CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Soil or water is said to be contaminated when either solid or liquid hazardous substances get mixed with the naturally occurring soil or water. These hazardous substances might either have been spilled or buried directly in the soil or might have migrated to the soil and water from a spill that has occurred elsewhere (Okaeanti, 2001). Oil spill is one of the major causes of soil contamination and is defined as discrete event in which oil is discharged through neglect, by accident or with intent over a relatively short time (Etkin, 2000b). Oil spill on land causes damage to properties, shrines, farm lands, surface and groundwater. These have led to youth restiveness and agitation by habitants of oil producing communities which made the regions ungovernable (Oghenero *et al.*, 2005).

Causes of oil spillage include accidents and errors during bunkering, lightering, loading, and structural and equipment failures not attributable to accidents, damage to pipeline, storage facilities, fixed industrial facilities, air transport facilities, road and rail tankers carrying oil, fuel or other hydrocarbons (Etkin, 2000b). Heavy metal pollution of soil, surface and groundwater from oil spillage has been reported (Kostecki and Calabrese, 1989; Barenboim *et al.,* 2014). Heavy metal can bio-transform and bio-accumulate in man and other living organisms (Dara, 2008 and Ademoroti, 1996).

Other pollutants associated with oil spillage are benzene, toluene, PCBs, chloroform, phenols, petroleum hydrocarbons (C_{1-} C_{40}), oil and grease and other aromatics (Kostecki and Calabrese, 1989; Osuji *et al.,* 2006).

Management of oil spill on land include physical removal with a machine called tarry hump collector, burning, use of adsorbent materials like talc, vermiculite, saw dust, peat, polyurethane, polystyrene, polyester, urea formaldehyde and use of dispersants (Wardley Smith ,1979 and Grolier, 2000).

It is well known that pH, colour, organic matter, organic nitrogen, texture, carbon/ nitrogen ratio, moisture content, water holding capacity, bulk density and mineral content (trace & bulk elements) of soil indicate the condition or status of soil (Olaitan and Lombin, 1984; Aziz and Karim, 2016) . Recent studies have shown how some of these parameters affect soil characteristics positively or negatively (Azlan *et al*., 2012; Aziz and Karim, 2016).

Soil sampling for atmospherically deposited pollutants will normally be based on shallow sampling (0-2.5 or 0.5cm) in top soils. Materials which contained contaminants (sewage sludge, fertilizers and manures) and which were subsequently ploughed into the soil need to be studied in samples of both top soil (normally 0-15cm) and samples from lower depths in the soil profile, 15-30cm (Okaeanti, 2001; Okop and Ekpo, 2012). The greatest part of the organic matter in soils occurs in the top soil (Olaitan and Lombin, 1984; Azlan *et al*., 2012).

Soil properties and composition change with depth. Consequently, the characteristics of sub soil could be different from those of the surface layer. The sub soil layer has been shown to be an important geochemical barrier against the migration of metals in the soil system, including penetration into groundwater. (Zacharyasz *et al*., 2012 and Alloway 1995). Trace element uptake by roots depends on both soil and plant factors (e.g source and chemical form of elements in soil, pH, organic matter, plant species, plant age etc).

Interactions between elements occurring at the root surface and within the plant can affect uptake as well as translocation and toxicity (Luo and Rimmer, 1995; Baum, 2012). Heavy metal uptake by plant grown in polluted soils have been studied to a considerable extent. All findings have shown that elevated levels of metals in soil may lead to increased uptake by plants. However, there is generally not a strong relationship between the concentrations in soil and plants (Xian, 1989).

With increase in industrialization, pollution by organic substances has become a major threat to our environment. Our atmosphere, surface water bodies and soil are now polluted with toxic gases generated from the combustion of fuels in electricity generators, petroleum refineries, steel mills and smelters, kerosene and petrol may leak out of their storage tanks and contaminate water supply. Likewise crude oil through leaking pipelines, over flown tanks, leaking tanks, oil drilling, faulty valves and burst hoses during transfer operations (Cheremisinoff, 1976 ; Okop and Ekpo, 2012). Oil wells themselves are major polluters. In the course of a year, a single oil well throws into the atmosphere up to 2 tons of carboniferous soot, 8 tons of carbon oxides, over 30 tons of nitrogen oxides,5 tons of sulfur dioxide and a large quantity of heavy metals. All of this later settle to earth (http//www.cdi.org//Russia/Johnson/6168-11.cfm).

Poisoning from kerosene and petrol could be by inhalation of the fumes or by ingestion of the product (Ademoroti,1996). Symptoms of intoxication from kerosene and petrol include restlessness, incoordination, confusion and excitement. Inhalation of high levels of petrol vapours could cause depression of central nervous system, coma and eventually death; usually from respiratory failure. Also pulmonary damage which progresses to pulmonary oedema has been reported (Das and Chandran, 2011).

Aromatic compounds like benzene, toluene and phenol found in petroleum when ingested, predisposes man to cyanosis, tachycardia, cancer, infertility and other deadly diseases (Ademoroti, 1996; Thomas and Ringen, 1985).

Soil pollution also affects the surrounding water supplies (Egboka *et al*., 1989 and Zacharyasz *et al*., 2012).These pollutants in one way or the other via the hydrologic cycle reach the groundwater systems to pollute them. Through the circulation of water within the hydrologic cycle, pollutants on the ground surface are transferred through the soil zone into the aquifer horizons where they damage potable water supplies.

1.2 Statement of the Problem

Petroleum substances pose a threat to the environment as they negatively affect plant production and put health of people and animals at risk (Zacharyasz *et al.,* 2012 and Kolwzan *et al*., 2001). They cause carcinogenic, mutagenic and toxic effects (Ribes *et al.,* 2003, Freitag *et al*., 1985 and DEC, 1992). Chemicals associated with oil spillage are benzene, toluene, petroleum hydrocarbons, phenol, oil and grease, heavy metals etc. Some of these substances are volatile, have moderate solubility in water and are readily absorbed by the organic components of the soil. They can enter the body by ingestion of contaminated crops, inhalation of vapour from the soil, intake of contaminated drinking water and skin exposure while bathing. They are all toxic but benzene is a recognized carcinogen. When inhaled for long periods in low concentrations they can cause brain damage. Metal poisoning and other forms of toxicity are caused by heavy metals.

Oil spillage brings death and barrenness. Babies in Nigeria are at double risk of dying before they reach a month old if mothers lived near the scene of an oil spillage before conceiving (Edozie, 2017). A 2011 report by the UN Environmental Program estimated that after decades of repeated oil spillage in Ogoni land, it would take 30 years to reverse damage to public health and ecosystem.

Oil spillage affects soil physical, biological and chemical properties. The daily maximum surface temperature of hydrocarbon-contaminated soils is often higher than that of adjacent control sites (Aislabie *et al.,* 2004). Oil spillage usually causes anaerobic environment in soil by smothering soil particles and blocking air diffusion in the soil pores thus affecting soil microbial communities (Townsend *et al*., 2003, Labud *et al*., 2007, and Sutton *et.al*., ,2013). Other effects of crude oil spillage on soil physical properties include decreased pore spaces (porosity), saturated hydraulic conductivity and increased bulk density..The decreased pore spaces apart from reducing soil aeration, minimize infiltration of water into the soil (Abosede, 2013). Hydrocarbon contamination can also increase soil total organic carbon (Ekundayo and Obuekwe, 2000) and change soil pH values (Hu *et al.,* 2006; Wang *et.al*., 2010) and other soil chemical properties (Kisic *et al.,* 2009). pH values can be increased to 8.0 and available phosphorus concentration reduced (Wang *et al*., 2013).

Maximum permissible levels of substances in soil and water are given by National Environmental Standards and Regulations Enforcement Agency (NESREA), WHO, The Environmental Management (Soil Quality Standards) Regulations, and other environmental agencies. To ensure that these maximum permissible levels are not exceeded, determination of the levels of these substances in environmental samples is done and remedies proffered where they exceed maximum permissible levels.

1.3 Aim and Objectives of the Study

Aim of this study is to determine physicochemical properties, organic and inorganic pollutants in petroleum contaminated soils and to establish best soil management practice.

The specific objectives of the study are to:

1. determine the physicochemical properties of petroleum contaminated soils .

2. relate the physicochemical properties of the petroleum contaminated soil with the extent of contamination.

3. determine the level of toxic and non toxic metals in the petroleum contaminated and non petroleum contaminated soils for comparison using AAS.

4. determine total petroleum hydrocarbon, phenol, benzene, oil and grease contents of the petroleum and non petroleum contaminated soils for comparison using standard methods

5. determine the various petroleum hydrocarbons inherent in the petroleum contaminated soils.

6. determine a material that can be used for oil adsorption (i.e. for management of oil spillage).

1.4 Scope of the Study

The study area comprised petroleum contaminated soil around crude oil storage tank Eleme petroleum refinery Port-Harcourt and non petroleum contaminated soil around utility building Nnamdi Azikiwe University, Awka. Soil samples were collected at depth of 0-12cm at five different points, mixed homogenously to obtain a grab sample representative of the study area. A total of seven homogenous soil samples were obtained and they were preserved by freezing before analysis. Some portions of the samples were prepared for organic matter, organic carbon and organic nitrogen determinations. The remaining portion was used for other analysis.. The selected physical and chemical properties of soil investigated were texture, bulk density, colour, soil moisture, soil water holding capacity, pH, %organic carbon, %organic matter,% organic nitrogen. Trace metals like Fe, Ca, Mg,V, Ni, Cr, Cd, Zn, Pb, Se, Mn and As were also investigated as well as total petroleum hydrocarbons, benzene , phenol, oil and grease which are associated with oil spillage. Atomic absorption spectrophotometry was used for trace metal analysis and some organic pollutants were analyzed by gas chromatographic method and the charts produced. Adsorption of crude oil with bamboo particles of various sizes was conducted and the results obtained were translated graphically. Statistical analysis of some of the data using ANOVA was then performed.

1.5 Justification of the Study

The problems encountered in crude oil spillage include destruction of vegetation and farmlands, aquatic animals and plants, drinking water supplies as well as pollution of the atmosphere (Tolulope, 2004, Oghenero *et al*., 2005, Nelson Smith 1979 and Nwankwo, 1987). There are also cases of defoliated bushes and deforestation (Imevbore,1981 and Texaco Funiwa,1981) .There is therefore need to monitor oil pollution of soil because of these devastative effects.

Bamboo wood which is cheap, renewable and abundant would be of immense importance in the management of oil spillage in Nigeria. Oil ad sorption pattern of this material would be investigated as this will diversify the already existing knowledge on spill management.

Further recommendation on management of oil spillage will be proffered and preventive measures outlined.

1.6 Significance of the Study

Some of the importance of this study are to:

1. gain an insight into the methods used in analyzing physicochemical properties of soil, benzene, phenol, oil and grease and total petroleum hydrocarbon content of polluted soil sample.

2. gain adequate understanding of the effect of oil spillage on the soil and the surrounding biota so as to provide the required awareness needed to check the menace.

3. employ effective and affordable method of oil cleaning using background knowledge of pollutant behaviour and information gathered from the experiment.

4. curb the youth restiveness and agitation by inhabitants of oil producing communities which have made the regions ungovernable by relating to government agency.

CHAPTER TWO

LITERATURE REVIEW

2.1 Soil and Soil Characteristics

Soil and soil characteristics comprise definition of soil, how it differs from land and earth, soil structure, composition of soil, classification of soil, types of soil, properties of soil etc (Anikwe, 2006 ;Olaitan and Lombin, 1984).

2.1.1 Definition of the Term Soil

Soil has been defined as a natural body of loose unconsolidated material which constitutes a thin layer several metres deep on the earth's surface (Olaitan and Lombin 1984). It is derived from weathered parent rock materials and decaying organic matter and is composed of solid particles.

2.1.2 How Soil Differs from Land and Earth

Earth was one of the eight planets of the universe known to man. Today millions are known. It consists of concentric layers of geochemically and geophysically different kinds of material, including water and land masses. The soil is the topmost or surface layer and it is the one most often exploited for the benefit of mankind. The difference between land and soil is that while soil refers essentially to the products of weathered rocks plus organic matter, the land includes all the conditions of the physical environment of which the soil constitutes only one component. Other factors may include the underlying geology, the hydrology, the relief or topography, the plant and animal populations and the results of human activity, both past and present (Olaitan and Lombin, 1984).

2.1.3 The Composition of Soil

A well formed soil is made up of the following components:

(1) Organic materials including humus

(2) Mineral particles

(3) Air

(4) Water

The organic material and mineral particles are intimately associated in the topsoil. If the organic material is removed or destroyed, the mineral particles will remain. The soil or mineral particles can be divided up according to the diameter of the particles:

Clay: less than 0.002mm in diameter

Silt: between 0.002 and 0.02mm in diameter

Sand: between 0.02 – 2.00mm in diameter (Olaitan and Lombin, 1984)

2.1.4 Mineral Soils and Organic Soils

Mineral soil is a soil which consists predominantly of mineral recast of inorganic matter. The organic matter is rarely more than 10%, most of which is accumulated in the top 30cm. virtually all cultivatable soils in the tropics are mineral soils. (Olaitan and Lombin, 1984).

Organic soils contain about 70 – 95% of organic matter and this high organic matter content characterizes the whole profile. Organic soils are not formed through the normal soil forming processes but through accumulation of vegetative matter in swamps, marshes and bogs. Peat deposits are common in the cool temperate regions of the world because the low temperatures permit only a minimum of microbial activity which results in the accumulation of organic matter. Organic soils are rare in the tropics because the temperatures are high throughout the year and this accelerates microbial decomposition or mineralization of organic matter. (Olaitan and Lombin 1984; Brady & Weil, 1996).

2.1.5 Surface and Subsoil

The terms surface soil, arable layer or topsoil generally refer to the top 15 to 20cm of the soil. In an undisturbed state, the surface layer of a typical mineral soil is usually darker than the layer below it. The dark colour is due to the presence of organic matter.

The subsoil is found below the surface layer or topsoil. It is almost always lower in organic matter than the surface layer and so the soil colour may change quite markedly. Generally, subsoil colours are more striking and show greater variation. The red, brown, yellow or brownish yellow colours of soils are due mainly to the presence of iron compounds. The colour is dependent on the amount and form of iron present (Olaitan and Lombin, 1984).

2.1.6 Genesis of Soils and Factors of the Soil Formation

Soil formation is a complicated natural process of soil origination from mountain rock under effects of the soil forming factors in natural or anthropogenic ecosystems of the earth. Soil formation is a global biospheric process and as a result of its manifestation a soil attains a number of typical features which are absent in the soil forming rock and distinguish the soil from other components of the biosphere. The soil forming process takes place under the influence of certain soil forming factors. Five factors of the soil formation are distinguished: climate, relief, mountain rocks, organisms and time. Each of these has its influence upon the soil formation and this process is impossible without contribution of one of them. In this sense, all these factors are equivalent and irreplaceable.

In the course of its formation, every soil passes through a number of successive stages whose direction, duration and intensity are determined by a concrete complex of soil forming factors in each particular point on the earth: the stage of initial soil formation, the stage of development, the stage of equilibrium and the stage of evolution.

The whole process of soil formation can be separated into component processes of a lower level which are called elementary processes of soil formation. The diversity of natural conditions in different landscapes results in manifestation of very varied combinations of soil formation. Diversity of these combinations is determined by both evidence or absence of one or another process under certain natural conditions and the intensity of each of these processes. This extremely wide diversity of complexes of the soil forming processes leads finally to a large diversity of soils on the land (Anderson and Cerkowniak, 2010 : Queensland, 2013)

2.1.7 Soil Classification

There are many systems of soil classification but the method chosen must be related to the reason for classifying one or a number of soils. Soils may be grouped quite simply according to particle diameter into sand, silt and clay (particle size classification) and these are shown in Table 2.1.

Table 2.1: Soils separates and their diameter ranges

Soil separate name	Diameter range (mm)	Visual size comparison of maximum size
Very coarse sand	2.0-1.0	House key thickness
Coarse sand	1.0-0.5	Small pin head
Medium sand	0.5-0.25	Sugar or salt crystals
Fine sand	0.25-0.10	Thickness of book page
Very fine sand	0.10-0.05	Invisible to the eye
Silt	0.05-0.002	Visible under microscope
Clay	Less than0.002	Most are not visible even with a microscope.

Source : Miller and Donahue (1992)

This classification may be adequate only if the main purpose is to try and show the main differences in soil texture, drainage or aeration. Detailed description of the soils are shown in the U.S. Comprehensive Soil Classification System presented in Table 2.2.

Table 2.2:U.S comprehensive soil classification system

Soil order	Description and areas where found
Oxisols	The intensely leached ,oxidized red soils of the tropics (laterites)
Utisols	Soils that have chemically weathered under warm moist climatic conditions, support forest canopy, dominant in south-eastern U.S, China, Brazil, Australia and West Africa.
Alfisols	Fine textured, yellow brown soils that are low in humus, clay-rich B horizon, moderate to high fertility. Texas, Ohio valley, Mississippi valley regions, Russian Steppes and Australia.
Spodosols	Acidic soils developed on quartz rich sandy soils in cool climates. Low fertility and short growing season make these poor soils except for root crops such as potatoes.
Mollisols	Thick humus, soft consistency when dry, Almost all are developed on transported parent material, loess or alluvium. Prairie and steppe grasslands of mid-latitudes, the choice fertile soils of the Midwest (Pedalfers).
Aridisols	Alkaline with caliche (petocals).Productive when water and good drainage are available. Desert regions, areas that receive less than 25cm rainfall per year.
Vertisols	Clay-rich soils that expand upon absorbing water and shrink upon drying. Desiccation cracks are common and their expensive nature requires special foundation design. Mostly in California, Colorado and Texas.
Histosols	Organic soils in bogs or swamps. Least important and least extensive soil order. Florida, the Everglades and the Mississippi River and delta.
Entisols	Poorly developed, recent soils with little or no profile. Sandy deserts, tundra areas and areas recently glaciated or covered by alluvium or volcanic ash.
Inceptisols	Immature soils (containing weatherable minerals) better developed than entisols. Tundra regions, steep mountain areas and flood plains or deltas; very productive along the Mississippi, Nile and Ganges Rivers.

Source: Pipkin (1994)

2.1.8 Physical Properties of Soil

2.1.8.1 Sand

Sand particles are large enough to be seen with the naked eye. They feel gritty when rubbed between fingers and do not adhere to one another. Sand particles are well aerated and have good drainage but they will not hold water or nutrients. Coarse sand particles have a diameter of 2.0 to 0.2mm and fine sand particles range in size from 0.2 to 0.02mm.

2.1.8.2 Silt

Silt particles are somewhat smaller (0.02mm to 0.002mm). They are too small to see without a microscope or to feel individually. Silt particles feel smooth but not sticky even when wet. Compared with sand, silt contains less silica ($Si0_2$) and more of the cations important in plant nutrition. The physical properties of silt are intermediate between sand and clay: silt occurs more abundantly in temperate soil than in tropical soil.

2.1.8.3 Clay

The smallest class of soil or mineral particles are the clays (<0.002mm) which adhere together to form a sticky mass when wet and hard clods when dry. The smaller particles (<0.001mm) of clay (and similar-sized organic particles) have colloidal properties. When fine clays are shaken up in water they show some of the properties of solids and liquids. They are therefore called colloids. The individual particles of clay can only be seen with the aid of an electron microscope. Since the surface of soil colloids (both mineral and organic) exhibit electromagnetic charges that attract positive and negative ions as well as water, this fraction of the soil is the seat of most of the soil’s chemical and physical activities. Clay colloids are important because they can hold nutrients on their surface in a form which is readily available to plants. They are also spongy and can hold water better than sand. Unfortunately they can become waterlogged and partly aerated (OLaitan & Lombin, 1984; Brady &Weil, 1996).

2.1.8.4 Soil Colour

The colour of a soil indicates certain physical and chemical characteristics of the soil. Soil colour is as a result of the humus content and the chemical nature of the iron compounds present in the soil. Humus is dark brown or black in colour. Iron oxides are green, yellow, brown or red . Mineral soil particles may contain 5% or more of iron (Olaitan and Lombin, 1984). Iron exists in two main forms namely Iron (II) oxide (FeO) and Iron (III) oxide Fe_20_3. Fe^{2+} cations, which exist as the pale green hydrated complex, $[Fe(H_2O)_6]^{2+}$, in aqueous solution, are formed when the metal is reacted with dilute acid. At pH values higher than about 3, the colloidal hydrated iron(III)oxide $Fe_2O_3.xH_2O$, separates as a reddish brown precipitate. In solutions which are not strongly acidic, the pale purple $[Fe(H_2O)_6]^{3+}$ cation hydrolyses to yellow aqua/hydroxo complexes. In alkaline solution, the hexa aquairon(II) cation forms the dirty pale green hydroxide which readily undergoes air oxidation to the hydrated iron(III)oxide which is red-brown (Murray,1982).

Too much water and an absence of oxygen cause anaerobic micro-organisms to reduce the ferric iron to the ferrous form and this produces a characteristic grey colour. The munsell colour system is used to describe soil colour (Olaitan and Lombin, 1984).

2.1.8.5 Soil Texture

This is determined by the size of the soil particles and it refers to the proportion of sand, silt and clay in a soil. Terms such as sandy, loamy, silty clay and clay loam are used to identify the soil texture. Texture may be used to describe how a soil feels or behaves under cultivation and it has a profound influence on many soil properties. Texture affects the suitability of a soil for many uses (Olaitan and Lombin,1984). Fine textured surface soils such as silt loams, clays and clay loams generally have lower bulk densities than sandy soils (www.agriinfo.in/default as px>page)

Determination of textural class by the feel method (Brady and Weil, 2013). Interpret your observations as follows:

1. Soil will not cohere into a ball, falls apart: **Sand.**

2. Soil forms a ball but will not form a ribbon: **Loamy sand.**

3. Soil ribbon is dull and breaks off when less than 2.5cm long and

a. Grinding noise is audible; grittiness is prominent feel: **Sandy loam.**

b. Smooth, floury feel prominent; no grinding audible: **Silt loam.**

c. Only slight grittiness and smoothness: grinding not clearly audible: **Loam.**

4. Soil exhibits moderate stickiness and firmness, forms ribbon 2.5-5cm long and

a. Grinding noise is audible, grittiness is prominent feel: **Sandy clay loam.**

b. Smooth, floury feel prominent; no grinding audible: **Silty clay loam.**

c. Only slight grittiness and smoothness; grinding not clearly audible: **Clay loam.**

5.Soil exhibits dominant stickiness and firmness, forms shiny ribbons longer than 5cm and

a. Grinding noise is audible, grittiness is dominant feel: **Sandy clay**.

b. Smooth floury feel prominent: no grinding audible: **Silty clay.**

c. Only slight grittiness and smoothness; grinding not clearly audible: **Clay**

2.1.8.6 Primary and Secondary Minerals

Primary minerals are minerals that have persisted with little change in composition since they were extruded in molten lava e.g quartz, micas and feldspars. They are prominent in the sand and silt fractions of the soil. Other minerals such as silicate clays and iron oxides were formed by the breakdown and weathering of less resistant minerals as soil formation progressed. These minerals are called secondary minerals and tend to dominate the clay and in some cases silt fractions.

The inorganic minerals in the soil are the original source of most of the chemical elements essential for plant growth (Brady and Weil, 1996).

2.1.8.7 Soil Structure

The building blocks from which soil is constructed are sand, silt and clay. The manner in which these are arranged together is called soil structure (i.e. arrangement of soil particles in aggregates of varying consistency). The particles may remain relatively independent of each other but more commonly they are associated together in aggregates of different size particles. These aggregates may take the form of roundish granules, cube like blocks, flat plates or other shapes. Soil structure (the way particles are arranged together) is just as important as soil texture (the relative amounts of different sizes of particles) in governing how water and air move in soils i.e., drainage and aeration and the ability of the soil to release plant nutrients (Olaitan and Lombin, 1984).

2.1.8.8 Classes of Soil Structure

1. **Structureless:** This includes single separate grains such as sand.
2. **Granular:** These are roughly spherical aggregates with spaces between the granules. They are the most favourable for plant growth and water can be held between the granules. A good crumb structure is found here.
3. **Structured:** Structured refers to individual natural soil aggregates which are characteristically platy, blocky or prismatic. The soil aggregates may be referred to as peds (Olaitan and Lombin, 1984).

2.1.8.9 Bulk Density

To get the bulk density of a soil, the weight of a particular volume of oven dried soil with its natural structure intact is compared with its volume to obtain a figure for bulk density. The fewer the pore spaces, the greater the bulk density. Pore space in the soil refers to the volume occupied by air and water. Cultivation reduces the amount of organic matter in the soil compacting it and thereby increasing the density (Miller and Donahue, 1990; Olaitan and Lombin, 1984).

2.1.8.10 Soil Temperature

Microbial activity, seed germination and root growth are affected by soil temperature. When the soil is cold there is little or no biological activity. In the soil the most important microbial activity takes place within the temperature range 20 to 28^0C. The temperature that is most favourable for seed germination varies according to the plant species. Warm soils are generally well drained soils and waterlogged soils are usually cold because water has a high specific heat capacity (Olaitan and Lombin, 1984).

2.1.8.11Soil Aeration

An excess of water in the soil usually means that the soil pores are filled with water. Cultivation of the soil by digging, ploughing and hoeing all help to loosen the soil particles and encourage circulation of air in the soil. Poor aeration causes anaerobic condition which reduces the population of nitrifying bacteria in the soil and increases the number of denitrifying bacteria. In severe cases, this will deplete nitrate levels in the soil dramatically.

The most harmful effect of poor aeration is that the anaerobic bacteria start carrying out reduction producing toxic byproducts such as simple fatty acids for e.g. acetic acid and hydrogen sulphide both of which are poisonous to plant roots. In general reducing conditions increase the soil pH and oxidizing conditions reduce the soil pH. Reducing conditions reduce the concentration of aluminum but increase the concentration of ferrous irons.

2.1.8.12 Soil Moisture

Water trapped in the soil is the solvent for plant nutrients. It helps to control soil aeration and temperature and provides a good medium for microbial activity in the soil. It also satisfies the evapotranspiration requirements of plants. A basic knowledge of soil-water relationships will help in understanding the factors associated with:

1. The movement of water into and within the soil.
2. The storage of water in the soil and its utilization.
3. The availability of soil moisture to higher plants.

Under optimal field moisture conditions, representative loam soil contains 25% solids, (sand, silt, clay and organic matter), 25% air and 25% moisture. In such optimal conditions only half of the moisture in the soil is actually available to plants because of the mechanics and physics of soil water storage. Water is held in fine pores by surface tension forces. It follows that the more surface area a soil has (e.g. where there is plenty of clay and/or organic matter); the more water it can absorb (Olaitan and Lombin,1984).

2.1.8.13 Water Holding Capacity

Soil water holding capacity can be defined as the amount of water absorbed per unit weight of dry soil when immersed in water. The soil water holding capacity determination is a useful index in pot experiments. It provides means of monitoring moisture levels required to maintain good plant growth (Ibitoye, 2006).

Precision and accuracy depend on the handling. Loose packed soil tends to increase in weight when immersed in water for at least 12 hours. The water holding capacity of sand, silt and clay varies and it depends on the spaces between their particles. In sandy soil, there are more macrospores than microspores and therefore the ability to retain water for long is low. In clay soil, there are more microspores than macrospores and therefore the ability to retain water is higher than either sand or silt. In a well drained loam soil, there is a balance in the number of microspores and macrospores.

The force with which water is held in soil is measured as the force required to dislodge the water from the soil or to pull the water off the soil. The terms suction or tensions are used to describe this force. Forces of water retention are measured in bars (of suction or pressure) which are approximately the same as atmospheres of pressure (1atm = 1.013 bars). The moisture content of a soil may be described as one bar suction. This means that at least one bar is required to remove the most loosely held water from that particular soil (Olaitan and Lombin, 1984;)).

2.1.9 Chemical Properties of Soil

2.1.9.1pH

pH is a unit that describes the degree of acidity or alkalinity of a solution. It is a measure of the active acidity or hydrogen ion $[H^+]$ of the sample solution. pH is defined as the negative logarithm of the hydrogen ion concentration (activity) in solution i.e. pH = - log $[H^+]$ where$[H^+]$ = activity of H^+ in moles/litre. Sample with pH between 0-7 is acidic, pH 7 is neutral while pH between 7-14 is alkaline (APHA, 2000).

Many processes in aqueous solutions depend on the hydrogen ion concentration. For instance, many chemical reactions are catalyzed or influenced by hydrogen ions including land toxic ions. Plant growth may be correlated with hydrogen ion concentration in the soil and processed in living tissues. Therefore determination of hydrogen ion concentration cannot be over-emphasized.

The property of a soil is a measure of its acidity or alkalinity. pH of a soil can provide useful information such as how acidic or basic the soil is, % base saturation, H^+ formation from cation exchange sites, H^+ formation from hydrolysis of Al and plant nutrient availability (Bates, 1954).

There are several factors that affect the pH measurement obtained for a particular soil sample. Some of these factors include:

i. Drying
ii. Soil water content
iii. Content of soluble salts
iv. Content of CO_2 is influenced by season or drying.
v. The level of grinding given to the soil
vi. Field variation or composite samples

vii. Weathering
viii. Leaching
ix. Soil micro organism activity (Olaitan and Lombin, 1984).

2.1.9.2 Methods of pH Determination

Colorimetric methods (measurement by indicator) Electronic method or measurement by pH meter (Ibitoye, 2006).

2.1.9.3 Cation Exchange

The replacement of one cation by another on the exchange complex is called cation exchange. Factors that control cation exchange in soils include the relative concentration of the ion involved, the number of charges on the ion and the speed of movement or activity of the ion. The greater the number of charges an ion caries, the more efficient it is in replacing others on the exchange complex. The speed of movement of an ion is essentially a function of its size. Hydrated ions, for instance, are usually less active than non-hydrated ions of the same species. The replaceability series of some of the common cations in soils is Al>Ca>Mg>K>Na and the ionic exchange is on a chemical equivalence basis. Thus, when an ammonium fertilizer e.g. $(NH_4)_2$ $S0_4$ or potash fertilizers e.g. KCl is added to the soil, the NH_4^+ or K^+ ions will replace other cations on the exchange complex and these will go into soil solution. Cation exchange takes place on the surfaces of clay and humic colloids as well as on the surface of plant roots.

Under natural conditions the process of cation exchange accounts for the fact that calcium and to a lesser extent, potassium, magnesium and sodium are lost by leaching. At the same time aluminum and hydrogen ions both of which enhance soil acidity are increased. This is why soils in humid regions tend to become acid rather quickly (Olaitan and Lombin, 1984).

2.1.9.4 Cation Exchange Capacity

Cation Exchange Capacity (CEC) is a measure of the number of adsorption sites per unit weight of soil at a particular pH. It is often defined as the sum of exchangeable cations adsorbed per unit weight of soil. It is measured in millequivalents per 100g of soil (meq/100g). The cation exchange capacity is affected quite dramatically by pH change. Soils high in organic matter or certain clay notably vermiculite and montmorillonite have a high CEC. In contrast soils dominated by kaolinite and hydrous oxide clays generally have a low CEC. Soils which contain small amounts of clay are also invariably low in organic matter and therefore the CEC is poor. Fine textured soils are usually rich in organic matter and hence their CEC values are often high. The organic matter in many weathered tropical soils is maintained in order to ensure maintenance of CEC at a satisfactory level.

2.1.9.5 Anion Exchange

Colloids low in cation exchange are high in anion exchange generally. Some of the cations such as iron, have hydroxyl (OH^-) ions that can be exchanged with sulphate (SO_4^{2-}), phosphate ($H_2PO_4^-$and HPO_4^{2-}) and molybdate ($M_00_4^{2-}$) ions.

Soils high in hydrous oxide clays (oxides of iron and aluminum) and amorphous clays such as alophane are particularly high in anion exchange. This explains why tropical soils fix considerable quantities of phosphate and sulphate. Kaolinite soils are not necessarily high in anion exchange but they are if they also contain hydroxides of iron and aluminum (Olaitan and Lombin, 1984).

2.1.9.6 Causes of Soil Acidity

The acidity of a soil is due to the following reasons:

1. **Soil is Formed from Acid Rocks:** Rocks such as granite and rhyolite contain an excess of quartz or silica which combines with various proportions of water to form

acids such as silicic acid and trisilicic acid. Considerable areas of sandy soil have been produced from acid rocks.

2. **Presence of Humus:** Reactions may take place between humus, iron and aluminum ions forming complexes which subsequently undergo hydrolysis to yield hydrogen ions which will increase soil acidity.

3. **Presence of Soluble Salts:** Soluble salts arising from fertilizer salts, mineralization or organic matter and the weathering of minerals may also undergo hydrolysis to form acids. Soluble salts can be acidic, neutral or basic.

4. **Water-Logging:** Excessive water causes hydrolysis of some of the cations in the soil. These are replaced by hydrogen ions.

5. **Rain Water:** Atmospheric carbon dioxide dissolves in rain water to form carbonic acid which is a weak acid $CO_2 + H_2O \rightarrow H_2CO_3$. The atmosphere also contains acidic gases such as sulphur dioxide. These gases dissolve in rain water to form dilute acid solutions in the soil.

6. **Cultivation:** During cultivation nutrient elements (cations) are removed by plants through absorption. These are replaced by hydrogen ions which cause acidification of the soil.

7. Application of Fertilizers

Fertilizer application increases the cation and anion content of the soil. However, all nitrates are soluble and when they are leached from the soil they take cations with them. Ammonium nitrate fertilizers have acidifying effect on the soil.

8. Biological Activities in the Soil

Biological activities in the soil like aerobic oxidation of organic matter and anaerobic decomposition of organic matter influence soil acidity. Anaerobic decomposition of organic matter may release weak acids such as lactic acid, acetic acid, butyric acid and propionic acid which acidify the soil. Nitrification increases soil acidity and is of great importance when commercial fertilizers containing ammonium salts are used.

9. Removal of Bases

The removal of bases from soil minerals make them unstable and subject to disintegration. The products of the mineral decomposition may contain replaceable hydrogen ions which increase soil acidity.

9. Sulphides

The presence of sulphides in the soil can cause soil acidity due to the production of hydrogen ions (Olaitan and Lombin, 1984).

2.1.9.7 Alkalinity

The pH of the soil indicates whether the soil is alkaline or acidic. Total alkalinity (soluble hydroxides, carbonates and bicarbonates) of a soil is determined by titration with a standard acid (H_2S0_4 or HCl) using phenolphthalein and methyl orange as indicators.

Alkaline soils contain more hydroxyl ions than hydrogen ions. This is because of the chemical reaction that takes place between carbonates of calcium, magnesium, sodium and potassium and hydroxyl ions. For example, sodium carbonate is readily hydrolyzed to form sodium hydroxide (Bates 1954;Olaitan and Lombin,1984).

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2.$$

2.1.9.8 Liming

Unfavourable soil acidity may be corrected by the application of lime. Lime may be said to be any compound of calcium or of calcium and magnesium that is capable of counteracting the harmful effects of an acidic soil.

Phosphorus is generally most readily available to plants in a neutral or slightly acidic soil. When soils become deficient in bases, the solubility of aluminum, iron and manganese increases and the high concentrations of aluminum and manganese may be toxic to crop plants.

Liming materials include:

(1) Calcium carbonate from calcitic limestone

(2) Calcium magnesium carbonate(dolomitic limestone),

(3) Corals, shells or marl which are sources of calcium carbonate

(4) Calcium oxide (burned lime, quicklime, caustic lime or lump lime)

(5) Calcium hydroxide

(6) Basic slag or Blast furnace slag (a by-product of pig iron manufactured from iron ore and limestone

(7) Paper mill refuse containing calcium carbonate

(8) Wood ash and

(9) Sugar factory lime. (Santra, 2005;Olaitan and Lombin,1984).

2.1.9.9 Organic Matter

The study of soils has revealed that the amount of organic material in a soil controls its productivity. Organic matter in the soil is a mixture of materials. It consists of plant and animal remains, living and dead micro-organisms and the products of decay which has taken place over months or even years.

The quantity of organic matter in the soil varies widely, from comparatively small percentages in sandy soil to more than 70% in peat soil. There are many different sources of organic matter of which compost is the most popular. Other sources are poultry manure, horse and cow manure, sheep and goat manure, fish waste and fish meal, green manure, wood ash and night soil or sewage.

2.1.9.10 Composition of Organic Matter in the Soil

The materials that make up organic matter in the soil include:

1. Carbohydrates (starches, sugars and celluloses)
2. Lignin (wood)
3. Proteins (e.g. albumens)
4. Minerals (calcium, iron, magnesium and potassium)
5. Phosphorus and Sulphur
6. Fats (oils and waxes)
7. Resins
8. Tannins
9. Pigments

Of these components, lignin and proteins make up the greatest proportion of organic matter in the soil (Olaitan and Lombin,1984).

2.1.9.11 Functions of Organic Matter

1. Fresh organic matter supplies food for soil dwelling organisms such as earthworms, ants and rodents.
2. Humus which is the decomposed organic matter provides a store of exchangeable and available cations (e.g potassium, calcium and magnesium).
3. Fresh organic matter has a special function because it makes phosphorus more readily available in acidic soils.

4. Organic matter improves the soil texture.
5. Organic matter contains soil water and air which are important for absorption of nutrients by plants.
6. Organic matter improves the soil tilth and the rate of water percolation
7. Heat absorption by the soil is influenced by soil colour because darker soils absorb more heat. Organic matter makes soil darker.
8. Organic acids that are released during the decomposition and in the process of rock and mineral weathering.
9. Organic matter is the source of many plant nutrients.
10. Organic matter minimizes erosion hazards because soil particles covered with humus stick together more firmly.
11. Organic matter in the soil helps to buffer soils against rapid chemical changes which may result when there is addition of lime and fertilizer.
12. Organic matter improves the porosity of soil (Olaitan and Lombin, 1984).

2.1.9.12 Organic Carbon

Carbon is the chief element present in soil organic matter, comprising from 48 to 58% of the total weight. Therefore organic carbon determinations are often used as the basis for organic matter estimates through multiplying the organic carbon value by a factor. For many years the Van Bemmelen factor of 1.724 was used based on the assumption that organic matter contains 58% organic carbon. However a number of studies have shown that the proportion of carbon in soil organic matter is highly variable for a range of soils, and thus any constant factor selected is an approximation at best.

Recent evidence suggests that the factors most appropriate for converting organic carbon concentrations to organic matter contents are 1.9 and 2.5 for surface and subsoils respectively. Thus the factor varies not only from soil to soil but also between horizons in the same soil. This finding suggests that it is most appropriate to determine and report the organic carbon concentration in soil rather than convert the analytically determined organic carbon value to organic matter content through use of an approximate correction factor.

Organic carbon maybe determined by

(i) Analysis of a soil for total carbon and inorganic carbon and subtraction of the inorganic carbon concentration from the total cabon present

(ii) A total carbon determination on the sample after destruction of inorganic carbon and

(iii) Reduction of $Cr_2O_7^{2-}$ by organic carbon compounds and subsequent determination of unreduced $Cr_2O_7^{2-}$ by oxidation-reduction titration with Fe^{2+} or by colorimetric techniques.

The latter is the widely used because it is simple, accurate and reproducible (Page, 1982 and Verma, 2003).

2.1.9.13 Metallic and Non Metallic Elements

About 90 elements are found in the earth's crust, out of which a mere 9 elements (viz Al, Fe, Ca, Mg, O, Si, Na, K and Ti) only account for over 99% by weight. The remaining 81 elements together, which account for hardly 0.14% by weight, constitute the trace elements (Dara, 2008).

2.1.9.14 Nutrient Elements

Nutrient elements are designated as macro or micro elements (or nutrients) depending on the relative amounts needed by plants and animals (Hay 1991).

The macro-nutrients are required in much larger quantities than the micro-nutrients. For plants the macro-nutrients are N, P and K and the micro-nutrients are Fe, Cu, Zn, B, Mn, Mo, Cl and Co. Macro-nutrients are sometimes referred to as primary nutrients and they are frequently deficient in many soils. Under natural conditions, macro-nutrient deficiencies generally precede micro-nutrient deficiencies. Secondary nutrients (Ca, Mg and S) are those usually required in amounts approximately intermediate between macro and micro-nutrients. Deficiencies of secondary nutrients are relatively infrequent.

Metals can be classified as essential, non-essential and borderline for the biota growth or organism (Santra, 2005).

Table2.3: Essential, non-essential and borderline metals

Essential (for biota growth)	Borderline	Non-essential
Calcium	Zinc	Cadmium
Magnesium	Lead	Copper
Manganese	Iron	Mercury
Potassium	Chromium	Silver
Strontium	Nickel	
Sodium	Arsenic/vanadium	

Source: Santra (2005)

Trace metals of nutritional significance to man are shown in Table 2.4 (Pike and Brown 1967).

Table 2.4: Trace metal of nutritional significance to man

Element	Approximate Amount in a (70kg) man, mg	Some uses
Chromium	<6	Probably an essential cofactor to insulin (glucose metabolism)
Cobalt	Up to 3	Cofactor for vitamin B12
Copper	100	Cofactor for respiratory enzyme and in all body tissues
Iodine	30	Needed to make the hormone thyroxine, if deficient, goitre.
Manganese	20	In several enzymes, peptidases, decarboxy lases, kinases.
Molybdenum	Up to 5	Enzymes for metabolizing nucleic acids, enzymes for oxidizing aldehydes
Zinc	1,600	Many dehydrogenating enzymes, carbonic anhydrase

Source: Pike and Brown (1967)

In addition to these, there are those whose picture is incomplete but are important to man. They are aluminum, arsenic, barium, boron, selenium, strontium and vanadium.

Out of about 40 naturally occurring elements detected in living organisms about 25 of them seem to be highly essential for the higher animals and humans. These include the following metals and non-metals (Dara, 2008). Metals – Na, K, Ca, Mg, V, Cr, Mn, Fe, Co, Cu, Mo, Zn and Sn,Si,Se.

Non-metals – H, C, N, O , P, S, F, Cl, Br and I

The bulk metals which are essential to life are Na, K, Mg and Ca.

Some trace metals such as Pb, Cd, and Hg and metalloids like As, Sb and Se are considered to be toxic. However, some of the metals listed as environmental hazards also seem to play some useful role in the development and growth of animals and humans (Dara 2008). The physiological role of some essential trace metals is shown in Table 2.5.

Table 2.5: Physiological role of some essential trace metals in plants and animals.

Element	Physiological function
Zinc	Activator for several mammalian enzymes
Copper	Activator for several enzymes
Chromium	Phosphoglytamase
Cobalt	Methylmalonyl GA mutase in livers, constituent of vitamin B12
Manganese	Activator for pyruvate carboxylase and arginase in liver
Molybdenum	Found in metalloflavin enzymes and in xanthine oxidase in liver.

Source: Dara (2008)

Trace elements find their way into humans either by direct absorption via the air or drinking water or via the food chain. Trace elements in the atmosphere exist in particulate form and may be required in three roles: nutrients, potential toxic pollutants and tracers of transfer mechanism (Beavington, 1977).

2.1.9.15 Trace Elements in the Marine Environment

Unlike many terrestrial organisms, many marine organisms can concentrate pollutants to an alarming degree. The process is called bioaccumulation. For example, the levels of Cu and Cd in shell-fish in New Zealand were respectively 3000 and 2 million times higher in scallops (Pectinovae-Zelandiae) and 14,000 and 30,000 times higher in Oysters

(Ostreasinuata), than in environmental sea-water (Dara,2008). Enrichment coefficients of the order of 10^5 have been documented for trace elements in the marine organisms (Dara,2008). Also their enrichment coefficients increase with increasing basicity of the divalent metal ions in the following order

Cu>Ni>Pb>Co>Zn>Fe>Cd>Mn>Mg>Ca>Sr>Ba>Ra. (Dara,2008)

This order is particularly disturbing from the environmental pollution point of view because the most strongly absorbed ions such as Ni, Pb and Cd are also among the most toxic to living organisms. The situation is all the more difficult because the organisms where bio-accum0ulation was detected were also the lower members of the food chain. Progress through food chain successively increases the concentrations of some elements such as Hg to such an extent that the natural levels in some commercial fish are close to, or even exceed sometimes the lowest levels now set by the Public Health Authorities in many Countries (Dara, 2008).

2.1.9.16 Heavy Metals

A total of 65 out of the 105 elements discovered so far are metals. The rest are non metals or metalloids (semi-metals). Owing to their various properties, metals find extensive use in human civilization and some activities lead to their dispersion into the biosphere. From the point of view of environmental pollution, metals may be broadly classified into the following three categories:

(1) Non-toxic but accessible
(2) Toxic but non-accessible
(3) Toxic and accessible

The third category, potentially toxic and relatively accessible metals have attracted more attention from the points of view of environmental pollution and public health. These toxic metals occur in very small quantities in the earth's crust (less than 1000ppm) and hence are called "trace metals". These are further arbitrarily sub-divided on the basis of their densities: those having densities below 5g/cm^3 are called "light metals" and those with densities above 5g/cm^3 are designated as "heavy metals".

Thus metals like Hg, Pb, Cu, Cd, Zn, Ni etc are generally known as "toxic heavy metals". Surprisingly, even metalloids like As and Sb are also generally considered under this category, thus making it appear as if the term "heavy metals" is a misnomer. Although the toxic heavy metals are present in the earth's crust in trace levels, anthropogenic activities such as industrial processing and use of metals, alloys and metallic compounds disperse them into the environment, thus adding up to their natural background levels. Table 2.6 shows the various heavy metals found in the effluents from some major industries (Dara, 2008).

Table 2.6: Heavy metals found in the effluents from some major industries

Industry	Heavy Metals Present in the Effluents
Chloralkali	Cd, Cr, Cu, Pb, Zn, Hg, Se
Electroplating	Cu, Cr, Zn, Ni
Leather	Cr
Batteries	Pd, Cd Hg
Paint & Dyes	Cd, Cr, Cu, Pb, Hg, Se
Textiles	Cr
Paper and Pulp	Hg
Petroleum refining	Zn, Cd, Cu, Cr, Pb
Fertilizers	As, Cd, Cr, Cu, Pb, Mn, Hg, Zn
Motor Vehicles	Cd, Cr, Pb, Hg, Se, Zn
Pharmaceuticals	As, Hg
Mining and Metallurgy	As, Cd, Cr Cu, Hg, Se, Zn
Explosives	As, Hg, Pb, Cu
Pesticides	As, Hg, Se, Pb

Source: Dara (2008)

Cu, Co, Mn, Mo, Se and Zn are essential to both plants and animals. Minute traces of As, Cr, Ni and Sn have been found to be essential for animals but not for plants. Although some essential physiological roles have been inferred for As, Cd and Pb recently, Hg and Ag have not yet been confirmed to be essential both for plants and animals since they do not seem to serve any useful biological function (Dara, 2008). However, all the heavy metals, when present in excessive quantities have been found to be toxic for animal and vegetable life (Dara, 2008). In fact, the toxicity of all the essential trace elements follow the following general trend: under-supply leads to deficiency, optimum supply helps in healthy growth and over-supply leads to toxicity and even eventual death to the organisms.

The adverse effects of heavy metal toxicity in biological systems may result from the following reasons:

(i) Interaction of the metal with protein leading to denaturation.
(ii) Interaction with DNA leading to mutation.
(iii) Effect on cell membranes.
(iv) Effect on regulatory enzymes.

These adverse effects in mammals may manifest in the following disorders:

(a) Retardation of growth
(b) Decrease in longevity
(c) Detrimental changes in reproductive cycle leading to mortality of the offspring.
(d) Morbidity
(e) Pathological changes
(f) Symptoms of chronic disease
(g) Formation of tumors

The extent of heavy metal toxicity in mammalian systems is influenced by the following factors:

(a) Electrochemical character of the metal.
(b) State of oxidation of the metal.
(c) The solubility, stability and reactivity of the heavy metal or its compound or its complex under the existing conditions.
(d) The rate of transport of the heavy metal compound in blood and its distribution and retention in the body tissues.

(e) The ability of the heavy metal to chelate with the various ligands in the body tissues and the stability of the metal chelates thus formed.

(f) The rate of absorption of the metal in the body as against the rate of clearance.

(g) The efficiency of the enzymatic and homeostatic mechanism which controls the absorption, distribution, retention and excretion of the heavy metal ions or compounds or complexes.

Traces of Cu, Zn, Mn, Cr, Mo and Co have been found to be highly essential for human beings (Dara, 2008).These metals have been detected in different body organs but relatively higher levels of these metals were found in the liver. As stated earlier, higher levels of even the essential metals may lead to toxicity. The toxicity due to the metals and their compounds is mainly determined by:

(i) The delivery of the metal to the cell to attain a critical concentration level at the site of action and

(ii) The cellular biochemical defense mechanisms.

The “target organs” affected by different heavy metal pollutants are given in Table 2.7.

Table 2.7: The target organs affected by heavy metal pollutants

Heavy metal pollutant	Target organ
(As), Hg, Mo, Se	Liver
(As), Cd, Hg, Pb	Blood
(As), Pb, HgAS	Brain
(As), Cd, Hg	Lungs
(As), Pb, Hg, Cd	Kidney
Cd, Se	Bones and teeth

Source:Dara (2008)

Some metal dependent conditions are stated in Table 2.8 (Hay, 1991). Excepting in case of occupational and accidental exposures, we are constantly exposed in nature to low levels of different trace metals and other pollutants.

Table 2.8: Some metal dependent conditions

Essential or beneficial element	Disease arising from deficiency	Disease associated with an excess of the element
Calcium	Bone deformities, tetany	Cataracts, gall stones, atherosclerosis
Cobalt	Anaemia	Coronary failure, polycythaemia
Copper	Anaemia, kinky hair syndrome	S.A.K Wilson's disease
Chromium	Incorrect glucose metabolism	
Iron	Anaemias	Haemochromatosis, siderosis
Lithium	Manic depression	
Magnesium	Convulsions	Anaesthesia
Manganese	Skeletal deformities, gonadal dysfunctions	Ataxia
Potassium		Addison's disease
Selenium	Necrosis to liver, white muscle disease	Blind staggers in cattle
Sodium	Addison's disease, stoker's cramps	
Zinc	Dwarfism, hypogonadism	Metal fume fever
Cadmium		Nephritis
Lead		Anaemia, encephalitis Neuritis
Mercury		Encephalitis, neuritis

Source: Hay (1991)

For evaluating the toxic effects of any pollutant and for comparing the information regarding the toxicity of different chemicals, a measure called LD_{50} is generally used. LD_{50} represents the median lethal dose of a chemical that kills 50% of the population of experimental animals. These values are specific to the species studied, duration of exposure, mode of exposure and generally under certain dietary and experimental conditions.

Further health implications of heavy metals and the affected organs are found in Table 2.9 (Ademoroti, 1996).

Table 2.9: Further health implications of heavy metals and the affected organs

Organ/Area	Heavy Metal/Compound	Broad/Health Effects
Central Nervous System (CNS)	CH_3Hg^+, Hg (II)	Brain damage
	Pb	Reduced neuropsychological functioning
	Tl	Brain tumors
Peripheral Nervous System (PNS)	CH_3Hg^+, Hg	Abnormal movement and reflexes
	Pb(II)	Peripheral neurological effects
	As	Peripheral neuropathy
	Tl	Polyneuritis
Renal System	Cd	Tubular and glomerula damage, proteinuria
	Hg(II)	Tubular nephrosis (Inflanmation of the kidneys)
Liver	As	Tubular dysfunction
	As	Cirrhosis (i.e. chronic and often fatal disease of the liver)
Blood System	Pb(II)	Inhibits biosynthesis of haem
	Cd (II)	Slight Anaemia
	As	Anaemia, Oral or natal Mucosa
	Hg(II)	Stomatitis
	As	Ukers
Hair	Tl	Alopecia (loss of hair)
Respiratory tract	Cd	Seemphysema
	As	Emphysema and Fibrosis
	Hg	Bronchial effects
	Se	Respiratory inflammation
Skeleton	Cd	Osteomalacia (bona malformation)
	Se	Tooth caries
Cardiovascular System	Cd	Heart diseases often fatal
	As	Heart failure causing death
Reproductive System	CH_3Hg^+	Hg, As Spontaneous abortion
Teratogenesis	CH_3Hg^+	Brain or body deformation
	Tl	Deformed babies
Cancer	Cd	Prostrate gland, lung
	As	Skin,lung
Chromosomal aberrations	Cd As	Disorders in gene carrying chords or nerves

Source: Ademoroti (1996)

Among the metals studied Cr, Ni, Cd, and Be have been found to be potentially carcinogenic (i.e causing cancer). Be, Cr, radionuclides such as ^{90}Sr and ^{239}Pu have been found to be potentially mutagenic (i.e causing chromosomal aberrations and thus altering genetic characteristics of susceptible cells). Further Cd, Cu, Pb, Hg, Mo, Ni and Se in excessive amounts have been found to be potentially teratogenic i.e, embryotoxic, inducing anatomical birth defects.(Dara, 2008) on the basis of studies on test animals. Some arsenic compounds have been found to be potentially carcinogenic, mutagenic as well as teratogenic (Dara, 2008).

2.1.9.17 Bio-transformation of Metals in Living Systems

In marine and fresh waters, metals undergo biological changes (transformations) from one species to another through the activities of aquatic organisms. This is referred to as bio-transformation. The enzyme responsible for this in them is called S-Adonesyl Methionine (SAM).The aquatic organisms collect nearly all elements to levels higher than those in surrounding water. Heavy metals are transformed most of all, largely through chelation (multiple coordinate covalent bonding) by the organic material of living systems.

Table 2.10 shows the dramatic concentrating effect of living organisms on zinc, a typical heavy metal in sea water (Ademoroti, 1996). The last column shows that zinc concentrations are multiplied up to 150,000 times by these unique transformations in living systems.

Table 2.10: Concentration of zinc by aquatic organisms.

Site	Zinc concentration	Magnification factor (zinc concentration) relative to sea water
Sea water	0.01	1.00
Mime plants	150.0	1,500
Marine animals	6 to 1500	600 to 150,000

Source: Ademoroti (1996)

Microorganisms in natural waters have their own chemical influence on mercury. This was observed in 1986 by a chemist (Ademoroti,1996). The organisms have strong inclination to methylate i.e. attach methyl groups to atoms of mercury. By this methylation, dimethyl mercury (CH_3-Hg-CH_3) and methyl mercury (CH_3-Hg^+) are formed. This means that Hg (II) has been biologically transformed to dimethyl mercury and methyl mercury by the process of methylation. Some of the chemical steps of methylation are shown in Figure 2 .1

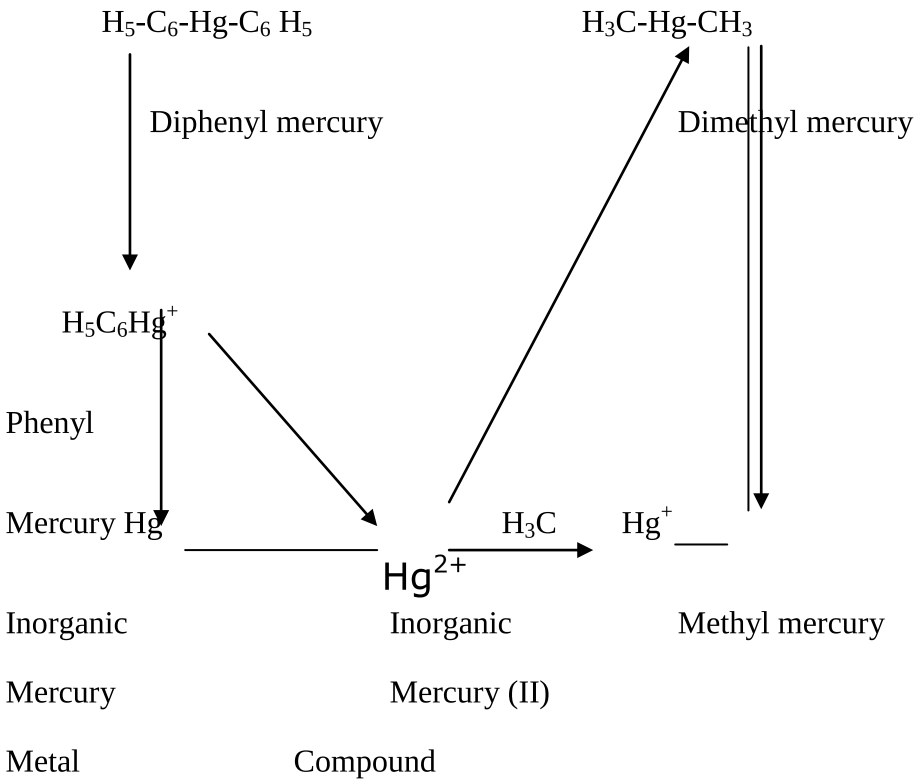

Figure 2.1 Methylation by Mercury

2.1.9.18 Bio-Accumulation of Metals in Living Systems

The process whereby organisms store up metals acquired from their surrounding food medium into their tissues by chelation process is bio-accumulation. The accumulation of a metal in an organism is the product of an equilibrium between the concentration of the metal in the organism’s environment and its rates of ingestion and excretion.

When organic forms of mercury are formed, they escape from water sediments onto the surface layers of the water. Aquatic organisms absorb them and the organisms are eventually eaten up by fish e.g. predator or tuna fish. The organic mercury contents pass into the gills and intestines and are stored up there for a long period of time. The fish is caught and eaten up by humans who get poisoned through it (Ademoroti,1996).

It was found in Japan that the run-of waste waters from a mine containing lead, cadmium and zinc were drained into a river called Jinzu in 1946 .The river was used as a source for drinking, rice irrigation and fishing. The toxic heavy metals thus discharged into the river accumulated in the agricultural and aquatic biomass and passed up the food chain to human consumers. In 1960, chemical analysis carried out on the body tissues of a patient who died of metal poison in the area revealed that 530mg Pb, 3,800mg Cd and 7000mg Zn were contained per kilogram of the bones of the patient (Ademoroti, 1996).

The following Table 2.11 shows levels of mercury in some foodstuffs (Ademoroti,1996).

Table 2.11: Levels of mercury in some foodstuffs.

Foodstuffs	Range in levels(ug/g)	Foodstuffs	Range in levels(ug/g)
Canned meat	0.001-0.01	Pike fish	0.19-0.59
Ham	0.001-0.05	Shell fish	0.01-0.23
Eggs(total Hg)	0.02-0.06	Baby foods	0.01-0.02
Eggs(methyl Hg)	0.02-0.03	Grain flours	0.004-0.018
Canned salmon and tuna fish	0.04-0.44	Fresh vegetables	0.001-0.05
Canned Sea Food	0.009-0.73	Cereals	0.004-0.008

Source: Ademoroti (1996)

2.1.9.19 Factors Affecting Bio-accumulation of Heavy Metals

Within the last 4 to 5 decades, evidence has been obtained to support the conclusion that heavy metal content of certain foods, particularly fish, is often directly related to an induced waste discharged into streams, lakes and oceans (Ademoroti,1996). These metals enter the living organisms either as inorganic salts or as organic metallic derivatives and can neither be degraded nor metabolized. Factors which influence bio-accumulation include:

(i) Persistence

(ii) Surface area or total size of organism and

(iii) Some biological factors like rates of food intake and metabolic rates (Ademoroti, 1996).

2.1.9.20 Lead

Lead is one of the oldest metals known to man. Since mediaval times, it has found wide range applications and is therefore prevalent in natural environment. However, lead is a dangerous and insidiously deceptive poison. Children are the most common victims of lead poisoning.

2.1.9.21Sources of Lead

The most important natural source of lead in the environment is the weathering of rocks. This is eroded by fast moving rivers. Wind-blown dust, forest fires, volcanic eruptions and sea salt sprays are some other natural phenomena leading to the distribution and concentration of lead in the environment.

2.1.9.22Uses

Lead is used in acid storage batteries, ammunition, solder and casting materials. Lead coated steel sheets have sound attenuation properties. Lead porcelain enamel is used as protection against radiation in nuclear powered reactors. Other sources of lead are paint, pottery (glazed with lead monoxide), gasoline additive or anti knocking agent known as tetraethyl lead, etc.

2.1.9.23 Lead Poisoning

Lead Poisoning also called plunbism or saturnism has proved to be more dangerous to the children than the adults due to their higher risk of exposure during play. Plumbism manifests itself in several forms:(1) Enzyme inhibition. It disturbs the biosynthesis of Heme (precursor to hemoglobin synthesis). Heme is also an essential constituent of other respiratory pigments, the cytochromes which play key roles in energy catabolism. (2) Kidney impairment (3) Neurological disorders (CNS), (4) Behavioural problems (with symptoms like excitement, restlessness, insomnia, nightmares, impairment of memory and loss of concentration.

2.1.9.24 Abatement Procedures

Transportation of lead ore in open rail road is being discontinued. The most commonly used technique to reduce air borne lead emissions is the electrostatic precipitator. Lead based commodities are being replaced by more environmental friendly materials (Sodhi, 2005). The reagent $CaNa_2EDTA$ has been found to chelate lead in the extra cellular fluid and it is excreted in urine (Ademoroti, 1996).

2.1.9.25 Arsenic

This is a semi-metal which belongs to group 15 of the Periodic Table. It exists in two oxidation states: III and V. Arsenic derivatives particularly in the lower valent state are deadly poisons. Just 0.1g of the element is enough to kill a human being. Despite its ban in commercial products, arsenic continues to command a cautious respect.

2.1.9.26 Sources

The sources of arsenic in the environment are weathering of rock, volcanism and pesticides (arsenicals like calcium arsenate, $Ca_3\ (A_sO_4)_2$, Sodium arsinite and lead arsenate. The leachate from gold mine of yesteryears is still a source of arsenic pollution.

Arsenic compounds have been used in textile dyeing, calico printing and as paint pigments. During the past few decades, environmental restrictions and regulations have limlted the amount of arsenicals produced and used (Sodhi, 2005).

2.1.9.27 Biomethylation of Arsenic

In aqueous environment, arsenic gets biomethylated to methyl arsenic compounds. This transformation is done by microorganisms both under aerobic and anaerobic conditions.

Methylated forms of arsenic are incorporated into benthic or benthonic organisms, algae, zooplankton and phytoplankton. These are then concentrated into aquatic food chain and have been detected in egg shells, seashells and fish.

2.1.9.28 Arsenic Poisoning

Arsenic Compounds are protoplasmic poisons that attack enzymes. Chronic exposure to arsenic leads to (1) Cardiac damage causing general weakness and respiratory distress.

2. Nervous disorders causing decreased motor coordination and neuritis.

3. Gastro intestinal problems causing abdominal pain, vomiting and diarrhoea.

4. Skin infections causing dermatitis and hair loss.

Arsenic is also known to cause lung cancer in humans.

2.1.9.29 Antidote to Arsenic Poisoning

The maximum allowable concentration of arsenic in drinking water has been set at 0.05ppm. Arsenic (III) compounds (Arsinites) are more toxic than arsenic (V) analogues, arsenates. This is due to the ability of arsenic (III) ion to be retained in the body longer since it becomes bound to the sulphhydryl groups of enzymes (Sodhi, 2005).

2.1.9.30Treatment of Arsenic Toxicity

One of the body's defence against arsenic is alkylation producing the less toxic alkyl arsenic (V) compounds: CH_3A_SO $(OH)_2$ and $(CH_3)_2$ AsO(OH) which are then excreted from the body. The British Anti lewisite reagent (BAL) which is 2, 3-dimercaptopropanol $H_{5cH2\text{-}C(SH)\text{-}CH2OH}$ could be used to remove arsenic from intracellular space and is excreted in urine and faeces.

Another method used is the antagonistic property arsenic and selenium have on each other. When one is present in a body, the other is injected into the body to counteract its toxicity (Ademoroti, 1996).

2.1.9.31 Abatement Procedures Against Arsenic Poisoning:

Arsenic compounds are no longer used as pesticides. Electrostatic precipitators are used to control the release of arsenic particulates to the atmosphere while electrodialysis prevents its release to aquatic systems. Waste stream of arsenic compounds are not discharged untreated to the environment.

2.1.9.32Cadmium

This is placed between zinc and mercury in group 12 triad of the Periodic Table. It's however more close to zinc than mercury in its physical and chemical properties.

2.1.9.33 Sources of Cadmium

Ores of zinc and cadmium occur in nature. During extraction of zinc, cadmium is released into the environment as a by-product. As a result soil and water in the vicinity of zinc smelters have abnormally high concentrations of cadmium. Cadmium is extremely resistant to corrosion hence it was as an electroplating agent. Plastic and ceramic items are coloured yellow by cadmium sulphide and cadmium selenide pigments. Cadmium selenide is also used in photoelectric cells as well as in TV screens, fluorescent lamps and cathode ray tubes.

Rechargeable nickel – cadmium batteries commonly called Nicad Batteries are used in calculators, satellites and missiles. Cadmium alloys find applications in solders, fIre detector apparatus, valve seals & high pressure gas containers. Soil receives cadmium from phosphate fertilizers and polluted irrigation water.

2.1.9.34 Cadmium Poisoning

Cadmium poisoning notably occurred in Japan in the 1950s (Sodhi,2005). About 200 people living in Jintsu River Valley suffered from a disease which came to be called itai itai (which means it hurts, lt hurts). The river received cadmium containing effluent from a zinc refinery located along its coasts. Downstream the river water was used for, irrigating rice fields. Once in the human body, cadmium replaced calcium in the bones (the two metals have similar size and charge). Symptoms similar to those of rheumatism set in. Subsequently the bones softened and became susceptible to fractures. During itai itai episode cadmium also damaged the kidney of victims causing renal dysfunction.

Consumption of cadmium containing sea foods causes enzyme poisoning. Cadmium displaces zinc in many vital enzymatic reactions resulting in disruption or cessation of activity. Epidemiological studies show that workers engaged in cadmium related jobs are more likely to suffer from prostate and nasopharynx cancers than their counterparts engaged in other activities (Sodhi, 2005).

2.1.9.35 Antidotes to Cadmium Poisoning

The limit of cadmium in drinking water has been fixed at 0.01ppm (Sodhi, 2005). The sea food containing more than 0.5ppm Cd is deemed unfit for human consumption. Beyond these limits, symptoms of cadmium poisoning set in.

The most effective antidote to cadmium poisoning is ethylenediamine tetra acetic acid (EDTA). This reagent chelates with cadmium forming a stable and soluble complex that is rapidly eliminated from the body.

2.1.9.36 Abatement Procedures

Modern zinc plants are endowed with electrostatic precipitators. Phosphate based fertilizers are treated to remove cadmium before being sprayed on agricultural lands. Cadmium is no longer used for electroplating other metals. Unwanted cadmium containing utilities are now not directly incinerated. These are subjected to waste separation technologies to isolate the cadmium content. The cadmium free waste is incinerated while the separated cadmium is immobilized preferably by vitrification (Sodhi, 2005).

2.1.9.37 Mercury

Mercury has featured in the most serious outbreaks of heavy metal poisoning among the general population especially in Japan, Iraq, Central America, Pakistan and Ghana.

The toxicity of mercury occurs at three levels depending on the chemical form of the metal. The order of toxicity is alkyl mercury (especially CH_3Hg^+) > mercury metal vapour > Hg (II) salts, phenyl and methoxy mercury salts. The last two organic species have weak C-Hg bonds. They are easily broken and the species soon transform to Hg^{2+}, in the body.

The toxic effects of mercury on physiological and neurological systems of the body have been well characterized (Ademoroti,1996). The most destructive is the effect of CH_3Hg^+ on the CNS.

2.1.9.38 Treatment of Mercury Toxicity

The treatment of mercury poison involves elimination of mercury from the body by two methods. One method is through the formation of mercury complex with a reagent (i.e. a ligand) which will allow the metal to be excreted. The other method involves trapping the metal in the gastro-intestinal tract.

A number of reagents have been used as ligands to complex mercury. Two very promising ones are N-acetylated, I-penicillamine, CH_3CO (NH)-CH ($C(CH_3)_2$-SH)-COOH and dimer captosuccinic acid, HOOC-CH(SH)-CH(SH)COOH. Other ligands employed for mercury elimination include penicillamine, glutathione and EDTA. As regards trapping of the metal, a thiol has been successfully used (Ademoroti,1996). Most of the reagent ligand make use of the strong interaction between their S content and mercury (Ademoroti, 1996).

2.1.9.39 Selenium

Among the toxic heavy metals, selenium is the only one that is both essential and toxic. Its deficient concentration in food is 0.04ug/g while the toxic concentration is 4ug/g. A lethal dose of the metal in food is 0.1-0.5 ug/g. Some of the diseases caused by selenium to mammals include accumulation of fluid throughout the body and destructive damage to the liver. In addition, animal can become ill and die due to too high selenium intake. This follows food chain. Grass, plants, fruits containing considerable quantity of selenium are eaten by animals, in turn, animals are killed for food by human beings.

The early symptoms of acute toxic effects of selenium are sore throat, fever, vomiting, irritation to eyes and nose, headache, gastrointestinal irritation, sleepiness or drowsiness, drop in blood pressure, dermatitis and garlic odour of the breath (Lucky and Venugopal, 1978, Berman, 1980). At a later stage, vascular disruption, pulmonary oedema, haemorrhage, respiratory failure and breathing with difficulty occur.

One of the ways in which selenium is toxic to human beings is in the replacement of sulphur in the body. As a result, sulphur metabolism is disrupted e.g. uptake of sulphate ions and the production of methionine (Shamberger, 1981).

2.1.9.40 Moderating Property of Selenium

Selenium has a moderating influence on the toxicity of other heavy metals e.g. arsenic. There is strong interaction between selenium and the metals. The toxic metals are strongly bound to selenium and they are therefore unable to form bonds with sulphur or nitrogen in the human body system.

Thus, the toxicity of arsenic, mercury, thallium, cadmium and tellurium are modified or counteracted by selenium (Nordberg 1976; Luckey and Venugopal, 1978).

2.1.9.41 Chromium

Chromium in (+VI) oxidation state is more toxic than in (+III) oxidation state and it can cause dermatitis, lung cancer, chest problems and ulceration generally in alkaline water. Leather tanning industries, glass and ceramic industries and waste from electroplating and paint industries are the source of chromium to water streams (Chawla, 2003).

2.1.9.42 Iron

After Aluminium iron is the most abundant metal in earth's crust (6.2percent by mass). It is found in many ores. Some of the important ones are hematite Fe_2O_3**;** siderite $FeCO_3$ and magnetite Fe_3O_4. Pure iron is a gray metal and is not particularly hard. It is an essential element in living systems. In the presence of oxygen, Fe^{2+} ions in solution are readily oxidized to Fe^{3+} ions. Iron (III) oxide is reddish brown and iron (III) chloride is brownish black (Chang, 2005).

2.1.9.43 Vanadium

Vanadium is the nineteenth most abundant element by weight in the earth's crust and is the fifth most abundant transition element. Over 75% of V_2O_5 is converted to an iron-vanadium alloy, called ferrovanadium, which is used to make steel alloys for springs and high speed cutting tools. V_2O_5 is an important catalyst in the conversion of SO_2 to SO_3 in the contact process of making H_2SO_4 (Sharma, 2011).

2.1.9.44 Manganese

Manganese is the twelfth most abundant element by weight in the earth's crust. Trace amounts of manganese are essential for plant and animal growth. For this reason small amounts of $MnSO_4$ are often added to fertilizers. MnO_2 is used in dry battery. Large amounts of MnO_2 are also used in the brick industry to colour brick red or brown. It is used to make red or purple glass. $KMnO_4$ is used for treating drinking water. It oxidizes and thus kills bacteria but does not leave an unpleasant taste as does chloride (Sharma, 2011).

2.1.9.45 Zinc

Zinc has been known to ancients as an alloy of Zn and Cu (very similar to brass) without knowing its actual composition. Zinc does not occur native. The chief ores of zinc are zinc blende (black jack) or ZnS, calamine (zinc spar) or $ZnCO_{3,}$ zincite or ZnO, zinc spinel or $ZnO\text{-}Al_2O_3$ and willemite or $ZnSiO_{4.}$ The principal source of zjnc is zinc blende ZnS. Zinc is probably best known in the laboratory for its role in generating hydrogen from dilute hydrochloric acid. The principal oxidation state is +2 (Bhatia, 2001;Murray, 1982).

2.1.9.46 Nickel

Nickel is used as an alloying element in ferrous as well as non ferrous alloys and hence enhances their properties considerably. Nickel is a silver coloured metal which is ferromagnetic. Above its curie point (415^0C), it becomes paramagnetic. It has face centered cubic crystal lattice. Its density is 8.9g/cc and its melting point is 1455^0C.

Pure nickel has the following important properties: (a) It has good mechanical as well as working properties. (b)It can be readily shaped into the desired form. It is resistant to corrosion and oxidation even at high temperatures. (d) It does not tarnish at ordinary temperatures and in corrosive atmospheres. (e) It can be easily alloyed to form important alloys with most metals and has a tendency to form solid solution.

For many corrosion resistant applications, nickel has also been used in the cast form, known as cast nickel. The latter is high nickel alloy containing 1.25% silicon, 0.5% manganese, 0.5% iron and small amounts of magnesium (Sharma, 2011).

2.2 Crude Oil

Another name for crude oil is Petroleum (Latin Petra, “rock” and oleum, “oil”). Crude oil is a liquid petroleum and petroleum is an extremely complex mixture of hydrocarbon compounds with minor amounts of nitrogen, oxygen and sulphur as impurities (Levorsen, 2003). In addition to hydrocarbons, crude oils contain other components both organic and inorganic which differ from one crude oil to another. Elements such as vanadium, sodium, nickel, iron have been detected in crude oil. The number and form of the individual components in the crude oil give the oil different physico chemical properties. Crude oil is immiscible with water and floats on it but is soluble in naptha, carbon disulphide, ether and benzene.

Petroleum gas commonly called natural gas consists of the lighter paraffin hydrocarbons of which the most abundant is methane gas (CH_4). The semi solid and solid forms of petroleum consist of the heavy hydrocarbons and bitumens. They are called asphalt, tar, pitch, albertite, gilsonite or grahamite or by anyone of many other forms depending on their individual characteristics and local usage. The general term bitumen has long been used interchangeably with petroleum for both the liquid and the solid forms. Hydrocarbon is a term often used interchangeably with petroleum for both the liquid and the solid forms. This is not strictly correct since hydrocarbons consist of only hydrogen and carbon whereas petroleum contains many impurities.

2.2.1 Formation

The origin of petroleum from organic matter in sedimentary rock is set forth by Tissor and Welte (Katz and Lee 1990). As early as 2500 X 10^6 years ago, remains of bacteria and primitive algae were deposited in pre-cambrian rocks. Photosynthesis of plants from CO_2 and H_2O by sunlight forming glucose and oxygen started some 2 billion years ago and reached a high yield at the time of coal deposits such as those in the carboniferous age.

When the organic matter was buried but still shallow, a process of digenesis took place often including consolidation of sediments. Temperature increased with depth of burial, forming Kerogen with generation of methane gas. The word catagenesis is used for the process by which oil and gas were generated at high pressure due to great depths. At great depths, metagenesis of organic matter (Kerogen) to anthracite coal and metamorphism of mineral phases also occurred.

The production of a large deposit of any fossil fuel requires a large initial accumulation of organic matter which is rich in carbon and hydrogen. Also the organic debris has to be buried quickly to protect it from the air, so that decay by biological means or reaction with oxygen will not destroy it.

When micro organisms in and around the oceans die their remains can settle to the sea floor. There are also under water areas near shore, such as on many continental shelves where sediments derived from continental erosion accumulate rapidly. In such a setting the starting requirements for the formation of oil are satisfied. There is an abundance of organic matter rapidly buried by sediment. Oil and natural gas are believed to form from such accumulated marine micro organisms. Continental oil fields reflect the presence of marine sedimentary rocks below the surface.

As burial continues, the organic matter begins to change. Pressures increase with the weight of the overlying sediment or rock. Temperature increase with depth in the earth and slowly over long periods of time chemical reactions take place. These reactions break down the large complex organic molecules into simpler smaller hydrocarbon molecules. The nature of the hydrocarbons changes with time and continued heat and pressure. In the early stages of petroleum formation, the deposit may consist mainly of larger hydrocarbon molecules (heavy hydrocarbons) which have the thick, nearly solid consistency of asphalt. As the petroleum matures and as the breakdown of the large molecules continues successively higher hydrocarbons are produced. Thick liquids give way to thinner ones from which are derived lubricating oils, heating oils and gasoline. In the final stages most or all of the petroleum is further broken down into very simple light gaseous molecules, natural gas.

Most of the maturation process occurs in the temperature range of 50-1000^{o}C (approximately 120^{o} to 210^{o}F). Above these temperatures, the remaining hydrocarbon is almost wholly methane. With further temperature increase methane can be broken down and destroyed in turn. A given oil field yields crude oil containing a distinctive mix of hydrocarbon compounds depending on the history of the material.

2.2.2 Distribution and General Composition of Crude Petroleum

If the residue of petroleum after removal of volatile compounds contains a large amount of alkanes or wax, the petroleum is classified as paraffinic or paraffinic base oil. If naphthenes predominate, the petroleum is classified as asphaltic or asphalt base oil. The crudes from the wells in Pennsylvania, Iran, Iraq and Rumania are paraffinic, those from Baku and Venezuela are asphaltic and those from Oklahoma, Texas and Mexico are intermediate in composition and may be classified as paraffinic and aliphatic (Finar, 1973). Crude oil from the delta basin of Nigeria are of two types, light and comparatively heavy. Both are paraffinic (Tuttle *et al*., 1999; Nigerian Finder, 2018). Typical hydrocarbon compounds found in crude oil and maximum concentration of certain elements found in crude oil are shown in Tables 2.12 and 2.13 (Pipkin, 1994 and IOPOPAC, 1974).

Table 2.12: Typical hydrocarbon compounds found in crude oil

MOLECULAR TYPE		Hydrocarbon compound	Percentage of weight of medium grade crude oil
Name	General formula		
Paraffins	C_nH_{2n+2}	methane,cH_4 ethane, C_2H_6 Propane,C_3H_8 Butane, C_4H_{10*} Pentane,C_5H_{12**} Benzene, C_6H_6	25
	$C_nH_{2n-6***}$		17
Aromatics	C_nH_{2n}		50
Naphthenes	(solid hydrocarbons)		8
Asphaltenes			100

Source: Pipkin (1994)

Table 2.13: Maximum concentration of certain elements found in crude oils

Element	Maximum level found, ppm
Aluminum	11
Antimony	11
Barium	3
Boron	<1
Cadmium	<1
Calcium	37
Chromium	3
Lead	2
Magnesium	8
Manganese	6
Phosphorus	98
Silicon	7
Tin	13
Tungsten	No data
Zinc	160+

Source: IOPOPAC (1974)

The soil quality standards of Nigeria (Contaminant limits for heavy metals) are found in Table 2.14.

Table 2.14: Soil quality standards (contaminants limits for heavy metals)

Parameter	Upper Limit (mg/kg)
Arsenic	1
Cadmium	1
Hexavalent Chromium	100
Lead	200
Manganese	1800
Mercury	2
Nickel	100
Selenium	20
Copper	200
Zinc	150
Molybdenum	5

Source: The Environmental Management Regulations (2007)

2.2.3 Oil Spillage

Oil spill is defined as discrete event in which oil is discharged through neglect, by accident or with intent over a relatively short time (Etkin, 2000a). It does not include an event in which oil leaks slowly over a long period of time, nor does it include operational spillages allowed by international or national regulations (such as MARPOL discharge from tankers), or that occur over a relatively long period of time (such as 25ppm oil discharges in refinery effluent) even if those discharges violate pollution regulation, (Etkin, 2000a). Oil spillage is divided into three classes, namely minor, medium and major oil spillages.

2.2.3.1 Minor: Any discharge of less than 25 barrels in inland waters or less than 250barrels on land, offshore or in coastal waters, that does not pose any threat to public health or welfare.

2.2.3.2 Medium: Any discharge between 25 and 250 barrels into inland waters or 250 to 2,500 barrels on land, offshore or in coastal water.

2.2.3.3 Major: Any discharge over 2,500 barrels on land, offshore or in coastal waters (Jaiyesimi and Thomas 1994)

2.2.3.4 Other Causes :

- flow-line / pipeline leaks
- over pressure failures /overflow of process equipment component
- sabotage to wellhead and flow lines
- Hose failures on the single bouy moorings (SBM) tanker loading systems
- Failure along pump discharge manifolds (vibrating effects)

There are also discharges of oil into surrounding waters by tankers during river and ocean transportation around the Delta Region, discharges from oil refineries and petrochemical plants as well as natural causes (Jaiyesimi and Thomas 1994).

2.2.3.5 Factors Responsible for Spillage in Nigeria

The major causes of oil spillage in Nigeria are failures in production equipment, pipeline and petroleum production equipment vandalization as a consequence of scarcity; deregulation and hike in product price, well blow outs during drilling activities and negligence on the part of the production operators who exhibit lukewarm attitude towards oil spillage incidences (Oghenero *et al.*, 2005)

The recent spillage on 29th July 2005 at Otu-Jeremi in Ughelli South Local government Area of Delta State is a typical case in which response by (SPDC) - the operator was slow, thus facilitating the spread of the spill and environmental contaminations of neighboring downstream communities in Burutu Local Government Area and other areas within the state.

Table 2.15 summarizes the major components of such factors responsible for oil spillage in Nigeria.

Table 2.15: Causes of oil spillage

Factor	Component
Production inadequacies as a result of technical/human errors	Operator/maintenance, Technical error
Production equipment failure	Equipment failure, seal failures
Corrosion	Internal, external corrosion/sand abrasion of pipeline, fitting etc.
Sabotage	Vandalization of oil production facilities example, flow lines, delivery lines manifolds, tempering (cutting and removal of gas lift etc)
Negligence	Operators slow response to clean-up activities each time spillage occur thus increasing impacted area and even causing more damages.
Others	Drilling operation(work-over fluid spillage), pigging operation, engineering activities, dredging flow lines replacement, flow station upgrade, tanks rehabilitation, natural causes, example, flooding heavy rainfall ,felling trees, lighting etc

Source:Oghenero et al., (2005)

Operational activities associated with oil production accounts for over 60% of oil spillage but in terms of volume sabotage accounts for more than 80% of oil spilled (Oghenero *et al.*, .2005) This scenario can obviously be due to slow response by the operators to sabotage- related spillage or spillage detection generally. For example, about 10,000 bpd was spilled from Friday to Saturday at the Otu-Jeremi case and more was spilled before the facility was shut down.

2.2.3.6 Oil Spill Trend in Nigeria

The frequency and magnitude of oil spills in Nigeria are shown in Table2.16 (Tolulope, 2004).

TABLE 2.16: Oil spill rate and volume spilled 1986-2000

Year	No of Spill	Quantity Spilled(Barrels)
1986	155	12,905
1987	129	31,886
1988	208	9,172
1989	195	7,628
1990	160	14,940
1991	201	106,827
1992	367	51,131
1993	428	9,752
1994	515	30,282
1995	417	63,677
1996	236	24,806
1997	280	15,004
1998	146	18,921
1999	198	29,337
2000	219	11,542
Total	3854	437810

Source: Tolulope (2004)

The first oil spillage in Nigeria was noticed in Araromi Ondo State in 1908 and one of the early major oil spill incidents in Nigeria was the TEXACO Funiwa No 5 oil well blew out, located in Funiwa fields about 5 miles offshore in the Niger Delta. This resulted in the loss of 200,000 barrels of crude oil in the environment on January 17,1980. Second to none in the Nigerian petroleum history was the Farcados terminal spill in July 1979. About 570,000 barrels were believed to have been spilled within 21 days of the blow out. The Abudu pipeline oil spillage of 2nd November 1982 offers another interesting case study of a different dimension. In this particular instance, it was neither an accident involving a tanker on the high seas nor a blow out. A privately owned loader accidentally ripped a hole in an C 16^{11} underground crude oil pipeline (system 2x, Warri-Kaduna) at km 90.95 in a location between Owa and Abudu spilling about 18,818 barrels of crude oil. In another instance, about 11,542 barrels were estimated to have been lost after slicks of oil were discovered along Egobiri Creek between wells 10 and $13^{''}$ in May 2000.

In the period, 1986 to 2000, Nigerian petroleum industry experienced three thousand eight hundred and fifty four (3,854) oil spill incidents (Tolulope, 2004). These oil spills resulted in the loss of 437,810 barrels of oil into the Nigerian environment. This loss amounts to millions of dollars in the Nigerian export from the petroleum industry.

From Table 2.16, it is obvious that oil spillage incident in Nigeria has been on a continuous increase. It could be observed that the largest number of oil spills 515 was recorded in 1994 resulting in a loss of 30,282 barrels of oil while, 1991 recorded the highest volume of oil spilled into the environment (106,827 barrels). The number of incidents and the corresponding volumes shown in the Table do not actually represent the true situation because the NNPC petroleum Inspectorate guideline on oil spillage reporting have provided companies the opportunity to overlook some incidents on the basis that the volumes involved have no significance.

2.2.3.7 Effects of Oil Spillage

Oil spillages affect land, marine and human lives as well as man made components (Tolulope, 2004).

2.2.3.8 Impact on the Natural Environment

Oil spillage occasioned by activities in the petroleum industry such as production, processing (tank farms, gas flaring), tank loading, storage depots, transportation, pipelining and refinery destroys aquatic animals and plants as well as flora and fauna on land. The land is also rendered infertile and sources of drinking water are polluted. Table 2.17 provides further illustration on the potential impacts of petroleum operations in the environment (Tolulope, 2004).

Table 2.17: Potential impact of oil operations on the environment

OIL OPERATION	POTENTIAL IMPACTS ON THE ENVIRONMENT
Exploration: a. Geographical Investigation. b. Geographical survey	Destruction of vegetation and farmlands/ human settlements
c. Drilling	Noise pollution and vibration, seismic shooting disturbance of fauna and flora habitat
	Accumulation of toxic materials from drilling materials, oil pollution of the sea, beaches or land.
Production processing	Destruction of breeding and spawning grounds for some marine organisms. Alteration of the taste of fishes, pollution of underground water.
a. Platforms and Tank farms b. Gas flaring	Water pollution from long-term cumulative effects of produced water (with high salinity), water and land pollution from sanitary wastes, used lubrication oil, solid waste.
	Air pollution from gas and oil processing and flaring production of heat.
	Kills vegetation around the heat area and suppresses the growth and flowering of some plants, diminish and reduce agricultural production destruction of mangrove swamps and salt marsh.
Tank loading locations and offshore	Water pollution from ballast and tank washing. Deck drainage and spillage during loading operations with all its accompanying of seabed by dredging.
Storage Depots	Land pollution from effluent water and solid waste of chemical cans and rums.
	Air pollution from storage tanks, destruction of farmland for the establishment of the storage depots.
Transportation:	Water pollution from the gaseous fumes during loading. Destruction of seabed by dredging for pipeline installation, sedimentation along pipeline routes.
Refinery	Water pollution from consequences of leaks from fracturing or breaking of pipe, caused by metal fissure, trawlers and dredging of seafloor or sabotages.
	Air pollution by transport tankers. Destruction of environmentally sensitive area e.g lowland where estuaries, wet land dune exist. Erosion and flooding.
Health	Water pollution from effluents which contain a wide range of organic and inorganic pollutants such as phenols, hydrogen sulphide, ammonia, oil and greases, phosphates, cyanide and toxic metals. All above have serious adverse effects on health.

Source: Tolulope (2004).

Some disaster episodes in Nigeria are stated in Table 2.18 (IPAN, 2006).

Table 2.18: Examples of some disaster episodes caused by industrial pollution and accidents in Nigeria

Area and Year	Nature of Disaster
Western Nigeria, 1960s	Many reported cases at University College Hospital, Ibadan of human poisoning by Gamalin-20 from the cocoa producing areas of the western Nigeria.
Idimangoro Agege, Lagos, Nigeria 1979	Combined industrial effluent from Ikeja Industrial estate through WEMABOD treatment plant which had broken down , spilled into Idimangoro area due to the blockage of one of the manhole on the effluent channel. Drinking well waters in the area were grossly polluted.The foundation of one of the houses affected by the spillage caved in. The occupants were evacuated.
Kaduna, Nigeria,1987	Petroleum product spillage from the Kaduna refinery into the Romi and Rido Rivers had occurred unabated. Well waters in Rido village and Romi Rivers were grossly polluted. Compensation of more than 3 milllion naira had been paid to the villagers affected by the pollution problems caused.
Koko Bendel State Nigeria, 1988.	3888 tons of assorted toxic wastes from Italy were found to have been illegally dumped at the fishing port at Koko. The Government ensured that the wastes were returned to Italy and promulgated Decree 42 of 1988 to forestall future reoccurrence. The environmental implications of this dumping episode are yet to be fully realized.

Source: IPAN (2006)

Pollution of rivers, lakes and other water bodies may lead to contaminated fish and other aquatic animals and eventually to fishless rivers and lakes like the fishless Scandinavian lakes (Imevbore, 1981}.

Groundwater may also be polluted making it unusable for a long time. Land pollution may result into pollution of vegetation growing on such land. Uncontrolled land pollution may ultimately lead to disastrous experience such as the Canadian treeless forest (Imevbore, 1981).

Information is fragmentary on the effects of environmental oil pollution on Nigerian plants (Imevbore, 1981). In the Funiwa blow- out of January 1980 in the Niger Delta, probably the largest single oil spill in the country, mangrove trees suffered heavy or complete defoliation and twigs were oiled. Along the beach, 0.5-2m^2 zones of defoliated bushes with greasy twigs were observed. On the whole 836 acres of mangrove trees were killed as a result of the blow out (Imevbore, 1981and Texaco Funiwa,1981)

This kind of destruction of the flora has grave implications. Apart from the economic loss of mangrove trees used for making poles and firewood, the possibility of a food chain transfer of dangerous components of oil e.g heavy metals in the ecosystem has never been addressed (Blummer,1970). The degree of biological damage depends on the kind of oil spilled, frequency of oiling, topography, hydrography and prevailing weather at the time of the spillage or discharge. If an effluent is discharged into small bays where hydrograph does not favour rapid dispersal, the effects of pollution may be severe. A table of toxicity data estimating typical toxicity ranges (ppm) for various organisms is available (Moore *et al.,* 1973) . Plants for instance have a toxicity range of 50-500ppm for fuel / kerosene and 10^4 - 10^5 ppm for fresh crude oil. Experimental evidences show that with plants toxicity increases along the series of alkanes (paraffins)-cyclo alkanes (naphthenes), alkenes (olefines) -aromatics.

As observed Dallyn, {1953), chlorophyll destruction appears to be the major, symptom of oil injury to green plants. Where oil pollution is light, leaves become yellow and drop soon after, but under heavy contamination complete shedding of leaves results.

Pollutants have a wide variety of adverse effects on phytoplankton which carry out primary production in fresh water.

These include:

- (a) Inhibition of photosynthesis
- (b) Prevention of biosynthetic production of nucleic acid
- (c) Retardation of the absorption of nutrient and
- (d) Reduction of the DNA and RNA concentration (Odum,1971, Divarvin *et al.*, 1978)

Unlike the sea which has the enormous capacity to absorb the various attempts by man to degrade it, the land, rivers, creeks, estuaries and swamps are not so lucky and well equipped to contain pollution emanating from human activities.

This is because the slow moving and stagnant nature of the creeks, estuaries and swamps result in limited reactivation and break down of oil films which enhance self purification capacity.

2.2.3.9 Man's Experience

Following several oil spillages, man experienced massive destruction of his farmlands, sources of drinking water, mangrove forest, fishing grounds and decimation of aquatic animals like crabs, molluscs, fishes, periwinkles and birds. The carcinogenic and the tetratogenic nature of oil to humans has been reported (Fabiyi, 2001).

2.2.3.10Management of Oil Spillage

Oil spillage management is necessary in Nigeria due to the fact that it occurs most in fragile rivers, stream, creeks, estuaries, swamps and land from which river-rine communities of Niger Delta, Bayelsa, River and Cross River depend solely for food (Oghenero *et al.*, 2005)

2.2.3.11 Oil on Water

Three general steps are taken to clean up floating oil (Grolier, 2000). First the oil slick is usually confined by booms, which act as floating fences and is then picked up by skimmers. Second, sorbent materials are added to the boomed, spilled oil causing the oil to adhere to the sorbents which can be controlled and removed more easily than the oil alone. Third, dispersants (similar to liquid detergents) may be used.

While their use is not as satisfactory as physical removal, since the oil is spread on and into the water rather than being removed dispersants may be very advantageous in preventing a floating spill from reaching the shore and causing greater damage there (Grolier, 2000).

Oil sorbent products are from three major sources, mineral, vegetable and synthetic. Some of the mineral products that have been tried as oil sorbents include perlite, talc and vermiculite. Commonly used vegetable products include straw, saw dust, bark, peat and corncob grindings. Synthetic products include polyurethane, polystyrene, polyester and urea formaldehyde, usually in the form of foam, chips or flexible strips (Grolier, 2000).

Detergents disperse the oil but can be pollutants themselves. They also spread the oil over a wider area possibly increasing the threat to marine life.

One method uses bales of straw thrown into the oil slick. These absorb the oil and are rounded up using a line of booms. The booms are attached at one end to a barge and the other end to a motor launch. The oil-sodden straw is transferred to the barge.

Some of the other methods which have been tried include the use of huge vacuum cleaners to suck up the oil into floating tankers. The oil can then be recycled. Floating barriers can be used to keep oil out of particularly sensitive areas of the coastline, such as a wild life sanctuary. BP have discovered a chemical that converts oil to a rubbery solid. If this can be developed and it is not a pollutant itself oil slicks can be made into an easily removed rubber sheet. Relatively non toxic chemical dispersants have also been developed. They may be sprayed onto floating oil from boats, helicopters and air planes (Grolier, 2000).

2.2.3.12 Oil Spillage on Land.

In the event of an oil spill on land, immediate action should be taken to limit and stop the escape of oil. Bunds of earth or sand around the spill to close access to road, drains and sewers should be put up as soon as possible, while inlets to drainage systems can be covered by using materials such as tarpaulins, blankets and plastic sheets. If possible any visible oil should be picked up by means of a gulley emptier or some other similar type of pump. Similar reservoirs made of holes dug in the earth and lined with plastic sheets can be prepared to act as temporary storage. If indeed the water does sink deeply into the ground and endangers underground water supplies, then much more elaborate and sophisticated remedial measures must be taken which involve pumping and the addition of further washing water (Wardley-Smith, 1979).

Oil which penetrates the sub soil will move down wards slowly until it reaches water or an impermeable layer. The maximum depth of penetration can be estimated from the following formula (Wardley-Smith, 1979):

$$D = \frac{K.V}{A} \qquad (2.1)$$

Where D = maximum depth of penetration (cm) K= constant, depending on the retention capacity of soil and viscosity of oil. V = volume of infiltrating oil ($m^{3)}$ A = area of infiltration at surface (m^2)

2.2.3.13 Methods Employed for Cleaning Oil from Beaches

The most obvious way of beach cleaning is physically to remove the oil. This is far from easy on many beaches as the oil gets mixed with and coats the beach material. Consequently, a number of other methods have been suggested. These include burning the oil, covering it up with an absorbent powder or washing it away using a dispersant chemical as each of these methods could be of value in particular circumstances and they are considered below.

2.2.3.14 Mechanical Removal

Mechanical removal is the most satisfactory method even if only some of the oil can be taken away. A sand beach firm enough to bear vehicles and with access from a road can be cleaned by removing the minimum amount of oily sand which can be collected by mechanical graders or bull dozers and loaded into lorries by fore loaders.

Viscous oil or lumps of oil deposited along the high hide line on a smooth sand beach can be collected by the use of a horticultural rake of fine spring loaded tines, of the type which is used on sports grounds to improve the turf.

Two machines have been developed for collecting tarry oil lumps from sandy beaches. One is wheeled aid intended to be hauled by a tractor while the other is mounted on a tractor to make a complete machine.

2.2.3.15 Burning

Oil on the shore is often wet due to contact with water or because the oil is mixed with seaweed and other wet detritus. It is very difficult even to ignite oil when it is on the shore and impossible to get complete combustion.

Lumps of oil mixed with flammable materials such as driftwood and plastic can be piled into heaps and set on fire. It will be found that the oil runs off materials and enter beach material and that as “tar balls” melt the oil does the same. If burning this sort of material is considered necessary, perhaps on an isolated beach difficult of access, then an improvised furnace such as a perforated 45 gallon drum with one end removed, will improve the air flow and catch melted tar. A pipe feeding in low pressure compressed air tangentially will help combustion.

2.2.3.16 Use of Adsorbent Material

If the ground is smooth as for example a cemented jetty, an oleophylic material such as silicon treated saw dust can be sprinkled over the oil and the whole lot brushed into heaps and removed. There are a number of substances which are sold in the market to clean garage and workshop. It can be seen that this method is impossible if the surface to be cleaned is made up of loose material like sand or is covered with holes like shingle. These absorbent materials therefore have a very limited use.

An alternative use of absorbent materials is to cover the oil with a powder to remove its oily properties and to leave the oil and powder to weather. A number of powders have been tried for this purpose but none of them is really satisfactory unless very large quantities are used. Liquid oil is absorbed by the powder but tends to exude if pressure is applied, for example by walking or sitting on it. Stearate treated limestone dust which is used for explosion control in coal mines has been used for one particular oil spill in the United kingdom with reasonable success(Wardley-Smith,1979}. The treatment makes the powder both waterproof and more ready to absorb oil. As it is a very fine powder, it is likely to be objectionable if used near houses in windy conditions.

2.2.3.17 The Use of Dispersants.

The cleaning fluid commonly used in garages, workshops and factories consists of a powerful emulsifying agent dissolved in a hydrocarbon solvent. It is therefore logical to attempt to use the same or similar materials to clean oil covered rocks and beaches in general. The current dispersants available are more effective and much less toxic than the previous ones. The quantity necessary to kill test animals exposed for 48 hours is few parts per thousand.

There are three steps in dispersing oil. First the oil must be treated with an appropriate amount of the dispersant chemical.

Then either time must be allowed for the dispersant chemical to become mixed with the oil or preferably some form of local agitation should be given and last, the treated oil must be mixed vigorously with as much sea water as possible both to produce a diluted dispersion and also to reduce the possible toxicity of the dispersing chemical by increasing its dilution. The dispersants are frequently flammable and being oil solvents, they can have a harmful effect on the skin, so caution must be exercised. Drums of the dispersant should be stored when not required in well ventilated sheds.

2.2.3.18 Biological Method

Repeated exposure of certain species of micro organisms to petroleum hydrocarbon pollutants with their consequent adaptive utilization of such has supplied man with biological waste cleaners for example biosurfactants (surface-active metabolites).

2.2.3.19 Biosurfactants

Biosurfactants have variously been defined/described as surface-active compounds derived from living organisms, compounds that are capable of decreasing surface tension of solutions, compounds that can solubilise and disperse hydrocarbons and those compounds that act as bioemulsifiers (Adelowo and Oloke, 2001).

2.2.3.20 The Useful Application of Biosurfactant

Biosurfactants can be used alone as chemicals (without organisms) or together with organisms (i.e. in the presence of organisms).

A prerequisite for surfactant enhanced biodegradation is that the microorganism survives, takes up substrate and degrades it in the presence of the surfactant.

A use that shows particular promise, is in the cleanup of oil spills both on water and on land. The oil can be in-oculated with an appropriate organism that will use it as a substrate. The organism will produce biosurfactants to improve accessibility to the substrate and allow further biodegradation by both the original organism and by others, which may show different preferences for different fractions of the oil. If the spill is on water, biosurfactants may aid in dispersing the oil.

Biosurfactants may be used in the enhanced oil recovery and the cleaning of storage tanks and oil tankers. Rocha et al isolated two strains of P. aeruginosa with several properties that are desirable for enhanced oil recovery operations. They are not affected by pH, temperature, calcium and magnesium concentrations in the ranges found in many oil reservoirs while their performance improves with salinity.

An indirect advantage of the enhancement of microbial growth on hydrocarbon is that a large number of useful by products can be obtained from these substrates, an important product is single cell protein and a number of individual amino acids, vitamins and pigments (Adelowo and Oloke, 2001).

Another useful application of biosurfactants is their ability to reduce the toxicity of heavy metal contaminants in the environment. Sandrin *et al.*, (2000) reported a reduction of cadmium toxicity during the biodegradation of naphthalene. Other workers have reported the ability of a rhamnolipid biosurfactant produced by various strains of P. aeruginosa to selectively complex cationic metal species such as cadmium, lead and zinc.

Remedial technologies adopted for petroleum contaminated soils and cost comparisons are presented in Table2.19 (Kostecki and Calabrese,1989).

Table 2.19: Summary of remediation technologies

Technology	Exposure Pathways	Applicable petroleum products	Advantages	Limitations	Relative Costs
In SituVolatilization	1-7	1,2,4	Can remove some compounds resistant to Biodegradation	VOCs only	Low
Biodegradation	1-7	1,2,4	Effective on some non volatile compounds	Long-term timeframe	Moderate
Leaching	1-7	1,2,4	Could be applicable to wide variety of compounds	Not commonly practiced	Moderate
Vitrification	1-7	1,2,3,4		Developing technology	High
Passive	1-7	1,2,3,4	Lowest cost and simplest to implement	Varying degrees of removal	Low
Isolation/Containment	1-7	1,2,3,4	Physically prevents or impedes migration	Compounds not destroyed	Low to moderate
Non-in situ land treatment	1-7	1,2.3	Uses natural degradation processes	Some residuals remain	Moderate
Thermal treatment	1-6	1,2,3,4	Complete destruction possible	Usually requires special facilities	High
Asphalt incorporation	1-6	1,2	Use of existing facilities	Incomplete removal of heavier compounds	Moderate
Solidification	1-6	1,2.3.4	Immobilizes compounds	Not commonly practiced for soils	Moderate
Groundwater extraction and treatment	1-6	1,2,4	Product recovery, groundwater restoration		Moderate
Chemical extraction	1-6	1,2,3,4		Not commonly practiced	High
Excavation	1-6	1,2,3,4	Removal of soils from site	Long-term liability	Moderate

Applicable petroleum products:1=gasolines; 2=fuel oils (diesel, kerosene); 3=coal tar residues; and 4= chlorinated solvents.

Costs are highly dependent on site conditions

Source: Kostecki and Carlabresse (1989)

Table 2.20 shows the most frequently used innovative remediation technologies at Superfund sites in the United States.

Table 2.20: Common innovative remediation technologies in projects at U.S. Superfund sites (as of 1996).

Technology	Sites in design or installation	Sites operational or completed	Total Number
Soil vapour extraction	69	70	139
Thermal desorption	22	28	50
Bioremediation(ex situ)	24	19	43
Bioremediation(in situ)	14	12	26
In situ flushing	9	7	16
Soil washing	8	1	9
Solvent extraction	4	1	5

Source: Baird (1999)

2.3 Chemical Nature of Soil Contaminants

Some common soil contaminants and their associated sources are shown in Table 2.21 (Connell, 1997).

Table 2.21: Chemical identity of some soil contaminants

Chemical	Source
Arsenic	Tanneries, wood preserving, mining wastes, cattle dips, smelters.
Copper	
Chromium	
Lead	Smelters, motor vehicles
Petroleum hydrocarbons	Petrol stations, fuel depots, accidental spillages, disposal of waste chemicals.
Polyaromatic hydrocarbons (PAHs)	As for petroleum hydrocarbons, coal gas plants
Polychlorodibenzodioxin s (PCDD)	
Polychlorodibenzofurans (PCDF)	
Pesticides (DDF, Dieldrin etc)	Agricultural areas, disposal of waste chemicals, cattle dips
Industrial chemicals (solvents, PCBs, acids, alkalis etc)	Disposal of waste chemicals, industrial operations

Source: Connell (1997)

2.4 Soil Contamination with Petroleum Hydrocarbon

Petroleum contaminated soil and water analysis and biodegradation was conducted by Zacharyasz, et al., (2012). Miedzychod Poland was heavily contaminated by petroleum substances. Due to a pipeline failure in 1996, 70 tons of petrol were dumped into water and soil. More than 3000m^2 of land was considered to be contaminated. In spite of the reclamation efforts, the analyses of water and soil samples continued to indicate their heavy contamination and presence of above-average petrol and oil concentration.

Furthermore, the hydrogeological conditions of Miedzychod were favourable for the contaminants to migrate from the surface into the groundwater. Therefore, subsequent and extensive reclamation works were still to be strongly recommended.

Analysis of petroleum hydrocarbons in soil from view of bioremediation process was carried out by Mracnova *et al.*, (1999). Hyphenation of capillary gas chromatography and mass selective detector operated in the selective ion monitoring mode which allows detailed specification of non polar extractable hydrocarbons used. Isoprenoid alkanes, alkyl homologues of aromatic hydrocarbons and polycyclic alkanes hopanes-like were investigated as markers for recognition of petroleum and biogenic contamination. C_{30}17&(H)21B(H)-hopane (C_{30}-hopane) seemed to be a suitable marker to identify hydrocarbons origin, to determine composting rates for non-polar extractable compounds and to calculate real content of non-polar extractable compounds in final composting status on the assumption that the contamination was of mineral oil type.

Aromatic hydrocarbons in the vicinity of the Ring Road in Siedice City was investigated to establish a level of polycyclic aromatic hydrocarbons (PAH_S) recognized by World Health Organisation as mutagenic and carcinogenic compounds in samples of soil collected along the ring road in city Siedice which is an element of the main route Berlin-Moscow. The investigation was carried out in selected points by collecting the samples from April to October 2000 i.e a period of growth and final vegetation of plants. Analysis was carried out using solid phase extraction (SPE) and reverse phase High performance liquid chromatography (HPLC). Concentrations of individual compounds were between 10^{-7} and 10^{-9}mgkg^{-1} (Kluska, 2003).

Total hydrocarbon contents in surface water and soil sediment samples from Ondo State coastal area were determined for a period of three years. In surface water samples, total hydrocarbon ranged from 0.05-0.2mg/L, 0.05-0.2mg/L and 0.03-3mg/L in wet seasons while it ranged from 0.00-0.2mg/L, 0.02-0.2mg/L and 0.03-1.1mg/L in dry seasons of 1994, 1995 and1996 respectively. Also in soil sediment samples, hydrocarbon content ranged from 1.00- 3.00mg/kg, 1.00- 3.00mg/kg and 1.60-3.20mg/kg in wet season while it ranged from 0.5-2.0mg/kg,0.51-1.75mg/kg and 1.00-75mg/kg in the dry seasons of 1994, 1995 and 1996 respectively. Generally, the total hydrocarbon contents in both the water and sediment samples fluctuated between the extreme ends of the sampling route. The concentrations of the total hydrocarbon in the soil sediments were in all cases higher than those obtained for the surface water (Asaolu, 2000).

Effect of crude oil contamination on soil physical and chemical properties in Momoge Wetland of China was investigated by Wang *et al*., (2013). Crude oil contamination was found to significantly increase soil pH up to 8.0, reduce available phosphorus, adversely affect soil fertility and physical properties and cause deterioration of the marshes in the Momoge National Natural Reserve.

Kinetics and thermodynamics studies of hydrophobic treatment of corn cob by acetylation was conducted by Nwadiogbu *et al.*, (2014). Fourier transform infrared spectroscopy (FTIR) was used to investigate the acetylation of corn cobs such that the effects of time were not significant but the effects of temperature and catalyst were significant. Kinetic analyses suggested surface reaction and intra-particle diffusion mechanisms for corn cob acetylation at 30^{o}C and100^{o}C. Thermodynamic models used enabled the evaluations of heat of acetylation (0.0291Jmol^{-1}), critical temperature(0.814^{o}C), heat capacity(4.157x10^{-4}Jmol^{-1}K^{-1}), entropy change (5.005x10^{-4}Jmol^{-1}) and values of Gibb's free energy changes at studied temperatures for corn cob acetylation respectively. The water absorption capacity studies showed that the raw corn cob had its water absorption capacity reduced after treatment indicating a considerable increase in hydrophobicity, thereby enhancing its potential for use in non-aqueous adsorption processes like oil sorptions and oil spill remediations.

2.5 Soil Contamination by Heavy Metals and Organic Substances

New Jersey examples of soil contamination by heavy metals and organic substances are highlighted below.

2.5.1 Universal Oil Products: The Universal Oil Products Chemical Division is in Bergen County. A waste treatment plant was constructed in 1956 and further expanded to contain wastewater holding lagoons in1959.Universal Oil Products adopted the facility to manufacture specialty organic chemicals (primarily benzyl alcohol and amyl salicylate). Based upon manifest records, it was estimated that approximately 4.5million gal of waste solvents and solid chemical wastes were dumped into the unlined lagoons located on the eastern part of the property. By1971,neither the onsite treatment system nor the two lagoons were in use. UOP terminated its operations at the site in 1979 and razed the plant in 1980. The contaminants found on site included chromium, arsenic, lead, benzene, chlorobenzene, 1,1,2,2 tetrachloroethane, trichloroethylene, vinyl chloride, toluene and other organic and inorganic chemicals (Kostecki and Carlabrese,1989).

2.5.2 Bridgeport

Bridgeport Rental and Oil Storage Services, Inc operated a facility in Gloucester County for waste oil storage and recovery, storage tank leasing operations and illegal dumping operations. Preliminary estimates indicated that their lagoon contained 50,000,000 gal of contaminated liquids, six to eight in. of free-floating waste oil and three to four ft of an oily sediment. Sampling of the lagoon indicated high levels of polychlorinated biphenyls

(PCBs), oil and grease, heavy metals, phenols and benzenes. Commercial waste-handling activities are presently prohibited at the site by court order.

The characteristics of the lagoon were such that it had contaminated local ground water, surface water and soil (Kostecki and Carlabrese, 1989).

2.5.3 Borne Chemical Company

Borne Chemical Company in Union County operated a now inactive lubricating oil manufacturing plant located on a five acre tract of land bordering the Arthur kill Waterway in a mixed residential and industrial section of the city of Elizabeth. In addition to petroleum processing and blending, the plant also manufactured products used in the leather tanning industry, tints for the textile industry and oil additives. The facility included several bulk storage tanks, warehouses and a rail-road car loading facility. The company also operated a leasing business for bulk storage tanks. Sampling at the site showed polychlorinated biphenyls (PCBs) present in the waste oil contained in the bulk storage tanks(Kostecki and Carlabrese,1989).

2.5.4 Nigeria’s Examples

2.5.4.1 Ebocha-8 Oil Spillage

The fate of associated heavy metals in Ebocha-8 oil spillage in Rivers State was conducted six months after by Osuji and Onojake (2004). It was found that while oil spillage might have been partly responsible for the significantly higher levels of nickels, copper and lead in the polluted soils, the slightly lower soil pH, higher moisture content, mobility of metals, total organic carbon (TOC) and total organic material detected in the affected soils as well as the intense rainfall that preceded the period of sampling might have also contributed in part to the enhanced concentration of the metals.

2.5.4.2 Legacy Spill Site

Soil and groundwater characteristics of legacy spill site was investigated by Adoki (2012). The results showed that TPH, BTEX and PAH levels were above the DPR intervention values at some of the sampling points. This was an indication that remedial intervention was required to restore the site to levels close to pre-spill conditions.

2.6 Remediation of Petroleum Contaminated Soils

Microbial degradation of petroleum hydrocarbon was reviewed by Das and Chandran (2011). Accidental releases of petroleum products were of particular concern in the environment. Hydrocarbon components had been known to belong to the family of carcinogens and neurotoxic organic pollutants. Accepted disposal methods of incineration or burial in secure landfills could become prohibitively expensive when amounts of contaminants were large. Mechanical and chemical methods generally used to remove hydrocarbons from contaminated sites had limited effectiveness and could be expensive. Bioremediation was the promising technology for the treatment of these contaminated sites since it was cost effective and would lead to complete mineralization. Bioremediation functioned basically on biodegradation which might refer to complete mineralization of organic contaminants into carbon dioxide, water, inorganic compounds and cell protein or transformation of complex organic contaminants to other simpler organic compounds by biological agents like microorganisms. Many indigenous microorganisms in water and soil were capable of degrading hydrocarbon contaminants. Petroleum hydrocarbon degradation by microorganisms under different ecosystems was reviewed.

In a study by Aisien *et al.*, (2003) on the potential of using rubber recycled from scrap tyres as an adsorbent in crude oil clean up, rubber particles of mesh sizes within the range of 0.15 to 2.36mm were used to adsorb crude oil at different temperatures (5 to 40^0C).

The rapid increase in oil adsorption within the first 20min was followed by a much slower rate, with the equilibrium adsorption being attained after 30min. The equilibrium absorption increased with decreasing particle size and decreasing temperature of absorption. At 30^{0}C, the oil adsorption for the 0.15mm rubber particles was more than twice that of the 2.36mm particle size. When regenerated recycled rubber was used, the equilibrium adsorption decreased by about 15-40%. The extent of reduction was higher for the larger particles and at lower temperature of absorption.

Other methods that have been adopted to address this problem included spraying an aqueous slurry of expanded graphite and chalk, burning the oil with wicking agents, disposing of oil with detergent, applying floating barriers or booms, using of polymeric foams and other absorbents and enhanced biodegradation (Lewicke, 1973, Grolier, 2000 and Lessard *et al.*, 1995). The various methods have proved promising with one disadvantage or the other. However the use of adsorbent material provided it is environmentally friendly, easily recoverable, of low cost and effective adsorbent has proved the fastest way of combating oil spillage (Labelle *et al.*, 1994),

2.7 Literature Gaps

It was observed from literature review that analysis of petroleum hydrocarbons, organic substances and various heavy metals had not been carried out on petroleum contaminated soils of Port Harcourt Refinery Nigeria.

Change of physicochemical properties of soil in relation to petroleum contamination in Port Harcourt refinery had not been investigated.

Oil adsorption pattern of bamboo particles (cheap, abundant, renewable and environmentally friendly) in view of remediation process had not also been studied.

This study therefore investigated the changes in physicochemical properties, organic substances and heavy metal levels as well as petroleum hydrocarbon content of soils from crude oil contaminated areas of Port-Harcourt refinery. Further, the oil adsorption pattern of bamboo particles as a remediation process was also studied.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 List of Apparatus

Oven

Water bath

Muffler furnace

pH meter (Baush and Lomb)

Electronic balance

Porcelain crucible with lid

Crucible tong

Hot plate

Specific gravity bottle

Polythene bags

Crucible

Stop clock

Universal pH paper

Thermometer

Forceps

Pasteur pipette

Viscometer

Mortar and pestle

Sieves

Sheet of asbestos

Hack saw

Knife

Fume hood

Deep freezer

3.1.2 List of Equipment

Atomic absorption spectrophotometer (Schimadzu AA 670)

Gas chromatograph (Bulk Scientific M910)

UV-VIS spectrophotometer (Apel Pd 300)

3.1.3 List of Chemicals and Reagents

Concentrated nitric acid	(BDH)
Concentrated hydrochloric acid	”
Concentrated sulphuric acid	”
Hydrogen peroxide	’’
Ferrous sulphate heptahydrate	”
Ferroin indicator	”
Cadmium chloride	”
Potassium chromate	”
Iron (iii) chloride	”
Magnesium chloride	’’
Manganese chloride	”
Nickel nitrate	”
Sodium chloride	”
Ammonium metavanadate	”
Zinc oxide	”
Lead nitrate	”
Arsenious oxide	”
Calcium carbonate	”

Anhydrous sodium sulphate (Sigma Aldrick)

n-Hexane (Sigma Aldrich)

Magnesium silicate (Sigma Aldrich)

Diethyl ether (Sigma Aldrich)

Pentanol (Sigma Aldrich)

Ammonium hydroxide (BDH)

Chloroform (Sigma Aldrich)

3.2 Study Area

The areas under study were soils under six crude oil storage tanks (50 TKOIA, 50TKOIB, 50TKOIC, 50TKOID 50TKOIE and 50TKOIF) Eleme Petroleum Refinery Port –Harcourt and soil directly behind utility building (CEP building) Nnamdi Azikiwe University, Awka. Eleme coordinates are 4.7994^{0}N, 7.1198^{0}E. it is located at east of Port Harcourt and covers an area of 138km^2. At 2006 census, it had a population of 190,884. Precipitation in Port Harcourt averages 2708mm and the average annual temperature is 26.4^{0}C. The average annual relative humidity is 71.0% (https//weather and climate.com). Awka is found in the south-eastern part of Nigeria. It is the capital of Anambra State and is located on latitude 6^{0}09$^{\prime}$N and longitude 7^{0}12$^{\prime}$ E. The climate is tropical with an annual rainfall of about 11,450mm, average temperature of 28^{0}C and relative humidity of 91% at dawn (Nwangwu, 2015).

3.3 Soil Sampling

Using a hand soil auger, samples were collected at depth of 0-12cm at five different points, mixed homogenously to obtain a sample representative of the study area (Wang *et al*., 2013). A total of seven homogenous soil samples were obtained by collecting samples of top soil from around six crude oil storage tanks in Eleme Petroleum Refinery Port-Harcourt and Nnamdi Azikiwe University, Awka premise behind utility building . The crude tanks were namely 50TKOIA, 50TKOIB, 50TKOIC, 50TKOID, 50TKOIE and 50TKOIF. Soil samples from around these crude tanks were labeled A,B,C,D,E and F respectively and the sample from Nnamdi Azikiwe University Awka was labelled G. The tanks were about 30years old and 200,000 liters in capacity. The crude oil tanks were about 30m apart and the samples were collected in black polythene bags in the month of November.

3.4 Sample Storage

Samples were stored in deep freezer prior to analysis (Asaolu, 2000).

3.5 Sample Preparation

Metal ion extraction was done by treating the samples with a 3:1 mixture of concentrated HNO_3 and HCl acid and heating at $1O5^0$ C on a hot plate for three hours (Voutsa *et al.*, 1996; Chen, and Ma, 2001).

For organic matter and total nitrogen determination, the soil samples were homogenized by shaking, air dried at room temperature and pulverized. They were then passed through 2mm sieve before use for analysis (Voutsa *et al.*, 1996).

3.6 Analysis

3.6.1 Determination of the Colour of Soil

The colour of the soils was examined with the naked eye and the results were recorded (Olaitan and Lombin, 1984).

3.6.2 Determination of Soil Texture

Textural class by feel was determined as follows:

1. Soil did not cohere into a ball, falls apart : **sand**
2. Soil formed a ball but would not form a ribbon: **loamy sand**
3. Soil ribbon was dull and broke off when less than 2.5cm long and

a. Grinding noise was audible; grittiness was prominent feel: **sandy loam**

b. Smooth, floury feel prominent; no grinding audible: silt loam

c. Only slight grittiness and smoothness: grinding not clearly audible: **loam**

4. Soil exhibited moderate stickiness and firmness, formed ribbon 2.5 to 5cm long and

a. Grinding noise was audible, grittiness was prominent feel: **sandy clay loam**

b. Smooth, floury feel prominent: no grinding audible: **silty clay loam**

c. Only slight grittiness and smoothness: grinding not clearly audible: **clay loam**

5. Soil exhibited dominant stickiness and firmness, formed shiny ribbons longer than 5cm and

a. Grinding noise was audible, grittiness was dominant feel: **sandy clay.**

b. Smooth floury feel prominent : no grinding audible: **silty clay**

c. Only slight grittiness and smoothness: grinding not clearly audible: **clay (**Brady and Weil, 2013).

Simplified key for identification of soil classes by texture in Table 3.1 was also followed before confirmation of the classes (Olaitan and Lombin, 1984; Ibitoye, 2006).

Table 3.1: Simplified key for identification of soil classes by texture

A	Air dried	Moist	Soil class
	Single grained. Loose	Gritty. No ribbon	Sand
Aggregated	Soft clods	Gritty. No ribbon	Sandy loam
		Intermediate. No ribbon	Loam
		Smooth. No ribbon	Silt loam
	Moderate pressure needed to break aggregates	Gritty. Medium ribbon	Sandy clay loam
		Intermediate. Gritty/smooth medium ribbon	Clay loam
		Smooth. Medium ribbon	Silty clay loam
Aggregated	Aggregates cannot be crushed with the fingers	Smooth. Good ribbon	Silty clay
		Gritty. Good ribbon	Sandy clay

Source: Olaitan and Lombin (1984).

3.6.3 Determination of Soil Moisture

A clean and labeled filter paper that has been oven dried was weighed (W_1). 2g of Soil Sample was added onto the filter paper and the weight taken (W_2).The filter paper containing the soil sample was transferred into a thermo-setting oven at 105^0C. Drying was carried out until constant weight (W_3) was obtained. The loss in weight after drying in the oven is the moisture content of the soil (Ibitoye, 2006).

$$\% \text{ moisture} = \frac{\text{Loss in weight}}{\text{wt of soil after drying}} . 100 \qquad (3.1)$$

$$\% \text{ moisture} = \frac{W2 - W3}{W3 - W1} . 100 \qquad (3.2)$$

3.6.4 Determination of Water Holding Capacity

The method of Olaitan and Lombin,1984 was followed:

Procedure

9.6cm filter funnels were lined with filter paper (Whatman No 42). The paper was wetted thoroughly and excess water was allowed to drain away completely. A graduated measuring cylinder was placed under each filter funnel and 10g of soil was put in each funnel. 6.7cm³ of water was poured onto each soil. The water draining out of each of the soils was collected and the volume recorded every 30 seconds. The volume of water that drains from each sample of soil was compared and the results recorded .The volume of water retained by each soil was also recorded.

% WHC (Water holding capacity expressed as percentage):

$$\frac{\text{Maximum water absorbed by soil}}{\text{Dry weight of soil}} . 100 \qquad (3.3)$$

3.6.5 Determination of Bulk Density of Soil

Bulk density was determined by measuring the oven dry weight of a unit volume of soil (Olaitan and Lombin,1984 ;Miller and Donahue,1990).

$$\text{Bulk density } (g/cm^3) = \frac{\text{weight of soil}}{\text{Volume of soil}} \qquad (3.4)$$

3.6.6 pH Measurement

This was done after calibration of the pH meter with buffers of pH 4.0 and 7.0.

20g of air-dried soil (passed through 2mm sieve) was weighed into a 50ml beaker. 20ml of distilled water was added and was allowed to stand for 30 minutes during which stirring was carried out occasionally. The electrode of the pH meter was inserted into the partly settled suspension and the pH measured. Result was reported as soil pH measured in water (APHA, 2000 and Bates, 1954).

3.6.7 Determination of Soil Organic Carbon and Organic Matter

1. Potassium dichromate ($K_2\ Cr_2\ O_7$), IN: 49.04g of reagent-grade $K_2Cr_2O_7$ (dried at 105^0C) was dissolved in water and diluted to a volume of 1000ml.
2. Sulphuric acid (H_2SO_4), Concentrated (98%)
3. Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) solution, 0.5N: 140g of reagent grade $FeSO_4.7H_2O$ was dissolved in water. 15ml of Conc sulphuric acid (H_2SO_4) was added and the solution cooled and diluted to a volume of 1000ml.
4. Ferroin indicator prepared by dissolving 14.85g of O-phenanthroline monohydrate and 6.95g of ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) in water and diluting to a volume of 1000ml. The commercial grade was used (BDH).

Procedure

Air dried soil sample was ground to pass through a 0.5mm sieve avoiding iron or steel mortars. 0.2g (for a very peaty soil) was transferred into a 500ml wide mouth Erlenmeyer flask. 10ml of $1NK_2Cr_2O_7$ was added and the flask swirled gently to disperse the soil in the solution. 20ml of conc H_2SO_4 was added rapidly, directing the stream into the suspension. The flask was immediately swirled gently until soil and reagents were mixed, then more vigorously for a total of 1min. The flask was allowed to stand on a sheet of asbestos for about 30 minutes, and then 200ml of water was added to the flask. 3 to 4 drops of O-phenanthroline indicator was added and the solution was titrated with 0.5N$FeSO_4$. As the end point was approached, the solution took a greenish cast and then changed to a dark green. At this point, the ferrous sulphate heptahydrate was added drop by drop until the colour changed sharply from blue to red (Maroon colour in reflected light against a white background). Blank determination was made in the same manner but without soil to standardize the iron (II) solution (Page 1982, Ibitoye, 2006 and Head, 1992)

3.6.8 Determination of Trace Metals

The conventional aqua regia digestion procedure consists of digesting soil samples on a hotplate with a 3:1 mixture of HCl and HNO_3.The nitric acid reacts with concentrated HCl to form aqua regia:

$$3HCl+HNO_3 \rightarrow 2H_2O + NOCl + Cl_2$$

This digestion procedure is so widely used that the European Community Bureau of Reference has certified several soil and sludge samples based on it, in addition to the total elemental concentrations.

Conventional aqua regia digestion was performed in 250ml glass beakers covered with watch glasses. A well mixed sample of 0.5000g was digested in 12 ml of aqua regia on a hot plate for 3hrs at 110˚C. After evaporation to near dryness, the sample was diluted with 20ml of 2% (v/v) dilute nitric acid and transferred into a 100ml volumetric flask after filtering through Whatman No 42 paper and diluted to 100ml with DDW.(Chen, and Ma, 2001)

3.6.8.1 Preparation of Standard Solutions for AAS

100mg/L stock solution= 1g of test element dissolved in one litre or molar mass of compound containing test element

$$\text{e.g } 1000\text{mg/L Ca} = \frac{\text{Molar Mass of } CaCO_3}{\text{Atomic mass of Ca}} \qquad (3.5)$$

2.5g dissolved in one litre to produce 1000mg/L or 1000ppm i.e the calculated mass was dissolved in volumetric flask and made up to one litre to give 1000mg/L stock solution. The solution was further diluted to 100mg/l by pipetting 10ml stock solution and making it up to 100ml with distilled water. Working standards of 0,2,4,6,8,10 and 20mg/L were prepared from 100mg/L. This was done by pipetting 2, 4, 6,8,10 and 20ml from 100ppm into 100ml standard flasks (volumetric flasks) and diluting to 100ml with distilled water.

3.6.8.2 Standard Solutions for AAS

1) Stock standard solution, cadmium, 1000mg/l. 2.0360g of cadmium chloride was dissolved in 250ml of deionised water and diluted to 1 liter in a volumetric flask with deionised water.

2) Stock standard solution, chromium, 1000mg/l. 3.735g of potassium chromate, K_2CrO_4 was dissolved in deionised water and diluted to 1 liter in a volumetric flask with deionised water.

3) Stock standard solution, iron, 1000mg/l. 4.8400g of iron (iii) chloride ($FeCl_3.6H_2O$) was dissolved in 200ml of deionised water and diluted to 1 liter in a volumetric flask with deionised water.

4) Stock standard solution magnesium, 1000mg/l. 3.9160g of magnesium chloride ($MgCl_2.6H_2O$) was dissolved in 200ml of deionised water and diluted to 1 liter in a volumetric flask with deionised water.

5) Stock standard solution manganese, 1000mg/l. 3.6077g of manganese chloride ($MnCl_2.4H_2O$) was dissolved in 50ml of concentrated HCl and diluted to 1 liter in a volumetric flask with deionised water.

6) Stock standard solution nickel,1000mg/l. 4.9530g of nickel nitrate ($Ni(NO_3)_2.6H_2O$)was dissolved in 1 liter volumetric flask with deionised water.

7) Stock standard solution selenium, 1000mg/l. 1.000g of selenium metal was dissolved in a minimum volume of concentrated HNO_3, evaporated to dryness and 2ml of water was added. It was evaporated to dryness 3 addition times, dissolved in 10%(v/v) HCl and diluted to 1 liter with 10%(v/v)HCl.

8) Stock standard solution vanadium, 1000mg/l. 2.2960g of ammonium metavandate (NH_4V0_3) was dissolved in 20ml of 100 volume hydrogen peroxide and diluted to 1 liter in a volumetric flask with deionised water..

9) Stock standard solution zinc, 1000mg/l. 1.2450g of zinc oxide (ZnO) was dissolved in 5ml of deionised water followed by 25ml of 5MHCl and diluting to 1 liter in a volumetric flask with deionised water.

10) Stock standard solution lead, 1000mg/l. 1.5980g of lead nitrate ($Pb(NO_3)_2$) was dissolved in 100ml of deionised water and diluted to 1 liter in a volumetric flask with deionised water

11) Stock standard solution arsenic, 1000mg/l. 1.320g of arsenious oxide As_2O_3 dried to110^oC was dissolved in 50ml of concentrated hydrochloric acid and diluted to 1liter in a volumetric flask with deionised water.

12) Stock standard solution calcium, 1000mg/l. 2.7693g of calcium chloride ($CaCl_2$) was dissolved in 100ml deionised ater and diluted to 1liter in a volumetric flask with deionised water.

3.6.8.3 Determination of Metal Concentration The solution of 0ppm or blank was introduced into the atomic absorption spectrophotometer and it was aspirated into the flame. The blank control was adjusted to set zero absorbance or 100% transmittance. Working standards were introduced separately and adjusted until agreeable readings were obtained. The absorbance of standards were recorded against concentration in ppm. The digested samples were introduced one after the other and absorbance was recorded. Dilution of the sample was carried out when required. The samples metal concentrations were read off from the calibration curve produced by plotting absorbance of standards against their concentration (Ibitoye, 2006).

3.6.9 Determination of Total Petroleum Hydrocarbon by Gas Chromatography

Preparation of Samples for Gas Chromatographic Analysis (AOAC 1990)

3.6.9.1 Soxhlet Extraction Method

Twenty grams (20g) of the homogenized sample was measured out.The sample was mixed with 60g of anhydrous sodium sulphate in agate mortar to absorb moisture. The homogenate was then transferred to 500ml beaker and 3ooml of n-hexane was added. Extraction was carried out with the 300ml of n-hexane using EPA 354^0C method (Environmental Protection agency) for 48 hours. The crude extract obtained was evaporated using a rotary vacuum evaporator at 40^0C just to dryness.The residue was transferred with n-hexane onto a 5ml florisil column for clean up.

3.6.9.2 Florisil Clean Up

Florisil was heated in an oven at 130^0C overnight for about 15hours and transferred to a 250ml size beaker. It was then placed in a desicator.0.5g of anhydrous $NaSO_4$ was added to 1.0g of activated florisil (Magnesiun silicate, 60-100nm mesh) on an 8ml column plugged with glass wool. Packed column was filled with 5ml n-hexane for conditioning. Stop cock was opened to allow n-hexane run out until it just reaches top of sodium sulphate into a receiving vessel whilst tapping gently the top of the column till the florisil settled well in the column. Extract was transferred to the column with disposable Pasteur pipette from an evaporating flask. Each evaporating flask was rinsed twice with 1ml portions of n-hexane and added to column. Eluate was collected into an evaporating flask and rotary evaporated to dryness. The dry eluate was dissolved in 1ml n-hexane for gas chromatographic analysis.

3.6.9.3 Analysis

The 1ml n hexane extract was dissolved was dissolved in 50 ml of chlolroform and transferred to a 100ml volumetric flask and diluted to mark. Most of the chloroform was evaporated at room temperature. 1ml of interesterification reagent (20vol% benzene and 55 vol % methanol) was added, it was sealed and heated at 40^oC in a water bath for 30 minutes. After interesterification, the organic sample was extracted with hexane and water so that the final mixture of the reagent, hexane and water were in the proportion 1:1:1(i.e 1ml each of hexane and water were added to the reaction mixture. The mixture was shaken vigorously by hand for 2 minutes. Any stable emulsion formed was broken by centrifugation. About half of the top hexane phase was transferred to a small testtube for injection. Care was taken to remove only the organic layer. Injection directly from the reaction vial was not done because of the risk of injecting water which can ruin the G.C column. ACCU standards for phytochemical analysis was used for the determination .The retention time was compared with standards.

3.6.9.4 Fixed Setting

Gas flow to the column, the inlets, the detectors, and the split ratio were adjusted. In addition, the injector and detector temperatures were set. The detectors were held at the high end of the oven temperature range to minimize the risk of analyte precipitation. All the parameters were set to the correct values and the instruments were also checked. Buck 530 gas chromatograph equipped with a column automatic injector, flame ionization detector, HP88capillary column (100mx0.25um film thickness) CA, USA

Detector Temperature A: 250^{o}C
Injector Temperature: 220^{o}C
Integrator Chart Speed: 2cm/ min
The oven temperature was set to 180^o C and the GC was allowed to warm up.
While warming, the following temperature conditions were set:

Table 3.2: Temperature Condition Initial

Temp	**Hold**	**Ramp**	**Final Temp**
70^{0}C	5min	10min	220^{0}C
220^{0}C	2min	5min	280^{0}C

When the instrument was ready the Not Ready light turned off and running of the sample was commenced.

A 1microlitersample was injected onto column A using paper injection technique.

3.6.10 Determination of Phenol Content of Soil Sample

The quantity of phenol was determined using the spectrophotometer method (AOAC,1990) . 20g of soil sample was boiled with 50ml of $(CH_3CH_2)_2O$ for 15minutes.5ml of the boiled sample was then pipetted into 50ml flask and 10ml of distilled water was added. 2ml of ammonium hydroxide (NH4OH) Solution and 5ml of concentrated $CH_3(CH_2\}_3CH_2OH$ was added to the mixture. The sample was made up to the mark and left for 30minutes to react for colour development and was then measured at 505nm wavelength in the spectrophotometer.

$$\text{Conc. of sample} = \frac{\text{Absorbance of sample x Conc. of standard}}{\text{Absorbance of standard}} \qquad (3.6)$$

3.6.11 Determination of Benzene

This was done according to AOAC, 1990.

3.6.11.1 Soxhlet Extraction

10g of the homogenized sample was weighed out. It was mixed with 60g of anhydrous sodium sulphate in agate mortar to absorb moisture. The homogenate was transferred to a 500ml beaker**.** Extraction was carried out with 300ml of n-hexane for 24hrs. The crude extract obtained was evaporated using a rotary vacuum evaporator at 40^oC just to dryness.

3.6.11.2 Preparation of Sample for Gas Chromatographic Analysis

1ml of filtered residue was dissolved in 50ml of chloroform and transferred to a 100ml volumetric flask. It was diluted to the mark and most of the chloroform was evaporated at room temperature. 1ml of the reagent (20 vol% benzene and 55 vol% methanol) was added. It was sealed and heated at 40^oC water bath for 30 minutes. After heating the organic sample was extracted with hexane and water so that the final mixture of the reagent, hexane and water was in proportion of 1:1:1 i.e 1ml each of hexane and water was added to the reaction mixture. The mixture was shaken vigorously by hand for 2 minutes. If a stable emulsion was formed it was broken by centrifugation. About half of the top hexane phase was transferred to a small test tube for injection. Only the organic layer was removed. Injection was not done directly from the reaction vial because of the risk of injecting water. Water could ruin the GC column.

Fixed Setting: Gas flows to the columns, the inlets, the detectors and the split ratio must be adjusted. The injector and detector temperatures were set. The detectors were generally held at the high end of the oven temperature range to minimize the risk of analyte precipitation. All of these parameters were set to the correct values and all the instruments were double checked. Buck 530 gas chromatograph equipped with an on-column, automatic injector, electron capture detector, HP 88 capillary column (100mx0.25um film thickness) CA, USA was used.

Detector temperature A: 280^0C
Column temperature: 210^0C
Injector temperature: 250^0C
Integrator chart speed: 2cm/min

Oven temperature was set to 180^0C and the GC was allowed to warm up. While warming the following temperature conditions were set:

Table 3.3: Temperature Condition

Initial Temp	Hold	Ramp	Final Temp
180^0C	4min	10min	200^0C
200^0C	2min	5min	300^0C

When the instrument was ready, the “NOT READY” light turned off and the run was begun.A1microliter sample was injected onto column A using proper injection technique.

3.6.12 Determination of Oil and Grease

The method of AOAC 1990 was followed.

3.6.12.1 Soxhlet Extraction Method

4.50g of each powdered soil sample was measured using electronic weighing balance. The sample was wrapped using Whatman Filter paper and inserted in the tube of the soxhlet apparatus. 250ml of hexane was poured into the round bottom conical flask of the apparatus and was heated. The extraction was carried out for eight hours. The remaining hexane in the extract was evaporated to get crude oil extract. This was done in vacuo using a rotary evaporator.

$$\%\text{Oil and grease} = \frac{\text{wt of oil + flask – wt of flash x 100}}{\text{wt of sample}} \qquad (3.7)$$

3.7 Statistical Analysis

Statistical analysis of the results of trace metals and organic matter were conducted as these were more affected by petroleum contamination than others.

3.8 Remediation Method

3.8.1 Materials Collection

Bamboo was collected from a bush in Awka. It was cut into small chunks for easy transportation. Crude oil was obtained from Eleme Refinery Port Harcourt, River State

3.8.2 Bamboo Particle Preparation

The chunks of bamboo wood were washed and dried to make them clean. The clean chunks of bamboo wood were cut into sections with a hack saw and later into very small pieces (4.75mm) with the aid of sharp hacksaw and knives. These wood chips were then transferred into a clean and dried electric grinding machine. This was used to reduce the wood to wood particles and fibres mixture. The mixture was then mechanically sieved into wood particles from 2.00mm to 0.425mm size range and the fibres were then separated and removed. The different sizes of wood particles were collected and kept in separate plastic containers.

3.8.3 Determination of Specific Gravity of Crude Oil and the Density.

Apparatus: Specific gravity bottle (50ml), weighing balance.

Reagents: Distilled water, crude oil.

Procedure

Specific gravity bottle was weighed empty as W_1 and then weighed filled with distilled water as W_2. The bottle was then filled with the crude oil and weighed as W_3 (Jacobs, 1999).

$$S.G = \frac{W_3 - W_1}{W_2 - W_1} = \frac{\text{Mass of Substance}}{\text{Mass of equal volume of water}} \tag{3.8}$$

3.8.4 Adsorption of Crude Oil with Bamboo Particles

3.8.5 Measurement of Time and Rate of Adsorption of Crude Oil:

Thirteen one-liter beakers were used for the adsorption test. The beakers contained 100cm^3 of crude oil each. 10g of a given particle size of bamboo were weighed into each of the beakers using an electronic balance. After 5mins, the contents of the first beaker were filtered until no further drops of oil were observed. Then the new weight of bamboo particles was determined. For the remaining beakers the same procedure was repeated at successive 10 minutes intervals until there was no further change in weight. The difference between the weight and the initial weight of each sample in each beaker was regarded as the weight of crude oil adsorbed at the particular time.

Crude oil adsorption (oil/g bamboo particle) =

$$\frac{\text{Mass of crude oil retained by bamboo particles}}{\text{Mass of bamboo particles}} \tag{3.9}$$

The results of adsorption of crude oil with bamboo particles of different sizes with time were recorded. Their graphs of adsorption or adsorption time curves were plotted.

The rate of adsorption was taken as the slope of the linear portion of the adsorption time curve. (Aisen *et al.*, 2003; Brown, 1976).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1Colour

The colour of the soil samples after eye examination are stated in Table 4.1.

Table 4.1: Colour of soil samples

Samples	A	B	C	D	E	F	G
Colour	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Reddish brown

The dark brown colour of soil samples A to F is due to the heavy contamination by petroleum which is dark brown or greenish brown in colour (Murray 1983; Sharma, 2011). This is absent in the sample G from Nnamdi Azikiwe Univerty Awka which appeared reddish brown in colour. The reddish brown colour of the sample G is as a result of the iron deposit in the soil which occurs as iron (iii) oxide, Fe_2O_3 (Olaitan and Lombin,1984; Egboka *et al.*,1989). At pH values higher than about 3, the colloidal hydrated iron(iii) oxide $Fe_2O_3.xH_2O$ separates as a reddish brown precipitate (Murray,1983)

The colour of a soil is an important indicator of certain physical and chemical characteristics. The dark brown colour of samples A-F emanated from petroleum which is formed from decayed organic matter (Montgomery, 2008) whereas sample G contains mainly minerals predominant of which is iron(iii) oxide. Humus which is a term used to describe well decomposed stable organic matter in the soil is usually dark coloured (Olaitan and Lombin, 1984)

4.2 Texture

The results of the identification of soil classes by texture are found in Table 4.2

Table 4.2: Soil classes by texture

Sample	A	B	C	D	E	F	G
Texture	silty clay loam	silty clay loam	silty clay loam	silty clay loam	silty clay loam	silty clay loam	Sandy Loam

Samples A-F being aggregated, moderate pressure needed to break aggregates after drying and forming smooth medium ribbon while moist are classified as silty clay loam. Sample G being aggregated, forming soft clods after drying, gritty and no ribbon formation while moist is classified as sandy loam (Olaitan and Lombin, 1984; Ibitoye, 2006). The oil of petroleum enhanced ribbon formation by samples A-F. This is because of the force of adhesion that exists in oil particles (Atkins and Jones, 1999). Forces of adhesion bind a substance to a surface and this occurs when there are favourable attractions between the molecules of the two substances, Aggregation is as a result of forces of cohesion which bind the molecules of a substance together.

Soil texture is determined by the size of the soil particle. It refers to the proportion of sand, silt and clay in a soil. In a more general way, texture may be used to describe how a soil feels or behaves under cultivation (Olaitan and Lombin, 1984)

Soil texture and organic matter content are two important factors which determine the amount of water a soil can hold.

4.3 Soil Moisture

The soil moisture contents are presented in Table 4.3

Table 4.3: Soil moisture content (%)

Sample	A	B	C	D	E	F	G
Soil Moisture Content	40.56	16.28	15.61	11.73	19.76	20.48	0.50

Samples A-F have higher moisture content than sample G. This is because samples A-F are contaminated with crude oil and are oil logged and partly aerated. The blocked pores in the samples slow down drainage of water and the oil hinders evaporation of water (Olaitan and Lombin, 1984). Aggregation due to force of adhesion existing in oil particles is also responsible for the high moisture content (Atkins and Jones, 1999). The moisture contents are also related to the clayey nature of the soils (Olaitan and Lombin,1984).

Sample G being sandy in nature allows for more drainage and evaporation due to the plenty unblocked pores present in the sample (Edori and Iyama, 2017).

4.4 Water Holding Capacity

The water drainage through soils, water retention of soils and water holding capacity results of soils are presented in Tables 4.4- 4.6 respectively. Water drainage through soil is the amount of water that drained through the soil at a specific period of time. Water retention of soil is the amount of water retained by the soil at a specific period of time.

Water holding capacity of soil expressed in percentage is maximum water absorbed by the soil divided by the dry weight of the soil times one hundred.

Table 4.4: Water drainage through soils, water retention of soils and water holding capacity

	Soil	Samples					
Volume of water drained at	A	B	C	D	E	F	G
30seconds	3.8ml	4.1ml	4.2ml	4.2ml	4.0ml	3.9ml	5.4ml
60seconds	4.5ml	5ml	5.2ml	5.2ml	5,0ml	4.6ml	5.6ml
90seconds	4.5ml	5ml	5.2ml	5.2ml	5.0ml	4.6ml	5.6ml
120seconds	4.5ml	5ml	5.2ml	5.2ml	5.0ml	4.6ml	5.6ml
Volume of water retained at							
30seconds	2.9ml	2.6ml	2.5ml	2.5ml	2.7ml	2.8ml	1.3ml
60seconds	2.2ml	1.7ml	1.5ml	1.5ml	1.7ml	2.1ml	1.2ml
90seconds	2.2ml	1.7ml	1.5ml	1.5ml	1.7ml	2.1ml	1.1ml
120seconds	2.2ml	1.7ml	1.5ml	1.5ml	1.7ml	2.1ml	1.1ml
Water holding capacity of soils (%)	29	26	25	25	27	28	13

Sample G has the highest amount of water drained through the soil and the least amount of water retained by the soil at the stipulated times. This is due to the soil texture which is sandy loam. The texture of samples A-F is silty clay loam but they differ in the amount of water drained and amount of water retained. This resulted in different values of water holding capacity.

Also due to the blockage of soil pores by oil and clayey nature of samples A-F, they have higher water holding capacity than sample G which is not contaminated by oil and is sandy in nature.

The aggregation of soil particles is an important factor affecting drainage, aeration and ability of the soil to release plant nutrients (Olaitan and Lombin,1984). Sandy loam soil (sample G) which is not highly aggregated with soft clods (when air-dried) has lower water holding capacity and higher drainage of water. The force of adhesion that exists in oil particles (Atkins and Jones,1999) tends to cause increased aggregation in samples A-F, thus increased water holding capacity. In general, the higher the clay and organic matter content, the greater will be the water retention capacity (Edori and Iyama, 2017). In sandy soil, there are more macropores than micropores and therefore the ability to retain water for long is low.

4.5 Bulk Density

The bulk density of soil samples are recorded in Table 4.5.

Table 4.5: Bulk density of soil samples

Samples	A	B	C	D	E	F	G
Bulk Density g/cm^3	0.80	0.94	0.90	1.03	1.05	0.95	1.42

The uncontaminated soil (sample G) has less amount of organic matter in it, as a result the bulk density increases (Olaitan and Lombin, 1984).The oil contaminated soils have higher amount of organic matter resulting in less bulk density.

The bulk density of uncultivated soils usually ranges from 1.0 to 1.6 g/cm^3 (Olaitan and lombin, 1984). Clay soils have bulk density values ranging from 1,10 to 1.40g/cm^3 .Loams, sandy loams and sand have bulk densities ranging from 1.20 to 1.80g/cm^3 (Olaitan and Lombin,1984).

4.6 pH

The soil pH values are shown in Table 4.6

Table 4.6: Soil pH values

Soil	A	B	C	D	E	F	G	Distilled water
pH $^{(electrode)}$	5.26	5.37	7.69	7.64	7.79	7.84	5.37	6.89
pH $^{(universal\ pH\ paper)}$	5 - 6	5 – 6	7.00	7 - 8	7 - 8	7 - 8	5 - 6	6 - 7

Soil pH indicates something about the percentage base saturation depending on the predominant clay type. It can also indicate something about the degree of dissociation of H ions from cation exchange sites or the extent of hydrogen ion formation by the hydrolysis of aluminum. Since the availability of most plant-essential elements depends on soil pH, it is an indication of relative availability of plant nutrient. Thus, soil pH is generally both a symptom of the soil's condition and a cause of many of the reactions that occur. Al^{3+} hydrolyzes to Al (OH) $^{2+}$ plus H^{+}, ($Al^{3+}+H_2O\rightarrow Al(OH)^{2+}+H^{+}$) at a higher pH than that where electrostatically bonded H ions begin to dissociate.

Similarly hydroxyl-Al[$Al(OH)^{2+}$or$Al(OH)^{+}{}_2$] hydrolyzes forming H^{+} at still higher pH values. Factors that may influence the measured pH include (i) The nature and type of inorganic and organic constituents that contribute to soil acidity (ii) The soil/solution ratio (iii) The salt or electrolyte content (iv) The CO_2 content and (v) Errors associated with equipment standardization and liquid junction potential.

The increased availability of cations in soil such as K^{+}, Ca^{2+} and Mg^{2+} as a result of petroleum contamination and decayed organic matter should have led to increase in soil pH of samples C-F (Adeleye *et al.*, 2005; Oladoja and Asia, 2003). Petroleum contamination blocks availability of nutrients to plants from the soil (Odum, 1971, Divavin *et al.*, 1978, Laws, 1981 and Dudd, 1974).

The acidity of samples A and B may be attributed to Aluminium toxicty due to soil contamination by refinery effluents or fertilizer contamination from the surrounding environment (Adeleye *et al.*, 2005).

The acidic nature of sample G may be due to intensive cultivation that had taken place on the site (Adeleye *et al.,* 2005).The atmosphere also contains acidic gases such as sulphur dioxide. These gases dissolve in rain water to form dilute acid solutions.

4.7 Organic matter, Organic carbon and Organic nitrogen

The organic matter, organic carbon and organic nitrogen content of the soils are shown in the Table 4.7.

Table 4.7: Organic matter, organic carbon and organic nitrogen content of soil samples

Sample	A	B	C	D	E	F	G
%Organic Carbon	14.41	15.09	10.68	12.40	10.85	10.68	7.29
%Organic matter	24.84	26.02	18.41	21.38	18.71	18.41	12.57
%Organic nitrogen	0.7205	0.7545	0.534	0.620	0.543	0.534	0.365

The organic matter results of samples A-F are similar to that obtained by Edori and Iyama (2017). This is because the samples were obtained from same geographical location, Port Harcourt

The organic matter content of samples A-F are higher than that of Sample G. This is because petroleum is formed from decayed organic matter and samples A-F are contaminated by petroleum (Montgomery, 2008).

The organic matter which gives soil its dark colour is primarily a material called humus and is derived principally from photosynthetic plants, some components of which (such as cellulose and hemicellulose) have already been decomposed by organisms that live in the soil (Baird, 1999).The undecomposed plant material in humus are mainly protein and lignin both of which are polymeric substances that are largely insoluble in water.

Crude petroleum contains alkanes (straight and branched chain from about C_1 -C_{40}), cycloalkanes or naphthenes and aromatic hydrocarbons (Finar, 1980). The carbon compounds add to the carbon content of samples A-F (petroleum contaminated soil). Other organic compounds that have been determined in crude oil are thiophene, mercaptans, organic disulphide, dithiols, sulphur containing heterocyclic aromatic compounds, triaromatic azaarenes, heterocyclic aromatics, carbazoles, benzocarbazole, polycyclic aromatic amines, diaromatic nitrogen bases, higher molecular weight primary ,secondary and tertiary amines, phenol and carboxylic groups, furan, dibenzofuran etc(Thomas and Ringen,1985). Total hydrocarbon content of water and sediment samples has also been determined (Asaolu, 2000).

Higher levels of organic nitrogen are observed in samples A-F than in sample G. This is again due to increased level of decayed organic matter and contamination by petroleum in samples A-F. Some carbon in plant material is transformed to carbon dioxide during decay process and is lost as a gas to the environment. This makes humus enriched with nitrogen relative to that in the original plant (Baird, 1999)

Nitrogen compounds detected in petroleum include polycyclic aromatic amines, triaromatic azaarenes, carbazole, benzocarbazole, heterocyclic aromatics and nitrogen heterocycles as well as diaromatic nitrogen bases (Thomas and Ringen, 1985).

4.8 Metals

The results of the metal determination of soil samples are presented in Table 4.8 and Figures 4.1 - 4.10

Table 4.8: Metal content of soil samples in mg/kg

	V	Ni	Cr	Cd	Zn	Pb	Fe	Se	Mg	Ca	Mn	As
Sample A	‹0.001	‹0.05	0.009	<0.005	2.70	<0.02	22.87	<0.001	0.86	0.18	0.008	<0.01
Sample B	“	2.05	‹0.005	‹0.005	0.47	0.14	12.32	‹0.001	0.31	0.14	0.011	‹0.001
Sample C	“	‹0.05	0.010	<0.005	2.87	0.16	20.67	<0.001	0.11	0.11	0.036	<0.001
Sample D	“	0.15	0.37	0.008	1.24	0.15	29.11	<0.001	0.09	0.04	0.008	<0.001
Sample E	“	0.15	0.009	0.008	0.36	0.19	27.46	<0.001	0.25	0.17	0.009	<0.001
Sample F	“	0.33	0.008	<0.005	0.29	0.14	21.64	<0.001	0.41	0.14	0.015	<0.001
Sample G Unizik soil	“	0.57	0.008	‹0.005	0.14	<0.02	15.61	‹0.001	0.52	0.13	0.013	‹0.001
Soil Quality standard	-	100	100	1	150	200	-	20	-	-	1,800	0.01
NESREA Draft Effluent Standard For Petroleum Based & Allied Chemical Industries (2007)	_	0.5	0.1	0.5	2	0.5	_	_	_	_	_	_

The results of the metal determination are within the range of soil quality standards. As, Ni and Cd are comparable with those obtained by Adoki, (2012) for legacy spill site but Pb, Cr and Zn are different. The concentration of all the metals are similar to those of Onojake, *et al.*, (2014).

The presence of heavy metal in virtually all the soil samples is a gross indication that heavy metals occur naturally in the soil (Gilman *et al*., 1975).

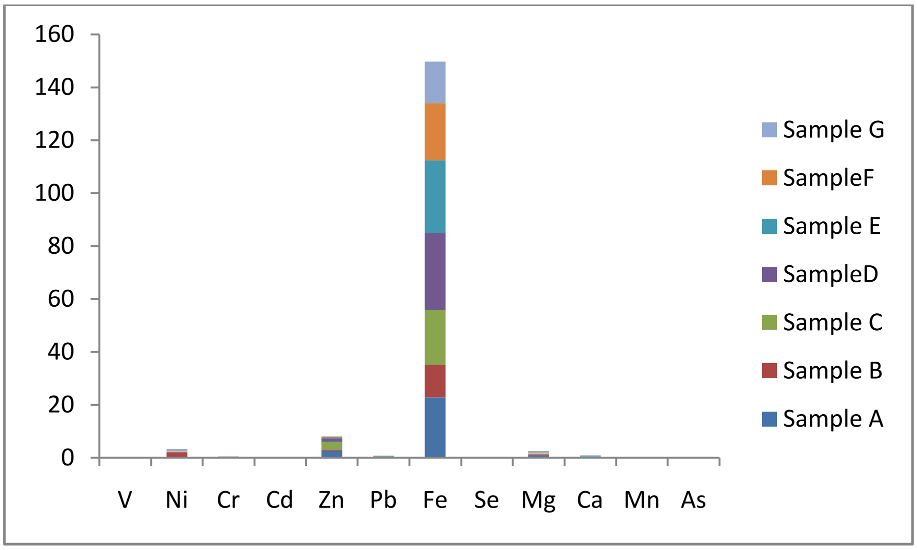

Fig 4.1 Variation of trace metals with soil samples (mg/kg).

In areas with high concentrations, metallic contamination of food and water probably lead to food poisoning. The emergence of the industrial age and large scale mining are major causes of heavy metal pollution in the environment (Gillman *et al*., 1975).

Among the metals, some appear to be essential at low concentration (calcium, magnesium, manganese, potassium, strontium, sodium etc) for biota growth and reproduction while there are a few non-essential but toxic (cadmium, copper, mercury and silver). Also a good number lies in the border line: zinc, lead, iron, chromium, nickel, arsenic and vanadium (Santra, 2005).

Virtually all metals including the essential metal micronutrients are toxic to aquatic organisms as well as humans if exposure levels are sufficiently high. The most undesirable trace elements -pollutants in ground water are mercury, lead, cadmium arsenic, barium, boron, selenium, chromium, uranium, sulphur and nitrogen (Egboka *et al*, 1989).

The highest concentrations of nickel and chromium occurred in sample B and Sample D respectively which are petroleum contaminated soils. They are observed in Figures 4.2 and 4.3 and they confirm the fact that petroleum is a rich source of trace elements like Ni, Cr, Cu, Zn, Na, Pb, Cd, Fe, Al, Sb, Sn, Mn, Ca and Mg (IOPOPAC, 1974).

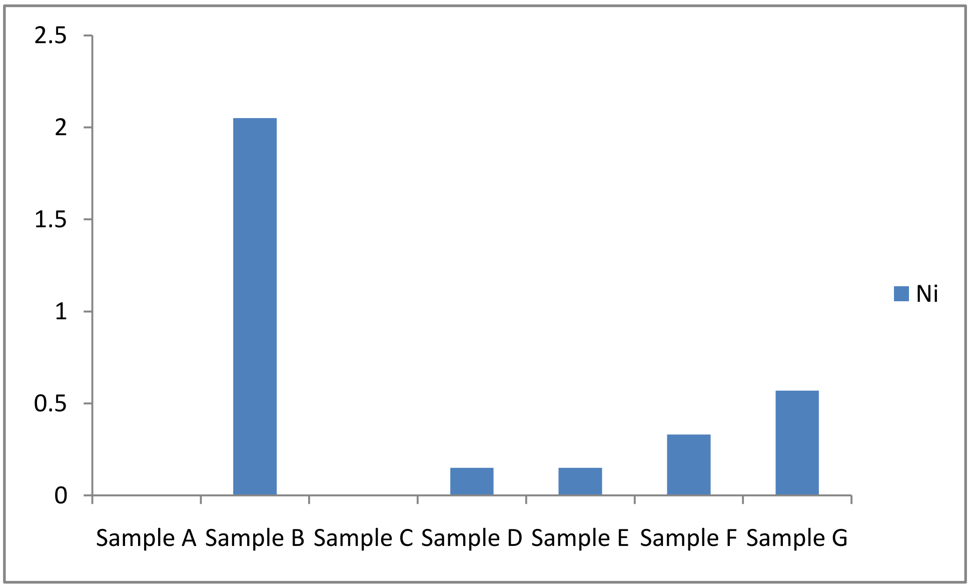

Fig 4.2 Variation of Ni with soil samples (mg/kg).

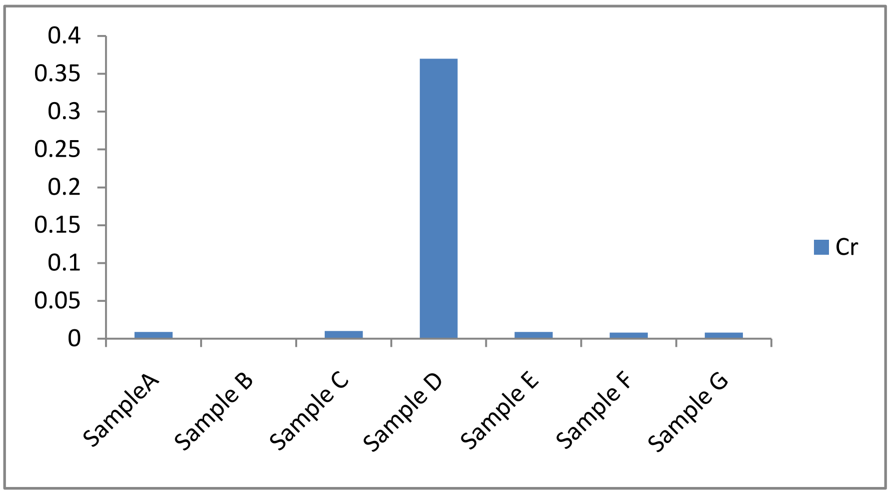

Fig 4.3 Variation of Cr with soil samples (mg/kg).

Highest levels of Cd, Zn, and Pb, were detected in samples D&E, C and E respectively (figures 4.4, 4.5and 4.6).

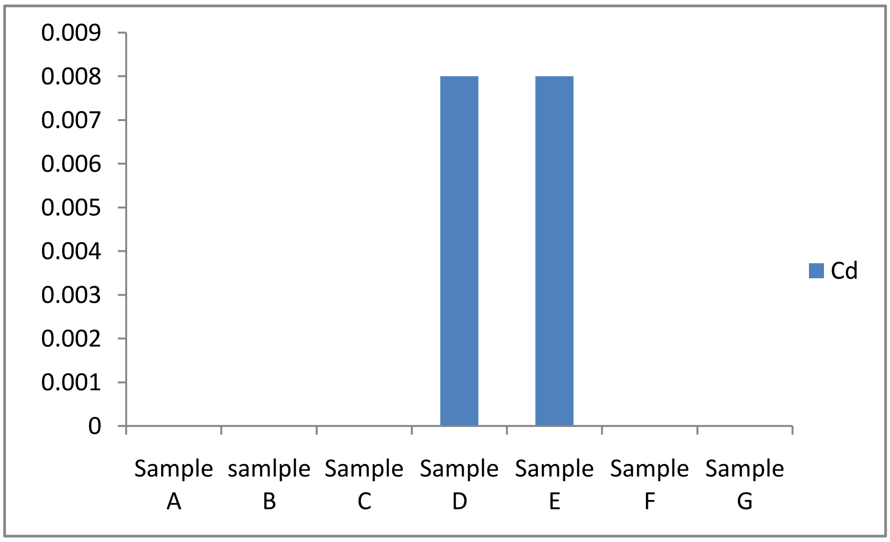

Fig 4.4 Variation of Cd with soil samples (mg/kg).

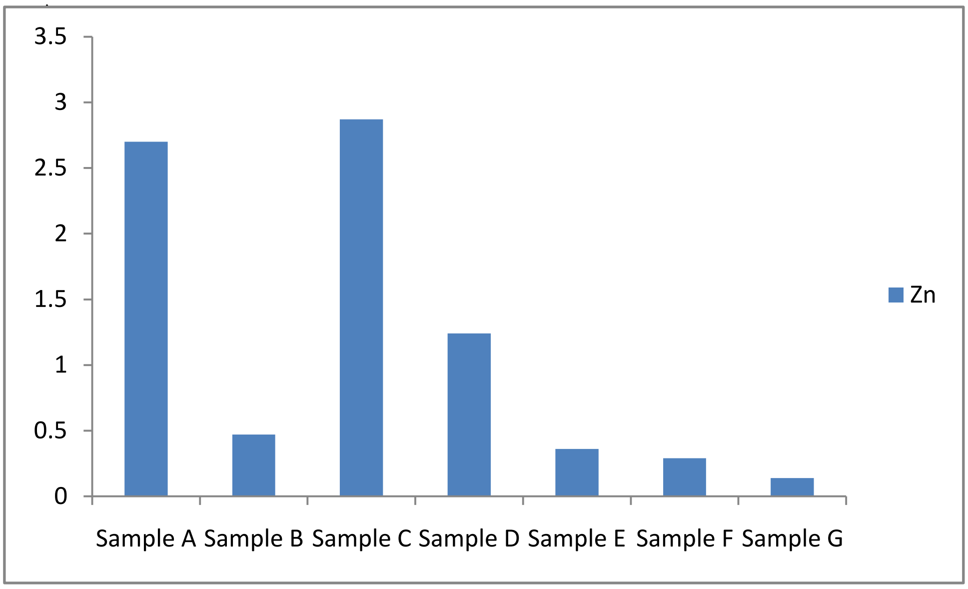

Fig 4.5 Variation of Zn with soil samples (mg/kg).

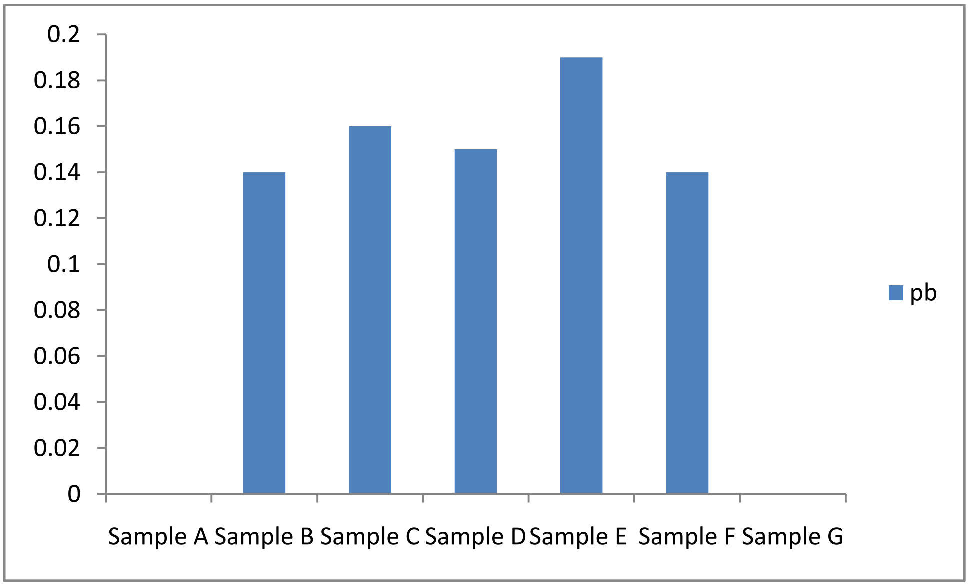

Fig 4.6 Variation of Pb with soil samples (mg/kg).

Also, highest levels of Fe, Mg, Ca and Mn were detected in samples D, A, A and C respectively (Figures 4.7, 4.8, 4.9 and 4.10).

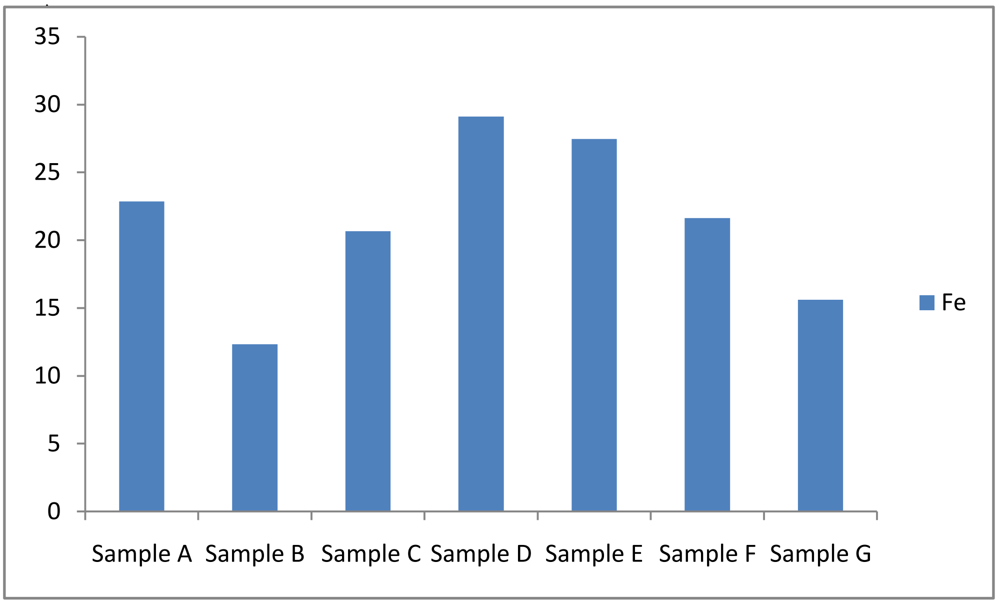

Fig 4.7 Variation of Fe with soil samples (mg/kg).

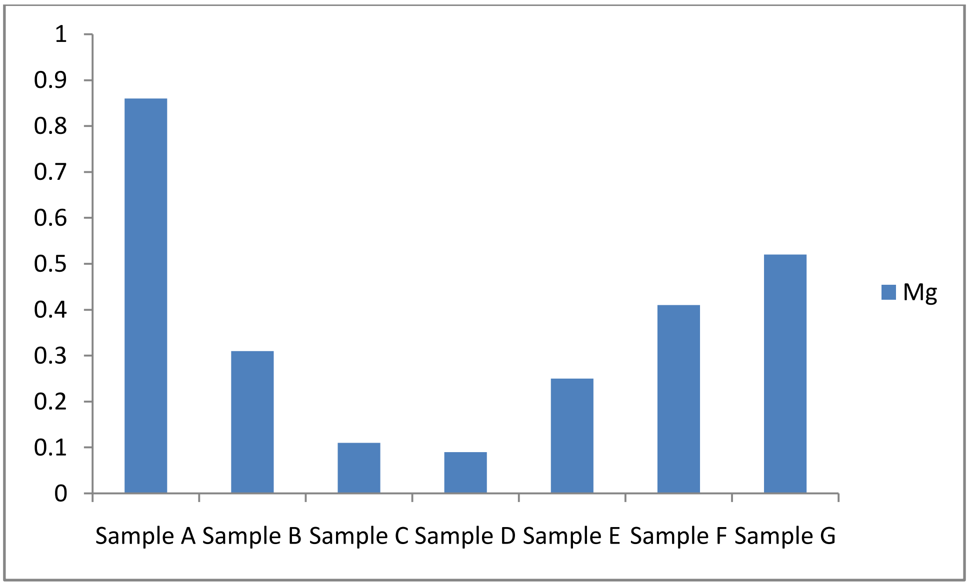

Fig 4.8 Variation of Mg with soil samples (mg/kg).

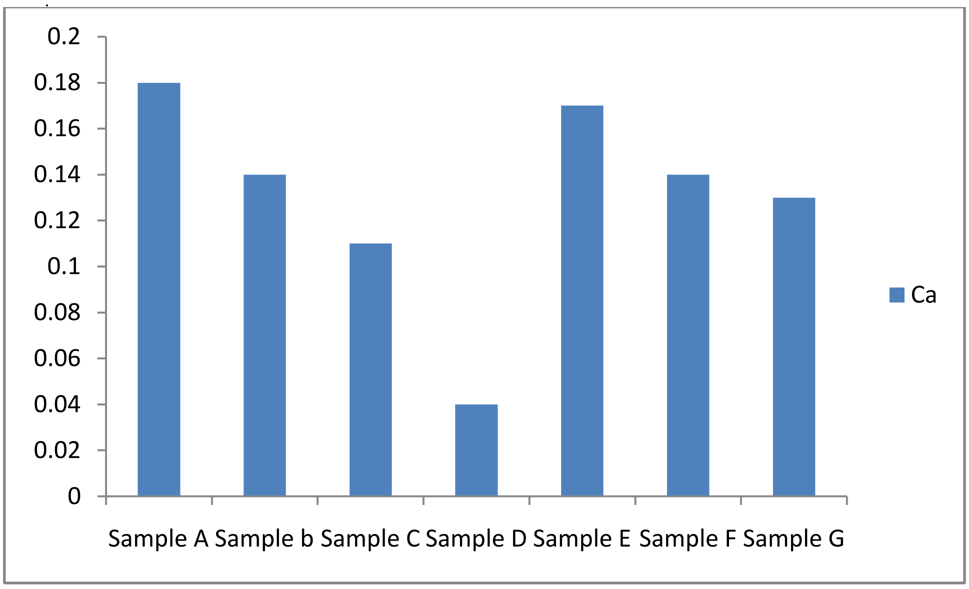

Fig 4.9 Variation of Ca with soil samples (mg/kg).

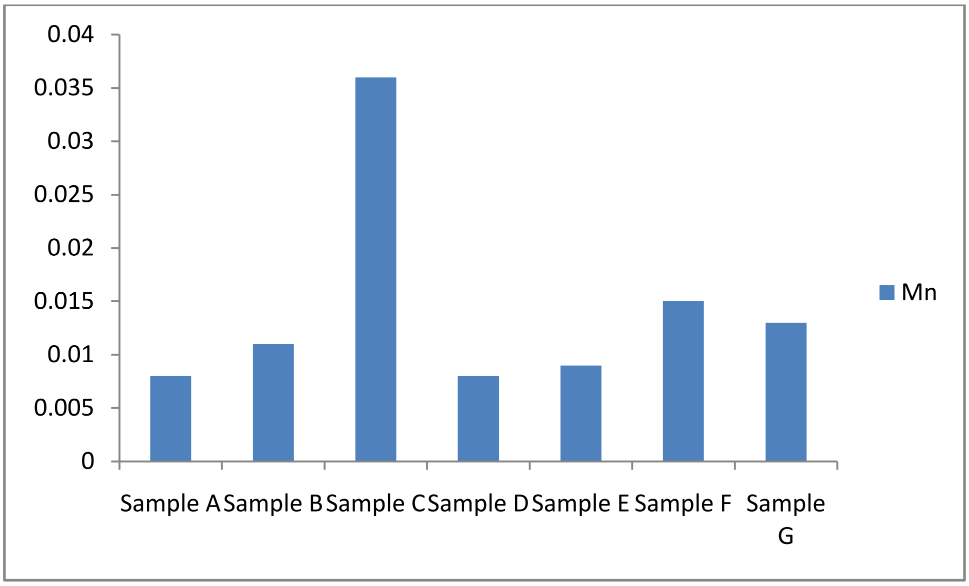

Fig 4.10 Variation of Mn with soil samples (mg/kg).

They are all petroleum contaminated soils with different soil properties and metal adsorption.

Heavy metal poisoning can result from food, air and water contaminated with lead (Wicke *et al.,* 2012). Lead induced inhibition of hemoglobin synthesis may lead to anemia. In addition, evidence for renal damage has been shown in some studies (Aydin *et al*., 2013).

The levels of iron are the highest when compared with levels of other trace metals in the result. Iron is traceable to corrosion of pipes conveying liquids (Fair *et al*., 1971) and is one of the trace metals found in crude oil (Fabec, 1985). Iron occurs in soil and water as Fe_2O_3 and Fe_3O_4 (Egboka *et al*., 1989). Magnesium, calcium and manganese are also present in the samples and biotransformation and bioaccumulation of these can lead to undesirable effects (Ademoroti, 1996). Ca, Mg and Mn are among the metals found to occur in petroleum (IOPOPAC, 1974). Limestone or Karstic terrains have also been reported to contain calcium and magnesium salts (Egboka *et al*., 1989). Mn is traceable to refuse incinerator, industrial scrubber water, paint formulation and mine drainage (Santra, 2005).

Cadmium in all the samples are lower than NESREA (National Environmental Standards and Regulations Enforcement Agency) Draft Effluent Standards for Petroleum Based and Allied Chemical Industries but continued deposition can result in toxic levels which lead to metal poisoning as well as stunted growth in plants (Gupt and Gupta, 1998, NIS 1985 and Ademoroti, 1996).

The concentration of chromium in sample D is higher than NESREA Standard. This can cause groundwater pollution when dissolved in infiltrating and percolating water (Egboka, *et al.,* 1989; Bhatia, 2001).Clinical effects of chromium toxicity are ulcer, perforation of nasal septum and respiratory cancer (Sharma, 2010).

Zinc concentrations in samples A and C are higher than NESREA Standard and can predispose man to metal fume fever, nephritis, anaemia and encephalitis (Hay, 1991).

The levels of nickel in sample B and sample G are higher than NESREA Standard and are traceable to industries of petroleum (Cempel and Nikel, 2006; Dara, 2008 ; Fabec, 1985). The target organs affected by nickel are pulmonary system and skin and the clinical effects are chronic rhinitis and sinusitis, respiratory cancer and dermatitis (Sharma, 2010).

Renal failure occur when the drinking water is polluted with cadmium and lead, liver cirrhosis to the pollution with copper and molybdenum, hair loss to the pollution with chromium and nickel and chronic anemia to the pollution with cadmium and copper (John *et al*., 2010).

4.9 Total Petroleum Hydrocarbon

The results of the total petroleum hydrocarbon are shown in Tables 4.9 to 4.15 and Figures 4.11- 4.17.

Table 4.9: Total petroleum hydrocarbon content of Sample A

Component	Name	Concentration (mg/kg)
C8	n-Octane	36.2501
C13	n-Tridecane	28.6524
C21	n-Heneicosane	255.1289
C23	n-Tricosane	300.9113
C36	n-Hexatriacontane	0.00

Table 4.10: Total petroleum hydrocarbon content of Sample B

Component	Name	Concentration (mg/kg)
C18	n-Octadecane	45.2412
C12	n-Dodecane	238.1888
C16	n-Hexadecane	35.8533
C37	n-Heptatriacontane	0.00

Table 4.11 Total petroleum hydrocarbon content of Sample C

Component	Name	Concentration (mg/kg)
C8	n-Octane	283.5023
C14	n-Tetradecane	25.5466
C16	n-Hexadecane	43.0247
C23	n-Tricosane	271.7028
C26	n-Hexacosane	2.6296

Table 4.12 Total petroleum hydrocarbon content of Sample D

Component	Name	Concentration (mg/kg)
C8	n-Octane	36.2501
C13	n-Tridecane	28.6524
C21	n-Heneicosane	255.1289
C23	n-Tricosane	300.9113
C36	n-Hexatriacontane	0.00

Table 4.13 Totalpetroleum hydrocarbon content of Sample E

Component	Name	Concentration (mg/kg)
C8	n-Octane	30.7240
C14	n-Tetradecane	16.0456
C16	n-Hexadecane	47.8746
C29	n-Nonacosane	18.6398
C32	n-Dotriacontane	50.0845
C37	n-Heptatriacontane	0.00
C39	n-Nonatriacontane	0.00

Table 4.14 Total petroleum hydrocarbon content of Sample F

Component	Name	Concentration (mg/kg)
C8	n-Octane	24.5640
C13	n-Tridecane	59.9962
C16	n-Hexadecane	35.9844
C20	n-Eicosane	0.00
C26	n-Hexacosane	5.0280
C29	n-Nonacosane	23.1911

Table 4.15 Totalpetroleumhydrocarbon content of Sample G

Component	Name	Concentration (mg/kg)
C8	n-Octane	54.8569
C15	n-pentacosane	26.5941
C24	n-Tetracosane	0.1719
C34	n-Tetratriacontane	25.9076
C39	n-Nonatriacontane	0.00

Different total petroleum hydrocarbons were detected in the samples analysed. Their levels were also determined; n-Octane(C_8), n-Tridecane(C_{13}), n-Heneicosane(C_{21}), n-Tricosane(C_{23}), n-Octadecane(C_{18}), n-Dodecane(C_{12}), n-Hexadecane(C_{16}), n-Tetradecane(C_{14}), n-Hexacosane(C_{26}), n-Nonacosane(C_{29}), n-Dotriacontane(C_{32}), n-

Heptatriacontane(C_{37}), n-Eicosane(C_{20}), n-Pentacosane(C_{25}), n-Tetracosane(C_{24}), n-Tetratriacontane(C_{34}) and n-Nonatriacontane($_{39}$) were determined in the samples.

Sample A contained n-Octane, n-Tridecane, n-Heneicosane, n-Tricosane and n-Hexatriacontane (Table 4.11) whereas Sample B contained n-Octadecane, n-Dodecane, n-Hexadecane and n-Heptatriacontane (Table 4.12).n-Octane, n-Tetradecane, n-Hexadecane , n-Tricosane and n-Hexacosane were found in Sample C (Table 4.13) and Sample D was found to contain n-Octane, n-Tridecane, n-Heneicosane, n-Tricosane and n-Hexatriacontane (Table 4.14). Presence of n-Octane,n-Tetradecane,n-Hexadecane, n-Nonacosane, n-Dotriacontane, n-Heptatriacontane and n-Nonatriacontane was detected in Sample E (Table 4.15) and Sample F showed presence of n-Octane, n-Tridecane, n-Hexadecane, n-Eicosane, n-Hexacosane and n-Nonacosane (Table 4.16). Sample G revealed the presence of n-Octane, n-Pentacosane, n-Tetracosane n-Tetratriacontane and n-Nonatriacontane(Table 4.17).

The total concentration of petroleum hydrocarbons in samples A,B,C,D,E,F and G are 620.9427mg/kg, 319.2833mg/kg, 626.4060mg/kg, 620.9427mg/kg, 163.3685mg/kg, 148.7637mg/kg and 107.5305mg/kg respectively. It increased in the following sequence, C>A,D>B>E>F>G. The TPH content of the samples are comparable with those of Adoki, (2012) but higher than those of Edori and Iyama, (2017) for abattoirs. Sample C (petroleum contaminated soil) has the highest total concentration of petroleum hydrocarbon while sample G (non- petroleum contaminated soil) has the lowest. This is attributed to petroleum contamination of the soil. Sample G was not collected from an area affected by petroleum contamination.

Tricosane in samples Aand D is the highest occuring followed by n-octane in sample C and Tricosane in sample C and then Hereicosane in samples A and D all petroleum contaminated soils (Asaolu,2000). All these occurred in levels greater than the amounts found in sample G (non-petroleum contaminated soil).N-Nonatriacontane appeared with levels of 0.00 in samples E and G i.e not detectable.The occurrence of petroleum hydrocarbons in sample G is traceable to contaminations from effluents of school laboratory (Cheremisinoff and Young, 1976).

4.10Phenol

The results of the analysis of phenol are recorded in Table 4.16.

Table 4.16 Phenol content of soil samples

sample	A	B	C	D	E	F	G
Phenol content(mg/kg)	0.9289	0.8610	1.8397	0.7285	1.1475	1.2932	0.9836

The results of analysis show the presence of phenol in all the samples. Highest level of phenol is obtained in sample C a petroleum contaminated soil, followed by sample F also a petroleum contaminated soil and sample E still a petroleum contaminated soil. Pollution of sample G may be traced to contamination by laboratory effluent. The presence of phenol in all the samples shows the possible contamination of virtually everything around us by phenol even foodstuffs. Higher levels are obtained near sources of pollution or in materials contaminated with phenol. Sources of phenol are petroleum (Kostecki and

Calabrese, 1989), coal tar (Finar, 1980; Murray, 1983) and burning of wood. Phenol is used as an antiseptic and disinfectant and in the preparation of dyes. drugs, bakelite etc (Finar,1980).

4.11 Benzene

The results of the benzene determination are shown in Table 4.17 and Figures 4.18 to 4.24

Table 4.17: Benzene content of soil samples

Samples	Benzene (ppm)
Sample A	0.8867
Sample B	0.2478
Sample C	1.0293
Sample D	0.4975
Sample E	0.2121
Sample F	0.2002
Sample G	0.1031

Benzene is present in all the samples including sample G which is not petroleum contaminated. However, sample G has the least concentration. Aromatic compounds occur naturally in petroleum and coal tar (Finar,1980 and Murray,1983) and are also traceable to laboratory and refinery effluents (Kostecki and Calabrese,1989). The presence of benzene in sample G is traceable to effluent from school laboratory. Benzene is known to cause cancer when inhaled or ingested (Sharma, 2010).

4.12 Oil and Grease

The results of oil and grease determination are presented in Table 4.18.

Table 4.18: Oil and grease content of soil samples

Sample Name	Wt of flask+ oil	Wt of flask	Wtof sample	% oil and grease
Sample A	63.832	62.943	4.50	19.756
Sample B	64.243	63.761	4.50	10.711
Sample C	60.286	59.431	4.50	19.000
Sample D	63.562	62.924	4.50	14.177
Sample E	60.426	59.873	4.50	12.289
Sample F	64.362	63.422	4.50	20.899
Sample G	60.186	59.886	4.50	6.667

Oil and grease are present in all the samples with the least concentration found in sample G. This is because sample G is not contaminated with petroleum which is the source of oil and grease. As observed by Dallyn (1953), chlorophyll destruction appears to be the major symptom of oil injury to green plants. When oil gets to leaf surface it penetrates the leaves thus interfering with its physiological functions mainly reducing transpiration and photosynthesis. Where oil pollution is light, leaves become yellow and drop soon after, but under heavy contamination, complete shedding of leaves results. The adverse effects of chlorosis and leaf fall is that the vigour of the plant may be reduced or death may result (Dallyn,1953).

Oil contamination on soil creates conditions which make nutrients unavailable to plants (Odu, 1977 and Imevbore, 1979).

Plants have a toxicity range of 10^4 -10^5 ppm for fresh crude oil (Moore *et al*., 1973) and experimental evidences show that with plants toxicity increases along the series, alkanes (paraffins)-cycloalkanes (naphthenes)-alkenes (olefins)-aromatics (Crafts and Riber, 1948; Havis, 1950).

4.13 Statistical Analysis

The results of the statistical analysis are shown in Tables 4.19 - 4.23.

Table 4.19: Raw data for metals and organic matter

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G
V	0.001	0.001	0.001	0.001	0.001	0.001	0.001
	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Ni	0.05	2.04	0.04	0.12	0.14	0.3	0.57
	0.04	2.06	0.05	0.18	0.16	0.36	0.57
Cr	0.009	0.004	0.01	0.36	0.009	0.009	0.007
	0.009	0.005	0.01	0.38	0.009	0.007	0.009
Cd	0.004	0.003	0.005	0.007	0.008	0.004	0.005
	0.005	0.005	0.004	0.009	0.008	0.003	0.003
Zn	2.5	0.46	2.85	1.22	0.34	0.29	0.17
	2.9	0.48	2.89	1.26	0.38	0.29	0.11
Pb	0.02	0.16	0.16	0.13	0.19	0.11	0.02
	0.01	0.12	0.16	0.17	0.19	0.17	0.01
Fe	22.86	12.34	20.65	29.01	27.45	21.66	15.6
	22.88	12.3	20.69	29.21	27.48	21.62	15.62
Se	0.001	0.001	0.001	0	0	0.001	0.001
	0	0.001	0.001	0.001	0	0.001	0
Mg	0.84	0.32	0.11	0.09	0.23	0.4	0.5
	0.88	0.3	0.11	0.09	0.27	0.42	0.54
Ca	0.19	0.16	0.11	0.01	0.15	0.14	0.14
	0.17	0.12	0.11	0.07	0.19	0.14	0.12
Mn	0.007	0.012	0.034	0.009	0.009	0.013	0.012
	0.009	0.01	0.038	0.007	0.009	0.017	0.014
As	0.01	0	0	0.01	0	0.01	0.01
	0	0	0.01	0.01	0	0.01	0

	ORGANIC MATTER	
Sample A	24.74	24.94
Sample B	26.02	26.02
Sample C	18.39	18.43
Sample D	21.36	21.40
Sample E	18.72	18.70
Sample F	18.42	18.40
Sample G	12.59	12.55

Table 4.20: The statistical analysis of metals using SPSS 17

		V	Ni	Cr	Cd	Zn	Pb	Fe	Se	Mg
Mean	**Sample A**	0.001	0.045	0.009	0.005	2.700	0.015	22.870	0.001	0.860
Std. Deviation		0.000	0.000	0.007	0.000	0.001	0.283	0.007	0.014	0.001
Std. Error		0.000	0.005	0.000	0.001	0.200	0.005	0.010	0.001	0.020
Mean	**Sample B**	0.001	2.050	0.005	0.004	0.470	0.140	12.320	0.001	0.310
Std. Deviation		0.000	0.000	0.014	0.001	0.001	0.014	0.028	0.028	0.000
Std. Error		0.000	0.010	0.001	0.001	0.010	0.020	0.020	0.000	0.010
Mean	**Sample C**	0.001	0.045	0.010	0.005	2.870	0.160	20.670	0.001	0.110
Std. Deviation		0.000	0.000	0.007	0.000	0.001	0.028	0.000	0.028	0.000
Std. Error		0.000	0.005	0.000	0.001	0.020	0.000	0.020	0.000	0.000
Mean	**Sample D**	0.001	0.150	0.370	0.008	1.240	0.150	29.110	0.001	0.090
Std. Deviation		0.000	0.000	0.042	0.014	0.001	0.028	0.028	0.141	0.001
Std. Error		0.000	0.030	0.010	0.001	0.020	0.020	0.100	0.001	0.000
Mean	**Sample E**	0.001	0.150	0.009	0.008	0.360	0.190	27.465	0.000	0.250
Std. Deviation		0.000	0.000	0.014	0.000	0.000	0.028	0.000	0.021	0.000
Std. Error		0.000	0.010	0.000	0.000	0.020	0.000	0.015	0.000	0.020
Mean	**Sample F**	0.001	0.330	0.008	0.004	0.290	0.140	21.640	0.001	0.410
Std. Deviation		0.000	0.000	0.042	0.001	0.001	0.000	0.042	0.028	0.000
Std. Error		0.000	0.030	0.001	0.001	0.000	0.030	0.020	0.000	0.010
Mean	**Sample G**	0.001	0.570	0.008	0.004	0.140	0.015	15.610	0.001	0.520
Std. Deviation		0.000	0.000	0.000	0.001	0.001	0.042	0.007	0.014	0.001
Std. Error		0.000	0.000	0.001	0.001	0.030	0.005	0.010	0.001	0.020

Table 4.21 Descriptive

		N	Mean
Sample A	V	2	.0010000
	Ni	2	.0450000
	Cr	2	.0090000
	Cd	2	.0045000
	Zn	2	2.7000000
	Pb	2	.0150000
	Fe	2	22.8700000
	Se	2	.0005000
	Mg	2	.8600000
	Ca	2	.1800000
	Mn	2	.0080000
	Organic Matter	2	.0050000
	Organic Matter	2	24.8400000
	Total	26	3.9644615
Sample B	V	2	.0010000
	Ni	2	2.0500000
	Cr	2	.0045000
	Cd	2	.0040000
	Zn	2	.4700000
	Pb	2	.1400000
	Fe	2	12.3200000
	Se	2	.0010000
	Mg	2	.3100000
	Ca	2	.1400000
	Mn	2	.0110000
	Organic Matter	2	.0000000
	Organic Matter	2	26.0200000
	Total	26	3.1901154
Sample C	V	2	.0010000
	Ni	2	.0450000
	Cr	2	.0100000
	Cd	2	.0045000
	Zn	2	2.8700000
	Pb	2	.1600000
	Fe	2	20.6700000
	Se	2	.0010000
	Mg	2	.1100000
	Ca	2	.1100000
	Mn	2	.0360000

	Organic Matter	2	.0050000
	Organic Matter	2	18.4100000
	Total	26	3.2640385
Sample D	V	2	.0010000
	Ni	2	.1500000
	Cr	2	.3700000
	Cd	2	.0080000
	Zn	2	1.2400000
	Pb	2	.1500000
	Fe	2	29.1100000
	Se	2	.0005000
	Mg	2	.0900000
	Ca	2	.0400000
	Mn	2	.0080000
	Organic Matter	2	.0100000
	Organic Matter	2	21.3800000
	Total	26	4.0428846
Sample E	V	2	.00100000
	Ni	2	.15000000
	Cr	2	.00900000
	Cd	2	.00800000
	Zn	2	.36000000
	Pb	2	.19000000
	Fe	2	27.46500000
	Se	2	.00000000
	Mg	2	.25000000
	Ca	2	.17000000
	Mn	2	.00900000
	Organic Matter	2	.00000000
	Organic Matter	2	18.71000000
	Total	26	3.64015385
Sample F	V	2	.0010000
	Ni	2	.3300000
	Cr	2	.0080000
	Cd	2	.0035000
	Zn	2	.2900000
	Pb	2	.1400000
	Fe	2	21.6400000
	Se	2	.0010000
	Mg	2	.4100000
	Ca	2	.1400000
	Mn	2	.0150000
	Organic Matter	2	.0100000
	Organic Matter	2	18.4100000
	Total	26	3.1845000
Sample G	V	2	.0010000
	Ni	2	.5700000
	Cr	2	.0080000
	Cd	2	.0040000

Zn	2	.1400000
Pb	2	.0150000
Fe	2	15.6100000
Se	2	.0005000
Mg	2	.5200000
Ca	2	.1300000
Mn	2	.0130000
Organic Matter	2	.0050000
Organic Matter	2	12.5700000
Total	26	2.2758846

		Sum of Squares	Df	Mean Square	F	Sig.
Sample A	Between Groups	1887.613	12	157.301	20176.158	.000
	Within Groups	.101	13	.008		
	Total	1887.714	25			
Sample B	Between Groups	1402.166	12	116.847	505579.201	.000
	Within Groups	.003	13	.000		
	Total	1402.169	25			
Sample C	Between Groups	1271.932	12	105.994	549302.779	.000
	Within Groups	.003	13	.000		
	Total	1271.934	25			
Sample D	Between Groups	2187.484	12	182.290	90433.871	.000
	Within Groups	.026	13	.002		
	Total	2187.510	25			
Sample E	Between Groups	1864.822	12	155.402	621607.194	.000
	Within Groups	.003	13	.000		
	Total	1864.825	25			
Sample F	Between Groups	1351.570	12	112.631	304375.964	.000
	Within Groups	.005	13	.000		
	Total	1351.575	25			
Sample G	Between Groups	669.948	12	55.829	185786.933	.000
	Within Groups	.004	13	.000		
	Total	669.952	25			

4.23: Metals and organic matter results expressed as mean ±standard deviation

	V	Ni	Cr	Cd	Zn	Pb	Fe	Se	Mg	Ca
Sample A	0.001±0.00	0.045±0.00	0.009±0.00	0.005±0.00	2.700±0.28	0.015±0.01	22.870±0.01	0.001±0.00	0.860±0.03	0.
Sample B	0.001±0.00	2.05±0.01	0.005±0.00	0.004±0.00	0.470±0.01	0.140±0.03	12.320±0.03	0.001±0.00	0.310±0.01	0.
Sample C	0.001±0.00	0.045±0.01	0.010±0.00	0.005±0.00	2.870±0.03	0.160±0.00	20.670±0.03	0.001±0.00	0.110±0.00	0.
Sample D	0.001±0.00	0.15±0.04	0.370±0.01	0.008±0.00	1.240±0.03	0.150±0.03	29.110±0.14	0.001±0.00	0.090±0.00	0.
Sample E	0.001±0.00	0.15±0.01	0.009±0.00	0.008±0.00	0.360±0.03	0.190±0.00	27.465±0.02	0.000±0.00	0.250±0.03	0.
Sample F	0.001±0.00	0.33±0.04	0.008±0.00	0.004±0.00	0.290±0.00	0.140±0.04	21.640±0.03	0.001±0.00	0.410±0.01	0.
Sample G	0.001±0.00	0.57±0.00	0.008±0.00	0.004±0.00	0.140±0.04	0.015±0.01	15.610±0.01	0.001±0.00	0.520±0.03	0.

Twelve metal elements were statistically analyzed for samples A, B, C, D, E, F, and G. The mean, standard deviation and standard error of mean was statistically analyzed and presented independently of the table above. Iron was found to be highest in the sample with mean values of 22.87, 12.32, 20.67, 29.11, 27.46, 21.64 and 15.61ppm respectively for samples A,B,C,D,E,F and G respectively. Vanadium and selenium were found to be lowest with mean value of 0.001ppm in sample A, B, C, D, E,F and G respectively.

The result showed that sample D had the highest amount of chromium (0.37ppm) while the highest amount of. Lead was found in sample E. Generally, the results which can be presented as mean ± standard deviation were found to be significant at P=0.05.

The statistical evaluation of the organic matter showed that sample B (26.02ppm) contained the highest level of organic matter followed by sample A (24.84ppm) while the least value of organic matter was found in sample G with a value of 12.57.

4.14 Oil Adsorption Studies (Management of Petroleum Contaminated Soil or Oil Spillage)

Tables 4.24- 4.26 showed the results of adsorption of crude oil with bamboo particles of different sizes with time.

The trend or pattern followed are expressed by graphs found in Figures 4.25-4.27 respectively.

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Table 4.24: Adsorption of oil by 2mm bamboo particle size

Time(minute)	Adsorption(g/g)
5	1.92
10	2.642
30	3.13
40	**3.52**

Table 4.25: Adsorption of oil by 1mm bamboo particle size

Time(minute)	Adsorption(g/g)
10	3.44
20	3.47
30	3.34
40	2.11

Table 4.26 Adsorption of oil by 0.425 mm bamboo particle size

Time (minute)	Adsorption (g/g)
10	3.15
20	3.18
30	3.61

40	3.68

Crude oil adsorption is expressed in terms of the ratio of the mass of crude oil retained to that of bamboo particles. Mass of crude oil retained comprises mass of crude oil adsorbed by the bamboo particles and that adhered to the bamboo particles surface and between the particles.

Crude Oil Adsorption(oil/g bamboo particles)

$$= \frac{\text{Mass of crude oil retained by the bamboo particles}}{\text{Mass of bamboo particle}}$$

The rate of adsorption is taken as the slope of the linear portion of the adsorption time curve. Adsorption time curves for various particle sizes of bamboo are Figures 4.25- 4.27.

Figure 4.25 shows a sharp increase between 5minutes and10minutes, then a slower increase within the rest of the time.

Figure 4.26 shows a slight increase between 10 minutes and 20 minutes, then a gradual increase between 20 minutes and 30 minutes and a sharp drop subsequently (between 30 minutes and 40 minutes)

Figure 4.27 shows a slow increase between 15 minutes and 20 minutes , sharp increase between 20 minutes and 30 minutes, and then slower increase between 30 minutes and 40 minutes .

The profile of adsorption of crude oil is due to concentration difference which acts as the driving farce.

The difference between the concentration of crude oil in the bamboo particles at the beginning of adsorption and that at equilibrium is high. This subsequently decreases to zero at equilibrium adsorption of oil.

Effect of the particle size of the bamboo on the adsorption of crude oil is shown in the graphs (Figures 4.25- 4.27).As the particle size is increased from 0.425mm to 2mm, the equilibrium adsorption of oil decreases from 3.68 to 3.52. This shows an increase in the level of oil adsorption for the 0.425mm particle size bamboo relative to the 2mm particle size bamboo. This confirms the fact that finely divided substances have large surface areas for increased adsorption (Brown, 1976).

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY

Oil spillage does indeed causes oily and chemically polluted soil and aforestation. It hampers nutrient availability to plants, pollutes surrounding water supplies and aquatic biota.

Elevation of trace metal and organic matter content as well as petroleum hydrocarbons, benzene, phenol, oil and grease in the petroleum contaminated soils were observed.

The results of the trace metals and organic matter which can be presented as mean ± standard deviation were found to be significant at P= 0.05.

Adsorption of oil increases with decrease in particle size of the absorbing material.

5.2 Conclusion

Once the spillage is detected, clean up should be initiated using bamboo particles which are effective in adsorbing oil .

Continuous monitoring of the levels of pollution of the soil and the surrounding water supplies should also be embarked upon. This will stem the tide of the menace by informing on the dangers posed by the action.

Government involvement is also necessary so as to achieve a greater degree of response.

More decrees protecting our environment should be promulgated and enforced by government.

5.3 Contribution to Knowledge

The study confirmed that the study area was polluted with petroleum hydrocarbons, benzene, phenol, trace metals, oil and grease. It was established that petroleum contamination of soil affected organic matter, bulk density, moisture, colour and water holding capacity of the soils. The study established that management of oil spillage can be sufficiently accomplished by covering with bamboo particles which absorb the oil and make way for a cleaner and fertile environment for man, plant and animals.

5.4 Recommendations

Contaminated soil is found most often not only near waste disposal sites and chemical plants but also near pipelines and gasoline stations. Removal of oil from petroleum contaminated soil can be accomplished by covering with bamboo particles which carry out the removal by adsorption process. Bamboo is relatively available, affordable and environmentally friendly.

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Client: UJU
Client ID: DA134
Collected: 25/09/15
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: TPH standard concentration.cpt
Data file: uju sample A.ASC ()
Sample: sample A TPH
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

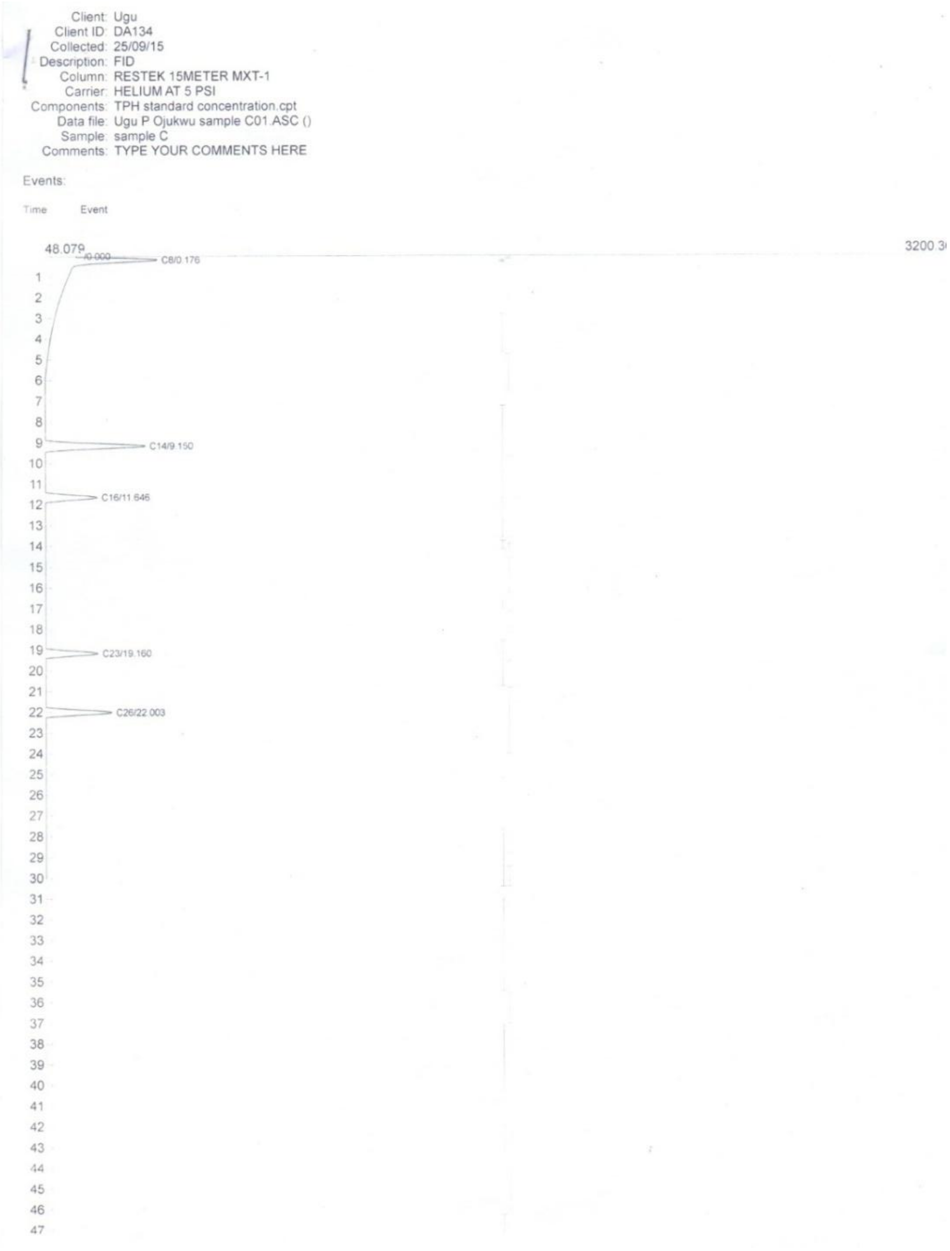
Figure 4.11: Gas chromatogram of sample A for TPH

Client: Uju
Client ID: DA134
Collected: 25/09/15
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: TPH standard concentration.cpt
Data file: Uju P ojukwu sample B.ASC ()
Sample: sample B TPH
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

Figure 4.12 : Gas chromatogram of sample B for TPH



Client: Ugu
Client ID: DA134
Collected: 25/09/15
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: TPH standard concentration.cpt
Data file: Ugu P Ojukwu sample C01.ASC ()
Sample: sample C
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

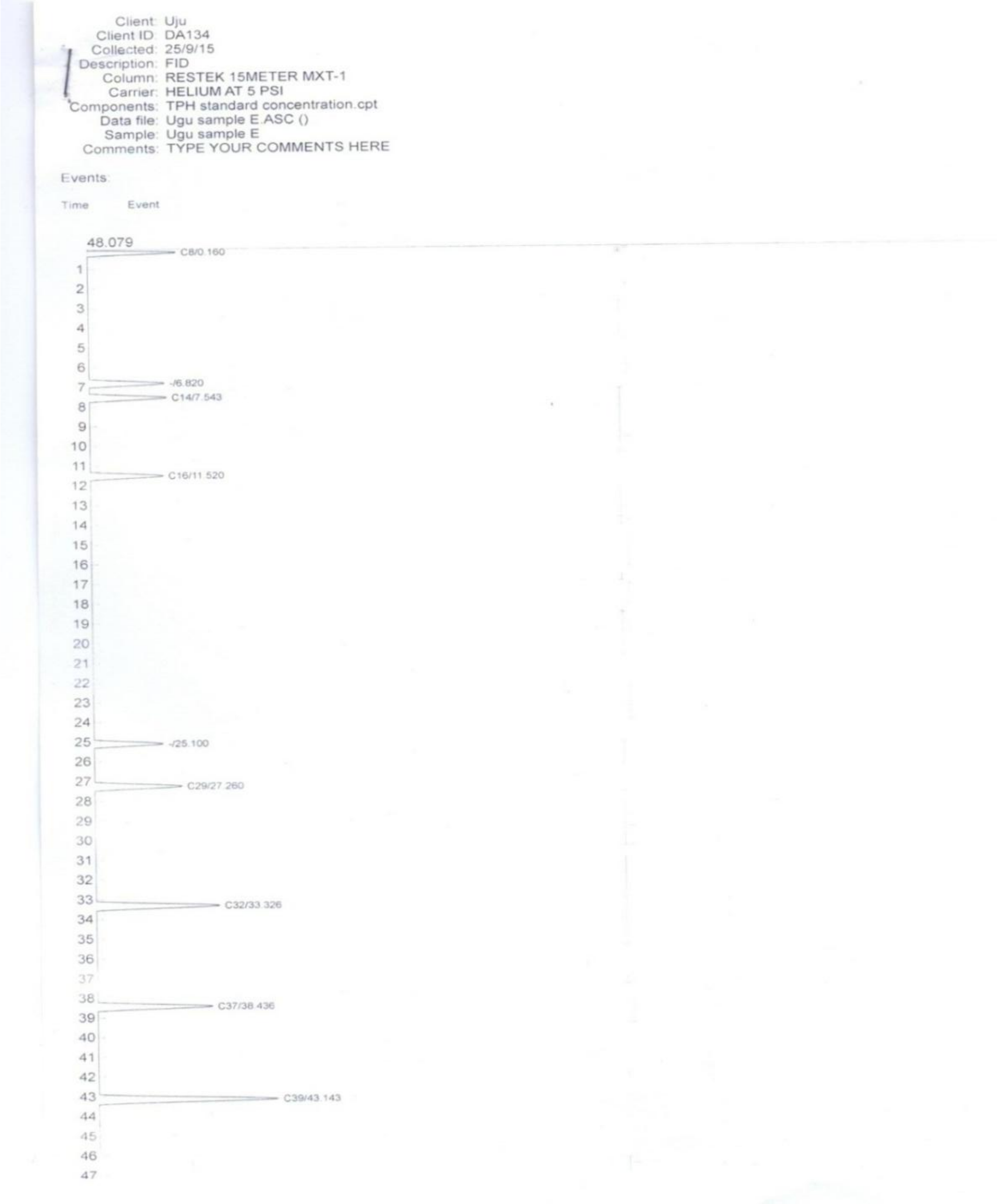
Figure 4.13:Gas chromatogram of sample C for TPH

Client: Uju
Client ID: DA134
Collected: 25/09/15
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: TPH standard concentration.cpt
Data file: Uju P Ojukwu sample D TPH01.ASC ()
Sample: sample D TPH
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

Figure 4.14 : Gas chromatogram of sample D for TPH



Client: Uju
Client ID: DA134
Collected: 25/9/15
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: TPH standard concentration.cpt
Data file: Ugu sample E.ASC ()
Sample: Ugu sample E
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

Figure 4.15 : Gas chromatogram of sample E for TPH

Client: Uju
Client ID: DA134
Collected: 1/10/15
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: TPH standard concentration.cpt
Data file: uju sample F TPH.ASC ()
Sample: sample F TPH
Comments: TYPE YOUR COMMENTS HERE

Events

Time Event

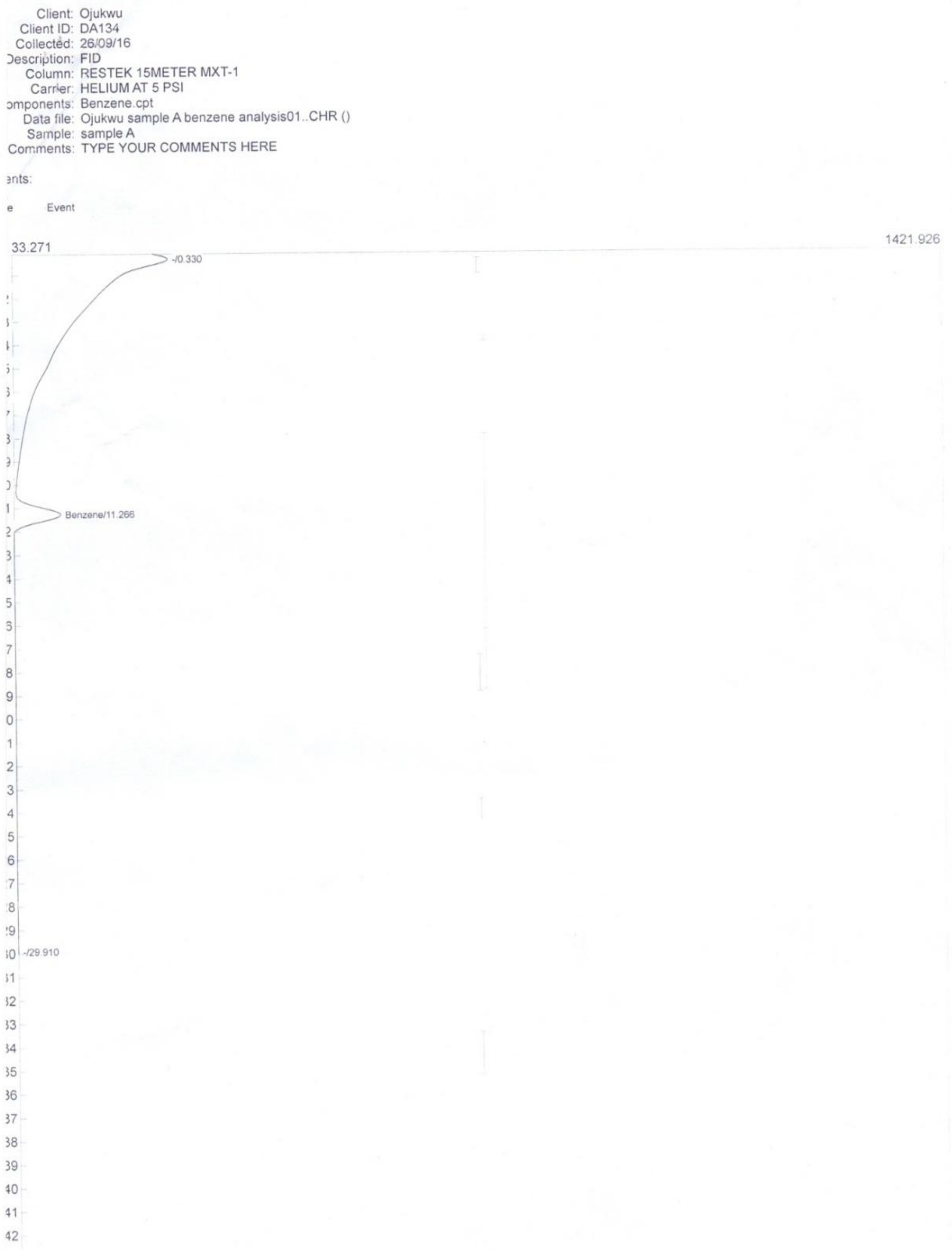
Figure 4.16 : Gas chromatogram of sample F for TPH

Client: Ojukwu
Client ID: DA134
Collected: 17/09/15
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: TPH standard concentration.cpt
Data file: Ojukwu sample G ()
Sample: sample G
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

Figure 4.17 : Gas chromatogram of sample G for TPH

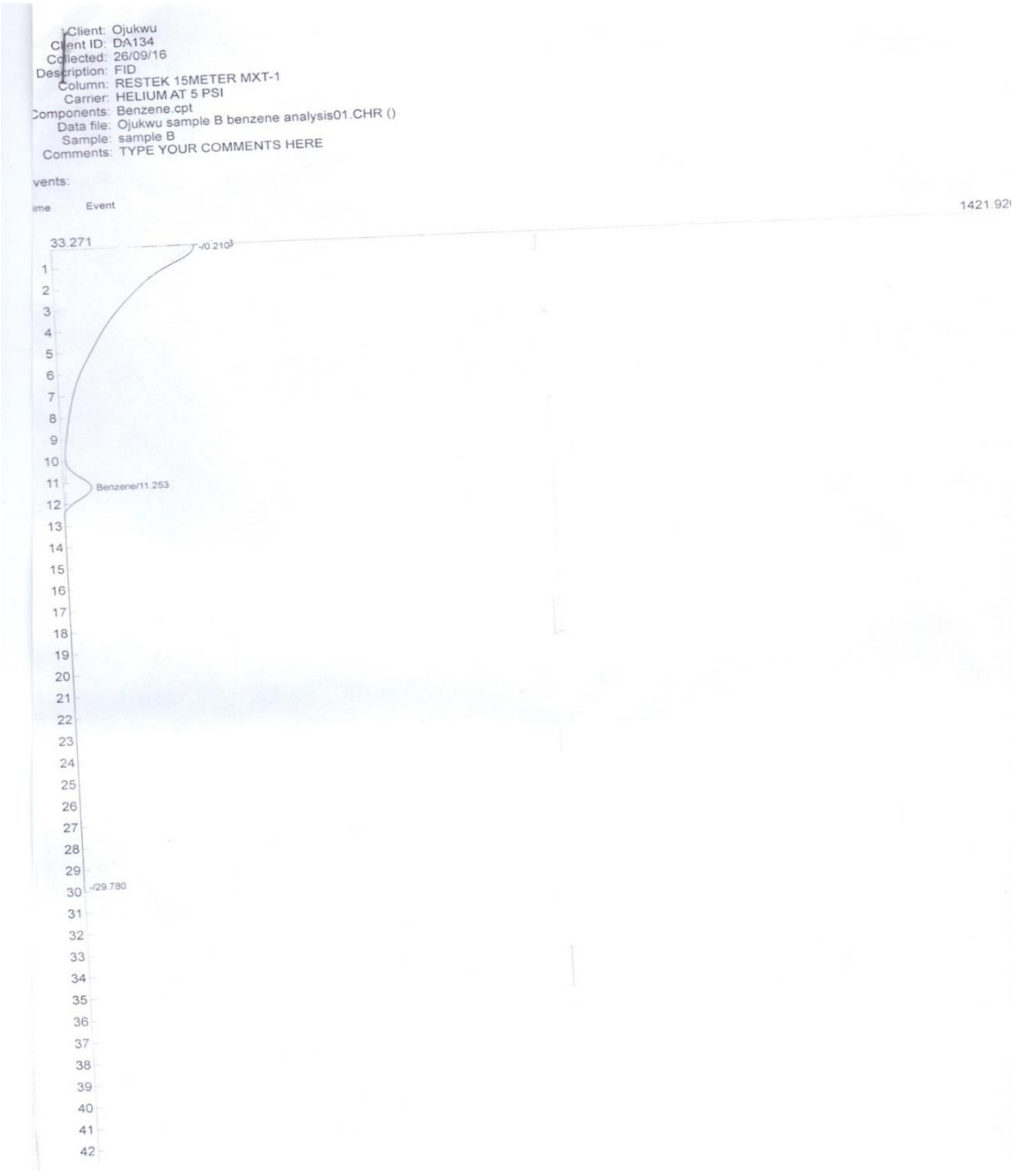


Client: Ojukwu
Client ID: DA134
Collected: 26/09/16
escription: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
omponents: Benzene.cpt
Data file: Ojukwu sample A benzene analysis01..CHR ()
Sample: sample A
Comments: TYPE YOUR COMMENTS HERE

ents:

e Event

Figure 4.18 : Gas chromatogram of sample A for benzene

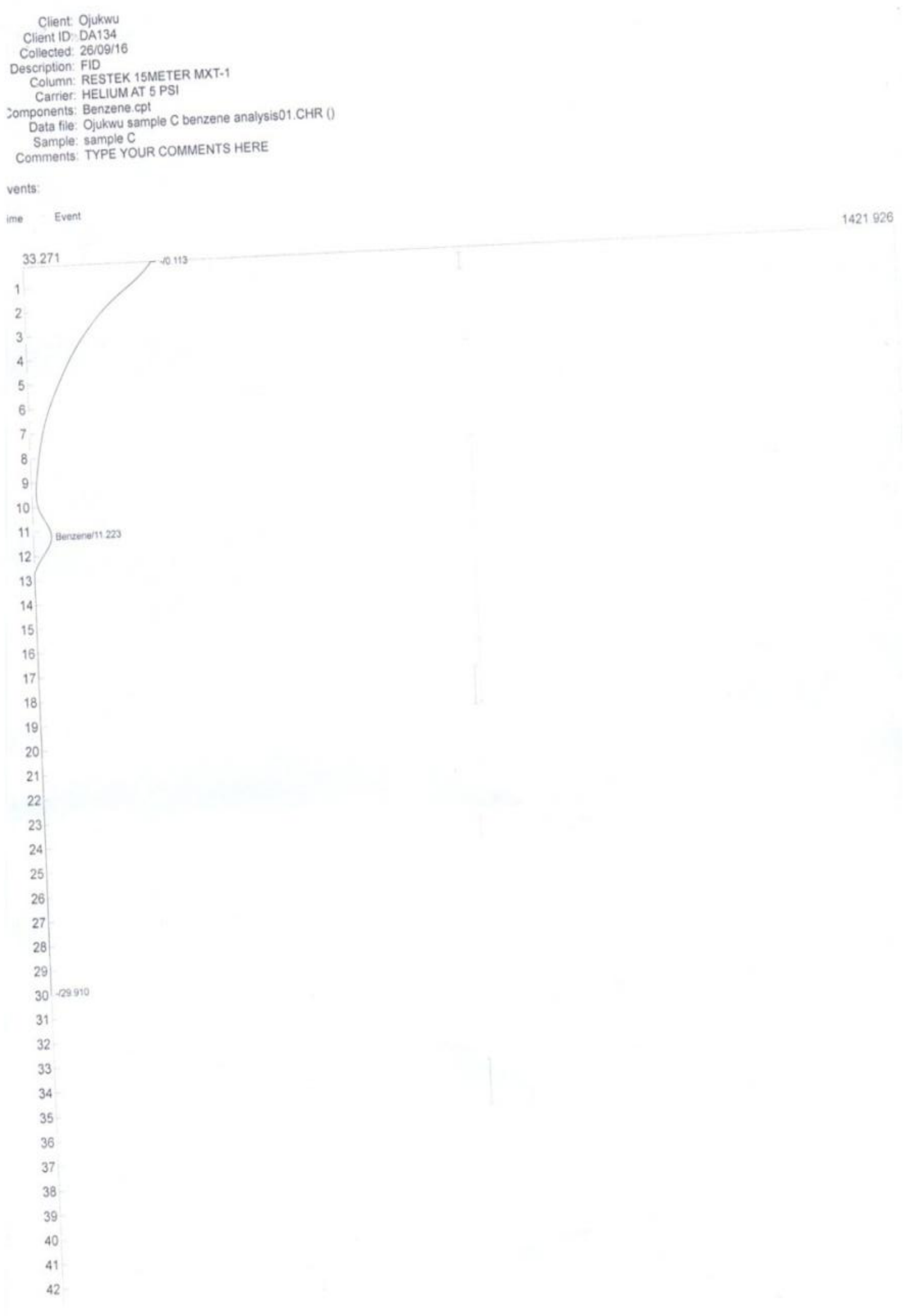


Client: Ojukwu
Client ID: DA134
Collected: 26/09/16
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: Benzene.cpt
Data file: Ojukwu sample B benzene analysis01.CHR ()
Sample: sample B
Comments: TYPE YOUR COMMENTS HERE

vents:

ime Event

Figure 4.19 : Gas chromatogram of sample B for benzene

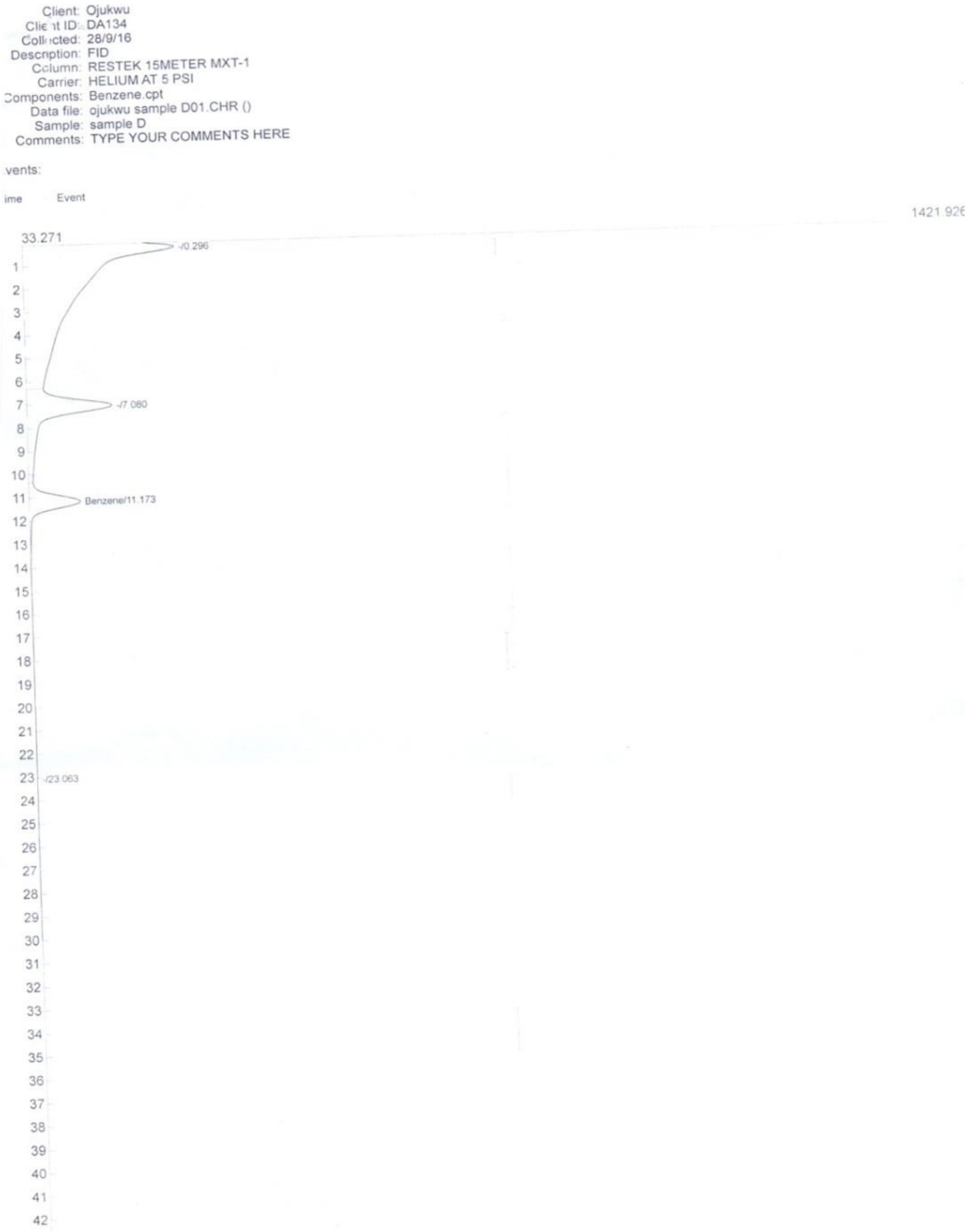


Client: Ojukwu
Client ID: DA134
Collected: 26/09/16
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
omponents: Benzene.cpt
Data file: Ojukwu sample C benzene analysis01.CHR ()
Sample: sample C
Comments: TYPE YOUR COMMENTS HERE

vents:

ime Event

Figure 4.20 : Gas chromatogram of sample C for benzene



Client: Ojukwu
Client ID: DA134
Collected: 28/9/16
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: Benzene.cpt
Data file: ojukwu sample D01.CHR ()
Sample: sample D
Comments: TYPE YOUR COMMENTS HERE

vents:

ime Event

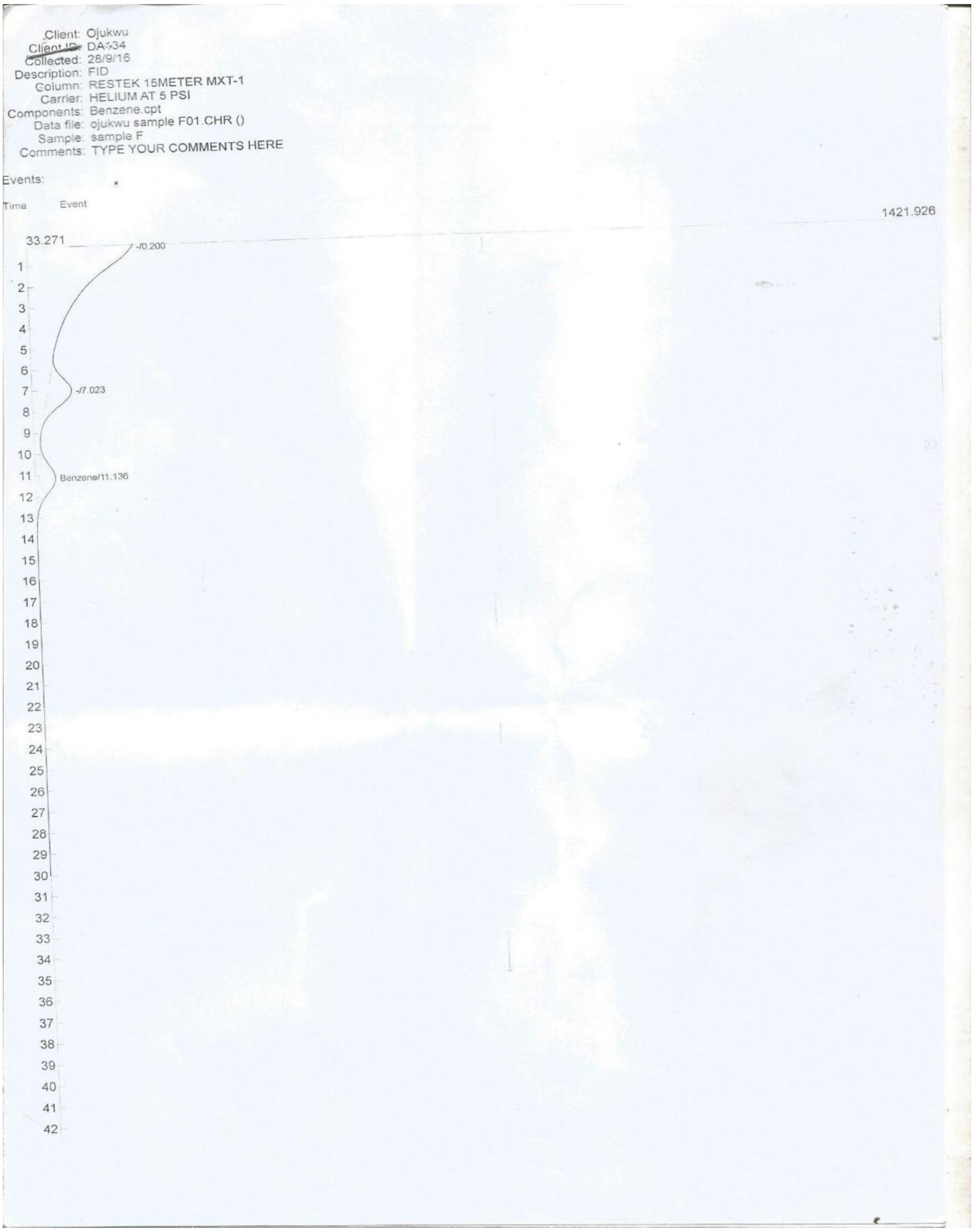
Figure 4.21 : Gas chromatogram of sample D for benzene

Client: Ojukwu
Client ID: DA134
Collected: 28/9/16
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: Benzene.cpt
Data file: ojukwu sample E01.CHR ()
Sample: sample E
Comments: TYPE YOUR COMMENTS HERE

vents:

ime Event

Figure 4.22 : Gas chromatogram of sample E for benzene

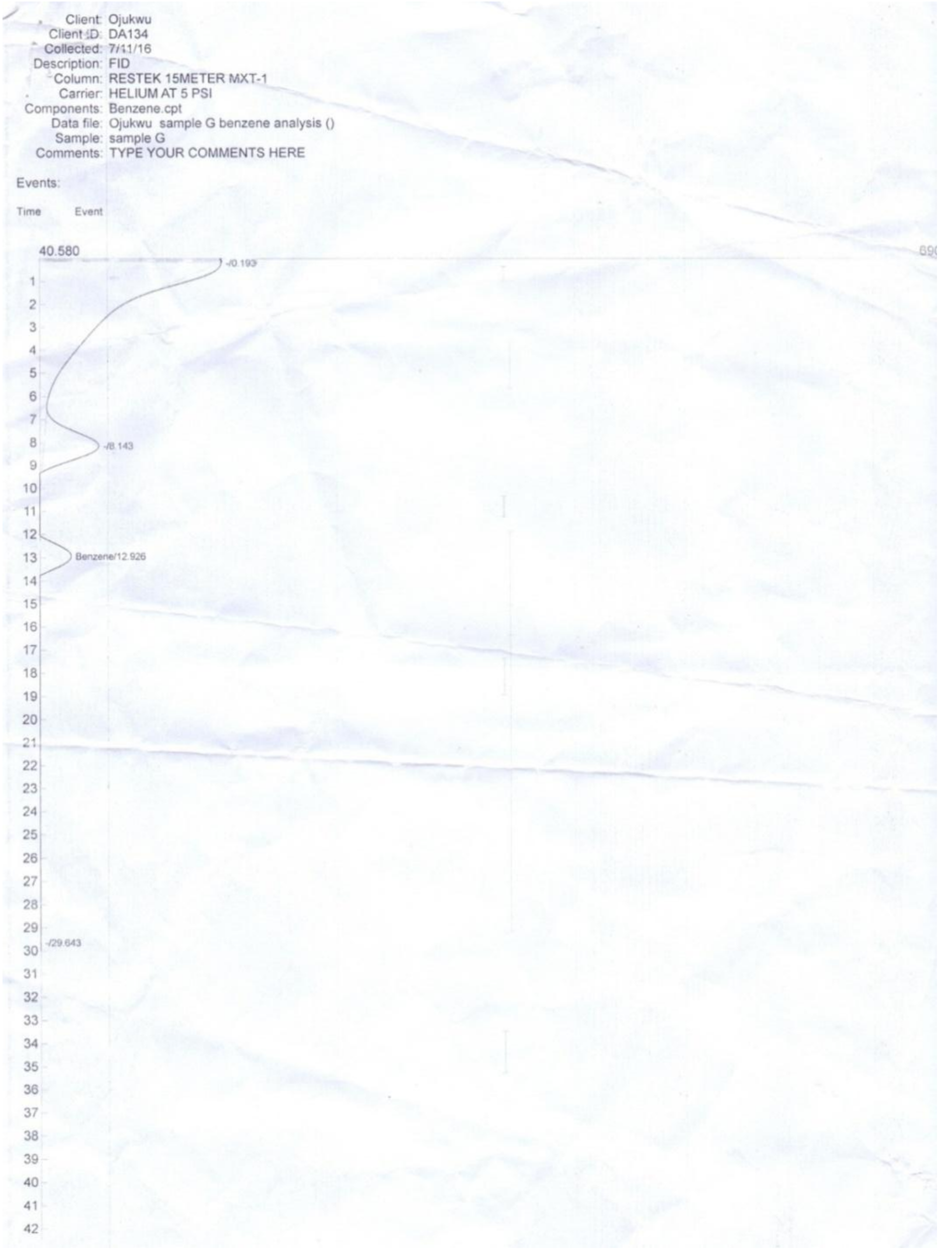


Client: Ojukwu
Client ID: DA134
Collected: 28/9/16
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: Benzene.cpt
Data file: ojukwu sample F01.CHR ()
Sample: sample F
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

Figure 4.23: Gas chromatogram of sample F for benzene



Client: Ojukwu
Client ID: DA134
Collected: 7/11/16
Description: FID
Column: RESTEK 15METER MXT-1
Carrier: HELIUM AT 5 PSI
Components: Benzene.cpt
Data file: Ojukwu sample G benzene analysis ()
Sample: sample G
Comments: TYPE YOUR COMMENTS HERE

Events:

Time Event

Figure 4.24: Gas chromatogram of sample G for Benzene

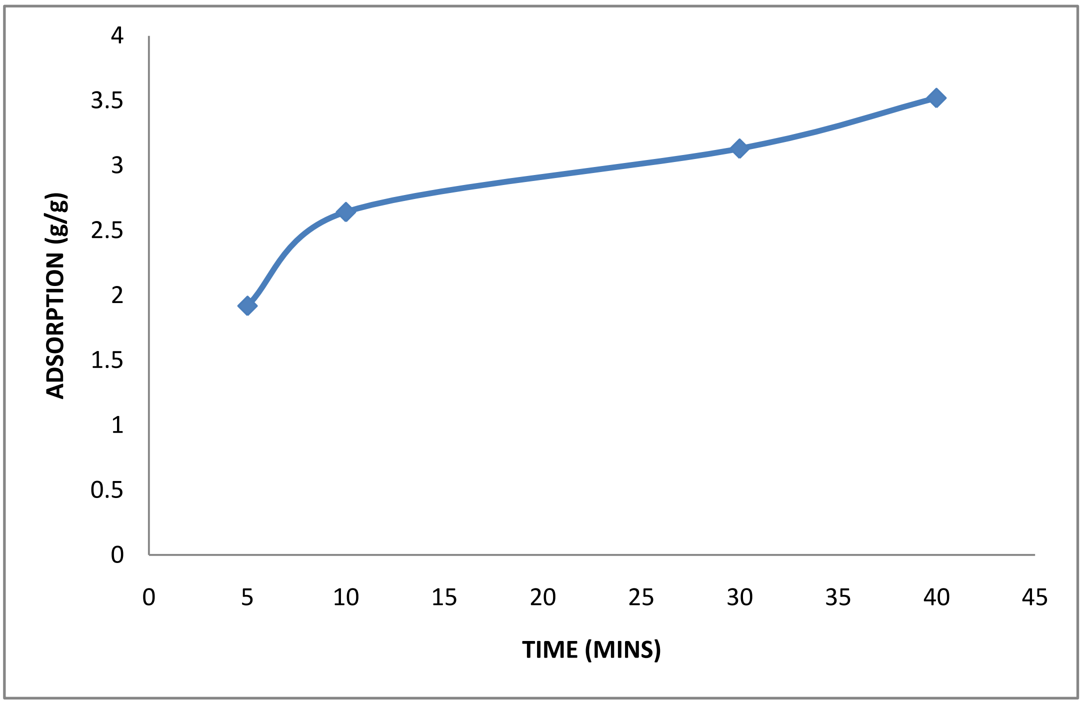


Figure 4.25: Variation of adsorption with time for bamboo particle size of 2mm

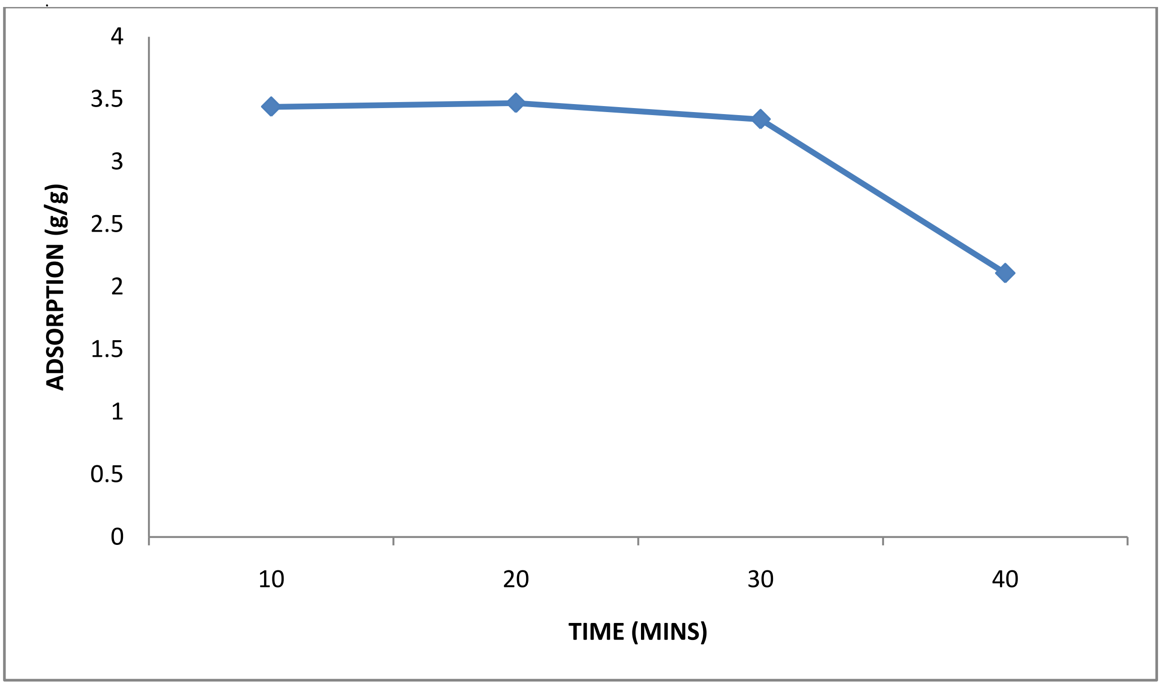


Figure 4.26: Variation of adsorption with time for bamboo particle size of 1mm

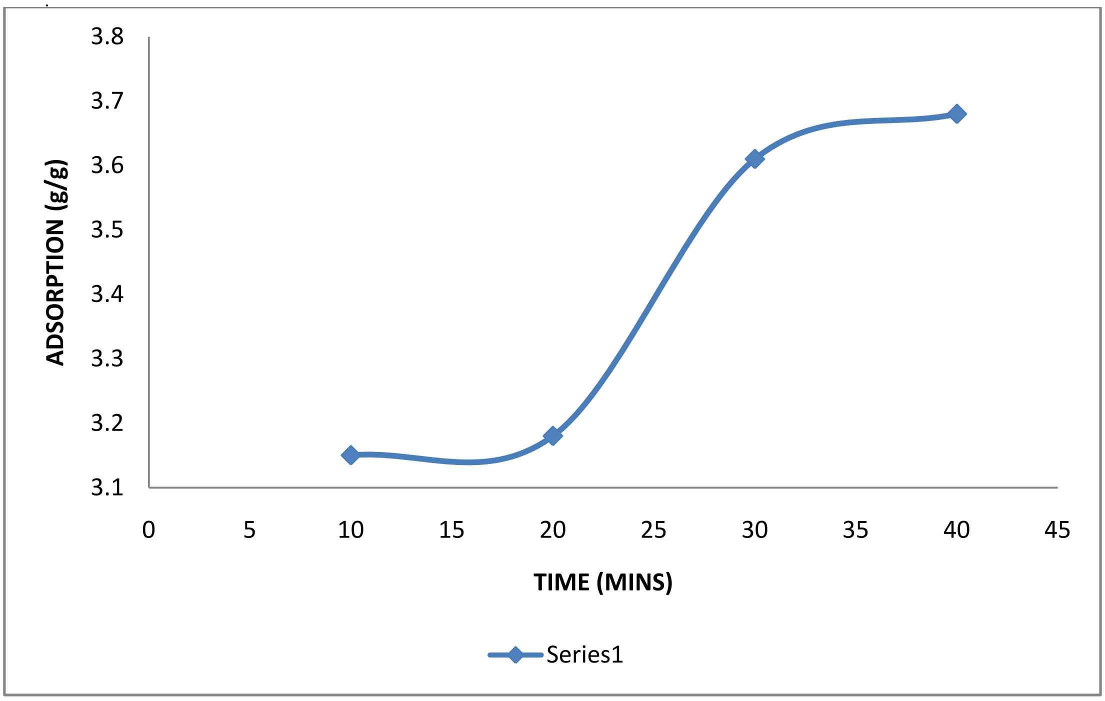


Figure 4.27: Variation of adsorption with time for bamboo particle size of 0.425mm