HYDROCARBON CONTAMINATION IN OGONILAND, NIGERIA, AND ITS MANAGEMENT VIA ADSORBENT-BASED REMEDIATION STRATEGIES

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DECLARATION

I declare that the research contained in this thesis, unless otherwise formally indicated within the text, is the original work of the author. The thesis has not been previously submitted to this or any other university for a degree and does not incorporate any material already submitted for a degree.

Signed

Dated 10/10/2018

DEDICATION

To my God for his unfailing love, mercies, grace, loving-kindness, and compassion upon my life, I know I never deserve this, but you made it possible. WOW to the most supportive wife Bernice, for her endurance and long-suffering during the long periods, honestly it will not have been possible with you.

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ABSTRACT

The Ogoniland axis of Rivers State, Niger Delta (Nigeria) is a heavily hydrocarbon-contaminated region, due to prolonged oil spillages and petrochemical activities on-going in the area. UNEP (2011) issued an environmental impact assessment report on the state of oil pollution in Ogoniland which highlighted the severe problem of hydrocarbon-contaminated groundwater and surface waters, which in turn profoundly impacts upon regional ecosystems and drinking water resources. Despite the acknowledged severity of surface and groundwater contamination in this area, understanding of (a) hydrocarbon migration and exposure pathways, and (b) practical methods of managing the impact of hydrocarbon-derived contaminants is limited.

This research has therefore investigated the distribution and concentrations of key hydrocarbon (and trace and major element) contaminants in groundwater and surface waters around major oil and petrochemical sites in Ogoniland; examined potential contaminant migration pathways between groundwater, surface water, and drinking water resources; and assessed the potential application of practical, more sustainable, water remediation or management methods, with particular emphasis on low-cost adsorption and enhanced natural attenuation approaches.

Field sampling identified gross contamination of surface and groundwater by phenol, with measured concentrations of 10.90-350mg/l exceeding the ATSDR (2008) phenol limit in drinking water of 0.03mg/l by several orders of magnitude. Laboratory core flooding studies were applied to examine contaminant migration and attenuation in simulated Ogoniland soils and to assess potential contaminant transfer pathways. The feasibility of the practical application of adsorbent-based remediation methods, based on testing of low-cost carbonaceous adsorbents, was examined in terms of the utility of these adsorbents (a) in reducing contaminant transfer to local receptors, (b) for local community use, and (c) for providing broader sustainability benefits to the local population. Commercial activated carbons were shown to be highly effective adsorbents for phenol removal (and removal of other contaminants of concern), although biochar adsorbents (based on *Miscanthus* grass, softwood, and rice husk) were less effective bulk adsorbents. Despite the relatively low adsorption efficiency of biochars observed here, however, their low-cost and potential for on-site (i.e., local) production suggest that they may still have application in combined, large area, soil improvement and contaminant risk management strategies. Commercial activated carbons, due to their higher cost, may find a potential demand at the point of water use but are unlikely to be effective community-level tools for large area application.

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CHAPTER 1.0 – BACKGROUND AND AIMS

1.1 INTRODUCTION

One of the most significant contemporary environmental problems is hydrocarbon contamination resulting from the activities of the oil and gas industry (Yakubu, 2017). The incidental or accidental release of hydrocarbons is of global concern to the health of humans and the environment. In particular, petroleum by-products such as polycyclic aromatic hydrocarbons (PAHs) are some of the most dangerous environmental contaminants due to the toxic and carcinogenic effect they pose to ecosystems (Leme *et al.*, 2007). The deliberate or accidental discharge of hydrocarbons and related petrochemical products are major causes of groundwater, surface water and soil pollution globally.

The accidental release of hydrocarbons is a phenomenon with an increasing trend across the globe. Some notable examples of oil spill incidents include the 1989 spillage from the Exxon Valdez (Figure 1.1) into Prince William Sound, Alaska, that resulted in severe surface and groundwater contamination, and has continued to affect local communities and wildlife over the following decades (Peterson *et al.*, 2003). The mass of the remaining subsurface oil from this incident is conservatively estimated at 55,600 kg (Nixon *et al.*, 2013). Elsewhere, the Amoco Cadiz disaster in the English Channel in 1978 released 220,000 tons of crude oil, resulting in an oil spill 29km wide and 129km long, affecting approximately 290km of coastline (Blackburn *et al.*, 2014). In Jilin, China, 1,842 oil wells were submerged by water due to coastal flooding, thereby causing water contamination, and the loss of seabirds and aquatic biota (Han *et al.*, 2009). Another example was the Deep-water Horizon oil spill which occurred in the Gulf of Mexico on the 20th April 2010. Sergei (2013) noted that this was the largest marine oil spill in the history of the hydrocarbon industry, and an estimated volume of 4.9 million barrels of oil was discharged into the marine ecosystem thereby causing marine pollution and damage to other surrounding water bodies.

Other significant oil spill incidents around the world (shown in Figures 1.1 and 1.2) include the Sao Sebastiao (Brazil) pipeline leakage, which occurred in 2006, and an oil tanker spillage, which occurred in Uruguay, around Jose Ignacio beach in Punta Del Este. Leme *et al.* (2007) suggest that total petroleum hydrocarbons (TPHs) and PAHs were the primary contaminants found to be present in the spillage above incidents.

1.2 SOURCES OF HYDROCARBON CONTAMINATION

Hydrocarbon contamination may arise from the following sources:

HYDROCARBON EXPLORATION AND EXPLOITATION – During the exploration for and exploitation of hydrocarbons, surface, and groundwater may become contaminated, which may be as a result of equipment failure or the seepage of hydrocarbon contaminants into the soil. These contaminants could pose a significant danger to the health of humans and the environment; Table 1.1 shows the contamination routes for both terrestrial and offshore drilling (Kadafa, 2012).

STORAGE TANKS – Storage tanks are used to conserve gasoline, oil, and other chemicals, etc. It is estimated that over ten million underground storage tanks are buried in the USA alone. However, fatigue, rusting and leakages may occur as a result of extended usage, thus allowing contaminants to escape and contaminate the groundwater aquifer (Wood *et al.*, 2013).

SEPTIC SYSTEMS - Septic systems are sewers where wastewater is collected from homes and offices and are not connected to a city drain system. When they are imperfectly designed, built, or sustained, they can leak bacteria, viruses, household chemicals, and hydrocarbon wastes into the groundwater causing harm to the environment (EPA, 2001; USGS, 1991).

LANDFILLS - Landfills are sites for disposal of hazardous and non-hazardous commercial, industrial and domestic waste. In 1999 the EU introduced legislation to prevent adverse effects of landfill disposal. Landfills should have an impermeable lining to stop contaminants from dispersing into surrounding surface and groundwater. When this lining is absent, contaminants (car battery acid, paint, household cleaners, hydrocarbons, etc.) can leach from the landfill and pollute the groundwater over time (Akinbile, 2006).

SHIPPING – Shipping incidents are major contributors of contamination (Table 1.1, Figures 1.1 and 1.2), due to tankers carrying petroleum products from one destination to another.

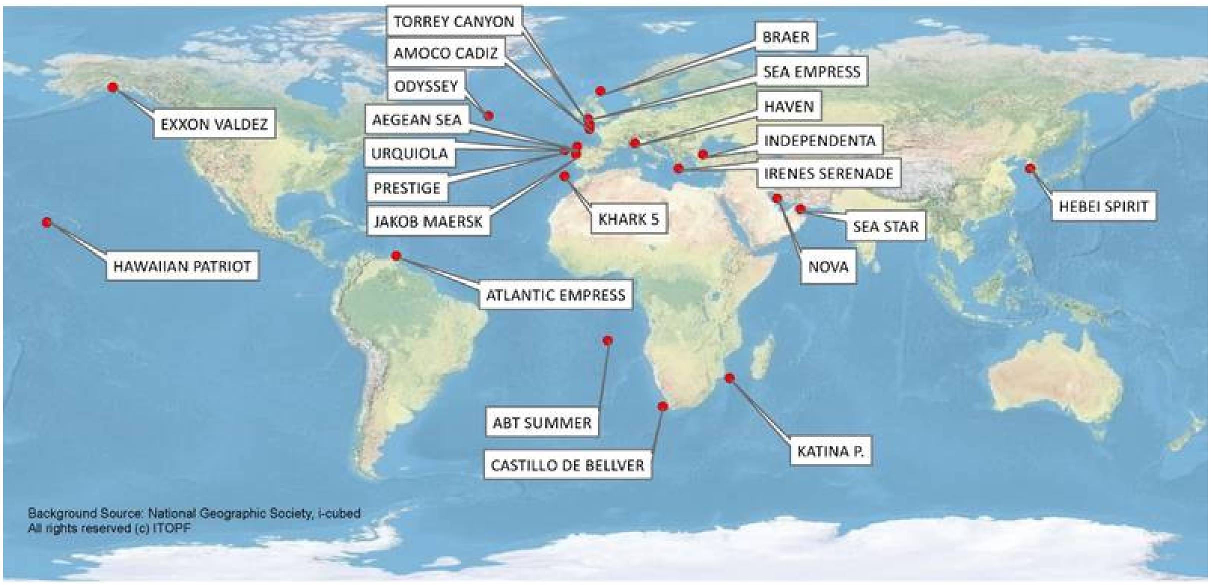

Figure 1.1 Location of major oil spills around the world over the period 2000-2010 (adapted from International Tankers Owners Pollution Federation Limited, 2018).

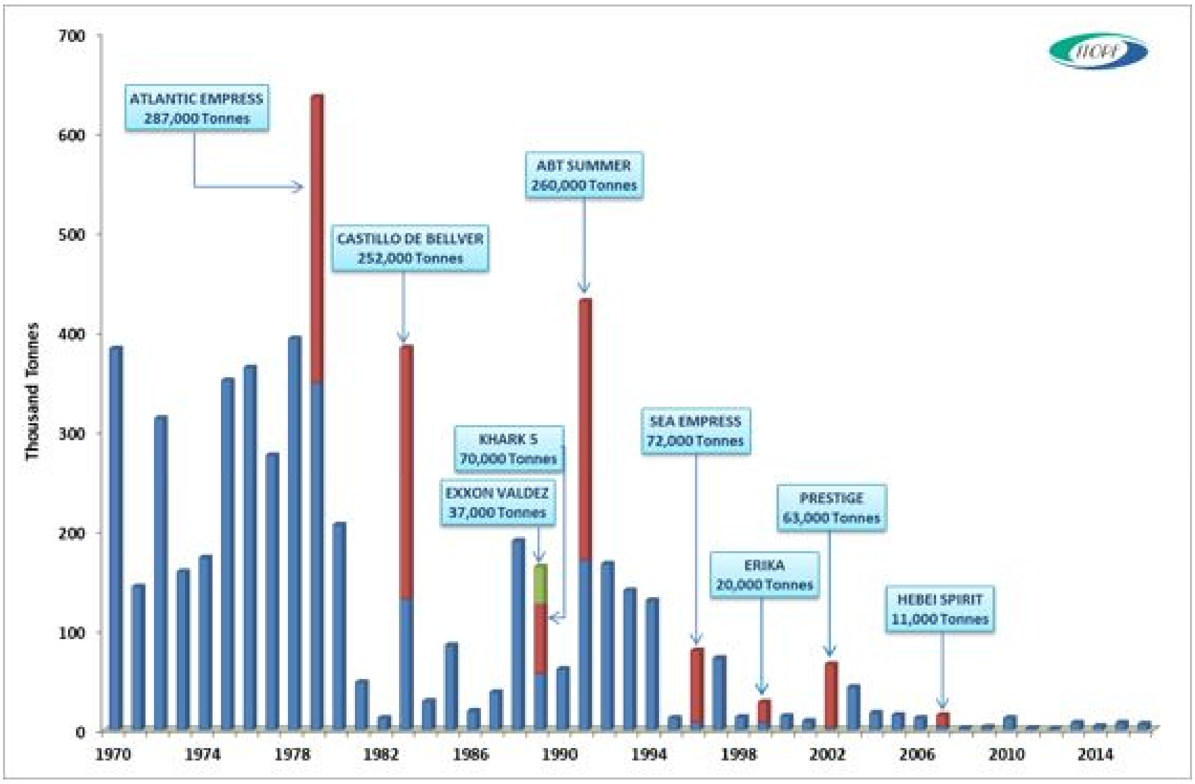

Figure 1.2 Quantities of oil spilled in major oil spillages (7 tonnes and over, rounded to nearest thousand), 1970-2016 (adapted from International Tanker Owners Pollution Federation Limited, 2018). Major shipping-related spills are highlighted.

1.3 NATURE OF HYDROCARBONS

Hydrocarbons are organic compounds that consist of hydrogen and carbon atoms. The carbon atoms are co-joined such that they form the framework of the compound. The hydrogen atoms are attached to them in different configurations, thus becoming principal constituents of petroleum and natural gas (Alireza and Smith, 2016). Hydrocarbons can be classified into the following, with crude oil or petroleum made up of varying proportions of these groups:

A) **SATURATED HYDROCARBONS (ALKANES) –** These are the simplest of the hydrocarbon species. They are made up of single bonds and undergo substitution reactions. They are found either as branched or linear compounds and are the basis for petroleum fuels. Their general formula is C_nH_{2n+2}.

B) **UNSATURATED HYDROCARBONS –** These groups of hydrocarbons are made of either double or triple bonded compounds with the general formula C_nH_{2n}.

C) **CYCLOALKANES –** These are hydrocarbons containing one or more hydrocarbon ring(s) attached to a hydrogen atom. The general formula of this species of hydrocarbon is C_nH_{2n}.

D) **AROMATIC HYDROCARBONS -** These are hydrocarbons that contain more than one aromatic ring, e.g., Polycyclic Aromatic Hydrocarbons (PAH).

1.4 STATEMENT OF PROBLEM AND CONTRIBUTION TO KNOWLEDGE

Nigeria is ranked as the largest producer of crude oil in Africa and fourth largest exporter of crude oil in the world (Klieman, 2012). The Niger Delta region is the heart of the Nigerian petroleum industry and accounts for 70% of the revenue generated by the Nigerian government. It is estimated that 1000km^2 of Ogoniland, a major administrative area in the southern Niger Delta, is heavily polluted by hydrocarbon contamination, which poses a significant risk to groundwater, the general environment and the local ecosystem (Table 1.1).

The United Nations Environment Programme (UNEP, 2011) carried out a detailed assessment of groundwater characteristics and contamination in Ogoniland in 2011. The assessment process was undertaken based on fieldwork, desk review and laboratory analysis which lasted for two years. The issue of pollution in this area has been ongoing for over 50 years, and problems are rapidly increasing rather than decreasing because efforts made to clean up this area have been poorly executed (UNEP, 2011).

Table 1.1 Environmental impacts associated with upstream and downstream petroleum operations (adapted from Ite *et al.*, 2013).

Activities	**Potential associated risks**	**Environmental, health and safety issues**
Exploration operations		
• Geological survey • Aerial survey • Seismic survey • Gravimetric and magnetic survey • Exploratory drilling • Appraisal	a. Noise pollution b. Habitat destruction and acoustic emission c. Drilling discharges, e.g., drilling fluids (water based and oil based muds) and drill cuttings d. Atmospheric emission e. Accidental spills/ blowout f. Solid waste disposal	Ecosystem destruction and interference with land use to access onshore sites and marines resource areas; environmental pollution (air, soil and controlled water) and safety problems associated with the use of explosives; land pollution which affects plants and poses human health risks; groundwater contamination and adverse effects on ecological biodiversity
Development and production		
• Development drilling • Processing: separation and treatment • Initial storage	a. Discharges of effluents (solids, liquids, and gases) b. Operation discharges c. Atmospheric emission d. Accidental oil spills e. Deck drainage f. Sanitary waste disposal g. Noise pollution h. Transportation problems i. Socioeconomic/ cultural issues	Ecosystem destruction and interference; Contamination of soils and sediments with petroleum-derived wastes; atmospheric emissions from fuel combustion and gas flaring/venting; environmental pollution (air, soil, sediments, controlled waters) and groundwater contamination; ecological problems in the host communities, adverse human health risks; safety-related

		risks and interference with sociocultural systems.
Decommissioning and rehabilitation		
• Well plugging • Removal of installations and equipment • Site restoration	a. Physical closure/removal petroleum-contaminated waste disposal c. Leave in situ (partial or total) d. Dumping at sea	Environmental pollution and human safety; pollution related to onshore and offshore operations; a hazard to other human activities such as fishing and navigation; marine pollution

Table 1.1 (cont.) Environmental impacts associated with upstream and downstream petroleum operations (adapted from Ite *et al.*, 2013).

Refining of petroleum products		
	a. Atmospheric emissions and air pollution b. Discharges of petroleum-derived wastes	Atmospheric emissions and air pollution; oil spillages; water effluents and production discharges.
Marketing operations		
• Product importation • Storage	a. Operational discharges b. Wastes disposal	Spillage; contamination of soils and sediments; emission of organic contaminants and environmental pollution.
Transportation and distribution		
• Pipelines • Barges, ships, and tankers • Road tankers and trucks	a. Emissions and accidental discharges b. Discharges from transporting vessels, e.g., ballast, bilge and cleaning waters	Air emissions (hydrocarbons from loading racks and oil spills); accidental discharges and operational failures; disposal of sanitary wastes; contamination of soils and sediments.

The UNEP team carried out various assessments starting from groundwater contamination, surface water, land, forestry, and public health and were able to access most contaminated sites with the help of local experts, academicians, support teams and security staff. According to the UNEP report, the survey team examined 122km of pipeline and visited all oil spill sites and oil wells as well as other oil facilities in Ogoniland (IET, 2012). More than 4,000 samples were collected and analysed, with samples collected from community drinking water, rainwater, fish, and sediments from creeks, surface water, and air. Groundwater samples were collected from 142 monitoring wells dug explicitly for this purpose. UNEP also held meetings with local communities on 264 occasions and examined more than 5,000 medical records. The resultant report focused on the major oil contaminants and their distribution and impacts. Other issues considered were environmental management systems, spill mitigation plans, and social engagement strategies. Despite this, there are notable gaps in the UNEP report relating to management practices and environmental standards.

The UNEP researchers targeted many groups of hydrocarbons that may have a substantial impact on human health. BTEX (benzene, toluene, ethylbenzene, and xylenes) are the most important, PAH compounds and Volatile organic compounds (VOCs), which were the primary target of the UNEP air quality team (Etechie *et al.*, 2011; Tse and Nwankwo, 2013). Regarding local geology, UNEP also discovered that there were no continuous clay layers across Ogoniland, which has exposed the groundwater to hydrocarbons spilled on the surface, as in 49 cases, hydrocarbons were found in the soil to depths of 5 m (Fyneface and Lillian, 2014). In 41 sites, hydrocarbon pollution has reached the groundwater, and now exceeds the Environmental Guidelines and Standards for Petroleum Industry in Nigeria (EGASPIN) (Adoki, 2011; Linden and Palsson, 2013).

The key groundwater contamination area was Nisisioken Ogale, in the Eleme Local Government Area, which can be found close to the Nigerian National Petroleum Company Product Pipeline (NNPC), where 400 ha of land are used for industrial activities. It was discovered that an 8 cm layer of refined hydrocarbons (benzene) could be observed floating on groundwater that serves community wells (Etchie *et al.*, 2011; UNEP, 2011). The oilfields in this local government area were discovered in October 1956, with the first shipment of 22,000 barrels of crude oil exported from Nigeria to Europe in 1958 (Watts 2008). This same local government area has a subsidy of the NNPC called the Eleme Petro-Chemical Company that was established in 1988. Its main aim is to produce polyolefins. To produce these resins, natural gas liquids are cracked in an olefin plant. Eleme Petro-Chemicals produced 240 metric tonnes of polyethylene, 95,000 metric tonnes of Polypropylene, and 22,000 metric tonnes of Butene-1 (a colourless, flammable and liquefied gas) per year (UNEP, 2011).

Benzene was identified in air samples, at a concentration of 0.155 to 48.2µg/m^3. A United States Environmental Protection Agency (USEPA) assessment noted that 1 in 10,000 of the population might be affected by cancer resulting from air pollution (Adoki, 2012; UNEP, 2011). VOCs were also detected in the air; these have caused chronic respiratory problems (Linden and Palsson, 2013).

In a second site, Ejamah Ebubu, in the Eleme Local Government Area, the petroleum hydrocarbon contamination profile was examined in the Ochani Stream site, where approximately 30 years ago there was major oil spillage. The key hydrocarbon contaminants across the Ochani Stream site have been well-defined, and there is also a major history of air pollution. Hydrocarbons were seen floating in nine dump pits around the site. The pits, which had an average depth of 1.14 m, represent a total surface area of about 184 m^2 and hold a total volume of the order of 220 m^3 of heavily contaminated mud (Adoki, 2011). The main contaminants are heavy metals, PAHs and BTEX compounds, which were also found in air and groundwater (Ana *et al.*, 2012). It was discovered that the depth of contamination was very shallow, with an average depth of 0.15m over an area of 6.05 ha, although hydrocarbon contamination may extend up to 6.7-8.1m in depth (Etechie *et al.*, 2011; Tse and Nwankwo, 2013).

The use of groundwater from shallow wells for domestic supply has been a long-standing practice in communities in Ogoniland. Ayotamuno *et al.* (2006c) stated that a study carried out in 1987 in the Port Harcourt area indicated that groundwater had high hydrocarbon concentrations of up to 1.8mg/l, well above the maximum of 0.1mg/l recommended by the World Health Organisation (WHO). Onifade *et al.* (2007) argued that the discharge of hydrocarbons into the environment ha caused severe contamination of shallow groundwater and surface waters, drinking water, and of local aquatic ecosystems. Local economic activity (agriculture and fishing) has also been severely impacted.

Several papers have been published on environmental contamination of the Niger Delta region specifically in Ogoniland, but the researchers (including UNEP) have concentrated on measuring total petroleum hydrocarbons (TPH), rather than examining different hydrocarbon components, which may show different environmental behaviour. Furthermore, a model of hydrocarbon migration pathways in the study area has not been developed, thus creating a vacuum of knowledge. According to the New Jersey Department of Environmental Protection

(2016), determining the migration pathway is important because pathways are the routes by which contaminants encounter receptors, and are a key conceptual component of risk-based contaminated land management strategies. Typical exposure pathways that are associated with groundwater contamination include direct consumption of contaminated groundwater taken from a well and irrigation of agricultural land with contaminated groundwater and the subsequent consumption of food products. There can also be contamination of surface water resources by groundwater discharge and recreational use of the contaminated surface water.

In light of the preceding discussion, this thesis will determine the major types of hydrocarbon-related contamination present in surface and groundwater in Ogoniland, and which methods are most appropriate for their remediation or management. It will also examine potential exposure pathways for key inorganic and Light Non-Aqueous Phase Liquid and Dense Non-Aqueous Phase Liquid contaminants and develop and test effective large area remediation strategies to manage contaminant risk in this area. There is an emerging body of research and practical applications on extensive (i.e., large area), less invasive remediation approaches, focusing on *in-situ* biological techniques (bioremediation and phytoremediation), contaminant stabilization and natural attenuation processes. These can be relatively low-cost options, but their detailed site-specific applicability in Ogoniland (and in surrounding areas of the Niger Delta) is yet to be assessed.

1.5 AIM

This thesis aims to investigate the extent of, and processes controlling, environmental contamination and exposure at hydrocarbon industry-impacted sites in Ogoniland, Nigeria, and to evaluate practical methods of managing this contamination.

1.6 RESEARCH QUESTIONS

This research has three inter-linked research questions:

What is the extent of environmental contamination around hydrocarbon industry-polluted sites in Ogoniland, Nigeria, and what are the key contaminants present?

What are the processes controlling migration and natural attenuation of this contamination?

What practical methods can be applied to manage the contamination present?

1.7 OBJECTIVES

To meet the aim stated in section 1.6, the following objectives will be addressed:

A) To investigate the distribution and concentrations of key organic and inorganic contaminants in groundwater and surface waters in Ogoniland.

B) To examine the processes controlling migration and natural attenuation of these contaminants.

C) To assess the application of practical remediation methods, with particular emphasis on low-cost methods such as enhanced soil adsorption and natural attenuation approaches.

D) Based on the above, to recommend systems of improved environmental management for hydrocarbon contamination in Ogoniland and the wider Niger Delta.

1.8 ORGANISATION OF THE THESIS

The thesis comprises eight chapters:

Following this introduction, Chapter 2 reviews the hydrogeological characteristics of the study area, relevant contaminant migration characteristics, and different options in remediating contaminated land; the current remediation options used in the Niger Delta are highlighted.

Chapter 3 reviews the methodological approach, the research methodology and specific instrumentation used in this thesis, and describes sites where samples were collected to assess the extent of oil pollution around hydrocarbon facilities and suburban areas in Ogoniland.

Chapter 4 presents concentration data for inorganic and organic contaminants found with ground and surface waters in Ogoniland, their exposure level, and guideline values compared with the current study. The guideline values recommended by various international organisations for assessing human exposure are reviewed to ascertain their applicability for use in the Niger Delta. A statistical correlation showing the elemental parameters of surface and groundwater is presented. Trace and heavy metal contaminants are reviewed, and the extent to which local surface and ground waters can be considered to be contaminated with these elements is examined. TPH fractions, petroleum hydrocarbon and levels of Phenol toxicity with background concentrations of benzene, toluene, ethylbenzene, xylene, naphthalene, and Anthracene are also reviewed.

Chapter 5 presents the results of core flooding experiments. The concept of core flooding as a tool and its previous application in the literature are discussed. Based on these data, the potential migration pathways for contaminants from the surface to groundwater through the soil, and potential for natural attenuation in the Niger Delta are assessed for adaptation in this study.

Chapter 6 uses batch adsorption studies to examine the potential application of carbon-based adsorbents as a large area and cost-effective remediation approach to protect key receptors, focusing on biochars and a commercially available activated carbon.

Chapter 7 integrates the results from previous chapters to discuss the potential applicability of low input approaches, particularly soil amendments using carbon-based adsorbents, given local supply routes and material availability and uses recently developed decision support tools to assess the wider applicability and benefits of less intensive remediation approaches in the Ogoniland region.

Chapter 8 presents the conclusions of the study and offers suggestions for further work.

CHAPTER 2.0 - LITERATURE REVIEW

2.1 INTRODUCTION

In the previous chapter, the topic of this thesis was introduced and the research problem, aim, and objectives were highlighted. In this chapter, the geological and environmental features of the study area are discussed, and relevant literature on hydrocarbon migration and the remediation of hydrocarbon-contaminated land and groundwater is reviewed.

2.2 STUDY AREA

The Niger Delta is a region in the southern part of Nigeria comprising nine states, namely Akwa Ibom, Bayelsa, Cross River, Delta, Edo, Ondo, Imo, Abia and Rivers states, as shown in Figure 2.1 and Tables 2.1 and 2.2. The Ogoniland area is found in Rivers State; covering about 1,000km^2 (Tanee and Albert, 2011) in the coastal area of the Niger Delta. The Ogoniland district is divided into four local government areas (LGAs), which are Eleme, Gokana, Khana, and Tai (Figure 2.3). These LGAs have a population of more than 832,000 according to the 2006 National Census and have been sites of oil exploration and production in the country since 1950. The people of Ogoniland have greatly suffered since then from chronic and persistent oil spills which have resulted in groundwater and surface water contamination (Zabbey and Olsson, 2017).

Figure 2.1 The Niger Delta state (taken from Adekola *et al.*, 2012). Note that Ogoniland, the focus of this study, is situated in Rivers State (see Figure 2.2).

Figure 2.2 Ogoniland and its four Local Government Areas (Eleme, Tai, Gokana and Khana) (adapted from, Shell, 2011).

Table 2.1 Niger Delta - summary statistics (adapted from Francis *et al.*, 2011).

Characteristics	
9 States 185 LGAs	South-South Zone: Akwa Ibom, Bayelsa, Cross River, Delta, Edo, Rivers Extended Niger Delta includes: Abia, Imo, and Ondo—all oil producing states
Population	32 million (22% of the Nigerian population), 2/3 under 30 years of age
Population density	265 people km^{-2}; 13,329 settlements, 94% with < 5,000 population
Ethnic groups	40 main ethnic groups; around 120 mutually unintelligible languages and dialects
Land area	112,000 km^2 of land area is oil affected; core delta is 75,000 km^2
Ecological zones	Coastal barrier sandy ridge; mangrove swamp; freshwater swamp; lowland rainforest
Natural resources	Petroleum, natural gas, tin, lead, coal, zinc, arable land
Livelihoods	Agriculture and fishing (48%); trading (17%); services (10%); Education/health (7%)
Social/Economic Indicators	
Infant mortality rate	120 per thousand (Nigeria: 100 per thousand)

Unemployment	Estimated youth unemployment (ages 15–24): 40% The official average for the South-South: 24% (2006)
Poverty	43% in relative poverty (2004); 75% perceive themselves as “poor.”
Water	76 to 80% in rural areas and 50 to 55% in urban areas do not have access to safe drinking water
Energy	Firewood is the primary energy source for 73% 34% of the population has access to electric power, when available

Table 2.2 Oil and gas production in the Niger Delta.

Crude oil production, mid- 2011	About 2.3 mbpd (million barrels per day, including condensate); 3.2 mbpd installed capacity; supplies 95% of Nigeria’s export earnings and 80% of federal government revenue. On average, 25% of production was stopped due to violence or sabotage (2006–09), at times up to 65%. Production fell from 2.6 mbpd in Feb 2006 to 1.3 mbpd in May 2009, during a major clash between combatants and the military
Main international operators and principal Nigerian companies; all have onshore operations except ExxonMobil	Shell (Shell Petroleum Development Company, Nigeria, Ltd); Chevron (Chevron Nigeria, Ltd.); ExxonMobil (Mobil Producing Unlimited); Eni (Nigerian Agip Oil Company); Total (Elf) (Total E&P Nigeria Limited, formerly EPNL)
Main terminals/offshore platforms	Bonny Island (Shell), Brass River (Eni/Agip), Escravos (Chevron), Forcados (Shell), KwaIboe platform (Mobil), Odudu platform (Total), Pennington (Chevron)
Naturalgas reserves	5 trillion cubic meters— seventh largest gas reserves in the world
Oil/gas pipelines/fields	Over 7,000 km of pipelines; 606 oil fields
Gas plants/LNG	30; NLNG Plant with six trains; 2 LNG plants in construction in Brass and Olokola
Environment	1958-2010: est. 546 million gallons spilled; av. 300 spills or nearly 10.8 million barrels/year (1986-2003): 50,000 acres of mangrove forest disappeared Q1 2010: 32% of associated gas flared (127 bcf)

2.3 HYDROCARBON-RELATED CONTAMINATION IN THE NIGER DELTA

The hydrocarbon contamination of the Niger Delta region is traceable mainly to oil spillages, which are due to the exploration and production of crude oil by multinational companies operating in the region. Oil spillages may arise from multiple sources such as corroded and vandalised pipelines, equipment failure, oil bunkering and illegal crude oil refining. The bulk of the spillages in the Niger Delta come from sabotage/theft (Figure 2.3 and Table 2.3). According to the Department of Petroleum Resources (Nigeria), 2.4 million barrels (total) of oil was spilled in the Niger Delta between 1976 and 1996, in 4,835 spill events (Adelena *et al.*, 2011). The Nigeria National Petroleum Corporation also stated that an average of 300 individual spills (2,300 cubic meters) happen yearly. The total oil spillage that occurred between 1958 and 2010 is estimated at 9.3 million barrels (Adelena *et al.*, 2011). These activities release large amounts of light and heavy petroleum hydrocarbons into water bodies, creeks, rivers, and land.

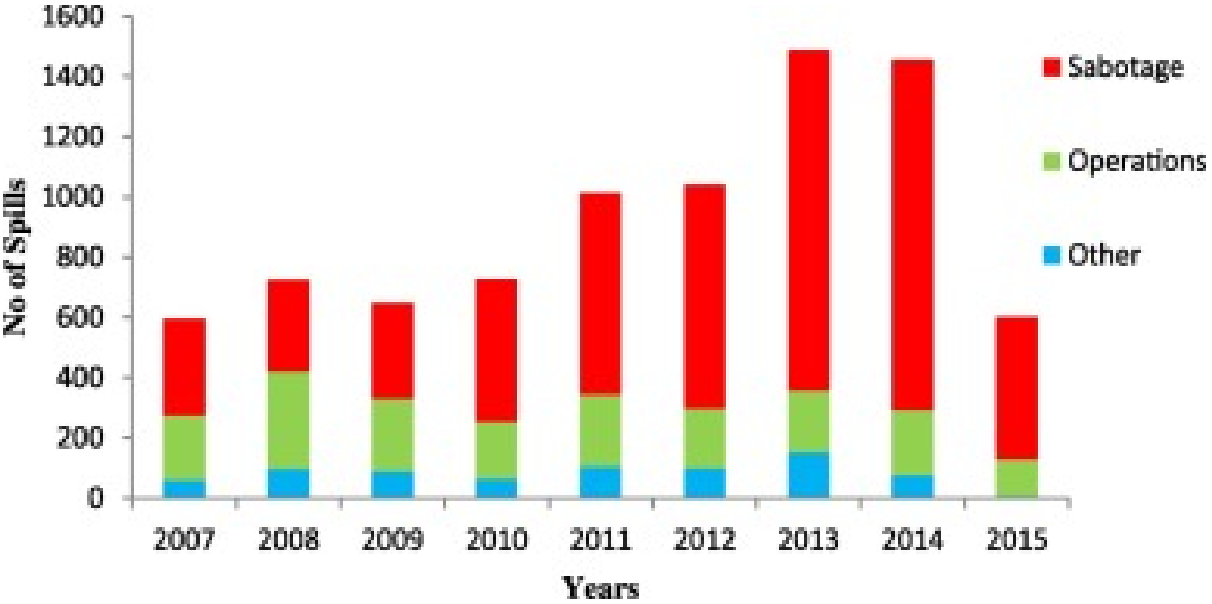

Figure 2.3 Yearly oil spill incidence in the Niger Delta during 2007 - 2015. The y-axis shows the number of incidents and x-axis the source of the monthly spillages (adapted from Christopher *et al.*, 2018).

Table 2.3 Causes of oil pipeline failures between 1999 and 2005 in the Niger Delta (adapted from Ordinioha and Brisibe, 2013).

Causes	**Number**	**Percentage**
Mechanical Failure	23	17.04
Corrosion	21	15.56
Operational error	17	12.59
Third Party activity	28	20.74
Natural hazard	3	2.22
Unknown	43	31.85

Recent data from Niger Delta areas such as Okpai and Beneku shows that groundwater contains a high level of various pollutants, although notably many of these do not seem to be hydrocarbon-derived (Dami *et al.,* 2013), indicating that remediation or management strategies need to consider both organic and inorganic contaminants. Pollution in Beneku was high due to elevated levels of dissolved salts and other organic materials, while in Okpai the pollution was because of acidic substances released into the environment, which later percolated into the groundwater (Dami *et al.,* 2013). The pollutants in the groundwater in these areas are elevated magnesium, iron, cadmium and lead. It was observed that magnesium concentrations were 1.173 mg/l during the dry season and 1.227 mg/l during the wet season; iron was found to be 0.036 mg/l in the dry season and 0.021mg/l in the wet season in the Okpai area. Amangabara and Ejenmi (2011) noted that magnesium and iron are more elevated than other groundwater constituents (such as calcium, sodium, potassium, chlorides, and bicarbonates). Meanwhile in the Beneku area the groundwater was found to contain cadmium (0.002 mg/l dry season, 0.005mg/l wet season), magnesium (1.21 mg/l dry season, 1.437 mg/l wet season), and lead (0.004 mg/l dry season, 0.005mg/l wet season) (Akpoborie and Aweto 2012; Dami *et al.*, 2013). Concentrations of cadmium, magnesium, and lead exceeded the guideline limits set by the National Agency for Food and Drugs Administration and Control (NAFDAC) and World Health Organisation (WHO, 2009), which are 0.003mg/l for cadmium and 0.001mg/l for the lead, raising significant health concerns. Samples were also taken from the Ekakpamre community in Ughelli, Delta State. It was found that contamination of aquifers of this area was due mainly to Cr, Pb, and PO_4^{3-} (Ogbuagu *et al.*, 2013).

From the report published in Ikwere LGA of Rivers State, it was observed that the total hydrocarbon concentration of the groundwater was 34 ppm, which is 680 times higher than the EU standard for drinking water (Dami *et al.,* 2013; Nwilo and Badejo 1995). Bayelsa State is also another region in the Niger Delta with significant oil extraction; this area is the location of the first discovery of oil reserves in commercial quantities in Nigeria. In Aleibiri, Bayelsa State, community members confirmed in August 1997 that a spill dating from March 1997 had not yet been cleaned up. Shell Petroleum Development Company (SPDC) stated that the spill was instigated by sabotage. The groundwater in a local government area called Yenagoa was also observed to be contaminated with heavy metals. Although the local community depends mainly on groundwater for drinking purposes, they were not aware of the effects of heavy metals on water quality and health. This contamination was due to industrial discharge into the water, and the pollutants were mostly magnesium, lead, and iron (Nwankwoala *et al.*, 2011).

In Cross Rivers State, areas around the Rumueke community have been polluted by thermal stress from gas flaring, heating from which led to the burning of mangrove trees and salt-tolerant vegetation around the flaring area and destroyed the growth and flowering of some plants. The flaring induces soil degradation and weakens agricultural productivity (UNDP, 2006; Egwurugwu *et al.,* 2013). Salau (1993) and Adeyemo (2002), conducted a study on the gas flaring impact on agriculture. It was reported as of 2006 that Nigeria flares 75 % of the gas it produces, which is more than any other country in the world (Kadafa, 2012). Elevated PAH concentrations of 1.8-334 mg kg^{-1} have been found in heavily contaminated industrial sites in Calabar due to gas flaring (Nganje *et al.,* 2006).

The UNEP (2011) report on the extent of contamination in Ogoniland revealed that PAHs, BTEX, arsenic, barium, mercury, and mineral oil were prominent in the list of contaminants from oil spillages in the area. An Ogoniland contamination report from Ite *et al.* (2013) corroborates the UNEP findings. At St Luigi town, it was observed that 18 ppm of hydrocarbon was seen to be floating on underground water (based on observations in wells). The hydrocarbon is 360 times higher than the level stipulated by the EU for drinking water. The total hydrocarbon product detected on the ground is more than 1 million micrograms per litre (µg/l), compared to a Nigerian standard of 600 µg/l, with groundwater PAHs concentrations ranging from 1.92 to 40.47 µg l^{-1} (Anyakora and Coker, 2009).

The WHO standard for water hardness is set as 100mg/l and 500mg/l (WHO, 1984) as the highest required and maximum permissible values respectively, but it was also observed by Ngah and Abam (2004) that the hardness of the water in most parts of the Niger Delta falls below the WHO standard. For example, at less than 10m below ground level, the water becomes very acidic, and hardness is a major quality issue (see Appendix 1 and 2). The WHO (1984) recommended a pH of 6.5 as the minimum desirable and 8.5 as the maximum permissible limits in drinking water supplies (Appendix 1). The acidity in groundwater in the Niger Delta is assumed to be linked partially to the long history of gas flaring from oil activities. When these happen, CO_2 is dissolved in rainfall and transferred to groundwater, causing acidity increases.

Chloride salts are made up of metallic elements, alkali metals, and alkali earth metals, and are readily soluble in water. However, chloride is present in all natural waters, but its concentration is lower than that of sulfates and bicarbonates especially in recharge areas (Nwankwoala and Ngah, 2014). Generally, the most common type of water in which chlorine is the dominant anion is one in which sodium is the predominant cation. Amadi (2004) and Ngah (2009) identified that chloride produces a salty taste in water which varies with the number of sodium ions (Na^+). The predominance of Na^+ imparts a highly noticeable salty taste even in small quantities of chlorine unlike when Ca^{2+} and Mg^{2+} predominate. Determination of chloride content is very important especially in coastal aquifers because the first sign of saline water intrusion is a progressive upward trend in chloride concentration in water obtained from the affected boreholes. From Appendix 4, the chloride content in Niger Delta groundwater appears to decrease from north to south, i.e., from the surrounding area to the coast. However, the localised chloride enrichments around the Old Government Residence Area, Port Harcourt, Borokiri, Moscow Road and Central Police Station in Port Harcourt is as a result of brackish water coming from nearby creeks and tidal channels. Chloride again is a significant quality issue mostly in groundwater in these areas, as also around the mangrove swamps and the coastal beaches (Nwankwoala and Ngah, 2014; Ngah and Abam, 2014).

Also, Appendix 3 indicates that iron is a severe problem in groundwater samples from the freshwater swamps/backswamp/meander belt region, the mangrove swamps and coastal ridges. Amajor (1987) clarified that the high amounts of iron in groundwater in the area are related to the geological history and source rocks of the deposits that constitute the aquifers in the Niger Delta. Thus, this originated from the northern highlands where the sediments rich in iron that make up the delta originate. With the high rate of deposition associated with the Niger Delta, these sediments may have preserved their iron-rich grains along with other iron minerals and incorporated them into the local strata.

According to Ngah and Abam (2014), three parameters, namely, pH, Cl^- and Fe^{2+}, are the major groundwater quality issues even in deep aquifers. The values of pH range from 3.8 – 8.4, with 62% of the samples having values below WHO recommended standards. Slightly acidic groundwater is prevalent in the eastern part of the area including Port Harcourt. All samples analysed indicated that values for iron ranged from 0.02 – 5.6 mg/l with 71% of the samples containing iron at more than 0.3 mg/l (the WHO highest permissible limit). The high iron concentrations occurred in boreholes drilled in the freshwater swamp/meander belt region.

Chloride concentrations vary from 5.6-710 mg/l, with 18% of samples showing Cl^- concentrations of greater than 250 mg/l (recommended by the WHO as the maximum permissible concentration in drinking water). See Appendix 4 for chloride distribution in the Niger Delta.

There is considerable public concern about the environmental impacts of oil pollution in the Niger Delta. However, reliable data on the effects of oil pollution on the physiological health of populations are extremely limited (see Ordinioha and Brisibe, 2013; Nriagu *et al*., 2016), and even less is known about the psychological effects of living with environmental contamination. One of the few investigations to consider the health impacts of oil pollution in the region is Adekola *et al*. (2017), who, in a study of 600 people from Akwa Ibom State, identified high levels of disease symptoms and environmental distress (including worry, annoyance and intolerance) associated with pollution. At the community level, the study identified that emotional distress from fear of the sources of exposure (including visible oil spills and gas flares) was an important mediator of health symptoms.

2.4 GROUNDWATER FLOW AND CHARACTERISTICS IN THE NIGER DELTA REGION

Several research papers have been published on the groundwater chemical characteristics in some parts of the Niger Delta (e.g. Etu-Efeotor, 1981; Amajor, 1987, 1991; Amadi *et al.*, 1989; Mecon Geology and Engineering Services Ltd, 2002; Ngah, 2002; Ngah and Allen, 2006; Ophori, 2007; Ofoma *et al.*, 2008). Specifically, the determination of water quality for consumption has been the subject of much research (e.g., Edet, 1993; Egbunike, 2007; Ige *et al.*, 2008, 2009; Edet *et al.*, 2011).

According to Ngah and Abam (2014), groundwater quality in deep aquifers has a considerable variation with local geology, depositional environment and degree of use and abuse. Situated within the deltaic plain and mega-depositional environment, the southern part of the study area comprises swamps, creeks, tidal channels, rivers and their distributaries and lakes. Brackish water resulting from tidal influx dominates the coast in the shallow aquifers. The groundwater flow and distribution can be seen in Appendix 4. The groundwater resources of the Niger Delta can be classified into hydrostratigraphic units, defined by the local geology, which are listed in Table 2.4. A schematic cross-section of the Niger Delta basin, and major aquifers and aquitards referred to in Table 2.4, is shown in Figure 2.4.

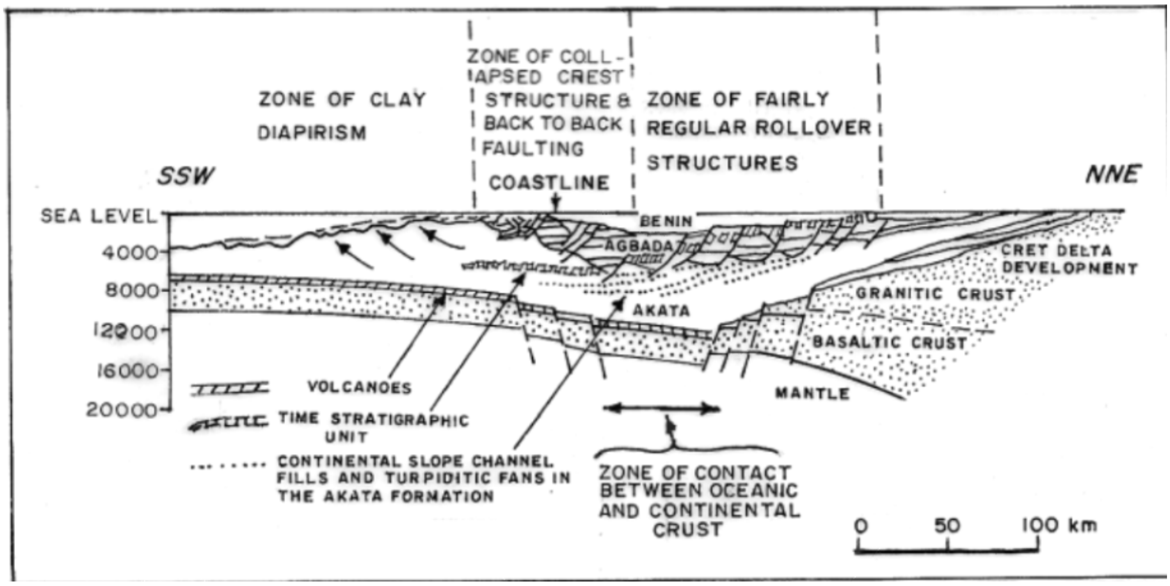

Figure 2.4 Schematic dip section of the Niger Delta region (Okiwelu and Ude, 2012). Growth fault trends are recognised, probably related to basement faults, but extensive shale tectonics did not occur, so that equivalent biostratigraphy and lithostratigraphy can be recognized on either side of fault trends.

Table 2.4: A summary of the hydrostratigraphic units of Nigeria, based on the work of Petters (1982), Offodile (1992), Akujieze *et al.* (2003), and Adelana *et al.* (2008).

Age	**Benin Basin**	**Niger Delta Basin**	**Nupe**	**SE Benue Trough**
Quaternary Pliocene Miocene Oligocene	Alluvial aquifer Deltaic aquifer Benin aquifer	Benin aquifer	Patti aquifer	Benin aquifer
Eocene	Ilaro aquifer Akimbo/ Oshosun aquifers	Agbada aquifer		Ogwashi-Asaba aquifer Nanka sand aquifer Ameki aquitard
Paleocene	Imo Shale aquitard Ewekoro aquifer	Akata Shale aquitard		Imo Shale aquitard

Table 2.4 (Cont.): A summary of the hydrostratigraphic units of Nigeria, based on the work of Petters (1982), Offodile (1992), Akujieze *et al.* (2003), and Adelana *et al.* (2008).

Age	**Benin Basin**	**Niger Delta Basin**	**Nupe**	**SE Benue Trough**
Maastrichtian Campanian	Nkporo Shale aquitard	Nkporo Shale aquitard	Lokoja sandstone aquifer	Nsukka aquitard Ajali Sandstone aquifer Mamu aquiclude Nkporo Shale aquitard Enugu Shale aquitard
Santonian Coniancian	Abeokuta aquifer			Agwu aquitard Agbani Sandstone aquifer Amaseri Sandstone aquifer New Netim marl aquitard
Turonian				Ekenkpon shale aquitard EzeAku aquitard Markurdi Sandstone aquifer Agala aquifer Ezillo aquifer
Cenomanian				Odukpani aquitard
Albian				Asu River aquitard
Pre-Albian	Basement Complex	Basement Complex	Basement complex	Basement Complex

Table 2.4 (Cont.): A summary of the hydrostratigraphic units of Nigeria, based on the work of Petters (1982), Offodile (1992), Akujieze *et al.* (2003), and Adelana *et al.* (2008).

Age	**NE Benue Trough**	**Chad Basin**	**Sokoto Basin**
Quaternary Pliocene Miocene Oligocene	Kerri Kerri aquifer	Chad aquifer Kerri Kerri aquifer	
Eocene			Gwandu aquifer
Paleocene			Kalambaina aquifer Dange aquiclude Wurno aquifer
Maastrichtian	Gombe Sandstone aquifer	Gombe Sandstone aquifer	Dukumaje aquiclude Taloka aquifer
Campanian			
Santonian Coniancian	Lamja Sandstone aquifer Numanha aquifer Sukuliye aquifer Jessu aquifer Gulani aquifer	Fika Shale aquitard	
Turonian	Pindiga aquitard Yolde aquifer	Gongila aquifer	
Cenomanian	Bima Sandstone aquifer	Bima Sandstone aquifer	
Albian			Illo-Gundumi aquifer/aquiclude
Pre-Albian	Basement Complex	Basement Complex	Basement Complex

2.5 SUBSURFACE MIGRATION OF HYDROCARBONS

Migrating hydrocarbons can be classified into non-reactive and reactive dissolved contaminants. Key controls for non-reactive pollutants are advection and hydrodynamic dispersion, which create a spreading pollution plume and cause a dilution in pollutant concentration (Guerin *et al.,* 2002). For active contaminant species, the attenuation of pollutant transport occurs by various processes, including chemical precipitation, sorption, and microbially mediated redox reactions (Gandy *et al.,* 2007). In cases where Non-Aqueous Phase Liquids (NAPLs) are involved, such as in Ogoniland, both immiscible and dissolved contaminants need to be considered. These classifications/considerations are key to achieve effective remediation practices. The NAPLs are petroleum-derived chlorinated solvents or oil, which are common causes of groundwater contamination in industrialized countries (Keely, 1989). These liquids exist as a separate fluid in the subsurface. Those lighter than water are labelled as LNAPLs (Light Non-Aqueous Phase Liquids). Those having a higher density than water are termed DNAPLs (Dense Non-Aqueous Phase Liquids), for example, chlorinated hydrocarbons (Palmer and Johnson, 1989; Youdeowei, 2012). Predicting the behaviour of these contaminants in the subsurface is a challenging problem that must be addressed at many sites before remediation results can be achieved (Youdeowei, 2012).

Predicting contaminant transport and fate in deltaic systems such as the Niger Delta is difficult because of the complexity of the sub-surface environment. Transport and fate assessments need inter-disciplinary analyses and interpretations because the processes involved in these activities are naturally intertwined (Keely, 1989). Integrating geologic, hydrologic, chemical and biological procedures into an effective contaminant transport assessment requires data that are accurate, specific, and appropriate. For example, while hydraulic conductivity can be measured correctly and with high reproducibility, it is challenging to accurately identify a value that is indeed representative of the vertical and horizontal distribution of conductivities found at a site (Keely, 1989).

The most important aspects of how hydrocarbons behave in the subsurface are the processes of transport, multiphase flow, volatilization, dissolution, geochemical reactions, biodegradation and sorption (Figure 2.5). There is a need for critical investigation of these processes to successfully assess the potential for migration of hydrocarbons in the subsurface. The transport of contaminants in the subsurface can be affected by advection, dispersion, diffusion, adsorption, and decay. These processes can work together or separately in groundwater flow (Miller and Hogan, 1996).

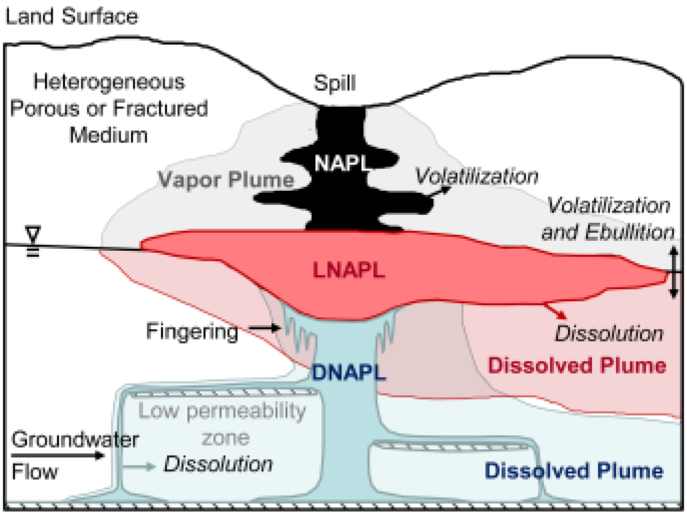

Figure 2.5 Processes critical to understanding the fate and transport of hydrocarbons in the subsurface (taken from (Hedeff *et al.*, 2009). A generalised vertical cross-section is shown illustrating the infiltration of a spilled LNAPL and DNAPL in the subsurface, and the subsequent development of vapour and dissolved organic contaminant plumes.

A report by Isehunwa and Onovae (2011) suggested that the production of hydrocarbon is usually associated with water (so-called ‘produced water’), which is naturally present in a petroleum reservoir and is a by-product of hydrocarbon exploitation in most onshore and offshore platforms. According to Avwiri *et al.* (2013), this produced water contains toxic contaminants such as BTEX and PAH which are hazardous to humans and the environment. To this effect, a range of studies has been made on analysing the migration pathways of these contaminants, which are discussed below.

2.5.1 Non-Aqueous Phase Liquids and Light Non-Aqueous Phase Liquids

Hydrocarbon spills have produced catastrophic problems resulting in groundwater contamination, which has made groundwater unsafe for drinking and irrigation purposes in Ogoniland. Most hydrocarbons in subsurface soil are characterized as immiscible and form a liquid phase separate from water and air. NAPLs and PAHs are the two groups of hydrocarbon contaminants that typically pollute water bodies (Ite *et al.*, 2018). Some multicomponent NAPLs also contain PAHs.

The Interstate Technology and Regulatory Council (2009) noted that the LNAPL distribution depends on soil properties (such as grain size and porosity); when small amounts of LNAPL are released, they will become trapped in the soil pores as a stationary, residual phase before reaching the water table. When large amounts of LNAPL are released, they may migrate to the water table while leaving immobile, residual LNAPL along the migration path. At the water table, LNAPL can accumulate and spread across the surface of the saturated zone, mainly in the direction of decreasing hydraulic gradient. The chemicals that constitute the LNAPL may be removed over time by numerous processes, such as sorption, volatilisation, and dissolution. When they are not removed and persist, the LNAPL "body" can lead to secondary impacts on adjacent soil, soil gas, and groundwater. It is important to note that LNAPLs may show varying degrees of solubility. Charles *et al.* (1995) noted that products like BTEX are slightly soluble in water, although these differ from other contaminants such as methyl tertiary-butyl ether, and alcohols which are highly soluble.

2.5.2 Dense non-aqueous phase liquids (DNAPLs)

DNAPLs have been commonly used in industries since the early 20th century. They are slightly soluble in water but exist in the subsurface as a separate fluid phase immiscible with both water and air. They are denser than water and can migrate to significant depths below the water table, and then dissolve into groundwater causing environmental challenges with global implications (Kueper *et al.*, 2003; Cheremisinoff, 2017). Due to limited industrial knowledge in the past, unregulated disposal and vast production and usage of DNAPLs has led to a large number of DNAPL-contaminated sites at present, particularly because little monitoring of these contaminants took place historically. Communities have also often used shallow soils to dispose of unwanted materials, including DNAPLs, which has also led to groundwater contamination. There are numerous sites in North America, Europe and other industrialised areas in the world impacted by DNAPLs (UNEP, 2010).

In the UK, major concerns have arisen from DNAPL-impacted soil and groundwater, which have been found to be toxic to mammals and other fauna (Kueper *et al.*, 2003). It has also been noted that these DNAPL-contaminated sites are difficult to inspect and are challenging to remediate. This is because DNAPLs can enter fractured rock, and in most hydrogeological environments many years are required for natural groundwater dissolution to dissipate DNAPL sources. In some areas where contamination has long affected the region, it may take more than 20 years to remediate the groundwater by the pump and treat and other methods.

The behaviour of DNAPL in the subsurface includes routes related to its transport; interphase chemical mass transfer into aqueous, sorbed, and vapour phases; and degradation reactions. Without any remedial measures, natural degradation reactions usually occur very slowly (Sale and Newell. 2011). For contaminants like chlorinated solvents, coal tar, and other DNAPLs, aqueous solubilities are very low, and DNAPL mass exchange to the aqueous phase is inadequate. As a result, DNAPLs may stay in the subsurface for several decades or more, depending on their site-specific solubility, type, mass, and distribution, as well as geologic conditions (Koch and Nowak, 2015).

DNAPL constituents represent a persistent reservoir of contaminants that will release dissolved contaminants for extended periods; thus, understanding the possible presence and distribution of DNAPL in the subsurface is critical to long-term environmental site management. Characterizing sites contaminated with DNAPLs must take into account the subsurface behaviour of DNAPL and subsequent phases, including the physics of DNAPL migration that controls three-dimensional distribution and dissolved-phase contaminants (USEPA, 2003; ITRC, 2015).

2.5.3 Migration processes of contaminants

With its essential objective of removing oil (that is, NAPL) from the subsurface, the oil industry has directed detailed research on the progression of immiscible liquids and the significance of subsurface permeability architecture (stratigraphic or in cracked media). In the 1990s, this abundance of understanding started to be connected to environmental studies of DNAPLs. As this work identifies with DNAPL transport in permeable media and multiphase systems, relevant data are summarised below.

DNAPL migration is represented by logical standards of multiphase streams in permeable media. The study of the parallel flow of various immiscible liquids began in the fields of soil water system science and oil production (Langevoort, 2009), and there is almost a century of scientific literature and understanding in this area. The use of multiphase stream ideas to water assets and the DNAPL issue was spearheaded by Schwille (1988), and early surveys of the essential immiscible liquid ideas were given by Corey (1986), Mercer and Cohen (1990), and Pankow and Cherry (1996).

LNAPL movement is controlled by a few procedures. When there is a release of LNAPL to the environment, the LNAPLs migrate under the force of gravity (Newell *et al.*, 1995). As noted earlier, if a minor volume of NAPL is released to the subsurface, it travels through the unsaturated zone where a portion of the hydrocarbon will be taken up by capillary forces as residual globules in the soil pores, thereby depleting the contiguous NAPL mass until movement ceases. If sufficient LNAPL is released, it will travel until it meets a physical barrier (e.g., low permeability rock) or is affected by resistance forces near the water table. As soon as it reaches the capillary fringe, the LNAPL may move as a continuous body along the water-saturated zone in the upper boundary of due to gravity and capillary forces (Cohen and Mercer, 1993).

Although LNAPL does not float in water but co-exists with water within the orifice network in the aquifer, it can fill the aquifer pore space incompletely, and LNAPL capacities decrease with depth until water fills all the pores. The amount of LNAPL saturation relies upon the soil and fluid properties. Site history and volume of LNAPL released are significant for remediation to become effective. For example, BTEX compounds will gradually dissolve out of mixed LNAPLs into the underground thereby creating a plume that will move with the groundwater (Lesage and Jackson, 1992).

As soon as a NAPL leaks from a storage tank into or onto the ground, it starts to penetrate the subsurface downward under the influence of gravity. The NAPL will continue to migrate through the unsaturated zone displacing the air that is in the pore spaces; this will continue until it reaches the water table. If the NAPL is a DNAPL, it will continue to penetrate the saturated zone moving through fractures, displacing water, and continuing downward, as seen in Figure 2.6 (lower diagram). On the other hand, LNAPLs will naturally resist migration below the water table because of the buoyancy effects arising from their lower density and will tend to migrate laterally across the top of the water table (Figure 2.6, top diagram) (CLAIRE, 2002).

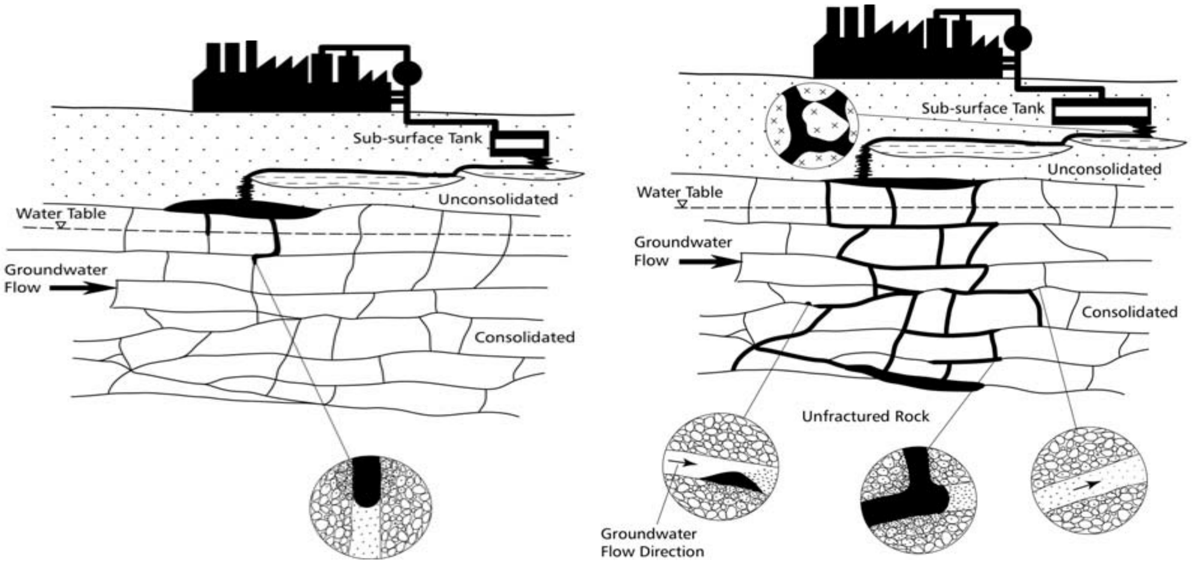

Figure 2.6 Contrasting outcomes of an LNAPL spill (left) versus a DNAPL spill (right) in a fractured rock aquifer, showing processes of contaminant migration to the water table and unfractured underlying rock (CLAIRE, 2002).

2.6 REMEDIATION OF CONTAMINATED LAND AND GROUNDWATER

Contaminated land is land containing harmful substances in concentrations that can harm humans and the built/natural environment directly and indirectly (Science Communication Unit, 2013). Groundwater contamination occurs when chemicals or contaminants are accidentally or incidentally released into the groundwater aquifer. Practically any activity whereby chemicals are released into the environment either intentionally or accidentally can pollute groundwater (ATSDR, 2016). In the USA, 50 per cent of the population depends on groundwater for drinking and other purposes, but most of the water is contaminated to some degree. Statistics have shown that 3.1 million cubic miles of saline groundwater exist compared to about 2.6 million cubic miles of fresh groundwater (Gleick, 1996). In normal conditions, the border between the clean water and saltwater tends to be quite stable, but when groundwater pumping occurs, it causes saltwater to migrate inland and upward, which causes saltwater contamination to occur when there is discharge (Mtoni, 2013). In the USA, the use of pesticides for agricultural purposes has also led to groundwater contamination because these can migrate into groundwater supplies over time. Furthermore, untreated waste from septic tanks or poisonous chemicals from underground storage tanks and waste landfills also contaminate groundwater (WHO, 2006b). The EPA acknowledged over 460,000 leaking underground storage tanks as of 2006 in the USA. Remediation work has been carried out for more than a decade, and almost 350,000 contaminated sites have been cleaned up (EPA, 2011).

The management of contaminated land and groundwater historically has been a significant issue. Recent and historical industrial activities have led to the incidence of high concentrations and prevalence of contaminants in soils, sediments and surface- and groundwater, thereby affecting the health of millions of people worldwide. The penalties can be severe for humans and the built/natural environment. Contamination can diminish the land value and constrain viable land re-use (Cundy *et al.*, 2008). In Europe, about 250,000 sites that are heavily contaminated require to clean up, whereas there are 3 million sites that have probably been occupied with polluting activities (Roberta *et al.*, 2013). The clean-up of these sites in the EU alone is projected to cost between 59 and 109 billion euros according to Peuke and Rennenberg (2005).

Groundwater and land contamination has severe consequences for both the economic and environmental value of that resource and human livelihoods (Gun and Lipponen, 2010). National and regional legislation has therefore been implemented to put into effect the clean-up of contaminated land, and the safeguarding of surface and groundwater resources. Two broad concepts have emerged in the management of contaminated land and groundwater over the past 30 years which are, the use of risk assessment to determine the seriousness of problems, and the use of risk management to mitigate problems found by risk assessment to be significant (Puschenreiter *et al.*, 2011). For a risk to be present there needs to be a source of contamination, one or more receptors (which may be adversely affected by the contamination) and one or more pathways (i.e., routes by which the contamination can reach the receptor; Figure 2.8). The risk management focuses on breaking the linkage between source and receptor, either by controlling the source (e.g. pumping out the contamination from the subsurface); managing the pathway(s) (e.g. preventing migration of contamination); protecting the receptor(s) (e.g., planning or institutional controls to avoid sensitive land uses), or some combination of these components Receptors are influenced by the contamination and include human health, water resources, building construction, or the broader environment. For example, in the UK, this combination of a source-pathway-receptor is referred to as a pollutant or contaminant linkage (DEFRA, 2012).

Breaking the contaminant linkage is one of the main aims of remediation. Hydrocarbon pollution on land and groundwater can create severe risk when this pollutant gets into or under the land where it reaches the receptor via any of the various pathways, for example, erosion, soil vapour to the surface, direct consumption of contaminated groundwater, or plant uptake via contaminated irrigation water. The essence of this risk management is to break the contaminant linkage by removing the contaminant from the subsurface or stop the migration of the contaminant (Cundy *et al.*, 2013). Conventional methods used in managing the risk of contaminated land have included cover and removal to landfill (or "dig and dump"), and pump and treat for groundwater. Some alternative treatment-based methods have been implemented since the 1990s, which include physical, chemical and biological *in-situ* and *ex-situ* treatment methods (Dermont *et al.*, 2008; Cundy *et al.*, 2013). In 1999, the EU issued a directive that was aimed at reducing the adverse effect of landfill disposal (i.e., dig and dump). A report by Alec *et al.* (2014) suggested that over 200 sites in the UK could not accept hazardous wastes due to the implementation of the EU directive on land waste disposal in 2004. Moreso, many consulting firms now turned to *in-situ* and *ex-situ* treatment because it was less expensive and sustainable when compared to the dig and dump method. Another limitation is its applicability in large areas of land. Cundy *et al.* (2013) reported that groundwater contaminants might be too deep to dig and dump, so therefore continued reliance on this method cannot address the issue of groundwater contamination.

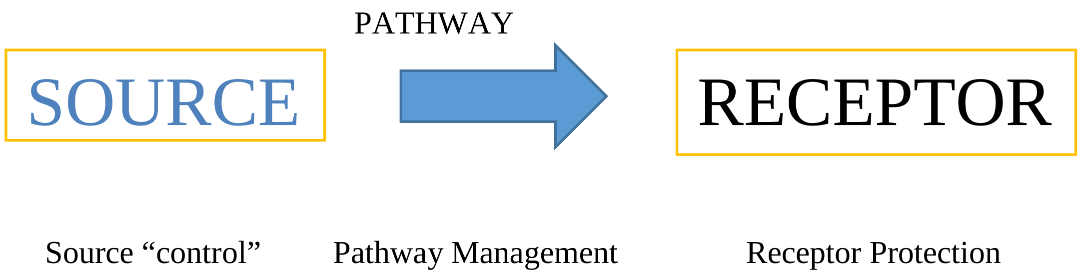

Figure 2.7 The Source-Pathway-Receptor model (Cundy *et al.*, 2013).

2.6.1 Low-Input Approaches to Remediation of Contaminated Land

Cundy *et al.* (2013) reviewed the concept of low-input or Gentle Remediation Options (GRO) for risk management, particularly for soft re-use rather than hard (e.g., built development) re-use, because there will be no net loss in soil functionality. The emergence of low input methods occurred as a result of the cost limitations of using invasive physical remediation (such as Dig and Dump options) in managing contaminated land risk over large treatment areas, alongside moves towards more sustainable land management. GRO includes a range of technologies based on phytoremediation and microbiological based methods, where plants and bacteria are used for site risk management. The benefits of low input methods include applicability in treating large land areas where contamination is active - if contaminant concentrations are too high, then plants will not efficiently grow. They are useful for contaminated sites with budget constraints and can be deployed where there are constraints in access for the process plant. Some notable examples of low input methods are phytovolatilisation, phytodegradation, phytoextraction, rhizofiltration, phytostabilisation and mycoremediation (Ruttens *et al.*, 2006; Grispen *et al.*, 2006; Chaney *et al.*, 2007; Vangronsveld *et al.*, 2009; Onwubuya *et al.*, 2009; Mench *et al.*, 2010; Table 2.2). The practical application of GRO in Europe has been successful at various sites and can bring about land regeneration where the cost for conventional remediation is very high (Friesl-Hanl *et al.*, 2009; Bert *et al.*, 2012; Herzig *et al.*, 2014).

Monitored Natural Attenuation (MNA) is the process of monitoring groundwater to confirm whether natural attenuation reactions are acting at an adequate rate to guarantee receptor protection and that risk management is accomplished inside a sensible timescale. The MNA method, as seen in Figure 2.8, is used for groundwater remediation and can be considered as a GRO. As illustrated in Figure 2.8, as the contaminant plume migrates it is influenced by various attenuation processes. Each process contributes to the overall attenuation of contaminants. In fact, what happens is a reduction of the amount of contaminant mass passing through a control plane per unit time (mass flux). The location of the control plane may be defined by a compliance agreement (cf. point of compliance) or may be associated with discharges to the receptor. As such, it has the potential for application in settings with large-area contamination issues such as Ogoniland.

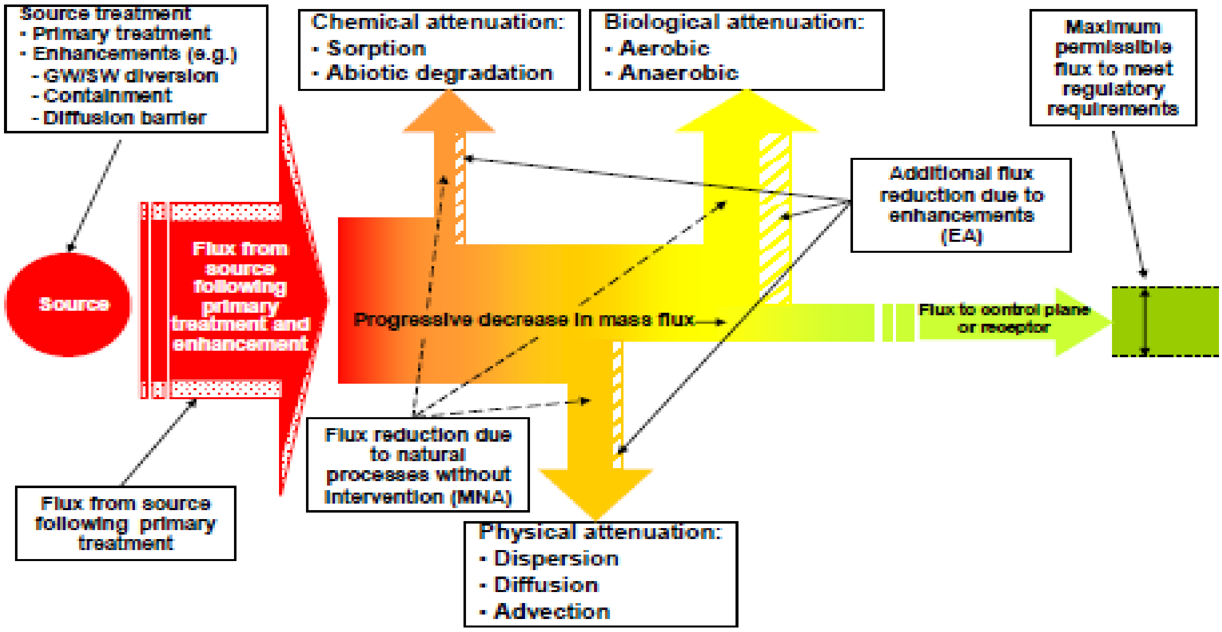

Figure 2.8 Various natural attenuation processes, and how they can be used to decrease the mass flux of contaminants reaching the receptor (adapted from Looney *et al.*, 2006).

Various studies have been carried out and published over the last few years regarding GRO, but the widespread use of these techniques is still limited in all but a few geographic areas. Sensibly applied GRO can provide rapid risk management via pathway control, through containment and stabilisation, coupled with a longer-term removal or immobilisation/isolation of contaminants. The application of GRO can also generate a range of additional economic (e.g., biomass generation), social (e.g., leisure and recreation) and environmental (e.g., C sequestration, water filtration, and management, ecosystem services) benefits, leading to recent discussion of its use as part of sustainable remediation strategies (e.g. Cundy *et al.*, 2016). The realisation of these benefits requires close and effective engagement with stakeholders, as illustrated by field applications of GRO at Betteshanger, England, the BIOGECO (biodiversity, genes, and communities) phytoremediation platform, SW France, and Krummenhennersdorf, Saxony, Germany (World Bank, 2012; Cundy *et al.*, 2013). Effective stakeholder engagement is also key in overcoming some identified barriers, largely around stakeholder confidence, to the large-scale use of GRO on a commercial land remediation basis (Cundy *et al.*, 2013). Other barriers include:

(1) The successful application of GRO is mostly dependent on changes in contaminant bioavailability, which is not considered by many legal frameworks (which are predicated on total soil concentration values).

(2) Effective management of large contaminated sites by GRO remains to be consistently demonstrated.

(3) Many existing national decision support tools do not sufficiently consider GRO, e.g., the UK's contaminated land guidance CLR-11 does not include photo-techniques in its list of remediation technologies.

2.6.2 Current Remediation Methods in the Niger Delta

The current main method of hydrocarbon clean-up and site remediation in the Niger Delta is bioremediation. Many authors (e.g., Adelena *et al.*, 2011; Asia *et al.*, 2007; Ayotamuno *et al.*, 2006c; Peter and Ayolagha, 2012; Okoro, 2010; Tanee and Albert, 2011) have emphasised that the use of bioremediation is useful in the Niger Delta. They argued that bioremediation is an advanced technology that can be used efficiently and quickly in treating hydrocarbon pollution, although some researchers have also suggested the use of bio-surfactants to make the process faster (Cameotra and Bollang, 2003). According to Adelena *et al.* (2011), bioremediation can also be enhanced using bio-augmentation and bio-stimulation (the use of microorganisms for biodegrading specific soil and groundwater contaminants and stimulating existing bacteria) in cleaning sites in the Niger Delta. Bioremediation as a process, however, has a number of limitations, specifically: (1) that if the process isn't controlled, the natural contaminants may not be separated completely, bringing about harmful side-effects that could be more damaging than the underlying pollution; (2) its success is dependent on the contaminant concentrations and ecological conditions, and if an ex-situ process is utilized, controlling unpredictable natural mixes (VOCs) might be difficult; (3) the treatment time is commonly longer than that for other remediation technologies since contaminants that can be successfully treated are restricted to compounds that are relatively readily biodegradable; (4) Execution assessments are difficult in light of the fact that there isn't a characterized level of a "clean" site and thusly, execution criteria directions are unverifiable (Concetta and Daugulis, 2013).

Shell (SPDC) outlines that bioremediation by land farming, remediation by stabilisation, and low-temperature thermal desorption, have been used to clean up sites in Ogoniland. International organisations such as UNEP, Friends of the Earth Nigeria, Netherlands (Millieudefensie), Europe and Germany (Bund) have criticised Shell for using remediation by Enhanced Natural Attenuation (EMNA) and Pump and Treat methods, which are not applicable in every setting and do not lead to clean-up of the entire region. However, Onifade *et al.* (2007) observed that natural processes of biodegradation, photo-oxidation, evaporation, and volatilisation without external inputs could attain remediation of polluted environments. Enhanced Natural Attenuation and Pump and Treat methods can be very expensive and may not achieve an adequate result on a broader scale regarding implementation. Edema *et al.* (2011) and Ndimele (2010) argued that phytoremediation is the optimum technique in terms of contaminated rivers/aquatic environments, and also for PAHs, although Ayotamuno *et al.* (2006b) argued that the use of activated carbon (AC) is also highly applicable for the remediation of petroleum hydrocarbon in contaminated groundwater (PHC).

2.7 SUMMARY

The sources of hydrocarbon, PAHs and BTEX contamination have been highlighted in this chapter. Also, the exposure pathways for contaminants such as DNAPL and NAPL have been discussed. A review of different remediation options and their applicability has also been presented, alongside an introduction to the concept of GRO and other low input methods. Also, the benefits and limitations of green technologies were introduced. The following chapter presents the research method, type of data collection and data analysis that will be used to achieve the aim and objectives of this study.

CHAPTER 3.0 – METHODOLOGY

3.1 INTRODUCTION

In the previous chapter, relevant literature in the context of the study was reviewed, and knowledge gaps identified. In this chapter, the research design to achieve the aims and objectives of this work, including research methods, and data collection and analysis methods, are presented. Also, this chapter provides details of the apparatus used, reagents, preparation of reagent solutions, analytical procedures used for determining concentrations in solution, and calculation of concentrations in the materials analysed.

3.2 RESEARCH DESIGN

According to Kothari (2004), research methodology is a systematic means of solving a research problem by collecting, analysing and interpreting research data. Research methodologies can be categorised into qualitative and quantitative methodologies. Quantitative methodologies involve the use of sample analysis and statistical tools in the study of a natural phenomenon in the examination of the relationships between variables in the context of the research (Yilmaz, 2013). The differences between these research designs are primarily related to strategies of an investigation. For example, a quantitative approach depends on the survey, sample measurement and so on, while a qualitative approach depends on ethnography and other non-quantitative methods. Mixed methods combine both strategies (quantitative and qualitative) through the use of collecting data quantitatively with instruments or collecting data with a thorough observation of a setting.

This research was carried out mainly through a quantitative approach, which was achieved by field studies and sample collection, combined with laboratory and core flooding experiments. The results of analyses of inorganic and organic contaminants in ground and surface waters are presented in Chapter 4; simulations of transport of contaminants to groundwater and natural attenuation processes using core flooding experiments in Chapter 5; and the results of experiments investigating enhanced natural attenuation through the use of carbon-based adsorbents in Chapter 6.

3.3 COLLECTION OF DATA

Data collection methods for objectives A and B (Chapter 1).

Given that:

(1) There is difficulty in measuring and quantifying all the components of complex mixtures of hydrocarbons, and

(2) The previous focus in the literature on Total Petroleum hydrocarbons does not allow adequate assessment of likely groundwater migration and exposure pathways for mixed Hydrocarbon contaminants,

This research targets key light and heavy hydrocarbon components with known health impacts, which can migrate into groundwater via different routes and may require different remediation methods. The targets (based on published literature, and field surveys in the Niger Delta; see Chapter 4) were phenol, toluene, and PAH. Heavy metal contaminants potentially associated with hydrocarbon exploitation and processing activities, and major groundwater cations and anions identified as groundwater contaminants from previous literature on Niger Delta groundwater (e.g., Fe, Mg – reviewed in Chapter 2), were also examined.

3.4 FIELD SAMPLING

The distribution of key contaminants in surface water, groundwater (via established boreholes), and drinking wells were examined around major oil production sites in Ogoniland. The study site is located in Rivers State on the coast of the Gulf of Guinea, east of the city of Port Harcourt (Figure 3.1). It extends across four Local Government Areas (LGAs), Khana, Gokana, Eleme and Tae. Site access was ensured through close contact with, and approvals from, the local government (e.g., Jackson Money Abikor, Paramount Ruler of Nyokuru Town). 500ml Nalgene bottles were used for water sample collection, which was prewashed with warm water and dried using a steam cleaner. The bottles were put in clean bags and transported via DHL to Nigeria. A local company (Engineering and Environmental Management Services Limited, EEMS) received the bottles. Before samples were collected, bottles were washed again with standard clean laboratory distilled water and ethanol to remove any contamination generated during the transportation to Nigeria. Local samples were collected by EEMS. Waters were tested for various field parameters (below) immediately and were then transported via DHL to the University of Brighton, East Sussex, UK. Samples arrived within two days. On arrival, the samples were collected, and parameters tested to compare with EEMS results, after which the samples were stored at 4°C in a laboratory cold room until further analysis.

Field methods included visual examination of hydrocarbons in boreholes and drinking water wells, water testing for pH, conductivity, temperature and oxygen content, and collection of water samples for further analysis. The collection of water was carried out from different locations in Ogoniland (Eleme and Gokana – Figure 3.1) and Port Harcourt City Local Government (Amadi Ama), to provide a series of sampling points upstream and downstream of hydrocarbon production facilities, from both surface water and drinking water boreholes. The well water samples were collected with the use of a depth-controlled bailer while the surface water was collected with a standard bailer. Sample collection devices were pre-washed with local water before sampling. A total of 31 samples were collected (in 500ml Nalgene bottles) from the sample locations. Due to political and safety pressures, sampling sites within Ogoniland were only able to be accessed once, with single surface and/or groundwater samples collected from each sampling point. Therefore, all water quality data presented are for $n = 1$ unless otherwise stated.

3.5 LABORATORY WORK/ DATA ANALYSIS

Analysis of hydrocarbon concentration (PAH, Toluene, and Phenol) and of heavy metals, and groundwater cations and anions, was carried out using standard methods (ion chromatography, Hach spectrometry, inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS)) (section 3.6). Also, a soil column was assembled to mimic near-surface soils around oil production sites in Ogoniland, and processes of hydrocarbon migration assessed by core flooding experiments to explore the role of soil type, porosity and other characteristics in hydrocarbon migration to groundwater. Core flooding experiments targeted the key hydrocarbon contaminant phenol (further methodological and experimental details are included in Chapter 5). Data collected were examined in the context of the source-pathway-receptor risk model to assess the potential risk to groundwater and drinking water.

Figure 3.1 Map of sample collection sites (blue circles), Adapted from UNEP (2011).

Data collection methods for Objectives C and D

Existing hydrocarbon treatment and management methods and their relative success were examined through a literature review, with a particular focus on large area, less intensive remediation methods (e.g., GRO – Chapter 2). Using results from this review, and from field and laboratory work under objectives A and B, the potential applicability of a range of groundwater remediation methods was assessed (including bioremediation, phytoremediation, and natural attenuation approaches). Additional laboratory experiments were undertaken on the effectiveness of applying carbon-based adsorbents as soil amendments, to absorb and stabilise key contaminants of concern in the soil subsurface. Based on this, systems of improved environmental management for hydrocarbon contamination in Ogoniland, and in the wider Niger Delta, were recommended using recently published Decision Support Tools to identify wider benefits (objective D).

3.6 ANALYTICAL METHODS FOR GROUND AND SURFACE WATER ANALYSIS

3.6.1 Cleaning of Glassware and Plasticware

Laboratory glassware and plasticware were pre-cleaned physically and chemically and then rinsed free of all cleaning agents. Initial physical cleaning and rinsing processes included soaking the glassware in acetic acid, rinsing in tap water and final rinsing in deionised water.

All glassware and plasticware selected for use were examined to ensure that it was free of chips and scratches, and before washing, a suitable solvent such as ethanol was used to remove all ink marks and previous labels. Self-adhesive labels were avoided as they were very often difficult to remove effectively, particularly after prolonged contact. After use, the glassware was rinsed with warm tap water immediately.

Care was taken to avoid scratching glassware during this process. After this stage, glassware appeared to be clean both inside and outside. Then the glassware was rinsed three times with warm tap water. The glassware that was already physically clean was soaked in a chemical cleaning agent. The cleaning solution used depending on the nature of the chemical contamination and the type of analysis. 2% of Decon 90 solution (Decon Laboratories Limited) is a general-purpose soaking solution which has good rinsing properties. Glassware was soaked in a container of this solution overnight. The flasks etc. were filled with and immersed in the solution.

After draining, glassware was rinsed five times with warm tap water to ensure complete removal of the chemical cleaning agent. This was followed by rinsing twice with deionised water and finally drying in an oven at 70° C. Care was taken to ensure that the oven-dried glassware did not become contaminated, e.g., by dust or contact with dirty surfaces. All laboratory analyses were carried out at the University of Brighton, U.K. unless otherwise stated.

3.6.2 Measurement of pH in Water

The pH was measured in the water samples using a pH meter (Mettler - Model: Delta 320). The meter was first standardised with buffer solutions of pH 7.0 and 4.0. The buffer solutions were prepared by dissolving buffer solution in 100 ml deionised water. 20 ml of the water sample was placed in a 50 ml beaker. The water sample was stirred by swirling the electrode slightly, and the pH value was recorded when the reading stabilised.

3.6.3 Measurement of the Electrical Conductivity (EC) of Water

The EC was measured in the water samples using a pH meter (Mettler - Model: Delta 320). The meter was first standardised with buffer solutions of pH 7.0 and 4.0. The buffer solutions were prepared by dissolving buffer solution in 100 ml of deionised water. 20 ml of the water sample was placed in a 50 ml beaker. The water sample was stirred by swirling the electrode slightly, and the EC value was recorded when the reading stabilised.

3.6.4 Measurement of PAH and other hydrocarbon components

The separation and the detection of PAH compounds were carried out with gas chromatography coupled to a quadrupole mass spectrometer equipped with electron impact ionisation source (GC-EI-MS) from Agilent Technologies (Santa Clara, US) model 7890, at Kingston University (UK). Electron ionisation was carried out at 70 eV. Chromatographic separation was carried out with a column 30m x 0.25mm I.D of 0.25µm of film thickness ID-BPX5 fused-silica capillary column with stationary phase 5% phenyl from SGE Analytical Science (Milton Keynes, UK).

The temperature of the injector was 240 ºC, and the samples (1µL) were injected in splitless mode (for greater sensitivity). Samples were injected in full scan (scan ranges m/z 49-150 and 150-300), the oven temperature was held at 65 ºC (held for 1 minutes), increased to 140 ºC at 25 ºC·min-1, followed by an increase to 290 ºC at ten ºC·min-1 and held at 290 ºC for 11 min. The mobile phase was He at 1.5 ml ·min-1

3.6.5 Hach spectrometer

The DR3900 photometer was used to perform tests in water analysis, used in identifying Total Petroleum Hydrocarbons (TPH) and Phenol in groundwater and surface water analysis. Use of this technique prevents measurement errors and simplifies water analysis, thus making it easier to ensure accurate and reliable results. The DR 3900 spectrophotometer delivers necessary improvements in quality control thereby eradicating false readings by taking ten readings of a prepared sample from diverse angles, and eliminates outliers caused by scratches, flaws or dirt on the glassware.

3.6.6 Ion Chromatography

Ion chromatography is used for analysing water chemistry, specifically for measuring concentrations of major anions, such as fluoride, chloride, and nitrate, and major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range (Michalski, 2018). The ion chromatograph measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently subject to species type and size. The sample solutions move through a maintained chromatographic column where column constituents absorb ions. As an ion extraction liquid, known as eluent, runs through the column, the absorbed ions begin separating from the column. The retention time of different species determines the ionic concentrations in the sample.

Ion chromatography is used widely to determine water chemistries in aquatic ecosystems, and sugar, salt, etc. in food content (Coskun, 2016). Here, it was applied to measure major ions in groundwater and surface water. Fluoride, nitrate, chloride, bromide, and sulfate were determined in water samples using a Dionex ICS-1100 Ion Chromatograph with an IonPac AS23 column. Water samples from Ogoniland were loaded in a 20ml plastic tube labelled with each site location. The ion chromatograph was calibrated using a Dionex seven anion standard at 5, 10, 20, 50, & 100% concentrations. A 5ml injection of a sample was used in the method. The samples were run, and their stable readings were recorded.

3.6.7 Measurement of inorganic contaminants using Optical Emission Spectrometer (ICP-OES)

According to Price and Burton (2011), an ICP-Optical Emission Spectrometer (ICP-OES), separates the light emitted from a sample injected into a plasma into its discrete component wavelengths using a diffraction grating. Each element in the periodic table has its own distinct set of emission wavelengths. Water samples from Ogoniland were loaded in a 20ml plastic tube labelled with each site location and analyed using a Perkin Elmer Optima 2100DV ICP-OES. The instrument was calibrated at 5ppm and 10ppm using Perkin Elmer standard solutions for the elements of interest. The volume of water sampled was 10ml, but this has no bearing on the outcome of the test.

A read delay of 80 seconds was used to avoid sample carry-over, with a 30-second wash sequence between each sample, and three replicates of each sample were recorded. After getting stable readings for the working standard solutions, the samples were run, and their stable readings were recorded.

3.6.8 Measurement of trace elements and heavy metals using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is an analytical technique used for elemental and isotopic determinations. The technique was commercially introduced in 1983, and it has superior detection capabilities. ICP-MS offer many advantages over other elemental analysis techniques, including:

- Detection limits for most elements are better than those obtained by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).
- It has higher throughput than GFAAS.
- Its ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source.
- Superior detection capability to ICP-AES with the same sample throughput.
- The ability to obtain isotopic information.

An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. Its source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer.

ICP-MS was used here to determine trace heavy metals in surface and groundwater samples. The ICP was tuned using Agilent tuning solution 7500cs and calibrated using Agilent Environmental acid solution (ultra-pure). Three replicates were run of each sample with a wash between each sample (5%Nitric Acid).

3.7 CORE FLOODING EXPERIMENTS

3.7.1 Core Flooding Set-Up

Core experiments were conducted in the laboratories at the University of Brighton to simulate the flow of phenol through, and possible natural attenuation in, simulated Niger Delta soils. This allowed for simulation of discharge of water containing phenol solution to the core zones, flow through the saturated zone, periods when the contaminants were left to react with the core, and flushing out of the contaminants. Results are presented and discussed in Chapter 5.

The core experiment laboratory setup is shown in Figure 3.2. Laboratory core experiments were conducted using a Hassler cell core holder and HPLC pump system. By using a pumped system, a greater range of controllable flows could be utilised for the experiments. The use of a gravity system would not have allowed sufficient downward migration of test solutions due to the capillary forces that exist within the core. A pumped system was selected for this reason and a

Hassler type cell holder chosen due to its ability to deliver a confining pressure that is required for this application.

The Hassler cell holder was constructed from stainless steel and allowed for core samples between 38 and 100mm in length, and 38mm in diameter, to be tested. The cores were prepared (drilled to the correct diameter) and trimmed so that the ends are flat and perpendicular (to the length). This ensured a tight fit and even distribution of the feed solution across the face of the core from the inlet platen and allowed for the effective collection of the eluted solution on the outlet platen. The core sample was placed in a Viton rubber sleeve, and the tapered ends of the inlet and outlet platens gripped by the inside of the sleeve.

The assembled sample within the Viton sleeve was placed inside the core holder and a confining pressure applied to the outside of the sleeve by a VJ-Tech automatic pressure controller (APC). Distilled water was used in the APC to apply the confining pressure within the core holder as this was assessed as being a safer medium than compressed air.

The APC delivered the required confining pressure to the cell holder, which was always selected as greater than the required delivery pressure of the HPLC pump, meaning that the pressure on the outside of the sleeve was greater than that on the inside. Not only does this reduce the likelihood of the sample breaking, but it also ensured that no short-circuiting of the delivery solution between the outside of the sample and inside of the sleeve could occur. The volume of confining distilled water was recorded during the experiments; and if there was no discernible increase/decrease in the volume, an effective tight fit of the sleeve on the core had been achieved. The APC was capable of delivering a confining pressure of up to 2000 PSI.

The test solution was delivered to the inlet of the core holder by a Jasco 980U HPLC pump. The HPLC pump can deliver a range of flows up to 10ml/min up to pressures more than the maximum permissible confining pressure of 2000 PSI.

The outlet of the pump and inlet to the core holder were connected with a 40cm length of PEEK tubing (with an internal diameter of 0.05mm). The outlet of the cell holder was connected to a length of PEEK tubing (with an internal diameter of 0.05mm) which was fed to a GE Healthcare Fraction Collector. The fraction collector can hold up to 96 15ml fractions (plastic centrifuge type tubes) and was programmed to collect fractions at chosen time intervals/volumes automatically.

When required, feed solutions were changed on the HPLC pump system by opening the waste valve (on the outlet of the pump head) which stopped the delivery of the solution to the core holder. The inlet tube and strainer were removed from the first solution and rinsed with distilled water and dabbed dry. They were then held out of solution for sufficient time to allow for a 4-5cm length of air to be drawn into the inlet tube. The tube was then placed into the second solution, which was then drawn into the inlet tube, separated from the first solution by the air bubble. A 50ml syringe was connected to the waste valve and, when drawn, the solution in the inlet tube is pulled into the syringe. Once the air bubble had been dragged into the syringe, the second solution was now in the pump head, and closing of the waste valve directed this flow to the outlet (delivery) side of the pump.

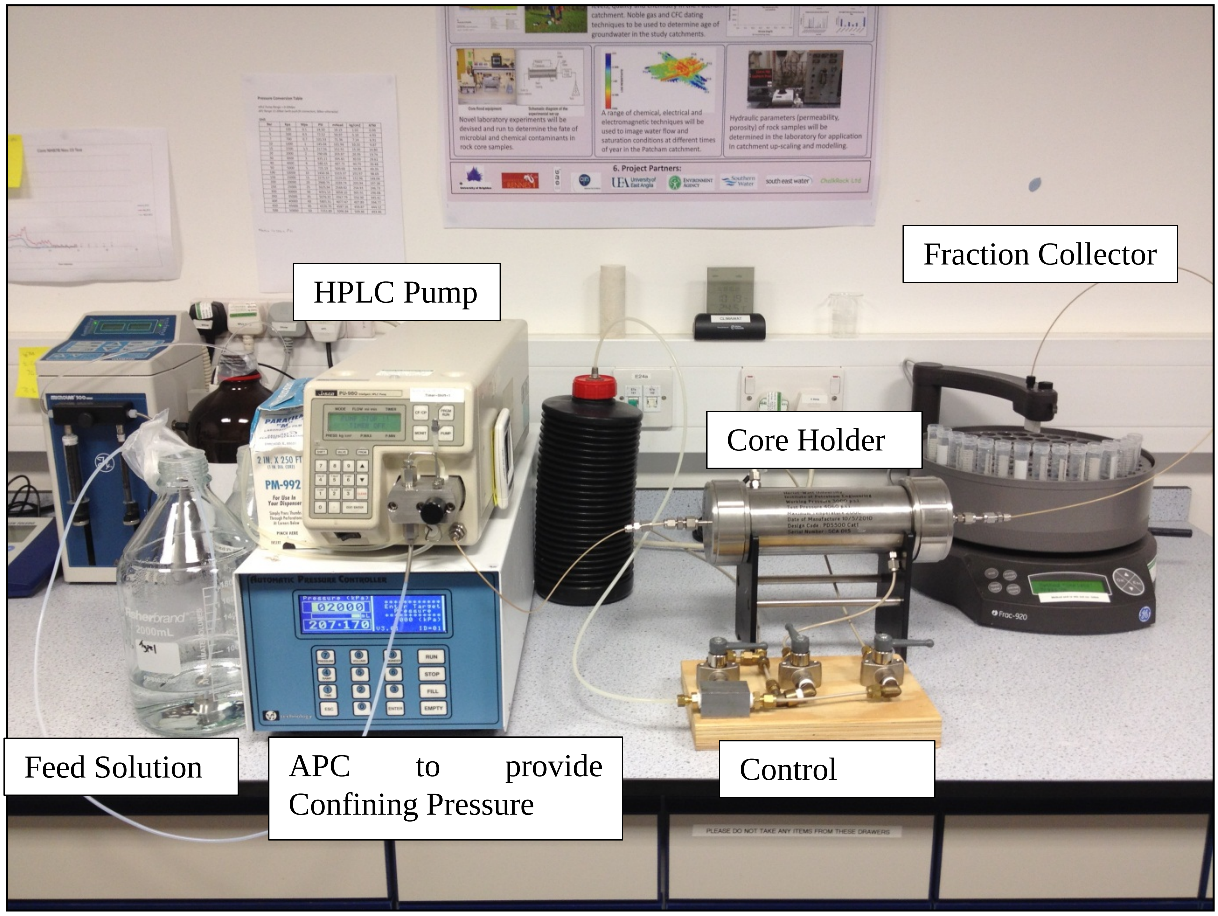

Figure 3.2 Core flooding experimental setup, showing core holder, and pumping and collection equipment.

3.7.2 Determination of system volume

The system volume can be seen as the dead volume within the experimental rig comprising of tubing and all fittings. The system volume was found so that this can be subtracted from the total collected cumulative volume, so when plotting pore volumes (PV's), this additional volume is not included in the pore volume calculation and appropriately offset.

The length of the coil is 11.3cm, the band length is 2cm, the filter is 0.6cm, and the sleeve diameter is 3.8cm and the volume of the coil =11.34-6.1=69.187cm^3. To calculate the density, the coil will be filled with 103.77g of the homogenised mixture. The density of the core was selected from Odigi (1994). This calculated by volume of the coil (69.18 multiply by 1.5=103.77g).

To find the system volume, a dummy core with a known sized drilled hole was inserted into the experimental rig. Lithium chloride tracer solution was pumped through the dummy core at 0.5ml/min and fractions collected at the outlet. The lithium chloride concentrations were measured, and the total volume of solution that passes through the experimental rig before the lithium chloride breaks-through was calculated. The volume of the drilled hole in the dummy core was subtracted from this total volume to give the system volume of the experimental rig.

3.7.3 Preparation of feed solutions

Synthetic water effluent was created to enable phenol and chloride breakthrough to be studied individually, with the chloride taking the role of a conservative flow tracer. Stock solutions were created by weighing out a dried quantity of the required compound to be tested and mixed with distilled water. All water used was Type 1 quality deionised water (with a specific resistance of 18.2MOhm).

Phenol was used to make stock solutions for phenol studies and sodium chloride used to make stock solutions used for chlorine studies. Stock solutions were diluted as necessary to provide the required concentration for a specific test, and in this experiment 50ml of each was used.

3.7.4 Core preparation

Several authors have presented mineralogical and compositional data for Niger Delta soils as seen in Table 3.1. As soil and rock directly sourced from the Niger Delta were not available, a simulated shallow aquifer material was generated, using sand and kaolin (40% each), which were mixed with standard garden compost (20%). Because of the available time frame, trying different compositional mixes in the experiment to assess if they caused any variability in the results obtained was not achievable.

Table 3.1 Minerals and organic content of soils in the Niger Delta.

Soil location	**Main minerals present**	**Organic content range (%)**	**Reference**
Aba soil	Quartz (40%), Kaolinite (40%), Gibbsite, allophane, smectite	-	Olorunfemi, 1984
Niger Delta		9.4 – 18.9%	Rim-Rukeh, 2013
Niger Delta	kaolinite, montmorillonite and a small amount of illite		Francisca, 1992
Niger Delta	Inter-stratified illite/smectite (I/S), kaolinite, and chlorite.		Velde *et al.*, 1986
Niger Delta	kaolinite, while authigenic kaolinite and smectite are present in the water-saturated sandstones		Lambert and Shaw, 1982
Niger Delta		7 – 30%	Ekweozor and Okoye, 1980
Niger Delta	kaolinite, while authigenic kaolinite and smectite are present in the water-saturated sandstones		Odigi,1994

3.8 BIOCHAR AND MAST CARBON PREPARATION

Adsorption studies using carbon-based adsorbents were undertaken using materials supplied under the EU FP7 WasClean project (grant no. 612250), at the University of Brighton and the Institute of Geotechnics, Slovak Academy of Sciences, Slovak Republic. Activated carbons were produced and supplied by MAST Carbon International Ltd (production methods are detailed in Busquets *et al.*, 2014). Pyrolysis of biochars was undertaken at the UK Biochar Research Centre (UKBRC, University of Edinburgh, UK) using the small-scale batch pyrolysis method described in Crombie *et al*. (2013). Samples of various feedstock types (held as standard biochar source materials at the UKBRC) were heated at a rate of $25^oC\ min^{-1}$ to the highest treatment temperature of 550^oC or 700^oC, held for 30 minutes. The resulting biochars were left in the reactor with N_2 flow overnight to cool before being transferred into an N_2-purged container. All biochars were used as provided by the EU WasClean project.

The biochars tested were produced using raw physically treated (boiled and dried) and thermally treated (heated at 550°C or 700^oC for 3 h to produce ash) softwood, grass and rice husk residues. For sample notation, RH550 is rice husk biochar produced at 550°C while RH700 is rice husk biochar produced at 700°C. Further details of batch adsorption methods used are given below and in Chapter 6.

3.9 ADSORPTION EXPERIMENT

3.9.1 Phenol: Preparation of phenol stock solution

Adsorption experiments were carried out in the Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova Kosice, Slovakia, in collaboration with the EU WasClean Project (PEOPLE-2013-IAPP-612250). All work was performed in a fume hood, and protective equipment was used during handling processes. Phenol stock solution was prepared using 50 mg phenol (accurately weighed) in 0.1 N sodium hydroxide in 1L of distilled water in a volumetric flask. Volumes of stock solution ranging from 0.1ml, 0.2ml, 0.4ml, 0.6ml, 0.8ml to 1.0ml were added to ranges of 10ml, 20ml, 40ml, 60ml, 70ml, 80ml and 100ml of distilled water. Calibration was carried out with several working standards covering the concentration range of the samples; pipets were used to measure 1, 2, 4, 6, 8, 10 and 20 ml calibration stock solution into 100ml of Distilled water volumetric flasks. Samples were measured via UV-vis spectrophotometry, and a calibration graph was prepared using absorbance area vs µg phenol concentrations in the 25 ml volume. The wavelengths were set from 200-800nm, and quartz cuvettes (1cm) were used. Deionised water was added into the cuvette, which should have a zero absorbance (Blank) and the peak response for phenol was seen at 270nm as shown in Figure 3.3, which was the wavelength used for all subsequent phenol determinations.

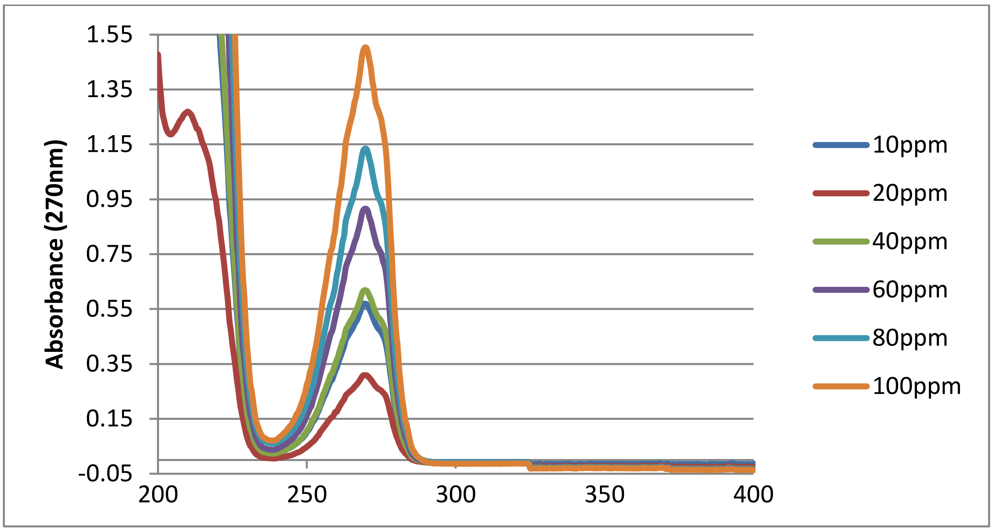

Figure 3.3 Phenol absorbance with wavelength, showing a maximum response at 270nm for various concentrations of phenol. The y-axis shows absorbance, while the x-axis shows wavelength in nm.

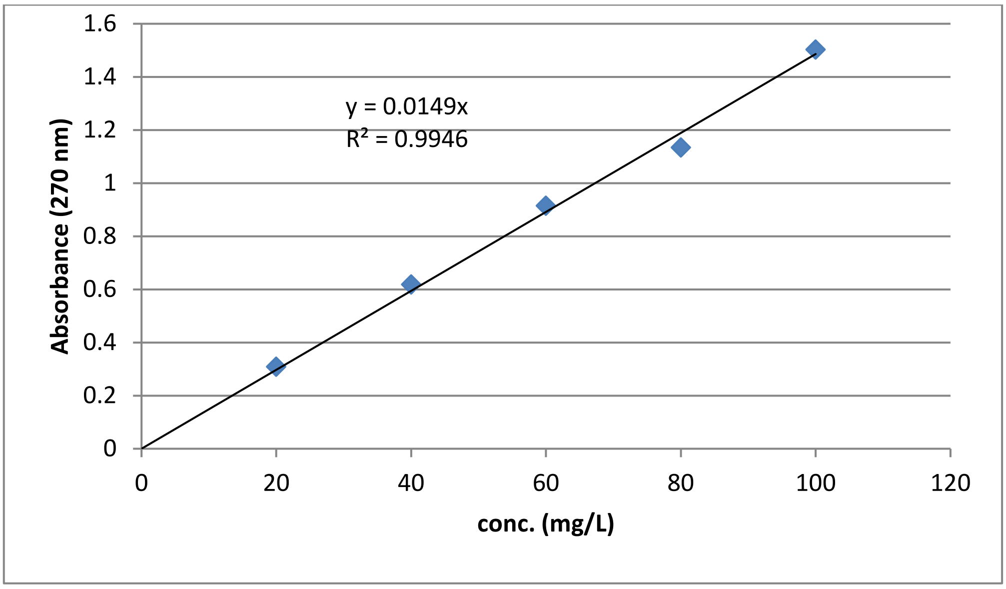

Figure 3.4 Phenol calibration curve. The y-axis shows absorbance at 270nm and the x-axis the concentration of calibration solutions in mg/l.

The slope of the calibration line (Figure 3.4) was used to correct the data. A straight line has an equation y = mx + c. C is the intercept on the y-axis, which here is zero (the calibration line passes through the zero points). The slope of the line (m) is 0.0149.

3.9.2 Preparation of MAST carbon and biochar adsorption experiment

The MAST carbon used was derived from the synthesis of phenolic resin. Pore distribution was carefully controlled; MAST carbons are designed as nanoporous, nano-mesoporous and nano-macroporous. The biochar utilised was provided by the UK Biochar Research Centre, University of Edinburgh. 0.05 g of sorbent/carbon (MAST carbon, Softwood (SW550/750), Miscanthus grass (MSP550/700) and Rice Husk (RH550/700)) were placed in 45 ml glass bottles and 25.00 ml of phenol solution, pH was measured. Experiments were performed at room temperature. All bottles were labelled using a marker pen. The tubes were shaken on a rotary stirrer for 48 hours. Solutions were filtered using filter paper and a 0.22 µm syringe filter. pH was measured again. 2 ml of all samples were removed and used for UV-VIS spectroscopy.

3.9.4 Preparation of pH experiment and pH effect after adsorption

To determine the effect of pH on contaminant adsorption, 0.05 g of sorbent/carbon was placed in 45 ml glass bottles with 25.00 ml of different concentration phenol solution (10, 20, 40, 60, 80 and 100 ppm). The effects of pH on adsorption were investigated using different concentrations of phenol solution over a pH range 3 to 9 (pH 3, 5, 7 and 9). The pH of the suspension was adjusted by adding 0.1M HNO_3 (acid-low pH) or 0.1M NaOH (base-high pH) as required. The tubes were shaken on a rotary stirrer for 24 hours then the solutions were filtered through filter paper and a 0.22 µm syringe filter. The pH was measured again, 6. 2 ml of all samples were removed and used for UV-VIS spectroscopy.

3.9.5 Anthracene: Preparation of stock solutions/standard curve (Anthracene 1 mg/l stock solution)

Solutions were shaken and put in an ultrasound bath for 15 minutes to ensure dissolution of anthracene. The standards used for the calibration curve are shown in Figure 3.5.

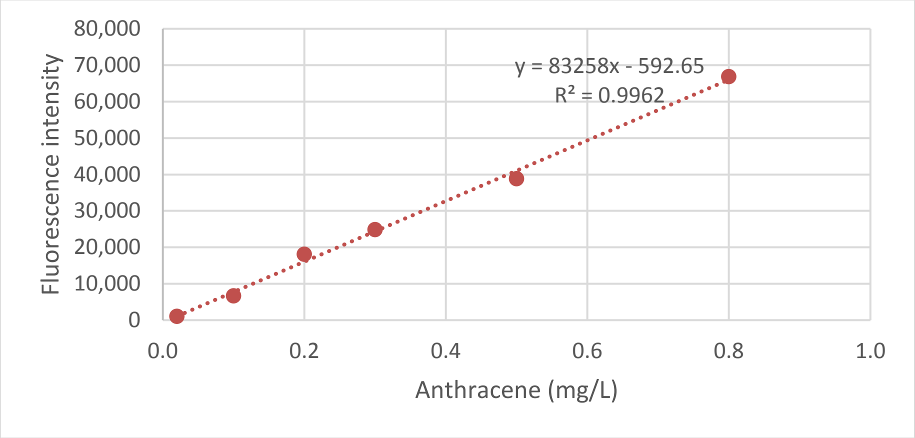

Figure 3.5 Calibration curve for anthracene. The y-axis shows the fluorescence intensity and the x-axis the anthracene concentration in calibration solutions in mg/l.

A portable fluorimeter was used in this study; the fluorimeter uses an ultraviolet LED (UV-LED) and a photomultiplier tube module as a light source and a detector. It is an advanced technique to estimate concentrations of UV-sensitive compounds in river-water, seawater, and industrial wastewater samples. The fluorescence intensities of samples (excitation wavelength, 245 nm; emission wavelength, 450 nm) were measured by this fluorimeter, their correlation, and values obtained by the conventional titration method using permanganate. The equations for the correlation at different sampling points were not identical. When the sample was taken from a specific point, the time course of its fluorescence intensity versus the sample value showed a good correlation

3.9.6 Selection of the excitation and emission wavelength

To identify the emission wavelength for anthracene, the stock solution was introduced in the cuvette, the excitation wavelength was fixed at 254 nm, and the emission wavelength was scanned from 260 to 800 nm. The emission wavelength that gives the highest intensity was selected. The excitation wavelength in the UV range (200-300 nm) was scanned, and the one that gave the best signal among the longest wavelengths was selected.

3.9.7 Preparation of MAST Carbon and biochars experiment

40ml of Anthracene solution was taken and placed into a glass tube. 20mg of adsorbent (MAST, Soft-wood, Rice Husk, and Miscanthus Straw) was added, and the tube was shaken for 48 hours at room temperature in an orbital shaker (Figure 3.6). The solution was filtered, and the filtrate (i.e., the filtered water) was measured for anthracene using the usual fluorimeter method.

Figure 3.6 Orbital shaking of samples.

3.9.8 Naphthalene: Preparation of Stock Solutions/Standard Curve (Naphthalene 30 mg/l Stock Solution)

Samples were shaken and put in the ultrasound bath for 15 minutes to ensure dissolution of naphthalene. Following, standards for the calibration curve were prepared. Glass volumetric pipettes were used, and the 50 ml was contained in volumetric glass flasks (rather than plastic that could adsorb the compounds of interest).

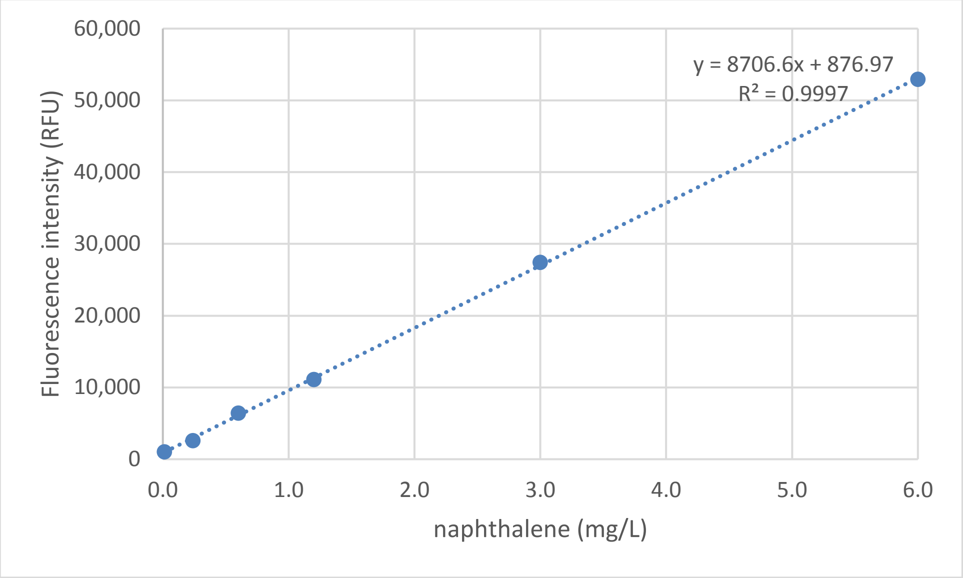

Figure 3.7 Calibration curve for naphthalene. The y-axis shows the fluorescence intensity (RFU) and the x-axis the naphthalene concentration in calibration solutions in mg/l.

3.9.9 Preparation of MAST carbon and biochars (soft-wood, rice husk, and Miscanthus straw) experiment

40ml of Naphthalene stock solution was taken and placed into a glass tube. 20mg of each adsorbent was added to the naphthalene solution (MAST, Soft-wood, Rice Husk, and Miscanthus Straw) and shaken for 48 hours at room temperature, on an orbital shaker. The solution was filtered, and the filtrate (i.e., the filtered water) was measured for naphthalene using the usual fluorimeter method.

3.9.10 Preparations of MAST carbon and biochars adsorption using Ogoniland water samples

Batch adsorption experiments were repeated with Ogoniland groundwater samples rather than deionised water, using activated carbon and the best performing biochars (Miscanthus straw (MSP550) and rice husk (RH550)) to assess the performance of the adsorbents under realistic conditions for their potential application in Ogoniland. The experiment was performed on water sample numbers 1 and 4 (Ogale), 1 (Bodo) and 1 (Amadi Ama), i.e., four groundwater samples in total, for phenol. For the adsorbent, the MAST carbon, MSP550, and RH550 were used (i.e., testing and comparing of 3 different adsorbents).

40ml of Ogoniland water was taken and place into a shaking tube with 20mg of adsorbent and shaken for 48 hours at room temperature, on an end-over-end or orbital shaker. The solution was filtered, and the filtrate was measured (i.e., the filtered water) for phenol using the usual spectrophotometric method.

3.10 SUMMARY

In this chapter, the research methodology used in the study was briefly discussed and the laboratory techniques used for analysing soil and water samples from the study area, and materials and materials set-up for core flooding and adsorption testing, were presented. The results obtained from these analyses are presented and discussed in subsequent chapters.

CHAPTER 4.0 – INORGANIC AND ORGANIC CONTAMINANTS IN GROUND AND SURFACE WATERS

4.1 INTRODUCTION

In this first results chapter, inorganic and organic contaminant data from surface and groundwater samples in Ogoniland are considered. The concentrations of key water contaminants from each Local Government Area in Ogoniland are presented and compared with the guideline values of regulatory bodies such as the World Health Organisation (WHO), United States Environmental Protection Agency (USEPA) and Standard Organization of Nigeria (SON). The results are also compared to relevant studies carried out in the Niger Delta and across the globe. This addresses objective A of the thesis, i.e., to investigate the distribution and concentrations of key organic and inorganic contaminants in hydrocarbon-contaminated groundwater and surface water in Ogoniland. Sample collection and analysis methods are detailed in Chapter 3.

4.2 INORGANIC CONTAMINANTS

Table 4.1 below shows a summary comparison of the sample results with the guideline values of various regulatory bodies. These inorganic constituents were detected in ground and surface water samples collected from oil spillage sites in Eleme, Gokana and Portharcourt local government area in Rivers State, Nigeria. These results are discussed on a constituent-by-constituent basis below.

4.2.1 Sodium (Na)

Na was detected in all groundwater samples collected from the study area at concentrations within the range 0.1 - 24 mg/l (Table 4.1), thus falling within the safe limits of the WHO (2008) guideline values of 250 mg/l for drinking water. The Australian guideline value for drinking water is 180mg/l, while USEPA, SON, and the EU have no fixed limits. Results are within the range identified by Dami *et al.* (2013) from analyses in Ndokwa East LGA of Delta State, Nigeria.

Figure 4.1 shows that concentrations at Ogale were low (ca. 1.5ppm), with Na not detected in two samples (Ogale 2 and 6). In Gokana LGA, concentrations at Bodo were low (ca. 3.28ppm), although Bodo 1 reported a higher value compared to Bodo 2 & 3. At B-Dere, Na was low (5.0ppm). B-Dere 1 shows a higher concentration compared to B-Dere 2 & 3 where the concentration was lower.

Table 4.1: Comparison of surface water (SW) and groundwater (GW) from Gokana, Eleme and Portharcourt Local Government Areas of Ogoniland for selected parameters against guidelines of USEPA, EU, Canada, and Australia (WHO, 1993; EU, 1998 and SON, 2007).

Parameter	**Range in current study GW**	**Range in current study SW**	**Recommended limits**					
			WHO	**EU**	**Australia**	**Canada**	**USEPA**	**SON**
Na (mg/l)	0.1-24.2	1.78-913	30-250	-	180	-	-	-
K (mg/l)	0-4.1	0.31-204.8	200	-	-	-	-	-
Ca (mg/l)	0.04 – 14.0	0.38-141.54	50-200		-	-		-
Fe (mg/l)	0.069	0-2.32	0.3	0.2	0.3	-	0.3	0.3
Mn (mg/l)	0.01 – 0.06	0-0.03	0.02-0.05	0.5	0.1	0.05	0.05	0.2
Mg (mg/l)	0.07 – 2.25	0.14-107.55	7- 50	-	-	-		0.20
Fluoride (mg/l)	0 – 0.16	0-0.48	1.5	1.5		1.5	2.0	1.5
Chloride (mg/l)	10 – 20.1	0.33-9.96	250	-	250	-	250	250
Nitrate (mg/l)	0 – 279.42	0-1.28	10	11	50	45	10	50
Sulfate (mg/l)	0.7 – 7.8	0-1006.26	200	250	-	-	250	100
Bromide (mg/l)	-	0-16.33	10	-	-	-	-	-
pH	4.2 – 8.17	6-8.08	6.5-8.5	6.5-8.5	6.5-8.5	-	6.5-8.5	-
TDS	3 - 168	3-65	500	500	-	-	500	500
EC	6 - 279	10-100	40	-	-	-		100
Turbidity	12.2 – 25.3	12-66.6	1	1	5	1	5	5

Table 4.2 Comparison of surface and groundwater from Gokana, Eleme, and Port Harcourt Local Government areas of Ogoniland for selected parameters against other current studies in the Niger Delta.

Parameter	**Range in current study GW**	**Range in the current study) SW**	**Values from selected studies**				
			Dami *et al.* (2013)	**Egirani *et al.* (2014)**	**Ayata-muno *et al.* (2006)**	**Ngah and Abam (2014)**	**Edet *et al.* (2011)**
Na (mg/l)	0.1- 24.2	1.78-913.1	0.28-0.87	2.6-22.82			10.77
K (mg/l)	0.1-4.1	0.31-204.8	0.1-0.29	1.5-11.7			3.05
Ca (mg/l)	0.04-14.0	0.38-141.5	2.39-3.0	2.2-21.8	30.60		6.24
Fe (mg/l)	0.06	0-2.3	0.2-0.68	0.001-0.23		0.1-5.6	2.41
Mn (mg/l)	0.01-0.06	0-0.03		0-0.098			0.10
Mg (mg/l)	0.07-2.3	0.14-0.3	2.39-3.08	2-12.6	2.80		3.35
Fluoride (mg/l)	0- 0.05	0-0.5	0-0.001				0
Chloride (mg/l)	10-20.1	0.33-1.96	0.01-0.18		790.4	66.4-408.2	23.6
Nitrate (mg/l)	0-279.4	0-1.3	0.02-0.12	0.12-1.45	3.5		4.73
Sulfate (mg/l)	0.7- 7.8	0-106	1.10-1.54	0.5-3.5	15.23		8.04
Bromide	-	0-16.3					
pH	4.2-8.1	6-8.1	6.5-6.81	5.5	5.5	5.3-7.9	5.89
TDS	3-168	3-65	23.76-65.24	14	108.5		87.9
EC	6-279	10-100		14	155	23-250	136.2
Turbidity	12.2-25.3	12-66.6	2.12-3.78	14	2		2

Eleme and Gokana LGAs (Ogale and Bodo & B-Dere) have lower Na concentration than samples from Port Harcourt city LGA (Amadi-Ama) (Figure 4.1). This is because Amadi-Ama is in a brackish part of the delta, with known tidal inputs of seawater, whereas Ogale and Bodo/B-Dere are in freshwater areas. The concentration of sodium observed in this study area still falls below regulatory standards and generally agrees with the findings of Todd (1980) that the concentration of Na is less than 100mg/l. Na is usually low in drinking water and causes no known health effects (Sengupta, 2013). However, studies carried out in the Niger Delta region show that Na concentration varies from region to region. Its concentration in the current study is higher compared to other studies in the region (Table 4.2). Sodium is not, however, a significant issue in the quality of groundwater in the locations studied.

Figure 4.2 shows that Na was not detected in the surface water samples collected in Gokana LGA, while the concentration of Na in Bodo was high (ca. 900ppm). A report by Amadi *et al.* (2012) suggested that the concentration of sodium in this location may be due to ongoing industrial activity. Hence sodium is a major water quality issue in this location.

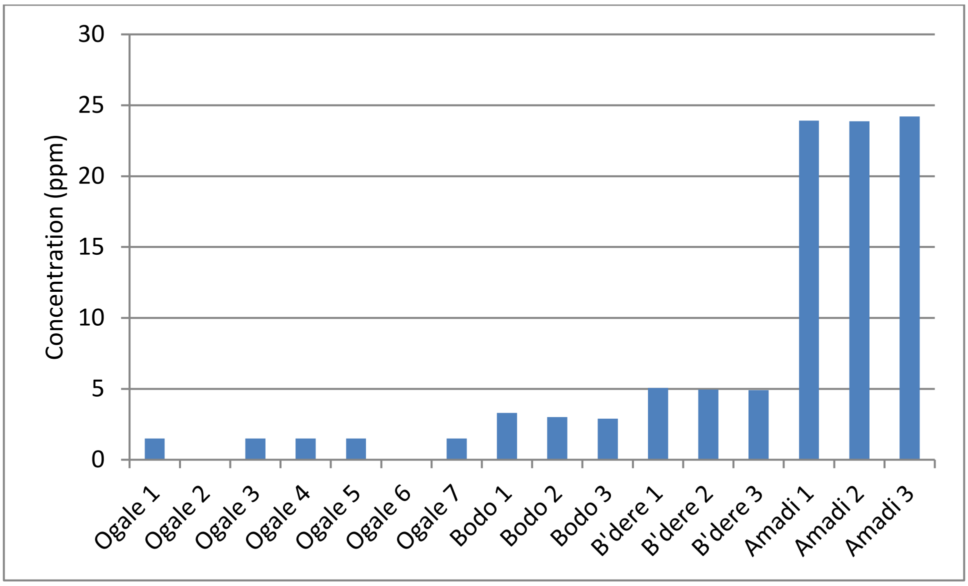

Figure 4.1 Concentration of Sodium in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Sodium concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

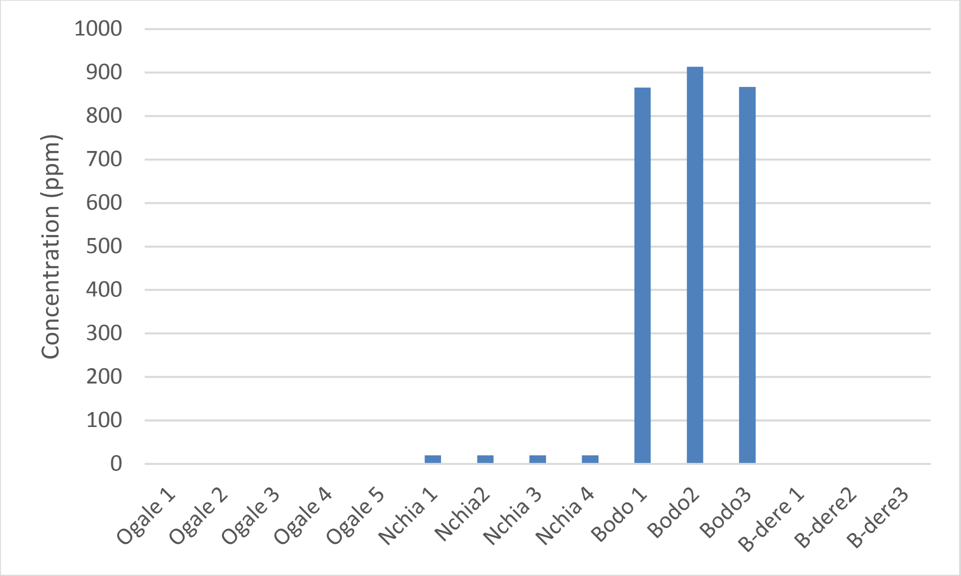

Figure 4.2 Concentration of Sodium in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Sodium concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.2 Potassium (K)

Potassium is an essential constituent of many fertiliser formulations, and its determination is often carried out in lakes, where an assessment of its nutrient input is undertaken. Potassium is fixed in soils, and as such, there are no toxic implications, except when exposure is at a gross level (UNEP 2008). WHO (2009) gave a guideline value for intake of potassium in drinking water as 10mg/l, while SON, USEPA, and the EU have no fixed limits.

K was detected in all the samples collected from the study area and the concentrations observed were within the range of 0.1 – 4.17 ppm. A similar study by Petronella *et al.* (2009), in Sabah east (Malaysia), presented values that were within the ranges of 0.25 – 4.28mg/l. Furthermore, their research suggested that the increase in the concentration of potassium may be as a result of the consistent use of NPK fertilisers by Malaysian farmers in the region, giving rise to elevated concentrations of potassium in the groundwater aquifer. Figure 4.3 below shows that groundwater samples tend to be very low in potassium.

In Gokana and Eleme LGA (Figure 4.3), the concentration of K in surface water samples was found to be high at Bodo when compared to the guideline values of the regulatory bodies. The elevated level of K in the surface water may have been due to the discharge of brines, salts and other by-products of the petrochemical industry in the area. A study by Liang *et al.* (2017) suggested that elevated levels of K could affect groundwater quality and the soil, thereby affecting the quality of food because of the presence of toxic elements in edible leaves. Hence, potassium contamination is an issue to be addressed in the sample collection site.

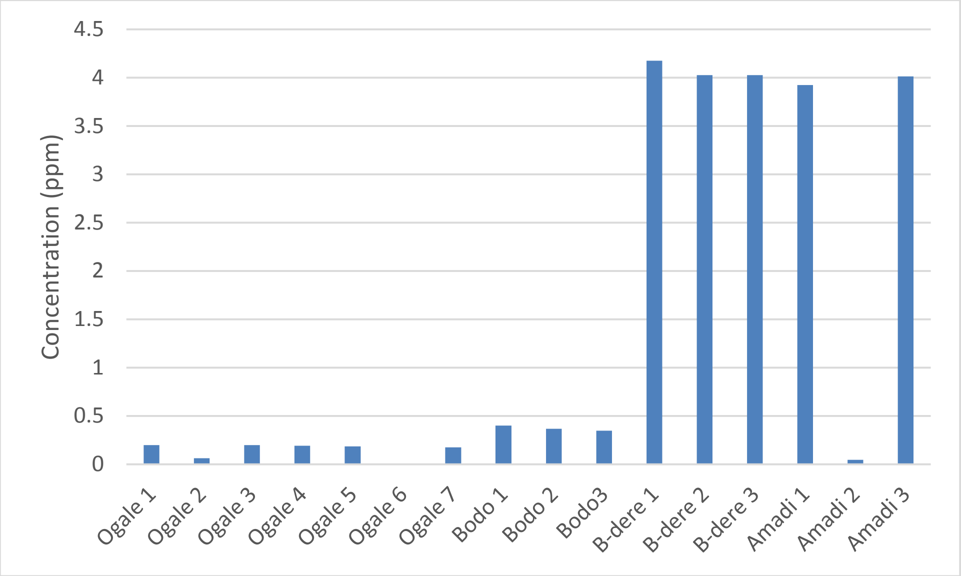

Figure 4.3 Concentration of Potassium in the groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Potassium concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

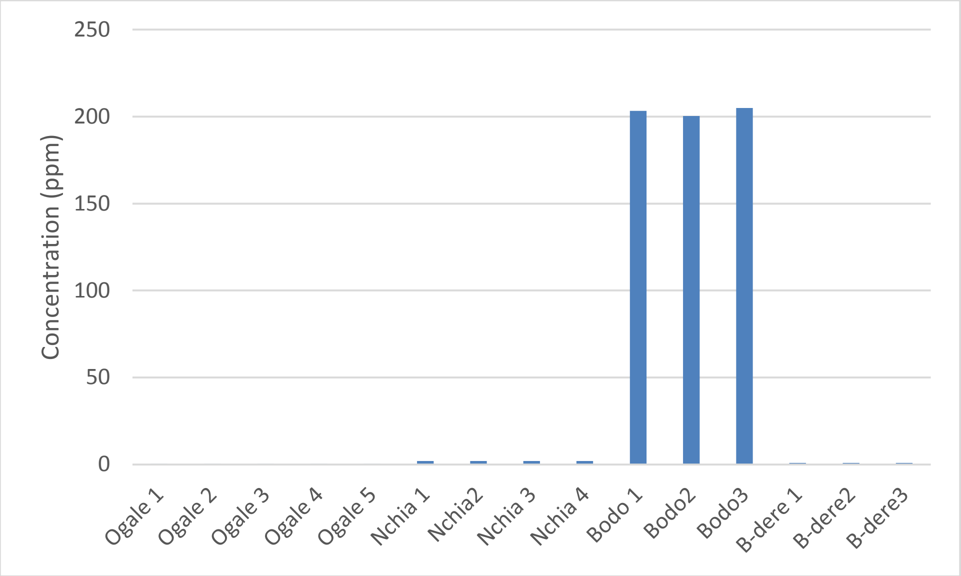

Figure 4.4 Concentration of Potassium in the surface samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Potassium concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.3 Calcium (Ca)

WHO (2004c) gives an objectionable limit for calcium in drinking water as 50-200 mg/l, while the Australian guideline value is 180 mg/l. Ca was detected in all groundwater samples collected from Ogoniland, and concentrations ranged from 0.04-14.7 ppm, thus falling within the range of the WHO (2006) permissible limit for calcium in drinking water. Figure 4.5 shows that the concentration of Ca was uniformly low, while analyses from Bodo and B-Dere showed similar concentrations of 4ppm in each sample.

Ca was detected in all surface samples in Ogoniland. The values ranged from 0.38-141.54 ppm, as seen in Table 4.2. In Figure 4.6, Ca was relatively low in Ogale, Nchia, and B-Dere (0.038ppm), while in Bodo, calcium concentrations were higher than the maximum WHO (2006) permissible limit for calcium in drinking water.

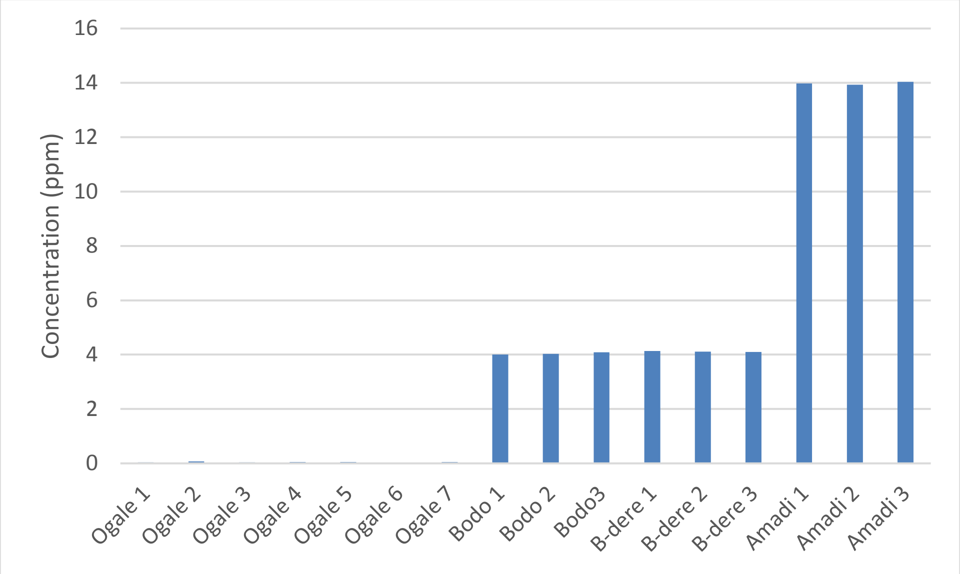

Figure 4.5 Concentration of Calcium in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Calcium concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

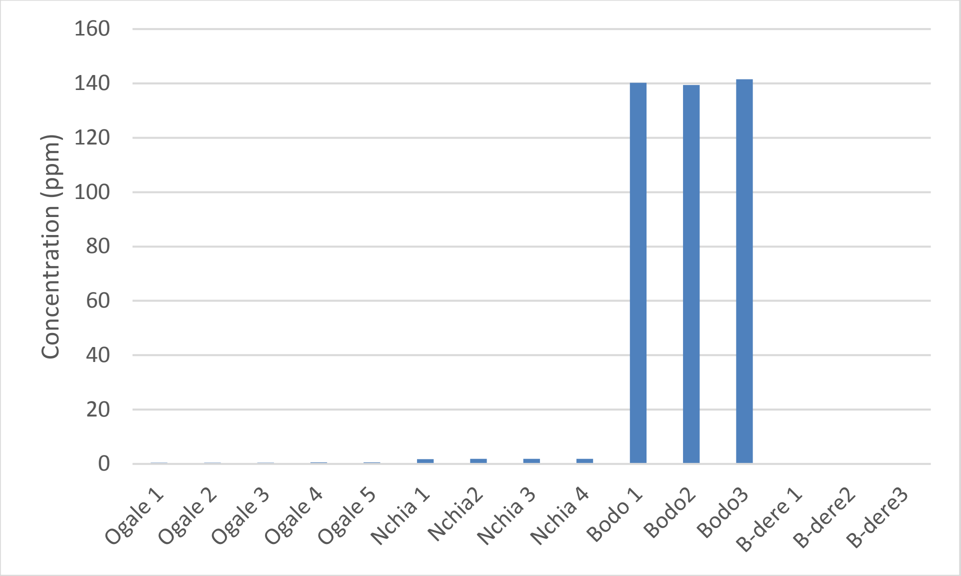

Figure 4.6 Concentration of Calcium in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Calcium concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.4 Iron (Fe)

Fe occurs in high abundance in soils and rocks and exists mainly in insoluble forms. Nevertheless, many complex reactions which occur naturally in ground formations can increase other soluble forms of iron in the groundwater aquifer (Harvlicka, 2011). DEFRA (2001) noted that large amounts of iron present in groundwater could result in severe problems such as blockage of pipes, and change in colour and taste in drinking water supplies. When in excess, iron can be quite harmful to aquatic life, as evident in laboratory studies (Zubrycki *et al.*, 2011). However, the degree of toxicity may be lessened by the interaction of the iron with other constituents of water (Emamverdian *et al.*, 2015).

Fe was detected in all groundwater samples, with the values ranging from <0 – 0.06ppm, as seen in Table 4.1. Figure 4.4 shows that Ogale 1, 3, 4, 5 & 7 reported relatively high, and consistent, concentrations, although there was a reduced concentration in Ogale 6 and no concentration was measurable in Ogale 2. Fe was not detected in B-Dere, Gokana, and Amadi-Ama.

Ngah and Abam (2014) suggested that some closed areas in Port Harcourt city showed high amounts of Fe (Table 4.2). Amajor (1987) explained that this was due to the geological history and type of rock deposits that constitute the aquifer in the Niger Delta. According to A major, the aquifers are made up of sands that originated from northern highlands of Kogi State, with solid brown colouration due to iron oxide coatings and stains; most of the sands are third cycle sands with very long transport history. The high rate of deposition associated with the Niger Delta may have preserved these iron-rich grains along with other iron minerals such as hematite, limonite, and magnetite and incorporated them into the geologic record. With slightly acidic and corrosive groundwater, the iron may have been leached from the iron minerals, stains, and coatings and liberated into groundwater flow systems. Pyritic clay interbeds, organic matter and lignite which abound in the area may also have provided sources for the leaching of iron from sedimentary rocks into the groundwater systems.

Higher Fe concentrations were observed in some of the surface water samples in Ogoniland. The values range from 0-2.23ppm, as seen in Table 4.1. Figure 4.7 shows that in Ogale 1, 2 & 3, the concentration of Fe was relatively high, and consistent, while there was a reduced concentration of Fe in Ogale 4 & 5.

The concentration of Fe was found to be high in Eleme-Nchia, though it fell under all regulatory guideline standards except that of the EU; other studies carried out in the Niger Delta show that Fe is a major quality issue in surface water in Bodo LGA.

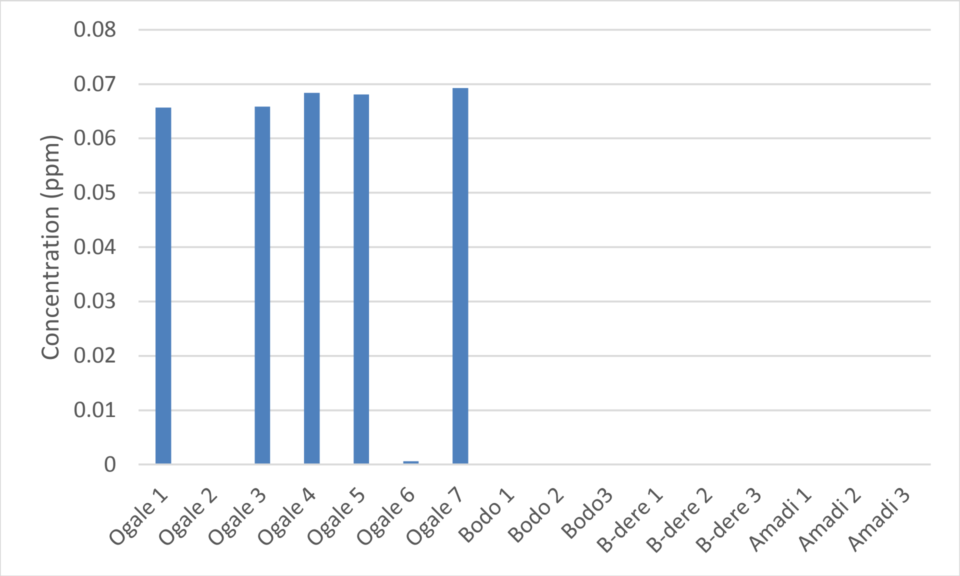

Figure 4.7 Concentration of Iron in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Iron concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

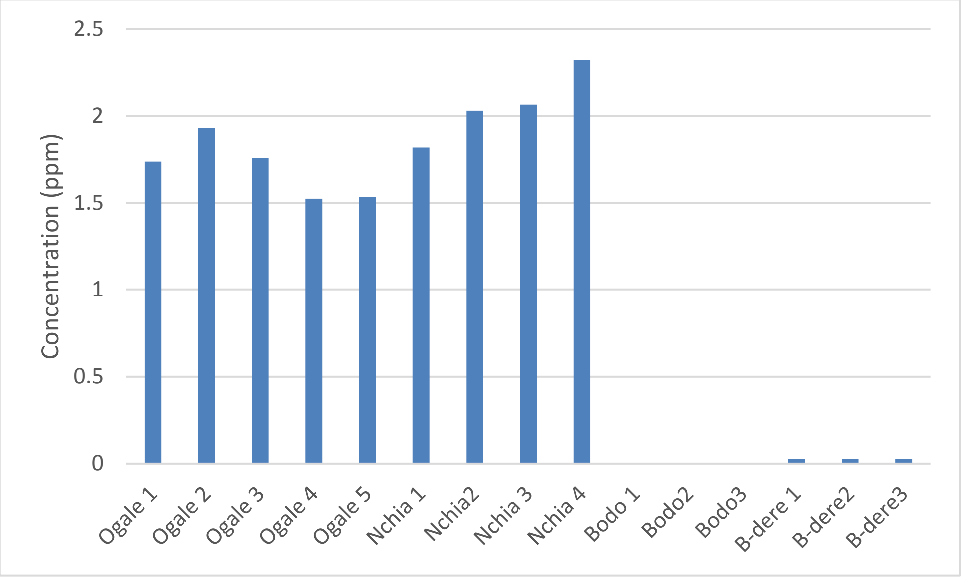

Figure 4.8 Concentration of Iron in Surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Iron concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.5 Manganese (Mn)

Manganese is a naturally occurring element, which is found in surface water, groundwater, or oxygen-depleted systems. The concentration of manganese is dependent on factors that include the aquifer lithology, rainfall chemistry and geochemical environment (Guo, 2018). Manganese also occurs in many food sources and, as such, reference limits of intake have been set by different regulatory bodies across the globe (WHO, 2004a).

In Gokana LGA, the groundwater samples (Figure 4.9) showed uniform Mn concentrations of below 0.1ppm, in B-Dere concentrations of less than 0.002 ppm, while Amadi Ama showed the highest Mn concentrations of 0.06ppm, which exceeds the WHO regulatory standard limit.

Figure 4.10 shows that the concentration of Mn in surface water samples from Ogale 1, 2, 3, 4 & 5 was within the range of 0.026-0.031 ppm. In Gokana LGA, Bodo and B-Dere, the results showed uniform concentrations of just below 0.003ppm Mn, which are within the WHO regulatory standard limit. Therefore, Mn is not a major water quality issue in Ogoniland.

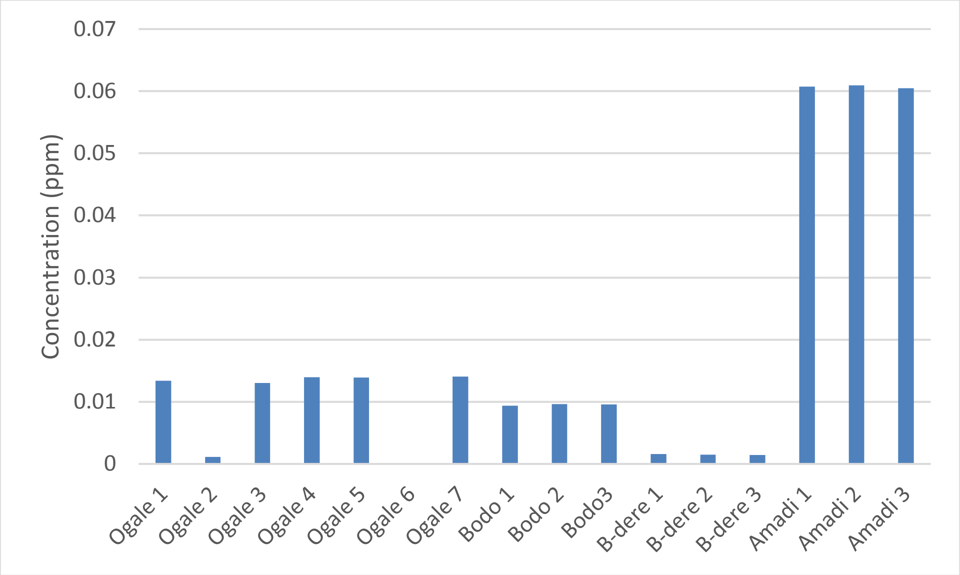

Figure 4.9 Concentration of Manganese in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Manganese concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

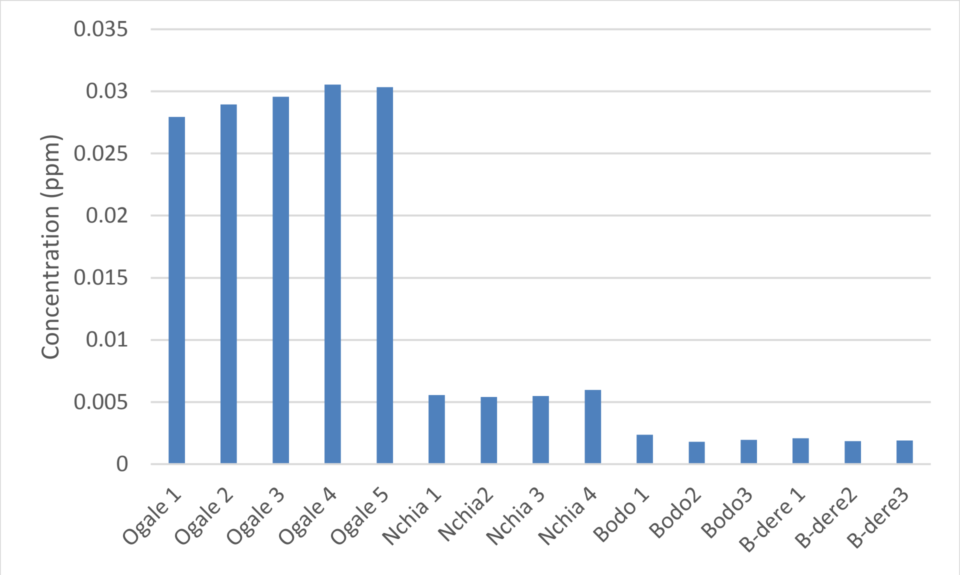

Figure 4.10 Concentration of Manganese in surface samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Manganese concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.6 Fluoride (F)

Several researchers around the world have reported fluoride contamination of ground water. A notable example is the assessment of the groundwater quality in Osor, Spain, that observed the concentrations of 2-8.26 mg/l, significantly higher than the WHO (2006) permissible level of

1.5 mg/l (Pandey *et al.*, 2012). Fluoride has beneficial effects on teeth at low concentrations in consumed water, but excessive exposure to fluoride in drinking water, or in combination with exposure to fluoride from other sources (e.g., diet), can give rise to some adverse effects, from mild dental fluorosis to crippling skeletal fluorosis (WHO 2006a).

In the current study, F was only detected in groundwater samples from Amadi Ama, in Port Harcourt City LGA (Figure 4.11). Amadi 1, 2 & 3 showed fluoride concentrations between 0.05 and 0.16 ppm in groundwater samples. Nwankwoala *et al.* (2011) noted a very high level (ranges from 0.010-2.33) of fluoride concentration in some parts of Port Harcourt city LGA. Fluoride was below detection limits at the three locations (Ogale, B-Dere & Bodo) in Ogoniland. Fluoride data from some water sources in different studies in Nigeria showed concentrations of 1.48 mg/l. Also, it has been found that 42 (45.16%) water sources out of 93 sources had fluoride above the WHO standard (Table 1). Therefore, the presence of slightly high fluoride concentration in water relative to the WHO standard and presence of almost fifty per cent of water sources with fluoride concentration above 1.5 mg/l in Nigeria, increases the chances of fluoride exposure. This, in turn, increases fluoride's negative impact in Nigeria, classifying it as a fluoride affected Country (Malago *et al.*, 2017). The findings in this study area, however, show low concentrations compared to the WHO limit, indicating that F is not a major groundwater contaminant in the study area.

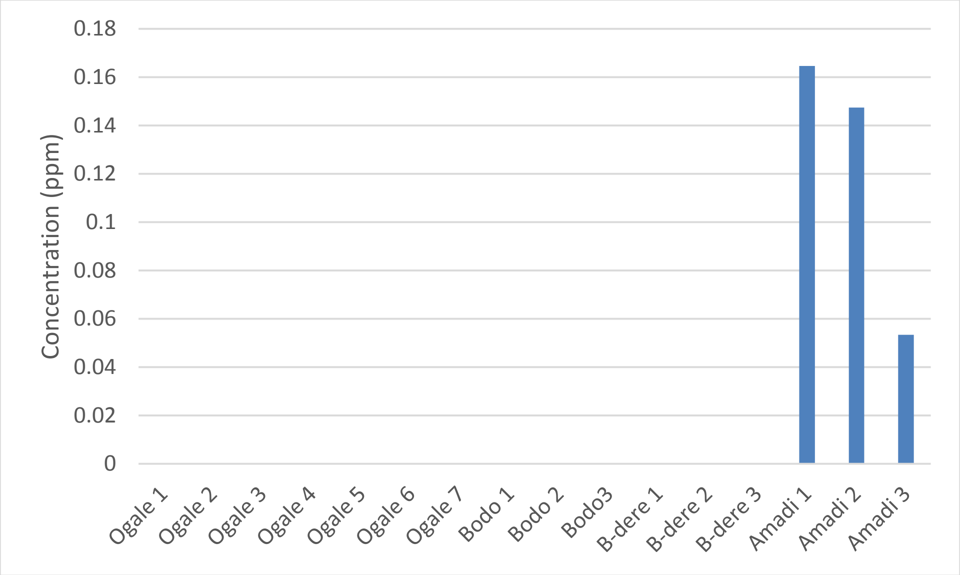

Figure 4.11 Concentration of Fluoride in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Fluoride concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

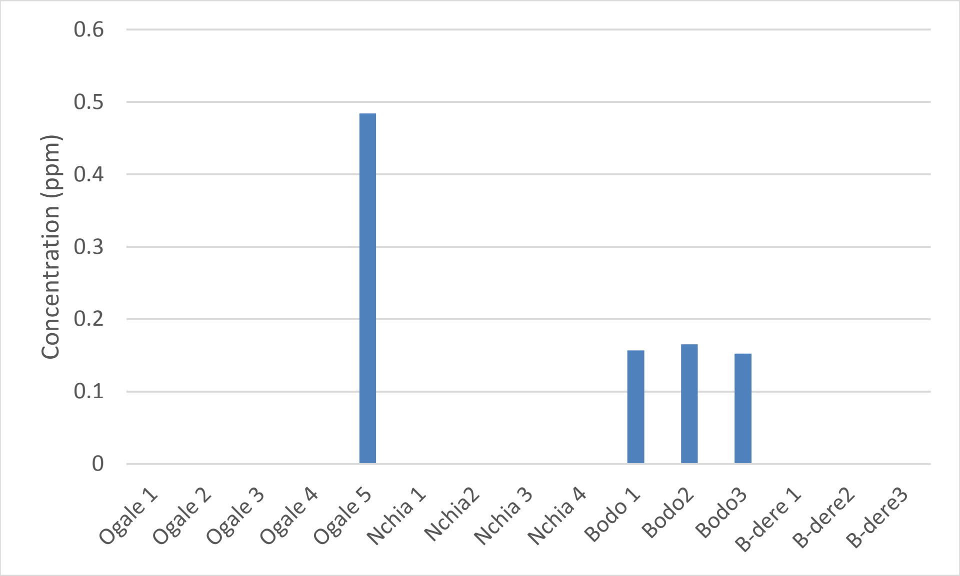

Figure 4.12 Concentration of Fluoride in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Fluoride concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.7 Chloride (Cl)

The WHO have not placed any guideline values on chloride in drinking water but have an objectionable limit of 200mg/l. Chloride exists in all natural waters, the concentrations varying very widely and reaching a maximum in seawater (up to 35,000 mg/l Cl).

The findings of this study show that chloride was detected in all groundwater samples in Ogoniland, with values ranging from 0.10 – 20.1ppm (Figure 4.13). The concentration of Cl in Amadi Ama (20ppm) was much higher than that observed at all other locations. According to Ngah and Abam (2014), the concentration of chloride may be as a result of brackish water infiltration from nearby creeks and tidal channels. The findings in this study show that the concentration of chloride was within the WHO objectionable limit. In previous works in the Niger Delta, Amadi (2004) suggested that chloride was very high mostly in the coastal areas bordering saltwater creeks and tidal channels, and also in coastal areas due to sea spray, or seawater infiltration, and was not necessarily caused by industrial discharges.

The finding of this study (Figure 4.14) shows that chloride was detected at deficient levels in all surface samples in Ogoniland. The concentration of Cl in Bodo 1 (10ppm) was much higher than those observed at all other sample locations.

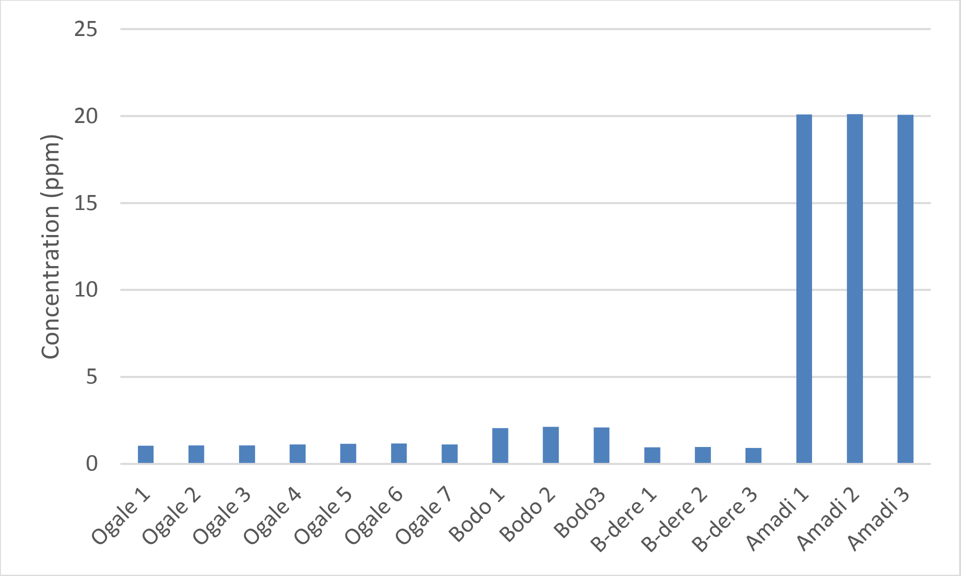

Figure 4.13 concentration of Chloride in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Chloride concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

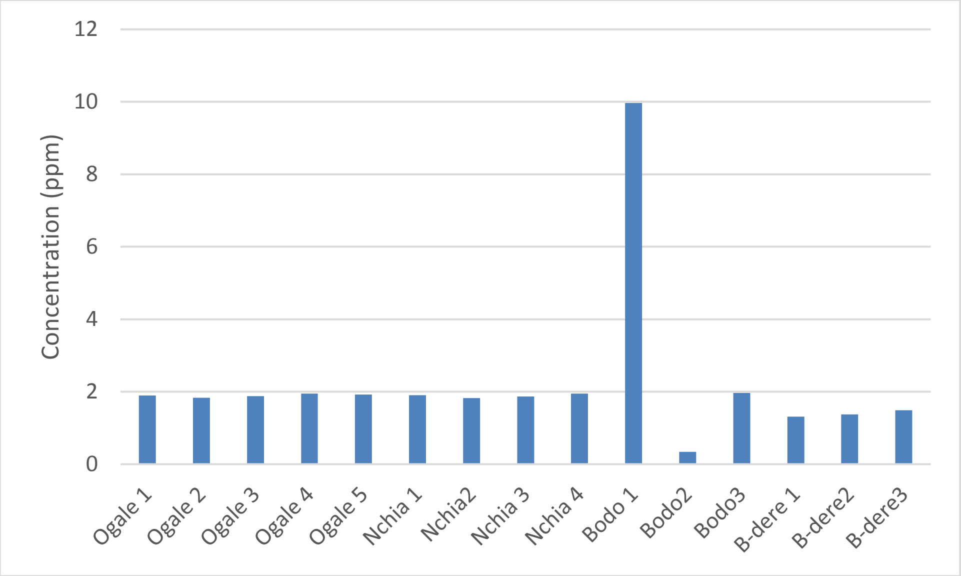

Figure 4.14 Concentration of Chloride in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Chloride concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.8 Nitrate

Nitrate contamination is a problem to drinking water sources (groundwater and well water) and can occur via leaching of the soil (due to prolonged use of NPK fertiliers) or accumulation due to mishandling or accidental spillage of nitrogenous materials (Wick *et al.*, 2012). To this effect, the WHO (2006) established a guideline value for nitrate intake in drinking water, the ultimate aim of which was to reduce the contaminant's concentration to levels near to those prescribed in the maximum concentration level. The WHO gave a harmless acceptable limit of 10 mg/l; the EU gave a fixed limit of 11mg/l, while the maximum permissible limits given by SON and Australia were 50 mg/l.

According to the findings of this research, Nitrate was detected in groundwater in all sample locations (Figure 4.15). The values present ranged from 0 – 279 ppm, as seen in Table 4.1. The concentration of nitrate was highly variable in the Ogale samples, with a maximum recorded value of 279ppm in Ogale 6. Ogale 1, 3, 4 and seven recorded concentrations below detection limits. In Gokana LGA, Bodo and B-Dere samples showed similar concentrations in all samples. The findings in this study area show a very high concentration of nitrate in groundwater compared to every acceptable regulatory limit. Hence, nitrate is a major groundwater contaminant in the study area; the populace of the study area may be at risk of health effects such as methemoglobinemia, stomach cancer and blue baby syndrome (WHO, 2006a) if exposed at gross levels.

In Ogale, the concentration of Nitrate in the surface water samples was below detection, while in Nchia it was also relatively low. In Gokana, samples from Bodo were low in concentration while B-Dere was below detection (Figure 4.16). Nitrate concentration in the surface water samples is very low compared to all regulatory standards and other studies carried out in the Niger Delta.

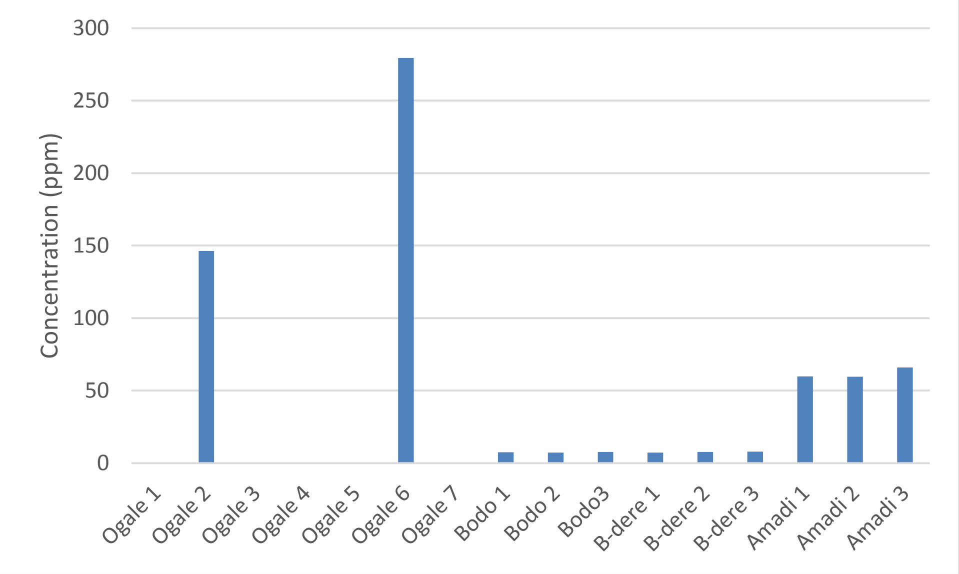

Figure 4.15 Concentrations of Nitrate in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Nitrate concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

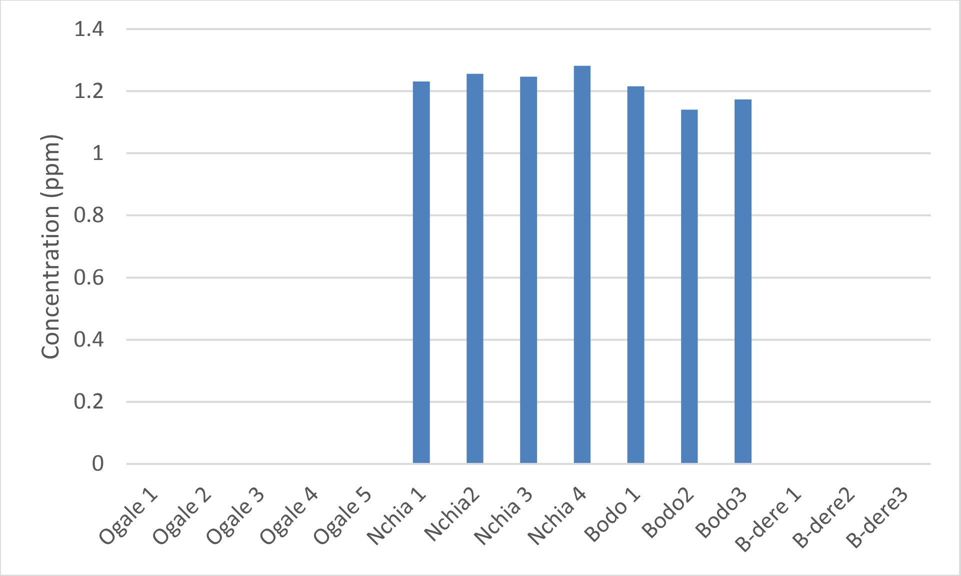

Figure 4.16 Concentrations of Nitrate in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Nitrate concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample.

4.2.9 Sulfate

Sulphur is present in deposits of iron sulphides, which dissolve to release sulphates, which leak into the groundwater aquifer and may contaminate the groundwater. This prompted world regulatory bodies such as the EU and USEPA to present guideline values which would provide a permissible limit of exposure to sulfate in groundwater. According to Otokunefor and Obiukwu (2005) and Riley and Chester (2016), iron sulphides are present in the marine sediments in the Niger Delta.

Sulfate was detected in all groundwater samples in the study area, at concentrations ranging from 0.7 – 7.8ppm, well below the EU and USEPA permissible limits of 250mg/l. Figure 4.17 shows that the B-Dere and Amadi samples, while still low, show a higher concentration than at Bodo and Ogale. B-Dere and Amadi samples are broadly similar. The findings in the study area indicate a very low concentration of sulfate compared to every acceptable regulatory limit. Figure 4.18 shows that the concentration of sulfate in surface waters was very high at Bodo (2 out of 3 samples) and exceeds all regulatory standards. Therefore, sulfate is a major quality issue in surface water in Gokana LGA.

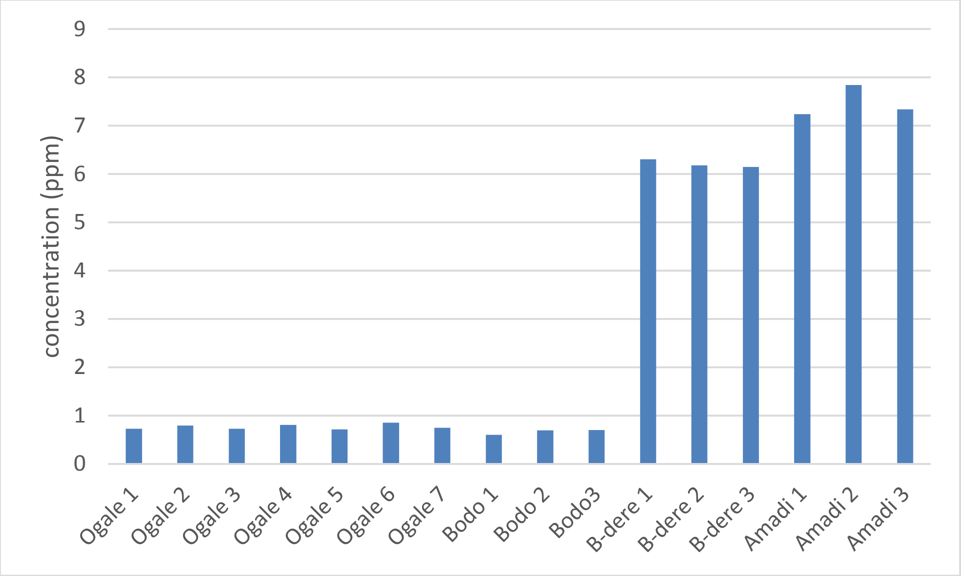

Figure 4.17 Concentrations of Sulphate in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Sulphate concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

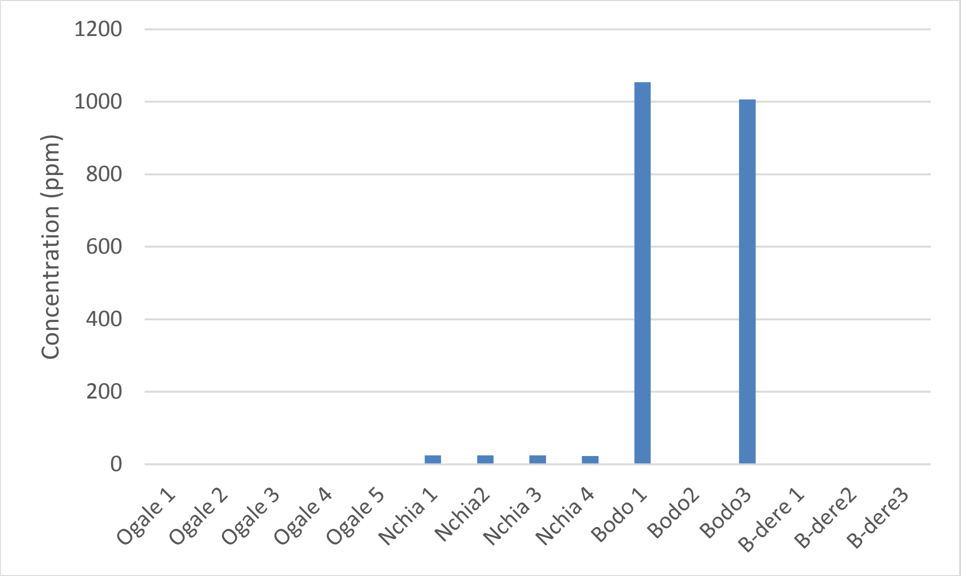

Figure 4.18 Concentrations of Sulphate in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Sulphate concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.10 pH

pH is the negative logarithm of the hydrogen ion concentration of a solution, which measures whether the liquid is acidic or alkaline. The pH scale (derived from the ionisation constant of water) ranges from 0 (very acidic) to 14 (very alkaline) (Chapman and Kimstach, 1992). Low pH, which means that there is a high concentration of hydrogen ions, can affect water taste, but the corrosive effect on distribution systems is a more urgent problem; this has also led to fish mortality due to increased acidity.

pH values observed in Ogoniland groundwater samples fell within the range 4.2 – 8.1, which is within the limit of the WHO (1983) standard for drinking water. Figure 4.19 shows that all samples in Ogale had a low pH, within the range of the minimum desirable limit, except for Ogale 4 which showed an alkaline pH above the minimum desirable limit. In Gokana LGA, Bodo samples analysed showed a high pH which exceeds the minimum desirable limit. At B-Dere, samples analysed showed neutral to slightly acid pH.

From Figure 4.19, Ogale, Bodo, and B-Dere recorded a higher pH value when compared to the Port Harcourt city LGA (Amadi-Ama). The findings in this study area show that pH seems to be very acidic at Amadi-Ama (4 – 5); this may be as a result of gas flaring from oil-related activities carried out in the region. The flaring of gas may be responsible for the acidity of the pH value because the methane gas which is flared may have reacted with moisture to form carbonic acid which penetrates the ground surface with rainfall and leaks into the groundwater aquifer.

Figure 4.20 shows that all surface samples in Ogale showed a neutral to alkaline pH which was within the range of the guideline limit, while Nchia showed a uniform pH above the minimum desirable limit. In Gokana LGA, Bodo and B-Dere samples analysed showed neutral to slightly alkaline pH.

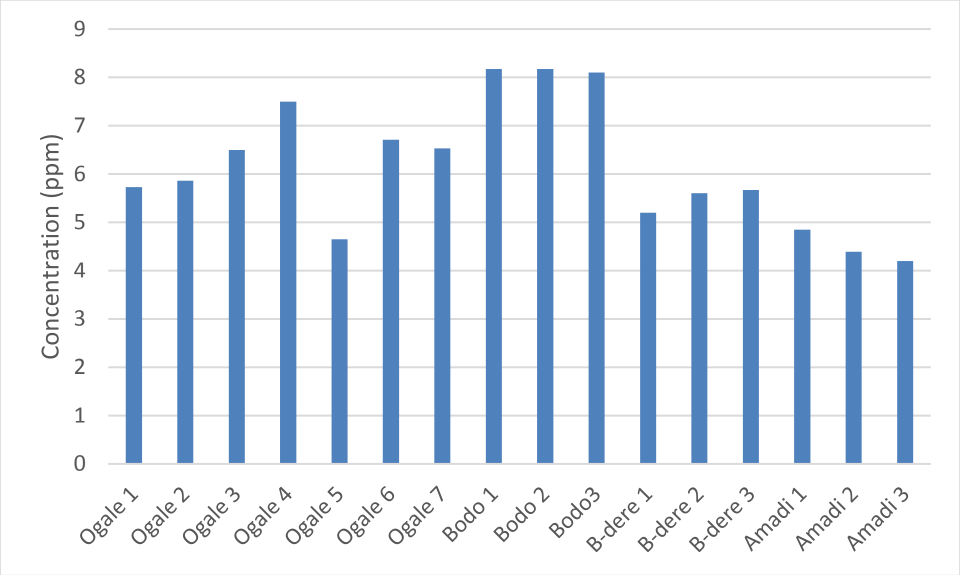

Figure 4.19 pH value in groundwater samples collected from Eleme, Gokana and Port Harcourt LGA. The y-axis shows pH (from 0, acid, to 9, alkaline). The x-axis shows the regions in the local Government areas being explored and the sample numbers.

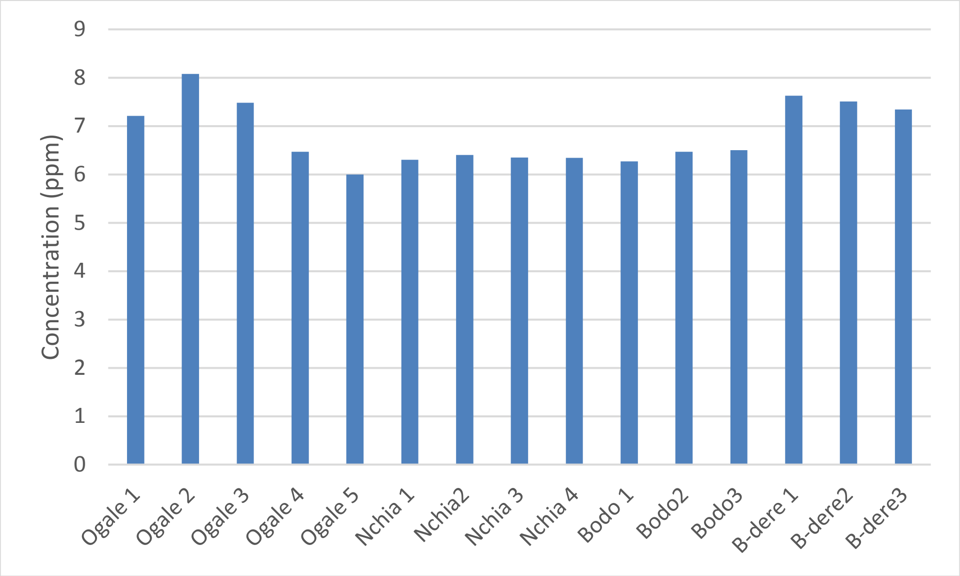

Figure 4.20 pH value in surface water samples collected from Eleme, Gokana and Port Harcourt LGA. The y-axis shows pH (from 0, acid, to 9, alkaline). The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.11 Total Dissolved Solids (TDS)

Dissolved solids were detected in all groundwater samples in Ogoniland. Values range from 3 – 168ppm (Table 4.1). WHO (1984) gave an acceptable upper limit of 500mg/l. Figure 4.21

shows that TDS in all groundwater samples in Ogale were low when compared to the other sample locations. In Gokana, Bodo LGA, samples analysed show a slightly higher (but still within acceptable limits) concentration of TDS. In B-Dere, the samples analysed show a low concentration level of TDS. Thus, dissolved solids are not a major water quality issue in groundwater and surface water across the study area.

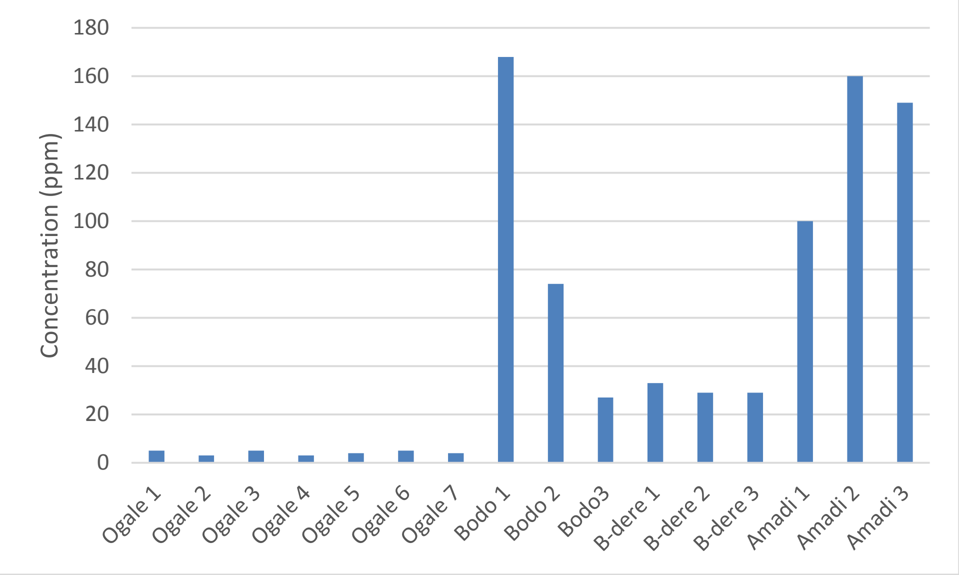

Figure 4.21 Total dissolved solids (TDS) in groundwater from Eleme, Gokana and Port Harcourt LGA. The y-axis shows TDS concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

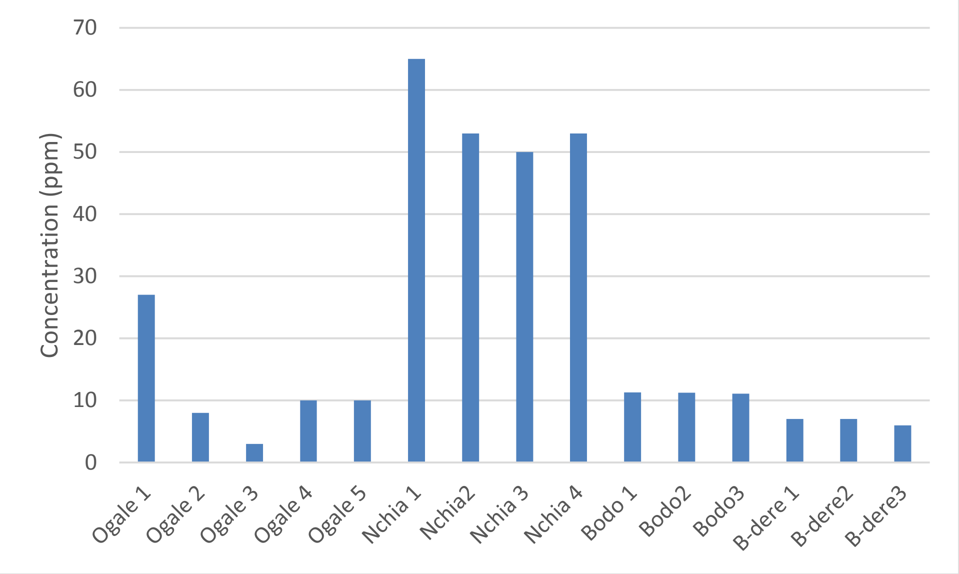

Figure 4.22 Total dissolved solids (TDS) in surface water from Eleme, Gokana and Port Harcourt LGA. The y-axis shows TDS concentrations in parts per million. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.12 Electrical Conductivity (EC)

The WHO (1983) standard for electrical conductivity (EC) in drinking water is 40µS/cm. EC reflects the mineral salt content of water and presents no significant hazard to health. The conductivity of water is an expression of its ability to conduct an electric current. As this property is related to the ionic content of the sample, which is, in turn, a function of the dissolved (ionizable) solids concentration, the relevance of easily performed conductivity measurements is apparent (Weaver *et al.*, 2007).

EC values in Ogoniland range from 6 – 279µS. Figure 4.23 shows that all groundwater samples in Ogale showed very low salinity, although WHO EC standards were still exceeded. In sample locations such as Gokana LGA, Bodo, the Bodo-1 sample showed a very high EC value of > 250 µS, while Bodo-2 and -3 showed significantly lower values. The Amadi-Ama samples also showed relatively high EC values. Of the surface water samples (Figure 4.24), the Nchia samples show the highest EC, at 80 – 100 µS.

The findings in this study area agree with previous reports. For example, Egborge (1994) reported that the water was brackish in his study of Warri River, in the Niger Delta, while a further study on EC carried out by several authors in the Niger Delta by Nwadiaro (1989), Agbozu and Emperor (2004), Agbozu and Izidor(2004), and Obunwo (2003), indicated high levels of EC in this area. This indicates that EC is a major quality issue in the ground and surface water in these locations and all the groundwater samples studied have a higher salt concentration than the required WHO standard for drinking water, except Ogale.

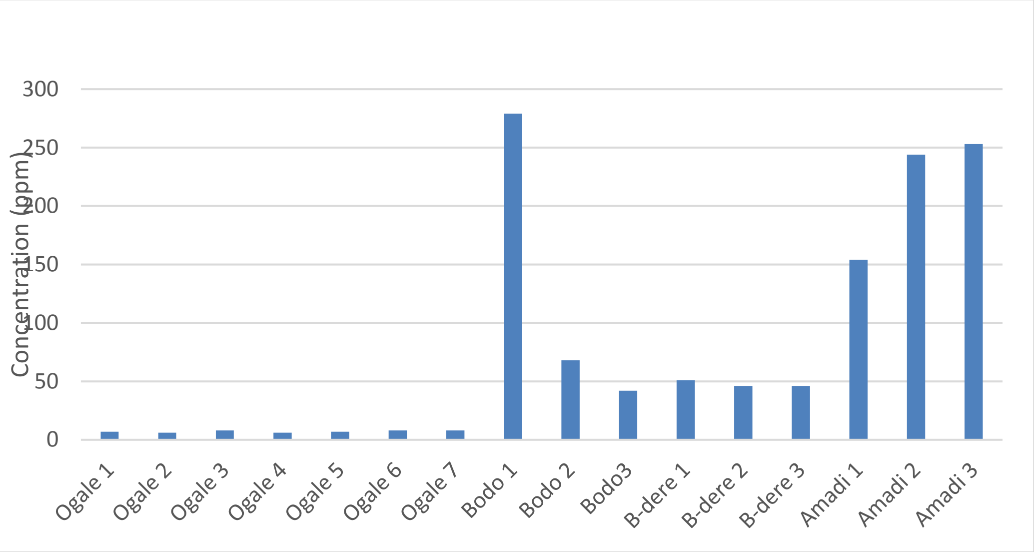

Figure 4.23 Value of Electrical Conductivity in ground water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Electrical Conductivity in microsieverts (µS). The x-axis shows the regions in the local Government areas being explored and the sample numbers.

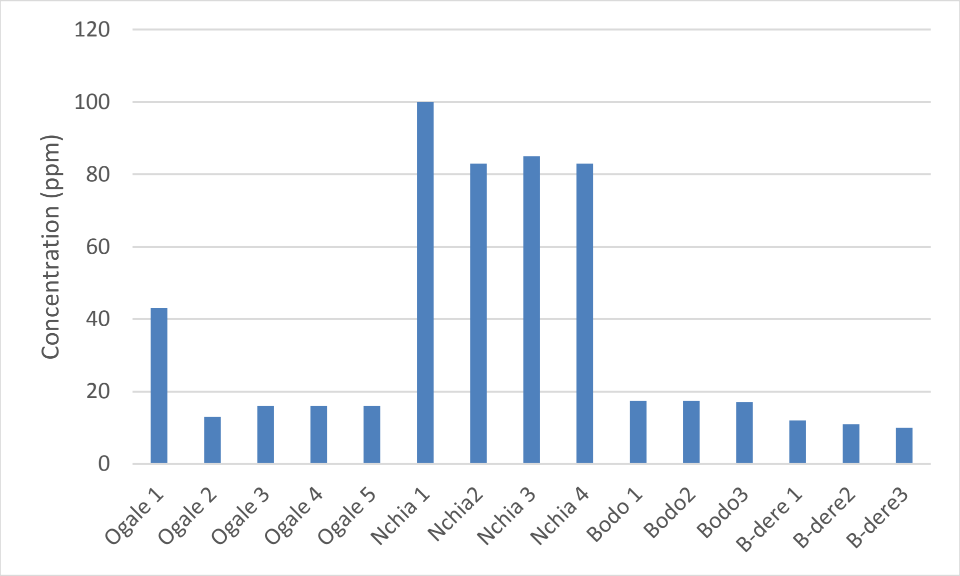

Figure 4.24 Value of Electrical Conductivity in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Electrical Conductivity in microsieverts (µS). The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.2.13 Turbidity

The WHO (1983) standard for turbidity in drinking water is 1 NTU. Turbidity is analysed via a range of methods, although the Aqua-probe was used in this study. Its origins are from very finely separated clay particles, sewage solids, silt, etc. (Omar and Mohd, 2010), which cannot be filtered by a standard approach.

Turbidity values were recorded for all groundwater samples in Ogoniland (Figure 4.25). The values range from 12.2 – 25.3 NTU, as seen in Table 4.1. WHO (1984), EU and Canada gave a permissible limit of 1 NTU. However, Australia, SON, and USEPA gave a limit of 5 NTU. Studies from several authors from the Niger Delta give ranges from 2-14 NTU as seen in Table 4.2. Figure 4.25 shows that all samples from Ogale showed high turbidity, ranging from 12 – 30 NTU; Bodo, B-Dere, and Amadi-Ama show similar concentrations.

Very high turbidity levels in surface water samples from the study area (Figure 4.26) are likely due to washing of debris, silt, and clay into the creeks. Obunwo (2003) and Asuquo and Etim (2012) also reported that high turbidity could result from the presence of colloidal particles arising from clay and silt during rainfall, or from discharges of sewage and hydrocarbon waste or the presence of large numbers of microorganisms. Turbidity is an important operational parameter in process control and can indicate problems with treatment processes, particularly coagulation/sedimentation and filtration (Chinda *et al.*, 2008). Turbidity is a major water quality issue in ground and surface water in the sample locations, and all water samples studied have a higher concentration than the required limit for drinking water.

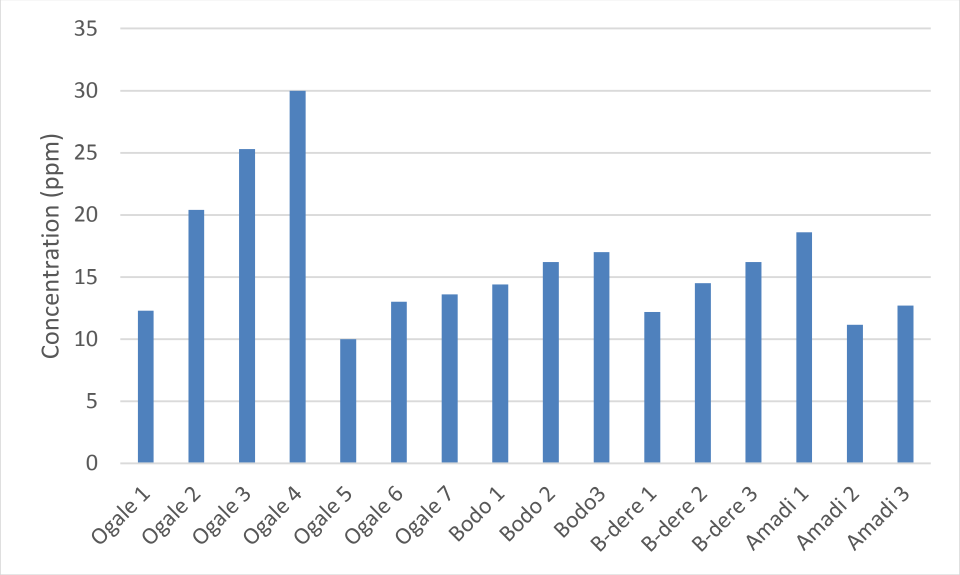

Figure 4.25 Value of Turbidity in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Turbidity in NTU. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

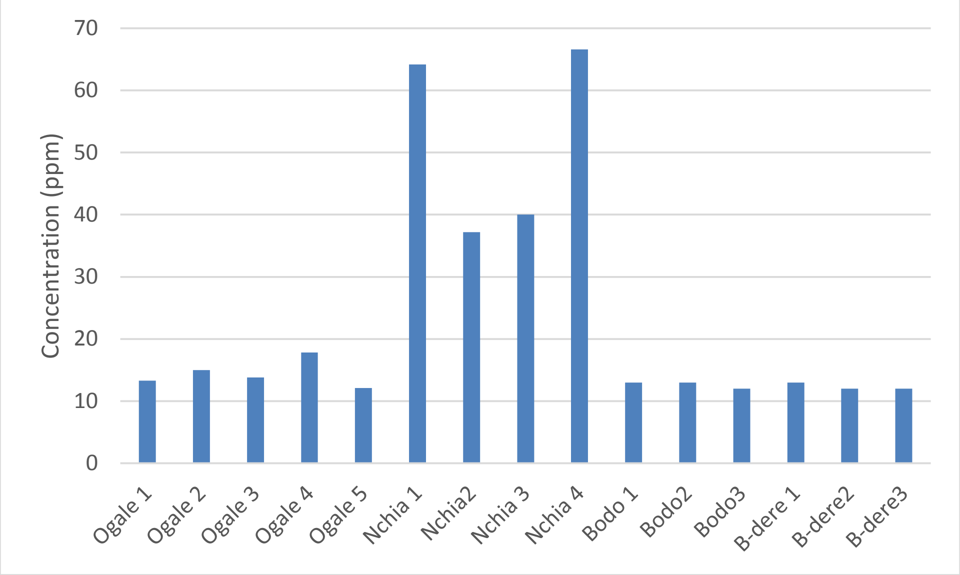

Figure 4.26 Value of Turbidity in surface water samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Turbidity in NTU. The x-axis shows the regions in the local Government areas being explored and the sample numbers.

4.3 ELEMENTAL AND PARAMETER CORRELATIONS

4.3.1 Correlation of chemical parameters in groundwater in Eleme and Gokana LGAs

The correlation coefficient is generally used to evaluate the relationship between two variables (Bahaz and Reza, 2010). It is a simple measure taken to predict how one variable is influenced by the other. A correlation coefficient (r) of +1 indicates that two variables are perfectly related in a positive linear sense, but r = -1 indicates a negative linear correlation. However, no relationship between two variables exists if r = 0.

In Table 4.3 below, red values show a statistically significant correlation (at 95% confidence). The data illustrate that Na and Ca show a statistically significant positive correlation at 95% confidence, with Mn, Fluoride, Chloride, Sulphate, EC and Salinity. According to Edet *et al.* (2011), these correlations indicate that the ions are derived from the same source. The strong positive correlation between Na v Chloride may represent the influence of saline water, either from seawater ingress or saline/brine discharges from local industry. The high positive correlation between Na – Ca represents ion exchange or brine discharges. Of the other parameters:

- Potassium has a statistically significant correlation with calcium and sulphate
- Calcium also has a significant correlation with Fe, Mn, Mg, Chloride, sulphate, TDS, EC, salinity
- Iron has a significant correlation with TDS, salinity
- Manganese has a significant correlation with Mg, Fluoride, chloride, sulphate, pH, TDS, EC, salinity
- Magnesium has a significant correlation with Fluoride, Chloride, Nitrate, sulphate, pH, TDS, EC, Salinity
- Fluoride has a significant correlation with Chloride, Mg, sulphate, pH, TDS, EC
- Chloride has a significant correlation with sulphate, pH, EC, Salinity
- Nitrate has a significant correlation with sulphate, pH, TDS, EC, Salinity
- TDS has a significant correlation with EC and Turbidity
- EC has a significant correlation with Turbidity

Overall, and despite local (inter-sample) variability, correlations indicate a dominant control of salinity (either via seawater ingress or industrial (e.g. brine) discharges) on groundwater major ion composition, coupled with the influence of local geology, with a lesser control exerted by pH and other environmental parameters such as turbidity.

Table 4.3 Correlation matrix between major ions (surface water samples). N = 16. Values shown in red exceed the critical value (95% confidence) of 0.497 for 16 data points. Corresponding critical values for 90% and 99% confidence are 0.426 and 0.623

	Na	K	Ca	Fe	Mn	Mg	Fluoride	Chloride	Nitrate	Sulfate	pH	TDS	EC	Turbidity	Salinity
Na		0.46	0.97	-0.35	0.94	1.00	0.90	0.98	-0.04	0.81	-0.61	0.22	0.65	-0.28	1.00
K			0.51	-0.46	-0.21	0.48	-0.24	-0.32	-0.15	0.80	-0.49	-0.22	-0.24	-0.16	0.43
Ca				-0.52	0.87	0.98	0.24	0.94	0.00	0.80	-0.49	0.81	0.80	-0.25	0.71
Fe					-0.09	-0.39	-0.25	-0.29	-0.33	-0.49	0.00	-0.50	-0.48	-0.26	-0.56
Mn						0.93	0.89	0.97	0.00	0.59	-0.54	0.68	0.68	-0.13	0.51
Mg							0.90	0.98	-0.05	0.82	-0.61	-0.74	-0.74	-0.22	0.66
Fluoride								0.91	-0.12	0.66	-0.52	0.61	0.59	-0.12	0.49
Chloride									-0.13	0.70	-0.57	0.07	0.73	-0.18	0.58
Nitrate										-0.03	-0.10	-0.04	-0.03	-0.11	-0.10
Sulfate											-0.71	0.50	0.51	-0.28	0.61
pH												0.49	0.47	0.43	
TDS													1.00	0.92	
EC														0.91	
Turbidity															
Salinity															

4.3.2 Correlation of chemical parameters in surface water in Eleme and Gokana LGAs

In Table 4.4 overleaf, as previously, red values show a statistically significant correlation (at 95% confidence). From Table 4.4:

- Sodium has a significant correlation with K, Ca, Fe, Mg, Chloride, Bromide, Nitrate, sulfate, Salinity
- Potassium has a significant correlation with Ca, Fe, Mg, Bromide, Nitrate, sulfate, Salinity, TDS
- Calcium has a significant correlation with Fe, Mg, Bromide, Nitrate, sulfate, salinity
- Iron has a significant correlation with Mn, Mg, Bromide, TDS, EC, Salinity
- Mn has a significant correlation with Nitrate

- Mg has a significant correlation with bromide, Nitrate, sulfate, salinity
- Chloride has a significant correlation with sulfate,
- Nitrate has a significant correlation with pH, TDS, EC, salinity
- TDS has a significant correlation with EC, Turbidity
- EC has a significant correlation with Turbidity

As observed for groundwater samples, correlations indicate a dominant control of salinity (either via seawater ingress or industrial (e.g., brine) discharges) on surface water major ion composition, coupled with the influence of local geology. Based on the correlations observed, the control of salinity is more pronounced in surface water than in groundwater samples.

Table 4.4 Correlation matrix between major ions (surface water samples). N = 16. Values shown in red exceed the critical value (95% confidence) of 0.497 for 16 data points. Corresponding critical values for 90% and 99% confidence are 0.426 and 0.623.

	Na	K	Ca	Fe	Mn	Mg	Fluoride	Chloride	Bromide	Nitrate	Sulfate	pH	TDS	EC	Turbidity	Salinity
Na		1.00	1.00	-0.60	-0.42	1.00	-0.36	-1.00	1.00	0.52	0.76	-0.34	-0.24	-0.27	-0.28	1.00
K			1.00	0.61	0.41	1.00	-0.36	-0.44	1.00	0.50	0.79	-0.33	-0.81	-0.28	-0.29	1.00
Ca				-0.60	-0.41	1.00	-0.36	-0.44	1.00	0.51	0.78	-0.34	-0.25	-0.28	-0.29	1.00
Fe					0.54	-0.61	-0.19	-0.20	0.61	0.09	-0.46	-0.16	0.62	0.65	0.19	-0.61
Mn						-0.41	-0.17	0.12	-0.41	-0.60	0.33	-0.19	-0.23	-0.26	-0.25	-0.41
Mg							-0.37	-0.44	1.00	0.50	0.78	-0.33	-0.29	-0.26	-0.30	1.00
Fluoride								-0.17	0.37	-0.01	0.27	-0.49	-0.28	-0.30	-0.30	0.37
Chloride									0.44	0.27	0.71	-0.26	-0.07	-0.08	-0.09	0.45
Bromide										0.50	0.78	-0.33	-0.26	-0.29	-0.30	1.00
Nitrate											-0.42	-0.68	0.67	0.65	0.61	-0.50
Sulfate												-0.29	-0.18	-0.20	-0.21	0.25
pH													-0.49	-0.47	-0.43	
TDS														1.00	0.92	
EC															0.91	
Turbidity																
Salinity																

4.4 TRACE ELEMENTS AND HEAVY METAL CONTAMINANTS

Trace metals are elements which are naturally occurring at 1000mg/kg or less in the earth's crust. These elements can be categorised as heavy or light, concerning their density. Heavy metals have densities greater than 5g/cm^3 while light metals have densities less than 5 g/cm^3

(Osuji and Onojake, 2006). Extreme levels of trace heavy metals may occur in the environment, because of normal geological occurrences such as ore formation, weathering of rocks, and leaching (e.g., Hg). Meanwhile, their toxic effects can be long-lasting, unlike the organic contaminants that decompose into other, less toxic, molecules with time (Raymond and Okieimen, 2011).

Heavy metals can be very toxic even at low concentration, and their concentrations in biota (for some metals) can increase through bio-accumulation (Mahipal *et al.,* 2016). Many activities can lead to an excessive release of these metals into the environment; these include burning of fossil fuels, smelting, and discharges of industrial, agricultural, and domestic wastes, as well as the deliberate application of pesticides on crops in farmland (Singru, 2011). Human activities such as petroleum drilling and mining, as well as oil spillage, are also major sources of these metals (Nkpaa *et al.,* 2013).

This section focuses on those metals (As, Cu, Cd, Ni, and Pb) which are reported as being normal constituents of crude oil spillages around the Niger Delta (Avwiri, 2013). Table 4.5 below shows a comparison of guideline value of trace metals in drinking water by different world regulatory bodies.

Table 4.5 Comparison of guideline values by world regulatory bodies measured in ppb. Where NI means Nigeria Standard, and Ns means No Standard.

Parameters	**WHO**	**NI**	**USEPA**	**Australia**	**EU**	**Canada**
As	10	10	10	7	10	10
Cu	2000	1000	1,300	Ns	Ns	Ns
Cd	3	3	5	2	5	5
Ni	70	20	Ns			
Pb	10	10	15	10	10	10
U	15	Ns	30	20	Ns	20
V	Ns	Ns				

4.4.1 Arsenic (As)

Arsenic contamination in groundwater may occur as a result of the oxidation of sulfide found in rock deposits, or due to agricultural activities such as irrigation, which depletes the groundwater of oxygen and releases sediment-bound arsenic (Punshon *et al.*, 2017). Arsenic is present in the groundwater of some countries, and in Ogoniland, where most communities depend primarily on groundwater use. Recent studies have indicated the presence of gross concentrations of arsenic in some countries; a notable example is a study by Shiv *et al.* (2014), who stated that the groundwater arsenic contamination in Bangladesh is reported to be the biggest poisoning event in the world regarding the affected population. Furthermore, the groundwater was severely contaminated above any permissible limits in guideline values provided by appropriate regulatory bodies around the globe.

Arsenic was found to be present in groundwater in all of the sample locations. The concentrations detected were within the range of 0.02 – 0.12 ppb (Figure 4.27), and are consistent with a similar study by Arpan and Paul (2016) and Ejike *et al.* (2017) who recorded values of 0.04 – 0.09 ppb in Delta state, Nigeria. Highest concentrations of As were found in Ogale and Amadi-Ama, although all As concentrations are well below regulatory guideline values.

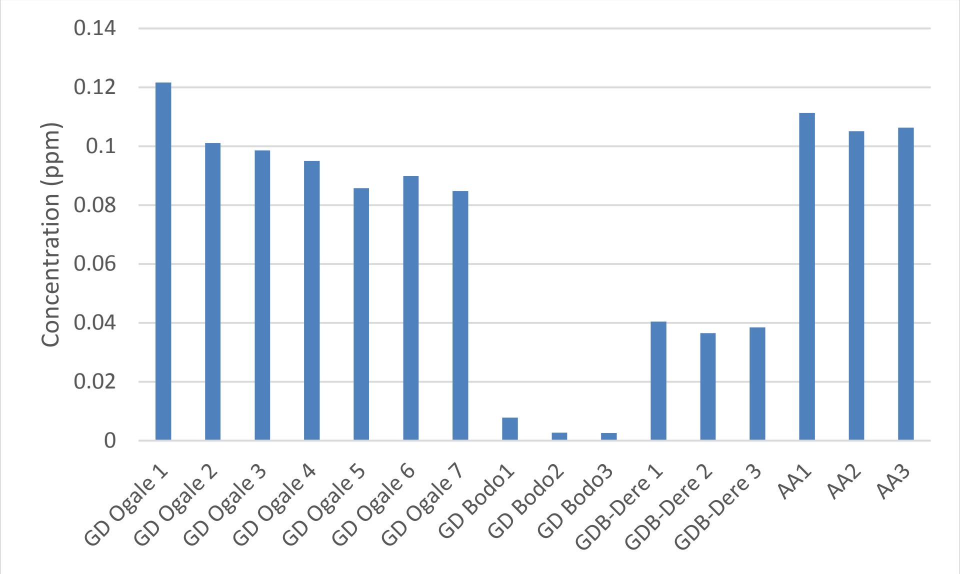

Figure 4.27 Concentration of Arsenic in groundwater samples from Eleme, Gokana and Portharcourt LGA. The y-axis shows Arsenic concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

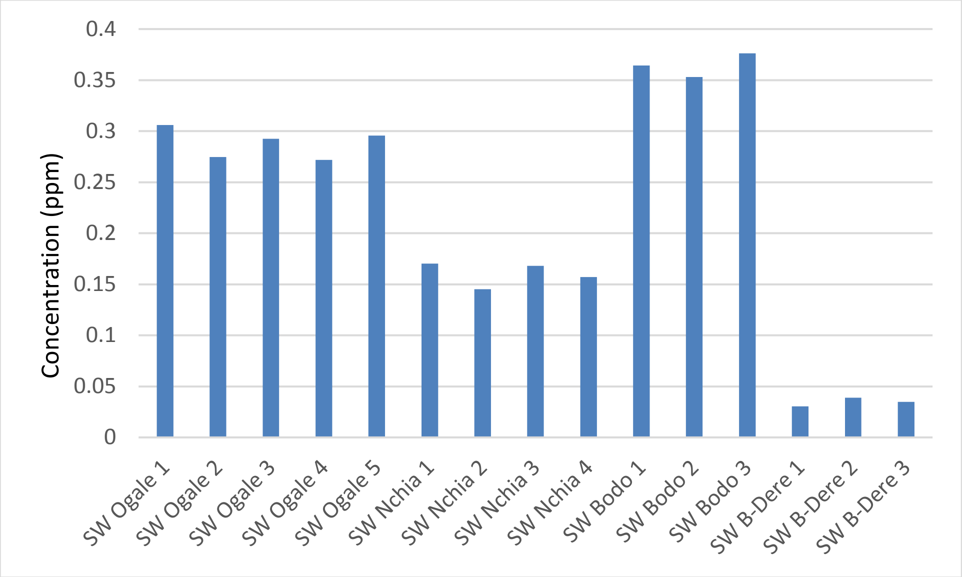

Figure 4.28 Concentration of Arsenic in surface water samples from Eleme and Gokana LGA. The y-axis shows Arsenic concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

According to the findings of this research, arsenic was detected in all surface water sample locations. The values detected were within the range 0.03 – 0.37 ppb (Figure 4.28). This contrasts with a similar study by Nduka and Orisakwe (2011), who reported that Niger Delta surface waters were contaminated above the USEPA guidance threshold for most heavy metals, and noted that this constituted a serious public health problem. All locations recorded a low level of arsenic, which was within the guideline value of 10ppb stipulated by ATSDR (2007).

4.4.2 Copper (Cu)

Copper is naturally found in rocks, soils and plants, occurring as a mineral deposit in sulfides, oxides, and carbonates (Fashola *et al.*, 2016). The concentration of copper is usually low in groundwater and, unlike other contaminants, elevated levels of copper do not naturally occur in ground or surface water. Copper concentrations were very low in some of the sample locations and were well below guideline limits (Figure 4.29 and 4.30). Copper was detected in all surface water samples, except those from B-Dere. Concentrations were uniformly low, at <5 ppb. Hence, copper is not a major ground or surface water contaminant in Ogoniland.

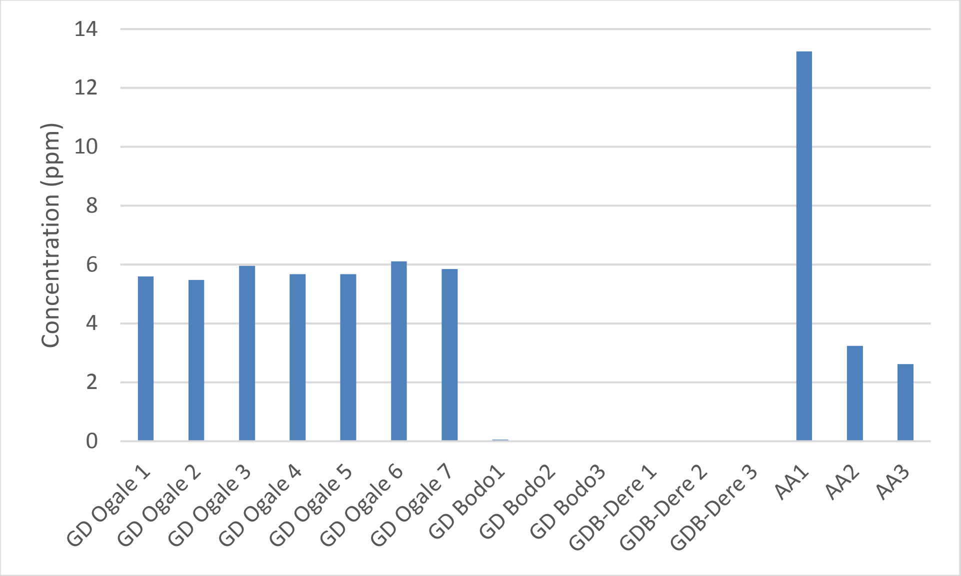

Figure 4.29 Concentration of Copper in groundwater from Eleme, Gokana and Portharcourt LGA. The y-axis shows Copper concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

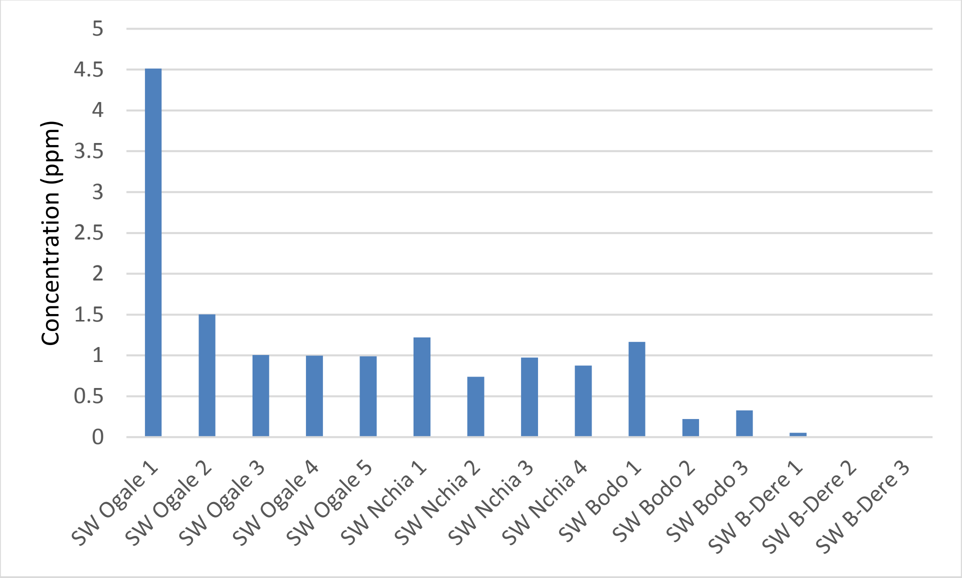

Figure 4.30 Concentration of Copper in surface water samples from Eleme and Gokana LGA. The y-axis shows Copper concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

4.4.3 Cadmium (Cd)

Cadmium is a natural constituent of most ground and surface water aquifers and may exist in the form of hydrated or complexed ions such as hydroxides, carbonates, and chlorides (Faroon *et al.*, 2012). Cadmium contamination may occur when it enters a groundwater aquifer through weathering of soils, erosion or direct discharges from hydrocarbon industries. According to

WHO (2004b), cadmium is more mobile in soil than in air and water, thus putting plants at risk when tissues and roots take up the contaminant.

The results from the groundwater sample locations show that the concentrations obtained were within the range of 0- 0.12 ppb, with Amadi-Ama 1 recording the highest values (Figure 4.31). However, the cadmium concentrations in the study area were within the permissible guideline value of WHO and USEPA, and thus cadmium is not a groundwater quality issue in the study area.

The results from the surface water sample locations show that the Cd concentrations obtained were within the range of 0-0.02ppb (Figure 4.32). These low levels are in agreement with previous findings for the Niger Delta (Otitoju and Otitoju, 2013; Vincent-Akpu and Mmom, 2012; Ideriah *et al.*, 2012; Issa *et al.*, 2011; Adeleye *et al.*, 2011). Cadmium concentration in the study area was highest at Bodo but was still well within the permissible guideline values of WHO and USEPA in all samples.

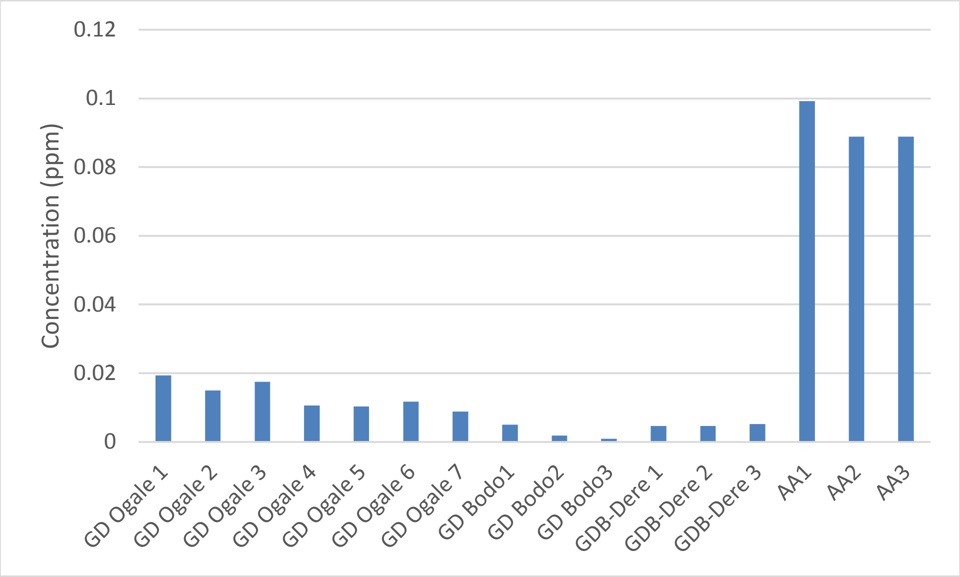

Figure 4.31 Concentration of Cadmium in groundwater samples from Eleme, Gokana and Portharcourt LGA. The y-axis shows Cadmium concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

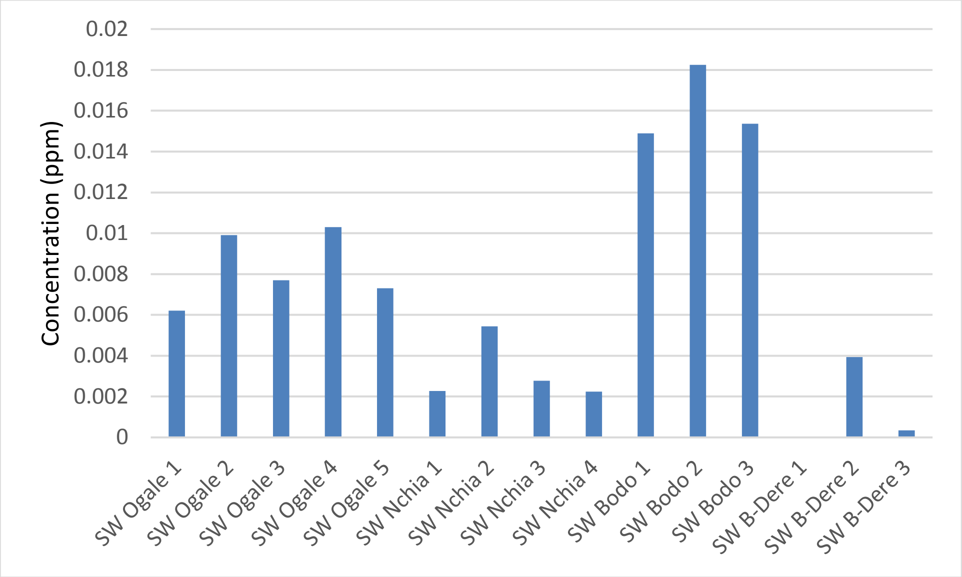

Figure 4.32 Concentration of Cadmium in surface water samples from Eleme and Gokana LGA. The y-axis shows Cadmium concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

4.4.4 Nickel (Ni)

Nickel is one of many trace metals that is widely distributed in the environment. It is naturally occurring in soil, water, and air in a variety of forms. Nickel may exist in soils and sediments in the form of sulfides, oxides, and disulfides, depending on soil pH (Jaishankar *et al.*, 2014). Nickel pollution has been reported across the globe by many researchers. For example, Rahman *et al.* (2016) reported that nickel concentrations in Joy Nagar, India, were between 0.029mg/l and 0.154mg/l, which was due to the discharge of heavy metals by industries in Mysore city.

However, in this study, nickel was not detected in most groundwater samples except in Bodo 1, Amadi Ama 1 and Amadi Ama 3 (Figure 4.33). The nickel concentration of 350ppb at Amadi Ama 1 is a potential water quality issue in the study area according to WHO and Nigerian Standard (NI) guideline values, although its concentrations in groundwater are highly heterogeneous.

Nickel was detected at very low concentrations in all surface water sample locations (Figure 4.34), except for two B-Dere samples where Ni exceeded the Nigerian standard Organisation limit but was below the WHO guideline value.

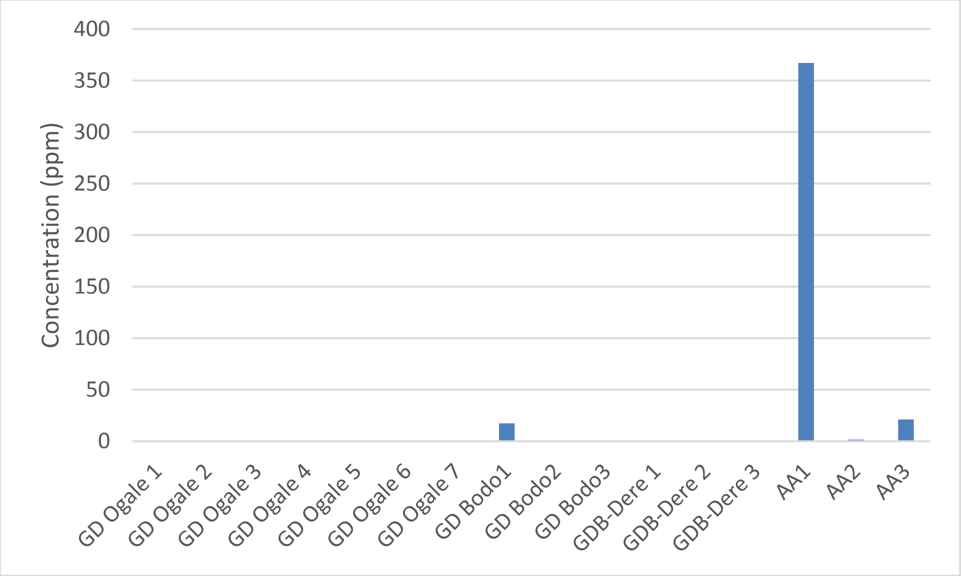

Figure 4.33 Concentration of Nickel in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Nickel concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

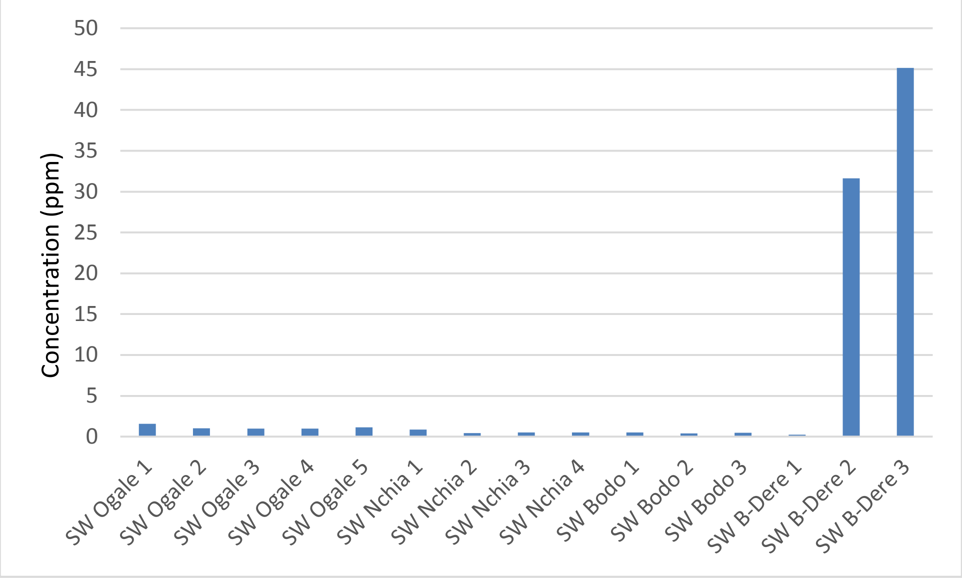

Figure 4.34 Concentration of Nickel in surface water samples from Eleme and Khana LGA. The y-axis shows Nickel concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

4.4.5 Lead (Pb)

Lead is a toxic metal that is profoundly harmful to humans, and thus there are no safe exposure limits. The degree of exposure to lead is dependent on age, route of exposure and current medical situation of the receptor. This has prompted the formulation of guideline values by different governing bodies across the globe. For example, the EU, WHO and Australia gave a guideline value of 10 ppb, while USEPA presented a value of 15ppb as an upper limit for the concentration of lead in drinking water.

The findings in this research indicated that the concentration of lead in the study area was within the range of the guideline value as given by the world bodies. The highest concentrations were observed in Ogale as 0.63 ppb, and were much lower in Bodo and Amadi Ama and below detection in B-Dere (Figure 4.35). Lead is not a major groundwater contaminant in the study area.

Pb was detected in all surface water samples (Figure 4.36) except for those from Bodo. Low concentrations from 0-0.25ppb were recorded in this study and agreed with previous work in the Niger Delta by Adeleye *et al.* (2011) and Chindah *et al.* (2009).

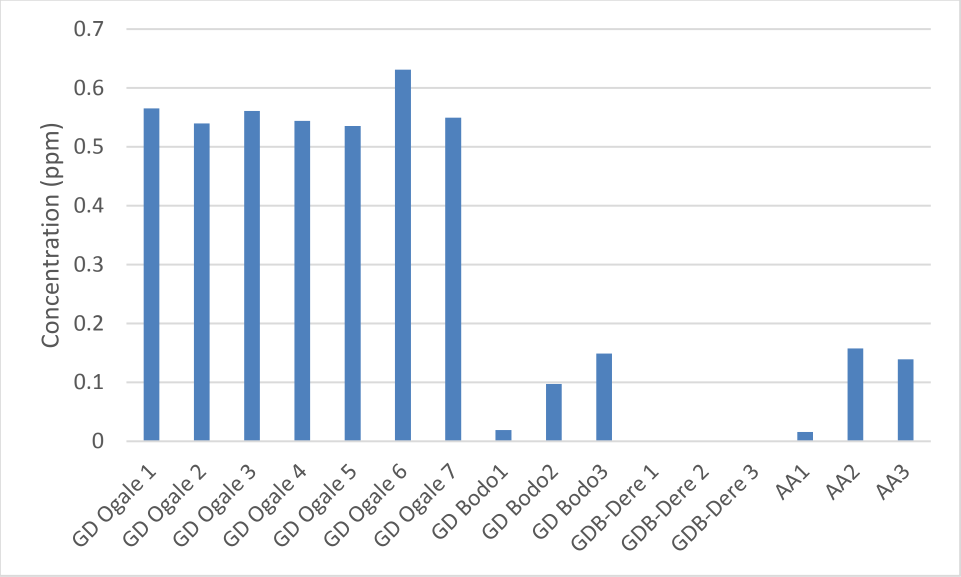

Figure 4.35 Concentration of Lead in groundwater samples from Eleme, Gokana and Port Harcourt LGA. The y-axis shows Lead concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

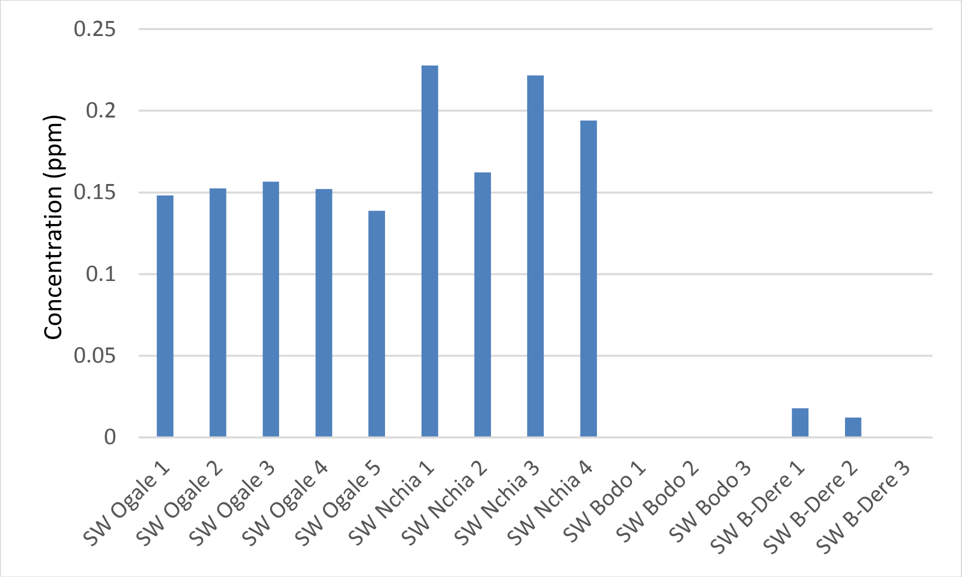

Figure 4.36 Concentration of Lead in surface water samples from Eleme and Khana LGA. The y-axis shows Lead concentrations in parts per billion. The x-axis shows the regions in the local Government areas being explored and sample numbers.

4.5 STATISTICAL CORRELATIONS OF TRACE ELEMENTS IN GROUNDWATER SAMPLES

Table 4.6 below shows the following:

- Beryllium gave a statistically significant correlation with aluminium, manganese, cobalt, nickel, copper, arsenic, selenium, cadmium, barium, lead and uranium.
- Aluminium gave a significant correlation with manganese, cobalt, arsenic, selenium, cadmium, antimony, barium, lead and uranium.
- Titanium gave a significant correlation with silver, arsenic, and lead.
- Vanadium gave a significant correlation with selenium and lead.
- Chromium gave a significant correlation with selenium and lead.
- Manganese gave a significant correlation with cobalt, nickel, copper, arsenic, molybdenum, cadmium, antimony, barium, lead and uranium.
- Cobalt gave a significant correlation with copper, zinc, arsenic, cadmium, molybdenum, antimony, barium, and lead
- Nickel gave a significant correlation with copper, zinc, molybdenum cadmium, barium, and uranium.

- Copper gave a significant correlation with zinc, arsenic, molybdenum, silver, cadmium, and lead.
- Zinc gave a significant correlation with arsenic, molybdenum, and lead.
- Arsenic gave a significant correlation with molybdenum, cadmium, and lead.
- Selenium gave a significant correlation with cadmium, antimony, barium, lead, and uranium.
- Silver gave a significant correlation with lead.
- Cadmium gave a significant correlation with antimony, barium, and uranium.
- Antimony gave a significant correlation with barium and uranium.
- Barium gave a significant correlation with uranium.

Table 4.6 Correlation Matrix between Trace elements in Groundwater samples, N=16. Values shown in red exceed the critical value (95% confidence) of 0.444 for 16 data points. Corresponding critical values for 90% and 99% confidence are 0.378 and 0.561

	Be [He]	Al [He]	Ti [He]	V [He]	Cr [He]	Mn [He]	Co [He]	Ni [He]	Cu [He]	Zn [He]	As [He]	Se [He]	Mo [He]	Ag [He]	Cd [He]	21 Sb [He	Ba [He]	Pb [He]	U [He]
Be [He]		0.98	-0.19	-0.37	0.20	0.95	0.64	0.57	0.46	-0.28	0.51	0.45	-0.27	-0.30	0.56	0.19	0.69	-0.81	0.98
Al [He]			-0.22	-0.26	-0.09	0.94	0.63	-0.36	-0.36	-0.20	0.45	0.57	-0.23	-0.31	0.99	0.96	1.00	0.33	1.00
Ti [He]				-0.08	-0.17	-0.20	-0.27	-0.27	-0.22	0.30	0.48	-0.31	-0.22	0.72	-0.27	-0.07	-0.24	-0.60	-0.19
V [He]					0.96	-0.39	-0.16	-0.13	-0.43	-0.12	-0.31	0.63	-0.24	-0.06	-0.30	-0.21	-0.24	-0.46	-0.30
Cr [He]						-0.17	-0.12	-0.14	-0.26	0.00	0.25	0.73	-0.07	-0.02	-0.12	-0.09	-0.07	-0.56	-0.14
Mn [He]							0.82	0.77	0.61	0.41	0.52	0.39	0.45	-0.26	0.96	0.84	0.93	-0.63	0.92
Co [He]								1.00	0.67	0.50	0.29	0.35	0.65	-0.20	0.68	0.46	0.64	-0.30	0.57
Ni [He]									0.68	0.51	0.26	0.32	0.66	-0.18	0.61	0.38	0.56	-0.29	0.50
Cu [He]										0.92	0.78	-0.17	0.67	0.67	0.48	-0.30	0.33	0.49	0.33
Zn [He]											0.82	-0.06	0.54	0.33	0.33	-0.19	-0.18	0.54	-0.18
As [He]												0.00	0.48	0.38	0.56	0.17	-0.42	-0.59	0.46
Se [He]													-0.03	-0.24	0.51	0.57	0.59	-0.59	0.54
Mo [He]														0.28	0.35	0.19	-0.22	-0.27	0.20
Ag [He]															-0.21	-0.19	-0.32	0.49	-0.29
Cd [He]																0.96	0.96	-0.22	0.98
Sb [He]																	0.96	-0.23	0.97
Ba [He]																		-0.11	0.99
Pb [He]																			-0.29
U [He]																			

4.6 STATISTICAL CORRELATION OF TRACE ELEMENTS IN SURFACE WATER SAMPLES

Table 4.7 below shows the following:

- Beryllium gave a statistically significant correlation with arsenic, cadmium, antimony.
- Aluminium gave a significant correlation with, titanium, vanadium, chromium, zinc, molybdenum, cadmium, barium, lead, thorium.
- Titanium gave a significant correlation with vanadium, chromium, zinc, silver, antimony, barium, lead, thorium.
- Vanadium gave a significant correlation with manganese, cobalt, zinc, barium, lead, thorium.
- Chromium gave a significant correlation with zinc, molybdenum, cadmium, antimony, thorium, uranium.
- Manganese gave a significant correlation with cobalt, copper, selenium, molybdenum, antimony, barium, uranium.
- Cobalt gave a significant correlation with nickel, zinc, copper, arsenic, selenium, cadmium, barium, lead, uranium.
- Nickel gave a significant correlation with arsenic, antimony, barium, lead.
- Copper gave a significant correlation with selenium, molybdenum, barium, and thorium.
- Zinc gave a significant correlation with barium, lead, thorium, uranium.
- Arsenic gave a significant correlation with selenium, molybdenum, cadmium, antimony.
- Selenium gave a significant correlation with barium
- Molybdenum gave a significant correlation with cadmium, antimony, lead, uranium.
- Silver gave a significant correlation with barium and thorium.
- Cadmium gave a significant correlation with antimony and thorium.
- Barium gave a significant correlation with thorium and uranium.
- Lead gave a significant correlation with thorium and uranium.

In conclusion, findings from the study show that there is little evidence for elevated concentrations of trace element contaminants in the surface and groundwater samples from Ogoniland. The correlation data show that the trace elements tend to correlate with other elements that show similar geochemical behaviour (e.g., Nickel gave a statistically significant correlation (95%) with copper, zinc, molybdenum, cadmium, and elements associated with sulfide minerals). Hence, the distribution and concentrations observed seem to be predominantly geologically controlled. The adverse effects of heavy metals usually result from a prolonged exposure (defined as a function of concentration and time) to them, often through food and water (Singh and Kalamdhad, 2011). These effects, and the mechanisms through which they are brought to bear, nonetheless vary depending on the heavy metal in question and could constitute physiological problems even at low concentrations of the metal.

Table 4.7 Correlation Matrix between Trace elements in Surface-water samples, N=16. Values shown in red exceed the critical value (95% confidence) of 0.444 for 16 data points. Corresponding critical values for 90% and 99% confidence are 0.378 and 0.561

	Be [He]	Al [He]	Ti [He]	V [He]	Cr [He]	Mn [He]	Co [He]	Ni [He]	Cu [He]	Zn [He]	As [He]	Se [He]	Mo [He]	Ag [He]	Cd [He]	21 Sb [He	Ba [He]	Pb [He]	Th[He]	U [He]
Be [He]		-0.20	0.33	-0.06	-0.23	0.35	-0.03	-0.31	-0.02	0.02	0.66	0.43	0.36	-0.03	0.59	0.45	-0.14	-0.02	-0.22	0.39
Al [He]			0.92	0.65	0.95	0.00	-0.27	-0.33	-0.27	-0.66	-0.18	-0.06	-0.52	-0.30	-0.49	-0.31	0.45	0.93	0.94	-0.42
Ti [He]				0.79	0.80	-0.37	-0.42	-0.20	-0.06	0.76	-0.33	-0.32	-0.33	-0.47	-0.27	-0.52	0.69	0.72	0.98	-0.25
V [He]					0.40	-0.55	-0.73	-0.42	-0.01	0.48	-0.13	-0.38	-0.26	-0.40	-0.04	0.40	0.95	0.44	0.77	0.34
Cr [He]						-0.19	0.00	-0.17	-0.30	-0.48	-0.32	-0.18	-0.75	-0.14	0.62	-0.55	-0.19	0.76	0.83	-0.65
Mn [He]							-0.53	-0.18	-0.53	-0.41	-0.38	0.96	-0.41	-0.30	-0.11	-0.28	-0.76	0.35	-0.26	-0.40
Co [He]								0.74	0.06	-0.48	-0.25	-0.91	-0.47	-0.35	-0.25	-0.57	-0.76	-0.13	-0.42	-0.51
Ni [He]									-0.34	-0.23	-0.59	-0.42	-0.21	-0.16	-0.38	-0.44	-0.88	-0.44	-0.29	-0.28
Cu [He]										0.09	-0.38	0.63	-0.64	-0.14	-0.02	-0.04	-0.72	0.43	-0.45	-0.19
Zn [He]											-0.11	-0.30	-0.14	-0.28	-0.02	-0.29	0.81	0.47	0.75	-0.76
As [He]												0.55	0.61	-0.02	0.86	0.77	-0.01	0.00	-0.22	0.64
Se [He]													-0.27	-0.21	-0.26	-0.08	-0.61	0.41	-0.18	-0.25
Mo [He]														0.34	0.82	0.94	-0.39	-0.60	-0.34	0.98
Ag [He]															0.05	-0.26	0.45	0.23	0.53	-0.09
Cd [He]																0.86	-0.06	-0.37	-0.44	0.82
Sb [He]																	0.46	0.33	-0.15	0.94
Ba [He]																		-0.18	0.65	-0.44
Pb [He]																			0.80	-0.50
Th[He]																				-0.25
U [He]																				

4.7 ORGANIC CONTAMINANTS

4.7.1 Total Petroleum Hydrocarbons (TPH)

TPH is a bulk family of numerous chemical compounds that originally come from crude oil. According to ATSDR (2014), TPH is a combination of chemicals, but they are all made primarily from hydrogen and carbon and can be straight chain, branched chain, or cyclic molecules. Petroleum hydrocarbon compounds that have an aliphatic structure will behave differently compared to aromatic compounds; petroleum hydrocarbon compounds that have fewer carbon molecules will also act differently (Wang *et al.*, 2013).

Petroleum hydrocarbons were detected in all samples at concentrations below 1ppm. Benzene, ethyl-benzene, and xylene were all below detection limits of 2, 1.5, 0.5 and 1ppm respectively. The findings of this study show that results of the TPH analyses cannot be compared with the drinking water standard of the regulatory bodies because there is no evidence of gross contamination by these organics in the study area. The results from other existing literature revealed that petroleum hydrocarbons were detected in some locations in the Niger Delta region. For example, Lindsen and Palsson (2013) reported that the levels of TPH found in contaminated sites in Ogoniland were high enough to cause severe damage to the ecosystem and human life. The results from their study showed that the TPH present in surface and groundwater was 7420 g/l and 42200 g/l respectively. The UNEP report showed that traces of petroleum hydrocarbons were detected in surface and groundwater, the values presented were within the range of 0.053 – 42.2 and 0.011-2.35ppm respectively. Hence, the results from the findings in this study cannot be generalised.

Table 4.8 WHO (2004c) and other drinking water standards for petroleum hydrocarbons (mg/l).

Hydrocarbons	**WHO**	**UK**	**USA**	**Canada**	**Australia**
Benzene	0.01	0.001	0.005	0.005	0.001
Toluene	0.7	0.7	1	-	0.8
Ethyl-benzene	0.03	0.3	0.7	-	0.3
Xylenes	0.05	0.5	10	-	0.6

While there have been some studies in the Niger Delta on petroleum hydrocarbons, individual hydrocarbon compounds have not generally been individually analysed. While TPH is a useful bulk measurement, it is insufficient when considering and developing site conceptual models because TPH comprises various elements that have varying pathways and likelihood of entering groundwater. Apart from UNEP report of 2011, which stated that there was a high level of petroleum hydrocarbon contamination in the study area, Etiche *et al.* (2011), Adeniyi and Afolabi (2002), Muniz *et al.* (2004) and Rauckyte *et al.* (2006) suggested that TPH is present in the oil region of the Niger Delta, while in the current study the values obtained were below 0.5 – 2ppm in all cases, so no gross contamination was indicated.

4.7.2 Hydrocarbon Constituents

Phenol is derived from polluted surface water and industrial effluents from the hydrocarbon industry. Phenolic compounds are corrosive and toxic to an extent, but their primary significance in waters is due to their organoleptic effects on sensory properties. Phenol is considered to be quite toxic to humans via oral exposure, which can cause anorexia, progressive weight loss, diarrhoea, vertigo, salivation, a dark colouration of the urine, and blood and liver effects, and in animals cause growth retardation, and abnormal development in offspring (ATSDR, 1998; Budavari`*et al.*, 1989; Hawley, 1981).

Concentrations in groundwater and surface water in various locations across Ogoniland indicate gross contamination of phenol. The permissible limit in drinking water according to WHO is 0.03mg/l, but Table 4.9 shows that this limit was exceeded in all samples. Phenol concentration varies from region to region, with samples from Ogale having the highest values. The results from this study are consistent with other similar investigations in the Niger Delta and the study location. For example, a report from Asibor *et al.* (2016) revealed that the concentration of phenol was at gross levels in oil spill polluted sites in Warri local government in Delta State. The results obtained were within the range of 1-30.4 and 1-67 mg/l for surface and groundwater respectively. Ana *et al.* (2012) reported elevated levels of phenol in Ahoada East Local Government Area in Rivers state, Nigeria. Deductions from this study indicated that the phenol contamination was due to the discharge of hydrocarbon waste into the groundwater aquifer. The values of phenol presented in the study were within the range of 1-35.1 mg/l. Hence, phenol contamination is a major water quality issue in the sample location and other areas in the Niger Delta region.

Table 4.9 Analysis of Phenol in Drinking water in the study area, WHO limit is 0.03mg/l.

Sample Location	**Result in mg/l**	**Sample location**	**Result in mg/l**
Groundwater Ogale1	321.68	SurfacewaterOgale1	34.23
Groundwater Ogale2	326.78	Surface water Ogale2	326.19
Groundwater Ogale3	342.47	Surface water Ogale3	23.05
Groundwater Ogale4	343.45	Surface water Ogale4	229.72
Groundwater Ogale5	334.03		
Groundwater Ogale6	267.76	Surface water Nchia 1	21.29
Groundwater Ogale7	300.11	Surface water Nchia 2	21.29
		Surface water Nchia 3	17.26
Groundwater Bodo 1	21.88	Surface water Nchia 4	20.90
Groundwater Bodo 2	20.90		
Groundwater Bodo 3	20.70	Surface water Bodo 1	25.21
		Surface water Bodo 2	27.17
Groundwater B-Dere1	10.90	Surface water Bodo 3	21.26
Groundwater B-Dere2	21.29		
Groundwater B-Dere3	13.25	Surface water B-Dere 1	22.07
Groundwater B-Dere4	26.78	Surface water B-Dere 2	167.56
		Surface water B-Dere 3	22.07

4.7.3 PAH and other hydrocarbon components

PAHs are generally hydrophobic, and so will tend to adsorb onto particles, mostly in the bed of the water system. Results obtained from GC-MS shows no trace of PAH contamination in filtered water samples, even though some authors have stated in the literature of some trace of PAHS in the Niger Delta. The sample bottles were washed with organic solvent to ensure that PAHs potentially adsorbed to the sample bottles were included in the analysis. This possibly due to the low concentration levels at which they may be in the samples or that they are bound to particulate matter. Some of the samples have shown peaks that could be compounds related to dodecane. Most of the peaks observed correspond to some loss of stationary phase (bleeding) from the column: samples were zoomed to see if there was any sign of the study compounds.

Regarding the lack of PAH observed in the water samples (PAHs were below limits of detection), this is consistent with the low TPH values observed, and the fact that many of the

PAHs analysed are relatively hydrophobic and so are likely to adsorb on to organic matter in soils. Phenol, on the other hand, is more soluble.

4.8 CHAPTER SUMMARY

This chapter has focussed on the various contaminants that were found in surface and groundwater samples from different locations in Ogoniland. A range of potential contaminants was analysed, including major and trace elements, TDS, TPH, and phenol. The key contaminants that exceeded world guideline values in at least some samples were: in groundwater – Mn, nitrate, pH, and turbidity; and in surface water – Na, K, Ca, Mg, Fe, sulfate, chloride, bromide, pH, and turbidity. The selected trace metals were within guideline limits set by the regulatory agencies. The study revealed that phenol levels were excessively high in Ogoniland, and the values presented ranged from 10.90ppm-340ppm, while those of PAHs were below detection.

Bulk significant and trace element (and contaminant) data can be used to group the samples by water characteristics, and potentially discriminate sources of water in surface and groundwater. The connectivity between groundwater and surface water can also be assessed, gaining insights into the potential transfer of contaminants from surface water to groundwater aquifer systems. Correlation data indicate a dominant control of salinity (either via seawater ingress or industrial (e.g., brine) discharges) on the surface and groundwater water major ion composition, coupled with an influence from local geology. Based on the correlations observed, the control of salinity is more pronounced in surface water than in groundwater samples. Phenol, identified as a major water contaminant in the study area, shows elevated concentrations in both surface water and groundwater, with a similar geographic distribution (e.g., the Ogale area showed greatest enrichments in both surface and groundwater), indicating significant connectivity between surface and groundwater in the study area.

The next chapter will build on these findings to examine the pathways of contaminant exchange and how these contaminants migrate from one location to another using a core flooding experiment, while Chapter 6 deals with results relating to potential remediation strategies.

CHAPTER 5.0 – SIMULATING TRANSPORT TO GROUNDWATER AND NATURAL ATTENUATION PROCESSES – CORE FLOODING EXPERIMENTS

5.1 INTRODUCTION

The success of any working model used to describe a process is directly related to how well the process is understood. A conceptual model is usually the first step in the understanding of a process. A more advanced understanding would result in the development of a more complex model (e.g., a quantitative model). To build a working model of contaminant transport in groundwater, and improve understanding of contaminant risk, it is expedient to understand how contaminants migrate from source to destination (or receptor). A key objective of recent pollution control programmes is to understand the biological, chemical and physical processes responsible for the migration of contaminants in groundwater. Environmental professionals designing improved remediation plans for polluted sites can use findings from these types of investigations.

Three factors affect the movement of contaminants in groundwater: advection, dispersion and chemical reactions (degradation and sorption), as well as the properties of the media (Maidment, 1993). The mass balance of a given contaminant could be expressed as (dispersion + advection by natural flow + artificially induced advection + other sources and sinks) = rate of change of contaminants mass stored in the aquifer. This can also be termed the advection-dispersion equation (Maidment, 1993). Advection describes the movement of contaminants as a result of the flow of groundwater. Dispersion in a media, on the other hand, describes the spreading of a volume of the contaminant as it flows through the subsurface (Anderson, 1984). For example, if a dye spot is injected into a porous media in which groundwater is flowing, the dye spot will spread in size as the media flows. With dispersion, contaminants tend to spread over a wider portion of the aquifer than they would have by mere predictions from analysis of velocity vectors of groundwater (Anderson, 1984). Therefore, via dispersion, contaminants could spread to uncontaminated zones. Hence there is a need to understand the movement of mechanisms of contaminants to design a more robust control strategy.

As shown in Chapter 4, phenol has been identified as a major contaminant in the study area in both surface and groundwater, and it is established that it has potential, in sufficient concentrations, to cause major damage to various life forms as well as the health of humans. Understanding the migration of phenol through the subsurface to potential receptors is essential in predicting its future occurrence in groundwater-sourced drinking water, and in designing its control mechanisms. Because the processes involved in contaminant migration are very complex, with diverse interactions of the various processes involved – advection, flow rate, dispersion, etc. – one must adequately understand these processes to make accurate predictions on (or model) migration patterns. Also, to attain a reliable degree of confidence about the predicted behaviour of contaminants (in cases where some quantitative predictive modelling has been carried out), predicted results need to be validated by comparison with simulated observations. As permeability distributions and the evolution of components of reservoirs in space and time cannot be observed directly, some authors have utilised one-dimensional laboratory-based models to simulate migration processes and help to validate theoretical and predictive models. Of these, core flooding experiments are viable laboratory-based models for simulating flow patterns, in this case, to estimate the dispersion and sorption parameters of the aquifers in groundwater migration in Ogoniland.

The aim of this chapter, therefore, is to examine potential groundwater migration pathways to local receptors for phenol, identified as a major surface and groundwater contaminant in Chapter 4 of this thesis. The chapter aims to assess the migration rate of phenol in groundwater and to investigate if sorption of phenols might occur in the aquifer materials, via core flooding experiments.

5.2 LITERATURE REVIEW

As established in previous chapters, spills and leakages of hydrocarbons via the Earth's subsurface have caused significant damage, resulting in contaminated groundwater systems which are unsafe for consumption and irrigation. Most hydrocarbons found in the subsurface environment are immiscible and form a separate liquid phase from groundwater. Heavier Polycyclic Aromatic Hydrocarbons (PAH) and Non-aqueous phase liquids (NAPL) are the two main categories of hydrocarbon contaminants under study in Ogoniland in this thesis. Results from the earlier UNEP assessment show that PAH sources have severely polluted Ogoniland's aquatic environment (UNEP, 2011). When these sources are spilled or discharged into the ground, NAPL contaminants are created, and some of these contain PAHs (Kamarudin *et al.*, 2011).

As discussed in Chapter 2, NAPLs in the subsurface can be light hydrocarbons with a density lower than that of water (light non-aqueous phase liquids, or LNAPLs), or dense hydrocarbons with a density higher than water (dense non-aqueous phase liquids, or DNAPLs). The light NAPLs migrate through unsaturated soils and rest on the surface of the groundwater while the dense NAPLs move through the saturated soils to deeper parts of the aquifer. Phenol is a component of complex DNAPLs such as creosote and coal tar, but in itself is not strictly a DNAPL due to its solubility. The structure of both saturated and unsaturated regions has a significant effect on the behaviour of dense NAPLs. Monitoring phenols under laboratory simulation conditions in association with some numerical modelling, therefore, should focus on both the unsaturated and saturated regions.

Over the last thirty years, more understanding has been developed in NAPLs. A comprehensive review was published by Mercer and Cohen (1990) exploring the features, characterisation, and remediation of these complex contaminants. Cohen argued that future research should be focused on improving in situ measurement of NAPL contaminants, their properties, as well as their mass migration mechanisms in simulation models. Such studies could potentially lead to a better understanding of NAPL characterisation and consequently an improvement in remediation strategies, as well as providing guidance at field level for site investigations. Driven by a lack of adequate field data, Gelhar *et al.* (1992) critically reviewed the literature on dispersivity observations spanning 59 different field sites, compiling differences in aquifer properties and characteristics. Chevalier and Petersen (1999) gave a summarising overview of experimental work involving the flow of NAPLs, their transport, and remediation technologies involved in two-dimensional aquifer models.

5.3 UNDERSTANDING CONTAMINANT MIGRATION PATTERNS

Studies aiming to understand contaminant migration patterns have been carried out for the better part of the last three decades. A well-established tool for understanding migration patterns of contaminants is via centrifugal modelling. Arulanandan *et al.* (1988) carried out one of the first centrifugal simulations in geo-environmental research, where they modelled the migration patterns of pollutants in saturated soils. For unsaturated soils, Nimmo (1990) also reported a successful simulation experiment using centrifuge technology. After that, groundwater flow and dissolved contaminant occurrences were successfully modelled by Cooke and Mitchell (1991) and Meegoda and Hu (2011). For spills relating to crude oil, these early studies proved that centrifugal modelling had the potential to be used in understanding transport architecture of contaminants in both saturated and unsaturated conditions.

A major limitation, however, of centrifuge modelling is the problem of adequately modelling realistic prototypes, and it is often suggested that centrifugal modelling is only suitable when there are no prototypes on which the verification of the model test results can be based; when applying the ‘modelling the models’ centrifugal technique (Arulanandan, 1988). More recently, however, geotechnical centrifuges have been proposed, as they can simulate two or more dimensional problems under situations where the experimental boundaries are controlled, with opportunities for reproducibility (Fox and Lee, 2008). Kumar and Singh (2012) utilied a geotechnical centrifuge to model the diffusion of chloride ions through a soil matrix. The study showed the potential of centrifuge modelling as a relevant technology alternative to field scale research; it also showed good data agreement with various mathematical models such as CTRAN/W and SEEP/W. These authors, however, highlighted a significant limitation, which is that the study only explains conditions within two soils, and recommended testing centrifugal acceleration at other levels with other soil types.

Jones *et al.* (2017) carried out some geotechnical centrifuge tests to understand the variably saturated flow and dispersion in soils as well as to address variably saturated flow in discrete fractures (both horizontal and vertical). Even though prevailing challenges associated with modelling the vadose zones still linger, Jones *et al.* (2017) showed that geotechnical centrifuge modelling is still a viable tool for modelling and observing variably saturated flow, physically. Centrifuge tests have also been used in many other different cases because of their reliability and reproducibility (Chen *et al.*, 2016; Zheng *et al.*, 2016).

More often, mathematical models governed by a set of guiding equations are used to predict contaminant migration patterns through soils. These kinds of models have been used for many years; from the widely cited Shackelford (1995), where analytical models were used to test mass columns, to the present, where diverse, more sophisticated, mathematical models have been developed. For example, Adhikari *et al.* (2014) constructed a mathematical model called HYDRUS-1D to predict the movement of phenolic compounds through groundwater and soil matrices with the help of column experiments. The breakthrough curve derived from this simulation fits well with those from the column experiments. Similarly, Nham *et al.* (2015) developed four one-dimensional flow and migration models based on field data retrieved from on-site data collection in Greece to predict the migration patterns of sixteen organic pollutants during the treatment of aquifers. Also, Al-Khaleda and Hajic (2016) developed two analytical methods to model the transport of solute and water flow in the unsaturated zone. They called these the ‘singular perturbation technique’ and the ‘Laplace transform method,’ and both were proven efficient tools to measure a closed form estimate of solute movement in the unsaturated zone. Findings from their study were consistent with real scenarios in Jordan and were argued to provide a reliable reference point in forming the basis of the Jordanian government’s decision making.

A third frequently used tool is that of core flooding experiments. These are a type of model-based simulation, usually performed at laboratory scales, used to represent chemical, physical and biological processes involved in liquid flow in a natural enclosed system. These systems are very advanced, they are modular and are a computer configured to simulate liquid permeability, water flood susceptibility, water floods, liquid/gas related permeability and other processes. Some of these core flood systems are customizable to meet the experimenter's research requirements for parameters like temperature, pressure, phase, flow measurements, etc. Core flooding is particularly advantageous because it is useful in giving a controllable one-dimensional laboratory model of contaminant transfer through a soil medium, allowing the soil characteristics to be varied, and is the approach adopted in this thesis.

5.4 BACKGROUND THEORY ON CORE FLOODING EXPERIMENTS

The degradability of phenols in groundwater has been well documented (Dimkic *et al.*, 2008). Under normal conditions, hydrocarbon degradation is favoured dramatically under suitable aerobic conditions. This research examines the migration and sorption of phenol (identified in this thesis as a key contaminant in the Ogoniland area; see Chapter 4) on simulated aquifer materials. The core flooding experiment was based on the null hypothesis that phenol solution in water and a conservative tracer solution (chloride ion Cl^-, in this case) behaves similarly (Dimkic *et al.*, 2008). In other words, no sorption of phenol occurs during subsurface transport. The core flooding test, therefore, seeks to measure by simulation the rate of migration of phenol in groundwater compared to a conservative Cl tracer. A breakthrough curve produced at the end of the experiment for both phenol and Cl allows assessment of differences in migration, and therefore a degree of sorption (or of other attenuation processes) under simulated flow conditions.

Core flooding experiments have been extensively used for different flow and permeability related simulations in the laboratory, and have been applied in a range of experiments relating to enhanced recovery of oil, quantifying water and nitrate fluxes, gel treatments, contaminant migration, etc. Enhanced oil recovery (EOR) appears to be the process where core flooding has been utilised the most. The process aims to increase the quantity of oil that can be extracted from an oil field using various techniques. Three different techniques could be utilised in this process; gas injection, thermal recovery, and chemical injection. Thermal recovery uses heat (e.g., steam) injection to lower the viscosity of the heavy oil and enhance its ability to flow through the reservoir; gas injection utilizes gases (e.g., CO2, natural gas, nitrogen) to expand the reservoirs to push left-over oil to designated production wellbores; chemical injection, which is the least used technique, involves the utilization of polymers to improve effectiveness of the waterflood process, or the use of surfactants to lower the surface tension that usually hinders oil droplets from flowing through the reservoir (Lake, 1989).

To actualie these field level EOR processes or experimentations, these ever-evolving processes are first tested in the laboratory using core flooding simulation experiments. The processes involved are represented at laboratory scales to ascertain recovery rates before the actual field trials are carried out.

On the SCOPUS database, the first time the phrase “core flooding experiments” was mentioned was in research by Healy and Reed (1977), where they investigated (using a core flooding simulation process) the potential of using microemulsions immiscible with oil and water to enhance the process of oil recovery. Even though the process was not as advanced as it is now, valid conclusions were drawn from the laboratory procedure. It was concluded that immiscible emulsion flooding was a viable alternative to conventional microemulsion processes as a means of enhanced oil recovery from reservoirs. In perhaps one of the most cited article relating to core flooding, Yakimov *et al.* (1997) tested the applicability of microorganisms as agents of enhanced oil recovery via in situ processes such as growth and metabolism. Injection of laboratory-grown microbial cells was carried out to model their suitability as agents to improve oil recovery.

Core flooding experiments have been used to quantify water, nitrate and other contaminant fluxes. Because of the difficulties in obtaining data via in situ measurements characteriing flow rates, transport process, and identifying dominant pathways of flows, it is necessary to quantify these processes using some laboratory modelling in addition to numerical modelling and field monitoring. Keim (2013) used data from field measurements to set up a core flooding model estimating the amount of water and nitrates entering the unsaturated zone. This was done in addition to field monitoring. To a significant degree, these simulations were a useful tool for understanding subsurface migration processes. Arab *et al.* (2014) also used core flooding experiments to understand and develop a means to remediate colloid-facilitated contaminants in saturated porous media. Because of an increase in the solubility of specific low solubility contaminants, as a result of their adsorption to colloidal fine particle surfaces, their transport in porous media could be facilitated. Arab *et al.* (2014) explored how the attachment of fine colloidal particles to rocks could potentially aid the remedying of this challenge. Core flooding tests were conducted, utiliing different nanofluids to saturate artificial porous media, and the theory was tested at lab scales. Results showed that by treating the porous media, fine particles (which are the main carriers of contaminants) could be absorbed by the treated media. These were compared with some quantitative extrapolations (Derjaguin-Landau-Verwey-Overbeek theory; Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) and confirmed by the calculation of total energy interaction between the rock surface and fine particles.

5.5 RESULTS AND DISCUSSION – CHLORIDE CORE EXPERIMENTS

5.5.1 Chloride result

The dead system volume of the core experimental setup (described in Chapter 3) was found to enable a correction to be made to the number of pore volumes of pumping when plotting breakthrough curves. The dead volume is the system volume from the pump outlet to the fraction collector that includes the tubing, plus any other volume in the apparatus that is not taken up by the core or packed sediment sample. The method of system volume calculation is described in section 5.6.1. The tabulated results are summarised as shown in Table 5.1.

Table 5.1 Calculation of system volume.

The volume of Solution Collected before LiCl solution fully breaks-through:	50ml
Dimensions of Dummy Core drilled hole:	Length = 11.3cm Sleeve Diameter = 3.8cm Volume = 69.187cm Density= 103.77 Filter= 0.6cm Band length= 2cm
System Volume Determination:	11.34-6.1=69.187cm3

From the results shown in Figure 5.1, using Ion chromatography, the calibration line was linear over the range 0 – 20ppm, with a high r^2 value showing limited scatter from the line of best fit. Cl is a conservative tracer, which is in accordance with the breakthrough curve, which shows a rapid breakthrough of Cl after less than ten samples (60mls, or less than one core volume). Following this, there was a continuous and steady increase up to 51 samples (510 MLS, or 14 core volumes).

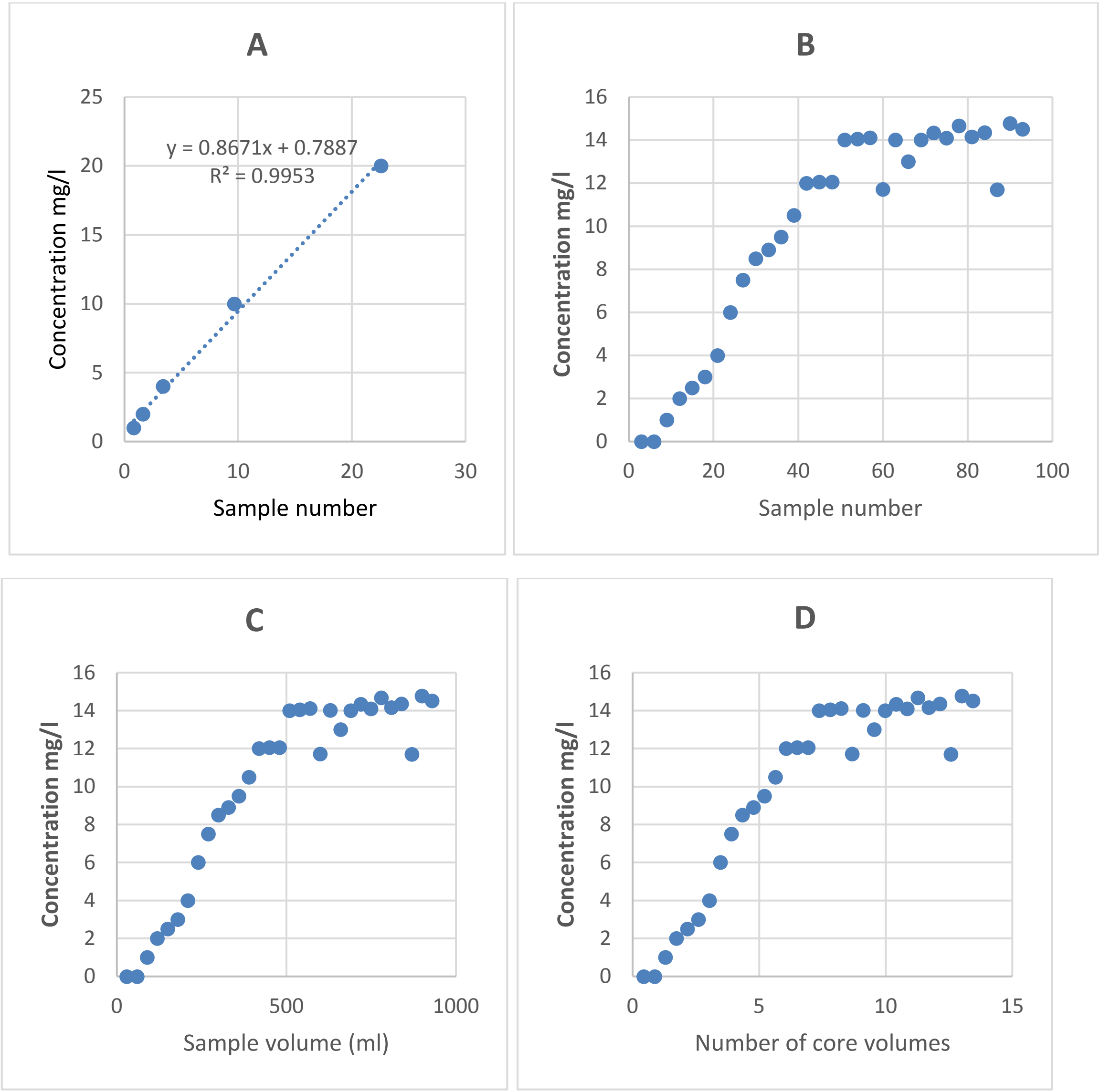

Figure 5.1 (a) Chloride calibration and (b-d) breakthrough curves, presented as (a, b) sample number, (c) sample volume, and (d) number of core volumes. The y-axis shows Cl concentrations in mg/l. The x-axis shows the sample number, sample volume and the number of core volumes respectively.

5.5.2 Results from Phenol Breakthrough Curve

The breakthrough curve was undertaken to simulate the reactive transport of phenol into groundwater. The result from the calibration curve (for spectrophotometric measurements) as seen in Figure 5.2 is a quadratic line over the range 0 – 50ppm, with a high r^2 value (showing limited scatter from the line of best fit). The phenol breakthrough shows a delayed breakthrough compared to Cl, after 40 samples, and an increase in the peak around 85 samples before a drop and rise between 90 and 93 samples. This means that there is some interaction between the phenol and the simulated aquifer material used; probably this is interaction with either the clay component or the organic matter fraction as these are the most reactive fractions of the sample, via adsorption. Phenol adsorption to clay/compost was fast because of a rapid increase of adsorbates adsorbed; previous findings on the adsorption of phenolic compounds by various clay-based adsorbents have shown a wide range of adsorption (Song and Sandi, 2001).

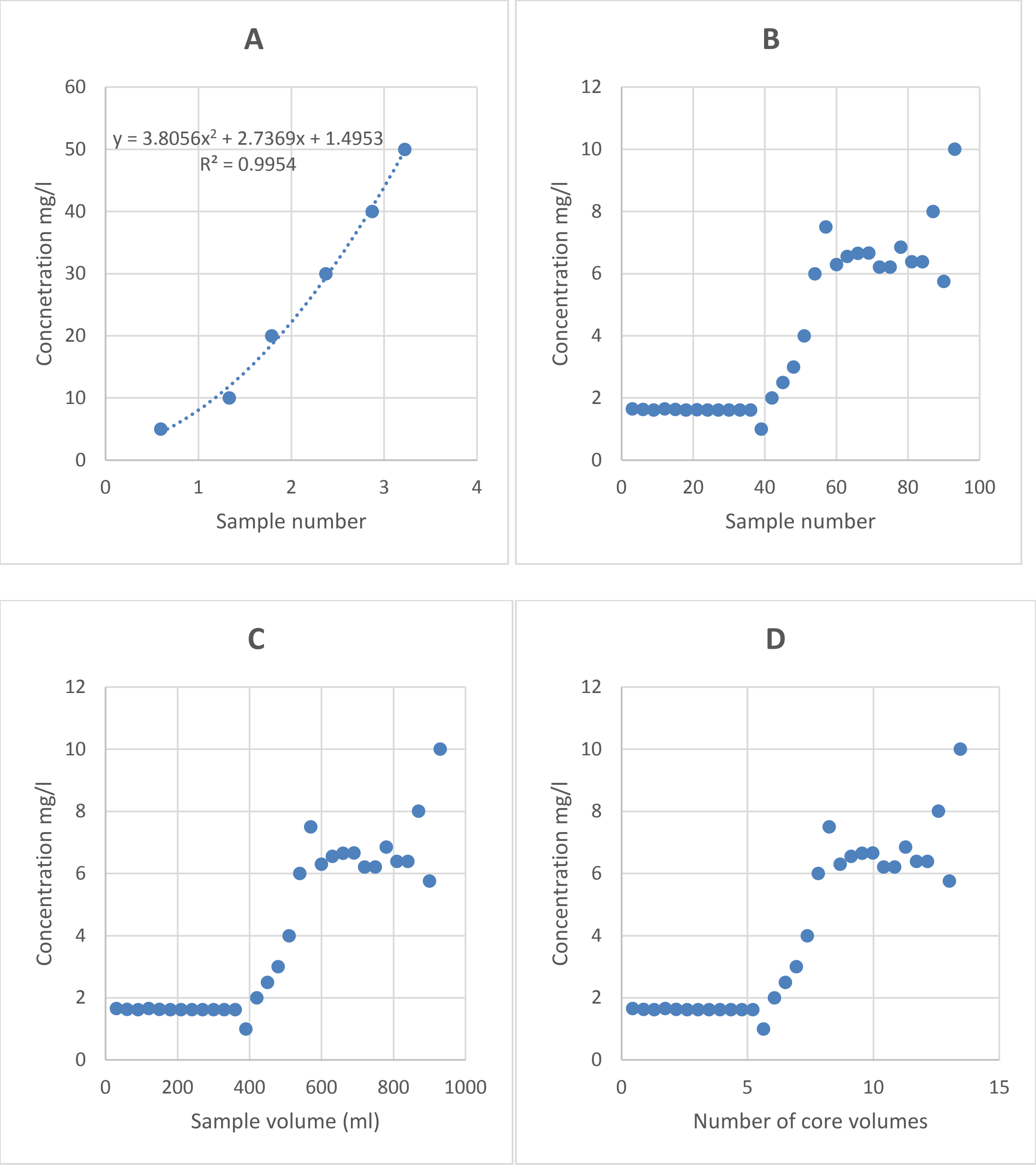

Figure 5.2 (a) Calibration and (b-d) Breakthrough curve of Phenol showing (a,b) sample number, (c) sample volume, and (d) core volume. The y-axis shows Phenol concentrations in mg/l. The x-axis shows the sample number, sample volume and the number of core volumes respectively.

Studies such as Djebbar *et al.* (2012) have suggested that phenol was absorbed onto clay surfaces; in this study, phenol was successfully adsorbed by compost from the aqueous solution up to 60-70%, and some is interacting with the organic components (compost) of the core. This proves the feasibility of activated natural clay as an effective adsorbent (Tahani *et al.,* 1999; Giles *et al.,* 1960). Moreover, phenol adsorption on organic matter particles and clay particles, as well as plant roots, plays a vital role in the removal of phenolic compounds. The data indicate that phenol may be subject to adsorptive-based natural attenuation processes in the Ogoniland aquifer, in addition to biological breakdown. These adsorptive processes will be further examined in Chapter 6.

5.6 CHAPTER SUMMARY

The above results simulate phenol transport and breakthrough to groundwater and show that despite some degree of natural attenuation via retention or adsorption processes (compared to the conservative tracer Cl), phenols can migrate into the groundwater, thereby causing pollution to the aquifer and human health. According to (Ruthven, 1984) retention can be viewed as a route by which contaminants from the leachate are retained on the solid surface through different mechanisms, such as sorption, complexation, and precipitation. This study was performed under uncontrolled pH conditions, and any process is leading to the removal of contaminants by the soil solids were considered as retention. Retention occurs until equilibrium is reached when a solution of contaminant passes from both sides of the core. A stability state is considered by the concentration of solute absorbed on the solid adsorbent and the equivalent solute concentration left over in the liquid phase (Deka and Sreedeep, 2017).

In this study, a pseudo-equilibrium was achieved as a result of the uncontrolled pH and temperature. However, the objective was to understand the retention that would occur under field conditions, which are genuinely uncontrolled. The result shows that there was some degree of phenol retention in the simulated aquifer materials, which indicates the suitability of natural attenuation as a means of managing contaminant transfer to the aquifer. A brief discussion on the use of natural attenuation as a low-input remediation option for groundwater contaminants is given in section 6.2. Also, chapter 6 explores the use of enhanced carbon-based soil amendments as an enhanced attenuation technique for remediation of phenol-polluted groundwater.

The leakage of phenol and other contaminants into underlying aquifers may have adverse impacts on aquifer drinking-water quality. This occurs due to transport via faults and fractures, through faulty wells or bores, or through leaky confining materials. The latter process has been simulated here, although it is recognised that fault and fracture transport, and leakage from well-bores, may accelerate transport of contaminants to aquifers, and reduce natural attenuation potential from adsorption and other processes within soils and near-surface geological materials. The hydrologic flow and transport parameters (degree of horizontal stratification, sorption, and local scale dispersion) are sensitive parameters in assessing overall risk. The magnitude that these processes impact the degree of uncertainty in overall risk in comparison to exposure and toxicity further promotes the importance of hydrologic flow and transport modelling in risk assessment, which is discussed in depth in chapter 7 (Siirila and Maxwell, 2012).

The next chapter will look at how the attenuation of phenol (and other contaminants) can be enhanced using carbon-based soil amendments. The addition of a monitoring system and remediation techniques is also discussed in Chapter 7 and will contribute to strategies for managing high-risk aquifers at potential sites across Ogoniland.

CHAPTER 6.0 - ENHANCED NATURAL ATTENUATION THROUGH USE OF CARBON-BASED ADSORBENTS

6.1 INTRODUCTION TO REMEDIATION STRATEGY

The previous chapter examined the migration and retention of phenol, identified as a major contaminant in the study area, in simulated aquifer materials. The retention of phenol on aquifer materials, coupled with its potential for biological breakdown, suggests that natural attenuation or enhanced natural attenuation approaches, which increase the retention of phenol and other contaminants in soils, could play a viable role in integrated remediation strategies in Ogoniland. Any approach used, however, needs to be applicable over large areas, and also relatively low-cost, ideally using local materials. This is examined further in this chapter, which firstly presents a review of low-cost remediation/risk management methods potentially applicable in the Ogoniland area, and then examines the potential application of low-cost adsorption and enhanced natural attenuation approaches for phenol and other contaminants, via a series of batch adsorption studies using a commercial activated carbon and a range of biochar products.

6.2 LOW-COST REMEDIATION/RISK MANAGEMENT METHODS POTENTIALLY APPLICABLE IN THE OGONILAND AREA

6.2.1 Approaches to the remediation of contaminated land

Pollutants enter the environment mainly via human activities; for example, hydrocarbon pollution can result from transportation-associated spills, accidents, waste disposal leakages or activities carried out in industrial facilities (Riser-Roberts, 1992). There is a consensus between government, the general public and industry on the potential health and environmental dangers associated with complex chemical pollutants such as polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPHs), polychlorobiphenyls (PCBs), pesticides and heavy metals. In response to these dangers, a variety of remediation techniques have been developed over the past 20 years to decontaminate soils, wastewater, groundwater and leachate polluted by these contaminants (Riser-Roberts, 1998).

Popular site cleanup or contaminant management methods that have been adopted include various physical, chemical or biological processes such as incineration, soil washing, vitrification, chemical oxidation, solidification/stabilization, electrokinetic treatment, excavation and offsite treatment (Pavel *et al.*, 2008; Cunningham *et al.*, 1995; Kumar *et al.*, 1995). Some of these traditional physicochemical remediation techniques could, however, be invasive and may sometimes be environmentally damaging (EPA, 2008). In addition to being potentially damaging, most of these conventional decontamination/ remediation techniques are incredibly cost-intensive (EPA, 2008). The US Environmental Agency has, since the 1981 fiscal year, appropriated US$1.2 billion in nominal dollars to its Superfund Programme, and annual costs to carry out remedial constructions for the 2010-2014 fiscal years were estimated to range from US$335 million to US$681 million (Gomes, 2012). It has, therefore, become expedient to explore alternative low-cost remediation/risk management techniques that could potentially apply to contaminated areas, particularly large contaminated areas in less economically developed regions.

Ultimately, the aim of any clean-up exercise is to maximise decontamination efficacy as well as reduce compliance cost, hence the need to develop technologies that are potent, less invasive and cost-effective. Remediation goals, however, could differ depending on varying specifications. For example, approaches could involve treatment to remove contamination, treatment to reduce the scale of contamination, treatment to limit the extent of contamination spread, institutional controls, as well as monitoring schemes. Irrespective of the specific remediation objective, the desire to achieve cost-effectiveness and limit associated risks remains.

6.2.2 Low-Cost Remediation Methods

Some lower-cost remediation methods potentially applicable to contamination sites have been identified in the literature, and some of these are highlighted as follows: Natural attenuation, phytoremediation, air sparging, bioslurping (mainly for treatment of non-aqueous phase liquids) and bioventing (mainly for remediating contaminated soils), amongst others.

Natural attenuation, which is an in-situ treatment method, relies on natural processes to check the spread of spills and reduce the pollutants’ volume and concentration in contaminated areas. The process can be destructive or non-destructive. Destructive processes aim at destroying pollutants, while non-destructive processes aim at reducing the concentrations of contaminants (USEPA, 1996). Natural attenuation is sometimes favoured because it is less intrusive, generates less remediation waste, is relatively cheaper and can combine effectively with other remediation technologies. However, the time to attain desired decontamination goals could be too long, requiring a robust monitoring programme, and the level of unpredictability is high. Also, with natural attenuation, contaminants may sometimes migrate before their degradation, and intermediate products from the degradation process may become more toxic than the earlier contaminant degraded.

Air sparging involves permeating the atmospheric air, under intense pressure, into saturated zones to render groundwater contaminants volatile. This technology has been used to remediate volatile organic compounds in groundwater that have been sorbed in the saturated soil zones or trapped within soil pores (Suthersan, 1997; Adams and Reddy, 2003). Its major drawback is that it is ineffective against non-biodegradable and non-strippable contaminants (Suthersan, 1997), and silt and clay sediments may not be appropriate for this kind of technology (Kirtland and Aelion, 2000).

Bioventing, on the other hand, involves a process where the air is infused into the contaminated media in such a way that it enhances *in situ* biodegradation and minimally reduces the release of gas / volatilized contaminants to the atmosphere. Unlike sparging, which aims to inject air into the saturated zones, bioventing pumps both nutrients and air into the vadose (unsaturated) zones (USEPA, 1998). This technology degrades less volatile contaminants, and because it usually requires less volume of air, it is effective in less permeable soils (FRTR, 1999). Equipment is easily installed and readily available, and the technology can be combined with other remediation technologies, but it is limited in that low cleanup limits cannot always be reached and it cannot always be applied in some site conditions with high clay content or low permeabilities (USEPA, 1998).

Phytoremediation has been considered an effective means of decontamination by some authors (e.g., Banks *et al.*, 2003; Reible and Demnerova, 2002). It involves the use of plants to degrade, stabilise or extract contaminants from polluted areas. Certain plants have the natural ability to take up contaminants into their above-ground parts. Some modes of phytoremediation seek to take advantage of this. Some of these plants are called hyperaccumulators because of their ability to store large amounts of contaminants; some plants can also degrade organic contaminants and process them for use in physiological processes (Vouillamoz and Mike, 2001). An aesthetically pleasing technology, phytoremediation produces little or no environmental disturbance and can be used for a wide range of contaminants. It can be a relatively cost-effective process, with low energy requirements and can cover a wide area expanse even though it is more effective when contaminant concentration is low. A major drawback of the process is in the time it takes to attain remediation goals (although Cundy *et al.*, 2016 noted that phytoremediation could, under some situations, provide rapid risk management via removal of labile soil contaminant components and contaminant pathway management), and contaminants may infiltrate the food chain causing severe consequences to animals in the process (Nedunuri *et al.*, 2000).

These highlighted low-cost remediation technologies are hardly an exhaustive list. There are some other lower impact technologies for remediating contaminated sites, such as soil washing, soil vapour extraction, aeration, biopiles, encapsulation, soil flushing, bioslurry systems, land farming, thermal desorption, bioslurping and other techniques.

This chapter's focus is on stabilisation of contaminants in soils, and reduction of groundwater contamination risk, by soil amendment application via an enhanced natural attenuation approach. Stabilization technologies are common and have certain peculiar advantages, i.e., a much greater cost certainty than most alternatives, capability for both *ex-situ* and *in-situ* applications, and stabilised soils can be reused (Akcil *et al.*, 2015). This technology does not just reduce risks associated with contaminated soils; it can also improve the geotechnical competency of the ground (Rahman *et al.*, 2016), and enhance soil structure for subsequent agricultural production.

6.2.3 Contaminant stabilisation by soil amendment application

The concentration of both organic and inorganic contaminants in soils and groundwater is increasing globally due to a combination of both natural processes and varying human activities (Mench *et al.*, 2010). Because traditional soil remediation methods are increasingly expensive, and willingness to allocate resources to remediation is lacking, it is expedient to develop cost-effective and environmentally tolerable alternatives. One such alternative technology is soil stabilisation by soil amendments. For this review, stabilisation would be defined as a process that converts pollutants or contaminants into a less mobile or less toxic entity within the soil or aquifer.

This section gives an overview of available published data on the immobilisation of phenol, and three PAHs: naphthalene and anthracene. These focus contaminants are some of the commonest groundwater contaminants; they are soluble in water and are very prevalent in the Ogoni area, evidenced either in this current study or previous literature.

The types of soil amendments used for stabilisation are mainly dependent on the type of contaminants present in the soil. Therefore, this review will explore the types of amendments that have been used in the past to stabilise soils contaminated with phenols or any of the mentioned PAHs.

6.2.4 Stabilization Techniques

The stabilisation of contaminants present in soils by the application of immobilising agents is a cost-effective remediation technique used to impede the mobility of contaminants. It describes a soil remediation process which depends on the application of certain additives to render contaminants immobile (EPA, 1986). This technique aims at contaminant fractions that can be released and percolated to ground or surface water, or can be taken up by soil organisms, sometimes due to changes in environmental conditions (Kumpiene, 2018). It can also be regarded as one part of the stabilisation/solidification (SS) method. While stabilisation is used to describe a technique that transforms contaminants into less mobile forms, solidification describes specifically a process that involves treating material to ensure its solidity and enhance its structural integrity. The SS technique essentially refers to a remediation method that involves a physicochemical means of stabilising soil by using cement-based materials through solid barriers or vitrification (Bates and Hills, 2015). When stabilisation (reduction of contaminant mobility) is achieved solely by chemical means, the process can be described as chemical stabilisation. The same can be said for physical stabilisation when the aim is achieved solely through physical means.

Contaminant stabilisation in soils can be attained if the applied soil amendments can adsorb, complex or (co)precipitate PAHs. This method is therefore not new, as agriculturally-based techniques like soil amelioration, which involves adding phosphates, lime or organic matter to soils has been in practice for centuries with the primary aim of improving plant growth, reversing nutrient depletion (e.g. P and K) as well as reducing the phytotoxicity of the soil to crop plants by the decrease of toxic elements' bioavailability and mobility. Hence, it can be said that the SS method borrows its concept from the field of agriculture with crop plants being its original focus. This process of reducing the mobility of contaminants by soil improvements or amelioration can be achieved through exploiting soil-plant pathways and in this case, is classified as a branch of soil remediation termed phytostabilisation (Berti and Cunningham, 2000).

Applying soil amendments in the field involves spreading the amendments across areas polluted by contaminant generating activities, e.g., around smelting, mining or oil exploration sites, or by mixing amendments with contaminated soils by, e.g., ploughing. Either way, vegetation can subsequently be applied to reduce contaminant spread and also to provide aesthetic value (Houben, 2013). When a chosen ecosystem recovery takes place, site colonization with surrounding plant species and vegetation establishment is achieved, and a clear indication is pointing to remediation success is attained.

6.2.5 Immobilization of PAHs in soils - assessment of biochar and Granular Activated Carbon (GAC) as practical, locally-produced soil amendments

PAHs are a group of organic pollutants mainly characterised by their carcinogenic properties, their resistance to biodegradation as well as their high hydrophobicity (Menzie *et al.*, 1992). The occurrence of PAHs on land and in groundwater has become a major environmental concern in recent years (Menzie *et al.*, 1992). With two or more aromatic rings in their structure, PAHs mainly occur as a result of anthropogenic activities ranging from incomplete combustion of fuel to industrial waste incineration and wood burning. Natural processes like forest fires or volcanoes can also be sources. Andersson and Achten, (2015) have listed some PAHs on its list of priority pollutants due to their mutagenic and toxic consequences.

Soils' sorption capacity plays a crucial role in checking the bioavailability of organic pollutants in the environment (Ahangar, 2010). Organic soil amendments can alter the structure of soils, its transport architecture as well as its sorption features. For example, organic amendment of soils may increase water retention capacity and porosity. It may also generate changes in pore size distribution as well as soil bulk density (Huang *et al.,* 2003). The distribution coefficient Kd, which describes the ratio of contaminant concentration in the solid to a liquid phase at equilibrium, can be increased significantly by the addition of carbon-rich materials to the soil. The sorption process of hydrophobic organic compounds on black carbon (including fly ash, char, soot, charcoal) has been reported in the literature to be 10-1000 times higher than on soil organic matter when treating soils to restrict desorption and migration of organic contaminants (Lohmann, 2003). Organic compound distribution (aromatic hydrocarbons, for example) between the solid phase and liquid solution is chiefly controlled by adsorption on both soil and black carbon organic matter (Lohmann, 2003). Some researchers (e.g., Lohmann, 2003; Denyes *et al.*, 2013) have shown that the interaction between soil organic matter and organic contaminants is dominated by adsorption to black carbon.

Biochar is a product derived from the combustion of biomass in the presence of little or no oxygen (pyrolysis). Its use as a soil amendment has increased over the last decade because it has potential to improve the fertility of the soil and also improve the soil's ability to sequester carbon in the long-term, hence contributing to a reduction of atmospheric carbon dioxide. The recalcitrant carbon structures present in biochar make its decomposition almost impossible. Therefore its addition to soils can assure sequestration of carbon for extremely long periods (Hernandez-Soriano *et al.*, 2016). Its prior use as a soil amendment has been to improve soil fertility and to bolster crop production, but an alternative application of biochar as a means of remediation is garnering increasing attention in more recent times because it has an inherent affinity towards organic compounds like PAHs (Mensah and Frimpong, 2018).

Another soil amendment which gained initial prominence for its use for other environmental purposes is activated carbon. It is likewise a sorbent and a carbonaceous material that is derived from the incomplete combustion of organic substances like coal or biomass, followed by the activation of its charred residues to maximise surface area, either by steam or chemical means (Hagemann *et al.*, 2018). Some researchers have shown that the application of biochar or activated carbon to soils can decrease the toxicity and bioavailability of certain organic contaminants (Denyes *et al.*, 2013; Gomez-Eyles *et al.*, 2011).

The ultimate objective of remediation strategies is to reduce the degree of risk associated with the presence of contaminants. This is mainly achieved by reducing or sometimes the complete breakdown of source-pathway-receptor linkages (Bardos *et al.*, 2002). When a contaminant can move in sufficient quantities from the source to the receptors to cause a possibility of significant harm, then remedial actions are required. In most cases, the most effective way of dealing with polluted sites is to eliminate the source of the contaminants or restrict access to the receptor. These propositions, however, are more probable in theory and are mostly impracticable in reality because of the high costs involved, especially in cases where contamination is very widespread and where contaminated sites are in still in active use.

Pathways through which contaminants move from source to receptors are varied, but in most cases, pathways require the dissolution of contaminants into the soil. By adsorbing contaminants on their surfaces, biochars break down the existing source-pathway-receptor linkages, hence causing a significant reduction in the concentration of contaminants in the soil solution (Beesley and Marmiroli, 2011). If there is irreversible adsorption of contaminants by biochars, thereby breaking the pathways of contaminants to the receptor locations where they can cause harm, then we can conclude that remediation is achieved.

Like biochars, activated carbon is produced by the valorisation of waste biomass products, mainly through pyrolysis. In this case, however, an activation stage is required for its manufacture, mostly using steam (del Campo, 2015); it is also possible to use chemical activators such as hydrogen peroxide and potassium peroxide. The purpose of the activation is to develop the inner pore structure of the carbon to give a very high surface area (around >900 m2/g N_2 BET) which greatly exceeds that of biochars (around 1–350 m2/g N_2 BET). This, in theory, makes activated carbon more suitable for remediation of hydrophobic organic contaminants because of their greater affinity for sites with the higher surface area (Bobbitt *et* *al.*, 2017). After some degree of success in the reduction of the bioavailability of hydrophobic organic contaminants in field plots (Cho *et al.*, 2009), a new direction in remediation has been created which involves using activated carbon to break down contaminant pathways, especially those that involve hydrophobic organic contaminants (Ghosh *et al.*, 2011). This approach has become popular in some areas of the sediment remediation industry (Cho *et al.*, 2009; Cornelissen *et al.*, 2011).

Because of their superior sorption capacity and the surface area about biochars, activated carbon has been recommended as the most appropriate carbon amendments for soil and sediment remediation especially for hydrophobic contaminant impacted soils/sediments (Gomez-Eyles *et al.*, 2013). However, biochars are more advantageous in some ways. For example, biochars are relatively inexpensive compared to activated carbon when production is in bulk (<USD$1000 per ton vs USD$2500 per ton); they may be less detrimental to the health of the soil biota than activated carbon (Hale *et al.*, 2013); and they may be more effective at plant growth stimulation than activated carbon because of the soil quality enhancements associated with biochars (Denyes *et al.*, 2013). Even though activated carbon has a higher amount of sorption sites for contaminants per unit mass and consequently is more effective at reducing contaminant bioavailability in most soils, it is still important to note that biochars are generally less dense than activated carbon. This could be positive for the kinetics of contaminants transfer from the soil to the carbon surface area because biochars possess a higher amount of particles per unit mass if both are amended at the same particle size and dose (Björklund and Li, 2017). The majority of comparative studies between the two soil amendments have shown better performance of activated carbon over biochars for hydrophobic organic contaminants (Cao *et al.*, 2009; Gomez-Eyles *et al.*, 2013; Rittenhouse *et al.*, 2014). However, in a field pilot study recently carried out, there was no significant difference between the two soil amendment procedures (Denyes *et al.*, 2013). For inorganic contaminants, on the other hand, the majority of the comparative studies between the two showed significantly superior performances of biochars over activated carbons (Cao *et al.*, 2009), except for mercury (Gomez-Eyles *et al.*, 2013). Ultimately, the choice of the amendment will depend on the type of contaminant in question and the kind of soils involved.

The following sections discuss experiments performed to assess the performance of a range of biochars, and a commercially available activated carbon (which has previously shown considerable utility in the removal of trace organic contaminants by Busquets *et al.,* 2014, 2016), in adsorbing and stabilising key contaminants found within Ogoniland surface and groundwater. Specifically, experiments examine the adsorption of phenol, anthracene, and naphthalene. Phenol adsorption is also examined in experiments using real Ogoniland groundwaters, to assess any impacts of background ions on the effectiveness of contaminant adsorption.

6.3 RESULTS FROM BATCH ADSORPTION STUDIES

This section examines the adsorptive effectiveness of (a) the commercially available MAST Carbon, and (b) biochars derived from everyday agricultural products and residues (softwood, rice husk, Miscanthus (Elephant) grass straw) for phenol, anthracene, and naphthalene.

6.3.1 Adsorption of phenol by MAST carbon 230°C

As indicated in Figure 6.1, the phenol in the water ranges from 10 -100 ppm before the batch adsorption experiments (blue diamond). Following adsorption, phenol decreased to around 1.3ppm (red bars). According to Busquets *et al.* (2014), phenolic resin-derived activated carbons with optimised structure, and surface chemistry have been found to be highly effective for metaldehyde removal in environmentally realistic situations in comparison to GAC currently used in tertiary water treatment. These results highlight their effectiveness for phenol removal of 98.73%, while the adsorption capacity (at 100ppm phenol concentration) is 49.37mg/g.

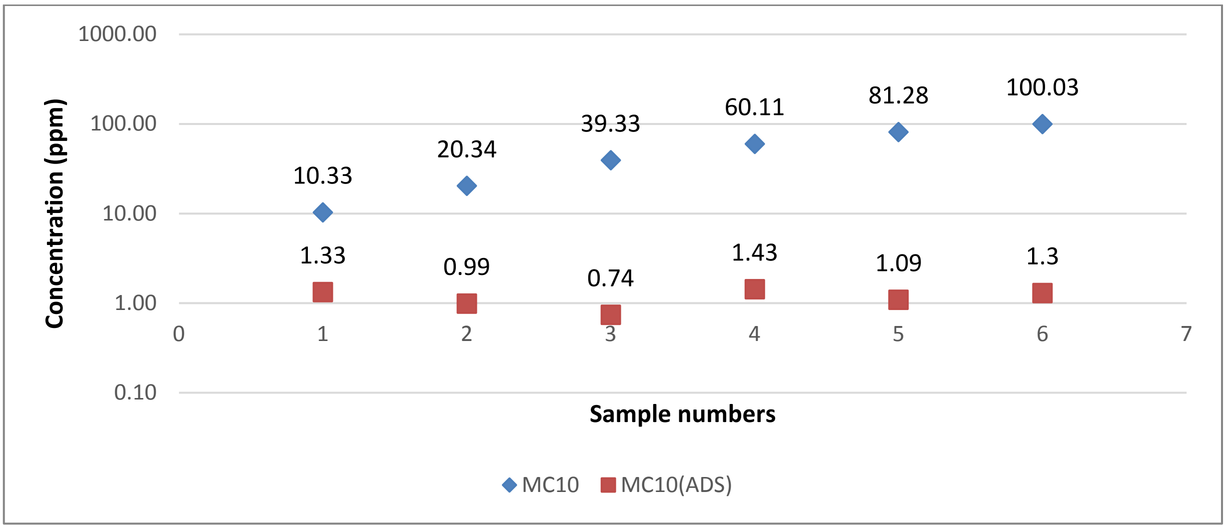

Figure 6.1 Adsorption of phenol using MAST Carbon, where MC10 means before adsorption and MC10 (ads) means after adsorption. The y-axis shows Phenol concentrations in parts per million from 0 to 1000 (logarithmic scale). The x-axis shows sample numbers. i.e. sample 1 has a starting phenol concentration of 10.33ppm; sample 2 is 20.34ppm etc.

The adsorption capacity in mg phenol / g carbon at each concentration is calculated as (Voco-Vtct) where V is the volume, C is the concentration in mg/l, 0 indicates initial concentration and t concentration at a particular time.

The adsorption capacity at 100ppm ((100mg/l*0.025)-(1.3*0.025))/0.05= 49.37mg/g

6.3.2 Adsorption of phenol using biochars

6.3.2.1 Rice Husk 550/700°C

Rice husk (RH), an agricultural waste, is abundantly available in rice-producing countries such as China, India, Bangladesh, Brazil, US, Cambodia, Vietnam, and Myanmar (Pode, 2016). Rice husk is the outermost layer of the rice grain that is separated from the edible rice grains during the refining process. The chemical composition of rice husk varies due to the differences in the type of paddy, crop year, climate and geographical conditions (Chandrasekhar *et al.*, 2006). Rice husk is pyrolysed carbon with a pyrolysis temperature of 550 or 700°C.

Before adsorption, phenol ranges from 10-100 ppm in both RH550/700 but after adsorption (Figure 6.2), rice husk was less effective than activated carbon, ranging from 7.60-86.38ppm remaining concentration, while RH700 ranges from 12.00-77.05ppm, which was due to a lower surface area, impurities, and other pyrolised organic matter. RH550 biochar adsorbed between 2.73 and 13.62% of the phenol, while RH700 adsorbed between -1.68 and 22.95%. RH700 performs significantly better than RH550; the adsorption capacity at 100ppm phenol concentration of RH550 is 6.83mg/g and RH700 11.49mg/g. There is some leaching of residual ash, which increased the pH. The adsorption capacity for phenol is relatively low, which contradicts Mahvi *et al.* (2004) and several authors who note that RH is very effective in removing phenol from groundwater. This is further discussed in Chapter 7.

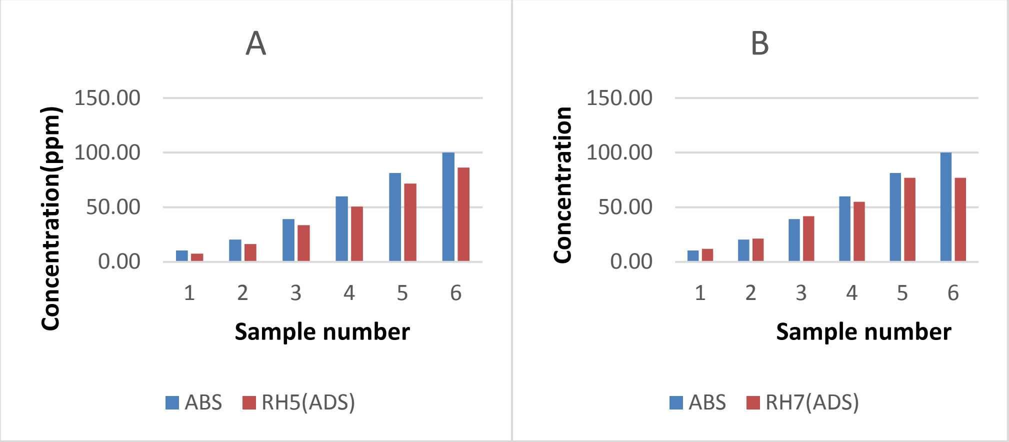

Figure 6.2 Adsorption of Phenol using (a) Rice Husk 550 and (b) 700 (ABS = absorbance before the experiment, while ADS = after adsorption experiment). The y-axis shows Phenol concentrations in parts per million. The x-axis shows sample numbers.

6.3.2.2 Miscanthus straw 550/700°C

According to Heaton (2011) and Howes *et al.* (2002), *Miscanthus* straw species are tall, woody, perennial, rhizomatous grasses. Most rhizomatous grasses retain a significant proportion of their nutrients in the rhizomes, retaining little in the biomass, so nitrogen and nutrient requirements are very low. These types of grasses are native to Nigeria, even though they originated mainly from Asia.

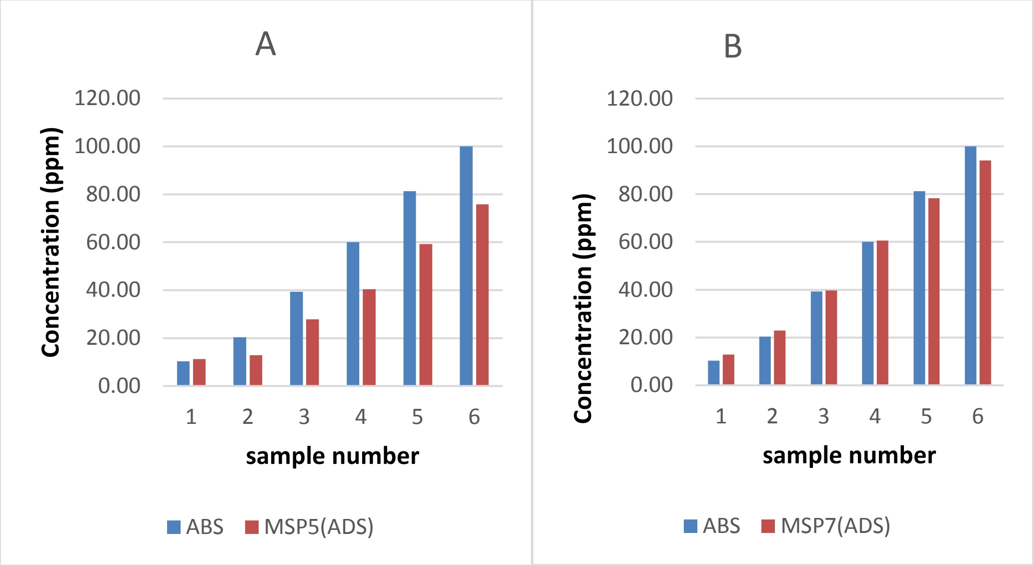

Figure 6.3 Adsorption of Phenol using (a) Miscanthus Straw 550 and (b) 700. (ABS = absorbance prior to experiment, while ADS = after adsorption experiment). The y-axis shows Phenol concentrations in parts per million. The x-axis shows sample numbers.

According to Figure 6.3, phenol ranges from 10.33-100.03ppm before absorption, but after adsorption, the MSP550 treated samples range from 11.31-75.83ppm while MSP700 ranges from 12.83-94.15ppm. Miscanthus straw shows very low adsorption of phenol. MSP550 biochar adsorbed between -0.98- and 24.17% of the phenol while MSP700 adsorbed between -2.5 and 5.85%. MSP550 performs significantly better than MSP700; the adsorption capacity of concentration at 100ppm for MSP550 is 12.1mg/g and MSP700 is 2.94mg/g.

6.3.2.3 Soft Wood 550/700°C

Pyrolysing-dried chips of debarked spruce (*Picea abies* (L.) H. Karst.) and pine (*Pinus sylvestris* L.) from Guildford, UK, were used to produce the biochar used in this experiment. The experiment was done according to Shi *et al.* (2016). The chips were pyrolysed in a furnace in a constantly pressurised laboratory at 550–700°C for 10–15 minutes at the University of Surrey. The process produced about 50% biochar, 30% gaseous products, and 20% bio-oil. The biochars were cooled overnight in an airtight silo and ground with a roller mill.

According to Figure 6.9, phenol ranges from 10.33-100.03ppm before absorption, but after adsorption, the SW550 treated samples range from 8.51-83.33ppm while the SW700 treated samples range from 9.78-95.51ppm. Softwood biochar shows very low adsorption of phenol. SW550 biochar adsorbed between 1.49-10.67% of the phenol, while SW700 adsorbed between 0.22-4.49%. SW550 performs significantly better than MSP700; the adsorption capacity at a concentration of 100ppm phenol for SW550 is 5.34mg/g and SW700 is 2.25mg/g.

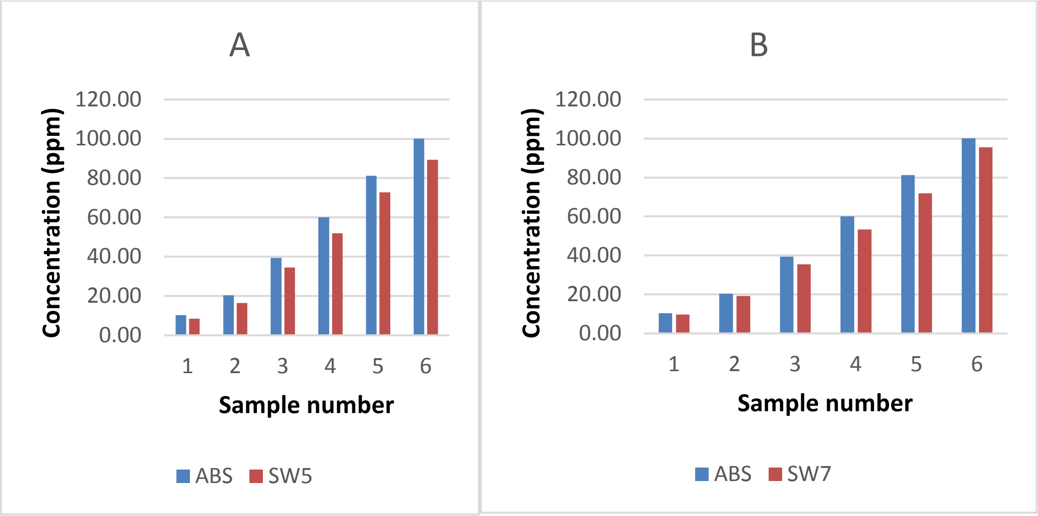

Figure 6.4 Adsorption of Phenol using (a) Soft-wood 550 and (b) 700. (ABS = absorbance prior to experiment, while ADS = after adsorption experiment). The y-axis shows Phenol concentrations in parts per million. The x-axis shows sample numbers.

6.4 pH EFFECTS

The pH is an essential factor in the adsorption process of phenolic compounds in aqueous solutions since it influences the ionisation status of phenols. The process of adsorption depends both on the behaviour of the adsorbate and the adsorbent. Generally, more phenol adsorption occurs in acidic conditions as compared to alkaline conditions (Bazrafshan *et al.*, 2016).

6.4.1 pH effect on the level of phenol absorption by MAST Carbon

From Figure 6.5, MAST Carbon activated carbon showed effective adsorption at all pHs tested (covering the range of pHs likely to be encountered under natural conditions in the Ogoniland area - see Figures 4.19 and 4.20). The adsorption capacity of MCpH3 at 100ppm phenol concentration is 47.29mg/g; pH5 is 46.61mg/g; pH7 is 48.72mg/g; and pH9 is 48.56mg/g.

This shows that pH did not have a major impact on adsorption capacity over the pH ranges used, although pH5 and pH7 gave the best adsorption behaviour, and adsorption was less effective at low pH ranges. This suggests that MAST carbon activated carbon can be utilised as a soil amendment in the Niger Delta region because most environmental waters are neutral to alkaline (see Chapters 2 and 4), while soil in Ogoniland ranges from less acidic to neutral.

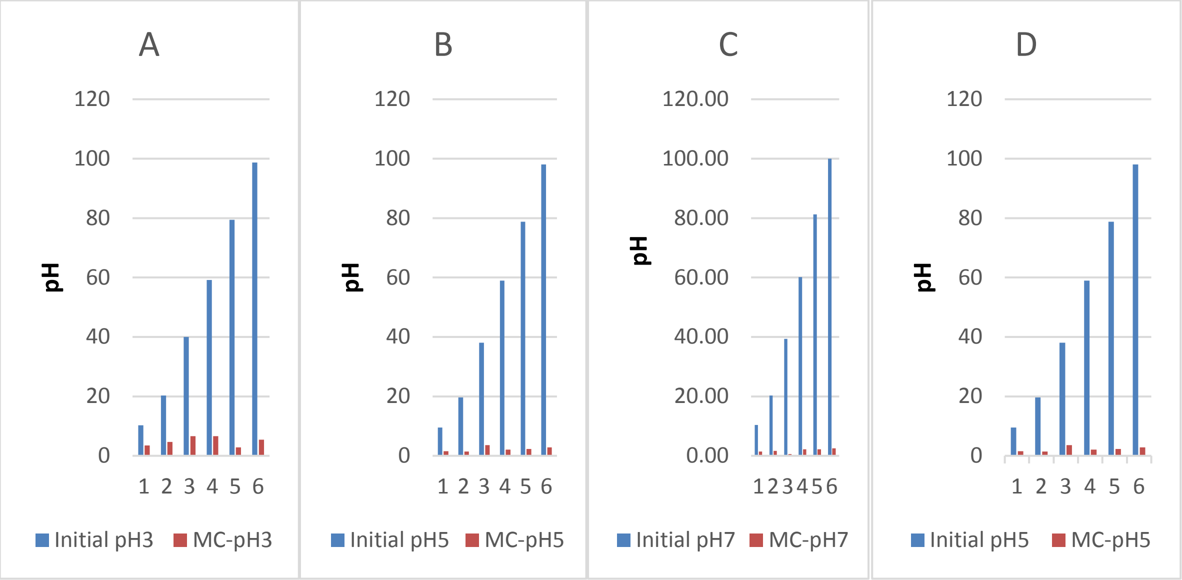

Figure 6.5 Effects of pH on the level of phenol adsorption by MAST carbon, at (a) pH 3, (b) pH 5, (c) pH 7 and (d) pH 9. The y-axis shows Phenol concentrations in parts per million. The x-axis shows sample numbers.

6.4.2 pH effect on MSP (pH3, pH5, pH7 and pH9)

From Figure 6.6, there was little difference in adsorption effectiveness with pH, over the pH ranges likely to be encountered in the Ogoniland soils and surface and groundwaters. The adsorption capacity of MSP550 at 100ppm phenol concentration at pH3 is 13.98mg/g, pH5 is 11.50mg/g, pH7 is 12.66mg/g and pH9 is 11.69mg/g.

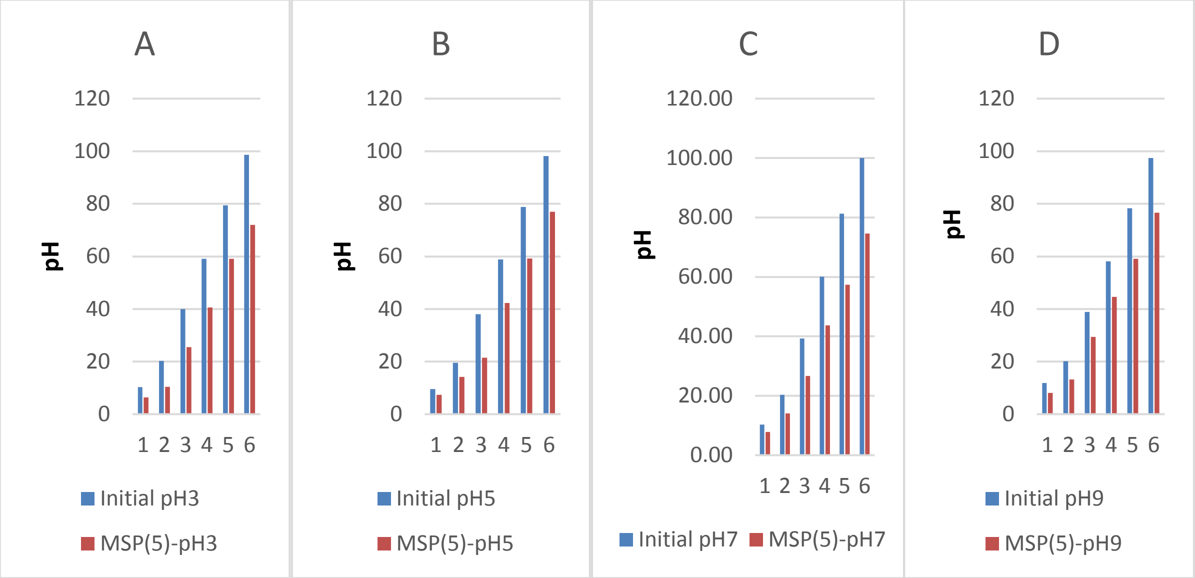

Figure 6.6 Effects of pH on Biochar adsorption by Miscanthus Straw, at (a) pH 3, (b) pH 5, (c) pH 7 and (d) pH 9. The y-axis shows Phenol concentrations in parts per million. The x-axis shows sample numbers.

6.5 RESULTS FROM OGONILAND GROUNDWATER SAMPLES

In the previous section, the results of batch adsorption experiments for a range of Biochars (and one activated carbon) in deionised water spiked with phenol were discussed. Here, adsorption in real Ogoniland groundwater samples is discussed, to assess the performance of adsorbents under realistic conditions for their potential application in Ogoniland. Representative samples from each local government area in Ogoniland were used, and three different adsorbents (MAST carbon, MSP550, and RH550) which had shown the best adsorption characteristics in deionised water were examined. Figure 6.12 shows the results from these adsorption studies, using samples from the two LGAs in Ogoniland Eleme LGA (Ogale) and Gokana LGA (Bodo), and Port Harcourt city LGA (Amadi-Ama).

As noted in chapter 4, the initial phenol concentration observed in the Amadi Ama (Port Harcourt city) groundwater sample was high, at 26.78ppm. After adsorption using MC, MSP5, and RH5, Phenol was reduced to 0.011-0.44ppm (Figure 6.7), with all adsorbents showing effective phenol adsorption. The phenol concentration observed in the Ogale1 sample is extremely high, at 321.68ppm. After adsorption using MC, MSP5, and RH5, Phenol was greatly reduced to 0.005ppm. Similarly, phenol concentrations in the Ogale4 sample were reduced from 343.45ppm before adsorption to 0.007-0.008 ppm after adsorption, and in the Bodo 1 sample from 21.88ppm before adsorption to 0.006-0.021 ppm after adsorption.

The Ogoniland water sample results, therefore, show that both MAST carbon and biochars have good adsorptive performance when added in sufficient quantities, with 99% adsorption in the study area as seen in Figure 6.12. The use of real environmental waters should have impacted on the adsorption capacity generally; data would be expected to show a lower adsorption capacity in mg phenol / g carbon in ‘real’ environmental waters than in the deionised water batch adsorption experiments, due to the presence of competing ions which may interact with the adsorbents and occupy some of the available binding sites. However, this effect is not expected to be of real significance, as the results in Chapter 4 showed high TDS values closer to what is obtainable in real environmental waters. It is important to note that even in the presence of high TDS values, optimal adsorption was maintained, and this signifies the effective adsorption capacity of these carbons irrespective of the degree of variability in ion content. Peng *et al.* (2016) agreed that pH had significant effects on the adsorption, which could well be explained by hydrophobic, hydrogen bonding, and electrostatic repulsion when using biochars.

Furthermore, they noted that the acid-washed biochars presented a higher adsorption capacity than the original biochars, which was probably due to the decrease in inorganic elements as well as the polarity of biochars. The biochars used for this experiment contained many impurities and were not washed, which resulted in relatively low adsorption uptake in batch studies. Hence, it is crucial to take necessary pre-processes (e.g., acid treatment and washing) of biochars into consideration, to achieve higher adsorption capabilities for environmental application.

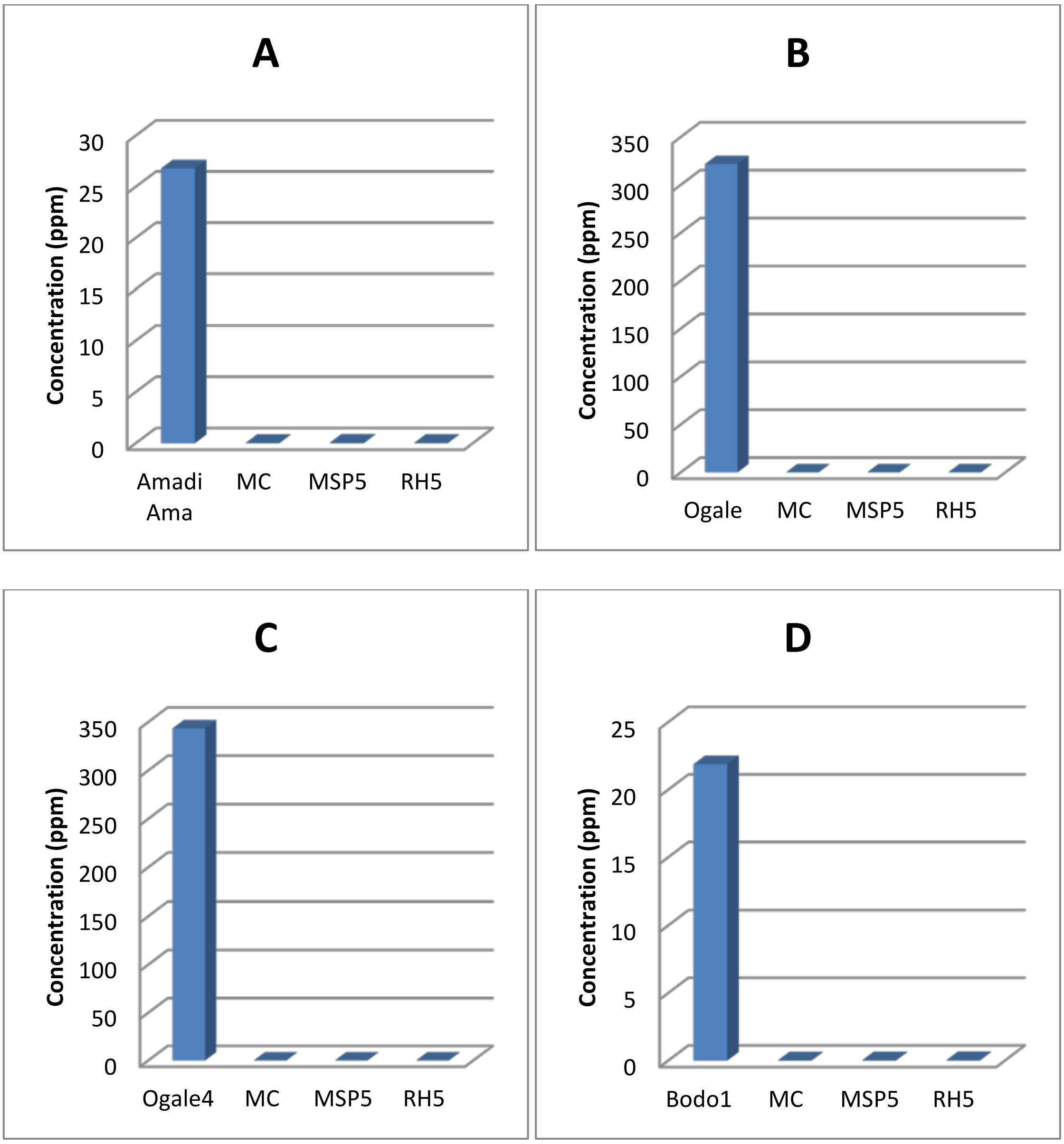

Figure 6.7 Adsorption of Phenol using MC, MSP5 and RH5 in (a) Amadi Ama, (b) Ogale1, (c) Ogale 4 and (d) Bodo 1 groundwater samples. The y-axis shows Phenol concentrations in parts per million; concentrations at Amadi Ama fall from ~30 to ~0 ppm, Ogale 1 and 4 from ~350 to ~0 and Bodo 1 from ~25 to ~0. The x-axis shows the material used (MC, MSP5 and RH5).

6.6 ADSORPTION ISOTHERMS

Adsorption isotherms are significant in describing how solutes interact with adsorbents and remain critical for enhancing the use of adsorbents (Kumar *et al.*, 2008). Numerous empirical models have been published in the literature to correlate the adsorption and desorption behaviour with experimental data from adsorption isotherms; among these the Langmuir and Freundlich models are the most frequently employed (Aliakbarian , 2015).

The Langmuir model can be expressed as follows:

(1) $Q_e=Q_{ob}C_e1+bC_e$

Where, Q_e (mmol/g) is the amount of sorbate adsorbed, C_e (mM) is the equilibrium concentration of adsorbate; Q_o (mmol/g) is the maximum heavy metal or phenol adsorption capacity, and b (L/mmol) is related to the affinity of the binding sites. Q_o and b are determined from the linear plots of $1/C_e$ versus $1/Q_e$ (Kumar *et al.*, 2008).

The Freundlich model can be expressed by the following equation:

(2) $Qe=K_FCe1/n$

Where, K_F and $1/n$ are constants and are related to the adsorption capacity and the adsorption intensity, respectively (Kumar *et al.*, 2008).

The results in the isotherms below (Figures 6.8-6.11) did not follow the typical profile shape expected for the Langmuir or Freundlich models. This is because higher phenol concentrations would be required to define the characteristic Langmuir profile. The Langmuir model assumes coverage of the sorbent with a monolayer of sorbate. A comparison between the performance of MAST carbon and biochars was carried out. This procedure was limited to how well these adsorbents remove phenol, and this was done by incubating the carbons with phenol-spiked aqueous solutions at a range of concentrations that represents accurately environmental levels, with high concentrations that would occur in the cases of spillages.

According to Busquets *et al.* (2014), if a further rise occurred, it might have been caused by a re-orientation of the sorbate or the formation of a second adsorbed layer, but this behaviour has not been observed here. Moreover, the slope of the curve in a Langmuir model is related to the so-called “Langmuir adsorption constant,” which increases with the binding energy of adsorption. Therefore, it can be distinguished that the adsorption of phenol is much stronger in the MAST carbon than in biochars .

6.6.1 Adsorption Isotherms for Phenol

From Figure 6.8, the adsorption isotherm of MAST carbon shows the highest adsorption capacity, as seen in Table 6.1. The temperature of biochar production significantly influenced the adsorption capacity, as biochars activated at a temperature of 550°C are more effective adsorbents than those activated at 700°C. The physical and chemical properties of biochars are also known to be strongly affected by pyrolysis conditions such as the highest treatment temperature, heating rate and residence time (Keiluweit *et al.*, 2010; Ahmad *et al.*, 2012). Among these variables, the temperature is considered as the main factor affecting biochar characteristics (Enders *et al.*, 2012). Accordingly, high pyrolysis temperatures (e.g., 750 °C) result in more crystalline and porous structure (Keiluweit *et al.*, 2010; Yuan *et al.*, 2011; Ahmad *et al.*, 2013, 2014). Thus, high-pyrolysed temperature biochars may have physical characteristics similar to those of activated carbon, including high mechanical stability and porosity. The samples indicate better performance however at 550-pyrolysis temperature (Keiluweit *et al.*, 2010; Moreno-Castilla and Rivera-Utrilla, 2001).

Alizadeh *et al.* (2016) noted that in both sorption and desorption batch equilibrium experiments, softwood 450°C biochar showed better remediation performance for phenol pollution compared to softwood 700°C biochar. This is in close accord with observations made in the present study.

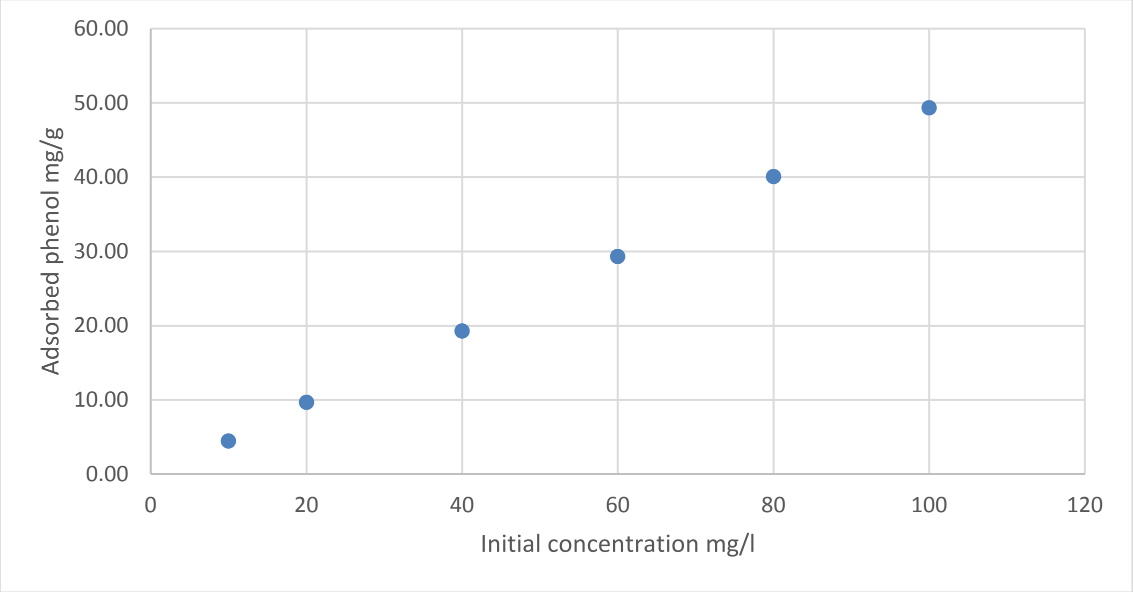

Figure 6.8 Adsorption isotherm for phenol using MAST Carbon. The y-axis shows adsorbed Phenol in mg phenol / g of adsorbent. The x-axis shows the initial phenol concentration in parts per million, from 0 to 120.

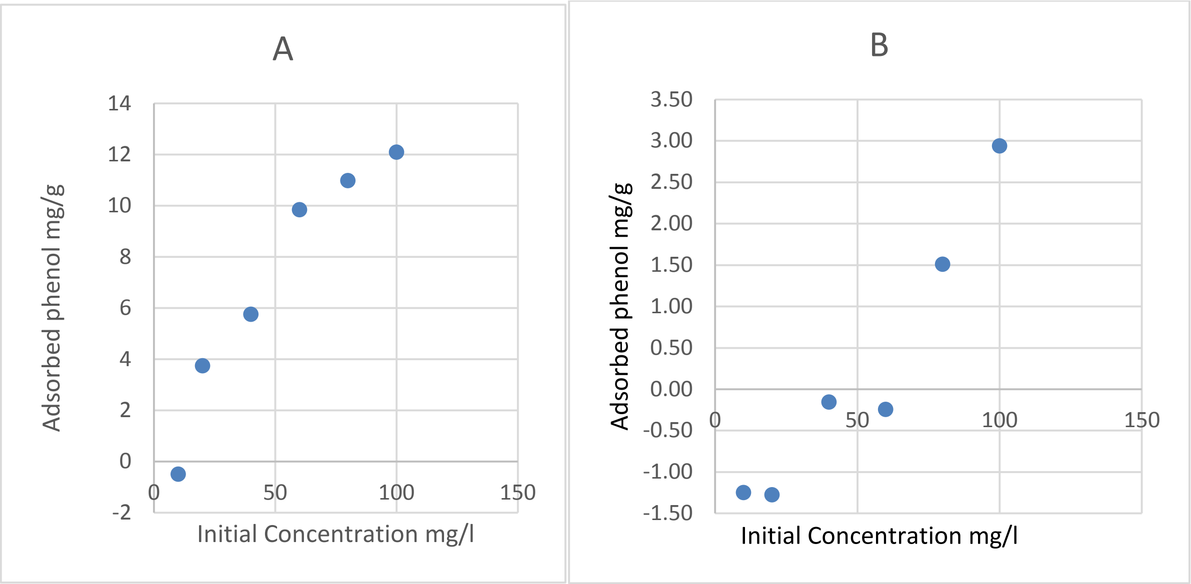

Figure 6.9 Adsorption isotherm for phenol, using (a) MSP550, and (b) MSP700. The y-axis shows adsorbed Phenol in mg phenol / g of adsorbent. The x-axis shows the initial phenol concentration in parts per million, from 0 to 150.

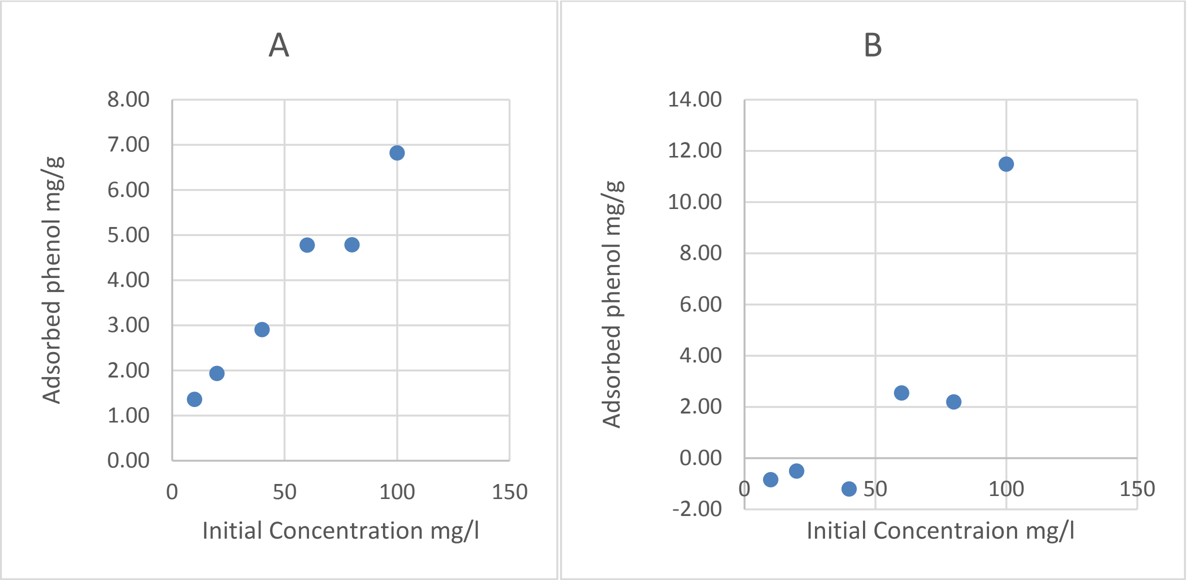

Figure 6.10 Adsorption isotherm for phenol, using (a) RH550 and (b) RH700. The y-axis shows adsorbed Phenol in mg phenol / g of adsorbent. The x-axis shows the initial phenol concentration in parts per million, from 0 to 150.

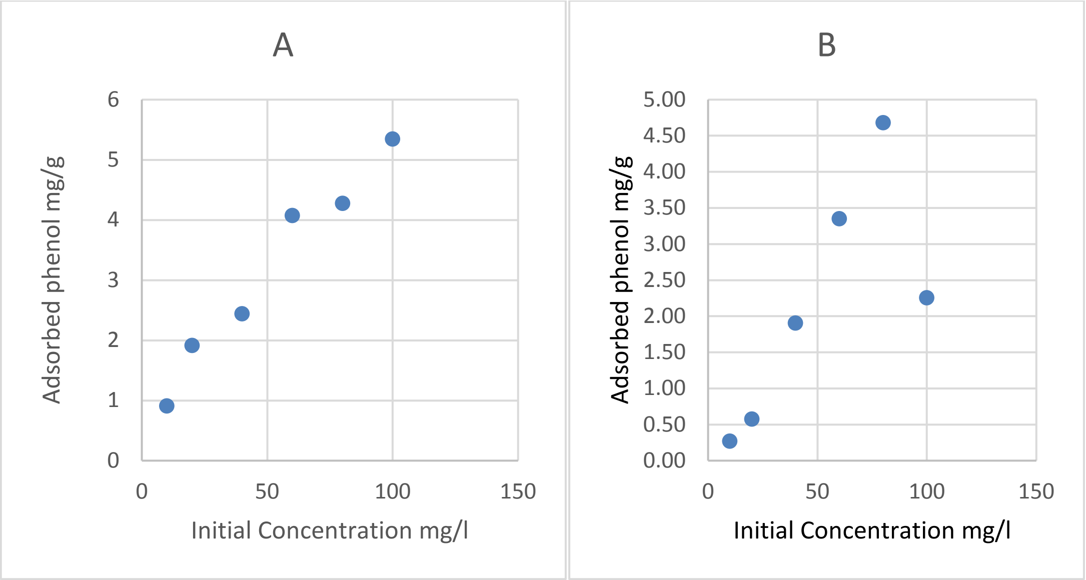

Figure 6.11 Adsorption isotherm for phenol, using (a) SW550 and (b) SW700. The y-axis shows adsorbed Phenol in mg phenol / g of adsorbent. The x-axis shows the initial phenol concentration in parts per million, from 0 to 150.

Table 6.1 Results of adsorption capacity of MAST carbon and biochars.

Sample type	**Adsorptive Capacity: at 100 (mg/g carbon)**
MAST Carbon	49.31
MSP5	12.1
RH7	11.49
RH5	6.83
SW5	5.35
MSP7	2.94
SW7	2.26

6.6.2 Adsorption of PAHs (anthracene and naphthalene)

Polycyclic aromatic hydrocarbons (PAHs) are organic micropollutants that are persistent in the environment due to their hydrophobic nature; this has resulted in extensive studies on removal methods for various types of PAHs. Adsorption is one of the most widely used PAH removal methods, as PAHs possess a great sorptive ability onto solid media and has low aqueous solubility (Lamichhane *et al.*, 2016). Numerous adsorbent media such as activated carbon, biochar, and modified clay minerals have been used to remove PAHs from aqueous solution and to immobilise PAHs in contaminated soils. This section focuses on the efficiency of adsorption using MAST carbon and other biochars (RH5 and MSP5) using Ogoniland waters.

Table 6.2 Results of adsorption of anthracene and naphthalene, presented in terms of adsorptive capacity by adsorbent type.

Sample type	**Adsorptive Capacity: Naphthalene (mg/g carbon)**	**Adsorptive Capacity: Anthracene (mg/g carbon)**
MAST Carbon	>60	0.681
Rice Husk	56.2	0
Miscanthus grass	56.4	0

As seen in Table 6.2, MAST carbon showed the highest adsorption capacity for naphthalene, although adsorption was also significant in rice husk and Miscanthus grass biochars. For MAST Carbon, the adsorption capacity could be significantly higher than the 60mg/g reported. Anthracene showed little adsorption. Ogbonnaya and Semple (2013) and Beesley *et al.* (2010) noted that, regardless of the presence of co-contaminants, biochars still strongly affected the total and bioavailable fractions of PAHs. As a result, biochar can be a crucial instrument to remove unacceptable risks by disrupting pollutant pathway of PAHs to humans and the environment. Kolb *et al.* (2009) and Yang *et al.* (2010) noted that the minerals within biochar serve as a source of nutrients to microorganisms and plants, which can additionally aid the growth of microbes and plants used for biodegradation of PAHs. However, the majority of studies have proven to be positive only within confined laboratory conditions (Yu *et al.*, 2009). Applying a large number of biochars in field studies should be more effective. Thus extensive investigations are required on field-contaminated land.

6.7 CHAPTER SUMMARY

Both biochars and MAST carbon are non-toxic substances. While MAST carbon is industrially produced, the biomass needed for mass production of biochars in Ogoniland is abundant and can be very cheaply obtained. Biochars are biological residues combusted under low oxygen conditions, resulting in an absorbent, low-density carbon-rich material. However, their large surface areas and cation exchange capacities, determined to a large extent by source materials and pyrolysis temperatures, enables enhanced sorption of both organic and inorganic contaminants in their most mobile forms. These surfaces serve to reduce pollutant mobility when amending contaminated soils and are a cost-effective approach (Xie *et al.*, 2014).

The experiments described in this chapter provide evidence of the potential of biochars and MAST carbon activated carbon to be used as an appropriate natural cleaning agent, particularly for phenol, and possibly as a partially alleviating soil treatment for oil spill contamination. The results are in line with similar assertions by many authors including Silvani *et al.* (2017), Xu *et al.* (2017), Huggins *et al.* (2016), Gupta and Tai (2016), and Gao *et al.* (2012) that natural biochars are practically suitable for remediation of contaminated soils, due to their malleability and high sorption capacity for contaminants. Biochars were found to be suitable and effective for sorption of contaminants. The measured rate of contaminants sorption by MAST carbon was significantly higher than biochars, but biochars have the potential to be re-used as soil amendments in oil-producing countries with crude oil spillage problems, which is in line with the current study location. According to Mahvi *et al.* (2004), and Gámiz *et al.* (2017), biochars are very effective as soil amendments. Furthermore, MAST carbon and biochars could be combined with other environmentally friendly techniques, such as phytoremediation, to achieve complete removal and remediation of oil contamination in soils. The results strongly suggest that MAST Carbon and biochar utilisation presents an environmentally friendly and suitable green technology for remediation of oil contaminants in sites around the Niger Delta.

Since modern environmental clean-up approaches are more focused on the effects of the most toxicologically relevant elements of contaminants, biochars can be an appropriate candidate for remediation. Nevertheless, pollutant immobilisation represents only one facet of contaminated land remediation. With the need for improvements to some soil physicochemical limitations of soils in the Niger Delta, biochars seem highly suitable for the amendment of these contaminated soils, but in some cases, this may require their combination with other amendments. For example, biochars have been found to be less effective in the amendment of phytotoxic elements like Naphthalene and Anthracene. However, their effectiveness may be further enhanced by manufacturing and increasing the number of biochars used and combining with other cost-effective and environmentally friendly remediation options.

Although the results vary according to the source material and production temperatures (550°C was more effective than 700°C), and the individual contaminant concerned, decreases in organic pollutant mobility ideally allow the same amendment to be deployed at multi-element polluted sites. This gives an attractive and cost-effective, multipurpose appeal to the continued use of biochars on a wide variety of contaminated soils, keeping mindful of certain key limitations.

In agreement with findings from past studies, it is possible to achieve a high removal efficiency using activated carbon and biochar adsorbents. PAHs adsorption capacity can be influenced by several parameters such as particle size of the adsorbent, pH, temperature, solubility, and salinity, as well as the production process of adsorbents. The results of the biochars experiment with anthracene and naphthalene show very low adsorption rates; this is likely because of the impurities found in the biochars in the production process. Even though many studies have been carried out to remove PAHs using the adsorption process, the findings from this study show that more work (e.g., washing and treating the biochars before experimentation) needs to be done to get the correct information for future studies in order to optimise the adsorption method to remove PAHs (Lamichhane *et al.*, 2016).

CHAPTER 7.0 – INCORPORATION OF CARBON-BASED SOIL AMENDMENTS INTO HYDROCARBON REMEDIATION STRATEGIES IN OGONILAND

7.1 INTRODUCTION

This chapter evaluates, based on research presented in the previous chapters, the potential use of carbon-based adsorbents in contamination risk management in Ogoniland, with particular reference to hydrocarbon contamination of surface and groundwaters. The chapter (i) summarises existing contamination problems in Ogoniland, (ii) synthesises the key findings from earlier chapters in this thesis, (iii) reviews contaminant linkages via presentation and discussion of a conceptual site model, (iv) examines how these linkages may be controlled or broken using carbon adsorbents (combined with other gentle remediation technologies), and (v) assesses how the HOMBRE soft re-use tool and Greenland DST may be used to identify wider benefits from these risk management strategies. The main considerations for the provision of potable/clean water systems in communities are outlined, and remediation cost issues discussed.

According to UNEP (2009), about 140 billion metric tons of waste biomass is produced globally from agricultural activities every year. Also, ineffective disposal of the waste biomass constitutes a problem for society because decomposition generates greenhouse gases. Nabegu (2011) indicated that the waste sector contributes up to one-fifth of global anthropogenic methane emissions, and so is a major contributor to global climate change. As this chapter demonstrates, much of the waste biomass in Nigeria could be used (via production of adsorbent materials) in the remediation of hydrocarbon-polluted contaminated land. It is important to mention, however, that the general criteria for the evaluation of biomass-utilising processes are their sustainability credentials and product yield. Other relevant factors, especially in developing nations, are the cost of production and the socioeconomic impact on the populace. There have been several investigations into the potential uses of corncob and sugarcane bagasse in both developed and developing countries, and these will be discussed (Gwenzi *et al.*, 2017).

7.1.1 Summary of existing contamination problems in Ogoniland

The literature review (Chapter 2) identified several examples of health and environmental problems in Ogoniland linked to land and water contamination, a lack of treated drinking water, and discharges from oil production and other activities. The affected communities are located in coastal and waterfront areas; whenever oil exploitation takes place, crude oils and other products can be released into the surface water and infiltrate to a local creek, soil, and surface water systems and groundwater. Contamination issues are caused by both organic (i.e., hydrocarbon and associated industry-derived by-products) and inorganic contaminants. In some communities, mainly where surface and groundwater are stagnant, the pollution problem increases due to pollutant accumulation.

In Ogoniland, three main sources of hydrocarbon pollution have been identified. These are (i) oil spills from petroleum industries, (ii) gas flares from petroleum industries, and (iii) effluent and waste discharges from petroleum industries.

7.1.1.1 Oil spill occurrences

In Ogoniland, between 1993 and mid-2007, around 35 incidences of oil spills were recorded, with presumably additional unseen leaks and unreported cases. The major sources of these incidences include pipeline and flow line leakage/blowouts, blowouts from well-heads (due to poor maintenance and damage), oil sabotage and spills from flow stations (Legborsi, 2007). Such releases, which include benzene, phenols, TPH and PAHs, not only pollute crops but also marine life and sources of water for domestic use. Depending on the spill area, oil may spread onto farmland and waterbodies. The more soluble components of the oil filter into the ground and might be taken up by plant roots. According to Numbere (2018), oil spills lower soil fertility and cause poor growth of plants. Mangrove forests are vulnerable to oil spills, as the presence of oil in the rooting zone may lead to oxygen starvation.

7.1.1.2 Gas Flares

Oil production includes the burning of hydrocarbon gases and the flaring– of natural gas as a by-product when drilling crude oil from reservoirs in which oil and gas are mixed. The flames release dangerous hydrocarbons, mostly methane and others that include sulphur and nitrogen oxides, into the atmosphere. The flares increase the temperature of the surrounding environment beyond the normal of 13-14,000 degrees Celsius and may cause noise pollution (Wuraola, 2016). Light pollution in the vicinity of the flare exposes living organisms to 24-hour daylight, and this affects day and night vision patterns in animals. The flares contaminate water bodies, which affects the reproduction of fish as well as forcing their migration away from the flaring areas. The gases released during gas-flaring mix with the moisture in the atmosphere to form acid rain with a pH <5.7 (Ajugwo, 2013).

Despite a 29% reduction in gas flaring in the Niger Delta between 2005 and 2010, Nigeria remains one of the worst offenders in gas flaring, second only to Russia (Oluduro, 2014). The result of this allowable emission of gases is the discharge of 35 million tons of carbon dioxide and 12 million tons of methane, which means that the Nigerian oilfields contribute more to global warming than similar settings anywhere in the world (Ajugwo, 2013). Nigeria recorded a huge revenue loss due to gas flaring and oil spillage, including ~$2.5billion annually through gas flaring (Agochi, 2014). Studies suggest that 100% of the gases in Ogoniland were being flared (Maduka and Tobin-West, 2017). Furthermore, Ogoni people’s daily activities such as farming, fishing, bathing, cooking, and most other domestic chores are conducted outdoors. Hence, exposure to toxic chemicals, including benzene, dioxin, and benz[a]pyrne, is inevitable (White and Bimbaum, 2009); this makes the Ogoniland area one of the most polluted in the world (Yakubu, 2017).

7.1.1.3 Effluent and waste discharges

Numerous multi-national companies in Ogoniland release effluents into the environment surrounding their operations, including into nearby waters. For instance, during oil exploration, boring mud and liquids are utilised for stimulating generation; various chemicals are also utilised as part of seismic exploration activities (Lee, 2016). The constituents of bore cuttings, for example, barytes and bentonitic dirt, once disposed of on the ground prevent nearby plants from developing to the point that characteristic procedures form new topsoil (Okoro *et al.,* 2016). According to Gregory (2009), these materials may be scattered and sink into nearby waters, and kill bottom-living plants and creatures by smothering. The transfer of waste into the ocean from oil industries affects fish stocks (Scott and Zabbey, 2013); this has influenced Ogoniland communities that rely upon fishing as one of their principal livelihood strategies.

7.1.2 Summary of key results from this thesis

The reconnaissance-level analysis of both surface and groundwater from Ogoniland (Chapter 4) generated data on several cations and anions, trace and heavy metals, TPH, and gross levels of phenol. Many of these exceed the national and international guidelines presented in Table 4.1 and 4.2 (see section 4.8). In the absence of centralised water treatment facilities, particularly in houses built on waterfronts, drinking water without treatment is the common practice in Ogoniland; therefore, consumption of this surface water and groundwater provides an important exposure pathway for local populations.

Findings from core flooding studies of simulated Ogoniland soils (Chapter 5) demonstrate that phenol shows a delayed breakthrough compared to a conservative tracer (Cl). This means that there is some interaction between the phenol and the simulated aquifer material used. Phenol appears to be subject to adsorptive-based natural attenuation processes in the Ogoniland aquifer, in addition to biological breakdown.

Findings from adsorption studies (Chapter 6) show the potential effectiveness of using carbon-based adsorbents such as activated carbons and biochars for removing contaminants from ground and surface waters. The findings also demonstrate the potential to use carbon adsorbents as soil amendments to remove key soil contaminants in the region, breaking the contaminant pathway to potable water sources, particular groundwater.

In this chapter, the following questions will be addressed: (i) What are the alternatives for reducing contamination in Ogoniland? (ii) In providing clean water systems, what are the essential factors to be considered? In identifying the key considerations for the provision of low-cost remediation strategies in coastal and waterfront communities, it is necessary to analye the environment, community structure and available services such as water supply, a collection of contaminated products, oil exploration and existing management of this problem.

7.1.3 Conceptual site model

A conceptual site model (CSM) is an illustration that sets out the critical contaminant linkages of concern for a particular land contamination problem. The CSM provides knowledge of what needs to be undertaken to achieve risk management, and from this point, appropriate remediation techniques for any set risk management goals can be chosen (McMahon *et al.*, 2001). Figure 7.1 presents an overall conceptual site model for contaminant linkages in the Ogoniland area. These linkages and the model are now discussed.

The integrity of natural environmental systems, food crop production, as well as human health, is threatened severely by contamination from industrial sites via groundwater pathways. As shown from the conceptual model in Figure 7.1, severe groundwater contamination can occur via some pathways. For example, spills from the petroleum industry can be leached into groundwater bodies via surface runoff. As groundwater is a major part of the hydrologic cycle, contamination from, for example, gas flares and effluents could indirectly have effects on groundwater systems; this has a corresponding effect on drinking water and food production.

From Figure 7.1, the CSM describes the pathway for each of the main contaminant sources. For example, pathway 1 shows percolation of contaminated waters arising from surface and groundwater pollution via industrial discharge into the water bodies. The discharge of waste effluents from industrial plant facilities is a further source via pathway 1. Gas flares will have a major atmospheric pathway to crops and animals via pathway 2. Humans are affected via pathways 1 and three as a result of oil spills. Humans, animals, and the wider ecosystem, including crops, are affected, as seen in picture 4 a and b, due to the consumption of contaminated water for drinking purposes, crop irrigation, and life processes.

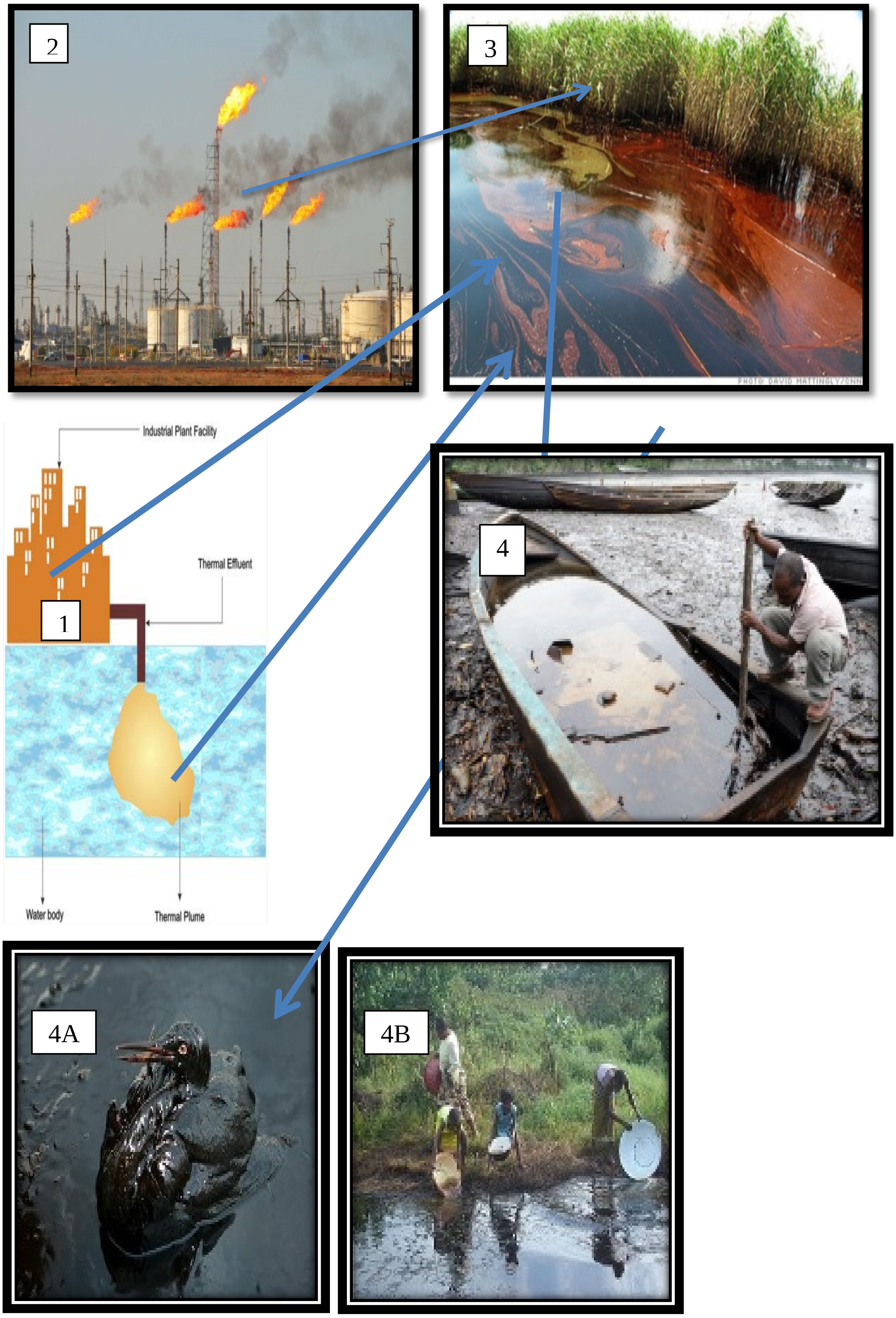

Figure 7.1 Conceptual site model (CSM) of contamination.

According to Caban (2018), oil spills in the Niger Delta can lead to as much as a 60% reduction in household food security, can reduce the ascorbic acid content of vegetables by as much as 36%, and can decrease the crude protein content of cassava by up to 40%. This can potentially result in a 24% increase in the prevalence of childhood malnutrition. Moving to better handling of crude oil, and the reduction of pollution, in the Niger Delta will lead to both healthier residents and a healthier environment. Akpokodje and Salau (2015) noted that using empirical findings, the increases in levels of oil spillage negatively affect agricultural production or productivity in the Niger Delta. Although the incidence of vandalism has reduced drastically in recent times, the low rates of bio-degradation of spillages and recovery rates of the deforested land still negatively affect agricultural output/production in the Niger Delta.

7.2 POTENTIAL USE OF CARBON-BASED ADSORBENTS TO MANAGE CONTAMINANT PATHWAYS IN OGONILAND

7.2.1 Comparison of results of adsorption experiments with previous studies

During the experiments in Chapter 6, it was observed that GAC is very effective in reducing contaminants (by up to 99%), while biochars were effective up to 50-70%. Despite the relatively low adsorption efficiency of biochars observed in the current study, their low-cost and potential for on-site (i.e., local) production suggest that they may still have application in combined, large area, soil improvement and contaminant risk management strategies. Commercial activated carbons, due to their higher cost (MAST carbons have an approximate cost of £50/kg, and Conventional GAC is about £2 - £5 per kg, depending on formulation) may find the potential application at the point of water use but are unlikely to be effective community-level tools for large area application**.** Zhang (2013) noted that the use of GAC was able to absorb a large amount of phenol, while Freitas and Farinas (2017) stated that the adsorption rate of phenol by GAC was rapid, and more than 80% phenol was absorbed within the initial 10 min following application. Carvajal-Bernal *et al.* (2018) stated that a prepared activated carbon showed high adsorption efficiency for the removal of phenol from aqueous solution. In light of these studies, the results for GAC presented here are consistent with other published work, giving high confidence in its applicability in Ogoniland, even though it is relatively expensive.

GAC is an effective material for eradicating contaminants from water but is expensive to produce. On the other hand, “sustainable” biochar involves less expenditure because it can be produced from locally-derived materials. Biochar is less carbonised than activated carbon. Significant hydrogen and oxygen remain in its structure along with the ash originating from the biomass. As discussed below, these percentages may vary depending on the kind of species pyrolysed or the pyrolysis temperature. While activated carbon has a surface area of 500 - 1500 m^2/g, biochars have a surface area of only 150-400m^2/g (Komnitsas *et al.,* 2017). Biochar could replace wood-based, and GAC activated carbons as a low-cost sorbent for contaminants (Hagemann *et al.*, 2018), potentially mitigating soil-groundwater and air-soil-plant pathways shown in Figure 7.1.

Several studies have shown that biochar derived from various biomaterials including crop residues and agro-processing wastes (e.g., sawdust) can effectively remove organic contaminants including dyes, phenols, hormones, endocrine disrupting compounds and pesticides. Komang and Orr (2016), for example, stated that there was a total decrease in PAH concentration using biochars because of their sorptive properties. There have been numerous successful biochar applications in other studies (e.g., Werner and Karapanagioti, 2005; Chen and Chen, 2009; Beesley *et al.*, 2010; Sigmund *et al.,* 2017; Duwiejuah *et al.,* 2017). Adsorption of PAHs using biochars from wood char was very effective and led to a reduction in phenanthrene exposure from the soil. There was a great reduction of phenanthrene using biochars produced from other biowastes like rice husk (Dong *et al.,* 2018). Biochars derived from rice husk were also reported to remove RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) in other studies (Lingamdinne *et al.,* 2015). The use of biochar-alginate beads derived from buffalo weed (Ambrosia trifida L. var. trifida) effectively removed TNT (2,4,6-Trinitrotoluene) in aqueous solution with adsorption capacities of 295.11 mg/kg (Moon *et al.*, 2013; Roh *et al.*, 2014). Other biochars derived from canola straw, peanut straw, soybean straw, and rice hulls have been used to effectively remove methyl violet, acid blue 25 (AB25), acid yellow 117 (AY117), and methylene blue. This agrees with the results in Chapter 6, which reported that biochars derived from softwood and rice husk effectively remove up to 99% phenol from Ogoniland groundwater (Mohan *et al.*, 2014a, b; Xu *et al.*, 2011).

Biochars have additionally been shown to be effective in removing a range of other contaminants. These include synthetic and emerging organics (Cao *et al.*, 2009; Chen *et al.*, 2011; Kasozi *et al.*, 2010; Hale *et al.*, 2012; Mohan *et al.*, 2012), pathogenic organisms (Lalander *et al.*, 2013; Molaei, 2014; Reddy *et al.*, 2014), and inorganics such as heavy metals (Gwenzi *et al.*, 2014; Uchimiya *et al.*, 2010) and arsenic, fluoride, phosphate and nitrate (Chen *et al.*, 2011; Yao *et al.*, 2011; 2013). This demonstrates the potential for water purification and soil amendment using biochars.

The effectiveness of biochar in soil amendment depends upon a range of factors, foremost of which is the temperature of pyrolysis. The results in Chapter 6 show that pyrolysis of all biochars at 550°C was more effective than 700°C pyrolysis. This is in line with Fushimi *et al.* (2003), who argued that softwood, having higher lignin content, produced the highest biochar yields at 500°C compared to lower and higher temperatures of pyrolysis. For illustration, biochar produced at a lower temperature of 350°C may contain large amounts of positive nutrients, whereas the sorption capacities are lower compared to those produced at a higher temperature of 800°C (Gundale and Deluca, 2006). The reason for this is because the carbon content increases with temperature, while oxygen, hydrogen, and polarity decline with a subsequent increase in the volume of micropores. At temperatures between 20°C and 150°C, wood dries, resulting in a loss of mass, after which hemicelluloses become modified (Correa *et al.,* 2017) by depolymerisation, whereby released acetic acid acts as a catalyst in the depolymerisation of the polysaccharides. The temperature (pyrolysis) dependence of the solvent-extractable PAH content of biochar was clearly demonstrated by Keiluweit *et al.* (2012); biochars produced at temperatures between 400 and 600 °C contained the maximum levels of PAH; this is in agreement with the current study where biochars pyrolysed at 500°C was more effective compared to those pyrolysed at 700°C.

Other factors in addition to species type and pyrolysis also influence the effectiveness of biochar as an adsorptive agent. Although the adsorption of phenol using softwood-based biochars in this study was low, Rozylo *et al.* (2017) have noted that lower pH produced more positive immobilisation conditions for heavy metals to the biochars and activated carbons studied; this is potentially very useful in Ogoniland because of low pH. Rozylo *et al.* (2017) also noted that at neutral pH soil conditions, the adsorption of phenol and heavy metals to biochars and activated carbons followed closely in a monolayer adsorption process. The mixture of reduced levels of microporosity and surface functional groups detected in the biochars produced by fast pyrolysis is attributable to the irreversible adsorption of phenol. Vapour activation did reduce not only the surface functional groups but also assumed a fast adsorption process for phenol.

Biochars have several benefits in addition to their use in soil remediation, including providing clean energy for domestic heating and cooking and improving soil quality and crop yields. Some studies, including batch experiments similar to Chapter 5, have demonstrated the effectiveness of biochars as a soil amendment to improve soil quality (e.g., Novotny *et al.*, 2015). According to Haring *et al.* (2017), charcoal and biochar addition to tropical soils has been shown to improve crop yields, sometimes dramatically. Their report provided data on costs of producing, transporting, storing and delivering biochar to the field when evaluating the mechanisms of biochar utilisation. This suggests that rice husk has important potential benefits for both subsistence and commercial agriculture. To maintain benefits to plant growth, these aspects should be explored robustly (Jeffery *et al.*, 2011; Chirwa and Matita, 2012). Although the design and optimisation of biochar-based systems for the treatment of drinking water remain largely unexplored, it has considerable potential in regions like Ogoniland (although some limitations may arise, such as limited knowledge, personnel, etc.). Finally, biochars may also be effective in carbon sequestration and the reduction of greenhouse gas emissions. Gurwick *et al.* (2013), for example, reported that applying biochar to the soil will mitigate climate change. The use of biochar as a source of soil carbon sequestration appears to have important adaptation/mitigation potential, providing economical solutions to its production. As well as risk management, the carbon-adsorbent application offers a wide range of additional benefits, which can potentially be used to provide economic value to offset the cost of its application. Biochar application may also generate a range of wider sustainability benefits, discussed further in section 7.3.

7.2.2 Potential for production of carbon-based adsorbents in Nigeria

The most important issues that need to be resolved to achieve an effective remediation strategy in Ogoniland using carbon-based adsorbents are (i) the volume of biochars that could be produced, and (ii) if this volume is sufficient for the large-scale application. In Ogoniland, many agricultural and forestry production systems produce extensive waste from crop residues such as (i) forest residues (logging residues, dead wood, excess saplings, pole trees terrestrial-forest, grasses); (ii) mill residues (lumber, pulp, veneers); (iii) field crop residues (corn stalks, corncobs, palm kernel shell, coconut shell, sugarcane straw, sugarcane bagasse, nutshells, and manure from cattle, poultry, and hogs); (iv) urban waste (yard trimmings, site clearing, pallets, wood packaging, wood chips, bark, sawdust, timber slash, mill scrap, waste paper and yard clippings); and (v) aquatic-algae and water plants (Walsh *et al.*, 1999; Australia Institute of Energy, Fact Sheet 8, 2004; Demirbas, 2004; Lehmann *et al.*, 2006; UNEP, 2009; Tumuluru *et al.*, 2011). In many cases, these waste materials have little value, and their disposal incurs costs (Adeyimi and Idowu, 2017), but they can be made useful in a sustainable manner by converting them into biochar. The most suitable materials yielding the most biochar have high lignin concentrations and include residues from sawmills, forest residues, or nut shells, all of which are abundant in Nigeria (Adeyemi and Idowu, 2017). However, crop residues also have considerable potential.

In Nigeria, traditional earthen and brick kilns have been used to produce charcoal for thousands of years, and the pyrolysis is a simple and inexpensive process that is very beneficial to communities. There are other methods used in producing biochar in Nigeria, namely gasification. This is a thermochemical method where biomass is heated with a small amount of air and leaves behind at most 10% of the biomass carbon as charcoal, alongside a byproduct (biochar). Hydro-thermal carbonisation includes steaming biomass together with different types of acid, which act as a catalyst. Hydrothermal conversion primarily focuses on using wet biomass to generate bio-oil, with biochar as a by-product (Zhang *et al.*, 2010). The capacity to remove multiple contaminants in aqueous solution makes biochar an ideal adsorbent for water treatment, compared to existing low-cost water treatment methods. Developing countries like Nigeria could gain from using biochars because they offer multiple environmental and agronomic benefits. One of the main reasons why such water treatment technologies have not been used in developing countries is because of a lack of technical skills and lack of electricity. Appropriate water treatment technologies should be relatively low-cost (Btatkeu *et al.*, 2016), implying that membrane technology and nano-technology relying on imported devices are at best bridging solutions.

The three biggest potential sources of organic materials for biochar production are the timber, corn production, and sugar cane sectors, of which the timber sector offers the greatest volume of waste by-products that could be converted to biochar. Wood businesses create expansive volumes of deposits which must be used, utilised or appropriately discarded. Buildups of residual wood are normal features in timber businesses. In Nigeria, this buildup is, for the most part, viewed as waste and this has prompted open burning practices, dumping in water bodies or dumping in an open region, which constitutes ecological contamination. Sawmills in Nigeria created more than 1,000,000 m^3 of wood waste in 2010, while around 5000 m^3 of waste was produced in plywood factories. Nigeria produces around 1.8 million tons of sawdust yearly and 5.2 million tons of wood waste (Owoyemi *et al.*, 2016). This improper disposal of waste wood on the environment impacts upon both aquatic and terrestrial ecosystems. Additionally, the burning of waste wood releases gases and particulates into the atmosphere causing various health issues. Reuse of these wood buildups in Nigeria will reduce the pressure on already diminishing timberlands, reduce ecological contamination, and have benefits for business.

The average production of corn in Nigeria is 8.18 million metric tons per annum, making the country the 10th largest producer in the world, with the crop cultivated in six geopolitical zones (see Figure 7.2). The North-central geopolitical zone output was about 31% of the national production in 2006, 58% in 2008 and dropped to 44% in 2009 (Cadoni and Angelucci, 2013; Foraminifera Market Research Limited, 2013). Unlike many developed countries where corn residues are used as raw materials for energy generation, the abundance of production in Nigeria has led to corn residues posing a significant disposal issue. The utilisation of corn residues as a potential biochar source and energy resource presents new opportunities and challenges and requires consideration of factors such as harvesting, handling, heating value, storage methods and energy conversion methods (Zych, 2008).

Sugarcane is widely cultivated in Nigeria, primarily for making juice and preparing feeds for animals. Currently, the country is the second largest importer of sugar in Africa. The increase in the land cultivated for sugarcane production has failed to meet the local demand for sugarcane products. For example, Galadima *et al.* (2013) stated that in 2007/08 and 2009/10, about 80,000 and 100,000 tonnes of sugarcane were produced, respectively. This is low when compared to the demand for sugarcane products, estimated at 1.5 billion tonnes. Mohlala *et al.* (2016) noted that Nigeria contributes only 1.9% to the production capacity of sugarcane in sub-Sahara Africa, valued at $30,155,345. However, because of the establishment of Nigeria's first sugarcane bio-refinery in Zaria in 2015, there has been an enormous increase in waste. Nigeria lacks the technical strategies to manage the residues such as straw and bagasse: 1 tonne of sugarcane generates about 270 kg of bagasse (Ogwo *et al.*, 2012). This indicates that if 50% of the demand for sugarcane production in Nigeria is met, sugarcane bagasse (*Miscanthus* grass) will constitute a massive waste if efforts are not in place to beneficiate it. The results in Chapter 6 demonstrate the potential benefits of using *Miscanthus* grass as a biochar precursor for organic contaminant management in Ogoniland.

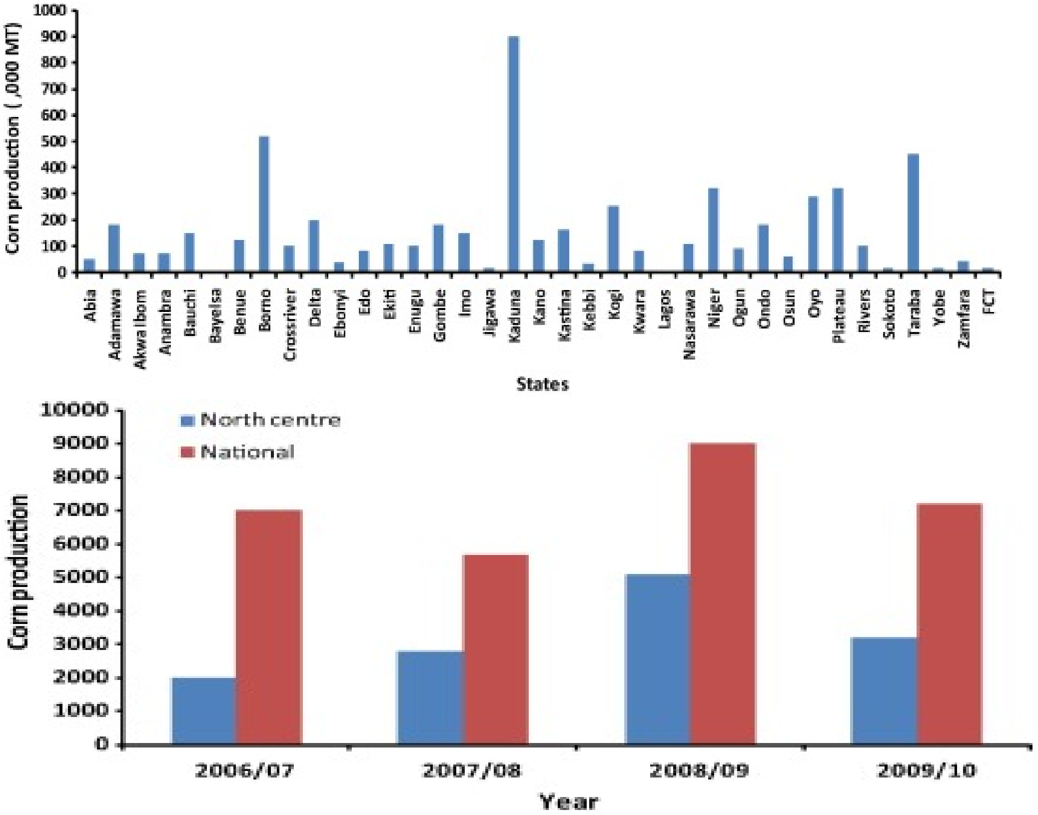

Figure 7.2 Corn production by state in Nigeria (top) and yearly national and north-central maize production (bottom), adapted from Mohlala *et al.* (2016).

7.3 ASSESSMENT OF THE WIDER SUSTAINABILITY BENEFITS OF USING CARBON-BASED ADSORBENTS VIA THE HOMBRE SOFT RE-USE TOOL

7.3.1 Introduction to the HOMBRE screening tool

In Europe, a variety of tools are available through which to assess the wider sustainability benefits of contaminated land remediation strategies. Some of the most useful of these have been generated by the Holistic Management of Brownfield Regeneration (or HOMBRE) project, which was designed to provide a scientific and technical resource to support the 'zero-Brownfield' concept (Table 7.1). HOMBRE was a major European Union FP7 project (see www.zerobrownfields.eu), which concluded in November 2014. The project generated a wide range of technical outputs and brownfield guidance across the land-use and management cycles (see Appendices 6.0, 7.0 and 8.0). To date, HOMBRE has been used to assess the remediation of various brownfield sites in the UK (see Chapter 2) but has yet to be applied in Africa.

Table 7.1 Concepts underpinning the "Zero-Brownfield" concept, and their explanation (www.zerobrownfields.eu).

Concept	**Explanation**
Land-utilize life cycle	The land is a vital limited asset. It is likewise an asset that is in a cycle of utilisation. Brownfield land can be a phase in this cycle. However, for financial, ecological, and social reasons it is imperative that a future Brownfield age is averted.
Intermediary land use	The best administration arrangement is avoidance; following that is remediation, where a few procedures are expected to bring land once more into reasonable re-use. It is critical to discover some type of go-between use for such relinquished land where its value can be promoted. The land can be step by step re-established until the point when it can be completely re-incorporated into the land use cycle.
Added value by combining technologies	Integrated arrangements offer an extraordinary chance to surmount the costs boundary by sharing the land administration costs with different administrations and open doors for society, for example, sustainable power source and urban green space and atmosphere control. The potential for income from various sustainable power source/atmosphere control innovations, from ground source warming and cooling to bio-vitality, can give income chances to empower remediation.

'Zero Brownfields'	Using several stakeholders, and developing more astute plans for Brownfield administration, possibly brings critical maintainability benefits. For the planet, there might be advantages of better asset advancement. To realise full benefits, there is a need for long-term and extensive stakeholder collaboration, e.g., masterplan for regeneration revised significantly in response to the public consultation.

7.3.2 Application of the HOMBRE Brownfield Opportunity Matrix (BOM) in Ogoniland

One of the most useful tools from the HOMBRE project is the “Brownfield Opportunity Matrix” (BOM), a simple Excel-based screening tool that essentially maps the services that might add value to a redevelopment project against the interventions that can deliver those services. The BOM can be used to identify potential wider benefits (and synergies and potential for added value) from remediation technology application and is designed for use during options appraisal, stakeholder engagement, and site planning. Here, the HOMBRE BOM is used to identify the direct benefits that can be generated by biochar and carbon adsorbent application in Ogoniland (including economic benefits), and indirect benefits for site management, such as improved options appraisal, stakeholder engagement, and planning. Benefits are discussed below based on the HOMBRE BOM benefits categories. Full details of the tool, as applied to Ogoniland, can be seen in Appendix 6-10.

7.3.2.1 Biosphere benefits (including associated human health) and amendment addition (GRO)

The understanding of receptor and pathway studies in Chapter 5 is crucial to managing risks to revegetation, ecological receptors, and human health, and in conjunction with other measures is a key to manage contaminant risk in Ogoniland sustainably. As discussed above and as seen in appendix 6.0, 7.0 and 8.0, it is possible to immobilise contamination with use of biochars and MAST carbon thereby preventing its migration off-site and reducing its bioavailability to vegetation and other ecological receptors. In situ stabilisation using amendments can also mitigate risks to human receptors, and may be useful in dealing with residual problems after hot spot removal in Ogoniland. In situ stabilisation also enables re-use of contaminated land for other services (such as farming), which needs adequate risk management.

As identified in the HOMBRE BOM, a wide range of stakeholders in Ogoniland could benefit from biosphere improvements, including Local Authority/government, National Environment

Agency/regulator, environmental consultants, and local residents. Investors and local communities could benefit greatly, especially if contaminated land liability lies with them. This would lead to an improved local environment regarding property value; Ogoniland currently suffers from a lack of investors because of the extensive contamination of land. If managed appropriately then a site could provide a source of revenue generation. The site owner and the community will benefit especially if contaminated land liability – and associated human health risks – lies with them, and the site could provide a source of revenue generation if managed properly. The local community will also benefit from an improved local environment, risk mitigation and subsequent land value/property value uplift. Depending on a site's final use, the wider community and other suppliers may benefit in the future. Key to the development of Ogoniland are services that will generate revenue; some sites may be important assets to support public investment in regeneration post-remediation. Due to the contamination in Ogoniland, many communities have suffered property depreciation due to people and companies leaving the area. An integrated, carbon-adsorbent based remediation strategy may impact on the value of built redevelopment (for example, providing a framing which enhances property values or providing local energy supply or other environmental services). These will attract companies to return to the community thereby creating more job opportunities.

7.3.2.2. Ecosystem services and amendment addition (GRO)

The need for conservation is important to the people of Ogoniland, thereby protecting ecological receptors, although some amendment additions may also be damaging to particular ecologies and conservation goals. The use of carbon-based soil amendment approaches will aid in the removal of contaminants affecting the ecosystems. The extent of protection depends on how ecological receptors have been considered in the risk appraisal and remedial target setting decision-making. To carry out effective remediation, the need for protecting the existing ecosystem must be recognised, and the use of remediated land for re-establishment of flora and fauna in former areas of contamination be considered. This will also improve food chains by reducing toxic loads and increasing crops yields.

7.3.2.3 Water resources (hydrosphere) and amendment addition (GRO)

The literature review in Chapter 2 discusses the importance of water to the people of Ogoniland, and also considers the level of water contamination. Ogoniland communities have many needs: provision of potable water; re-use of treated waters on site; and improved quality of water in the vicinity of a site; retention of surface water runoff and water storage; and flood mitigation (incorporating extreme weather events that may be linked to human-induced climate change).

As considered in Chapter 6, the need for managing risks to water resources is the main goal of amendment. The use of in situ stabilisation using amendments (biochars and MAST carbon) can immobilise contamination, preventing its migration off-site, and so reducing its input to groundwater and surface water. This will be a great benefit for the people of Ogoniland, adding to the fact that amendments can be deployed using readily available agricultural equipment. Primary value will initially be natural capital and cultural capital; however, revenue generation is also a real possibility if a site is managed appropriately. Contaminated land has little monetary value; however, once remediated, it can be a valuable commodity that attracts investors. Economic tangible and intangible benefits are associated with successful remediation of a contaminated site, as seen in appendix 5.0.

7.3.2.4 Soil fertility/structure and amendment addition (GRO)

Carbon-based soil amendments have the potential to increase soil fertility in Ogoniland (see appendix 6.0, 7.0 and 8.0), and some amendment may have a direct effect on soil fertility via the addition of plant nutrients (such as potassium or phosphorous), or the improvement of soil functionality (e.g. because of changes in pH or buffering capacity). If the soil in Ogoniland is managed properly, it has the potential to be a source of revenue generation and therefore benefit local communities. The revenue generation can come because of investors developing land after clean-up, and growing renewable crops on-site post-remediation. An additional benefit of soil amendment is improvement to the soil organic matter and hence soil structure. Excessive addition rates may not be beneficial, and different soil horizons may require different amendment rates. It is also important to select specific amendments so as not to lock away vital plant nutrients or damage the soil structure (for example by cementation).

7.3.2.5. Renewable energy/material generation and amendment addition (GRO)

Assessment via the HOMBRE tool indicates that Ogoniland could benefit from renewable energy production from the by-products of biochar production. On-site soil amendment may be highly compatible with on-site production of biomass for bioenergy. However, stakeholders need to implement some regulations about the re-use of recyclates, particularly away from the site where the waste originates. Ogoniland will benefit from material recovery, which will defray some costs and avoid disposal costs for site owners and investors. It is expected that value will include a revenue recovery or cost reduction. Ogoniland lacks good recycling use; material recovery and re-use is more feasible, especially where there are opportunities for on-site materials recycling operations and several waste reuse and regeneration projects in proximity to each other.

7.3.2.6. Greenhouse gas emissions and amendment addition (GRO)

The use of the HOMBRE BOM suggests that amendment addition (e.g. composts and biochars) may lead to sequestration of carbon in soil and be effective in the very long term (100s of years). Processes of biodegradation will ultimately release carbon dioxide from organic matter added to soil. However, ongoing management through additional amendment and the vegetation regime will allow for continued sequestration. The overall carbon balance for a remediation project is highly site-specific, and sequestration benefits may be negated by the energy inputs to the remediation process (and processing / production of amendments). The local community would be the primary beneficiaries of reduced greenhouse gas emissions and carbon sequestration. Both help to offset global warming and potential associated severe weather events, and help to improve local air quality. The wider community may be considered to be the secondary beneficiary, as human-induced climate change as a result of greenhouse gas emissions is a global problem.

7.3.2.7. Economic assets and amendment addition (GRO)

The value of both the site and land/property in the area will be uplifted as a significant risk issue is mitigated (see appendix 5.0, 7.0 and 8.0), and the range of potential site uses is potentially extended. Potential improvements in landscape and sense of place over the longer term may be an important factor in value uplift. Amendment addition approaches are highly compatible with interim land management solutions, pending a longer-term ambition or some other form of development. A remediation project will create jobs in the local area in the short term. There may be employment opportunities in maintenance of the system in the medium to long-term, depending on the nature of the ongoing site management and monitoring needs. Facilitation of site re-use for other soft end use functions may also create local economic benefits

7.4 POTENTIAL APPLICATION OF GENTLE REMEDIATION OPTIONS AND INTEGRATED ATTENUATION STRATEGIES.

Remediation of soils and waters contaminated with petroleum products is a challenging task. The results in chapter 5 suggest that the use of natural attenuation strategies is possible, due to observed adsorption of phenol on simulated aquifer materials in core flooding experiments. The Committee on Intrinsic Remediation, Washington DC, and UK Environmental Agency (2014) stated that before considering using natural attenuation as a means of cleaning contaminants from groundwater, it is necessary to assess the nature of the problem and the potential benefits. Natural attenuation may be suitable for contaminated groundwater, providing that the method will not create an adverse effect on human health, surface water or other potential receptors and that attenuation can achieve the site clean-up goals within a reasonable timeframe. The requirements will necessitate that natural attenuation is used in combination with active remediation of the source of the groundwater contamination. In the Ogoniland case, an integrated remediation strategy may be applicable, where soil amendments are utilised to provide enhanced natural attenuation in soils, coupled with more intensive remediation to remove contaminant “hot-spots.” To some extent, before natural attenuation of contaminants in groundwater is carried out, it must assess each of the following: risk to humans from contaminated groundwater; if the groundwater below the site is presently used for a water supply; and the likelihood that contaminated groundwater will migrate to used and unused aquifers and other constructions that are connected to useable aquifers. This is in line with the current situation in Ogoniland, as some water sources are still used for day-to-day activities despite being contaminated, and water may migrate from one location to another.

Soil amendments may also be applied in combination with plant-based or phyto-approaches, e.g., in aided phytostabilisation or phytoexclusion approaches, or in green or gentle remediation strategies. Phytoremediation is one of the most favourable remediation techniques since it is considered both cost-effective and environmentally friendly (Han *et al.,* 2016; Azubuike *et al.,* 2016). Plants give some benefits, including degradation, transformation, assimilation, metabolism, and decontamination of dangerous pollutants from soils and aquatic and atmospheric sites (Cai *et al.,* 2010). According to Khan *et al.* (2013), Mimmo *et al.* (2015) and Lu *et al.* (2015), numerous plant species, including ryegrass, *Axonopus sp*., *Cyperus sp*, legumes, trees, *Zea mays* (corn) and *Pennisetumpurpureum* (elephant grass), and several other monocots and dicots, can be successfully applied to the phytoremediation of soil contaminated with organic and inorganic pollutants. Hydrocarbon losses of 77.5% using *Z. mays* and 83% for *P. purpureum* were reported by Ayotamuno *et al.* (2006a). The question of how to increase the effectiveness and enhance the conditions of phytoremediation is one of the major concerns. Guo *et al.* (2014) noted that both the physicochemical properties and microbial activities of soil had a robust impact on the effectiveness of phytoremediation. The use of local species is better than importing alien species, regarding local ecosystem services.

By the results presented in Chapters 5-6, there is good potential for a combined gentle remediation approach in remediation of contaminants in Ogoniland. The use of natural attenuation plus carbon-based soil amendments can reduce available contaminant concentration in the soil, which then allows plant growth. This plant growth subsequently enhances contaminant stabilisation or degradation and reduces site risk – i.e., an aided phytostabilisation approach. Further tools can be used to assess and validate the potential of such approaches in Ogoniland – notably the GREENLAND (Gentle remediation of trace element contaminated land) decision tool (derived from the GREENLAND EU FP7 project). This tool includes applicability assessment for various plant-based approaches to remediate trace element contaminated soils at low cost and without significant adverse effects on the environment. The DST and the best practice guidance handbook are available at www.greenland-project.eu. Selected applications as seen in Appendix 9-11.

7.5 LOCAL BARRIERS TO THE USE OF CARBON-BASED AND GENTLE REMEDIATION CLEAN-UP APPROACHES

The preceding sections have demonstrated the potential of using biochars and other carbon-based adsorption methods to remediate areas of contaminated land and water in Ogoniland. There are, however, some potential barriers to the local uptake of these cleanup technologies. These barriers are discussed below.

7.5.1 Lack of knowledge and technical know-how on biochar production, use, and effectiveness for contaminant clean-up in Nigeria

Limited knowledge of carbon-based remediation strategies exists among communities due to little research (or publicity) on the subject. Knowledge sharing is needed to highlight that biochar can have beneficial impacts on soil quality, water clean-up, and crop growth, enhancing farming practice and allowing safer water use. This, in turn, highlights the need for effective stakeholder engagement (further discussed below). Barriers largely stem from limited empirical data on biochar-based water and land treatment systems and public and environmental risks associated with biochar production, materials, cost, areas requiring treatment, and local acceptability. A potential criticism for the proposed approach is that biochar produced at household level will be too limited in volume to have a significant impact on crop productivity and soil quality, yields, and large-scale water clean-up.

Further local barriers could arise from a lack of optimum design and operational parameters. Even though biochar has excellent potential as a renewable, low-cost and sustainable local product, the fact remains that a comprehensive, methodical study is yet to be carried out. There is limited literature about the cost of biochar production in Ogoniland. Kurniawan *et al.* (2006) noted that costs estimate can only be obtained from pilot scale studies instead of typical laboratory batch experiments commonly reported in the literature. Operating conditions are likely to be different in Ogoniland, with little information about the volume/quality of water and soil requiring treatment, the degree of purification required, the possibilities for adapting local equipment, and the need for specialist production and treatment plants. Poorly planned and built pyrolysis reactors may yield toxic fumes and potent greenhouse gases (Hale *et al.*, 2012), and biochar disposal issues (if used for water treatment) require careful consideration. The human food chain could also be affected adversely by using consumed biochar as a soil amendment which could contaminate soils with toxic pollutants (Chaukura *et al.*, 2016).

Using biochar as a substitute for activated carbon in existing water treatment processes may involve redesigning and retrofitting additional units, which means incurring additional costs. However, this may still be cheaper than activated carbon use because of its design parameters and operating conditions. Regardless, biochar water treatment systems still require standardised procedures for the production of biochar, and their subsequent application for water treatment in Ogoniland is yet to be developed.

Biochar benefits are partly offset by the costs of production, mainly hauling and processing feedstocks. Profitability of biochar systems will be especially sensitive to prices for energy and greenhouse gas reductions and offsets. Charcoal is naturally abundant, and in Nigeria, it has been used by indigenous people for centuries to improve the fertility of their soil. Yilangai *et al.* (2014) also noted that charcoal used as biochar stimulated greater food crop growth, suggesting that biochar as charcoal can effectively improve food security.

According to Yilangai *et al.* (2014), the effect of biochar amendment on crops such as maize (*Zea mays*), soybean (*Glycine max*), radish (*Raphanussativus*), sorghum (*Sorghum bicolor*), potato (*Solanumtuberosum*), wheat (*Triticumaestivum*), pea (*Pisumsativum*), oats (*Avena*sp), rice (*Oryza sativa*), and cowpea (*Vignaunguiculata*) (Lehmann *et al.*, 2003; Chan *et al.*, 2007) and on sweet potato (*Ipomoea batatas*) yield and quality has been studied in different parts of the world, but fewer studies have been carried out on water contamination. Research in Africa on the use of biochar as a means for cleaning contaminated water is lacking.

7.5.2 Deficiencies in national and local governance and decision-making structures

One of the barriers to the use of carbon-based and other remediation strategies in Ogoniland is a lack of environmental policies and policy implementation. The government needs to set up key policy goals for protecting existing water resources; improving the efficiency of use of water as a resource; managing rainfall runoff - principally through sustainable urban drainage systems; and rehabilitating contaminated water. Some of the local barriers to use of these clean-up technologies in Ogoniland and around the Niger Delta region relate to local community disempowerment, and conflicts over land ownership and use (Yusuf and Omoteso, 2016; Leach *et al.*, 2012). Addressing these barriers requires clear, transparent and enforceable environmental policies, and a robustly applied legal framework, to ensure that wider benefits from land remediation are realised both by local authorities and by local communities.

7.5.3 Stakeholder involvement in management decisions

Interventions aimed at addressing these limitations in Ogoniland require better knowledge-exchange, effective stakeholder engagement (including from government, international bodies and registered environmental agencies), and the development of supportive legal and policy frameworks. Effective stakeholder involvement will be a key requirement for the optimal application of sustainable remediation strategies, and in-site regeneration more widely (REVIT 2007, RESCUE 2005). Effective and sustained stakeholder engagement is critical to the acceptance of large-scale soil amendment-based remediation strategies and GROs generally, particularly for larger projects. This is because (a) GROs are most likely to be used for sites where a soft end use is envisaged, and the biological component of the remediation (e.g., plant cover) is likely to be an enduring part of the overall regeneration of the land, and (b) to ensure that wider economic, environmental and social benefits from GRO application are effectively delivered (Cundy *et al.,* 2013).

Stakeholder engagement is a broad, inclusive and continuous process between a project and those potentially affected by it. The World Bank (2012) describes the aims of stakeholder engagement as building up and maintaining an open and constructive relationship with stakeholders and thereby facilitating a project's management of its operations, including its environmental and social effects and risks. Effective stakeholder engagement is also seen as key to reducing remediation project risks, for example, failure to gain acceptance and delays due to antagonistic relationships; and also as means of reducing project management costs and timescale (RESCUE 2005; REVIT 2007).

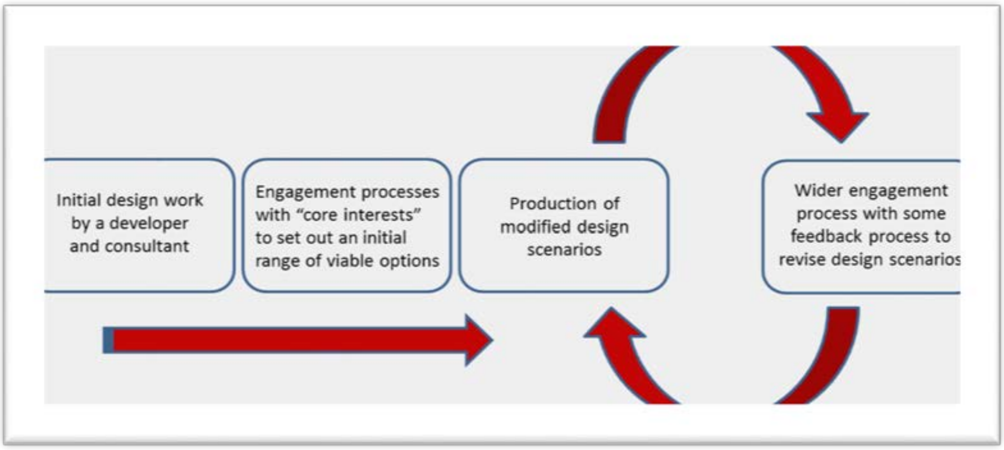

Figure 7.3 Principles of stakeholder engagement and GRO (Cundy *et al.*, 2013).

Given that drivers for dialogue often relate to the project context, locality, and stakeholders, rather than the technical means of achieving remediation, there seems little justification for developing detailed GRO technology-specific guidelines for Ogoniland. A more sensible approach is to draw out general principles of good practice for stakeholder engagement from existing sources for the benefit of those offering GROs (see review in Cundy *et al.*, 2013). These principles can be summarised as:

- Identify and engage the core and noncore stakeholders early in the process;
- Adopt a proactive not reactive approach to engagement;
- Engage stakeholders at all stages of the GRO process;
- Plan for long-term stakeholder engagement;
- Develop useful communication structures that allow a reciprocal, two-way dialogue and ensure engagement is transparent and recorded;
- Recognise that the criteria for assessing GRO may need to be subjective and objective;
- Set out all assumptions and procedures for implementing and monitoring GRO at the start of a project;
- Follow a logical, stepwise approach to engagement to avoid circular arguments and address subjective issues.

Applying the above principles of stakeholder engagement is critical to the effective management of remediated land problems in Ogoniland, as it will ensure that every stakeholder has the potential to benefit from each part of the application. The range of stakeholders who should be engaged with will be site- and project-specific, but a general (non-exhaustive) list is provided in Table 7.2, based on GREENLAND and other case study sites, to guide stakeholder identification. In Ogoniland, stakeholder identification will need to incorporate various groups, including traditional rulers, affected communities, financial specialists, and engineers. Everyday designs and targets will need to be established to accomplish this procedure, and outcome-situated objectives put in place. All central and non-central partners must be included in the process. One of the reasons for the current contaminated land problem in Ogoniland is that the legislature and multinational organisations communicate among themselves without including nearby communities. A particular issue in Ogoniland is the absence of long-term planning; this is essential for successful land management. Finally, effective communication is key to each project, regardless of how large or small. Problems emerge where community groups are not informed as to what work is to be completed. All partners should be informed of each procedure, and there had to be an open, straightforward and shared dialogue between all parties concerned. Importantly, all discussions should be fully documented and recorded.

Table 7.2 Framework for stakeholder identification (www.greenland-project.eu), giving examples of "core" and "non-core" stakeholders.

An example list of Most Affected or Affecting ("Core") stakeholders	***An example list of Moderate or Least Affected or Affecting ("Non-Core") stakeholders***
Developer (i.e., the individual or organisation seeking to develop the land area for alternative use)	Local community Investors
Site Owner (i.e., the legal owner of the site)	Insurers
Regulator (i.e., the local, regional or national body responsible for)	Campaigning groups
Planner	Future site users, Recreational users
Service provider (i.e. the contractor or consultant providing the remediation or regeneration service)	Local and regional press
Current and future site users (e.g. biomass producers)	Conservation bodies and Scientific community
Local authorities as owner, financer, regulator and Traditional Rulers	Biomass/bioproduct users

CHAPTER 8.0 – CONCLUSIONS

8.1 KEY FINDINGS OF THIS RESEARCH

This thesis aimed to investigate the extent of, and processes controlling, environmental contamination and exposure at hydrocarbon industry-impacted sites in Ogoniland, Nigeria, and to evaluate practical methods of managing this contamination. Following a review of the relevant literature (Chapter 2) and presentation of the study methodology (Chapter 3), the project results were presented and discussed in Chapters 4 – 7.

Chapter 4 addressed the question "What is the extent of environmental contamination around hydrocarbon industry-polluted sites in Ogoniland, Nigeria, and what are the key contaminants present?" The key findings were as follows:

- Groundwater in the study area shows elevated concentrations of manganese, chloride, nitrate, EC, and turbidity, while for surface water the main contaminants are Na, K, Ca, Fe, Mg, chloride, sulfate, and EC.
- A statistical correlation between samples indicates that despite local (inter-sample) variability, there is a dominant control of salinity (either via seawater ingress or industrial (e.g. brine) discharges) on groundwater major ion composition, coupled with the influence of local geology, with a lesser control exerted by pH and other environmental parameters such as turbidity.
- Analyses suggest little evidence for elevated concentrations of trace metals in the surface and groundwater samples from Ogoniland, with all selected trace metals within guideline limits set by regulatory agencies. Statistical data show that trace metals tend to correlate with other elements that show similar geochemical behaviour (e.g., nickel gave a statistically significant correlation (95%) with copper, zinc, molybdenum, cadmium, and elements associated with sulfide minerals). Hence, the distribution and concentrations observed seem to be predominantly geologically controlled.
- Results suggest no gross contamination by hydrocarbons (as indicated by Total Petroleum Hydrocarbon levels) within ground and surface water samples in the study area, with TPH values below 0.5 – 2ppm in all cases. This is in contrast to previous studies (including Etechie *et al.*, 2011; UNEP, 2011; Adeniyi and Afolabi, 2002; Muniz *et al.*, 2004; Rauckyte *et al.*, 2006), which stated that there was a high level of petroleum hydrocarbon contamination.
- The study, however, revealed that phenol concentrations were excessively high in Ogoniland, with concentrations present ranging from 10 - 340ppm, while those of PAHs

were below detection. Phenol shows elevated concentrations in both surface water and groundwater, with a similar geographic distribution (e.g., the Ogale area showed greatest enrichments in both surface and groundwater), indicating significant connectivity between surface water and groundwater in the study area.

Chapter 5 addressed the question "What are the processes controlling migration and natural attenuation of this contamination?" In the published literature, there are limited reports on core flooding experiments as related to contaminant migration in groundwater matrices. Most of the available studies relate to core flooding experiments carried out decades ago, investigating water and nitrate fluxes as well as simulating enhanced recovery of oil from oil fields. There are very few reports of core flooding experiments utilised to model contaminant migration in groundwater. This research uniquely utilised this simulation mechanism to understand phenol behaviour in aquifer materials as it migrates along groundwater pathways. The key findings were as follows:

- Results provide evidence of the potential for phenol transport and breakthrough to groundwater via surface soils.
- Results suggest, however, that there was some degree of phenol retention in the simulated aquifer materials, which indicates the potential suitability of natural attenuation as a means of (partially) managing contamination.

Chapter 6 addressed the question "What practical methods can be applied to manage the contamination present?"

- Based on results from batch adsorption studies, commercial activated carbons were shown to be highly effective adsorbents for phenol removal (and removal of other contaminants of concern), although biochar adsorbents (based on *Miscanthus* grass, softwood, and rice husk) were less effective bulk adsorbents.
- MAST Carbon activated carbon showed effective adsorption at all pHs tested (covering the range of pHs likely to be encountered under natural conditions in the Ogoniland area - see Figures 4.19 and 4.20). The adsorption capacity of this activated carbon at 100ppm phenol concentration was 47.29mg/g (at pH 3); 46.61mg/g (at pH 5); 48.72mg/g (at pH 7); and 48.56mg/g (at pH 9).
- When tested for phenol uptake from Ogoniland groundwater samples, both the activated carbon and biochar adsorbents showed ca. 100% phenol removal. The use of real environmental waters should have impacted on the adsorption capacity generally, due to the presence of competing ions which may interact with the adsorbents and occupy

some of the available binding sites. As the adsorbents were added at relatively high mass compared to the mass of phenol present in the groundwater samples, however, near complete removal of phenol was observed.

- The adsorption isotherms of MAST carbon and various biochars shows that the MAST (activated) carbon has the highest adsorption capacity. The temperature of biochar production (pyrolysis) significantly influenced the adsorption capacity, as biochars activated at a temperature of 550°C pyrolysis are more effective adsorbents than those activated at 700°C.
- Despite the relatively low adsorption efficiency of biochars observed here, their low-cost and potential for on-site (i.e., local) production suggest that they may still have application in combined, large area, soil improvement and contaminant risk management strategies.

Chapter 7 discussed the overall results of the thesis and considered the potential for the use of biochars in Nigeria as part of integrated remediation strategies.

- Key recommendations from this thesis are that the use of carbon-based adsorbents, derived from local agricultural and other waste processing streams, should be further explored as effective large-area in situ soil amendments for reducing contaminant exposure risk in Ogoniland.
- Effective stakeholder (including local community) involvement, clear, transparent and enforceable environmental policies and a robustly applied legal framework are needed to ensure that wider benefits from land remediation are realised both by local authorities and by local communities.

8.2 DIRECTIONS FOR FUTURE RESEARCH

Based on the results presented in this thesis, the following areas of further research are suggested as priority topics to support a wider understanding of contamination issues in Ogoniland, and the application of practical, large area remediation strategies:

1. Further detailed field sampling to assess the spatial extent of phenol contamination, and its persistence.
2. Core flooding studies with a range of simulated and real aquifer materials to more fully assess natural attenuation potential for phenol and other contaminants in the soil-groundwater pathway. These could, for example, include mixtures with lower clay percentages to more closely mimic the range of natural materials in Ogoniland aquifers.

3. Field trials of the use of local wastes as biochar for soil amendment application.
4. Field pilot studies on the application of integrated soil amendment - natural attenuation - phyto-based strategies in Ogoniland.

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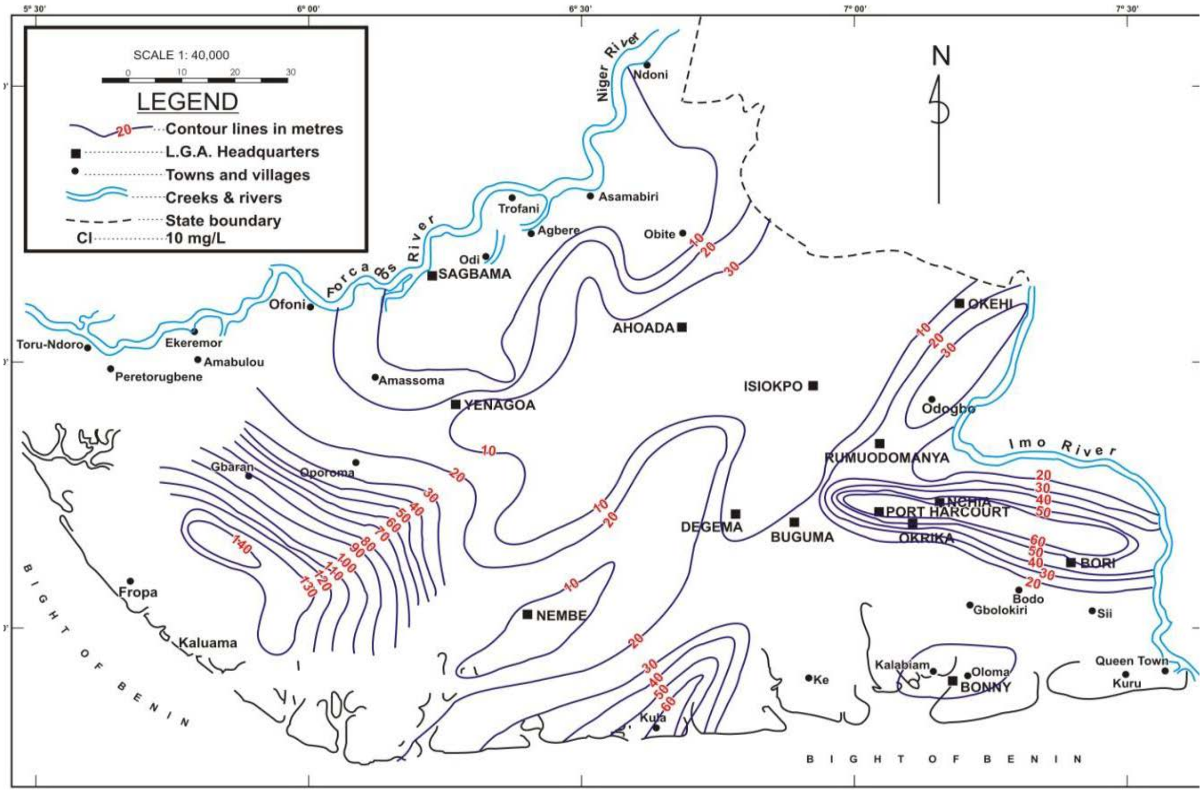
10.0. APPENDIX

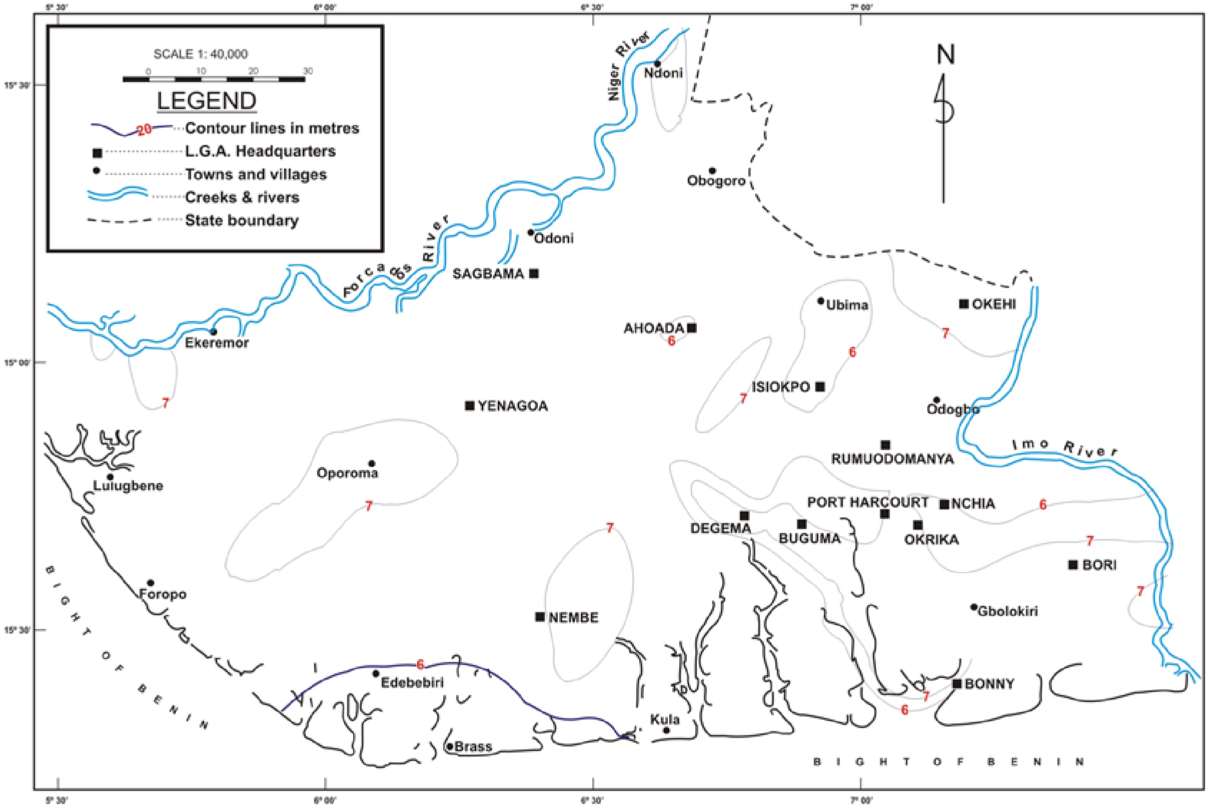
Table 1: WHO (1984) Guidelines for acceptability of water for domestic purposes.

S/N	Parameter		Highest Desirable	Maximum Permissible
1	Phenolic compound (as Phenol)	0.001	0.001	0.001
2	Fluoride (as F)	1.0 – 1.7[a]	-	0.2 – 1.7[a]
3	Nitrate (as NO_3)	50.100	-	-
4	pH	-	7.0 – 8.5	6.5 – 9.2
5	Copper (as Cu^{2+})	0.5[c]	0.05	1.5
6	Iron (as Fe^{2+})	0.1[c]	0.1	1.0
7	Manganese (as Mn^{2+})	0.05	0.05	0.5
8	Zinc (as Zn^{2+})	5.0	5.0	15
9	Magnesium (as Mg^{2+})	50 – 125[b]	50 – 150[b]	150
10	Sulphate (as SO_4^{2-})	150	200	400
11	Hydrogen Sulphate (as H_2S)	0.05	-	-
12	Chloride (as Cl^-)	200 – 600	200	600
13	Chloride (free)	-	-	-
14	Anionic detergent	0.2	0.2	1.0
15	Ammonia (as NH_4)	0.5	-	-
16	Carbon dioxide (free)	Nil	-	-
17	Calcium (as Ca^{2+})	-	75	200
18	Mineral oil	-	0.01	0.5
19	Mineral oil with high	-	-	-
20	Sulphur content	-	-	0.1
21	Turbidity (units)	-	5	25
22	Organics	0.2 – 0.5	-	-

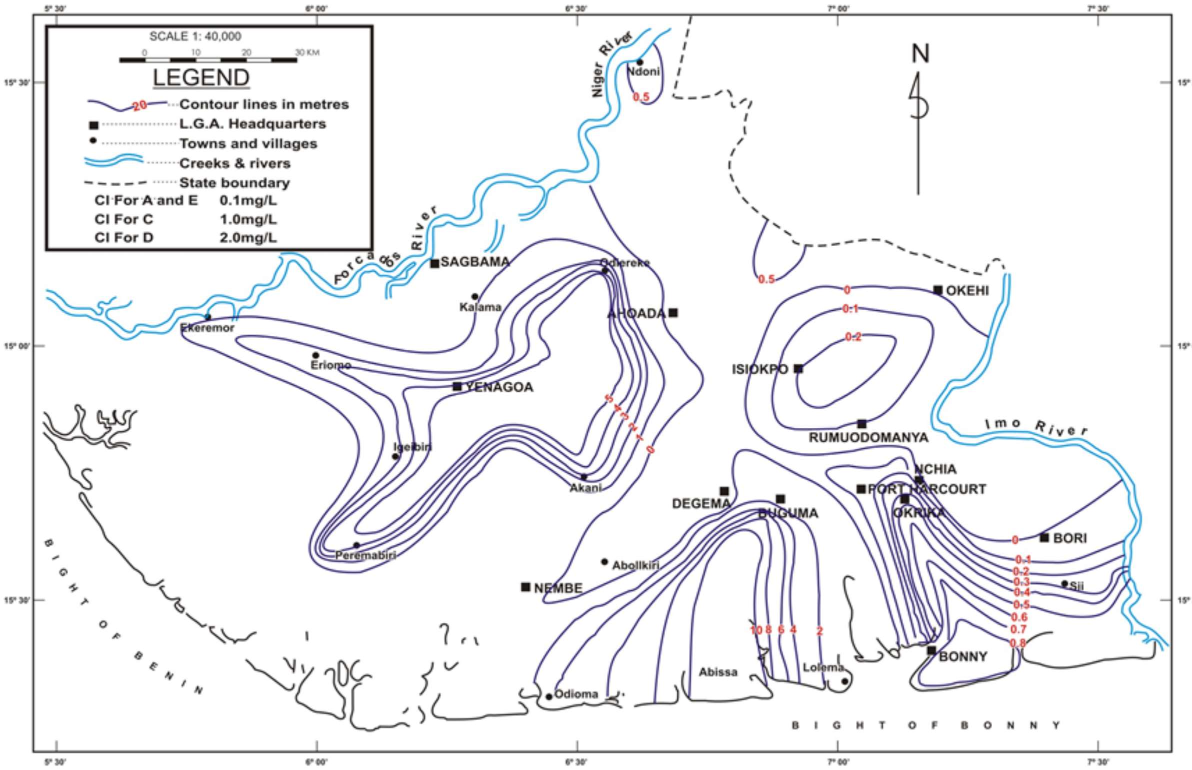
Note: (a) Depending on temperature; (b) Higher levels under certain circumstances; (c) Depending on sulphate concentration



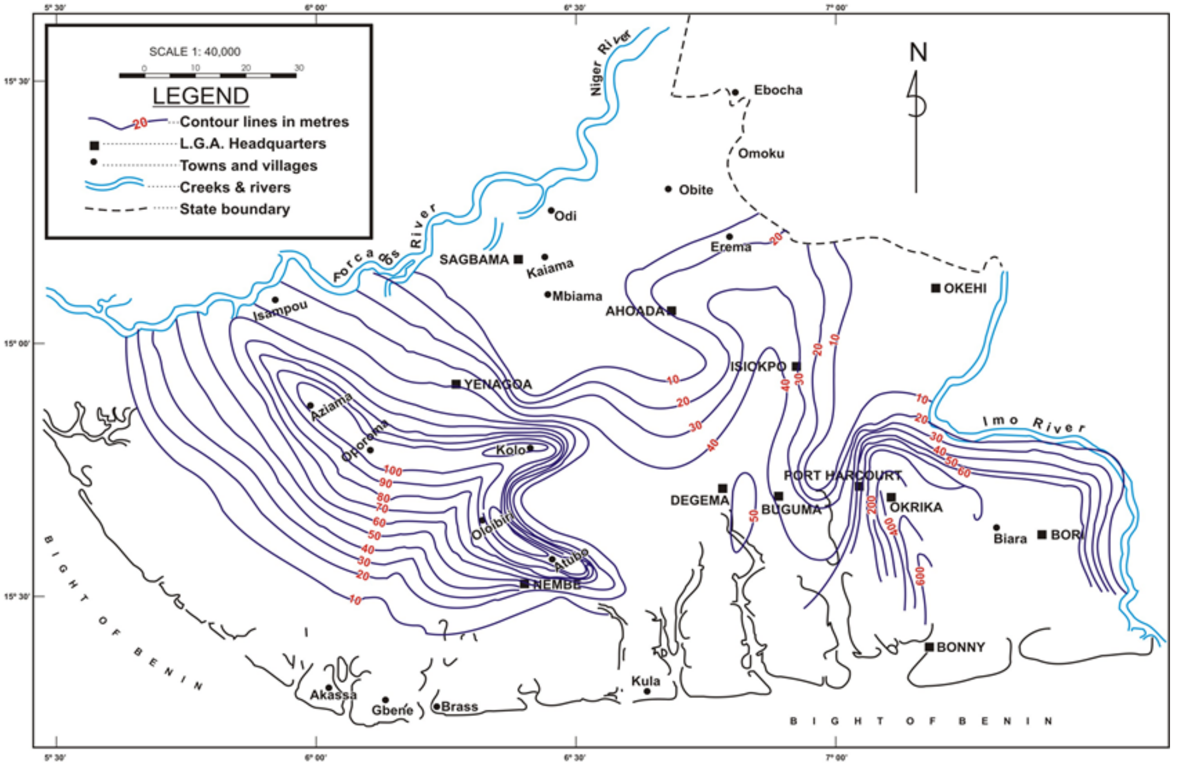
1.0 Pattern of distribution of hardness in groundwater samples from deep aquifers in some parts of the Niger Delta. Adapted from Ngah and Abams,2014



2.0 Pattern of distribution of pH in groundwater samples in some parts of the the Niger Delta. Adapted from Ngah and Abams,2014



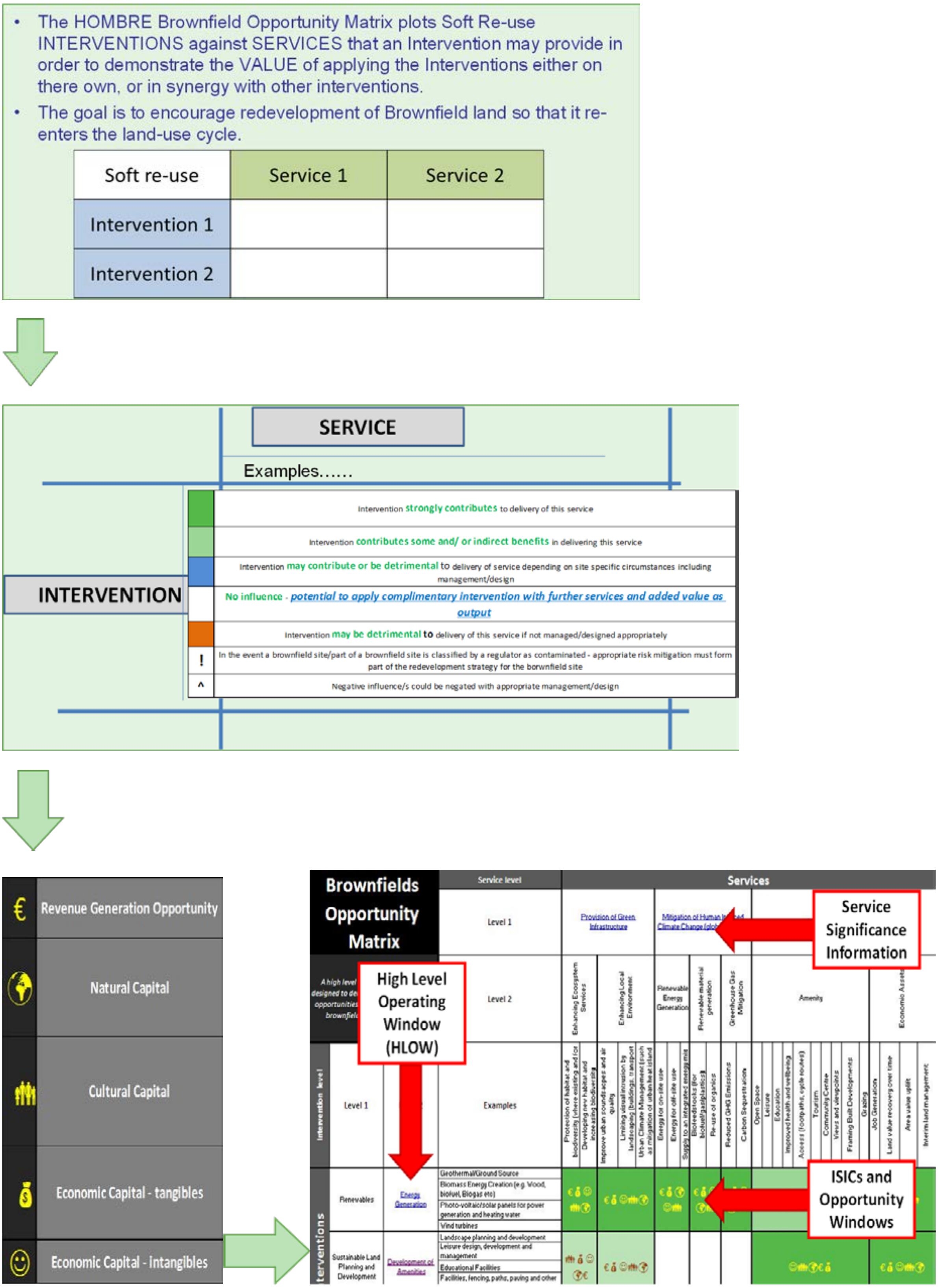
3.0 Pattern of distribution of iron in groundwater samples some parts of the Niger Delta. Adapted from Ngah and Abams,2014



4.0 Distribution of distribution of Chloride in groundwater samples in some parts of the Niger Delta. Adapted from Ngah and Abams.

Key: ***VALUE*** **of Applying Intervention to Provide Service**		
€	**Revenue Generation Opportunity**	Direct revenue generation opportunities. Revenue generation opportunities may be exploited by an INVESTOR, the LOCAL COMMUNITY, and/or by OTHER SUPPLIERS
☐	**Natural Capital**	Natural Capital may be generated, primarily for the LOCAL COMMUNITY and possibly for WIDER SOCIETY. Natural Capital is developed in a number of ways, including (but not limited to) providing green infrastructure, improvement of the local climate, improvement of water resources etc). The INVESTOR and or OTHER SUPPLIERS may benefit from Economic tangibles and intangibles.
☐	**Cultural Capital**	Cultural Capital may be generated, primarily for the LOCAL COMMUNITY. Cultural Capital is developed by improving the social environment (by improving the aesthetics of an area and/or creating a sense of place/belonging for e.g.) and can be a direct result of an increase in natural capital. The INVESTOR and may benefit from Economic tangibles and intangibles, whilst OTHER SUPPLIERS may benefit from direct revenue generation in the future, if for example, the intervention increases tourism.
☐	**Economic Capital – tangibles**	If intervention is applied to provide service then it is expected that Tangible Economic Capital may be the result. For example, land and property values in the area may increase (feeding back into Cultural Capital) providing benefits to the LOCAL COMMUNITY and also the INVESTOR. The INVESTOR may save money by facilitating planning and permitting processes.
☐	**Economic Capital – intangibles**	These benefits can only be valued on a stakeholder by stakeholder basis and include for example, reputational benefits, brand awareness etc
*	Value assuming intervention can be implemented in a way that positively delivers service.	
Nb. Please note that the value and beneficiaries noted in the above table are not intended to be exhaustive, rather they are illustrative examples of the value/benefits that can be achieved by implementing a project. It should be noted that the different types of value are often intrinsically interlinked, feeding back into each other. Value and beneficiaries WILL vary widely depending on the site specific circumstances.		

5.0 VALUE of Applying Intervention to Provide Service



- The HOMBRE Brownfield Opportunity Matrix plots Soft Re-use INTERVENTIONS against SERVICES that an Intervention may provide in order to demonstrate the VALUE of applying the Interventions either on there own, or in synergy with other interventions.
- The goal is to encourage redevelopment of Brownfield land so that it re-enters the land-use cycle.

Soft re-use	Service 1	Service 2
Intervention 1		
Intervention 2		

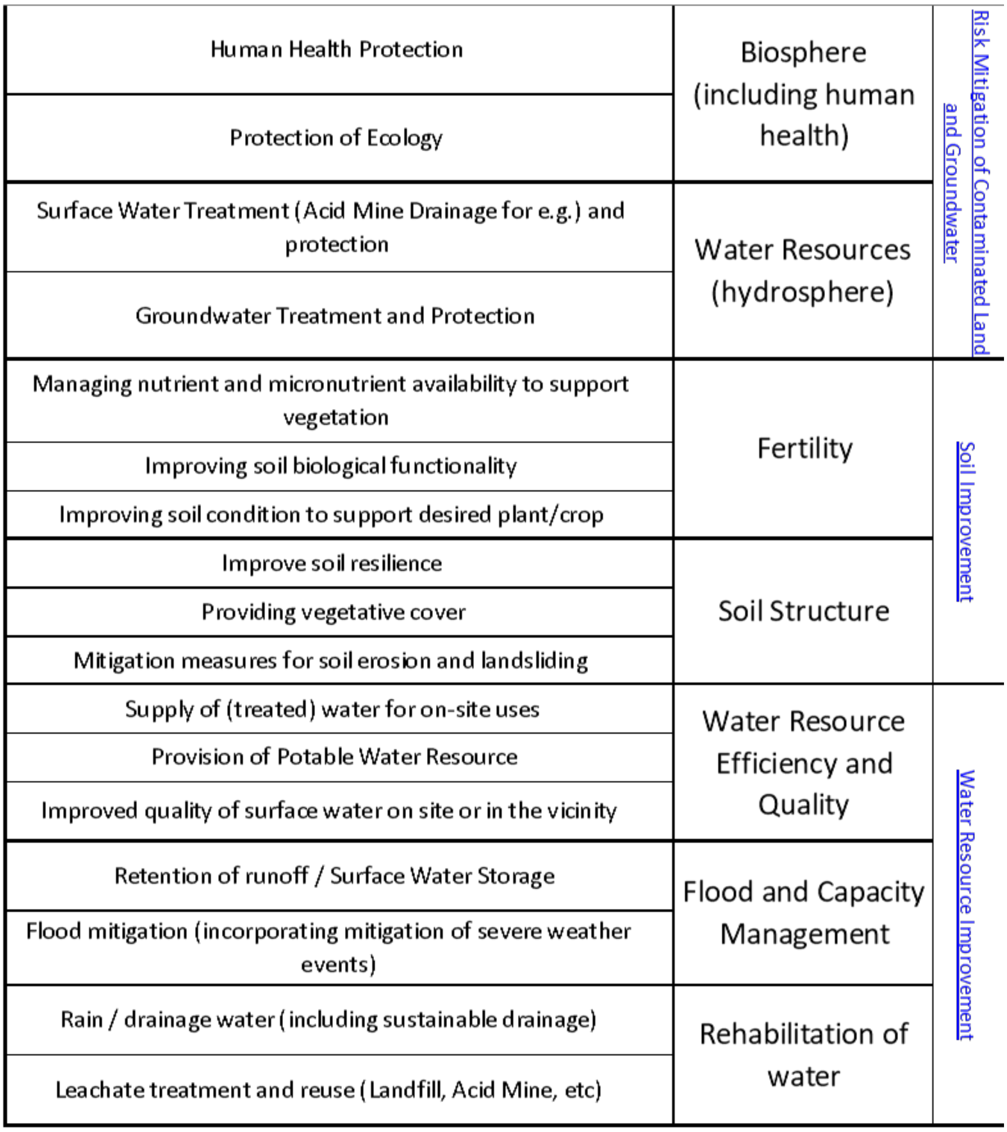
SERVICE

Examples……

INTERVENTION

🟩	Intervention strongly contributes to delivery of this service
🟩	Intervention contributes some and/ or indirect benefits in delivering this service
🟦	Intervention may contribute or be detrimental to delivery of service depending on site specific circumstances including management/design
	No influence - *potential to apply complimentary intervention with further services and added value as output*
🟧	Intervention may be detrimental to delivery of this service if not managed/designed appropriately
!	In the event a brownfield site/part of a brownfield site is classified by a regulator as contaminated - appropriate risk mitigation must form part of the redevelopment strategy for the borwnfield site
^	Negative influence/s could be negated with appropriate management/design

6.0 Application of the Brownfields Opportunity Matrix (source: the HOMBRE project)



Human Health Protection	Biosphere (including human health)	Risk Mitigation of Contaminated Land and Groundwater
Protection of Ecology		
Surface Water Treatment (Acid Mine Drainage for e.g.) and protection	Water Resources (hydrosphere)	
Groundwater Treatment and Protection		
Managing nutrient and micronutrient availability to support vegetation	Fertility	Soil Improvement
Improving soil biological functionality		
Improving soil condition to support desired plant/crop		
Improve soil resilience	Soil Structure	
Providing vegetative cover		
Mitigation measures for soil erosion and landsliding		
Supply of (treated) water for on-site uses	Water Resource Efficiency and Quality	Water Resource Improvement
Provision of Potable Water Resource		
Improved quality of surface water on site or in the vicinity		
Retention of runoff / Surface Water Storage	Flood and Capacity Management	
Flood mitigation (incorporating mitigation of severe weather events)		
Rain / drainage water (including sustainable drainage)	Rehabilitation of water	
Leachate treatment and reuse (Landfill, Acid Mine, etc)		

7.0 Brownfields Opportunity Matrix Dashboard (source: the HOMBRE project)

Protection of habitat and biodiversity (where existing and for protected sites)	Enhancing Ecosystem Services	Provision of Green Infrastructure
Developing new habitat and increasing biodiversity		
Improve urban soundsacpes and air quality	Enhancing Local Environment	
Limiting visual intrusion by landscaping (buildings, transport links etc)		
Urban Climate Management (such as mitigation of urban heat island effect)		
Energy for on-site use	Renewable Energy Generation	Mitigation of Human Induced Climate Change (global warming)
Energy for off-site use		
Supply to an integrated energy mix		
Biofeedstocks (for biofuel/gas/plastics)	Renewable material generation	
Re-use of organics		
Re-use of aggregates		
Reduced GHG Emissions	Greenhouse Gas Mitigation	
Carbon Sequestration		
Open Space	Amenity	Socio-Economic Benefits
Leisure		
Education		
Improved health and wellbeing		
Access (footpaths, cycle routes)		
Tourism		
Community Centre		
Views and viewpoints		
Framing Built Developments		
Grazing		
Job Generation	Economic Assets	
Land value recovery over time		
Area value uplift		
Interim land management		

8.0 Brownfields Opportunity Matrix Dashboard (source: the HOMBRE project)

For each category, choose only 1 of the 3 options by writing "Yes". Examples are shown	
What is the typical soil pH range at your site?	**pH**
5 - 8	yes
4 - 5 / 8 - 9	
2 - 4 / 9 - 11	
What is the relative diversity and density of current plant species present on your site?	**Plant Community**
Diversity and density of plant species are similar to surrounding areas (on non-contaminated soil)	yes
Diversity and density of plant species is visibly less/different to surroundings (non-contaminated soil)	
No plant species are growing on the contaminated site	
What is the overall climate of the region in which your site is located?	**Climate**
Arid	
Semi-Arid	
Humid/Temperate	yes
What is the typical soil type / composition on your site?	**Soil Type**
Clay	yes
Loam	
Sand	
What is the typical soil depth to which contaminants of concern are present?	**Depth of contamination**
Top Soil (0-30 cm)	yes
Sub Soil (30-90 cm)	
Deep Soil (> 90 cm)	
Recommendation	
Good to go!	

9.0 Application of Phyto-extraction (Source: the GREENLAND project decision support tool).

For each category, choose only 1 of the 3 options by writing "Yes". Examples are shown	
What is the typical soil pH range at your site?	**pH**
5 - 8	yes
4 - 5 / 8 - 9	
2 - 4 / 9 - 11	
What is the relative diversity and density of current plant species present on your site?	**Plant Community**
Diversity and density of plant species are similar to surrounding areas (on non-contaminated soil)	yes
Diversity and density of plant species is visibly less/different to surroundings (non-contaminated soil)	
No plant species are growing on the contaminated site	
What is the overall climate of the region in which your site is located?	**Climate**
Arid	
Semi-Arid	
Humid/Temperate	yes
What is the typical soil type / composition on your site?	**Soil Type**
Clay	
Loam	
Sand	yes
What is the typical soil depth to which contaminants of concern are present?	**Depth of contamination**
Top Soil (0-30 cm)	
Sub Soil (30-90 cm)	
Deep Soil (> 90 cm)	yes
Recommendation	
Expert advice and plant toxicity tests are recommended	

10. Application of Phytostabilization (Source: the GREENLAND project decision support tool).

For each category, choose only 1 of the 3 options by writing "Yes". Examples are shown	
What is the typical soil pH range at your site?	**pH**
5 - 8	yes
4 - 5 / 8 - 9	
2 - 4 / 9 - 11	
What is the relative diversity and density of current plant species present on your site?	**Plant Community**
Diversity and density of plant species are similar to surrounding areas (on non-contaminated soil)	yes
Diversity and density of plant species is visibly less/different to surroundings (non-contaminated soil)	
No plant species are growing on the contaminated site	
What is the overall climate of the region in which your site is located?	**Climate**
Arid	
Semi-Arid	
Humid/Temperate	yes
What is the typical soil type / composition on your site?	**Soil Type**
Clay	
Loam	
Sand	yes
What is the typical soil depth to which contaminants of concern are present?	**Depth of contamination**
Top Soil (0-30 cm)	
Sub Soil (30-90 cm)	
Deep Soil (> 90 cm)	yes
Recommendation	
Good to go!	

11.0 Application of Immobilization and Phytoexclusion (Source: the GREENLAND project decision support tool).