ow}, it is not ideal as it is prone to errors. This is because the K_{ow} is normally based on the chemical properties of the compound whereas the K_d is based on both the properties of the chemical and the soil. Properties of soil are accounted for in the formula via f_{oc}, however, biochar tends to be a much stronger sorbent than ordinary soil organic carbon. The measure K_d value were therefore used in the calculation en lieu of $K_d = f_{oc}K_{oc}$.

Table 3-3 Naphthalene Concentration Factor (CF) calculation for the 'ingestion of contaminated fruits and vegetables' pathway. (Only green vegetables is considered in this illustration)

	A	B	C	D	E
Treatment	**No oil**	**No oil + biochar**	**Oil + biochar added at start**	**Oil + biochar 5mths**	**Oil**
Log K_{ow} (dimensionless)	3.29	3.29	3.29	3.29	3.29
ρs (g/mL)	1.145	1.145	1.145	1.145	1.145
θ_w (cm^3/ cm^3)	0.07	0.07	0.07	0.07	0.07
K_d (cm^3/g)	2144.372	2320.164	9710.106	834655.3	774.6742
CF (mg/ g fw plant over mg /gdw soil)	1.95E-04	1.80E-04	4.31E-05	5.02E-07	5.40E-04

Equation 3-4

$$IR = \sum_{all\ produce\ groups} C_s\ CF_x\ CR_x\ BW\ HF_x$$

IR is the chemical intake rate from consumption of homegrown produce, mg day^{-1}

Cs is the total concentration of the chemical in soil, mg g^{-1} dw

CFx is the soil-to-plant concentration factor for each produce group, mg/ g fw plant over mg /g dw soil [calculated CF$_{green\ vegetables}$ in equation 4 above]

CRx is the food consumption rate per unit body weight for each produce group, g fw kg^{-1} bw day^{-1} [6.85 toddler aged 2-4]

BW is the body weight, kg [19.7 for a six year old female]

HFx is the homegrown fraction for each produce group, dimensionless

Equation 3-4 calculates the Intake Rate (IR) for green vegetables from the CF values obtained in Table 3-3 above.

Table 3-4 Naphthalene intake rate calculation for the 'ingestion of contaminated fruits and vegetables' Pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
Cs (mg g^{-1} dw)	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
CFx (mg/ g fw plant over mg /g dw soil)	0.0002	0.0002	0	0	0.0005
CRx (g fw kg^{-1} bw day^{-1})	6.85	6.85	6.85	6.85	6.85
BW (kg)	19.7	19.7	19.7	19.7	19.7
HFx (dimensionless)	1	1	1	1	1
IR (mg/day)	5.0567E-07	4.0580E-07	0.0000E+00	0.0000E+00	1.1129E-05

3.7.4 *Dermal contact with soil/ outdoor dermal uptake*

This pathway considers uptake of contaminants from soil through contact with the skin. It is generally assumed that solids adhere to the skin only on areas of the body not covered by clothing (USEPA, 2006) and even though a certain amount of contaminant may be absorbed from the surface of the skin, not all of this is expected to be absorbed into systemic circulation. Dermal uptake is greatly impacted not only by the amount of soil which the subject comes in contact with but also by how long and how much of the soil adheres to the skin hence in addition to the Cs, the skin-soil adherence factor (AF) is another parameter that is important to this pathway. AF estimates the amount of soil that adheres to the skin per unit of skin surface area. (MADEP, 1995). Exposure estimations studies often assume that the

material to which humans are exposed is the same as the matrix that was studied in order to characterize exposure. Dermal bioavailability studies by Ruby and Lowney (2012) however demonstrates that the soil particle size which is used in oral bioavailability and bioaccessibility studies impacts on the accuracy of the estimated exposure. Results by (McLeod *et al.*, 2007) showed that sediment amendment with activated carbon decreased bioaccumulation not only with increase of dosage but also with decrease in particle size. Bioaccumulation reductions of by 41, 73 and 89% were observed upon amendment with carbon particles of 180 to 250, 75 to 180, and 25 to 75μm respectively. These studies illustrate just how complex the pathway is indicating a need to pay careful attention to what fraction of the soil is actually adhering to the skin.

Passive sampling experiments in Chapter 2 used polyethylene passive samplers as a proxy to measure the pollutant availability. The sheet of plastic (polyethylene) embedded in soil is not dissimilar to skin with adhering soil. Polyethylene passive sampler results suggest that the availability of PAHs for mass transfer from soil to a sheet of plastic (or skin) is strongly altered by biochar amendment, coinciding with a higher derived sorption coefficient in the biochar amended batches compared to the unamended batches. In Equation 3-5, the dermal absorption fraction ABS_d is, on the other hand, a constant and there is no provision to incorporate K_d into the formula, even though passive sampling results would suggest lower uptake from biochar- amended microcosms for an equal total soil concentration Cs. This pathway does therefore not explicitly consider cutaneous bioavailability. It has been argued that bioavailability processes are an implicit component of human health risk assessment (NRC, 2003). It would therefore be beneficial if this pathway incorporated the effect of biochar sorption into the dermal absorption fraction (ABS_d), perhaps by deriving ABS_d from polyethylene passive sampler or pig skin tests as an in-vitro assessment for dermal uptake, similar to the suggested use of digestive fluid extraction methods for the derivation of oral bioaccessibility factors.

Equation 3-5

$$IR = C_s \, n \, AF \, ABS_d \, A_{skin} \, X \, \frac{1}{1000} \, g \, mg^{-1} \, x \, 10000 cm^2 m^{-2}$$

Where: IR is the chemical uptake rate from outdoor dermal contact with soil, mg day^{-1}

Cs is the total concentration of the chemical in soil, mg g^{-1} dw

AF is the soil-to-skin adherence factor, [1 mg/cm^2 for residential exposure for a child]

ABS$_d$ is the dermal absorption fraction, dimensionless [0.1 is CLEA model default value for organic chemicals]

A$_{skin}$ is the exposed skin area, m^2 [0.068 for a 6 year old female for residential & allotment land use]

n is the number of daily soil contact events, day-1 [1 is default CLEA assumption]

Table 3-5 Naphthalene intake rate calculation for the 'outdoor dermal uptake' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
Cs (mg g^{-1} dw)	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
AF (mg/cm^2)	1	1	1	1	1
ABS$_d$ (dimensionless)	0.1	0.1	0.1	0.1	0.1
A$_{skin}$ (m^2)	0.068	0.068	0.068	0.068	0.068
n (day^{-1})	1	1	1	1	1
IR (mg/day)	1.87E-05	1.50E-05	1.42E-04	6.82E-03	1.65E-04

3.7.5 *Dermal contact with Household dust/ indoor dermal uptake*

Referred to in the CLEA model as 'indoor dermal contact with indoor dust', this pathway and its parameters are similar to the 'outdoor dermal uptake', however it has an additional parameter; the 'minimum transport factor' (TF). In Equation 3-6, the TF is assumed to be proportional to the mass fraction of soil in indoor dust and the default value for the mass fraction is 50 percent. The default value of 0.5 g g^{-1} dry weight (DW) for the soil-to dust

transport factor is therefore used and would be considered a conservative assumption (Jeffries and Martin, 2009a). The CLEA framework models outdoor and indoor dermal contact separately, however, in terms of rationale concerning bioavailability considerations, they are the same. As mentioned previously, not much is known about the fate of dust. Bioavailability should be considered here as well; evidence for this has been given in section 0.

Equation 3-6

$$IR = C_s \, TF \, n \, AF \, ABS_d \, A_{skin} \, X \, \frac{1}{1000} \, g \, mg^{-1} \, x \, 10000 cm^2 m^{-2}$$

Where: IR is the chemical uptake rate from indoor dermal contact with soil, mg day^{-1}

Cs is the total concentration of the chemical in soil, mg g^{-1} dw

TF is the soil to indoor dust transport factor, g g^{-1} dw [default value = 0.5]

AF is the soil-to-skin adherence factor, [=0.06 mg/ cm^2 for residential exposure for a child]

ABS$_d$ is the dermal absorption fraction, dimensionless [0.1 is CLEA model default value for organic chemicals]

A$_{skin}$ is the exposed skin area, m^2 [0.068 for a 6 year old female for residential & allotment land use]

n is the number of daily soil contact events, day^{-1} [default CLEA assumption value = 1]

Table 3-6 Naphthalene intake rate calculation for the 'indoor dermal uptake' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
Cs (mg g^{-1} dw)	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
TF (g g^{-1} dw)	0.5	0.5	0.5	0.5	0.5
AF (mg/ cm^2)	0.06	0.06	0.06	0.06	0.06
ABS$_d$ (dimensionless)	0.1	0.1	0.1	0.1	0.1
A$_{skin}$ (m^2)	0.068	0.068	0.068	0.068	0.068
n (day^{-1})	1	1	1	1	1
IR (mg day^{-1})	3.82E-08	3.07E-08	2.89E-07	1.39E-05	3.36E-07

3.7.6 *Inhalation of fugitive dust from soil /outdoor dust inhalation*

Factors affecting estimation of exposure via the inhalation route include; inhalation rate, airborne chemical concentration and bioavailability (Paustenbach, 2015), however, not much is known about the fate of dust in the body. For soil, we know when ingested, it is eventually excreted and our concern is usually what the uptake is between ingestion and excretion. For the dust however, it is uncertain if it is excreted or if the dust stays in the lung. The author is not aware of any studies which link bioavailability to the exposure that is derived from dust and there is no evidence that sorption reduces exposure via this pathway. It thus seems appropriate to take a cautious approach and assume that all of the contaminant is potentially bioavailable.

In order to determine the IR, the PM10 emission flux from soil, J_w, and then the particulate emission factor PEF, must first be calculated.

Equation 3-7

$$J_w = 0.036 \, (1 - V) \left(\frac{u}{u_t}\right)^3 F(x) \, X \, \frac{1}{3600} \, hr \, s^{-1}$$

Where: *Jw* is the PM10 emission flux, g m^{-2}s^{-1}

V is the fraction of outdoor surface cover (equals zero for bare soil), dimensionless [0.75 for residential land use]

u is the mean annual wind speed at height of 10 m, m s^{-1} [5]

u_t is the threshold value of wind speed at height of 10 m, m s^{-1} [7.2]

F(x) is an empirical function of *x*, dimensionless [1.22]

J$_w$ = **1.02144E-06**

Equation 3-8

$$PEF = \frac{Q}{C_{wind}} \, X \, \frac{1}{J_w}$$

Where: *PEF* is the particulate emission factor, [m^3 kg^{-1}]

Q/C$_{wind}$ is the air dispersion factor, [2.4E + 03 g m^{-2} s^{-1} per kg m^{-3} representative of a six year old child exposed to residential land use at a height of 0.8m]

J$_w$ is the PM$_{10}$ emission flux, [calculated = 1.02144E-06 g /m^2 /s]

PEF = **2.35E+ 09**

Equation 3-9

$$IR = C_s \left[\frac{1}{PEF}\right] V_{inh} \left[\frac{T_{site}}{24}\right] X \, 1000 \, g \, kg^{-1}$$

Where: IR is the chemical intake rate from inhalation of dust from ambient air, mg day^{-1}

Cs is the total concentration of the chemical in soil, mg g^{-1} dw

PEF is the particulate emission factor, m^3 kg^{-1} [calculated = 2.35E+09]

V_{inh} is the daily inhalation rate, [10m^3/day for a six year old child]

T_{site} is the outdoor site occupancy period, [1 hour day^{-1} for a six year old child in the garden]

Table 3-7 Naphthalene intake rate calculation for the 'outdoor dust inhalation' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
Cs (mg g^{-1} dw)	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
PEF (m^3 kg^{-1})	2.35E+09	2.35E+09	2.35E+09	2.35E+09	2.35E+09
V$_{inh}$ (m^3/day)	10	10	10	10	10
T$_{site}$ (hour day^{-1})	1	1	1	1	1
IR (mg day^{-1})	3.32E-12	2.67E-12	2.51E-11	1.21E-09	2.92E-11

3.7.7 *Inhalation of fugitive household dust/ indoor dust inhalation*

This pathway is similar to inhalation of outdoor dust and although it is modelled for separately within the CLEA framework, the arguments are the same.

Equation 3-10

$$IR = \left[C_s \left[\frac{1}{PEF} \right] \ X \ 1000 \ g \ kg^{-1} + (C_s \ TF \ DL) \right] V_{inh} \left[\frac{T_{site}}{24} \right]$$

Where: IR is the chemical intake rate from inhalation of dust from indoor air, mg day^{-1}

Cs is the total concentration of the chemical in soil, mg g^{-1} dw

TF is the soil-to-dust transport factor according to soil type, g g^{-1} dw [0.7]

PEF is the particulate emission factor, m^3 kg^{-1} [2.35E+09]

DL is the indoor dust loading factor, [5.0E-5g m^{-3}]

Vinh is the daily inhalation rate, m^3 day^{-1} [10m^3 day^{-1} recommended for a six year old child]

Tsite is the indoor site occupancy period, [19 hour day^{-1} for a six year old child in the garden]

Table 3-8 Naphthalene intake rate calculation for the 'indoor dust inhalation' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	O+ biochar 5mths	Oil
Cs (mg g^{-1} dw)	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
TF (g g^{-1} dw)	0.7	0.7	0.7	0.7	0.7
PEF (m^3 kg^{-1})	2.35E+09	2.35E+09	2.35E+09	2.35E+09	2.35E+09
DL (g m^{-3})	5.00E-05	5.00E-05	5.00E-05	5.00E-05	5.00E-05
V$_{inh}$ (m^3 day^{-1})	10	10	10	10	10
T$_{site}$ (hour day^{-1})	19	19	19	19	19
IR (mg day^{-1})	5.25E-09	4.22E-09	3.97E-08	1.91E-06	4.63E-08

3.7.8 *Inhalation of vapours outside*

Volatilization experiments in chapter 2 demonstrated how foam plug acts like a sink for all contaminants evaporating from the soil. Results showed a clear effect of sorption on volatilization as well as a clear biphasic dissipation of the VOCs in which there was rapid dissipation followed by a much slower release phase. (Beck *et al.*, 1995) argue that this sort of biphasic desorption kinetics has implications for existing soil-quality guidelines. They discuss the unlikeliness of any significant change in contaminant concentration occurring during the residual phase in the absence of any engineering/remedial intervention/action or

change in environmental conditions. They defined the concentration in the residual phase as a kinetically constrained soil quality limit (KCSQL) and have applied it to selected examples of contaminant dissipation from the literature, including PAHs and PCBs in a range of soils. Even though there is no provision to directly substitute the measurements from the volatilization experiment into the equation, inputting different K_d values for K_{sw} (which has the same definition as K_d) in the CLEA formulas helps account for difference in volatilization which are due to sorption. Results in Table 3-9 below therefore indicate less volatilization with biochar addition. This is in line with the experimental results that showed that soils with a high K_d produced lower uptake by foam plugs.

This pathway incorporates K_{aw} (air-water partition coefficient) as well as K_{sw} (total soil-water partition coefficient) in the CLEA model, and K_{sw} is the same as K_d. The benefits of sorption are thus accounted for within this formula hence the vapor pathway can be influenced by inputting empirical K_{sw} (or K_d) values.

In order to determine IR; D_{eff}, VF and then C_{air} first need to be determined.

$D_{eff} =$ is the effective diffusion coefficient for unsaturated soils

$D_{air} =$ Diffusion coefficient in air $= 5.90E\text{-}02$ cm^2/s

$D_{water} =$ Diffusion coefficient in water $= 7.50E\text{-}06$ cm^2/s (USEPA, 1996)

$\theta_a =$ air-filled soil porosity (Lair/Lsoil) 0.28 cm^3/cm^3

$\theta_w =$ water-filled soil porosity (Lwater/Lsoil) 0.15 cm^3/cm^3

$\theta_T =$ total soil porosity (Lpore/Lsoil) 0.43 (DEQ, 2007)

$K_{aw} = 1.74 \times 10^{-2}$ (Jones, 2013) cm^3/cm^3

Equation 3-11

$$D_{eff} = D_{air}\frac{\theta_a^{3.33}}{\theta_T^2} + D_{water}\frac{\theta_a^{3.33}}{K_{aw}\,\theta_T^2} \; X \; 10000 cm^2 m^{-2}$$

$D_{eff} = 0.374$

Equation 3-12

$$VF = \frac{\rho_s}{\frac{1}{10} \, X \, Q/C_{wind}} \sqrt{\frac{4D_{eff}}{\pi \tau \, X \, 31536000 \, s/yr} \, X \, \frac{K_{aw}}{K_{sw} \, \rho_s}}$$

Where: VF is the volatilization factor from surface soil to ambient air, g cm^{-3}

ρ_s is the dry bulk soil density, g cm^{-3} [Density of naphthalene at 20°C = 1.145 g/mL (ATSDR, 2005)]

Q/C_{wind} is the air dispersion factor, [2.4E + 03 g m^{-2} s^{-1} per kg m^{-3} representative of a six year old child exposed to residential land use at a height of 0.8 m]

D_{eff} is the effective diffusion coefficient for unsaturated soils, 0.374 cm^2 s^{-1} (calculated)

τ is the averaging time for surface emission vapour flux, year (CLEA default value = exposure duration = 6 years)

K_{aw} is the air-water partition coefficient at ambient temperature, cm^3 cm^{-3} 1.74 x 10^{-2} (Jones, 2013).

K_{sw} is the total soil-water partition coefficient, cm^3 g^{-1} (measured K_d values)

Table 3-9 Naphthalene volatilization factor calculation for the 'outdoor vapour inhalation' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
K_d	2144.4	2320.2	9710.1	834655.3	774.7
VF (g/cm3)	6.296E-10	6.053E-10	2.959E-10	3.191E-11	1.048E-09

Equation 3-13

$$C_{air} = C_s \, VF \, X \, 1000000 \, cm^3 m^{-3}$$

Where: C_{air} is the ambient air concentration at the receptor height, mg m^{-3}[ ]

C_s is the total soil concentration, mg g^{-1}[ ]

VF is the volatilisation factor from surface soil to ambient air, g cm^{-3}[ ]

Table 3-10 Naphthalene ambient air concentration calculation for the 'outdoor vapour inhalation' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
C_s (mg g^{-1})	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
VF (g cm^{-3})	6.296E-10	6.053E-10	2.959E-10	3.191E-11	1.048E-09
C_{air} (mg m^{-3})	1.18E-08	9.10E-09	4.19E-08	2.18E-07	1.73E-07

Equation 3-14

$$IR = C_{air} V_{inh} \left[\frac{T_{site}}{24} \right]$$

Where: IR is the chemical intake rate from inhalation of vapour from ambient air, mg day^{-1}

C_{air} is the ambient air concentration of the chemical, mg m^{-3} [ ]

V_{inh} is the daily inhalation rate, [10m^3/day for a six year old child]

T_{site} is the outdoor site occupancy period, [1 hour day^{-1} for a six year old child in the garden]

Table 3-11 Naphthalene intake rate calculation for the 'outdoor vapour inhalation'' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
C_{air} (mg m^{-3})	1.18E-08	9.10E-09	4.19E-08	2.18E-07	1.73E-07
V_{inh} (m^3/day)	10	10	10	10	10
T_{site} (hour day^{-1})	1	1	1	1	1
IR (mg day^{-1})	4.92E-09	3.79E-09	1.75E-08	9.07E-08	7.20E-08

3.7.9 *Inhalation of vapours inside*

This pathway is similar to inhalation of outdoor vapour and although it is modelled for separately within the CLEA framework, the arguments are the same.

In order to determine IR, Q_b, α and then C_{air} first need to be determined.

Equation 3-15

$$Q_b = \left(H \; X \; A_{foot} \; X \; Ex\right) X \; 1000000 cm^3 m^{-3} \frac{1}{3600} s hr^{-1}$$

Where: Q_b is the building ventilation rate, cm^3 s^{-1}

H is height of living space, m [2.4m for residential bungalow]

Afoot is the building footprint, m^2 [78m^2 for residential bungalow]

Ex is the building air exchange rate, hour^{-1} [0.5/hr]

Q_b = 26,000cm^3/s

Equation 3-16

$$\alpha = \frac{\left[\left(\frac{D_{eff}A_B}{Q_b L_T}\right) exp\left(\frac{Q_s L_{crack}}{D_{crack}A_{crack}}\right)\right]}{\left[exp\left(\frac{Q_s L_{crack}}{D_{crack}A_{crack}}\right) + \left(\frac{D_{eff}A_B}{Q_b L_T}\right) + \left(\frac{D_{eff}A_B}{Q_s L_T}\right)\left[exp\left[\left(\frac{Q_s L_{crack}}{D_{crack}A_{crack}}\right)\right] - 1\right]\right]}$$

Where: α is the steady-state attenuation coefficient between soil and indoor air, dimensionless

D_{eff} is the *effective diffusion coefficient for unsaturated soils, 0.374 cm^2 s^{-1} (calculated)*

AB is the area of enclosed floor and walls below ground, cm^2 [100m^2 for a Residential - Slab On Ground building] (URS, 2014)

Qb is the building ventilation rate, cm^3 s^{-1} [26,000 cm^3/s]

LT is the source-building separation, cm [0.5 m = 50 cm; generic CLEA model assumption] (Jeffries and Martin, 2009a)

Qs is the volumetric flow rate of soil gas into the enclosed space, cm^3 s^{-1} [25 cm^3/s for residential land use]

Lcrack is the foundation slab thickness, cm [0.15m = 15cm]

Acrack is the floor crack area, [706.5 cm^2]

Dcrack is the effective diffusion coefficient through the cracks, [*Deff* = 0.374 cm^2 s^{-1}]

α = **2.35E-05**

Equation 3-17

$$C_{air} = \alpha \, C_{vap} \, X \, 1000000 \, cm^3 m^{-3}$$

Where: C_{air} is the indoor air concentration, mg m^{-3}

α is steady-state attenuation coefficient between soil and indoor air, dimensionless

C_{vap} is the soil vapour concentration, mg cm^{-3}

K_d gives an indication of the concentration in water, so dividing air-water by soil-water gives the air-soil distribution coefficient which is found in the literature.

$$C_{vap} = C_{soil}/K_{sw} \, x \, K_{air-water} = C_{water} \, x \, K_{air-water}$$

Table 3-12 Determination of C$_{vap}$ values

	A	**B**	**C**	**D**	**E**
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
C_s (mg g^{-1})	0	0	0.0001 ± 0.0001	0.0068 ± 0.0006	0.0002 ± 0
K_{sw} (cm^3 g^{-1})	2144.4	2320.2	9710.1	834655.3	774.7
K_{aw}	1.74E-02	1.74E-02	1.74E-02	1.74E-02	1.74E-02
C_{vap} (mg cm^{-3})	1.52E-10	1.13E-10	2.54E-10	1.42E-10	3.70E-09

Table 3-13 Naphthalene indoor air concentration calculation for the 'indoor vapour inhalation''' Pathway

	A	**B**	**C**	**D**	**E**
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
α (dimensionless)	2.35E-05	2.35E-05	2.35E-05	2.35E-05	2.35E-05
C_{vap} (mg cm^{-3})	2.67E-04	7.82E-05	2.23E-02	9.31E-02	9.16E-02
C_{air} (mg m^{-3})	3.57E-09	2.65E-09	5.96E-09	3.34E-09	8.71E-08

Equation 3-18

$$IR = C_{air} V_{inh} \left[\frac{T_{site}}{24}\right]$$

Where: IR is the chemical intake rate from inhalation of vapour from indoor air, mg day^{-1}

C_{air} is the indoor air concentration of the chemical, mg m^{-3}

V_{inh} is the daily inhalation rate, [10m^3/day for a six year old child]

T_{site} is the indoor site occupancy period, [19 hour day^{-1} for a six year old child indoors]

Table 3-14 Naphthalene intake rate calculation for the 'indoor vapour inhalation''' pathway

	A	B	C	D	E
Treatment	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
C_{air} (mg m^{-3})	3.57E-09	2.65E-09	5.96E-09	3.34E-09	8.71E-08
V_{inh} (m^3/day)	10	10	10	10	10
T_{site} (hour day^{-1})	19	19	19	19	19
IR (mg day^{-1})	2.83E-08	2.10E-08	4.72E-08	2.64E-08	6.90E-07

Tables 2-15, 2-16 and 2-17 show the cumulative IR values for the ingestion, dermal and inhalation pathways respectively. Comparison of the 'oil' sample with the biochar-amended samples does not fully reflect the results from the experimental study which demonstrates that biochar addition reduces naphthalene availability and hence potentially exposure via the ingestion and dermal pathways. Risk assessment that does not fully account for the benefit of sorption would be a hindrance to the adoption of sorption-based technologies.

Table 3-15 Summary of IR values for the different ingestion pathways within the CLEA model based on calculation using empirical data where possible in the model calculations.

Pathway	IR (mg/day)				
	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
Direct soil & household dust ingestion	0.00E+00	0.00E+00	1.00E-05	6.80E-04	2.00E-05
Ingestion of soil attached to vegetables	4.85E-08	3.90E-08	3.67E-07	1.77E-05	4.27E-07
Ingestion of contaminated vegetables	5.06E-07	4.06E-07	0.00E+00	0.00E+00	1.11E-05
Total ingestion	**5.55E-07**	**4.45E-07**	**1.04E-05**	**6.98E-04**	**3.15E-05**

Table 3-16 Summary of IR values for the different dermal pathways within the CLEA model based on calculation using empirical data where possible in the model calculations.

Pathway	IR (mg/day)				
	No oil	**No oil + biochar**	**Oil + biochar added at start**	**Oil + biochar 5mths**	**Oil**
Dermal contact with soil/ outdoor dermal uptake	1.87E-05	1.50E-05	1.42E-04	6.82E-03	1.65E-04
Dermal contact with Household dust/ indoor dermal uptake	3.82E-08	3.07E-08	2.89E-07	1.39E-05	3.36E-07
Total dermal	**1.87E-05**	**1.50E-05**	**1.42E-04**	**6.83E-03**	**1.65E-04**

Table 3-17 Summary of IR values for the different inhalation pathways within the CLEA model based on calculation using empirical data where possible in the model calculations.

Pathway	IR (mg/day)				
	No oil	No oil + biochar	Oil + biochar added at start	Oil + biochar 5mths	Oil
Inhalation of fugitive Soil dust/ outdoor dust inhalation	3.32E-12	2.67E-12	2.51E-11	1.21E-09	2.92E-11
Inhalation of fugitive household dust/ indoor dust inhalation	5.25E-09	4.22E-09	3.97E-08	1.91E-06	4.63E-08
Inhalation of vapours outside	4.92E-09	3.79E-09	1.75E-08	9.07E-08	7.20E-08
Inhalation of vapours inside	2.83E-08	2.10E-08	4.72E-08	2.64E-08	6.90E-07
Total inhalation	**3.85E-08**	**2.90E-08**	**1.04E-07**	**2.03E-06**	**8.08E-07**

Table 3-18 Summary of equations for the different pathways within the CLEA model indicating the level of consideration given to bioavailability for each equation.

Pathway	Bioavailability accounted for in pathway?	Equation(s) & parameter which accounts for bioavailability
Direct soil & household dust ingestion	No	Does not currently account for bioavailability. Exposure is estimated based on total soil concentration. An additional bioaccessibility factor should be included in the formulas, and parameter values and could be derived from in-vitro gastro-intestinal bioaccessibility tests.
Ingestion of soil attached to vegetables		
Ingestion of contaminated vegetables	Yes, but not K_d dependent.	Accounts for bioavailability by enhanced adsorption in the sense that CF depends on K_d. However, the estimation formula $K_d=f_{oc}K_{oc}$ does not account for the fact that "not all organic carbon is the same". It would be best to use measured K_d instead.
Dermal contact with soil/ outdoor dermal uptake	Yes, but not K_d dependent	The dermal absorption fraction (ABS_d) accounts for bioavailability, but is a constant independent of soil properties. It would be useful if ABS_d was a function of K_d, or determined in vitro, for example with pig skin tests.
Dermal contact with Household dust/ indoor dermal uptake		
Inhalation of fugitive Soil dust/ outdoor dust inhalation	No	Safer to exclude bioavailability assumptions due to insufficient information on the fate of inhaled dust.

Inhalation of fugitive household dust/ indoor dust inhalation		
Inhalation of vapours outside	Yes	Accounts for bioavailability by incorporating K_{sw} (K_d) values in the prediction of vapour concentrations. Measured K_d values should be used for K_{sw}.
Inhalation of vapours inside		

3.8   Chapter conclusion

Current regulatory frameworks for characterizations of risk to humans and ecological receptors do not generally include bioavailability and bioaccessibility considerations, often because of the precautionary principle. Soil and sediment quality decisions, even when using risk assessment modelling software, are therefore mostly based on total contaminant concentrations. There is however growing evidence to show that this may be an overly conservative approach which may lead to inappropriate remediation decisions. Especially, greater use of measured instead of estimated parameter values in exposure risk calculations should result in more accurate predictions. The most obvious benefit to incorporating bioavailability considerations within a risk management framework is better accuracy (Frankenberger, 2001) and the opportunity it provides to use new remediation approaches, which reduce risks of exposure rather than total contaminant concentrations. New and innovative technologies such as the sorption-based technology explored in this work have the potential to reduce exposure and/or uptake by living organisms by reducing contaminant bioavailability and mobility. Results and discussions within this chapter demonstrate the importance of bioavailability and bioaccessibility considerations, which could often be represented by K_d and K_d-derived parameters in risk estimations. These effects are however generally not yet addressed within the CLEA model although they are implicitly considered for some exposure pathways. There are therefore considerable benefits to be derived from further progress in this area with regards to the setting of risk-based cleanup criteria in risk assessments and site management decisions (Bridges *et al.*, 2008), and such progress is

needed for a more widespread uptake of sorbent-based soil and sediment remediation technologies.

According to (CARACAS, 1998), integration of technical frameworks with socio-psychological views is likely to produce further advancement in contaminated land risk assessment. It is generally known that risk perceived based on scientific evidence is usually very different form risk as it is perceived by members of the public (CARACAS, 1998). 'Novel' risk generally arouses greater concern and risk perception may impact on the priorities assigned to addressing competing risks (van Leeuwen and Hermens, 2012). After formal risk assessment has been completed, it is important to appropriately communicate the results to stakeholders and members of the public. Chapter four of this work therefore introduces the social aspects of this research that involve exploration of factors affecting implementation of remediation technologies and more specifically how those relate to biochar. The chapter addresses potential concerns about biochar and the incorporation of bioavailability assumptions in risk assessment models that may impact on the stakeholder's perception of the risk and potential acceptance. It helps buttress the fact that risk assessment approaches need to be constantly reviewed in order to ensure that approaches remain relevant to the needs and challenges that stakeholders face. A change in approach would potentially help decrease the scope and cost currently required for remediation and possibly help to ensure that sites which currently go 'unremediated' have a chance of being addressed.

Chapter 4.   Framework of Enquiry for Social Research

4.1   Introduction

The overall aim of this research as outlined in chapter one is to investigate the viability of biochar as a novel approach to the remediation of crude oil spills not just from a scientific standpoint but also from a social perspective. The social objectives are geared towards identifying the drivers for the decisions taken by key actors. This chapter is devoted to providing a clear understanding of the approach that is taken for the social aspect of the investigation as will be seen throughout this chapter and the two that follow.

4.2   Chapter scope and outline

This chapter acts as a precursor to chapter five (5) which is the result of an extensive desktop study and chapter six (6) which is an analytical presentations of data derived from social interactions with stakeholders in Nigeria and the USA. The chapter provides an understanding of the framework and methods that are employed in successive chapters (five and six). It discusses the justification for choice of study locations. Research questions and objectives for the social enquiry are outlined within chapters five and six as well.

4.3   Research location rationale

4.3.1   *Nigeria*

In choosing a suitable location of reference for the research, a number of factors were considered; one of which was the author's affiliation and knowledge of the Niger-Delta region. The research was mainly funded by Nigeria's Petroleum Technology Development Fund (PTDF). Despite enormous research by Nigerians locally and in the diaspora, prevailing challenges with oil spill in the Niger-Delta indicates that there is a need to bridge the gap between available science and technology implementation in Nigeria. The desktop study (chapter five) indicates the potential for utilisation & implementation of biochar as a technology option for oil spill remediation in the Niger Delta. Very little research has however been done regarding the use of such sorbent-based remediation technologies in Nigeria despite a gradual shift in approach globally. In terms of understanding the legislative and institutional framework, this had to be done at the level of the Federal Government. Government agencies were visited in Lagos and oil companies in Lagos and Port Harcourt were therefore also approached. Physical accessibility in terms of security of the author was also considered.

4.3.2 *USA*

The author visited the USA via a research exchange programme and this provided an opportunity to interact with carbon-based remediation technology stakeholders there. The USA was an appropriate location for comparative study with Nigeria as carbon-based remediation technology originated in the USA, and field scale pilot studies and full scale projects have recently been implemented there. The USA data provides a very useful prelude to the work in Nigeria in addition to serving as a platform for comparison based on the understanding that was derived from interviews. Leading researchers, industry experts, academics and regulators in the field provided information about factors which were relevant for implementation of the new technology in the USA.

4.4 Research strategy/Worldview

The research strategy employed was chosen to suit the research questions and objectives presented in the social enquiry chapters. In this work, I justify the use of mixed-method research based on the convergence that would be derived from combining the experimental, risk and social elements/ components of my research interest in sequential order. Creswell (2013) refers to this model of research as explanatory-sequential mixed method research. Even though Creswell (2013) refers to this sort of combination in the context of social research methods, the argument holds for this work as well because the quantitative result is explained further by the qualitative findings. The core assumption of a mixed-method research, (one involving quantitative as well as qualitative methods) as employed in this work, is that the combination of the two is more likely to produce a better understanding of a research problem than each individually (Creswell, 2013). Even though there is a broad consensus that the rational for a mixed-method research has to be a pragmatic one, this is not always the case.

The philosophical approach used for this analysis is 'critical realism'. Critical realism is a theory which argues for the necessity of ontology (i.e. what is real, the nature of reality). It emerged in the 1970s and 1980s through the work of Roy Bhaskar and can be applied to social science as well as natural science (Fletcher, 2017). The critical realism research process focuses on the relationship between the real world and the concepts we form of it. Critical realism views scientific activity (production of scientific knowledge) as a working process just like any other production activity, which is able to produce temporarily readymade products, which may be fallible. It assumes that science is fallible at any time

(Danermark *et al.*, 2001). Reality is categorised into three strata; i) the *empirical* level, (where events or objects can be measured empirically and explained through 'common sense') ii) the actual level (where events occur independent of the human experience and knowledge) and iii) the real level (where causal structures or causal mechanisms exist) (Fletcher, 2017). Figure Figure 4-1 below shows the three-layered 'iceberg' of reality.
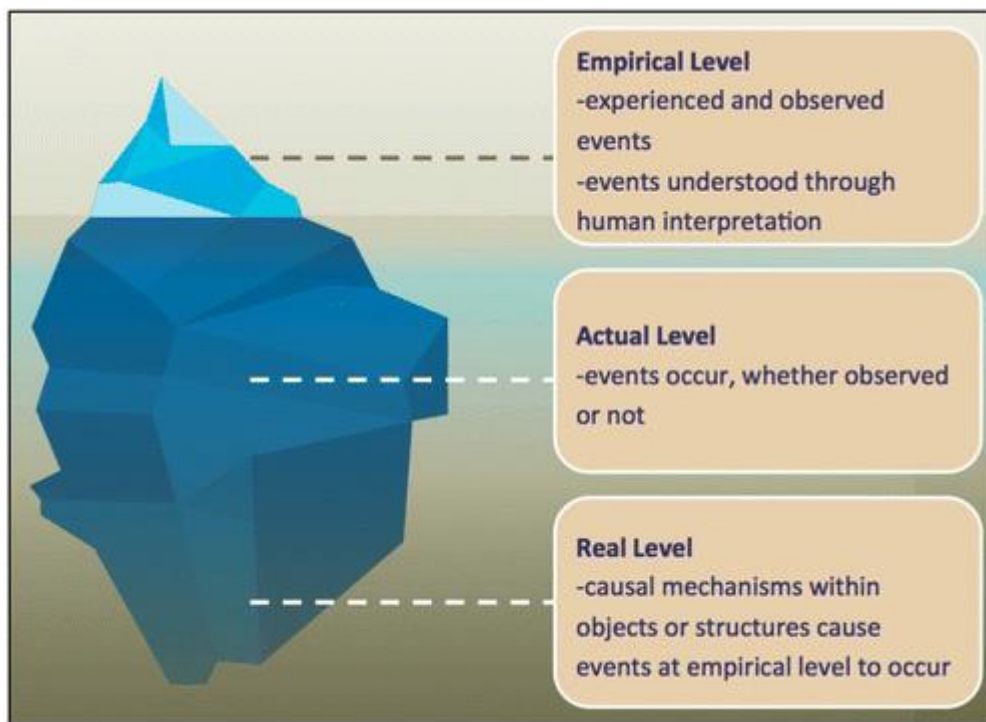
Figure 4-1 three-layered 'iceberg' of reality (Fletcher, 2017).

CR suggests that natural and social reality need to be understood as an open stratified system of objects with causal powers (Morton, 2006). CR's dual nature of ontological realism and epistemological relativism is an excellent foundation for a mixed-method approach. CR is therefore attractive for use in this work as it helps to integrate physical and social realities within the research environment. My application of this method is above all, pragmatic in the sense that I am concerned with practical success more than with the generation of theory. Pragmatism is generally used to refer to 'a commitment to success in practical affairs' (Talisse and Aikin, 2008). It is not usually concerned with abstraction or theories. The pragmatist worldview agree that research always occurs within a historical, social and political context (Creswell, 2013). As this research employs both qualitative and quantitative

methods, the author is more interested in practical rather than theoretical considerations when it comes to achieving the research objectives. This pragmatic approach underpins all aspects of this research work.

4.5   Approach to Desktop study

Chapter five is a high-level institutional analysis of the Nigerian oil and gas industry which resulted from of a desktop study. Data for the analysis was obtained by reviewing online articles, journals, government reports, theses, as well as legislative and policy documents. The data was critically analysed under two major themes; firstly, oil and gas legislation and secondly, organisational and institutional setting of major stakeholders laid the foundation for subsequent investigation done through interaction with stakeholders.

4.6   Design & Methodology for the Fieldwork studies

4.6.1   *Sampling*

Participants for interviews and questionnaires were chosen by means of 'Purposive non-probability sampling' based on their role/involvement in the Remediation Decision Making Process (RDMP). This is an informant selection tool which is also known as judgment sampling and involves deliberately choosing an informant because of the qualities the informant possesses (Tongco, 2007).

4.6.2   *Collection of primary data*

Data was collected in three major stages as illustrated in Table 4-1 below.

Table 4-1 Phases of data collection

	Description of research work
Phase I (Nigeria)	Preliminary field visit; to gain a broad understanding of factors that affect remediation decisions within the oil and gas industry in Nigeria. Semi-structured interviews were conducted with a wide range of system actors including government officials, academic and oil company operators.

	Second field visit; to investigate the viability of biochar technology in Nigeria. Semi-structured interviews were conducted with a wide range of system actors: regulators, academics and oil company operators.
Phase II (USA)	Third field visit; to understand the factors that enabled implementation of sorbent-based remediation technology in the USA. Semi-structured interviews were conducted with campus faculty, students, industry experts and regulators. In total 16 questionnaires administered.

4.6.3 *Interviews & Questionnaires*

Stakeholder interactions involved a combination of semi-structured, face-to-face interviews and questionnaires. Phone interviews were however held on three occasions where it was not possible to meet in person. Key stakeholders had been identified prior to the interviews and letters of introduction (see Appendix D) were obtained from Newcastle University in keeping with Nigerian bureaucratic requirements. Information obtained from the desktop study was used to define target objectives for interaction with the system and oil industry stakeholders in Nigeria as well as to determine the decision-making domains. Questionnaires (Appendix B) were aimed at acquiring quantitative data to examine the diversity of views about remediation technologies that exist across different stakeholder participatory categories in the USA (see Appendix A). A combination of list questions, rating questions, open questions and closed questions were employed based on the nature of data that was anticipated by the author. Interviewees were presented with a one-page research brief of biochar technology (see Appendix A) and a brief oral introduction of the aim of my research. All interviews (N=28) were conducted in English language with complete integration of ethical considerations. Interviews lasted an hour on average and information provided by key informants was treated as representative of the organisation. Practical reasons for selecting interviewees included ready access to participants and their position in an organisation of interest. The interviews were designed to help achieve the objectives of the social science aspect of the thesis as outlined in chapter six (section 6.1).

4.6.4 *Data analysis*

Interview recordings were transcribed using Nvivo software and thematic cross-content analysis was performed on the data (Reis and Judd, 2000; King and Horrocks, 2010). Findings are presented in chapter six (6) as a summary narrative pulling together data from several interviews and providing direct quotes in some cases.

4.7 Conceptual framework for analysing sociotechnical system of oil spill remediation in Nigeria - Overview of the IAD framework

The analytical framework chosen for understanding the socio-technical systems in this work was inspired by the Institutional Analysis and Development framework (IAD) which is a legacy of Elinor Ostrom's theoretical and empirical foundations on long term sustainable resources and their management (Ostrom, 1999). The IAD framework was initially developed to help researchers structure the analytical tasks involved in understanding the complexity of institutions. Institutions in this work is used in the broad context of shared rules, strategies, and norms that are used within or across organizations. The IAD framework has been used within the authors research group (Clement, 2008) as well as by other researchers for organising research on institutions and governance structures (Andersson, 2006; Abel *et al.*, 2014). It helps to identify key variables required for systematic analysis of situations that humans face as well as how these situations are impacted over time by rules, the nature of the events and community attributes (Ostrom, 2005). The IAD is explicitly compatible with CR as proposed by (Clement, 2017) because CR provides a strong ontological basis for applying the IAD framework due to its reliance on realist and constructivist approaches.

Ecologists have criticized the IAD for treating the biophysical context as an external force, and not explicitly acknowledging the degree of control that it possesses over a natural resource via the management policies and monitoring of the resource. they have also criticized the IAD as being weak at explaining exogenous factors beyond a community level (Lundqvist, 2004). Consequently, Ostrom developed another framework subsequent to the IAD; the SES (Socio-Ecological Systems) framework which is more elaborate because of the disparate numbers of sub-variables included in it (Bal, 2015). The IAD is, however, preferred for this research because the modifications made to the SES were geared towards better solving ecosystem-based problems whereas this work is focused more on technology implementation. The theoretical framework for the social aspect of the thesis is essentially a pragmatic one hence a flexible approach is taken in the author's use of the IAD. In adapting

the framework for this investigation and attainment of the desired objectives, the focus was to identify findings that were generalizable, within reason. The modified framework therefore provides a basis for orientation of the analyses and is used as a tool to examine how institutions affect social actors in the design and implementation of remediation approaches in Nigeria. The understanding of oil spill remediation in Nigeria is built on three broad aspects; the legislation, stakeholders and governance.

4.8 Structure and Key elements of the IAD framework

4.8.1 IAD framework as a multi-level conceptual map

An important characteristic of the IAD framework is the multi-level structure for analysis which it offers. On one hand, it focuses on factors affecting decisions and on the other, it analyses the multiple levels affecting these decisions. It acts as a tool with which one can zoom in and out of specific hierarchical parts of the regularised interactions in an established social system (Ostrom, 2005). Analysis is categorised into three levels; constitutional-choice, collective-choice and operational-choice (McGinnis, 2011) which correspond to the policy-making, policy-implementation and application level respectively as adapted for analysis in chapter six of this thesis.

4.8.2 Action arena

The action situation is the core component of the IAD framework. It refers to the social space where individuals interact with each other and jointly affect outcomes that are valued differently by those actors (McGinnis and Ostrom, 2014). The action situation is also where information is observed, actions are selected. Analytic deliberation refers to the design principle that defines one kind of outcome in an action situation (Ostrom, 2005). Understanding the action arena produces an understanding of the patterns of interactions that exist as well as outcomes. Action arenas can be linked together either sequentially or simultaneously (Ostrom, 2005). The IAD framework will be used to code the data in such a way that conditions which could lead to deliberative and cooperative outcomes are identified instead of those that could lead to conflict and mistrust. For the purpose of this research, the action arena will be used to refer to the action situation and the relevant actors.

Individual decision makers in an **Action Situation** are usually surrounded by four contexts which influence their choices. These are

1. The biophysical world

2. The community in which the individual is embedded

3. Sets of institutional rules that incentivize or constrain certain actions

4. Group interactions (Koontz, 2005; Ostrom, 2011)

In adapting the IAD framework, these contexts are the 'exogenous factors' which affect decisions of actors and are considered as part of the focal action situation. They capture the political, social and physical settings around partnerships (Kim, 2012). The IAD treats these four contexts as 'external' based on the premise that whenever an action arena is the focal level of analysis as shown in Figure 4-2 below, these contexts generate interactions that produce outcomes. These outcomes feed back to the participants and action situation and may affect some of the external variables over time. This is viewed as the simplest and most aggregated way in which arenas can be represented (Ostrom, 2005).
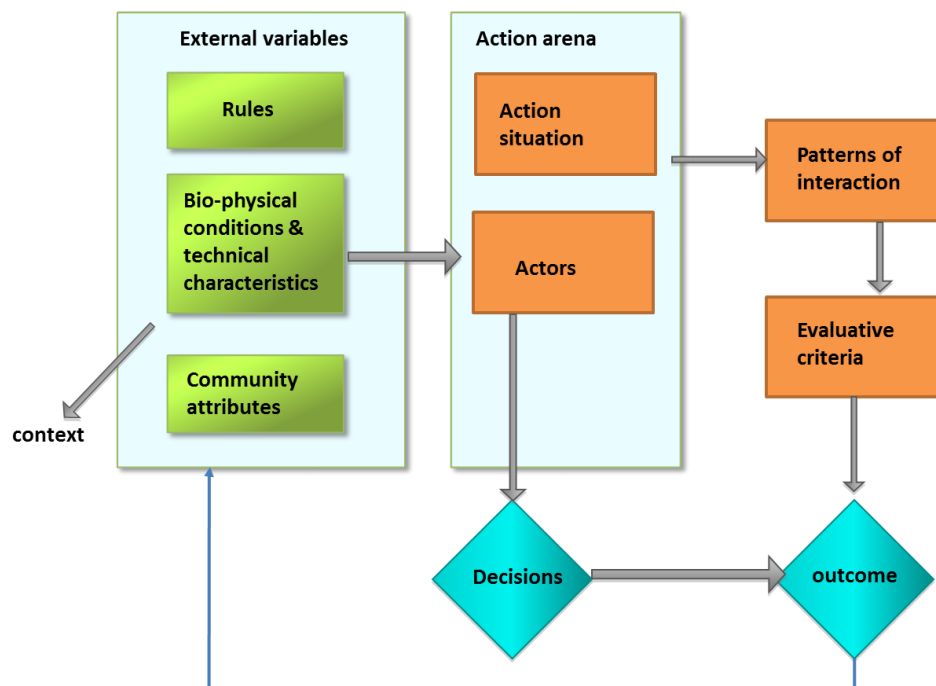
Figure 4-2 Framework for the analysis, adapted from the IAD framework (Ostrom, 1999)

4.8.3 *Biophysical conditions & technical characteristics*

These focus on the nature of the good/service that is being shared in the interactions. They usually include factors such as number & size of sites, level of contamination, pollution typology and historic and future usage, and operational (remediation) activities.

4.8.4 *Community attributes*

This represents a set of attributes for a community where actors are located. Common attributes are levels of trust among members, reciprocity, cooperation, shared values and goals, social capital, and repertoires of deliberative processes (McGinnis, 2011). These attributes are critical in shaping behaviour (Abel *et al.*, 2014).

4.8.5 *Outcomes*

Outcomes refer to output generated from an action situation. They feed back into the action arena and may transform it over time. They may also impact slowly over some of the exogenous variables over time (Ostrom, 2005; McGinnis, 2011; Prior *et al.*, 2011) identified readily recognised outcomes of RDMPs to include the minimisation of environmental risk, the removal of blight on property and the reduction of the impacts of hazardous substances on human health. Outcomes of concern in this research include process-related (remedial), environmental, socio-economic and partnership outcomes.

4.8.6 *Rules*

The concept of rules is central to the IAD framework hence it is important to consider the effect of rules at all three levels. Rules within the IAD context refers to understandings that are shared by participants about enforced prescriptions regarding what actions (or outcomes) are required, prohibited or permitted (Ostrom, 2005). A diverse set of rules guide and govern the way that outcomes can be attained by actors (Prior *et al.*, 2011). Rules considered within the IAD framework are closely-linked to the elements of an action situation. They help in the explanation of policy-related actions, interactions, and outcomes (Polski and Ostrom, 1999). Humans are able to adopt norms about the actions that they must, must not, or may choose to take hence many rules emerge as a result of individuals cooperating to proffer solutions to commonly faced problems. It is important to notes that these rules are not necessarily an 'agreed-upon set of rules' and they need not be written either (Gibson, 2005). Rather, rules emerge in the action situation as individuals seek to change the structure of repetitive situations that they face in an attempt to improve the outcomes achieved (Ostrom, 2005).

Rules that affect behaviour in the action arena are grouped into formal and informal. Formal rules also known as the rules-in-form are discussed in chapter five while rules-in-use which are those used in 'actual settings' (McGinnis, 2011) are presented in chapter six.

4.8.7 *Evaluation Criteria*

Evaluative criteria are used to access the system's performance by determining what aspects of the project have a positive or negative impact on the likelihood of successful outcomes. Some of the potential evaluative criteria recommended by Ostrom are Efficiency, Equity, Adaptability/Resilience, Accountability and Conformance to General Morality (Ostrom, 2005).These criteria have been implicitly incorporated into my analysis. Measurement of the value created was also based on whether the outcomes sought and valued by stakeholders are met (Prior *et al.*, 2011).

4.9   Ethical considerations

It is important to report research ethically hence consideration was given to the fact that values can be implicated into research as discussed by Hammersley and Atkinson (2007). The researcher was introduced as a PhD research student from Newcastle University to all participants and organizations. Ethical approval for the research was granted by the university. For confidentiality reasons, codes were used to identify participants. Where individual acted as representatives of organizations, it was made clear if their views were to be taken as that of the organization. Participants were informed that data obtained would be used for research purposes only.

Chapter 5. Legal and institutional framework for remediation of oil pollution in Nigeria

5.1   Introduction

Effective environmental management demands that policy and legislation be made which protect human health and the environment. Environmental laws are often made to meet political aims and goals, as well as to set scientific standards. Policy on the other hand, refers to intentions of action of government and is usually brought about by shifts in environmental values as a result of new priorities and required action (Bell and McGillivray, 2008). A sound knowledge of the legislative and institutional framework of the oil and gas industry would help in understanding how decisions are made and what factors inform the choice of remediation technology employed at contaminated sites. It would also highlight how relevant organisations work; their structures, capabilities and degree of efficiency as well as any relationships that may exist amongst them.

5.2   Chapter Scope and Outline

This chapter is the product of a desktop study which was carried out on the Nigerian oil and gas industry with major focus on the legal and institutional framework for oil pollution remediation in the country. Chapter four (4) provided details of the methodological approach taken for this desktop study. This high-level analysis critically analyses relevant laws, policies and programs as well as the roles that key stakeholders play within the existing institutional framework. It provides a systematic understanding of the environment in which rules and decisions that affect clean-up of oil contaminated lands are made. A purely theoretical approach is taken at this stage to concentrate on how things are on paper (rules-in form), bearing in mind that the practicalities might differ slightly or greatly from what is presented here. Section 5.3 provides background information on the current oil pollution and remediation situation in Nigeria. Research questions and objectives are outlined in sections 5.4 and 5.5. A historical timeline of the development of environmental laws in Nigeria is presented in sections 5.6 and 5.7. The provisions of the laws are critically discussed to evaluate their adequacy for environmental management as it relates to oil pollution remediation particularly within the upstream sector of the Nigerian oil and gas industry. I also highlight any defects or shortcomings in legislation or administrative framework and make

recommendations for improvement where possible. Institutional analysis is presented in section 5.8. The chapter ends with a brief summary of chapter findings and conclusion.

5.3   Background to Nigeria

5.3.1   *The Niger-Delta Region*

Figure 5-1 Map of Nigeria showing states typically considered as a part of the Niger delta (Idemudia and Ite U, 2006)

The oil-rich Niger Delta region of Nigeria which is situated on the West African continental margin at the apex of the Gulf of Guinea is one of the largest Tertiary delta systems in the world (Doust, 1990). It occupies an area of about 75,000 km^2 with a total sediment volume of 500,000 km^3 (Oforka, 2012). Most of the terrestrial ecosystems and shorelines within the nine (9) oil-producing states of the region are required by the communities for agricultural cultivation (Osuji and Onojake, 2004). According to the National Population Commission (NPC), the region had an estimated total population of 33.8 million in 2010 and an anticipated population of 39.2 million by 2015 and 45.7 million by 2020 (Omuta, 2011). The climate is

equatorial, characterized by high relative and specific humidity, and intense rainfall, which occurs almost throughout the year in the core delta, although wide internal variations exist from one part of the region to the other. The delta which is a vast sedimentary basin is mostly a flat, low-lying swampy region, separated by a dense network of rivers and creeks. The mangrove swamp zone is scattered with islands; some of which are inhabited and the population is therefore discontinuous and sparsely distributed. Fishing camps do however exist within the mangrove (Omuta, 2011).

5.3.2 *Oil Pollution in Nigeria*

Figure 5-2 A Niger-Delta crude oil spill site

Nigeria is presently considered to be among the most oil polluted nations of the world (Akpomuvie, 2010) as a result of the exploration of crude oil which is a smelly yellow-to-black liquid usually found in underground areas known as reservoirs (Eneh 2011). According to DPR, an estimated 1.89 million barrels of petroleum was spilled into the Niger Delta between 1976 and 1996. The Nigerian National Petroleum Commission estimates the quantity of oil jettisoned into the environment yearly at 2,300 cubic metres with an average of 300 individual spills annually (Adelana *et al.*, 2011). During the period; 1970–2000, the Department for Petroleum Resources (DPR) revealed that approximately 6%, 25% and 69%

of total oil spilled in the Niger Delta environment were on land, swamp and offshore respectively (Udoudoh, 2011).

Oil spills have contributed to widespread environmental devastation across the coastal area of the Niger delta where the main oil fields are situated (Barale and Gade, 2014). Instead of development and poverty reduction, the local population has been brought to the brink of economic and social disaster. It is generally known that oil spills on soil can make land useless for grazing or agriculture (Karl, 2005). One of the major impacts of oil spills is groundwater contamination which inadvertently affects aquatic and terrestrial lives, causing devastation, diseases and infertility (Udoudoh, 2011). In the Nisisioken Ogale community for instance, drinking water from wells are contaminated with benzene, a known carcinogen, at levels over 900 times above the World Health Organization (WHO) guideline (UNEP, 2011). Large-scale spills on a global level such as the Gulf oil spill have triggered research into this area and there is therefore a growing literature, which describes the impact of such spills on health (Goldstein *et al.*, 2011). Short-term effects that are usually of concern to clinicians and the pubic include nausea, dizziness, headaches, eye irritation as well as respiratory and dermal irritation (Goldstein *et al.*, 2011). The greater concern however relates to more long-term toxicological effects such as mutagenesis and carcinogenesis; as well as systemic effects such as those relating to the endocrine, neurologic, hematologic, respiratory, hepatic and renal systems (Goldstein *et al.*, 2011). There has thus been serious health concerns regarding oil spill in the Niger Delta over the years.

Oil pipelines vandalization by locals; aged pipelines; oil blow outs from the flow stations; releases, oil tankers releases and the disposal of used oil into the drains by the road side mechanics are the major sources of oil spills in Nigeria (Nwilo and Badejo, 2005). According to Nwilo and Badejo (2005), vandalization of pipelines is by far the most serious source of oil spill usually as a result of civil disaffection with the political process or as a criminal activity. Similarly, Adelana *et al.* (2011) states that the most common causes of oil spillage in Nigeria is corrosion of pipelines and tankers (accounting for 50% of all spills), sabotage (36%), and oil production operations (6.5%), with 1% of the spills being accounted for by inadequate or non-functional production equipment. According to Ekpu (1995-1996), the greatest health risk posed to all organisms in Nigeria from the oil industry is via oil field pollution with water bodies being the most impacted. USEPA (United States Environmental Protection Agency) defines oil spill as an accidental or intentional discharge of oil which reaches bodies of water.

The name 'Petroleum' refers to both naturally occurring unprocessed crude oils and petroleum products that are made up of refined crude oil (Science, 2010). For the purposes of this research, the term 'oil' will generally be used to refer to crude oil. There are six (6) major stages that produce and generate waste, hazardous materials and toxic chemicals within the oil industry. These are exploration, production, terminal operations, hydrocarbon processing, oil transportation and marketing operations (Kusamotu and Kusamotu, 2013). Petroleum industry operations are classified globally into upstream and downstream operations. Upstream operations have to do with the search for, development, and extraction of oil and gas (Conaway, 1999). Upstream operations are of greater concern in this research. The downstream sector on the other hand, involves the refining of the crude oil and/or raw natural gases as well as the sale and distribution of the refined product (Bhardwaj 2013).

According to Akpomuvie (2010), the most pronounced devastation of the Delta ecosystem occurs in the process of transportation of crude oil. 98% crude oil transportation in Nigeria takes place within the Niger Delta, because of the numerous oil fields, flowstations and terminals through which crude oil flows (Ikporukpo, 2004). The Ogoniland oil spill (discussed in section 5.8.4) is unarguably the most notorious case of oil spill in Nigeria. Spill sites in Ogoniland constitutes about 50% of spills in the Niger Delta (Onwuteaka, 2016), however, over two decades after the incident, it remains unresolved.

5.3.3 *Oil Spill Remediation in Nigeria*

The concept of oil pollution remediation has already been explained in chapter two. The approach and technologies that are used however varies from country to country and are usually impacted by factors such as legislative restrictions; regulatory framework, risk perception of decision-makers, socio-economic considerations and pollution typology. According to Onwuteaka (2016), attempts at clean-up and remediation in Nigeria are recorded in less than 0.2% of sites and a dearth of testing of remedial best practices has made innovation of indigenous and cost effective technologies difficult. Remediation by enhanced natural attenuation (RENA) is the most common remediation technique utilized by MOCs (Multinational Oil Companies) in Nigeria due to its low cost requirement. There have however been outcries from various quarters about the ineffectiveness of this preferred technology, which is usually applied both on land and water. The UNEP (United Nations Environment Programme) report on Ogoniland criticized Shell for relying solely on RENA as it failed to achieve legislative compliance (UNEP, 2011) as well as its own company

guidelines (Shoraka and Emmanuel, 2014). Amnesty International stated that the current clean-up methods are ineffective and need to be fully overhauled if progress is ever to be made in remediating the Niger-Delta (Vidal). The comparatively large-scale pollution in Nigeria poses a serious remedial challenge. It is thus becoming increasingly expedient that remediation technologies are sought which are not only effective but also inexpensive.

5.3.4 *Legislative and Institutional Analysis Framework for Oil Pollution Remediation in Nigeria*

The discovery of crude oil in Nigeria in 1956 engineered a focus of environmental legislation on oil which was the economically important natural resource at the time (Ogunba, 2011). There currently exists a robust environmental regime with specific and specialized organisations to administer the law on environmental issues in Nigeria (Otu, 2011). Despite these laws and policies on environmental protection and conservation, environmental degradation has continued to worsen in the Niger Delta. Remediation is generally subject to an array of regulatory requirements, and may be based on assessments of human health and ecological risks where no legislated standards exist or where standards are advisory (AirClear, 2013). Institutional analysis within the context of this research refers to the rules that govern the actions of stakeholders and how institutions interact with each other. Implementation of legislation depends to a large extent on the quality of stakeholders (people or organisations) responsible for executing specific actions. Stakeholders are actors with a vested interest in something; for instance a policy, programme, action or organisation (INBAS, 2011). A change in trajectory of the current remedial situation cannot be brought about without effective legislative and institutional framework for effective management of contaminated sites.

5.4   Research Questions

This desktop study aims to answer the following questions;

- Is the legislative framework for oil spill remediation robust enough?
- Who are the key stakeholders and what rules govern their behaviour?
- How much power do they have?
- Does stakeholders' perception of risk have a significant impact on the Remediation Decision Making Process (RDMP)?

5.5   Chapter Objectives

- Identify and analyse the laws which govern oil spill remediation operations in Nigeria
- Identify the stakeholders involved in oil pollution remediation and the rules that govern their behaviour
- Present a situational analysis of current institutional framework for oil spill remediation in Nigeria
- Identify and discuss the challenges and prospects, if any, within the institutional framework

5.6   Laws with Specific Relevance to Oil Spill Remediation

5.6.1   *EGASPIN (Environmental Guidelines & Standards for the Petroleum Industry in Nigeria) 2002*

Issued by the Department of Petroleum Resources (DPR) in 1992, EGASPIN sets out the powers of DPR and forms the operational basis for environmental regulation of the oil industry in Nigeria. It provides the performance standard that governs the oil spill response process in Nigeria and also sets out monitoring programmes & schedules to ensure environmental quality control for the oil and gas industry. EGASPIN sets out the remediation guidelines for contaminated soil and groundwater and stipulates penalties for responsible parties (Cragg *et al.*, 2013). This key legislation however, is plagued by a major inconsistency concerning the remedial guidelines. A target value of 50 mg/g TPH is stated as the desired end point for restoration after a spill however an intervention value of 5,000 mg/Kg TPH is given for remediation closure (DPR, 2002). EGASPIN states that the DPR is responsible for remediation of sites where the source of contamination is not known. It stipulates that this should be done through funds established by the government. It mandates monthly inspection of pipelines and clean-up of all spills within 24 hours with the complete containment and removal of spilt oil. There is also the question of whether the guidelines are feasible. For instance, it requires companies to continue to monitor spill sites after clean-up and demands that for all waters, there is to be no visible sheen after the first 30 days and in swamp areas no sign of oil after 60 days (Cragg *et al.*, 2013). The oil companies however admit that they cannot start clean-up operations within 24 hours and regard themselves as lucky to get clean-up started within several days. It also recommended in a review of EGASPIN, that more emphasis should be placed on the social and health impacts of oil spills and that the approach taken to clean up be clarified. EGASPIN also suggests that there is a

fund to compensate operators for any clean-up costs incurred, if the spill is not their responsibility. Reference is made to this in the Petroleum Industry Bill (see section 5.6.2). There have been concerns about EGASPIN mainly because it is not clear whether it is just a guideline document or whether it does in fact represent law. An UNEP report states that it is uncertain if EGASPIN falls under the Petroleum Act of 1969. This uncertainty makes it unclear whether EGASPIN is legally enforceable or not; in which case, they are merely guidelines. The EGASPIN makes (Environmental Impact Assessment) EIA studies mandatory. The study must be prepared by the project proponent/initiator (proponent), together with DPR-certified consultants (where necessary) and in conjunction with the DPR. There is however, a closed category of projects that do not require EIA studies. These include;

     i.   Projects that the President or the Federal Environmental Protection Council feel are likely to have minimal environmental effect

     ii.   Projects carried out during national emergencies

     iii.   Projects carried out in circumstances that, in the opinion of NESREA, are in the interest of public health or safety

5.6.2 *The Petroleum Industry Bill (PIB)*

This is another very important piece of legislature proposed since 2008, and it has been submitted to the National Assembly for approval but remains unpassed due to power tussle between the legislative and executive arms of government. As the long title implies; it is "an Act to establish the legal and regulatory framework, organisations and regulatory authorities for the Nigerian petroleum industry, to establish guidelines for the operation of the upstream and downstream sectors, and for purposes connected with the same''. If enacted, it would also precipitate a major restructuring of the NNPC as it proposes to create a framework that would unbundle of the powers, functions and objectives of the Nigerian National Petroleum Corporation (NNPC) including its assets and liabilities. The NNPC currently functions as a regulator as well as an operator and this is a source of concern especially with regards to accountability for remedial responsibilities. Licensees and lessees under the act are required to submit an environmental programme or an environmental quality management which will contain among other things;

  i.   their environmental policy, objectives, and targets

ii.   established baseline information concerning the affected environment to determine protection, remedial measures and environmental management objectives

iii.   description of the manner in which they intend to modify, remedy, control or stop any action, activity or process which causes pollution or environmental degradation

iv.   description of the manner in which they intend to contain or remedy the cause of pollution or degradation and migration of pollutants

v.   description of the manner in which they intend to comply with any prescribed waste standard or management standards or practices

Part I, Section 6 (1), states that 'The Federal Government shall, to the extent practicable, honour international environmental obligations and shall promote energy efficiency, the provision of reliable energy, and a taxation policy that encourages fuel efficiency by producers and consumers'.

Part I, Section 6 (2), states that 'the Federal Government shall introduce and enforce integrated health, safety and environmental quality management systems with specific quality, effluent and emission targets for oil and gas related pollutants, without regard for fuel type such as gas, liquid or solid, in order to ensure compliance with international standards'.

According to part 2, chapter 1, section 9, The Minister in charge of petroleum resources shall be responsible for the co-ordination of the activities of the petroleum industry and shall have overall supervisory functions over petroleum operations and all the organisations of the industry. The functions of the minister include advising the Federal Government on all areas pertaining to the oil and gas industry. This legislation if passed would impact on the current administrative framework in the sense that the set-up of individual will have to change significantly.

Chapter 2, section 13 (k) states that 'the National Petroleum Directorate shall promote the use of locally available raw materials in preference to previously imported materials, without at any time compromising quality, safety and environmental standards in the petroleum industry'. This would potentially drive innovation for use of locally produced solutions for remediation and consideration could be given to waste materials from which biochar can be produced.

When considering an environmental management plan or environmental management programme, the Inspectorate is required to consult with the Federal Ministry of the

Environment and the State Ministries of Environment within which the licence or lease is situated and with any other relevant bodies within which the licence or lease is situated. This hopefully would facilitate greater involvement of states in remediation decisions as currently the Federal Government dominates in discussions and decisions. Section 286 of the bill addresses financial provision for remediation. It stipulates that every state and local government within which any licence or lease is located shall pay a sum equal to 1% of the state's annual derivation allocation, and 0.5% of the local government's annual derivation allocation into a 'Remediation Fund'. This shall be utilised solely and exclusively for the restoration and remediation of the environment in cases where the said damage to the environment has been caused by sabotage. This Remediation Fund is to be kept in the custody of the Inspectorate and is to be utilized only in accordance with prescribed regulations made under this Act. There is currently an 'Ecological Fund' based on existing legislation however the functionality of it is questionable, perhaps due to corruption.

5.6.3 *Oil Pollution Act (OPA) of 1990*

This Act is responsible for many of the nation's improvements in oil spill prevention, mitigation, clean-up and liability (Ugochukwu, 2008). The majority of its provisions were targeted at reducing the number and quantity of oil spilled. It provides guidance for government and industries in this regard and also created a comprehensive scheme to ensure availability of funds to clean up a spill and to compensate for subsequent damages.

It mandates that

  i.   The federal response system be adequately prepared to manage the impacts of oil spills that occur;
  ii.   Industry implements prevention and preparedness measures.
  iii. Tankers and inland oil facilities develop individual response plans.
  iv.   Enhancements be made to the national response system, and development of area Contingency Plans (Ugochukwu, 2008).

5.6.4 *EIA (Environmental Impact Assessment) Act (1992)*

The Environmental Impact Assessment Act (1988, cap. E12, LFN, 2004) is a tool of the Federal Ministry of Environment (FME) that prohibits the public or private sector from authorising or embarking on a project without prior consideration to its environmental

effects. Part I, section 1 (a) indicates that the jurisdiction of the act covers 'any activity that may likely or to a significant extent affect the environment'. This Act which regulates environmental pollution was promulgated to protect and sustain the Nigerian ecosystem. Its principal function is to enable the prior consideration of impact assessment of public or private projects on the environment before approval is granted for the project. The law makes it mandatory for environmental impact assessments and environmental audits to be carried out by polluting industries in Nigeria. This means that an EIA report must be prepared in respect of all major projects and approved by the Federal Ministry of Environment (FME) and the Environmental Agency of the State in Nigeria in which the project is located. Anyone who fails to comply with the provisions of the EIA Act is liable on conviction to a fine and imprisonment (Okenabirhie, 2008). Implementation of the EIA is usually done under the supervision of FEPA (Federal Environmental Protection Agency) (Kadafa, 2012).

5.6.5 *National Oil Spill Contingency Plan (NOSCP)*

This is a blueprint/manual for checking oil spill through containment, recovery, and remediation/restoration (NOSDRA, 2012). The management of this plan is the primary mandate for NOSDRA (National Oil Spill Detection and Response Agency). NOSDRA cooperates with the Federal Ministry of Transportation to implement the National Oil Spill Contingency Plan (NOSCP) and with the International Maritime Organization (IMO) Convention on Marine Pollution especially in the area of tanker accidents. TheThe contingency plan and the agency were established in compliance with the International Convention on Oil Pollution Preparedness, Response and Cooperation 1990 (OPRC 90) to which Nigeria is a signatory' (Ugochukwu, 2008). Parties to the OPRC, which is managed by the International Maritime Organisation (IMO), are required to establish measures for dealing with pollution incidents, either nationally or in co-operation with other countries (I.M.O, 2011). The Agency has a standing agreement with relevant Government Ministries, Departments and Agencies for their prompt support in cases of Tier 3 oil spill response as well as surveillance. Similar plans exist in other oil-producing countries around the world including Trinidad & Tobago and the United States. Oil spills in Nigeria are categories into three (3) tiers of implementation based on the National Oil Spill Contingency Plan (NOSCP). They are outlined below;

Tier 1; This tier covers operational type spills which may occur at or near a company's own facility as a consequence of its own activities. The size of this type of spill is usually less than or equal to 7 metric tonnes (50 barrels) and under the OPRC, the company responsible for the spill would typically provide resources to respond to it (Kadafa, 2012).

Tier 2; This is a larger spill; usually greater than 7 metric tonnes (50 barrels) but less than 700 metric tonnes (5000 barrels). It usually occurs in the vicinity of a company's facility just like the Tier 1 spill but requires resources from another company, industry and possibly government response agencies. Companies help out through local cooperative efforts on a mutual aid basis. An example of this is the Clean Nigeria Associates. Every member of the CNA pools it's Tier 1 resources and has access to equipment which have been jointly procured for the cooperative (Kadafa, 2012).

Tier 3; This type of spill which may be close to or far from a company's facilities is usually greater than 700 metric tonnes (5000 barrels). It requires substantial further resources from a National (Tier 3) or international cooperative stockpile such as the Oil Spill Response Limited (OSRL) may be required. It is usually subject to governmental control and direction because of its magnitude (Kadafa, 2012).

5.6.6 *National Policy on Environment*

This is an instrument of the Federal Ministry of Environment of Nigeria (FME) and is enforced by NESREA. Issued in 1989, it describes guidelines and strategies for achieving the policy goal of sustainable development. This can be found on the NESREA website. Nigerian possesses this document as do a lot of other countries.

5.6.7 *Oil Pipelines Act (1990)*

 This law seeks to prevent the pollution of land and waters by oil pipelines. It regulates the granting of licenses for the establishment and maintenance of oil pipelines. It mandates that compensation be paid any person suffering damage as a consequence of any breakage of or leakage from the pipeline or an ancillary installation (except when the spill is the result of the malicious act of a third person). The act however creates an easy defence for the permit holders in the event of an action for compensation because of the clause 'other than on account of the malicious act of a third person' (Orji, 2012). Despite the existence of this law, spills from oil pipelines are still one of the major causes of pollution in Nigeria.

5.6.8 *International Conventions*

The key function of international agreements/treaties is the regulation of oil pollution damage. International treaties relevant to the oil and gas sector to which Nigeria is signed up to which have an impact on the legislative framework include;

   i.   OPRC (oil pollution preparedness, response and co-operation) convention *(see section 4.3)*

   ii.   African convention on the conservation of nature and natural resources, 1968.

   iii.   Convention on the prevention of marine pollution damage, 1972

   iv.   International convention on the establishment of an international fund for the compensation for oil pollution damage, 1971

   v.   International convention for the prevention of pollution of the sea by oil (1954)

   vi.   International convention on the continental shelf and high seas (Geneva, 1958)

5.7 Laws Relevant to the Oil & Gas Industry in General

5.7.1 *1999 Constitution of the Federal Republic*

Provision is made within the country's constitution for the protection of the environment. Section 20 which is the basis of environmental law in Nigeria states that 'The State shall protect and improve the environment and safeguard the water, air and land, forest and wild life of Nigeria'. Furthermore, Section 12(2) establishes, though impliedly, that international treaties (including environmental treaties) ratified by the National Assembly should be implemented as law in Nigeria. It states that 'The National Assembly may make laws for the Federation or any part thereof with respect to matters not included in the Exclusive Legislative List for the purpose of implementing a treaty'.

5.7.2 *Petroleum Act 1969*

This is a major law that has been amended by the Petroleum Act Cap. 350 L.F.N. 1990. It vests the entire ownership and control of all petroleum in the state and charges the minister of petroleum resources with the task of regulating the activities of the Nigerian petroleum industry by making regulations regarding licences, leases and operations. It also covers regulations which prevent the pollution of waterways and the atmosphere (Orji, 2012). There are seven (7) subsidiary legislations under this Act. Most of the regulations of this act are related to the prevention of oil spillage. Even though there are references to the payment of

compensation, nothing specific is mentioned in relation to oil spill remediation or any type of remediation at all.

i. **Minerals Oils (Safety) Regulations 1963**; this act replaced the repealed 'mineral oils regulations'. It deals with safe discharge of noxious or inflammable gases and provides penalties for contravention and non-compliance. It stipulates that any unusual escape of petroleum oil or gas from any well, pipeline or installation or anything unsafe or likely to produce damage should be reported to a manger or competent person.

ii. **Petroleum Regulations.**

iii. **Petroleum (Drilling and Production) Regulations 1969;** requires license holders to take all practical precautions, including the provision of up-to-date equipment approved by the appropriate authority to prevent pollution of inland waters, river water courses, the territorial waters of Nigeria or the high seas by oil or other fluids or substances (Ugochukwu, 2008).

iv. **Petroleum Refining Regulations 1974;** prohibits discharge or escape of petroleum into waters within harbour areas and deals, among other things, with construction requirements for oil storage tanks to minimize damage from leakage (Ugochukwu, 2008). It provides that the disposal of residue, sludge, rusts, and similar matters from tanks which may have contained leaded petroleum products shall be according to good refining practices (Orji, 2012).

v. **Crude Oil (Transportation and Shipment) Regulations.**

vi. **Deep Water Block Allocations to Companies (Back-in-Rights) Regulations.**

vii. **Oil Prospecting Licences (Conversion to Oil Mining Leases, etc.) Regulations.**

5.7.3 *Oil Terminal Dues Act 1969*

It prohibits oil discharge to areas of the continental shelf within which any oil terminal is situated (Ugochukwu, 2008).

5.7.4 *Associated Gas Re-Injection Act (1979)*

The act was enacted to discourage gas flaring in Nigeria. It provides for the utilization of gas produced in association with oil and for the re-injection of such associated gas not utilized in an industrial project. The Government has raised the penalty for gas flaring and this

increase was due to the government's determination to protect the environment and ensure the optimal and functional use of Nigeria's gas resources (Ugochukwu, 2008).

5.7.5 *Harmful Waste Cap 165 LFN 1990.*

As the name implies, it is 'an Act to prohibit the carrying, depositing and dumping of harmful waste on any land, territorial waters and matters relating thereto'. Under Act, where any damage (e.g. contamination of land or groundwater) is due to harmful waste, any person who deposited, dumped or imported the harmful waste or caused the harmful waste to be so deposited, dumped or imported shall be liable for the damage. It is a preventive legislation that was enacted after the dumping of toxic waste at the Koko port by an Italian firm in 1988. It applies to toxic substances which would also relate to the oil and gas industry, however, there is no reference whatsoever to remediation.

5.7.6 *Oil in Navigable Waters Act (ONWA) 1968*

The act was enacted to implement the terms of the International Convention for the Prevention of Pollution of the Sea by Oil 1954 to 1962 and to make provisions for such prevention in the navigable waters of Nigeria. It prohibits discharge of oil or any mixture containing oil into the territorial or navigable inland waters (Ugochukwu, 2008). It makes provision for precautions in the conveyance of petroleum and rules for safe operation of pipelines. Many cases for exemption are, however, contained within this act and may be used to evade responsibility to remediate pollution in navigable waters.

5.8 Organisational and institutional framework for oil spill remediation

This section looks at specific regulatory agencies that have been mandated to ensure a wholesome approach to oil remediation in Nigeria as well as formal and informal stakeholders whose roles may or may not be well defined. It also analyses the setting of major actors including private sector and host community involvement. An attempt is made to elucidate the roles, power and realms of jurisdiction of these agencies. National policies and programs will be discussed within this section. The major stakeholders in the Nigerian oil industry are highlighted in the diagram below.
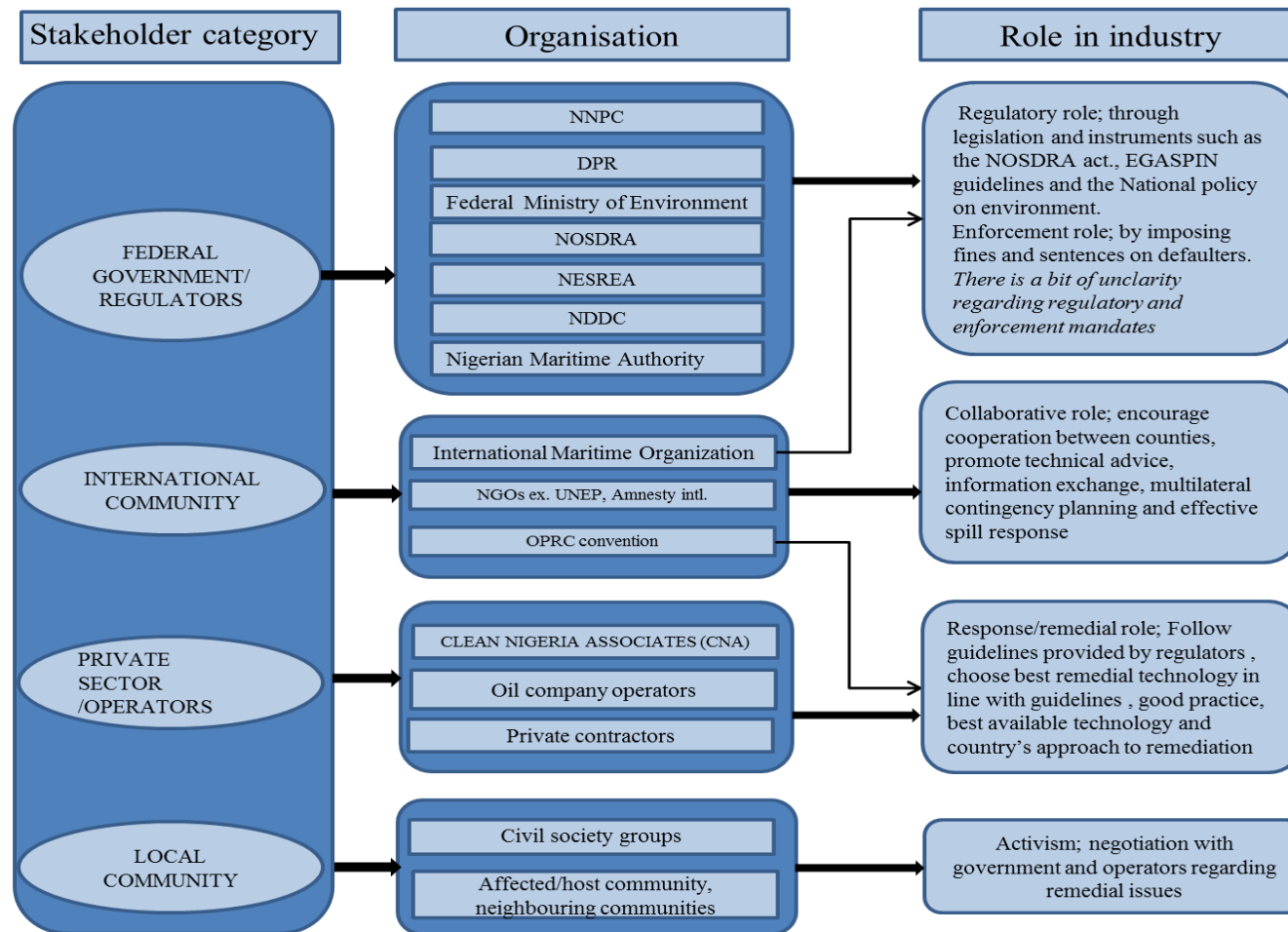
Figure 5-3 Key oil industry stakeholders and their roles in oil pollution remediation in Nigeria (designed based on primary findings of this research)

5.8.1 *Federal Government*

The Land Use Act (1978) vests all land in the territory of each State in the Federation in the Governor of that State to be held in trust and administered for the use and common benefit of all Nigerians. Hence this act places the Federal government in complete ownership and at the helm of affairs as far as oil pollution is concerned. The Federal Government of Nigeria deals with the problems of oil spill in Nigeria through a number of Federal and State parastatals and agencies with specified roles and functions (Nwilo and Badejo, 2006). The key Federal regulatory agencies for the petroleum industry are DPR and NOSDRA and they function via Acts & Instruments. According to Iledare (2010), the high international environmental safety standards required of petroleum industry operators in their activities are either weakly enforced or respected because of the limited technical capacity of these federal regulatory agencies. The FGN acts in a response (operator) as well as regulatory capacity within the industry. Relevant agencies, acts and instruments worth mentioning are listed below.

DPR (Department of Petroleum Resources)

This is the first statutory agency that was set up to supervise and regulate the Nigerian petroleum industry. It started as a Hydrocarbon Section of the Ministry of Lagos Affairs in the early fifties and was later upgraded to a Petroleum Division within the then Ministry of Mines and Power. It became the Department of Petroleum Resources (DPR) in 1970. The Department has since continued to oversee all the activities of companies licensed to engage in any petroleum activity in the country. It was realigned with the Ministry of Energy in December, 2006, when the government merged the Ministries of Petroleum Resources and Power & Mines together to form a single entity (DPR, 2012). The Department of Petroleum Resources (DPR) is responsible for technical/environmental regulation of all activities of the oil and gas sector of Nigeria (DPR, 2012). Its key objective is to ensure that oil companies carry out their operations according to international oil industry standards and practices in line with National goals and aspirations. It does this by issuing guidelines to regulate the impact of such industries on the environment, namely the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). EGASPIN empowers DPR to issue permits for all aspects of oil-related effluent discharges from point sources (gaseous, liquid and solid), and oil-related project development. The DPR also has powers to seal up premises, seize offending substances, impose fines and require the clean-up of environmental damage where such facilities have been licensed by the DPR.

Violators may be fined and in certain cases, have the polluting facility shutdown until they comply (Okenabirhie, 2008). DPR is empowered by various legal provisions to discharge a number of other functions which cover all activities in petroleum operations; upstream and downstream, as well as petrochemicals (DPR, 2012). These include;

• Supervision of all petroleum industry operations in order to ensure compliance with applicable laws and regulations. Companies who are under licences and leases in the country are required to carry out operations in line with good oil producing practices. This does not say anything specific about the choice of remediation technology that should be used.

• Enforcement of safety and environmental regulations to ensure that those operations conform to national and international industry practices and standards.

• Appropriate and updated record keeping of the oil industry's operations particularly on matters relating to petroleum reserves, production and exports of crude oil, gas and condensate, licenses and leases. It also keeps records of and keeps government informed about activities and occurrences in the petroleum industry by rendering regular reports on them to Government.

• Provision of advice to government and relevant agencies on technical matters and policies which may have impact on the administration and control of petroleum.

NNPC (The Nigerian National Petroleum Corporation) and the NNPC Act

The NNPC which in 1977 defines itself as an integrated Oil and Gas Company, engaged in adding value to the nation's hydrocarbon resources for the benefit of all Nigerians and other stakeholders (NNPC, 2010). The role of the Nigerian Government in the oil industry has evolved over time, from just regulatory and supervisory to include direct involvement in oil exploration and development (BEG, 2006). Its statutory duties as provided within the NNPC Act relate to the production, refining, treating, processing, handling, purchasing, marketing, storage and transportation of petroleum and petroleum products. It is therefore involved in environmental protection in the oil and gas sector by virtue of these responsibilities. The corporation is particularly charged with the duty of providing and operating pipelines, tanker-ships or other facilities for the carriage or conveyance of crude oil and other products related to the corporation's operations. It is also involved in the construction, equipping and maintaining of tank farms and other facilities which are used for handling and treating petroleum and its products and derivatives (Okenabirhie, 2008). Their involvement in environmental protection in the sector stems from the fact that

they are liable for any spillages, discharges, escape or leakage from their facilities hence they ought to take due care and diligence thereof to avoid such liability. Furthermore, it is listed within the National Oil Spill Contingency Plan (NOSCP) as one of the agencies to be mandatorily co-opted and engaged by NOSDRA in the event of a Tier 3 oil spill. In the event of a spill, according to Okenabirhie (2008), NNPC is mandated with the following responsibilities;

i. Cooperation with the oil spiller in determining appropriate measures to prevent excessive damage.

ii. Prompt referral of the response effort proposal made to her to the Federal Ministry of Environment.

iii. Mobilization of their internal resources and also assist in obtaining any outside resources that may be required to combat the spill.

iv. Assistance in the assessment of damage caused.

The above functions were imposed on the NNPC because by equity participation in oil operations with her joint venture partners, the NNPC absorbs a good proportion of the expenditure incurred by her operating partners including compensations and claims arising from damage caused by oil spill disasters (Okenabirhie, 2008). The Pipelines and Products Marketing Company Limited (PPMC) is a subsidiary of NNPC and is responsible for all pipelines in Nigeria including crude oil pipelines.

FEPA (Federal Environmental Protection Agency) and the FEPA Act

The FEPA Act Cap 131 LFN 1990 was the principal environmental legislation that regulated environmental pollution in Nigeria until 2007 when it was **repealed** by the National Environmental Standards and Regulations Enforcement Agency (NESREA) Act. The FEPA Act stipulated that where there has been a discharge of any hazardous substance in violation of environmental laws/permits, the person responsible for the discharge would bear the liability of the costs of removal and clean up. FEPA was empowered to protect and develop the environment throughout Nigeria and contained provisions which addressed challenges in the oil and gas industry. NESREA however is not empowered to enforce environmental laws and regulations in the oil producing communities in Nigeria. It possesses specific legislative exemption from the oil and gas sector (Okenabirhie, 2008). In 1999, the Federal Ministry of Environment (FME) was established and it took over FEPA's duties (Ogunba, 2011).

The Federal Ministry of Environment of Nigeria (FME)

The Federal Ministry of Environment (FME) is the main body tasked with administering and enforcing environmental laws on behalf of the Federal Government of Nigeria (FGN). It administers the rules set out in the FEPA and the Environmental Impact Assessment Acts (EIA) (Okenabirhie, 2008). It was established in 1999 to ensure effective coordination of all environmental matters under a single ministry. It plays a strategic role in the achievement of the objectives of the country's socio-economic reforms such as the National Economic Empowerment Strategy (NEEDS) and other regional and global initiatives such as the New Partnership for African Development (NEPAD), Millennium Development Goals (MDGs) and Johannesburg Plan of Implementation (JPOI). It handles problems of environmental degradation in Nigeria through guidelines and standards for environmental pollution control and other regulations that deal with effluents, industrial pollution, waste management, and environmental impact assessment.

Other instruments of the ministry include the revised **National Policy on Environment**, 1999 and the **National Agenda 21** (published in 1999), which touches on various cross-sectoral areas of environmental concern and maps out strategies on how to address them.

Key functions of the ministry include;

i.   Preparing National Policy for environmental protection and conservation of natural resources.

ii. Defining procedure for environmental impact assessment of all relevant projects.

iii. Providing advice to the Federal Government on National Environmental Policies and priorities, conservation of natural resources, sustainable development and scientific & technological activities affecting the environment and natural resources.

iv. Promoting cooperation in environmental science and conservation technology with similar bodies in other countries and as well as with international bodies connected to environmental protection and natural resources conservation.

v.   Ensuring cooperation among government bodies and research agencies on matters and facilities relating to the protection of the environment and the conservation of natural resources.

vi.   Prescribing standards and making regulations on water quality, effluent limitations, air quality, atmospheric protection, ozone protection, noise control as well as the removal and control of hazardous substances.

vii.   Monitoring and enforcement of environmental protection measures (F.M.E., 2010).

There are five (5) Parastatals which exist under the Federal Ministry of Environment including the National Environmental Standards and Regulations Enforcement Agency (NESREA) and the National Oil Spill Detection and Response Agency (NOSDRA).

NESREA (National Environmental Standards and Regulations Enforcement Agency)

NESREA was established by the NESREA (Establishment) Act, 2007, thus repealing the Federal Environmental Protection Agency (FEPA) Act 2004. The key thing to note about the NESREA act which repealed the FEPA act is that it can enforce environmental laws and regulations other than in the oil and gas sector (Okenabirhie, 2008). It is thus excluded from many issues that have to do with oil spill remediation. It has been endowed with a mandate to ensure the protection and development of the environment, biodiversity conservation and sustainable development of Nigeria's natural resources as well as enforce compliance with laws, guidelines, policies and standards on environmental matters. NESREA is also responsible for coordination, and liaison with, relevant stakeholders within and outside Nigeria on matters of enforcement of environmental standards, regulations, rules, laws, policies and guidelines (NESREA, 2008). Several of its functions clearly state that its jurisdiction covers all areas of the environment 'other than the oil and gas sector', however, certain of its functions do not make this distinction. In fact, one of the outlined functions requires NESREA to enforce compliance with the provisions of international agreements, protocols, conventions and treaties on the environment to which Nigeria is a signatory including within the oil and gas sector and such other environmental agreements as may from time to time come into force' (NESREA, 2008). This is a contradiction that may make it difficult to carry out enforcement of relevant laws. The 'National Policy on Environment' is enforced by NESREA.

NOSDRA (National Oil Spill Detection and Response Agency) & the NOSDRA Act

This is a special Agency established specifically for the oil and gas sector and is the foremost organisation for environmental protection in Nigeria in this regard. It is of key interest as far as oil spill response and remediation in Nigeria is concerned. The agency was initiated by the Ministry of Environment in 2004, and approved by the Federal Executive Council of Nigeria

with a mandate to manage the reviewed draft National Oil Spill Contingency Plan (NOSCP). The mission of NOSDRA is "To restore and preserve our environment by ensuring best oil field, storage and transmission practices in exploration, production and use of oil in the quest to achieve sustainable development in Nigeria" (NOSDRA, 2012).

Its key functions include;

- Ensuring compliance with all environmental legislation and the detection of oil spills in the Petroleum Sector.

- Coordination of oil spill response activities throughout Nigeria.

- Co-ordination of the implementation of the NOSCP (National Oil Spill Contingency Plan).

- Encouragement co-operation among member States of the West African Sub-region and Gulf of Guinea for combating oil spillage and pollution in contiguous waters (NOSDRA, 2012).

There were several calls for an Act to amend the NOSDRA establishment Act 2006 and for other related issues and thus the NOSDRA Amendment Bill 2012 was designed to redress the legal loopholes in the existing Act (Umoru, 2012).

The Niger Delta Development Commission (NDDC), CAP N68, LFN 2004

This agency was formerly known as Oil Mineral Producing Areas Development Commission (OMPADEC). The NDDC master plan is designed to cover specific areas to facilitate improvement of the lives of the people of the Niger Delta Region of Nigeria. One of these key areas is environment and hydrology (NDDC, 2012). NDDC mandate is majorly regulatory not remedial hence they do not intrude in the remediation process. The NDDC's major mandate is the formulation and implementation of policies and guidelines for the development of the Niger Delta area. It is also charged with tackling fund and environmental problems that arise from the exploration of oil mineral in the Niger Delta region as well as advising the Federal Government and the member states on the prevention and control of oil spillages, gas flaring and environmental pollution. Additionally, it is required to liaise with the various oil relevant companies on all matters of pollution, prevention and control (NDDC, 2012). It can be clearly seen that some of these responsibilities overlap with those of DPR and NOSDRA.

5.8.2 *Host community involvement*

Affected communities have a right to the land that has sustained them for centuries, and a right to a voice when decisions that impact their communities are taken. However due to several conflicting interests, these rights are often drowned, ignored and neglected. They are therefore one of the most important stakeholders in the oil industry. Although not directly involved in the remediation process, they do have an impact on the success of remediation activities. In recent times, they have been getting increased recognition and attention by the Federal government (Akinjide-Balogun, 2001). For instance, part 1 section 7 of the EIA decree No. 86 1992 states that before decision is taken on an activity to which an environmental assessment has been produced, opportunity shall be given to government agencies, members of the public, experts in any relevant discipline and interested groups to make comment on environmental impact assessment of the activity. In considering specific remediation technologies, it is worth noting that members of communities near contaminated sites often believe that natural attenuation is a "do nothing" approach (Committee on Intrinsic Remediation *et al.*, 2000). Such technologies may be perceived as an attempt to evade responsibility and such issues will need to be anticipated and addressed where necessary. We however note from the Ogoniland case that Remediation by Enhanced Natural Attenuation (RENA) is the primary remediation technique employed at oil-impacted sites (see section 5.3.3).

5.8.3 *International cooperation*

A notable example of international community involvement is the OPRC Convention, which calls for cooperation between countries and the technical advisers in order to promote exchange of information, multilateral contingency planning and effective oil spill response. This convention which was conceived primarily for the assistance of developing nations has been adopted by Nigeria (Moller and Santner, 1997). It encourages government and industry cooperation in contingency planning and coordinated response procedures as well as research and development (R&D) programmes. Other forms of assistance that the international community may provide include advice on-site at the time of an incident as well as case studies and provision of subsequent reports and recommendations. The key challenge with such cooperation in the Nigerian context has usually been in the implementation and how recommendations have been taken on board. In July 2012, for instance, the Federal Government set up HYPREP (Hydrocarbon pollution restoration project) for the restoration of areas devastated by oil pollution in the Niger delta in furtherance of its commitment to

implement the UNEP (United Nations Environment Programme) Assessment Report on Ogoniland – a severely battered area of the Niger Delta. The Ogoniland oil spill is one of the most renowned incidents of oil pollution in Nigeria. Ogoniland covers an area of about 1,000 km^2 in Rivers State, southern Nigeria and has a population of 830,000 people (UNEP, 2011). The Ogoniland spill drew international media attention in 1995, when Ken Saro-Wiwa, along with eight others were hung to death in a prison yard after being sentenced to death by a military tribunal for alledgedly masterminding the gruesome killing of some Ogoni-chiefs at a pro-government meeting. The trial and execution of these environmental activists by Nigeria's military government at the time have since been described as fraudulent and resulted in Nigeria's suspension from the Commonwealth of nations for three years (Okome, 2000; Doron and Falola, 2016). Ken Saro-Wiwa received several human rights awards including the 'Right Livelihood Award' and 'Goldman Environmental Prize' for leading nonviolent campaign against the environmental degradation of the land and waters of Ogoniland (UNPO, 2015). Despite continued activism for the remediation of Ogoniland and efforts by the government and operators, it is still heavily polluted. This situation has thus resulted in lack of trust among actors; political tensions among communities and government; security considerations as well as technical and logistical challenges among other things (UNEP, 2011). UNEP was commissioned by the Federal Government of Nigeria in 2009 to carry out a comprehensive assessment of the environmental disaster in Ogoniland. An extensive study was therefore carried out by UNEP in consultation with relevant stakeholders which provided the 'scientific basis on which a concerted environmental restoration of Ogoniland could begin' (UNEP, 2011). The report noted widespread oil contamination in Ogoniland, which is impacting severely on land areas, sediments and swampland. Most of the contamination reported was from crude oil although refined product was found at three locations (UNEP, 2011). The UNEP involvement highlighted several areas of deficiency including remediation approach and guideline values. The project was charged to implement the recommendations of the UNEP report on Ogoniland as well as investigate, evaluate and establish other hydrocarbon impacted sites and make appropriate recommendations. There has been scepticisms about HYPREP being inadequate to sort out the issue of oil spill due to the change of scope of the clean-up intervention, from an Ogoniland clean-up to the clean-up of all polluted areas in the Niger Delta, while it is still being referred to as a project instead of a programme. Also, there have been allegations already that the 'oil majors' are behind it hence the 'Ministry of Environment and suppression of the National Oil Spill Detection and Response Agency (NOSDRA)' (Alabo-George 2012). Another example of international

cooperation can be cited in the UNDP collaboration with NOSDRA. UNDP provided support to NOSDRA, particularly in the development of its regulations and strengthening of its policy framework for oil spill management under the international development body's Control Programme Action Plan (CPAP) (FOSTER, 2011).

5.8.4 *Private sector involvement*

Private sector players are perhaps the most dominant actors in the field of oil pollution remediation. SPDC (Shell Petroleum Development Company of Nigeria Limited) commonly known as Shell is a dominant actor in the private sector being the largest fossil fuel company in Nigeria. Other notable actors are oil servicing companies, remediation contractors (who are usually consulted by oil companies) and other multinational oil companies such as Total which form part of the CNA (Clean Nigeria Associates).

SPDC remediation in Ogoniland

It is important to note the focal position of SPDC in the oil remediation process in Nigeria. As the foremost oil operator, most of the remediation work is carried out by them. UNEP's Environmental Assessment of Ogoniland showed many areas contaminated way beyond the 50 mg/kg of total petroleum hydrocarbon EGASPIN target range and sometimes well above the 5,000 mg/kg EGASPIN intervention level (UNEP, 2011). The company's main operating document for guiding clean–up activities is the SPDC Oil Spill Clean–up and Remediation Procedure (SPDC–2005–005716) (UNEP, 2011). It possesses other documents including the Remediation Management System 2010 which were reviewed during the UNEP assessment of Ogoniland (UNEP, 2011). Intervention measures that were employed in Ogoniland included laying a skirt boom or absorbent boom to contain the spill although the equipment used was often observed to be in poor condition, rendering it ineffective (UNEP, 2011). The UNEP report noted that

i. RENA was the primary method of remediation of oil-impacted sites (UNEP, 2011). (Cragg *et al.*, 2013).

ii. Provisions for using risk-based screening exist for soil, however, a TPH value of 5,000 mg/kg (same as the EGASPIN intervention value) was validated as the end point (UNEP, 2011).

iii. Despite the EGASPIN recommended Target level of 10 ppm of dissolved TPH"., there is no location in Ogoniland where groundwater remediation has been attempted (UNEP, 2011).

iv.   'Up till the time of the report in 2011, there still remained pollution of outrageous proportion which still needs to be remediated'.

The situation has not changed much till date implying a need for further research in this area. Apart from RENA, two other methods of remediation are commonly employed by SPDC globally. These are Remediation by Stabilisation / Solidification and Low Temperature Thermal Desorption.

Clean Nigeria Associates (CNA)

CNA is a non-profit oil spill response cooperative organisation formed by the Oil Producers Trade Section (OPTS) for the main purpose of assisting the Nigerian Petroleum Industry in its efforts of oil spill containment and minimisation of the impact of oil spills on sensitive ecosystems. It started out with 11 member companies operating in Nigeria, which aimed to enhance their individual clean-up capabilities. Its mission is to identify and execute actions necessary to establish CNA as an appropriate, well managed, sustainable and evolving tier-two oil spill response organization relevant to the evolving needs of its members. It was formed in November 1981, became fully operational in 1985 and was incorporated as a company limited by guarantee in 2000 with a constituted Board of Directors as well as a Technical Committee which serves as its advisory arm. A constituted management team overseas the day-to-day running operations of the company. According to Nnubia (2008), CNA stores and maintains in a state of constant readiness, the most comprehensive and advanced containment and clean up equipment available in Nigeria under an experienced and seasoned management team. According to Nnubia (2008), CNA has an equipment investment valued at over $ 20 Million which are strategically located in manned bases and storage deports to provide prompt and effective response to an oil spill emergency. The operating bases are at Onne, Warri, Eket, and Kaduna. New bases are being planned for Brass, Forcados, and Atlas Cove/Mosimi. Although CNA's equipment stockpiles are primarily for use in the inland, coastal and offshore exploration and production areas, CNA makes equipment available for members and non-members spill anywhere within Nigeria and bordering countries. Fast response equipment can be at an oil spill site up to 160 kilometres away within six hours of notification depending on time of call out (Nnubia, 2008).

The Company main aim is to minimise the impact of oil spills on sensitive ecosystems. Objectives also include providing training and conducting or supporting research into, subjects pertaining to the environment (CNA, 2015).

During oil spill containment and clean-up operations, CNA functions under the sole direction and control of the member company requesting the assistance, providing specialist advise and full response activities. Request for CNA assistance is made directly to CNA management who then mobilizes its personnel to the site and subsequently report its operational activities to the CNA. It has the capacity to respond to a 2nd-tier oil spill. The CNA has 2 distinct operational phases of spill response as outlined below

Phase 1 (critical phase of response) which involves assessment, dispersion or containment; organisation of response activities at the spill site and initial recovery of spilled product for disposal as directed.

Phase 2 (clean-up phase of response) involves complete recovery of spilled product to the extent determined to be appropriate; complete clean-up of polluted debris or similar materials; safe disposal of waste and conducting remediation measures as appropriate (Nnubia, 2008).

Existing clean-up technologies currently in use by the CNA for oil spill response include skimmers and pumps, dispersant spraying system and sorbents (Nwilo and Badejo, 2005). There is a need for synergy between the government and private sector as well as international NGOs.

5.9   Chapter findings

The desktop study helped to provide an understanding of the biophysical, social and political context of oil pollution remediation in Nigeria. It showed that Nigeria has a robust environmental legislation that has developed over time however, challenges in enforcement do exist. Stakeholder mapping identified the roles of key stakeholders and classified them broadly as regulators, community members, experts/academics and oil companies. Information obtained from the desktop study helped to set the following target objectives for the stakeholder interactions presented in chapter six (6).

5.9.1   *Characteristics of the legislative framework for oil spill remediation in Nigeria*

i. **Defences and Exceptions;** a number of these are allowed which water down the law and make it easy for the offender to escape liability for example, Under the *Oil in Navigable Waters Act*, six (6) special defences are outline. These defences relate to issues such as reason for leakage, claim of accidental spill or sabotage (Ezeibe, 2011).

ii. **Lack of harmonization of laws;** some of the roles mandated to agencies are duplicated and this poses a challenge to effective remediation. A typical example is

the duplication of functions that exists between the NIMASA (Nigerian Maritime Administration and Safety Agency) and NOSDRA. As oil spill is harmful to maritime life, NIMASA has a mandate to make regulations and give directives in this regard. Hence the oil spiller is compelled to report incidents of leakage, spill, escape or discharge to not only NOSDRA but also to the Chief Fire officer, harbour master and NIMASA by the individual acts of these agencies (Ezeibe, 2011). Also worthy of note is the NESREA Act which although granted legislation enforcing powers 'including that of the oil and gas sector' at section 7(c), to NESREA, expressly excluded the oil and gas sector from the jurisdiction of NESREA in the same section of the Act. Also, the merchant shipping act grounds the major stake of the Ministry of Transport in environmental protection as it relates to the oil and gas sector, particularly with regards to the marine environment (Ezeibe, 2011). ''Divide and rule' is a well-recognised strategy which governments use to avoid taking action on politically sensitive issues (Bar-Joseph, 2010). There is however no evidence that the competing bureaucracy observed within the oil and gas industry in Nigeria is the result of such intentional act. Rather, negligence and lack of due diligence within the industry; government instability due to several military coups and interim governments; power-play between the legislative and executive arms of government, perceived executive dominance and the relative newness of democracy are more likely culprits (Shinsato, 2005; Godswealth *et al.*, 2016).

iii. **Low ineffective penalties;** these tend to be inappropriately small and hence do not serve as an effective deterrent or punishment (Orji, 2012) typical instances are

  a. a fine of one million naira for failure to clean up an oil impacted site is about the only penalty provided in the NOSDRA act with regard to oil spillage (Ezeibe, 2011).

  b. A fine of 100.00 naira (₦) or six (6) months imprisonment is the penalty for failure to comply with the approved eluent specifications of the Petroleum Refining regulations.

  c. According to Ezeibe (2011), the ONWA act penalty that ranges between ₦20 to ₦200 were carried over into the 2004 legislation from the 1960s due to laxity.

iv. **Age;** many of the laws are archaic and this is usually evident in the inappropriate amount stipulated as penalties for many of the laws.

v. **Enforcement/ implementation;** despite a large number of laws, environmental laws and policies in Nigeria are rarely enforced. Lack of enforcement capability can also be attributed to the limited technical capacity of the regulatory agencies and the shallow rule of law, corruption and inadequate funding (Ngoran, 2011).

vi. **Ambiguity/ lack of clarity in language;** the Petroleum Act for instance stipulates that 'all operations shall conform to good oil field practice'. This does not indicate specific requirements for safety or environmental protection hence ambiguity in wording of legislation makes it difficult to implement relevant legislation (Edu, 2011).

5.9.2 *Characteristics of the operational & administrative framework for oil spill remediation in Nigeria*

This section highlights the approach to oil spill clean–up and remediation in Nigeria as well as challenges that are characteristic of the industry.

i. **Principle for clean-up;** Nigeria approach to clean–up is based on the 'polluter pays principle' which is interpreted to mean that the polluter must pay for any clean up exercise as well as compensate for losses suffered (Okenabirhie, 2008). Based on this, the oil companies are usually the Potentially Responsible Party (PRP) whenever a spill occurs. The responsibility for enforcement of remediation activities lies mainly on the shoulders of the Federal Government through the various agencies and parastatals reviewed above. Although this principle is in place, a major challenge is the acceptance of responsibility for clean-up. While the oil companies tend to say it is due to sabotage, government and action groups would generally hold a contrary opinion usually tilted towards claims of a lack of maintenance of pipelines and storage tanks. For instance, SPDC (Shell Petroleum Development Company) claimed in 1996 that sabotage accounted for more than 60% of all oil spilled at its facilities in Nigeria (SPDC, 1996). The British Advertising Standards Authority reviewed this claim by Shell in 1996, due to complaints from members of the public and from Friends of the Earth. It resulted in the advertisers (Shell) being asked not to repeat the claim as it had not given enough information to support the claim. DPR statistics indicate that only 4% of all spills in Nigeria between 1976 and 1990 were caused by sabotage. These statistics however include offshore spills, which constitute a significant proportion of spills and are unlikely to be caused by sabotage (Manby and Human Rights, 1999). In actuality, oil spill is caused by a combination of several

different factors including old pipelines, operational malfunctions and sabotage (Shinsato, 2005). Despite the fact that DPR is supposed to confirm sabotage and inspect the damaged installation in the presence of community members , regulatory agency representatives and other prescribed partners under a JIV (Joint Investigation Visit), there are often no genuinely independent experts present (Manby and Human Rights, 1999). A report by Amnesty international regarding flaws in the oil spill investigating and report system in Nigeria states that the oil companies themselves are the primary investigator of the JIV. The report also stated that regulatory certification of the cause and volume of an oil spill as well as the status of clean ups is not credible (AmnestyInternational, 2013).

ii. The approach of regulatory agencies in Nigeria is largely focused on prevention of environmental damages and the regulation of potentially harmful activities as they are too ill equipped and poorly funded to prosecute and thereafter punish offenders when the harmful damage occurs (Okenabirhie, 2008).

iii. Multiplicity of agencies and disparity in roles ex. Regulatory and response roles of DPR and NOSDRA.

iv. Weak emergency response to spills and remediation procedures.

v. Lack of trust, secrecy and corruption surrounding remediation efforts.

vi. Inability of regulators and response agencies to carry out their roles effectively due to insufficient funds, which culminates in dependency on the polluters who are meant to remediate.

vii. Ineffective enforcement of remediation responsibilities.

viii. Security challenges for visiting communities during oil spills.

ix. International community involvement; usually in collaboration with government and local stakeholders.

x. PRPs attempt to evade responsibility for remediation. Evidence of this is demonstrated in the magnitude of spills that have been documented in Nigeria versus in more developed countries where these same multinational companies operate. For instance, 40% of all of Shell's oil spills between 1982 and 1992 occurred in the Niger Delta. This is despite the fact that Shell drilled for oil in 28 different countries during that same period (Shinsato, 2005).

5.10   Conclusion

The study provides an understanding of the context for the RDMP (Remediation Decision-Making Process) in Nigeria. It was discovered that there is a robust legislative framework even though it is plagued by many inconsistencies and anomalies. It is commonplace in developing countries for enforcement to be epileptic despite robust legislation. In fact, a phenomenon known as ''implementation deficit'' has been used to describe this sort of situation. Implementation deficit may be defined as failure to achieve policy objectives (Carter, 2007) or the difference between ambition and actual performance (Crabb and Leroy, 2012). The observed deficit in the enforcement of remediation regulation in Nigeria may be attributed to the fact that the monitoring, compliance and enforcement elements of regulatory activities are often very expensive and time-consuming (Carter, 2007). It may also be due to lack of political willingness and motivation on the part of the regulatory bodies.

The institutional framework is similarly robust however, duplicity of roles makes it difficult for objectives to be consistently achieved. There have been reforms proposed by the government; of which the PIB is paramount. It can be noted from this chapter also that the existing remedial techniques have proven inefficient at remediating contaminated sites in the Niger Delta. Considering the dwindling financial climate due to recent fall in oil prices, it is expedient that a sustainable alternative is found to replace or be combined with RENA to achieve remedial goals in a reasonable amount of time. The key legislations and stakeholder interests identified within this chapter will be integrated into discussions in chapter five which are based on interactions with stakeholders.

Chapter 6. Understanding the status of the institutional context for oil spill remediation and biochar implementation in Nigeria and the USA

6.1   Introduction

Chapter five explored legislation and institutional settings for oil spill remediation in Nigeria based on the formal rules-in-use. It therefore set the foundation for the empirical analysis done in this chapter which is based on semi-structured interviews carried out in Nigeria and the USA. A detailed discussion of the methodology and framework for obtaining and processing the data presented here can be found in chapter four.

An opportunity to visit the USA on a research exchange programme made it possible to interact with remediation stakeholders in the USA. Useful insight into the oil spill remediation framework, particularly carbon-based remediation was obtained.

There is presently a wide disparity in the approach taken for remediation of contaminated sites in the USA compared to Nigeria. This is evidenced not only by the difference in scale of pollution that persists but also by the social outcries from impacted parties. Differences can be seen in technology choices and the decision-making process for selecting technologies. Public engagement and the impact that stakeholders have in remediation matters also differ greatly. Carbon-based remediation technology has advanced rapidly in the last decade and in 2013 alone, 25 field-scale demonstrations or full-scale projects were performed in the United States, Norway, and the Netherlands (Patmont *et al.*, 2015).

Even though the social aspect of this study explored the Nigerian environment first, the USA research can in a way be considered a sort of preliminary work to the Nigerian research. This is because it gives a good understanding of the technology and the different perceptions that exist regarding the functionality and effectiveness of carbon-based remediation and consequently biochar as a technology. Interviewee coding information can be found in Appendix B while Interview questions are in Appendix C.

6.1   Chapter scope and objectives

This chapter is an empirical work which involves analysis of the existing remedial system for oil spills in Nigeria. It analyses the implementation of sorbent-based remediation technology in the USA with the aim of exploring biochar viability in Nigeria.

The following targets are explored within this chapter;

- To understand the physical, social and organisational context of oil pollution remediation in Nigeria
- To understand how biophysical conditions and technical characteristics may affect stakeholder perception and decisions relating to implementation of carbon-based remediation in the USA
- To understand community attributes and the rules which govern implementation of carbon-based remediation in the USA
- To highlight similarities and differences in the factors enabling biochar implementation between Nigeria and the USA
- To make recommendations for implementation of biochar in Nigeria based on learnings from implementation of the technology in the USA

In terms of scope, the analysis of the Nigerian environment examines the challenges and prospects of the oil spill remediation framework in Nigeria at the policy-making, policy-implementation and application levels. Analytical work of the USA environment however focuses mainly on the application level within the context of technology implementation. This is because the objectives pursued as well as the data acquired for the USA aspect of the research were more focused on the implementation of the biochar technology itself which is more developed in the USA.

The two scenarios discussed above have been synthesised into Action Arenas as outlined below and constitute the first two core sections of this chapter.

- Action arena (AA)1: oil spill remediation decision making process in Nigeria

AA1 (Section 6.3) discusses the current realities surrounding oil spill remediation in Nigeria as well as the factors which affect decision making regarding remediation technologies. The discussion, which is based on interview data from Nigeria echoes some of the issues highlighted in the desktop study (chapter four) therefore reference will be made to those issues where necessary.

- Action arena (AA) 2: Decision making process for biochar implementation in the USA

AA2 (section 6.4) explores the factors which facilitate choice of remediation technology; particularly carbon-based remediation technology in the USA.

The USA interviews were conducted alongside questionnaires with the aim of evaluating the contrasts of opinions which may exist regarding carbon-based remediation technology. The results obtained were however of different quality as it was not feasible to statistically analyse the questionnaires based on the total sample population. The focus of the discussion

therefore is on the interviews even though data from the questionnaires is incorporated into it to provide supporting evidence where necessary.

The third section (6.5) is a comparative analysis of the two action arenas which explores the potential for biochar implemenmtation within the Nigeria context while making comparisons with the USA and highlighting similarities where necessary.

Recommendations/ the conclusion based on the findings of the analysis are presented in the fourth major section (6.6).

6.2   Action arena 1: oil spill remediation decision making process in Nigeria

This section summarizes views from the Nigerian interviews while employing the use of selected direct quotations for simplicity. It analyses the oil spill remediation framework in Nigeria highlighting the prospects and potential challenges to be faced when implementing a remediation technology. Figure 6-1 (below) shows the framework for analysis of the oil spill remediation decision making process in Nigeria at the policy-making, policy implementation and application levels.
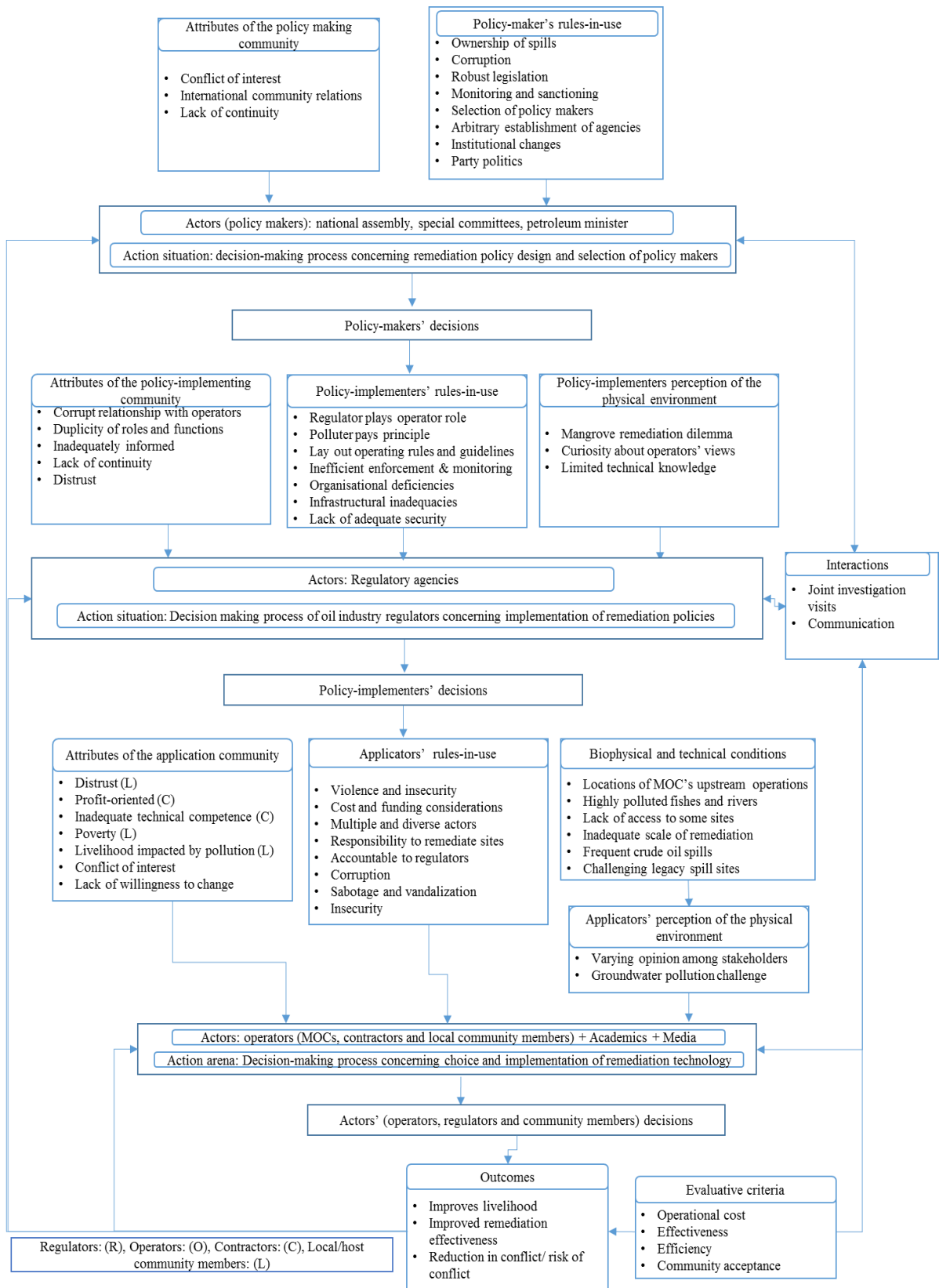
Figure 6-1 diagram for analysis of the oil spill remediation decision making process in Nigeria (designed based on primary findings of this research)

6.2.1 *Policy-making level:* **Decision making process of actors (legislators) in relation to** *design of organisational structure*

Attributes of the policy-making community

The key actors here are senators and speakers of the house of assembly who form the upper and lower house of the Nigerian national assembly respectively. A prominent issue that has plagued the policy-making community is Conflict of interest. Individuals often put their personal interest ahead of national agenda. This often leads to inefficiencies in the legislative process in policy implementation as environmental remediation is not a priority for them. For instance, the Petroleum Industry Bill (PIB) has been proposed since 2008 but remains unpassed through different dispensations of government. The current administration have been accused of 'dragging feet' on the PIB (Ogunmade and Okafor 2016). One of the National Dailies (This Day Newspapers) suggested that the delay in the passage of the Bill is due to a power-play between the National Assembly and the executive arm of government (Ogunmade and Okafor 2016). The bill proposes to provide a comprehensive legal framework for the oil and gas industry as well as address anomalies in the oil and gas sector such as the duplicity of regulatory agency roles as discussed in chapter five among other things (Ogunmade and Okafor 2016). Despite legislation mandating HYPREP to handle the Ogoni spill, the project has also suffered neglect through different dispensations of government. Also, there is a history of arbitrary establishment of agencies and institutional changes as discussed in chapter five**.** The establishment of DPR and NOSDRA has been a source of frustration for operators as they need to satisfy the requirements of different regulators before progress can be made regarding remediation. Lack of continuity has also been a major challenge as different administrations of government often have different priorities.

Policy makers' rules-in-use

Formal rules (legislation) have already been discussed from a theoretical standpoint in chapter five. We focus here on rules-in-use which refer to laws applied in the real world and do generally tend to differ from rules-in-form.

 It was observed from the desktop study that a robust array of laws exist which evolved over the years as a result of efforts to improve the way oil spills were being remediated in Nigeria. *''we have a million and one legislations, policy is not the issue… our problem is not a dearth of policies, no, it is about implementation''* (KII-11).

One major factor that is relevant to oil spill remediation legislation is responsibility for spills and ownership of spills. Nigerian legislation stipulates that operator is responsible for spills within their operational location (DPR, 2002). Legacy spills are the responsibility of the government and an ecological fund exists which was designed to handle legacy spills however, its functionality appears to be nearly non-existent. This may be due to embezzlement of funds as it is not unusual for such monies to be taken by individuals in authority for their own personal use (Donwa *et al.*, 2015). For instance, a former governor of Delta state, James Ibori, was arrested on 129 count charge by Nigeria's EFCC (Economic and Financial Crimes Commission) for laundering over N9.1 billion which eventually resulted in a 13 years prison sentence by the Southwark crown court, UK in 2012 (Mohammed, 2013; Odorige, 2017).

The inability of legislation to culminate into significant progress in remediation is illustrated by the disparity between policy intentions and final outcomes as in the case of Ogoniland which has been attributed to corrupt practices among other reasons (Babalola, 2014; Barima, 2014). Corruption has eaten deep into the fabric of the Nigerian society and this is reflected in the politics and consequently in the selection of policy-makers. Corruption has also been pointed out as the reason for lack of progress in remedial efforts (Shoraka and Emmanuel, 2014). Nepotism and appointment of incompetent directors is a plague that riddles public service life in Nigeria (Yaro, 2014). One of Nigeria's former petroleum minister was arrested in 2015 for allegations of colossal corruption. Corruption also affects establishment of legislation as in the case of the PIB.

'' It depends on if government really wants it… and companies don't want it. The oil companies don't want it. It is government that wants it. So now it is to the highest bidder. That's what the lawmakers, isn't it? In the last assembly session, the highest bidder prevailed which is the oil companies. So in this dispensation, we are hoping that government will be the highest bidder this time around? Like I said, the oil companies don't want it. All the money they should have been investing in projects, they are investing it in ensuring that the bill is not passed. By frustrating it. Making sure that the lawmakers have other diversions. They give them treats, take them on retreats, and sponsor their programmes. You cannot sponsor me on something and then I come and start ... no, I won't do that. cos I will think of all that money'' KI-11

As is the case in many parts of the world, party-politics plays a key role in Nigerian governance. For instance members of the House of Representatives from the Niger Delta would often speak in the interest of those in the region and the government in power often

determines which issues are given priority. When a new dispensation of government comes to power, they often want to bring in new policies that favour them, often abetted by the high politicization of Nigeria's public administration system (Nwogwugwu and Adiro, 2015).

6.2.2 *Policy-implementation level: decision-making process of actors regarding policy design*

The key actors in the policy-implementation community are oil industry regulators who are responsible for translating legislation into policies. We discuss here how regulators policies and actions impact on remedial activities. The major stakeholders are NOSDRA, DPR and State Ministry of Environment.

Attributes of the Policy-implementation community

As with the policy-implementing community, one of the challenges of the regulatory community identified is conflict of interest. One interviewee alleged that some regulatory officials themselves have companies that engage in remedial activities. This is not an unlikely or foreign practice in Nigeria as it is common knowledge that government officials have been reported to own many of the Niger Delta oil blocks.

Ok, putting national interest above self. That's what our problem is because all of them in those regulatory agencies, most of them have companies and because the operators know that virtually every Nigerian has a price, 'what is your price?' they pay and they do not... (KI-11). Duplicity of roles and functions exists among certain regulatory bodies as has been the case between DPR and NOSDRA. DPR is the Petroleum regulatory agency of Nigeria while NOSDRA has a mandate to deal with oil spills. Another important factor to consider which has been a cause for controversy in the past is the fact that the regulator also plays the role of operator as NNPC which is an operator also acts a regulator. These issues are some of the anomalies that the PIB proposes to rectify. It is also alleged that regulators have a corrupt relationship with operators.

Regulators are often inadequately informed on operator activities**.** They tend to depend on information that is given them by operators about remedial activities.

Policy implementers' perception of the physical environment

Regulators pointed out groundwater pollution as a particularly challenging issue to deal with. Also, mangrove remediation was described as a dilemma due to the sensitivity of the ecosystem coupled with legislation which prohibits the application of intrusive remediation technology. The author noted during interactions with regulators that they are curious to

know what the views of operators are concerning the state of remediation work in the country.

Policy implementers' rules-in-use

One of the issues highlighted by most interviewees was enforcement of legislation. The responsibility for this lies almost entirely with the regulators. They lay out operating rules and guidelines as guided by legislation, mostly in the form of agency mandates, remedial guideline values and policy documents.

Ownership of spills is one of the central themes that dictates how regulatory activities are carried out hence the Polluter Pays Principle (PPP) is at the forefront of many remediation decisions in Nigeria. Operators are obligated to adhere to the PPP and are liable to penalties such as fines and levies if they falter. Regulators are usually focused on getting the operators to take responsibility and very little is done therefore to manage legacy spill sites. The viewpoint that government ought to be involved with regulation as opposed to actual remediation seems to be a common expectation in Nigeria. It might be beneficial if government was more involved in remediation through its own contractors.

''government has no business being ... involved in these things as it were. Even government don't have those expertise. The service companies do, so what government needs to do is to enforce implementation'' KI-11.

Discussions with interviewees revealed that policies are constantly changing with new government administration and this causes instability, lack of continuity and organizational deficiencies.

Infrastructural inadequacies mean that regulators are often handicapped in carrying out their regulatory function effectively and often need to rely on operators for assistance. One of the formal operators who is head of remediation services of an oil company stated;

''Regulators should be separate from us. We arrange all their logistics. This is not ideal and not good enough. The company provides accommodation and land transport'' (KI -19)

Lack of adequate security affects their ability to carry out their regulatory roles properly as there is a risk of being kidnaped or attacked so what is found is that they tend to rely on third party information.

Enforcement, also affected by corruption, is also an issue with regulators as is the case with the policy-makers and this impacts on their ability to enforce policies effectively.

''It is enforcement that is our problem and even the enforcement agencies are cutting corners. They come, they settle them and they look the other way.'' (KI-11).

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Regulators must approve remedial technologies used by operators. Limited technical knowledge of the environment and technology being used means that regulators may find it challenging to assess the viability of a new technology independently.

Another major area that has been impacted by corruption is monitoring and sanctioning such that even when legislation is available to curtail remediation lapses, corrupt practices within the policy-making arena mean that responsible parties are often able to evade responsibility due to either high quality legal representation or officials who accept bribes to overlook lapses.

In terms of monitoring, interviewees confirmed that a joint task force, which would usually include regulators, operators and community members, is responsible for conducting a Joint Investigation Visit and for closing out remediation projects.

''...DPR, NOSDRA, and then the community and then the local government of the area and the security officials. Usually there are about five parties, five or more that are represented. They are supposed to report ok, they have reported this, this is the quantity spilled, and how soon they are going to swing into action but like I said, mostly, they will give the excuse that because of lack of access, they cannot swing into action as they would like to'' KI-11*

Lastly, fines for defaulting on remedial obligations are often impractical; being either grossly insufficient or arbitrarily extortionate. Oftentimes, they do not get paid as it is easy for operators to have lawyers who can counter penalties via loopholes that exist within the legislation.

...it's like gas flaring. When it's much cheaper to flare gas than to harness it. And even though it is cheaper to flare it, the flare penalties, they don't pay. Nobody enforces the payment (KII-11)

A newspaper energy editor also revealed that regulators may be relying on third party information or information from the operators themselves to verify remedial work done perhaps due to logistic constraints.

...and then if you say I have done remediation, [you go there and ensure that indeed yes, remediation has been done and you don't take their word for it. 'oh! we have done remediation and that's ok by me and you sign them off... KI-11

Involvement and willingness of regulators could be improved by ensuring that they are adequately trained and feel competent enough to do their job.

6.2.3 *Application level: Decision making process of actors concerning choice and implementation of remediation technologies*

This part of the analysis consists broadly of actors (operators, contractors and local community members) whose decisions impact on the choice of technology employed for oil spill remediation. The impact (which may be direct or indirect) does however vary among actors depending on how much power and influence they possess. The table below shows the categories of actors identified within the application level of the action arena.

Table 6-1: categories of actors at the application level

Actor	Description of actor
Oil company operators	Formal/legal operator
Operators of illegal refineries	Informal/illegal operator
Government agencies	Formal regulators
Media/local community members /academics	unofficial actors

Biophysical characteristics and technical conditions of the application community

As stated in chapter four, the Niger-Delta was chosen as the biophysical study area because of the relatively high scale of pollution from oil exploration activities. In terms of pollution typology, the major contaminant of concern in the Niger-Delta is from crude oil as pollution from refined products are often easily volatilised and are more of a fire hazard than a toxic hazard. It is vital that in choosing a remediation technology, the phase of the crude oil is taken into account as this is fundamental determinant of the fate and transport of the contaminant in the environment. Since a major challenge is ground water pollution and biochar is likely to contain the pollutant so that it does not reach groundwater.

''downstream is more from tankers and the depots, the depots. They are not really as serious as the crude, upstream because these ones, you know the effects of crude is much more than the refined'' KI-11

Legacy spills sites are prevalent and spills are still occurring at an alarming rate. As fishing and farming are vital to the livelihood of people in the communities, spills have caused low soil fertility and productivity and hence impacted negatively on the community's land use capabilities.

''It is legacy sites which usually contain tar–like products. They are sites from long time ago. Recent spills are light crude and are generally not an issue. Issues may be with the illegal refineries which are not within Shell's scope. 'I do not want to go looking for contaminated lakes in Nigeria to remediate. It is not within our scope as a company'' KI-14

The UNEP report for instance stated that contaminant levels tend to be quite high in certain areas even though there operators disagreed with the outcome of the report.

Remediation projects are being carried out however the scale and quality needs to increase to cater for the magnitude of pollution in the region and improve livelihood.

There is more awareness about clean-up than remediation. It was noted during interviews that most respondents when asked about remediation tended to give answers relating to clean-up or immediate response even among experts. When questioned further for clarity, it appeared that remediation is much less of a priority than immediate response (clean-up) after a spill. This is understandable as only after satisfactory clean-up has been conducted can remediation commence at a spill site.

''Remediation is really, really something else. Look at Ogoni. Ogoni has been on for how many decades now and we are still talking about remediation and they have not even started'' KI-1.

Also, there are claims that the contractors are often not technically competent to carry out the job required.

''Yes, they do clean-up. I think the issue is more on the quality of the clean-up. Because the companies like to cut corners, they usually use people who are not technically, who do not have the required technical capacity to do a thorough job. Like I said, they cut corners and use local people who will just assemble one or two clean-up equipment and they think they are good to go, but of course in their home countries they don't do that. That's not how they do it but here because of policy **lapses,** *they get away with blue-murder literally so no one cares''* KI-11

When asked about the challenges of activated carbon production, one of the Nigerian academics said: *''heating system for pyrolysis would be a big challenge… Are you considering the end–use of the contaminated land?''*KI-16

It appeared that remediation approaches used tend to be more generic than site-specific. Responses from interviewees gave an indication that a general approach is employed routinely for specific types of spills but not much reference was made to site-specific remediation. Interviews revealed that currently RENA (Remediation by Enhanced Natural Attenuation), which is commonly referred to as land-farming, is one of the most commonly-

used and most preferred remediation technologies for soil remediation by oil company operators.

''...the best is land farming ... good temperature (here in Nigeria) and cost effective for bioremediation. Soil is rich in microorganisms. If nitrogen or phosphorus is in short supply, simple fertilizer is used. We do not introduce exogenous microorganisms'' KI-18.

According to the head of remediation services in one of the oil companies visited in Nigeria, *'the company has carried out pilot trials of different additives and products recently and realized that all that is needed for land remediation is basically NPK fertilizer'KI-14.*

In disagreement with this view, the Engineering Faculty Dean of one of the universities said, *''Harrow and plough is all that RENA is about''* KI-15.

He argued that the oil companies would usually tell '*good stories and make you believe that nothing is wrong*'. He further stated that natural attenuation is only effective if most of the contaminant is removed and even then oxygen level and the movement of wind are of concern.

(Wilson and Jones, 1993) stated that on-site 'land-farming' methods had only been successful in degrading PAHs with three or fewer aromatic rings from contaminated soil effectively and within a reasonable period of time. The author also notes that there may be issues with remedial by-products by natural attenuation if not properly monitored.

It was noted that due to the sensitive nature of the Niger-Delta ecosystem, particularly the mangrove swamp, there is a dilemma between adopting the commonly-used RENA which is viewed by many as a do-nothing approach and employing more intrusive remediation procedures. This is due to legislation that prohibits damaging the mangrove during remediation. According to a technical spokesperson for one of the regulatory agencies also visited,

''Mangroves…, they do not allow the use of dispersants there so it is difficult to regenerate so they prefer to use natural methods. These terrains are difficult to access, people sink in quick sand, and wild animals… you cannot cut down trees easily…. torn between cutting down trees and destroying the environment'' KI-3

Legislation does not support introduction of microorganisms during bioremediation. One of the regulators did however state that some contractors might be going against this. This is just one of many indications that existing technologies may not be sufficient to handle present

remediation challenges. Other technologies used in Nigeria apart from RENA include cement fixation, biocells, thermal desorption units and sludgers.

Perception of the biophysical environment at the application level: scale of pollution and choosing appropriate technology

Just like the rules in use, opinions do vary among stakeholders regarding the scale and seriousness of pollution in the region. Views also differ regarding the effectiveness of existing technologies at the application level. According to (Ekpu, 1995-1996), hydrocarbons contamination in groundwater is a widespread and growing environmental problem in Nigeria which is considered particularly problematic due to the ability of hydrocarbons particularly PAHs to persist in the environment. Groundwater pollution was repeatedly mentioned as a major challenge by both formal and informal members of the application community, although disparity exists in the extent of damage that pollution is thought to have caused to groundwater.

''It (biochar) would be more relevant for groundwater issue. It could be considered for oil–impacted groundwater in pump and treat groundwater remediation. Rather than soil, biochar could be considered for dissolved phase compounds. What is a real challenge is remediation of groundwater. Activated carbon is a recognized method for treating dissolved–phase hydrocarbon'' KI-14

Studies indicate that the low viscosity and high permeability of Nigerian geological formations and shallow depth aquifers play a notable role in the level of groundwater contamination in Nigeria (Ekpu, 1995-1996). This is in contrast to claims that a natural 'clay pan' in the Niger Delta protects groundwater from contamination. One academic interviewee did however state vehemently that claims by oil companies about a clay pan that protects the groundwater are invalid. He cited the UNEP report on Ogoniland to support his argument;

''UNEP 2011 says RENA is not efficient. UNEP said clay–pan claim by Shell is false. There are micropores which exist and it is not possible for the pan to be all across the Niger Delta. Almost everyplace especially the farmlands are contaminated'' KI-16.

The effectiveness of RENA in the Niger-Delta remains a major cause of disagreement as the operator who is the Potentially Responsible Party (PRP) contests the credibility of the research that led to the UNEP report on Ogoniland while outcries continue nationally for the implementation of the recommendations of the UNEP report. Remediation of mangrove swamp was also stated as a major remedial challenge. Based on the interviews, land farming

is majorly used in Nigeria however according to (Wilson and Jones, 1993). Academics however stated that claims by operators that existing technologies (particularly RENA) are highly effective is untrue.

'' Challenge is more in mangrove; the ecosystem is sensitive… no technology. They do not have technology apart from booms and pads to absorb. Natural attenuation is effective if most of the contaminant is removed. Oxygen level, as well as the movement of wind is important. It would be useful if more research is done in this area but (the companies) look at cost'' KI-15

In terms of pollution residuals, a spokesperson for one of the oil company operators stated that they did not consider residuals after bioremediation to be toxic to the environment because it is usually below the intervention level of 5,000 units stipulated by the EGASPIN framework. He also said that their decision-making process is guided by ALARP (As Low As Reasonably Practicable) principle. He however commented on bioavailability considerations, which they factor into their decision-making process.

''normally bioremediation does not totally remove everything. It removes the short chained compounds however C_{32} and above stay in the environment. The beauty is that they are not mobile so they are not toxic. Based on EGASPIN which is the major guideline that they use those that stay behind are not very mobile so they do not make contact with plants, organisms or animals'' KI-18

The Nigerian EGASPIN guideline gives intervention and target values for soil, groundwater, sediment and drinking water. The soil intervention value is 5000 mg/kg and the target value is 50 mg/kg. There are concerns however that the Nigerian standard does not require action for PAHs at concentrations below the intervention values even where relatively high risk of contaminant exposure and presence of carcinogenic PAHs exists. It also overestimates the risks to exposures as bioavailability and bioaccessibility are not considered (Ogbonnaya et al., 2017).

With respect to contamination from illegal refineries, a spokesperson for one of the oil company operators appeared not to think it harmful to the environment and again suggested that RENA was a suitable remedial option for this.

''Coal tar for instance sits in the environment but poses no problem. It is just an aesthetic problem. It is handled by land farming'' KI-18

There are also claims that the pollution problem is blown out of proportion. For instance an interviewee stated that results presented by Amnesty International on Ogoniland about PAH

levels in water were incorrect due to issues with the chromatograms. A number of respondents expressed dissatisfaction with the efforts of MOCs and their preferred choice of technology for remediation. It appeared that this was due to the perception that the remedial options commonly used are low-cost.

Attributes of the application community

Oil company operator usually carry out remedial activities through contractors whose activities they oversee. Contractors are profit-oriented and are therefore often motivated to use a technology that is most profitable for them. This however means that they may not be patient enough to go through the rigorous application process required for a new remediation technology to be approved. They are likely to be content with existing technology and less willing to implement a new technology. A member of the media claimed that contractors are often incompetent and this may be linked to corruption.

Operators on the other-hand, though they are conscious of cost, are also mindful that the work needs to be done effectively as they are accountable to regulators and liable to penalties if they default. Contractors may however get away with doing a sub-standard project due to corruption. One major attribute that seems to be characteristic of the host community members is distrust of government and operators which is usually due to previous experiences and failed promises.

Lack of will on the part of operators may also be affecting the scale of remediation being carried out presently. One of the respondents used the Ogoni case as an example;

''It's not a lack of expertise. It's a lack of will (emphasized). Shell has the expertise to engage world-class environment experts but they will give you the excuse of lack of access… the Ogoni people do not want them to so much as step an inch into their land but that is crap. In the Netherlands or in England, they won't do that. Access or not, you would clean it up. How you do it is your business but clean-up you will. And even despite the UN report on the emergency situation required in Ogoniland, nobody is bothering. Government is there setting up panel after panel, white papers after white papers. Nothing is happening'' KI-11

The willingness of companies to remediate may also be impacted by sabotage occurring in communities.

''restoration; plant trees. Here sabotage is our problem. Do I keep planting trees because the law says to restore? As a company, we say until things change, we will not do restoration. Spills are occurring almost every month on lines. We will not go down that route and it is a deliberate policy from the company (SPDC)''

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The media and action groups are often a voice that amplifies the sentiments of deprived communities and may be biased in their views. Most community members are concerned about the betterment of their environment as it impacts greatly on their livelihood. However, there are also community members within the region who are more interested in their own personal gain than the state of the environment. Host community members often view contractors and operators as one and the same. This conflict of interest is illustrated in the scale of sabotage in the form of pipeline vandalization and illegal refining of crude oil which have been frequent occurrences in the region (Ambituuni *et al.*, 2015). It is important to note however that these acts cannot be dissociated from socioeconomic factors such as unemployment and poverty that are prevalent in the region in comparison to some other non-oil producing communities in the country. This further aggrieves community members and there have been repeated issues of pipeline vandalization and more recently the blowing up of Chevron's platform. Illegal refineries are a major source of concern. There are those that say they should be legalized however there has been no known official move or discussion toward this. There is a need to balance between the call for increase in 'local content' as required by government policy and the quality of hands employed.

''Yes, sabotage is an issue but it is only an issue to the extent that that is the only way they see that they can get something out from the natural resource that they are seeing. Until the government is able to douse restiveness in the oil region, sabotage will always be an issue…it's going to be a cycle until. Ok, until we improve industrialization, employment generation projects, it will always remain an issue… '' KI-11.

Additionally, the local community tends to respond differently depending on who or what party is in power based on the level of trust that they have for the incumbent government.

''I personally don't believe in those post-remediation checks. Why? Because it is the same companies, the same culprits that will take them there and you know how it is, if I know you are coming to look me up, of course I will tidy my house… that is why I don't have confidence in those post-remediation checks'' KI-11.

Stakeholder willingness to move beyond status quo is likely to impact on whether or not they choose to drive/support a new technology. This may however also be driven by personal interest. Community involvement in remediation is low as the expectation is for government or PRPs to carry out their responsibility. Interaction between communities involves a joint investigation visit before and after a remediation project. Communication involves oil and gas industry stakeholder forums however improvement needs to be made in ensuring

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adequate awareness and involvement of community members in the decision-making process for remediation technology.

In summary, members of the application community are often seek their own interest and hence may not be willing to drive new and innovative technology unless they are sensitized to do so.

Rules-in-use at the application level

The standard across the world is that operators have a duty to be mindful of communities in which they operate and to do so to a level that is deemed satisfactory by regulators. It is commonly thought however that the standard has been lowered in Nigeria because of inadequate regulation and monitoring.

'' The oil companies are required to report every spill even if it's just a drop. They are supposed to record how much chemical was spilled and if they have ...'' KI-11

There are allegations that operators bribe regulators to evade responsibility however one interviewee expressed dissatisfaction at the fact that operators often had to cater for regulators' expenses. Cost implications are usually a major consideration when exploring a new technology and this is also the case in Nigeria. In terms of organisational structure, one of the oil company operators confirmed that they have separate remediation personnel/department for land and swamp remediation. This suggests an organizational structure that could facilitate improved remediation outcomes with proper planning. Host communities are often keen to designate contractors for the operators to use however interview data suggests that these contractors are often incompetent and often work contracted out is not carried out or improperly carried out. Also, contractors approach operators for contracts as they are keen to make money but as is typical, there is likely to be corruption.

Due to the activities of saboteurs, oil company operators also have taskforce team that inspect/secure pipelines however there is the risk of these personnel being kidnapped by host community members as they are seen as representative of the oil companies. One of the interviewees who heads the remediation department of one of the MOCs stated;

'I have been kidnapped for nine days on the mangrove' KI-13

Lack of access was stated as one of the reasons for delay in remedial work.

A journalist stated;

'' The challenge more often is access, having access to the spill sites is key and the locals are now aware ... whatever chance or opportunity they have to get some piece of the cake, they usually would juice it and the first opportunity is usually the spill so you find that even when

the companies come and say we need to relocate you to a particular place so that we can, they say no, we have lived here for centuries. This is our great-grandfather's house. We are not going anywhere'' (KI-11)

Oil company operators have however been accused of using this as an excuse to evade responsibility;

''They will give the excuse that because of lack of access, they cannot swing into action as they would like to'' (KI-11).

Host communities are greatly impacted by spills and it may be expected that they would be in a position to prevent the issue of sabotage from escalating since the perpetrators of these acts often reside in their midst. This however might not be a realistic expectation citing recent bombings of oil platforms/pipelines by Niger Delta militants. Access to sites is often granted through community chiefs or private owners of contaminated sites. Community remedial effort is often non-existent or ineffective as it would usually involve crude means such as bailing oil off surface of waters or burning oil off farmlands which is bound to leave high concentration of pollutants in place. Community members however often want local contractors to carry out remedial work even though they may not be well qualified. Regional/tribal conflicts, violence and kidnapping are vices which have evolved within the region. An Amnesty payment initiated by the government makes payments to Niger Delta militants however they seem to have acquired more ammunition based on this support.

The author notes that the issue of restiveness in the Niger Delta region is linked to the state of the environment, which is in turn based on the quality of remediation work that goes on in the country. In terms of improving the situation, the expectation is for operators and government to ensure that adequate compensation is made for damages caused. The compensation procedure is however crippled by corrupt practices resulting in people being defrauded of their entitlement. There needs to be a re-orientation in the minds of these militants if a change is to be seen. The activities of these saboteurs have further aggravated the level of environmental degradation and inadvertently, poverty in the region as it impacts on the approach that MOCs take towards remediation. They feel their efforts are not likely to make sustainable and effective long-term impact as expected and also security issues often prevent or forestall the progress remediation plans. One interviewee however alleged that the prevalence of pipeline vandalization might not be disconnected from the nature of the pipeline themselves (A *et al.*, 2015).

...The companies can save themselves so much burden. Pipelines are no longer running on the surface. They should bury them deep, because they are seeing them, it is easy to break them open... KI-11

As with many social vices in Nigeria, people are often of the belief that the government is somehow involved in it. For instance, the government have been accused of sponsoring the Boko Haram insurgence that has ravaged the north of Nigeria for their own motives.

''...the kind of pipelines we are talking about are not pipelines you can use an axe or a cutlass to open up. You need sophisticated equipment to open them up and those equipment do not come cheap. It therefore means that some people also are helping them so it is not just about the natives because for them, they wouldn't even know how to. The sight of the pipeline alone is scary. But it is some people who are promoting them... '''KI-11

MOCs have historically had a dominant presence within certain locations in the country based on when and where they started operations. Recent happenings and unrest have made some begin to pull out of these locations.

In a bid to palliate aggrieved communities, there have been initiatives and release of funds by operators to compensate communities however these has often been followed by stories of embezzlement/ misappropriation of funds. In Nigeria, 'oil is big money' and leaders often see public offices as an opportunity to get rich rather than to serve the people. Corruption in the form of misappropriation, bribery, embezzlement, nepotism and money laundering are all elements of corruption that have permeated the fabric of the Nigerian society. Various policies and measures have been introduced to fight corruption in Nigeria however, these have had little effect on the situation. The effects of corruption in Nigeria are far-reaching and have been particularly pronounced within the oil industry as it is the main source of revenue for the economy.

''The will to say yes, this is what the law is and we are going to follow it by the book, that's what we need'' (KI-11)

Apart from the issues mentioned above, inadequate technical competence his also another limitation that plagues the application level and just as in the policy-making level.

''Because the companies like to cut corners, they usually use people who ... do not have the required technical capacity to do a thorough job'' (KI-11)

Corruption is also a major challenge here and this corresponds with studies by (Obuah, 2010)

''No one is held responsible. Once they are finished, they are gone. Bunkers are brutal so researchers should stay clear because they are very easily agitated'' KI-16

There is a robust legislative and organizational structure for oil spill remediation in Nigeria however these are plagued by anomalies. Corruption has played a major rule in the current state of affairs, which is characterized by inadequate technical competence among other factors. If significant progress is to be made in the region in terms of remediation of spills, all stakeholders need to be sensitized and motivated to cause a change.

6.3   Action arena 2: Understanding the framework for biochar implementation in the USA

This area of the study that focused on implementation of sorbent-based remediation technology involved analysis of semi-structured interviews supported by structured questionnaires with the aim of extracting lessons and practices for potential implementation in Nigeria. Due to time constraints and limited population sampling, the interviews and questionnaires were of different quality so focus of analysis is on interview data with reference made to the questionnaire data where necessary. Industry professionals, regulators, students and academic researchers were interviewed in three states: Baltimore, Washington DC and Delaware. The interviews attempted to capture experiences and general opinions of these different groups of people regarding the implementation of remediation technologies particularly sorbent-based technologies such as biochar. As has been mentioned in chapter four, the USA case study and indeed most other field trials and full-scale projects involved the use of activated carbon which is quite similar to biochar. A copy of the interview questions for this phase of the study can be found in Appendix A.

Traditional technologies usually have a framework that is enshrined in regulations. This makes it easy to access information relevant to the technology and to make an informed decision when presented with a range of technology options. It is therefore imperative to demonstrate the viability of the approach by showing that the rules-in-use can be used to develop workable rules-in-form.

The **Mirror Lake Remediation and Restoration Project**, which is the first full scale implementation of activated carbon based sediment remediation and was used as a case study below (section 6.4.1), highlight the elements that have enabled the implementation of activated carbon technology for contaminated sediment remediation in the USA. Subsequent sections give an understanding of the fundamental factors that drive choice of remediation technology; particularly carbon-based technology in the USA.

6.3.1 *Mirror Lake Remediation and Restoration Project (Delaware)*

The Delaware Department of Natural Resources and Environmental Control (DNREC) successfully carried out the first full-scale example of direct placement of activated carbon for sediment remediation in the United States in Dover. The Mirror Lake spans about 2.5 acres ($10117.5m^2$) and the contaminants of concern included PCBs and PAHs. The project involved remediation of the lake sediment with the aim of lifting a fishing advisory as well as improving the general aesthetics of the area. Scientifically, the major aim was to reduce PCB bioavailablity to the food chain without great alteration to the existing sediment bed. It involved application of Sedimite[TM] pellets over the lake using heavy equipment which were positioned on the bank of the lake to minimize intrusion (Patmont *et al.*, 2015). SediMite[TM] is a proprietary form of activated carbon consisting of PAC mixed with a weighting agent (sand), and a binding agent (Menzie *et al.*, 2016). It was successful and widely publicised in the State of Delaware and beyond via numerous public outreach efforts. An in-depth, semi-structured interview was conducted with two key environmental regulators who were directly involved in the conception and implementation of the project. They gave insight into their motivation for initiating and carrying out the restoration project. Vital information was obtained regarding the science and engineering aspects of the project as well as the dynamics of the relationship between stakeholders. Interview data were very rich in content however emphasis was put on the Delaware project as these informants were much more knowledgeable about the technology than others. The project was greatly supported by the ITRC (Interstate Technology and Regulatory Council) which was a platform for developing a framework for innovative remediation technologies. It will be noticed that most of the cases where carbon has been applied in the USA is in sediments**.** Interview data will be categorized and discussed under the three IAD exogenous factors used in the previous section (6.3).

6.1.1 *Biophysical conditions and technical characteristics*

Pollutant typology

The type and state of the pollutant to be remediated is important in determining if sorbent-based remediation is an ideal choice for a site. Laboratory and field trial research in the USA has shown activated carbon to be effective at dealing with various organic pollutants including PCBs, PAHs, dioxins, furans, mercury, TBT (tributyltin) in the USA (Patmont *et al.*, 2015). PCBs in sediments are a major remedial challenge in the USA because of release of legacy pollutants. As a result of this, fish advisories (advisories against the consumption of fish) are prevalent in many states in the USA. Passive sampling results from Mirror Lake

showed 75% reduction of total freely dissolved PCBs after one year (Patmont, 2016). Even though the **Mirror Lake Remediation & Restoration Project** was more concerned about PCBs, opinions were sampled about the effectiveness of carbon for crude oil spill remediation.

'AC actually does a better job with PAHs than PCBs because of the fundamental chemistry'' KI-22

A number of interviewees *(KI-22, -23, -24 and -25)* gave their opinions about the suitability of carbon for crude oil remediation and the resounding theme was that carbon is best used as a mop-up option and would not be ideal for highly concentrated pollution. The consensus is that if there is free products, it needs to be dealt with first and then carbon can be used as a 'polishing technique'.

''Crude oil has a lot of lighter end compounds in it which would biodegrade easily and volatilize versus a coal gasification stuff; tar, creosole that's like glue, real heavy end stuff. If you have free product, throwing carbon it is going to make it carbon goo. This all works when you have more dilute concentrations'' KI-22

Characteristics of remedial material and placement technique

The properties of carbon affect its quality which in turn impacts on its sorption ability. The AC used was applied at 4.3% (Patmont *et al.*, 2015). A major consideration for the application of sorbent-based remediation is the means of deployment. They considered dewatering the lake in order to till the carbon into the sediment. However, there were concerns about what might happen if there was a huge storm. In this project, placement of activated carbon was done using two different application methods one of which involved pneumatic delivery of SediMite[TM] from a boat and onshore locations, They eventually opted for SediMite[TM] as one of the placement options which even though was costlier than regular carbon, overall, it was cheaper than dewatering the lake. Ease of application needs to consider when choosing placement methods. Research has however progressed and there are currently several options available for carbon deployment be it in sediment or in soil (Patmont *et al.*, 2015).

Technical requirements and procedures

Due diligence was applied to ensure that proper procedures were followed in order to gain access to the site.

''We had to get approval for site access because some of this is all private–property'' KI-22

The project could have been managed either internally or contracted out and a decision had to be made based on funds available. The technicality of the work required and risk involved also influenced the decision about whether or not to have contractors from outside the agency.

''We hired a firm, a design firm to put together those engineering plans and specifications. We told them this is what we want. We worked with them on developing the plans'' KI-22

People driving the technology needed to be very knowledgeable about the technology in order to 'sell' the idea. They needed to be able to gather and analyse relevant data and paint a picture of what the project would deliver in the minds of stakeholders.

''Rick did a lot of modelling to say this is what we would expect to see'' KI-23

The right technical expertise was necessary for carrying out the much-needed engineering feasibility and eventual success of the project.

''Once we had plans, specs and permits, we had to go into construction. Also we hired a construction manager to oversee the day-to-day operations… Luckily, we had firms that we could hire in my group that do this so we just hired a local consulting firm who took their cut'' KI-23

Effectiveness of existing remediation technologies

Certain traditional technologies such as air-sparging and soil vapour extraction have been effective historically and are still well favoured in the USA for remediation of contaminated soils.

''Terrestrially, I would put things like air sparing, soil vapour extraction, and things like that ahead of a carbon-mixing thing… but you reach your asymptotic level of recovery with those types of systems which I think are probably more effective still and then you could consider a polishing. It's just the stuff you can't get out any other way. I think carbon would be great in a terrestrial setting for that…'' KI-23

Traditional technologies should continue to be used as long as they are cost effective and are able to bring pollutant concentrations down to acceptable levels. There have however been challenges with pollution residuals where existing technologies work effectively only up to a certain point. In such cases, sorbent-based technologies should be considered as it works well as a polishing technique for residual pollution.

'I would say that is more like the tail end of the process, that's when you've got this residual that still represents a problem'' KI-22

6.3.2 *Perception of biophysical attributes and technical characteristics*

It has been established from Chapter Three that risk assessment decisions are usually based on risk calculated empirically based on certain assumptions. Risk is an important element of perception and tends to drive decisions affecting the approach that is taken towards remediation as a whole. It is viewed differently by different stakeholders hence the factors that affect risk perception directly translate into how decisions are made. We will discuss within this section, the various factors that have been identified as impacting on risk perception of the technology in the USA. We also discuss how major concerns may be effectively managed under a risk management framework.

Knowledgeability of interviewee

Stakeholder views and acceptance of the technology is impacted by how much they know about the technology. Regulators for instance, appear to be most accepting of sorbent-based remediation because they possess adequate knowledge about the technology and related policy framework. Members of the general public on the other hand, tend to be less knowledgeable about technologies being applied and are more likely to be apprehensive about implementation of a new technology. Out of 16 respondents, 6 stated carbon-based remediation as their most preferred over bioremediation (biostimulation) and monitored natural attenuation. After presentation of the biochar brief and explanation of the technology however, the number of respondents who stated carbon-based remediation as their most preferred techniques increased to 9. Two regulators however did not indicate a preferred method as they stated the decision would have to be site-specific (KI-22 and KI-23).

''We were mindful that just doing the sediment remediation wasn't going to be really that visible. They had seen that we had heavy equipment in and were dropping stuff into the pond but most people were like; what did you just do'' KI-22.

Effectiveness of carbon amendment

A number of interviewees in the USA were more positive about the use of carbon for treating sediments than soils. Their reasons were either because they were of the opinion that it would be more effective in an aqueous medium or because they felt there were other options more suited for remediation of residual contaminant in soil other than carbon. AC has been applied much more in an aqueous medium in the USA perhaps because sediment

remediation was a priority and the technology is thus more advanced in sediment than in soil. This however does not mean that it cannot be applied effectively in soil.

''I think there's a lot more of a good effect you could have by adding carbon in sediments as opposed to doing the same thing terrestrially… KI-23

It's a lot easier to excavate on land and work around on land than it is walk in water and dredging is really expensive'' KI-22.

AC is generally known to be more effective at sorbing HOC (Hydrophobic Organic Compounds) than biochar by over on order of magnitude (Gomez-Eyles *et al.*, 2013) and has been used more commonly for remediation however biochar is been explored as a more environmentally friendly alternative.

''Biochar of course is like a lower grade AC and so it's probably 10% as effective as AC but it's a lot cheaper to produce and shows some promise in mildly contaminated situations and actually is being used now'' KI-22.

Biochar stability and long-term effectiveness

There are concerns about the long-term effectiveness and possibility of contaminant leaching from the biochar however, it is generally known that the release rates of HOCs from soil, sediment, or aquifer solids are usually very slow due to binding which occurs between the HOCs and the soil or sediment. This means that 'residual HOCs may be significantly less leachable by water and less toxic as measured by simple tests' (Luthy *et al.*, 1997). Proper understanding of phenomena which affect bioavailability (such as release rates and contaminant binding mechanisms) are bound to be useful tools in making quality decisions about soil/sediment quality criteria and remediation clean-up goals. (Luthy *et al.*, 1997). It is important that such decisions are made on assumptions that are neither too strict nor too conservative as the levels that are deemed 'acceptable treatment endpoints' have far-reaching effects on remediation costs and efforts (NRC, 2003). Risk assessment and risk management decision making should be supported by an appropriate consideration of the degree of bioavailability which is as accurate as possible. It is important to be able to communicate these technicalities effectively to stakeholders as it will go a long way in influencing their perception. This also transients into how stabilization by sorption is viewed or perceived.

Newness of the technology

Sorbent-based remediation technology has developed rapidly over the last decade and interest has grown with regards to incorporating bioavailability measurements into site management

decision making. Many of the methods which had been used in these site-specific assessments were however yet to be critically reviewed or validated (NRC, 2003). This gave room for skepticism and there was a lot of caution around use of this approach among scientists as the presence of readily-available information is essential for proper decision-making. This is gradually changing in the USA with development of frameworks as was done under the ITRC.

Secondary environmental impact

There have been concerns about potential pollution from the biochar itself as well as the effects of carbon on benthic invertebrates. It is important to use biochar which comply with limits on pollution residues as stipulated by relevant legislation (Lehmann and Joseph, 2009). Other secondary environment concerns include impacts which could potentially be produced due to emissions and resource use caused by the remediation activities (Lemming *et al.*, 2010). A risk management process should be used to select a remedy designed to reduce the key human and ecological risks effectively'. Another concern usually is that the biomass itself might be contaminated. It is therefore important that the biochar is carefully characterized to analyse its specific surface area, sorption capacity, cation exchange and mostly importantly to check for any contaminants (Denyes *et al.*, 2012).

Ecosystem sensitivity

This is often one of the major drivers for using carbon amendment. In Mirror Lake, a decision had to be made between dewatering the lake to apply the carbon or directly unto the surface of the lake as SediMite^{TM}. It is highly beneficial that the carbon can be applied in-situ without much mechanical interference with the ecosystem.

6.3.3   *Community attributes*

The major actors here are regulators, contractors, host community members and state government officials. In this section, we look at the characteristics of the communities involved in the decision-making process of carbon implementation. We highlight hurdles that needed to be tacked and how they were overcome in the **Mirror Lake Remediation & Restoration Project**. We also highlight progress that can still be made and actions that are critical for such progress to occur. Drivers of technologies need to engage with politicians and work with different departments or facilitate cooperation between departments.

Conflict of interest

Interest and concerns relating to remediation activities usually differs from stakeholder to stakeholder. Contractors are reputed for being profit motivated. Regulators are tasked with the responsibility of ensuring that proper environmental standards are adhered to while members of the local communities are usually concerned about harm that may occur in their environment.

''Attorneys and engineers, they want a piece of it''. KI-22

''They're in it for the money. And that's where it's different from a regulatory perspective. We're in it to help the environment''. KI-23

On the Delaware project however, stakeholders, particularly contractors were able to set aside their varying interest to collectively develop a framework that worked so that the technology could be accepted by the state. There was a conscious effort to influence the perception of actors. Hence we see at the end of the project, a community that is more homogenous than at the initial stage and more importantly, the different communities were happy with the outcome.

''The egos get checked at the door, these different technologies are all new enough that their concern in how they are going to make their money is when the technology is accepted… so let's put our agenda away and get the technologies accepted and then I'm going to make my money'' KI-23.

It is important to acknowledge that there is usually a net social gain to society that results from the production or consumption of a particular good or service. Adam Smith laid the foundations of this free market economic theory. It might thus be beneficial to consider the net social gain that such projects may have on communities. (Kelso, 1966).

Community involvement and team work/cooperation

The team was made of people with different levels of technical competence. Local community members who may have been sceptical at the beginning were seen volunteering towards the project once they understood the potential benefits. The process afforded the volunteers the privilege of skill acquisition from professionals. Even though there were concerns raised by labour unions about 'taking money out of labourers' pockets', this was overcome by pointing out the benefit of demonstrating the viability of the technology. It was

important that the benefits of the project were highlighted as appropriately for the different groups of stakeholders.

''We did a lot of this work with volunteer labour. We solicited division directors and upper level management to say; 'can we use your people?' and teach them, something new in the process… we had government officials and their staff volunteering this gave them opportunity for some visibility as well. KI- 23

''We were able to generate team work over the period of planning'' KI- 23

The ITRC, which was a major actor in the Mirror Lake Remediation & Restoration Project, is an organization that was set up and funded by some federal agencies to expedite the 'acceptance and use of innovative environmental technologies and approaches'. The role of ITRC in the project is a good example of how communities can be brought together in partnership to develop a framework that benefits all stakeholders in a remediation effort. A consortium of different stakeholders worked on developing the framework.

''The teams are made of industry professionals, consultants, technology vendors, federal agency personnel, and state agency personnel. So you've really got every facet of the industry sitting at a table together and the idea is to work on a problem that in many cases is difficult…'' KI-23

''...requires collaboration between different people, skillsets and programmes and that's other unique thing about this project, the partnerships that were built because you're not going to do this by yourself...'' KI-22

Trust and reputation

It is important that companies and regulators have a good image in the eye of the public as this helps to build trust and facilitate productive partnerships.
In the USA, PRPs are legally required to remediate polluted sites however difficulties are often experienced in getting them to accept responsibilities as sites can often have many PRPs. It has been identified that being open to the application of innovative technologies could be a form of incentives for companies to engage more readily in remediation. It was noted from interview with one of the regulators that the temptation to be involved in corruption exists in the USA.

''I never tried to taint it based on whose ox was going to be gored or what the political fallout of it was going to be. I pissed off all kinds of different people but at the end of the day, they at least understood why I was making the recommendations. You anger people at first

but eventually, they understand where you're coming from and hopefully, they respect it. And so we've built some support by knowing that we're straight shoes'' KI-22

People driving the technology need to be trusted. It is important to note however that certain communities may be biased about others perhaps due to past experience hence it's important to consciously build trust.

''Sometimes, you're just dealing with people who hate the government and it doesn't matter what you say. They either think you're in bed with industry and allowing them to walk all over you, or you're being unfair to them… Environmental groups think that you're way too lenient and you're not being strong enough'' KI-22

This lack of trust for regulators may also be applicable to operators as members of the general public are usually sceptical of them perhaps because of their profit-oriented nature.

''Some of it is reputation. Rick has a reputation in the state for what he is doing… they trusted us enough to do it and give us close to one million dollars for this project...'' KI-23

People investing money may be averse to risk and sceptical about accepting liability for an innovative technology.

''There was a point where we were planning on managing the whole thing ourselves to save money. But then it was pointed out to us that what if something goes wrong. It was people saying; as the state, we're not going to take on that liability of you doing this'' KI-23

Technical competence

There were different levels of competence even though the team was passionate about the work. It is important that drivers of the technology possess a wholesome understanding of the technology in order to be successful at driving implementation.

''The only way you're going to solve a problem is when you acknowledge it and you've done enough homework that you understand the problem backwards and forwards. You know what the limitations and the barriers are, the science of it and you are able to speak clearly and completely about'' KI-22

''People who were working heavy equipment were well trained and paid but the volunteers weren't… the science and technology associated with dealing with remediation of sediments or even properly characterising sediments is a very specialized skill'' KI-22

Decision to use a technology has to also be made by technically competent people.Apart from being able to communicate the technology clearly and succinctly to stakeholders, technical competence also involves being transparent about uncertainties surrounding the technologies and how they may be eliminated.

''You can take these kinds of tests and better characterize the situation and what may be characterized now as likely to be a problem, that problem may go away but you have to do certain things'' KI-22

With regards to the level of competence of the contractors, one regulator stated that it varies.

''A lot of times, it's good and it's adequate and other consultants, not so good and we need to kind of bring them along and so really again, it depends'' KI-22

Openness to innovative technologies

Oftentimes, innovative technologies are not accepted by regulators because they have not been proven or they are not knowledgeable about it. It is important that regulators are open to exploring new technologies and allow discussions to occur which could lead to development of a framework for such technologies.

''You can't use that carbon technology because there's not enough information to show that it's going to work, you have to dredge it, period! People get that from regulators'' KI-23

From a contractor's perspective, they are more comfortable doing what they have done in the past.

''There are certain consultants that we work with all the time and they've got their own kind of skillsets and they like doing things their way and it works for them…'' KI-22

6.3.4   *Rules*

Interviewees made reference to a number of different rules-in-form which are a reflection of legislation and standard industry expectations that pertain to technology implementation. More importantly, however, they provided an understanding of rules-in-use, which are a better description of how things work in reality; factors that make for good implementation as well as the challenges which need to be addressed in order for the technology to be implemented effectively.

Nature of policy and legislative framework

Policy guidelines that were identified as catalysts for carbon technology implementation in the USA include remediation target guidelines and values. ALARP (As Low As Reasonably

Practicable) and BMP (Best Management Practices) are among the principles that are used in deciding whether a remediation technology would be effective at a particular site.

''You've got rid of the majority of the mass but you're still at a concentration that's causing ill effect to something or has potential to, then this (carbon) is a good way to get those concentrations down to a safe range''KI-23

Legislation in the USA is currently changing to accommodate innovative remediation technologies. Regulators who were involved in the **Mirror Lake Remediation and Restoration Project** pointed out the importance of having laws that are sufficiently flexible to consider innovative technologies such as carbon amendment.

''When you have programmes that are overly enforcement-based and restrictive... wooden ways of doing things have this unintended consequence of intentionally slowing everything down...'' KI-22.

One of the interviewees highlighted that one of the unintended consequences of overly restrictive technologies was the fuelling of corrupt relationship between companies and lawmakers.

''...companies that get shafted are going to hire really good attorneys and those attorneys are going to lobby lawmakers. And lawmakers are going to say what can we do, then the attorney say; I'll help you with some legislation. Let me write that for you and it favours the clients...'' KI-22.

Motivation for using carbon technology

A major trigger for the changing approach to remediation/risk assessment in the USA appeared to be the enormous sums that PRPs were having to pay for remediation options that were being 'imposed' by regulators particularly dredging of sediments as there are many sediment contamination cases across the USA.

'' This costs the PRP millions, billions of dollars and it's not clear that that was really justified... it got their attention that they were being forced to do these things. People saying well, you know what, these other things need to be considered... it's good science'' KI-23

''The way EPA has dealt with it is to force these deep-pocketed companies to pay to dredge it out and so the companies were going, wait a second, we need to bring some sanity, some structure to it'' KI-22

Cost was also a major motivation for using the chosen technology in the Delaware project.

''It was cost. It would have been a million and a half just to dredge it and then we would have to take that material and haul it somewhere, do something with it. And as Rick likes to

say, we just take one problem and move it from here to there so we've done nothing but create it somewhere else so that wasn't really an attractive option for us... from the outside, you would say why wouldn't you just get rid of it. It was too costly'' KI-23.

Another motivation was the fact that it was an in-situ remedial option which meant there was no need to worry about what to do with waste material that would have been dredged out. Recent research has shown that carbon amendment works towards breaking pollutant linkages and changing biophysical conditions and full-scale implementation helps in advancing the science. Carbon is well-suited for remediation of legacy sites as it provides a reduced-cost alternatives for sites that might otherwise get no attention. Legacy pollution has resulted in numerous fish consumption advisories that presently cover 43% of the area of lakes and 39% of all river miles in the United States (USEPA, 2009).

''We also said if you don't do this, you're going to have to wait 30, 40, 50 years in order to be able to lift this fish advisory and so if you want to speed that up and give people the public resource that they deserve, then let's try doing this and we believe that it's going to speed things up significantly...What happens when there's not an accepted solution? What happens is nothing.... This idea that we can't accept that, it's not worth taking the risk of doing it really is counter-productive because then what you're saying is you're either consciously or you're implicitly accepting the no-action alternative'' KI-22.

Need to influence stakeholder perception

Community and political acceptance is impacted by perception. It was important to proactively engage stakeholders in order to influence public opinion and overcome reservations. Initially all communities were not aligned in terms of opinions and so we see that there was a starting community and a final community. Community became more homogenous because of this active effort to evolve or change their perception.

There was a conscientious effort to increase public awareness about the project and to sensitize the public in order to improve stakeholder involvement and willingness.

''There were three different videos that DNREC PR group put together, Upal, Rick and myself (John). They filmed before, during and after the project. Then put three little summary videos on the DNREC YouTube channel. There are a number of newspaper articles'' KI-22.

Another proactive move was to strategically locate the site so it could be noticed by stakeholders.

''... It was very important that we chose this site in a strategic manner. There are places all over the state that have more contaminant, but this particular location, you drive into historic

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Dover which is the capital of the state. This intertidal wetland that we built, we planted it with native plants, flowery plants so people could actually see it… Not only is it there at the historic Dover, the legislative building is right there. People that drive over that bridge include state lawmakers and city of Dover officials. So they are going to be looking. We wanted them to see and be curious about what we were doing'' KI-22.

Also, it was important that the idea was sold with passion to all stakeholders, particularly people who were going to provide funds for it.

''…we had to get our management to buy into it first. Because they ultimately were releasing funds for us to pay for it. So we did presentations to our management…'' KI-23

''When we could show the public, this is what we want to make, we intend to lift this fish advisory so you can fish in this lake. Now this lake is surrounded on one side by a city park. We have all these little pieces that probably affected the way people thought about the project and its success…'' KI-22

Restoration elements were included in project to endear members of the public to the project.

''If you drop carbon pellets in a pond, everything looks the same before and after. You collect technical data and that is convincing to a scientist but the public doesn't care about that. They want to see something else. So what we decided to do was marry this sediment remediation with some habitat restoration... that's what people see but that was at most 25% of the project.''

Part of the process of overcoming reservations about novel technology has to come from convincing people about the authenticity of the technology from a scientific standpoint. The ITRC helped play a major role in doing this in the USA.

'Where are these barriers for getting things accepted, can we identify what those are and what can we do to help break down those barriers'. KI-23

Need for inter-disciplinary projects

In order to work across compartmentalised organisational structures, projects that cross the lines of discipline need to be designed.

''Many of the programmes in our agency are compartmentalized, they are in silos. We recognized the need to build a bridge and sold this a multi-disciplinary thing. A lot of the bosses talk about that but they cannot give you an example of where it's really been done so we created that for them'' KI-22

Regulatory/Decision making framework

The technology approval process involves the PRP gaining approval from a regulator to use a specific technology or combination of technologies for remediation of a particular site.

''We tell somebody, they do a feasibility study and say this will work and this will work and this won't work and won't and they look at all these factors and oftentimes, they rank these factors. They say our recommended remedy is this and this is what it's going to cost but you know what, we don't always agree'' KI-23.

It is important that decision about what technology to use for a particular site is based on sound science.

''Anything's possible if you don't know what you're talking about'' KI-22

Evaluation and monitoring of spill sites is a key element of the remediation process. Following initial response after an oil spill, a decision usually needs to be made by experts about *''whether or not that residual risk is high enough to even worry about''* (KI-22) based on the relevant policy guidelines. If after assessing the system, it is determined that the pollutant would degrade in an acceptable time period, then that is usually the preferred option in order to save cost and attend to sites of greater priority. This process is usually referred to as natural attenuation or monitored natural recovery.

Another rule-in-use is that any active sources of pollution need to be handled first before remediation or restoration work commences at a site. This is particularly important when applying carbon because pollutant concentration plays a key role in its effectiveness.

''Normally, you would only use carbon say in a pond or something like that when you know that you've seen the worst of it. There might be some residual stuff coming in like you always want to make sure that you've cleaned up the active source ...job one is to control sources'' KI-22

A decision making framework for choice of technology is important because it considers all of the different factors such as resources available, remediation time, priority of site hence decision is not usually based on one factor alone.

''We want to see something done that's going to be effective at reducing the risk in a reasonable amount of time...cost benefit analysis... we have to make a good management decision based upon the resources that we have or that someone else has…'' KI-23

It's important to note however that in terms of ranking of factors, priorities differ based on who is deciding.

''They're going to fight for the cheapest option that they can and we run into that issue all the time especially in my programme where we're regulating what remedies are done'' KI-23

Choosing the technology in the USA is usually a reasonably elaborate process and there is usually a framework for making such decisions.

''…Those decisions don't get made by any one person. It's usually a joint decision to do… KI-22.

6.3.5 *Development of a conceptual Plan*

A consensus among experts that were interviewed is that opinions alone would not suffice, there needs to be trials done to determine the suitability of the technology from a scientific standpoint. This usually takes the form of pilot- or full-scale field projects as in the case of Mirror Lake.

''And so we had this conceptual plan. We knew what we wanted to do but you just can't go out there and -do it. You're not allowed to do that. You have to have permits, plans, engineering plans and specifications because as a part of the permit approval process, you have to have all that. You have to have something for the regulatory agencies to look at and ask questions and ultimately to approve… the best way to determine whether or not it works is to do bench scale, pilot studies… let's develop a framework, let's develop a broad-based, consensus-based set of guidance documents that can be used in the future'' KI-22

When implementing novel technology in a new environment, it is critical to the whole thing to have a conceptual framework that demonstrates the circumstances under which it would work. The ITRC with prompting from the USEPA, helped in developing a guidance document that helped in assessing innovative remediation technologies facilitates decision making about what technology to use.

''Each document takes about three years to write and you have a group of people that work on it for three years. What we tackled was remediation of contaminated sediments but we didn't just look at new innovative technologies. We looked at the body of technologies available… it's pushing the boundaries of how things are accessed. What we did was add rules of thumb making the document they call technology assessment guidelines. Where we look as specific criteria that you might use to evaluate a technology…. KI-23

This conceptual framework involved characterization of the pollutant to predict its fate in the environment. In a soil setting, it would be recommended to apply carbon where the pollutant cannot be gotten out any other way as options such as excavation, and thermal stripping work well for dealing with heavily contaminated sites in a terrestrial setting. In sediment, the options are fewer with dredging being quite expensive. Certain technical requirements had to be complied with. Permits, write proposal, as mentioned under technical characteristics.

Site-specific considerations

Decision making process for choosing technology is usually site-specific. The ITRC guidance document provided a guideline for carrying out a feasibility study when evaluating the different technology potions to be used. It points out things which need to be considered and checks the suitability of the technology for that specific site.

''I mean all of these things are site-specific. There is no one technology that would work overboard. SediMite^TM is not the only game in town. Carbon is not the only game in town. It depends on the contaminants, the setting you're in, accessibility, implementability, a myriad of other factors that go into deciding on what to do in a specific place… We'll help you evaluate all of them together and help you come up with the best two or three that might work and then you have to go and figure out which one is going to work best for your site. KI-23 Site specific also entails considering if the technology chosen will meet the remediation goals for that site. Feasibility study should involve collection of technical data. In making plans for the actual construction, it is important to ensure compliance with technical requirements and that it is suitable for the proposed plan. The means of deployment of the carbon material is perhaps one of the most vital elements that needs to be considered and this would depend on the medium to which it will be applied.

Cost considerations

Government funding and budgeting have an impact on the rate of progress of innovative technologies however a state regulator stated that environment generally comes low in priority in terms of funding.

''Politicians don't get support unless they've done good things and let's face it. Environment isn't always on peoples' agenda. I mean it costs a lot of money… In our case on the Mirror lake project, we were given a large sum of money out of our hazardous substance clean up act fund. We had some money that a colleagues's group brought together to do plans and specifications, we had some other groups that had the money to do the restoration so we were able to pull it all together to say we just have enough to do this one project because we didn't have anybody responsible for that. That's the other big problem with a lot of what this stuff is… you have 50-100 different people or companies or whatever that helped cause that and the way most government structures work is you've got to after those people and make them pay. You could get caught in litigation for decades over that stuff cos nobody wants to pay'' Decision-makers process numerous issues simultaneously, often away from public view hence the process should not be viewed as simplistic. Important changes tend to be made only

when an issue becomes severe or when stakeholders highlight such issues (Jones and Baumgartner, 2005).

Acknowledging that fund for remediation of sites, especially legacy sites cannot always be gotten from industries is a major step towards getting more sites remediated. Conceptual framework would need to take cognisance of how much carbon is needed to effectively remediate a site. These projections are usually based on information about the amount and composition of contaminant in the site and percentage carbon required. Site-remediation technologies are categorised into ex-situ and in-situ remediation techniques. One of the problems associated with ex-situ remediation however is the cost of operation (Geng *et al.*, 2001). Funding for development of framework came from multiple sources including the contractors.

''The industries pay the ITRC to be involved on this…so we're going to pay to help with these things. We'll give information where asked but we're more in tune with getting the technologies or getting the process or whatever that is into these documents so it can be disseminated to people throughout the US cos that's going to help our business and we want to see these technologies used more'' KI-23

6.4 Comparative analysis of factors affecting biochar implementation between Nigeria and the USA

It does not matter where in the world a spill occurs, risk assessment approaches should deal effectively with health risks and risks to ecological receptors that may arise from polluted sites. Section 6.4 provided vital insight and understanding into the framework for implementation of sorbent-based remediation technology in the USA by highlighting key factors that influenced the outcome of the **Mirror lake project.** Though some of the factors discussed bear similarities with the Nigerian situation, several areas are vastly different from the conditions obtainable in Nigeria. This section therefore provides a comparative assessment of the impact of 'exogenous factors' (discussed previously) on remediation outcomes in Nigeria and the USA. It extracts learnings from the USA case study analysis by contrasting it with the situation in Nigeria, with a view to making cogent recommendations for biochar implementation in Nigeria. Prospects and challenges likely to be faced in implementing the technology in Nigeria will be highlighted and recommendations about these will be made in chapter 7.

6.4.1 *Biophysical conditions and technical characteristics*

Pollution source, scale and typology

Sediment contamination is clearly a major challenge in both countries however, advisories prohibiting fishing activities are not common place in Nigeria as in the USA. This nonetheless does not undermine the fact that a vast majority of locals in the Niger Delta region of Nigeria are unable to fish or farm because of the devastation caused by oil pollution. Apart from sites that need to be remediated, clean-up of crude oil spills is still a major issue in Nigeria as sites are often rendered inaccessible due to security concerns. Crude oil spills in Nigeria are frequent and are often due to vandalism of pipelines, improper maintenance of pipelines and illegal refineries. This is in contrast to the USA where clean-up after a spill is not usually a challenge and contingency plans are judiciously followed. It is important that clean-up is done on sites before remediation can be carried out effectively and before biochar can be considered. The phase of the contamination is a key determinant for considering the potential for biochar application in a specific site. This is because it determines the means by which the carbon will be deployed and also has effect on cost. PCBs were the major Contaminant of Concern (COC) on the **Mirror lake project** however a field experiment in Trondheim Harbor, Norway involved testing of AC as a thin-layer capping material for polycyclic aromatic hydrocarbon (PAH)-contaminated sediment (Cornelissen *et al.*, 2011).

Remediation challenges and current remediation

Sediment remediation appears to be a greater concern in the USA than land remediation because of cost-effective in-situ options that abound for land remediation. Similarly, it is claimed that RENA is effective at remediation of contaminated land in Nigeria however the fate of pollution residuals is uncertain. Groundwater pollution is a concern in both countries and activated carbon seems to be an option that would be considered for groundwater remediation in both countries. Additionally, Nigeria has its own unique challenges one of which was identified as remediation of mangrove swamp. Most trials using AC in the USA have involved sediments as opposed to soil mainly because sediment remediation is a major challenge there but also because it is easier for carbon to work in aqueous medium. This is not to say that soil remediation should not be pursued in Nigeria but perhaps the preferred choice should be mangrove and groundwater. The scale of remediation activity in the USA is definitely greater and more effective than in Nigeria. One easily identifiable reason is legislation, which stipulates that operators are responsible for spills within locations of their

operation whether they are responsible for its occurrence or not. Also, the Ecological Fund, which is Nigeria's version of the Superfund in the USA has not been efficient. The fund was established in 1981 to ensure adequate provision of funds for ecological problems such as flood, soil erosion, desertification and general environmental hazards and it receives 2% of the Federations account. It however has a history of mismanagement and there have been several instances where funds allocated for specific projects have been diverted into private pockets (DailyTrust, 2017).

Another peculiar attribute of the Nigerian environment is tar, which is a by-product of illegal refining of crude oil. At the time of this write-up, there has been no documented field-trial conducted in Nigeria regarding the use of biochar for crude oil remediation although AC is generally known to be used for treatment of aqueous solutions.

Engineering feasibility

In the USA, access to sites is gained by following the outlined procedure for site permits however in Nigeria, it is a more complex situation. Access is often prohibited by security restrictions such as risk of being kidnapped or being caught in a local conflict. A major consideration for application of the technology is the means of placement which in the case of **Mirror Lake** required heavy-duty equipment which had to be rented. This sort of equipment may not be readily available in Nigeria but can also be sourced if there is a clear plan for a project. In contrast to the constraints which are often encountered in Nigeria with regards to technical competence and infrastructure, we see that major parts of the project such as the construction had to be contracted out to professionals. As in the case of Mirror lake, it may be possible to pneumatically apply biochar to mangroves in Nigeria although site-specific considerations will need to be made. Although ease of implementation needs to be considered in both countries, it is particularly important for Nigeria if a project is to be successful. One must take account of the unique challenges to be faced, foremost of which is power supply and technical expertise.

Carbon source

The major motivation for considering biochar in Nigeria in contrast to AC, which has been used more widely in the USA, is cost. According to (Denyes *et al.*, 2012), biochar is about 50 – 75% cheaper than activated carbon. This, in addition to the benefits of agricultural enhancements and carbon sequestration are motivation for its use in oil spill remediation. Biochar has been produced from a wide range of organic matter including corn stalks, sawdust, chicken manure and construction wastes. It is important that attempts are made to

limit secondary environmental impact from biochar itself. It would be greatly beneficial to explore the potential for sourcing biochar locally. In doing this however, one must take into account the fact that different feedstock require different pyrolysis conditions in order to produce biochar and these differences are expected to change the biochar's physiochemical properties as well as its sorption capabilities (Yao *et al.*, 2011). In Nigeria, feedstock such as cocoa pods, plantain peels and corn cobs are readily available and could serve as a suitable option for biochar production (Ogunjobi and Lajide, 2013; Ogunjobi and Lajide, 2015). In addition to feedstock type, the technology used for pyrolysis impacts on the quality of biochar that is produced (Ronsse *et al.*, 2013). The stability of biochar has been shown to be related to not just the feedstock (material) property, but how efficiently fixed carbon in the feedstock is converted to fixed carbon in the biochar during the pyrolysis process (Enders *et al.*, 2012). There is very limited data regarding biochar research in Nigeria and available data tend to be laboratory or small pilot scale field projects (Ogunjobi and Lajide, 2013; Ndor1 *et al.*, 2015). There is however significant knowledge about small-scale biochar production in developing countries which could potentially be replicated within the Nigerian scenario. There is not so much concern about carbon footprint in Nigeria like in developed countries.

 Disparity in remediation statistics and views

In both countries, stakeholders' opinions about remediation activities vary. PRPs are usually of the opinion that they are being forced into doing too much while government and actions groups usually see the need for more to be done. This is quite a generalized statement, however, challenging this view may be a bit more challenging in Nigeria as statistics may not always be available to support claims. This can again be linked to issues of instability and insecurity in host community as well as corruption.

6.4.2   *Community attributes*

Need to influence stakeholder perception

Knowledgeability of stakeholders affects their perception greatly and so it is important to ensure relevant information is made available and accessible to the public. On the Mirror lake project, there were numerous public outreach efforts including meetings, press releases and door-to-door flier updates (Cargill, 2015). Conscious efforts were made to make the community more homogenous and to overcome the lack of trust and conflict of that had been prevalent hitherto. Similar actions may need to be taken in Nigeria to encourage stakeholders

to put aside their personal agendas in order to reach goal of advancing technology and solving remediation issues that otherwise may not be resolved. In Mirror Lake, elements were added to the project that would appeal to the public and this may also need to be implemented in any potential projects in Nigeria. Willingness of contractors could be influenced if the trade-offs from implementing a new technology is envisaged to provide sufficient financial remuneration. There is a need to address specific concerns about the technology while being as transparent as possible.

Networking

Networks that were formed in the USA were helpful in influencing stakeholders to adopt new approaches. The views and concerns of stakeholders were taken into account during planning and execution process. Collaborative participation was encouraged by employing both volunteer and paid labour from the host community as this gives them a sense of ownership. Also, this would foster unity and hopefully acceptance. There have been suggestion from members of the general public that the activities of illegal oil refiners in Nigeria be legalized and small refineries be encouraged. Network links should be created both nationally and internationally with people who have successfully implemented the technology in the USA. That way, Nigerian stakeholders can be more assured that it has been successful in other places, and that it is cost-effective. This would create has a greater chance of it being embraced by experts as well as non-experts. There is usually a wide spectrum of expertise in the community so they can be involved in tasks as little as taking readings for monitoring or being actual contractors on trial projects. Organisational structures should allow for collaborative projects and people with diverse skills should be involved on projects.

6.4.3   *Rules*

Legislative framework

Legislation and policies guide decisions about technology in the USA. The USA system of governance is characterized by states that are highly autonomous whereas in Nigeria, major decisions center on the Federal government and so the states do not have as much influence in the Nigeria as the USA when it comes to policies. Corruption exists in both countries and in the USA, there is a challenge with lobbying of Law-makers to influence legislation. The USA however has well-developed institutions and procedures as well as a powerful judiciary. One way that USA has positioned itself to deal with this is to be more open-minded to potential remedial approaches particularly innovative technologies such as carbon amendment. In addition to consultative forums, Nigeria should consider making its rules

more flexible as the USA experience showed that rigid rules may instigate corrupt practices. There needs to be a balance to this as regulatory agencies in Nigeria already have issues with enforcement of legislations and some stakeholders already think they are too lenient. In introducing biochar therefore, it is important to be able to cite successful projects outside Nigeria and within Nigeria because people want to see how it would work locally. Policy makers' in Nigeria have limited knowledge of the technology and even though forums already exist in Nigeria, they need to be places where framework for innovative technologies such as carbon amendment can be developed holistically.

Responsibility for pollution

The US has issues with legacy spills which they have only recently begun to handle more effectively. Nigeria on the other hand has major issues with sabotage which need to stop. Even though this is an indisputably serious challenge in both countries, the situation in Nigeria is not improving at nearly the same rate as in the USA. In the USA, PRPs are responsible, however the Superfund takes on a lot of responsibility for legacy sites. The Ecological Fund which is Nigeria's version of the Superfund needs to be re-hauled so that it becomes functional. If one is to see a change in trajectory, the way that funds are generated for legacy sites and the entire framework for dealing with legacy spills needs to change. If government is actively involved in remediation, they are more likely to be effective regulators as they would feel more obligated to stop the activities of saboteurs.

Regulatory design and risk assessment framework

In terms of regulatory design, the regulatory approach in the USA is gradually changing towards sorbent-based remediation technologies. Perhaps Nigerian regulators could provide incentives for operators to consider new technologies as this was recently incorporated into EPA guidelines in the USA and is currently one of the major drivers for innovative remediation technologies. The chemical risk assessment framework used in Nigeria is the EGASPIN (Environmental Guidelines and Standards for Petroleum Industries in Nigeria) framework. It is quite similar to the UK's CLEA model and the EPA guidelines and stipulates. An integral principle of the framework is the 'suitable for use' approach as well as the fact that a 'significant pollutant-receptor linkage' must be identified. Also, intervention values and target values are used to assess risk (DPR, 2002). Approval for execution of any remediation project is usually in two stages. The first being provisional approval based on pilot scale experimentation and a final approval for large scale application based on the findings of the pilot scale experiment (DPR, 2002).

Cost and funding considerations

Oil has historically been viewed as a high priced commodity of the extractive industry and one of the most influential commodities in the world market (Aroh *et al.*, 2010). Oil prices have however dwindled severely in recent times and impacted on Nigeria's economy. Careful thought must therefore be given to the cost implications of choosing a technology as it impacts on the quality of infrastructure that is accessible. This however needs to be a balanced with the quality of remedial work required and estimated time to achieve remedial goal. The Nigerian EGASPIN framework stipulates that the cost burdens on individuals, companies and society are 'proportionate, manageable and economically sustainable' (DPR, 2002). There are well-defined systems for evaluating cost and analysing efficiency of remediation options however this is beyond the scope of this research work.

6.5   Chapter conclusion

Findings from this chapter show that there are similarities between Nigeria and USA with regards to the factors that enable the implementation of remediation technologies. These similarities exist across the spectrum; from biophysical conditions and technical characteristics, to community attributes and even unto the rules that dictate stakeholder actions. Significant differences were however noted in many aspects. The USA is not encumbered with the many social vices that Nigeria faces at this time of its development as a nation. Sabotage of oil pipelines and installations, insecurity and corruption are some of the factors that would make implementation in Nigeria more challenging. This is because they impact on the typology of the spills that are prevalent in the area. Oil and gas legislation in Nigeria is however at the brink of undergoing a historic re-haul which promises to impact positively on the industry in general. Fortunately, present risk assessment framework in Nigeria is able to accommodate implementation of the technology as long as the Nigerian environment is uniquely considered in any plans for implementation. The weight of the chapter findings provide a basis to believe that there is considerable potential for implementation of biochar in Nigeria. The low-intrusive nature of the technology indicates that it may be a viable choice for remediation in the mangrove swamps of Nigeria. In light of these, recommendations are made in the concluding chapter (seven).

Chapter 7.   Conclusion

7.1   Introduction

This chapter presents the overall conclusion for this thesis by triangulating a summary of the key findings with the overall objectives of the research. It demonstrates how the objectives have been met by the data presented in the thesis. Recommendations are made for potential implementation of biochar technology in Nigeria taking into account the country's unique biophysical, institutional and social characteristics. Limitations of the study are highlighted and finally, recommendations are made for future study.

7.2   Re-stating the scope and objectives of the study

This study was aimed at determining the viability of biochar as a suitable remedial technology option for Nigeria from a technical as well as social perspective. The three core areas of enquiry therefore were laboratory experiments, risk assessment modelling and social analysis in both Nigeria and the USA. In order to address the research aim, the study was divided into six main objectives. In the following section (7.3), the key findings from the research are linked to the corresponding objective.

7.3   Summary of main findings

> ***Objective 1*** *- Investigate the effectiveness of biochar in remediating contaminated soils in comparison to more conventional bioremediation technologies i.e. biostimulation and natural attenuation based on laboratory evidence (**Chapter 2**)*

Laboratory results showed that the volatilization flux of aromatic hydrocarbons was significantly lower (t-test $p < 0.05$) in biochar-amended microcosms between day 0 and day 14 as evidenced by the data from the foam plug experiment. This indicates the ability of biochar to inhibit pollutant volatilization into the gaseous phase as postulated, however, an equilibrium plateau was observed for all treatments by 91 days, when volatilization was no longer significant in any of the investigated soils. After six months, biochar was shown to inhibit desorption of alkanes from bulk soil in contrast to unamended microcosms, where alkanes were degraded to a large extent. This suggests that bioremediation may be a better remediation strategy for the early phase of remediation as applying biochar too early in the process would prohibit potential bioremediation. Nonetheless, biochar amended soil could be utilized as a covering layer to minimize volatile losses of pollutants to the atmosphere. PAHs did not degrade as easily as the alkanes and relatively high amounts of residual oil were

obtained from unamended microcosms compared to amended batches upon Accelerated Solvent Extraction (ASE), despite the evident activity of crude oil degrading microorganisms. Passive sampling experiments showed much higher available concentrations, i.e. in the aqueous phase, for unamended microcosms. Overall, the laboratory work done provided useful evidence that biochar could be effective as a mop-up technology in Nigeria to reduce contaminant spreading and deal with recalcitrant crude oil residuals after bioremediation has been used to remove the readily biodegradable portion of the pollution.

> ***Objective 2*** *- Evaluate residual risks for all treatments using the contaminated land exposure risk assessment (CLEA) model of the UK Environment Agency* **(Chapter 3)**

The author carried out a literature review of relevant UK government publications resulting in a written summary of the CLEA guidance which highlighted and discussed key components of the framework. Naphthalene residual concentrations in soil for all five treatments (C_s) in the experimental work were used as an input into the CLEA model, to exemplify potential biochar amendment benefits. Out of the nine exposure pathways considered by the model, only two were observed to have explicitly accounted for bioavailability in the current version of the CLEA model. Ingestion of contaminated vegetable was dependent on K_d (which relates to the pollutant bioavailability), while inhalation of outdoor vapour was dependent on K_{aw} which is a K_d derivative. Indoor and outdoor dermal uptake did however consider bioavailability implicitly as ABS_d (dermal absorption fraction) was incorporated into relevant equations, however, it is currently unclear how ABS_d might relate to K_d or other measures for the pollutant availability. Modelling results showed that uptake rates were lower for biochar-amended batches than unamended batches for all exposure pathways indicating that biochar may reduce extractable pollutant concentrations. The effects of this sorption would, however, not be observed in certain pathways within the CLEA model, such as the important soil ingestion and soil attached to vegetables ingestion pathways, unless there is a change in the framework that incorporates bioavailability assumptions in all pathways. In light of these, it was recommended that in attempting to implement the technology in Nigeria, efforts should be made to influence legislation such that the risk management framework assumptions are not overly conservative. Soil, sediment and groundwater quality in Nigeria is assessed based on 'total hydrocarbon concentrations' (DPR, 2002) and so the benefits of sorption may currently not be accounted for. It should, however be noted, that activated carbon is such a strong sorbent for some organic pollutants, that it prevents their extraction even with rigorous methods such

as accelerated solvent extraction, and may thereby indirectly result in lower measured total hydrocarbon concentrations in activated carbon amended soil.

> ***Objective 3*** *- Draw up a framework for the social enquiry into the potential for implementing biochar in Nigeria based on social interactions in Nigeria and the USA (Chapter 4).*

Nigeria was initially the focus of the social enquiry and so interactions in Nigeria were split into two phases; firstly to gain an understanding of the remediation environment and secondly to explore biochar implementation in the country. Stakeholder mapping revealed relevant stakeholders and helped in planning and logistics for contact with informants and also in deciding on best method for data collection. An opportunity arose to carry out research in the USA and so it was decided that the most beneficial information to obtain from the USA would be data about the technology as full scale implementation had just then been carried out in the USA for the first time. The Mirror Lake restoration project was therefore used as case study. Semi-structured interviews were deemed as the most appropriate means for obtaining required data in Nigeria and the USA. Questionnaires were however administered alongside interviews in the USA although interviews were of greater quality in terms of relevance to the research objectives and so they were only used to echo points from the interviews. After consideration of different potential frameworks/models, it was decided that an adaptation of the IAD framework would be ideal due to the pragmatic nature of the research.

> ***Objective 4*** *- Conduct a desktop study to understand the legislative and institutional framework for oil pollution remediation in Nigeria (Chapter 5)*

A historical review of existing legislation relevant to the Nigerian oil and gas industry revealed that environmental protection legislation has evolved in Nigeria through the last six decades and there is presently a plethora of such. It was however observed that legislation is often incomprehensive and enforcement is a major challenge for regulators. The desktop study which also involved a high-level institutional analysis revealed the major actors in the Nigerian oil and gas industry and their roles through stakeholder mapping. The Federal government as one of the major player carries out its regulatory activities through a number of Federal and State parastatals and agencies with specified roles and functions (Nwilo and Badejo, 2006). DPR (Department of Petroleum Resources) is the main regulatory agency even though NOSDRA was established with similar roles and functions. The EGASPIN

(Environmental Guidelines and Standards for the Petroleum Industry in Nigeria) framework was issued by DPR in 1991 and revised in 2002. It gives directives concerning the control of pollutants from the various petroleum exploration, production and processing operations in Nigeria and may be considered the single most important piece of legislation for oil spill remediation in Nigeria. The Petroleum Industry Bill (PIB) was proposed in 2008 to reform the oil and gas industry and address anomalies including the issue of duplicate role and function among agencies. Despite several revisions, it has not yet been passed and remains the subject of intense debate among stakeholders. Another major category of actors are Oil company operators who carry out their remedial activities through contractors. Members of host communities, media and action groups are also major actors.

> ***Objective 5*** *- Analyse data from social interactions to provide an understanding of factors that influence oil spill remediation in Nigeria and the implementation of carbon-based remediation technology in the USA (Chapter 6).*

Several interesting observations were made, some of which were more relevant than others. Major findings about the Nigerian oil spill remediation environment include institutional and legislative deficiencies, corruption and remediation challenges such as security and access issues, and a lack of effective technologies for oil spill remediation in mangrove swamps, due to ecosystem sensitivity. The remediation of legacy spill sites is also of serious concern as it is often the expectation that oil companies should take responsibility for these sites however this is not the case.

Major findings from the USA include historic challenges with sediment remediation, recent changes in legislation and a community of stakeholders that are gradually embracing sorbent-based remediation technologies. Increased flexibility for innovative technologies within regulations had a positive impact on the success of carbon based remediation technology implementation in the USA.

The comparative analysis showed that the remediation environment in Nigeria is quite different from the USA although similarities exist. It also highlighted a need for greater stakeholder involvement in driving new and innovative remediation technology in Nigeria.

Based on the findings of the chapter, it was concluded that there is a potential for implementation of the technology in Nigeria. The author is of the opinion that the potential for biochar implementation as a polishing technique for crude oil residuals be explored in Nigeria through engagement with all stakeholders. Technical, legislative and institutional

aspects should be taken into account in conducting pilot studies which would potentially lead to full-sale implementation. The unique challenges of the Nigerian environment should also be taken into consideration.

> ***Objective 6*** *- Triangulate all research findings with initial objectives in a coherent conclusion and make recommendations based on these (Chapter 7).*

The three main aspects of the research as outlined in the initial objectives were thoroughly investigated using methods from varied disciplines as required and resulting in data of varied nature. The IAD was useful in that it provided a framework to present and analyse the data from the social aspect of the research to meet the research objectives. This complementarity of technical and social aspects provided a robust understanding of the current realities surrounding the use or potential use of sorbent-based technologies globally. It thus allows for potential multi-dimensional conceptualisation of the viability of biochar in Nigeria.

7.4   Recommendations for biochar implementation in Nigeria

1.   Advancement of the technology in Nigeria should begin by engaging stakeholders in initial discussions about what aspects to consider implementation, challenges that are likely to be faced and how to mitigate against these. It should also entail encouraging research through experimental work, field trials and full-scale implementation projects. Field scale demonstrations should be conducted in the Niger-Delta across different environmental conditions and using different application methods that would be deemed conducive for specific sites. As was done in the USA and as stipulated in Nigeria's EGASPIN guideline, full-scale projects should follow successful field studies. The pilot study must be compatible with existing legislation and conditions in Nigeria. It is important to be able to translate the deductions made from this work into terms that can be easily interpreted and applicable within the Nigerian context. Effective test and monitoring during field trials would be essential for success.

2.   In developing a conceptual plan for trial of the technology, the following need to be considered;

•   The potential for use in treating dissolved–phase hydrocarbons in mangrove and groundwater contamination should be explored. As it appears that RENA may be suitable for most soil sites in Nigeria, the possibility of using biochar as a polishing step after RENA should be explored particularly in mangrove swamps.

- Nigeria needs to invest in capacity building to build technical competence and infrastructure. Workshops that pro-actively address the concerns and reservations that people have about biochar would be helpful.

- Competent contractors that can effectively execute and monitor the project innovatively based on the Nigerian environment.

- Remediation Technologies Roundtable Meeting

- A cordial relationship between all members of the application community would be beneficial for a change in trajectory of the existing remedial approach.

- Create incentives for contractors to explore new technology by pointing out benefits to them.

- Design activities to address community attitudes and build trust among stakeholders. Members of the local community can be employed on such projects.

- Cost-benefit analysis

- Determine means of deployment

- Multi-disciplinary projects

3.   Efforts need to be made to stop or significantly decrease the level of pollution that arise from sabotage/malicious activities before biochar can be considered on many sites. Stricter penalties and enforcement need to be put in place for maintenance of pipelines.

4.   A review of policy and regulation in order to review the way in which risk is currently addressed particularly as it relates to contaminant bioavailability would be beneficial. Law-makers should be part of this because unless legislation enables it, little or no progress can be made.

5.   Secondary environmental impact are not usually at the fore-front of decision making in developing countries. It is however important that biochar has to be produced from feedstock which have no other obvious use because of impact on greenhouse gas emissions (Lehmann and Joseph, 2009). Potential source materials include corn cobs and palm husk. Under no circumstances should biochar production for soil and sediment remediation contribute to deforestation or similar negative impacts on local ecosystems.

6.   Government agencies should be empowered to take the lead on "orphan sites", ideally with financial support from an invigorated Ecological Fund.

7.5   Direction for further research

The research objectives of the research have been met to a large extent however, despite the contributions of this work, a few limitations still exist. Further study should consider

characterization of biochar produced from local Nigerian feedstock as well as local production techniques. Work should be done on resolving policy challenges. Overall there is scope for taking the work further based on learnings from successful implementation in the USA.

Sediments are generally not as easily accessible as soils and research is advancing in terms of application techniques to sediments (Hilber, 2010). It would thus be beneficial to conduct more research on biochar application in mangrove in order to advance techniques that would involve minimal intrusiveness during application.

Research should be done on how to motivate change and make the most of the results for Nigerian stakeholders. For instance, social media has helped in advancing the credibility of Nigeria's democratic process in recent years (Lewis, 2011).

Also, the massive overhaul that was seen in Nigeria's pharmaceutical industry regarding the endemic problem of fake drugs shows that positive change is possible in Nigeria (Akunyili).

In order to see a significant and lasting change in all segments of the Nigeria oil and gas industry, particularly regarding remediation issues, institutional reform needs to occur.

Chapter 8.   Appendices

Appendix A: Tables of experimental data

Table 8-1 aromatic hydrocarbon volatilization flux for days 0-14

Compound	no oil (ug/g)	no oil + biochar (ug/g)	oil + biochar (ug/g)	oil + biochar after 5mths (ug/g)	Oil (ug/g)
Toluene	0.0156 ±0.0088	0.0081 ±0.0010	0.0092 ±0.0008	0.0091 ±0.0031	0.0079 ±0.0007
Ethylbenzene	0.0004 ± 0.0001	0.0004 ± 0.0003	0.0008 ± 0.0001	0.0013 ± 0.0002	0.0012 ± 0.0001
m-xylene	0.0011 ± 0.0003	0.0010 ± 0.0007	0.0036 ± 0.0004	0.0048 ± 0.0009	0.0047 ± 0.0003
1,3,5-TMB	0.0002 ± 0.0001	0.0001 ± 0.0000	0.0009 ±0.0001	0.0143 ± 0.0026	0.0137 ± 0.0016
1,2,4-TMB	0.0003 ± 0.0001	0.0001 ± 0.0000	0.0036 ± 0.0005	0.0076 ± 0.0030	0.0090 ± 0.0024
P-isopropyltoluene	0.0003 ± 0.0003	0.0000 ± 0.0000	0.0087 ± 0.0019	0.1539 ± 0.0347	0.1513 ± 0.0135
n-butylbenzene	0.0002 ± 0.0002	0.0001± 0.0000	0.0004 ± 0.0000	0.0017 ± 0.0003	0.0018 ± 0.0004
naphthalene	0.0003 ± 0.0002	0.0001 ± 0.0000	0.0223 ± 0.0046	0.0931 ± 0.0300	0.0916 ± 0.0026

Table 8-2 Total concentration of 10 alkanes between C_{10} and C_{28} measured after Accelerated Solvent Extraction of soil

compound	no oil (ug/g)	no oil + biochar (ug/g)	oil + biochar (ug/g)	oil + biochar after 5mths (ug/g)	Oil (ug/g)
decane	0.00 ± 0.00	0.06 ± 0.02	16.19 ± 1.65	0.00 ± 0.00	0.00 ± 0.00
dodecane	0.00 ± 0.00	0.09 ± 0.02	15.65 ± 2.43	0.00 ± 0.00	0.00 ± 0.00
tetradecane	0.00 ± 0.00	0.09 ± 0.03	14.59 ± 2.36	0.00 ± 0.00	0.00 ± 0.00
hexadecane	0.00 ± 0.00	0.09 ± 0.03	15.82 ± 2.26	0.00 ± 0.00	0.00 ± 0.00
octadecane	0.00 ± 0.00	0.09 ± 0.05	14.33 ± 1.74	0.00 ± 0.00	0.00 ± 0.00
eicosane	0.00 ± 0.00	0.08 ± 0.05	12.76 ± 1.35	0.00 ± 0.00	0.00 ± 0.00
docosane	0.00 ± 0.00	0.07 ± 0.04	11.49 ± 0.91	0.00 ± 0.00	0.00 ± 0.00
tetracosane	0.00 ± 0.00	0.06 ± 0.03	11.55 ± 0.92	0.00 ± 0.00	0.00 ± 0.00
hexacosane	0.00 ± 0.00	0.06 ± 0.04	9.80 ± 0.45	0.00 ± 0.00	0.00 ± 0.00
octacosane	0.00 ± 0.00	0.08 ± 0.02	6.62 ± 0.47	0.00 ± 0.00	0.00 ± 0.00
	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
total	**0.00 ± 0.00**	**0.77 ± 0.31**	**128.81 ± 13.88**	**0.00 ± 0.00**	**0.00 ± 0.00**

Table 8-3 Total concentration of 16 EPA PAHs measured after Accelerated Solvent Extraction of soil

Compound	no oil (ug/g)		no oil + biochar (ug/g)		oil + biochar (ug/g)		oil + biochar after 5mths (ug/g)		Oil (ug/g)	
Naphthalene	0.019	± 0.005	0.015	± 0.002	0.142	± 0.085	6.821	± 0.597	0.165	± 0.020
Acenaphthylene	0.016	± 0.004	0.025	± 0.006	0.014	± 0.006	0.033	± 0.010	0.026	± 0.004
Acenaphthene	0.018	± 0.003	0.051	± 0.056	0.131	± 0.045	0.335	± 0.308	0.230	± 0.057
Fluorine	0.029	± 0.012	0.069	± 0.085	0.483	± 0.067	0.453	± 0.408	2.147	± 0.425
Phenanthrene	0.511	± 0.173	0.572	± 0.597	1.508	± 0.493	2.004	± 2.102	6.901	± 1.307
Anthracene	0.159	± 0.102	0.176	± 0.208	0.183	± 0.147	0.431	± 0.646	0.466	± 0.115
Fluoranthene	1.232	± 0.357	1.429	± 1.225	1.388	± 0.681	1.919	± 2.192	3.657	± 1.123
Pyrene	1.013	± 0.285	1.120	± 0.855	1.142	± 0.514	1.393	± 1.499	3.199	± 0.834
benz[a]anthracene	0.692	± 0.209	0.857	± 0.791	1.103	± 0.430	1.254	± 1.308	3.401	± 1.136
Table continued on next page										

chrysene	0.752	±	0.693	±	1.407	±	0.850	±	4.444	±
	0.193		0.533		0.354		0.966		0.821	
benzo[b]fluoranthene	0.769	±	0.750	±	1.269	±	0.932	±	3.232	±
	0.169		0.487		0.342		0.949		1.081	
benzo[k]fluoranthene	0.139	±	0.461	±	0.643	±	0.491	±	1.894	±
	0.041		0.304		0.200		0.473		0.436	
benzo[a]pyrene	0.815	±	0.807	±	1.226	±	0.884	±	3.579	±
	0.220		0.559		0.336		0.939		0.982	
indeno[1,2,3-cd]pyrene	0.618	±	0.838	±	1.412	±	0.954	±	3.866	±
	0.161		0.490		0.310		0.894		1.265	
dibenz[a,h]anthracene	0.118	±	0.198	±	0.397	±	0.238	±	1.011	±
	0.024		0.146		0.124		0.223		0.412	
benzo[ghi]perylene	0.405	±	0.464	±	0.741	±	0.493	±	1.825	±
	0.098		0.243		0.160		0.400		0.495	
Total	**7.306**	**±**	**8.524**	**±**	**13.187**	**±**	**19.485**	**±**	**40.042**	**±**
	2.019		**6.484**		**4.201**		**13.750**		**10.497**	

Table 8-4 Total alkane concentration in PE experiment after 7 months

compound	no oil (ug/g)		no oil + biochar (ug/g)		oil + biochar (ug/g)		oil + biochar after 5mths (ug/g)	Oil (ug/g)	
decane	0.014	± 0.012	0.010	± 0.009	0.083	± 0.104	0.010 ± 0.006	0.023	± 0.002
dodecane	0.014	± 0.004	0.011	± 0.009	0.142	± 0.111	0.012 ± 0.007	0.017	± 0.006
tetradecane	0.030	± 0.036	0.032	± 0.044	0.252	± 0.110	0.031 ± 0.035	0.056	± 0.059
hexadecane	0.350	± 0.404	0.221	± 0.033	0.382	± 0.077	0.123 ± 0.038	0.212	± 0.141
octadecane	0.507	± 0.487	0.234	± 0.114	0.437	± 0.146	0.257 ± 0.062	0.329	± 0.092
eicosane	0.439	± 0.625	0.314	± 0.112	0.477	± 0.142	0.341 ± 0.109	0.303	± 0.059
docosane	0.538	± 0.586	0.404	± 0.145	0.634	± 0.145	0.507 ± 0.258	0.574	± 0.193
tetracosane	0.597	± 0.525	0.386	± 0.070	0.617	± 0.188	0.484 ± 0.084	0.497	± 0.391
hexacosane	4.271	± 4.774	2.134	± 0.326	2.294	± 0.262	2.293 ± 0.172	2.425	± 0.177
octacosane	0.326	± 0.067	0.159	± 0.086	0.358	± 0.154	0.660 ± 0.311	0.451	± 0.097
total	**7.086**	**± 7.381**	**3.905**	**± 0.534**	**5.677**	**± 0.826**	**4.718 ± 0.685**	**4.887**	**± 0.897**

Table 8-5 Total PAH concentration in PE after 7 months

compound	no oil (ug/g)		no oil + biochar (ug/g)		oil + biochar (ug/g)		oil + biochar after 5mths (ug/g)	Oil (ug/g)	
naphthalene	0.015	± 0.002	0.011	± 0.001	0.025	± 0.016	0.014 ± 0.006	0.362	± 0.046
acenaphthylene	0.005	± 0.002	0.001	± 0.001	0.004	± 0.002	0.009 ± 0.003	0.062	± 0.044
acenaphthene	0.032	± 0.015	0.000	± 0.000	0.002	± 0.004	0.013 ± 0.004	2.342	± 0.359
fluorene	0.033	± 0.015	0.002	± 0.001	0.007	± 0.001	0.053 ± 0.018	26.375	± 4.590
phenanthrene	0.336	± 0.186	0.045	± 0.002	0.087	± 0.008	0.385 ± 0.067	70.914	± 14.914
anthracene	0.068	± 0.042	0.003	± 0.001	0.005	± 0.003	0.023 ± 0.005	1.788	± 0.522
fluoranthene	0.868	± 0.579	0.017	± 0.005	0.035	± 0.016	0.330 ± 0.070	17.052	± 4.455
pyrene	0.864	± 0.599	0.011	± 0.005	0.043	± 0.021	0.434 ± 0.125	16.632	± 4.516
benz[a]anthracene	0.289	± 0.223	0.001	± 0.001	0.012	± 0.010	0.300 ± 0.152	13.107	± 8.607
chrysene	0.597	± 0.445	0.005	± 0.005	0.062	± 0.023	1.443 ± 0.546	20.762	± 5.197
benzo[b]fluoranthene	0.293	± 0.228	0.000	± 0.000	0.020	± 0.024	1.087 ± 0.616	5.036	± 1.581

benzo[k]fluoranthene	0.252 ± 0.217	0.002 ± 0.003	0.017 ± 0.029	0.052 ± 0.090	3.464 ± 1.365
benzo[a]pyrene	0.239 ± 0.186	0.010 ± 0.012	0.030 ± 0.018	0.528 ± 0.306	4.327 ± 1.332
indeno[1,2,3-cd]pyrene	0.055 ± 0.085	0.002 ± 0.004	0.013 ± 0.012	0.225 ± 0.131	1.725 ± 0.514
dibenz[a,h]anthracene	0.032 ± 0.026	0.000 ± 0.000	0.004 ± 0.003	0.141 ± 0.092	0.940 ± 0.273
benzo[ghi]perylene	0.054 ± 0.079	0.004 ± 0.005	0.039 ± 0.017	0.328 ± 0.181	1.527 ± 0.413
Total	**4.030 ± 2.793**	**0.114 ± 0.046**	**0.406 ± 0.158**	**5.365 ± 2.224**	**186.414 ± 39.213**

Table 8-6 T-test comparing volatilization flux

oil + biochar	oil + biochar after 5mths	oil
0.052847	0.315084	0.268014
0.047709	0.203604	0.276846
0.048023	0.33842	0.298824

t-Test: Two-Sample Assuming Equal Variances

	oil + biochar	*oil + biochar after 5mths*
Mean	0.049526	0.285703
Variance	8.29E-06	0.005191
Observations	3	3
Pooled Variance	0.0026	
Hypothesized Mean Difference	0	
df	4	
t Stat	-5.67299	

t-Test: Two-Sample Assuming Equal Variances

	oil + biochar	*oil*
Mean	0.049526	0.281228
Variance	8.29E-06	0.000252
Observations	3	3
Pooled Variance	0.00013	
Hypothesized Mean Difference	0	
df	4	
t Stat	-24.8886	

	P(T<=t) one-tail	0.002382	P(T<=t) one-tail	7.74E-06
	t Critical one-tail	2.131847	t Critical one-tail	2.131847
	P(T<=t) two-tail	0.004763	P(T<=t) two-tail	1.55E-05
	t Critical two-tail	2.776445	t Critical two-tail	2.776445

Table 8-7 T-test results for eight aromatic hydrocarbons within the first 14 days of the volatilization experiment

	oil + biochar (ug/g)	oil + biochar after 5mths (ug/g)	P value of oil + biochar vs oil + biochar after 5 mths
toluene	0.009252	0.00853463	0.92715465
	0.008413	0.00623351	
	0.010029	0.01238418	
ethylbenzene	0.000822	0.0013513	0.03751462
	0.000718	0.00099052	
	0.000901	0.00142325	
m-xylene	0.003541	0.00540051	0.08160151
	0.003184	0.00382881	
	0.003952	0.00525205	
1,3,5-TMB	0.000932	0.01483176	0.00093357
	0.000754	0.01146838	
	0.001048	0.0166913	
1,2,4-TMB	0.003739	0.01102824	0.09042273
	0.003041	0.00626685	
	0.004083	0.00540368	
P-isopropylToluene	0.008861	0.16724614	0.00193401
	0.006793	0.11450674	
	0.010563	0.17990169	
n-butylBenzene	0.000359	0.00194276	0.00259763
	0.000336	0.00130348	
	0.000414	0.00181875	
naphthalene	0.025341	0.10474897	0.01560303
	0.02447	0.05900569	
	0.017032	0.11554536	

Table 8-8 T-test comparing PAH concentration in PE samplers after bioremediation and BC amendment

T-Test: Two-Sample Assuming Equal Variances

	No oil	*No oil + biochar*
Mean	4.030252	0.110133
Variance	7.80202	0.00212
Observations	3	3
Pooled Variance	3.90207	
Hypothesized Mean Difference	0	
Df	4	
t Stat	2.43051	
P(T<=t) one-tail	0.035971	
t Critical one-tail	2.131847	
P(T<=t) two-tail	0.071941	
t Critical two-tail	2.776445	

Appendix B: Biochar brief, questionnaire and interview questions for USA investigation

Biochar in oil spill remediation: a viable option for Nigeria?

Newcastle University

School of Civil Engineering and Geosciences

Policy brief · Jan 2015

Alero Arenyeka

Oil industry regulations around the world require that action is taken to clean up and rehabilitate land and water affected by pollution. Recent developments in contamination remediation apply a risk-based approach to restoring contaminated soils and aqueous/river sediments to useable conditions. In determining the viability and potential effectiveness of a remediation technology for a specific location, factors such as cost effectiveness, biophysical peculiarities and legislative requirements need to be assessed.

What is biochar?

Biochar in its simplest form may be defined as fine-grained charcoal applied to soils. It is a similar material to activated carbon (AC), but derived from modern biomass.

Biochar image (source: http://www.biochar-international.org/biochar/faqs)

Like all charcoal, biochar is made by exposing wood, grasses, crops, plant residues or other biomass to high temperatures but in this case, with limited oxygen in a process called 'pyrolysis'. The biochar can be 'activated' by heat or steam treatment to increase its surface area and microporosity. In recent years, there has been increased research relating to the use of biochar in the remediation of contaminated soils and sediments. Compared to other sorbents, biochar can also potentially be applied in carbon sequestration, soil fertility improvement, pollution remediation, and agricultural by-product/waste recycling.

What pollutants can biochar remediate?

AC amendment has been tested extensively in the laboratory and the addition of a few percent AC by soil or sediment mass has been effective in sequestering PAHs, PCBs and organochlorine pesticides (Ghosh *et al.*, 2011).

How does biochar remediate contamination?

When the contaminated soil or sediment is amended with biochar, it alters the sediment geochemistry, increases contaminant binding and reduces contaminant exposure risks to people and the environment (Ghosh *et al.*, 2011). It does not actually remove the contaminant from the system but makes the contaminant unavailable to biota through sorption into the biochar pore spaces.

Where has biochar been used?

Activated charcoal has been widely used in drinking water purification and in aquaria to keep fish healthy. Even though amendment by biomass-derived sorbent such as biochar is novel, sorbent amendment is not new to oil spill contamination. In fact, the USEPA as well as the Clean Nigeria Associates (CNA) both use sorbents. This research aims to investigate the viability of biochar in oil spill remediation in Nigeria from a scientific as well as social standpoint.

Reference: U Ghosh *et al.*, In-situ sorbent amendments: a new direction in contaminated sediment management. Environmental Science & Technology 45 (4), 1163-1168

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Figure 8-1 Biochar brief

Questionnaire for survey research

Age: ☐ 21-30 ☐ 31-40 ☐ 41-50 ☐ 51-60 ☐ 61-70

Occupation: ☐ student ☐ private sector ☐ government ☐ other

Gender: ☐ Male ☐ Female

Highest educational qualification: ☐ High school ☐ BSc ☐ MSc ☐
PhD

Nationality: _____

Initial open questions:

❖ Which remediation strategies in your opinion work best for remediation of oil contaminated land/ wetlands/sediments? Why do you think they are the best option?

❖ Are there any major concerns with pollution residuals at the end of a remediation effort? How are these dealt with?

Please view technology brief *

Please rate the following remediation approaches for crude oil-contaminated sites according to your overall preference

1. Bioremediation   2. Monitored natural attenuation   3. Carbon amendments

Most preferred _____

Least preferred _____

Please rank the following technology <u>approaches</u> for crude oil-contaminated sites from 1-3 (with 1 being the most preferred and 3 being the least preferred) for each of the <u>factors</u> outlined

Approach	Factor				
	Remediation effectiveness	Cost effectiveness	Regulatory concerns	Risk of damage to ecosystem	Public acceptability
Bioremediation					
Natural attenuation					
Carbon amendments					

Tell us your level of agreement with the following statements

- Legislation is a key factor in the choice of remediation technology?

☐ Strongly agree ☐ agree ☐ neutral ☐ disagree ☐ strongly disagree

- Current legislation in the US is compatible with the use of activated carbon/biochar for soil/sediment remediation

☐ Strongly agree ☐ agree ☐ neutral ☐ disagree ☐ strongly disagree

- Activated carbon/biochar would greatly reduce the risk of pollutants entering the food chain

☐ Strongly agree ☐ agree ☐ neutral ☐ disagree ☐ strongly disagree

- A concern about biochar-based remediation is the presence of biochar-associated pollutants in the long-term.

☐ Strongly agree   ☐ agree   ☐ neutral   ☐ disagree   ☐ strongly disagree

- Activated carbon/biochar can be applied without damaging ecosystems

☐ Strongly agree   ☐ agree   ☐ neutral   ☐ disagree   ☐ strongly disagree

- A concern about the use of activated biochar in remediation is that it would remain for hundreds of years in the soil or sediment

☐ Strongly agree   ☐ agree   ☐ neutral   ☐ disagree   ☐ strongly disagree

- The long term remediation effectiveness of activated carbon/biochar is uncertain
☐ Strongly agree   ☐ agree   ☐ neutral   ☐ disagree   ☐ strongly disagree

- The activated carbon/biochar itself is potentially beneficial to the soil/sediment ecosystem

☐ Strongly agree   ☐ agree   ☐ neutral   ☐ disagree   ☐ strongly disagree

- The sustainability of activated carbon/biochar production is of concern
☐ Strongly agree   ☐ agree   ☐ neutral   ☐ disagree   ☐ strongly disagree

- The involvement/participation level of all stakeholders in the decision-making process is satisfactory

☐ Strongly agree   ☐ Agree   ☐ neutral   ☐ disagree   ☐ strongly disagree

Please view results sheet**

Which assessment (total vs available vs volatile) is most and least relevant in your opinion?

Most relevant assessment_____

Least relevant assessment_____

Considering the evidence presented to you, which is your most preferred and least preferred remediation approach for crude oil polluted soils?

1. Bioremediation   2. Monitored natural attenuation   3. Carbon amendments

Most preferred _____

Least preferred _____

In your opinion, what is the better strategy for the stabilization of oil pollution residuals following bioremediation; monitored natural attenuation or Carbon amendments?

Better stabilization strategy _____

In what context would it be most practical/beneficial to implement activated carbon/ biochar for remediation of crude oil in your opinion?

_____

_____

*   *brief information sheet about biochar as a remedial option*
** *brief summary of relevant result from researcher's PhD work*

Follow on open questions, if there is time

❖ What in your opinion is the greatest driver/motivation for a risk-based approach such as activated carbon amendment for pollution remediation?

❖ What are the major limitations/concerns highlighted by stakeholders regarding the use of sorbent amendment in pollution remediation? Desorption, change in soil properties and impact on end-use, contaminant sequestration etc

❖ Where do you think it would be most practical /beneficial to implement the technology, soil/ aqueous sediment?

❖ Do you think sorbent amendment would be better used alone or as a mop-up technology after bioremediation?

❖ Do you think there is a potential for greater utilisation of sorbent amendment for remediation globally? Why do you think it has not been used more frequently?

❖ Is the adoption of this remedial approach impacted greatly by who is paying; i.e. superfund (for legacy pollution) or potentially responsible parties (PRPs)? How receptive are companies to the approach?

❖ Is activated carbon amendment viewed as a cheaper alternative/an easier way out by any stakeholders?

❖ Do you think this would be a suitable option for remediation of mangrove swamp? What would be your major challenges/concerns regarding the use of activated carbon/biochar in mangrove swamp?

❖ Would you be concerned about how the availability of activated carbon/biochar impacts on the environment?

❖ How could any legislative/regulatory barriers be overcome in order to implement the technology where risk assessment is mainly focused on total concentrations?

❖ Is there likely to be a relatively high demand for long-term monitoring?

❖ Is the stability of the AC material in soils and sediments of concern?

❖ Would you be concerned about spread of pollution by water currents, and surface runoff/leaching due to translocation of surficially applied AC in soil?

Appendix C: List of relevant interviewees

S/N	Organization	Role	Date	Location	Code	Stakeholder category	Method
1	NDDC	Environmental personnel	2013	Port Harcourt	KII1	Regulator	Semi-structured; face-to-face
2	DPR	Environmental personnel	4th Dec 2013	Lagos	KII2	Regulator	Semi-structured; face-to-face
3	DPR	Environmental personnel	5th Dec 2013	Lagos	KII3	Regulator	Semi-structured; face-to-face
4	NIMASA	Environmental personnel	5th Dec 2013	Lagos	KII5	Regulator	Semi-structured; face-to-face
5	NIMASA	Environmental personnel	9th Dec 2013	Lagos	KII6	Regulator	Semi-structured; face-to-face

6	NIMASA	Environmental personnel	9th Dec 2013	Lagos	KII7	Regulator	Impromptu chat
7	SPDC	Environmental personnel	10th Dec 2013	Port Harcourt	KII8	Operator	Brief phone-chat ; fixed interview
8	SPDC	Environmental personnel	11th Dec 2013*	Port Harcourt	KII9	Operator; expert	Semi-structured; phone
9	Lagos Ministry of Environment	Environmental personnel	2013	Lagos	KII10	Regulator	Semi-structured; face-to-face
10	vanguard newspapers	Chief editor	2013	Lagos		Media	Semi-structured; face-to-face
11	vanguard newspapers	Energy reporter	2013	Lagos			
12	vanguard newspapers	Energy editor	2013	Lagos	KII11		Semi-structured; face-to-face
13	KRPC	Environmental personnel	2014	Kaduna		Operator	Chat and scheduled phone interview

14	NOSDRA	Environmental personnel	2014	Lagos	KII4	Regulator	Semi-structured; face-to-face
15	CNA	Environmental personnel	2014	Port Harcourt	KII12	Regulator	Phone chat
16	Shell Port Harcourt	Environmental personnel	2014	Port	KII13	Operator	Semi-structured; face-to-face
17	Shell Port Harcourt	Environmental personnel	2014	Port Harcourt	KII14	Operator; expert	Semi-structured; face-to-face
18	RSUST	Environmental academic	2014	Port Harcourt	KII15	Academic	Semi-structured; face-to-face
19	Rivers State University of Science & Technology (RSUST)	Environmental academic	2014	Port Harcourt	KII16	Academic	Semi-structured; face-to-face
20	RSUST	Environmental academic	2014	Port Harcourt	KII17	Academic	Semi-structured; face-to-face

21	Chevron	Environmental personnel	2014	Port Harcourt	KII18	Operator;	Semi-structured; face-to-face
22	Chevron	Environmental personnel	2014	Lagos	KII19	Operator;	Semi-structured; face-to-face
23	CNA	Environmental personnel	2014	Port Harcourt	KII20	Operator;	Semi-structured; face-to-face
24	CNA;	Environmental personnel	2014	Warri	KII21	Operator;	Phone interview
25	DNREC	Environmental personnel	2015	Delaware	KII22	Regulator	Semi-structured; face-to-face
26	DNREC	Environmental personnel	2015	Delaware	KII23	Regulator	Semi-structured; face-to-face
27	UMBC	Postgraduate student	2015	Baltimore	KII24	Researcher	Semi-structured; face-to-face
28	UMBC	Postgraduate student	2015	Baltimore	KII25	Researcher	Semi-structured; face-to-face

This guided the actual questions used on the trip though the focus was mainly on phase 1 questions.

Phase 1 questions – Nigerian pollution & remediation situation

Typology of oil contamination in Nigeria; what is the most common oil contaminant in Nigeria; crude oil or refined petroleum product? What percentage of oil contamination in the Niger delta is on water? On land? Sediment–based? Where is there a greater challenge with Pollution; on land/ in river sediments?

Characterization of remediation; where does remediation primarily occur presently? Who carries out majority of the remediation work? How involved is the CNA (Clean Nigeria Associates) in the remediation process? What is the involvement level of companies/ government / private sector in remediation? Where would it be most practical /beneficial to implement the technology, soil/ aqueous sediment?

What technology is being used presently? What are the limitations of the current technology?

How is remediation outcome assessed? Target values? How do you assess endpoint for remediation? Do you use soil guideline values? Who carries out this assessment?

Prevailing technologies; what types of sorbents are used in oil remediation in Nigeria? What is the proportion/ percentage of sorbent utilisation compared to other technologies? Why is it not being used more frequently? Is there a potential for greater utilisation of sorbents?

Institutional/regulatory issues; who deals with legacy pollution? Who pays for remediation? Who decides choice of remediation technology used?

Phase 2 questions – biochar viability

Taking account lessons learnt from first phase, how can we make this happen in Nigeria?

How biochar could potentially be used?

Where would it be most valuable place to implement it in Nigeria? By whom?

In areas where remediation might have been carried out but there is still residual/legacy contamination, could biochar potentially be used as a mop–up technology?

What would be the concerns/benefits for contractors? How acceptable would biochar technology be to them?

How would regulation have to be different to fit in biochar? Ex the UK uses fit-for purpose approach not total concentration

Would it be feasible to apply a fit-for-purpose approach in Nigeria? Particularly in places where it cannot be returned to its original state as stipulated in legislation?

Would stabilization of residuals be considered?

How is remediation value assessed? Literature talks about EGASPIN target values. What is the reality around how remediation outcomes are assessed?'

Follow up questions after Dec 2013 interactions

What are the most commonly used remediation strategies?

Which are the strategies that in your opinion work best?

Why do you think they are the best option?

Are there any problems with pollution residuals at the end of a remediation effort? How are these dealt with?

What do you think about using sorbents like biochar to bind contaminants in-situ? Thus reducing bioavailability?

How much of what you do is driven by legislation?

What do you think about the role and behaviour of regulators?

Who are the regulators that you normally need to deal with?

Do regulators have a role in determining technology options?

Can companies adopt biochar independently or do they need to be prompted by regulators?

What regulatory hoops will companies have to jump if they were to adopt biochar technology?

Do you have any links or contacts for Clean Nigeria Associates?

The Oil Spill Response and Remediation team covers land and swamp assets. Is there a separate team for marine remediation?

Could you please throw more light on ''Shell's Risk Based Corrective Approach to Environmental Issues''?

Is it possible to gain access to the risk management framework documents (OG.02.47028 or OG.03.47062)?

Who is usually involved in JIV?

In which media do you have the greatest challenge with regards to remediation?

What kind of material is used in the sorbent boom?

Could biochar potentially be used to line excavated pits in order to minimize soil contamination?

Is your remedial work always carried out by external contractors?

Questions compiled before May 2014 trip (focuses on 2nd phase)

Identify good location for case study in order to explore the viability of biochar

Identify specific oil companies within this identified location

Identify challenges/concerns regarding use of biochar in mangrove swamp

Discuss potential for local production of biochar

Regarding trip to Nigeria & areas of focus for potential interview questions;

What is done with the soil at the end of the land farming treatment process?

What might people's reaction be regarding using biochar?

How would the availability of biochar impact on the environment?

Potential raw material for biochar production?

Before trip - May 2014

Find out more about mangrove swamp; physical characteristics & challenges

Design policy brief for application of biochar in wetlands

Characterize physical conditions for case study

Identify a particular location where we can do a more detailed study (hypothetical scenario) on how biochar can be applied

Potential regulatory barriers for biochar implementation

Appendix D: Sample of introductory letter

Newcastle University

2nd Dec, 2013

TO WHOM IT MAY CONCERN

School of Civil Engineering and Geoscien

Newcastle University
Cassie Building
Newcastle upon Tyne
NE1 7RU United Kingdom

Dear Sir/Madam

INTRODUCTION: MISS ALERO ARENYEKA

I am a member of the academic supervisory team of Miss Arenyeka, who has been registered as a full time PhD student within the School of Civil Engineering and Geosciences at Newcastle University since February, 2012. The ultimate aim of her research is to assess the social acceptance of biochar-based soil remediation in Nigeria. Against this backdrop, Miss Arenyeka will be conducting an extensive fieldwork in Nigeria to obtain her research data. This will entail:

* Conducting some semi-structured interviews with members of your organisation who may be involved in oil spill remediation within the regulatory or operational context

* Requesting access to remediation efforts/reports within the upstream and downstream oil sector in Nigeria as it relates to the nature of contaminated sites, choice of remediation technology applied and regulatory framework

Also, since Miss Arenyeka's research project is envisaged to offer a feasible approach to a risk-based oil spill remediation in Nigeria, it is our kind hope that she is able to explore and establish a collaborative partnership with your organisation so as to present her findings to you at the end of her research.
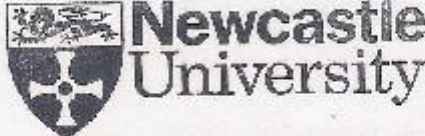
I would be very grateful if your organisation would be able to offer the necessary assistance to facilitate her work.

If you have any queries, please do not hesitate to contact me.

Yours faithfully,

Dr Jaime M. Amezaga

Senior Lecturer in Environmental Policy and Sustainability

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THE QUEEN'S
ANNIVERSARY PRIZES

2009

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