ASSESSMENT OF GROUNDWATER CONTAMINATION BY PETROLEUM PRODUCTS IN BARUWA COMMUNITY LAGOS, NIGERIA

BY

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ABSTRACT

Contamination of petroleum products in groundwater in Baruwa community, Lagos has been widely reported, as a result of ageing pipelines and vandalisation. Information on the types, nature of hydrocarbon and other contaminants that could assist in assessing the level of contamination is lacking. This study was therefore designed to assess the hydrogeochemical settings (delineate aquiferous units, quantify contaminated unit and define types of hydrocarbon present) in the groundwater resources of Baruwa community, Lagos state Nigeria. The study was also carried out to estimate areas that require remediation in the groundwater resources.

Based on preliminary studies, two boreholes (depth 36-42 m), one each in uncontaminated and contaminated areas were drilled to determine hydrogeological sequences in the Baruwa community. Twenty four sediment samples from the drilled boreholes were purposively selected for sedimentological analysis and determination of some hydraulic properties using standard methods. Thirty groundwater samples were collected purposively from the two drilled and other available boreholes and were analysed for heavy metals, cation / anions and the hydrocarbon content using Atomic Absorption Spectrophotometric, Colorimetric and Gas Chromatography- Mass Spectrometric methods, respectively. Data were compared with the WHO standards for potable water. Various thematic maps were developed using appropriate software. The area of contaminated land and volume of water that would require remediation were estimated hydrogeologically from the thematic maps.

Three aquifer units were identified at depths 9.0, 21.0 and 30.0 m. Aquifer grain size graphic mean was 1.64 indicative of medium to coarse grained moderately sorted leptokurtic sands. These were suggestive of materials deposited under low energy condition in a fluvial or tidal environment. The porosity ranged from 15.9 to 19.9%. The permeability coefficients of the aquifer were 9.469×10^{-5}, 4.105×10^{-5} and 5.102×10^{-5} mm/sec, respectively. The range of total hardness and pH were 2.6-248.6 mg/L and 4.4-6.7. Heavy metals, cations and anions concentration (in mg/L) in the groundwater samples ranged from 0.0-0.4 (Zn), 0.1-1.6 (Mn), 0.1-2.6 (Fe), 0.4-77.8 (Mg^{2+}), 0.25-13.20 (Ca^{2+}), 24.5-286.3(Cl^{-}), 0.1-1.2 (NO_3^{-}), 1.4-88.2(SO_4^{2}), 0.0-0.2(PO_4^{3-}), Lead, chromium, cadmium, nickel were below the detection limits. The samples from the contaminated area revealed enhanced concentrations of hydrocarbon, metals and anions when compared with the uncontaminated borehole samples. Data fall within the WHO limits except for Fe and Mn. Compounds identified were $C_{20}H_{34}O_8$, $C_{27}H_{56}$, $C_{21}H_{44}$, $C_{24}H_{50}$, $C_{21}H_{34}O_3$ indicating heavy oils. The estimated area in need of remediation was 9.9 million metre square with an approximate volume of 89.1 million cubic meter of water.

Groundwater contaminants in Baruwa community were mainly heavy oils and heavy metals. The area of contaminated land that needs remediation has been calculated and volume of water that needed remediation had also been determined.

Keywords: Aquiferous units, Sedimentological analysis, Groundwater Contamination, Hydraulic properties

Word count: 428

CERTIFICATION

I certify that this work was carried out by Mrs Adegbesan Omotolani in the Department of Geology, University of Ibadan.

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DEDICATION

This work is dedicated to my Husband Professor Olufemi Adegbesan, my children Moyo, Sharon, Adun and my mummy, Mrs G.O. Olaseinde.

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My deepest appreciation is to God Almighty, my maker, king, redeemer, my all in all, without Him, I am nothing. Thank you Lord for everything.

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CHAPTER ONE

INTRODUCTION

1.1 Background Information

Water is a constant gift of nature that defines peace in life. It remains a veritable endowment of nature necessary for life sustenance of plants and animals (Gray, 1997). The United Nations (UN) predicts that water shortages could retard the economic growth of some countries and lead to food shortages and possibly, to international conflicts (Turner, 2000).Groundwater and rivers constitute the main sources of water supplies that humans use (for drinking, cooking, cleaning, industry and agriculture). These several sources of water supplies are polluted by natural geological sources, pesticides, industrial discharge from various processing industries and oil spillage during oil exploration and exploitations or accidental discharge. Organic substances from oil spillage and petroleum products disposed into water bodies significantly contaminate and degrade them and could possibly elevate the concentration levels of heavy metals. Heavy metals are persistent and can easily enter food chain and accumulate until they reach toxic levels. Traces of heavy metals such as Hg, Cd, Pb, Co, Mn, Cu, Fe and Cr above stipulated levels are toxic to aquatic ecosystem and human (Bowen, 1979; Ademoroti, 1996). Incessant oil spills are known to have caused severe damage to aquatic and terrestrial environment. Crude petroleum, as well as many products derived from it, is shipped from oil-producing locations to oil-consuming locations in ocean going vessels having huge capacities. Accidents in which the hulls of such vessels are breached and their contents spilled can cause serious damage to the environment.

Unfortunately, such accidents are not at all uncommon. Land and offshore oil wells also can be a source of oil spills into ocean waters. Oil spills from such accidents may quickly spread over many square miles of water surface, for example in the Niger- Delta region of Nigeria where there is increasingly oil exploration and exploitation. Incessant vandalization of pipelines carrying petroleum and its products, massive destruction of oil facilities by irked youths, oil bunkering, industrial and domestic accidents which result in oil spillage and petroleum products deposits into existing water bodies have become the order of the day. Due to their complex composition, crude oils vary widely in their physical/chemical properties.

Release of hydrocarbons into the environment whether accidentally or due to human activities is a main cause of water and soil pollution. Soil contamination with hydrocarbons causes extensive damage of local system since accumulation of pollutants in animals and plant tissue may cause death or mutations. Petroleum hydrocarbons (PHCs) are common site contaminants, but they are not generally regulated as hazardous wastes. With the exception of the benzene, toluene, ethylbenzene, and xylene (BTEX) compounds, the United State Environmental Protection Agency (US EPA) regulates only sixteen compounds out of the thousands found in petroleum. Total petroleum hydrocarbons (TPH) is a term used to describe a broad family of chemical compounds that of water, soil, or air as a general indicator of petroleum content.

These are alkanes (paraffins), alkenes (olefins) and aromatics. Total petroleum hydrocarbon (TPH) is a term used to describe a large family of several hundreds of chemical compounds that originally come from crude oil. Crude oil is used to make petroleum products, which can contaminate the environment (Gustafson, 2007). Petroleum hydrocarbons released to the soil may move through the soil to the groundwater. Individual contaminant compounds at the site may separate from the original mixture, depending on the chemical properties of the compounds. Some of these compounds will evaporate into the air and others will dissolve into groundwater and move away from the release area. Some compounds will attach to particles in the soil and may remain in the soil in the groundwater. Individual contaminant remains in the soil for a long time, while others will be broken down by organisms found in the soil. It is useful to measure the total amount of all hydrocarbons found together in particular samples; individual hydrocarbons present in petroleum products are as follows: gasoline (C6 – C12), diesel (C8 – C26), kerosene (C8– C18), fuel oil (C17 – C26), and lubricating oils (C15 – C50). Used oil is significantly contaminated with aliphatic and polyaromatic hydrocarbons (PAHs). The content of aliphatic and aromatic hydrocarbons measured in used engine oil was (in ppm)

The fate-and-transport of liquid petroleum products in the subsurface is determined primarily by the properties of the liquid and the characteristics of the geologic media into which the product has been released. Important liquid properties include density, viscosity and interfacial tension. Soil properties that influence the movement of petroleum hydrocarbons include porosity and permeability. Other additional properties, which are functions of both the liquid and the media, include capillary pressure, relative permeability, wettability, saturation, and residual saturation. Site-specific physical conditions (*e.g.*, depth to groundwater, volume of the release, direction of groundwater flow) also contribute to the migration and dispersion of released petroleum products. To put the following discussion in the context of the types of petroleum hydrocarbons commonly found at UST sites, we begin with a brief description of the classification and composition of hydrocarbons.

The most common route of soil and ground water contamination are leaking underground storage tanks that are used by gas stations, commercial, industrial, and residential compounds. Underground storage tanks that are not protected against corrosion with cathodic protection and are not designed in double wall with reinforced fiberglass to withstand ground subsidence are very likely to fail and cause massive leaks in the ground.

The subsurface medium must be protected against any kind of hazardous contamination because soil acts as a permanent residence for pollutants and the dynamic movements of hydrological cycle transports them to ground water aquifers. Once a liquid petroleum product is released into the ground it partitions into three separate phases; dissolved, liquid and gas. A small fraction of the petroleum hydrocarbon dissolves in the soil moisture or ground water, a portion of the product remains in soil pore space in its pure liquid form as residual saturation and some of it evaporates into the air trapped in soil pores. Pure phase liquids that do not readily dissolve in water are called non-aqueous phase liquids (NAPL). In general NAPLs are subdivided into two classes: those that are lighter than water (LNAPLs) and those with a density greater than water (DNAPLs). Hydrocarbon fuels such as gasoline, heating fuel, kerosene, jet fuel and aviation fuel are LNAPLs. Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) are light aromatic hydrocarbons that have relative high water solubilities (150 - 1800 mg/L). Laboratory studies have revealed BTEX to be acutely toxic for laboratory animals. Long term gastrointestinal and respiratory exposure of mouse and rats to BTEX have produced liver cancer and leukemia. The volume fraction of BTEX in gasoline can be as high as 20%. BTEX may also be present in other petroleum products in lower fraction. Methyl tert Butyl Ether (MTBE), an octane enhancer is an oxygenate and a substitute for lead in gasoline. Due to the presence of an oxygen atom in its structure, MTBE has a high water solubility and its volume fraction in gasoline may range from 0–15%.The bulk products may also be classified on the basis of composition and physical properties. Products typically stored in USTs include the following main groups:

1. Gasolines
2. Middle Distillates
3. Heavy Fuel Oils

Fig. 1.1 presents a gas chromatogram of a hydrocarbon sample with the approximate ranges in which the various constituents fall. Compounds outside the normal ranges depicted are commonly found as contaminants in other products. For example, diesel fuel may contain minor amounts of benzene and other light hydrocarbons.

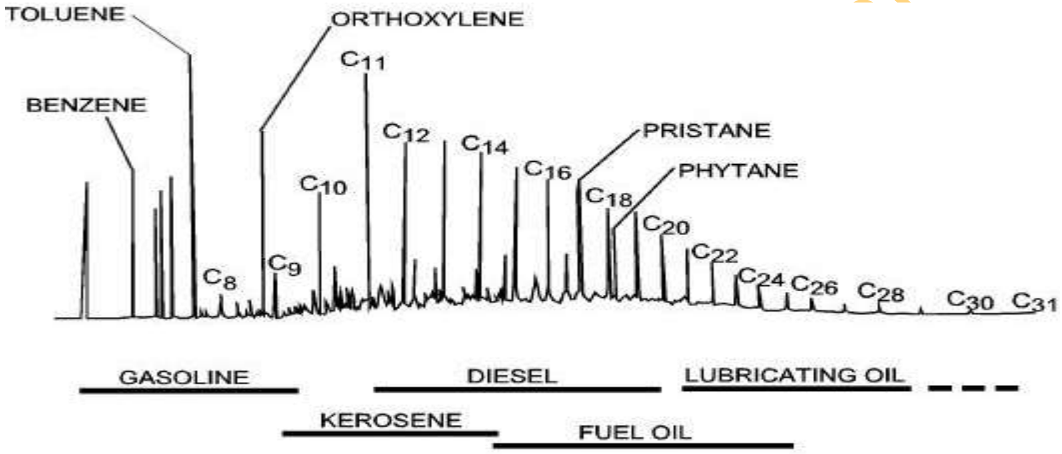


Fig. 1.1: Gas Chromatogram showing approximate ranges for individual hydrocarbon products

(source: Adapted from Senn and Johnson, 1985).

1.1.1 Gasolines

Gasolines are mixtures of petroleum hydrocarbons and other non-hydrocarbon chemical additives, such as alcohols (*e.g.*, ethanol) and ethers (*e.g.*, methyl tertiary-butyl ether, or MTBE). Gasolines are more mobile than either the middle distillates or the fuel oils. The higher mobility of gasoline is primarily due to the fact that its components tend to have lower molecular weights; hydrocarbon compounds usually found in gasoline have between 4 and 10 carbon atoms per molecule. The lower molecular weight results in lower viscosity, higher volatility, and moderate water solubility.

Fresh gasolines contain high percentages of aromatic hydrocarbons (*i.e.*, those with a 6-carbon benzene ring), which are among the most soluble and toxic hydrocarbon compounds. The most frequently encountered aromatic compounds are benzene, toluene, ethylbenzene, and xylene (BTEX). Because of their relatively high volatility, solubility, and biodegradability, BTEX compounds are usually among the first to be depleted from free product plumes. At sites of older gasoline releases, the free product plume may contain relatively little BTEX, being instead enriched in heavier, less soluble, and less readily biodegradable components. As a consequence, the product will be more viscous, slightly denser, less volatile, and less mobile than fresh product. The non-hydrocarbon additives (*e.g.*, ethanol, MTBE) are readily soluble and preferentially dissolve into groundwater, which diminishes their concentration in the free product, but results in formation of longer dissolved plumes. MTBE also moves away from the source faster than free product and because it is relatively non degradable, it is difficult to remediate. Discussions of methods to remediate dissolved plumes are beyond the scope of this manual.

1.1.2 Middle Distillates

Middle distillates (*e.g.*, diesel fuel, kerosene, jet fuel, lighter fuel oils) may contain 500 individual compounds, but these tend to be denser, much less volatile, less water soluble, and less mobile than the compounds found in gasolines. The major individual components included in this category of hydrocarbons contain between 9 and 20 carbon atoms each. Lighter aromatics, such as BTEX, are generally found only as trace impurities in middle distillates, and if initially present, they are generally not present in plumes at older release sites, because they have biodegraded, evaporated, and dissolved into groundwater.

1.1.3 Heavy Fuel Oils

Heavy fuel oils and lubricants are similar in both composition and characteristics to the middle distillates. These types of fuels are relatively viscous and insoluble in groundwater and are, therefore, fairly immobile in the subsurface. Most of the compounds found in heavy fuel oils have more than 14 carbon atoms; some have as many as 30. Like the older releases of middle distillates and gasolines, the lighter end components are present only in trace amounts as they are more readily biodegraded and dispersed.

Groundwater contamination differs from surface water contamination in several important aspects. Among them is that it does not typically flow to a single outlet, it can affect people through wells dug in a contaminated aquifer, as it can flow into streams or lakes. Groundwater contamination also occurs on a different timescale than surface water contamination. Flow rates vary widely and can be as slow as two-miles a year. Because of this, non-point source contamination can take years or even decades to appear in wells and just as long or even longer to dissipate or be converted. These distinctions depend on topography, hydrology and the sources of groundwater recharge and have implications for limiting as well as remediating contamination.

Many Nigerians are drinking water with high and dangerous levels of hydrocarbons due to the problem of petroleum sipping into groundwater. Ageing pipelines and tanks used by the Nigerian National Petroleum Corporation (NNPC), investigations have revealed are the major cause of the massive pollution, resulting in ailments and shorter life spans for the millions of the citizens.

Petroleum hydrocarbon originates from liquid fossil fuels called oil or more properly *petroleum*. Petroleum is a naturally occurring liquid with widely different composition and complexity. Except for a few surface seepages, the vast portion of petroleum is located well below the surface of the earth and it is extracted only by drilling. Crude oil is a complex mixture of hydrocarbons. Its elemental composition is carbon–hydrogen, with variable quantities of oxygen and sulfur, and trace amounts of nitrogen, metals and other elements. Modern refineries use a procedure called cracking to fractionate unused cuts. In this process, the material is heated to temperatures above 2308C at different pressures with or without a catalyst. Cracking converts heavy and complex hydrocarbons to more simple molecules with lower boiling points with the loss of hydrogen. Various fractions of petroleum products ranging from methane to asphalthene are produced during this process. At every point in the oil production, distribution, and consumption process, oil is invariably stored in storage tanks. The potential for an oil spill is significant, and the effects of spilled oil many times pose serious threats to the environment. Leaking underground and aboveground storage tanks, improper disposal of petroleum wastes, and accidental spills are major routes of soil and groundwater contamination with petroleum products. The most common route of soil and groundwater contamination is leaking underground storage tanks that are used by gas stations, commercial, industrial, and residential compounds.

Underground storage tanks that are not protected against corrosion with cathodic protection and are not designed in double wall with reinforced fiberglass to withstand ground subsidence are very likely to fail and cause massive leaks in the ground (U.S. EPA, 1998). The subsurface medium must be protected against any kind of hazardous contamination because soil acts as a permanent residence for pollutants and the dynamic movements of hydrological cycle transports them to groundwater aquifers (Huling and Weaver, 1996). Once a liquid petroleum product is released into the ground it partitions into three separate phases: dissolved, liquid and gas. A small fraction of the petroleum hydrocarbon dissolves in the soil moisture or groundwater, a portion of the product remains in soil pore space in its pure liquid form as residual saturation and some of it evaporates into the air of soil pores. Pure phase liquids that do not readily dissolve in water are called non-aqueous phase liquids (NAPL). In general NAPLs are subdivided into two classes: those that are lighter than water (LNAPLs) and those with a density greater than water (DNAPLs). Hydrocarbon fuels such as gasoline, heating fuel, kerosene, jet fuel and aviation fuel are LNAPLs. Benzene, toluene, ethylbenzene, and xylene (BTEX).are light aromatic hydrocarbons that have relative high water solubilities (150–1800 mgrl). (Howard et al., 1991). Laboratory studies have revealed BTEX to be acutely toxic for laboratory animals. Long-term gastrointestinal and respiratory exposures of mouse and rats to BTEX have produced liver cancer and leukemia (Budavari-et al., 1989).The volume fraction of BTEX in gasoline can be as high as 20%. BTEX may also be present in other petroleum products in lower fraction (American Petroleum Institute, 1985). Methyl-tert-butyl ether (MTBE), an octane enhancer is an oxygenate and a substitute for lead in gasoline. Due to the presence of an oxygen atom in its structure, MTBE has relatively high water solubility and its volume fraction in gasoline may range from 0% to 15% (Howard et al., 1997).

1.2.1 Distribution of Petroleum Contaminants in the Subsurface Zone

Petroleum hydrocarbon molecules are usually lighter than water and shortly after a spill they forma pool of NAPL over the surface of water table. Portion of the NAPL phase that is in contact with the groundwater slowly dissolves in groundwater and forms a plume of hydrocarbon in the flowing groundwater. The plume's front mostly contains the lighter and more soluble hydrocarbon compounds. Fig.1.2 shows a typical leaking underground storage tank with air sparging and vapor extraction systems for clean-up.

In the unsaturated zone, portion of petroleum products remains as residual pure product NAPL. Residual NAPL is held in soil pores either by capillary forces or as small pools of liquids over clay and silt lenses. If not removed, residual petroleum hydrocarbon acts as a permanent source of contamination in the ground. Soil vapor extraction _SVE.and air sparging have the capability of removing NAPL if the flow of air is not restricted by channelling or existence of natural barriers. If the density of the contaminant plume is significantly higher from the native groundwater, the contaminant plume moves deep into the aquifer and may not be detected with shallow monitoring systems.

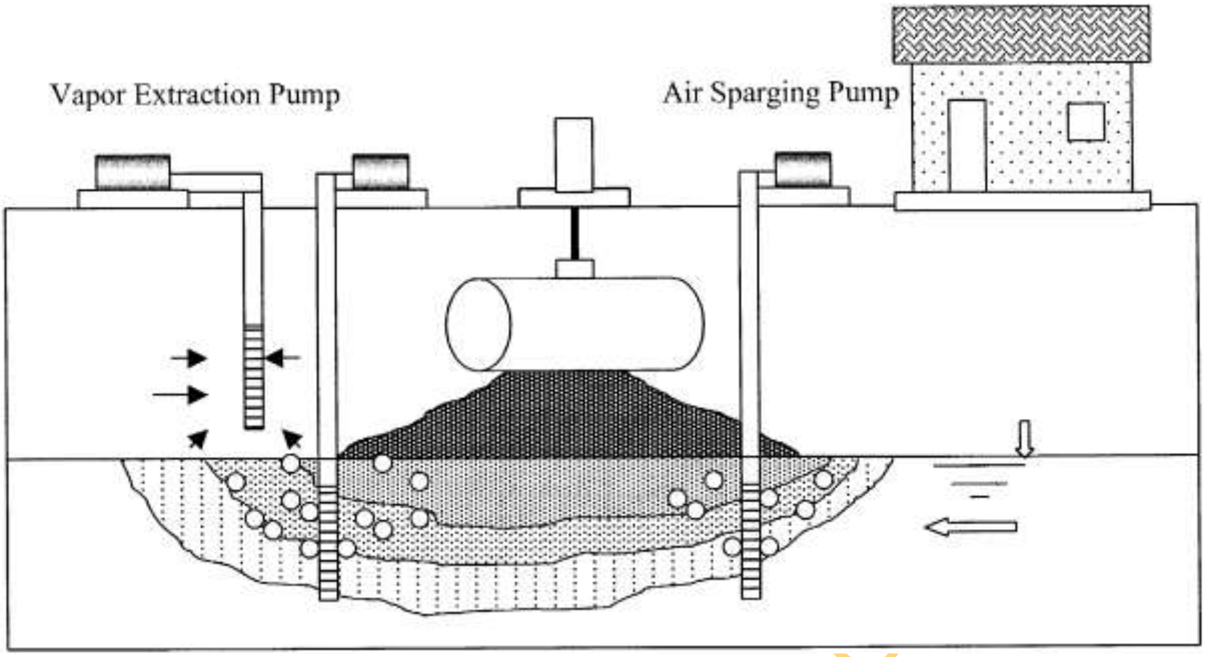


Fig. 1.2: A schematic illustration of a typical leaking underground tank with contaminant plume

1.2.2 Phase Distribution in the Subsurface

The petroleum hydrocarbon constituents that comprise free product may partition into four phases in the subsurface vapor (in soil gas), residual (adsorbed onto soil particles including organic matter), aqueous (dissolved in water), and free or separate (liquid hydrocarbons). Fig.1.2 illustrates the distribution of the hydrocarbon phases in the subsurface from a leaking UST. The partitioning between phases is determined by dissolution, volatilization, and sorption. When released into the subsurface environment, liquid hydrocarbons tend to move downward under the influence of gravity and capillary forces. The effect of gravity is more pronounced on liquids with higher density.

The effect of capillary forces is similar to water being drawn into a dry sponge. As the source continues to release petroleum liquids, the underlying soil becomes more saturated and the leading edge of the liquid migrates deeper leaving a residual level of immobile hydrocarbons in the soil behind and above the advancing front. If the volume of petroleum hydrocarbons released into the subsurface is small relative to the retention capacity of the soil, then the hydrocarbons will tend to sorb onto soil particles and essentially the entire mass will be immobilized. For petroleum hydrocarbons to accumulate as free product on the water table, the volume of the release must be sufficient to overcome the retention capacity of the soil between the point of release and the water table. Without sufficient accumulation of free product at the water table, there is no need for a free product recovery system.

However, in either case, there may be a need for appropriate remedial action to mitigate the residual (sorbed) phase so that it does not continue to act as a lingering source of soluble groundwater contaminants or volatile, and potentially explosive, vapor contaminants. Fig.1.3 illustrates the progression of a petroleum product release from a leaking UST. Frame A shows the hydrocarbon mass before it reaches the capillary fringe. If the release were to be stopped at this point, there would probably be no accumulation of free product. In Frame B, the release has continued and the volume of the release is sufficient for free product to begin accumulating on, and displacing, the capillary fringe. The free product is beginning to displace the capillary fringe and some of the soluble constituents are dissolving into the groundwater. The source of release has been stopped in Frame C. Residual hydrocarbons remain in the soil beneath the UST. The free product plume has spread laterally, and a plume of dissolved contaminants is migrating down gradient.

Portions of the hydrocarbon mass from both the residual and free phases will volatilize (evaporate) and solubilize (dissolve) to become components of the soil vapor and groundwater, respectively. Volatilization and solubilization of the lighter fractions tend to make the remaining hydrocarbon mass more dense and even less mobile. Hydrocarbons that are in the vapor phase are much more mobile and can migrate relatively great distances along preferential flow paths such as fractures, joints, sand layers, and utility line conduits. Accumulation of vapors in enclosed structures (*e.g.*, basements, sewers) potentially can cause fires or explosions. The more soluble components of the hydrocarbon mass will dissolve into groundwater, both above and below the water table.

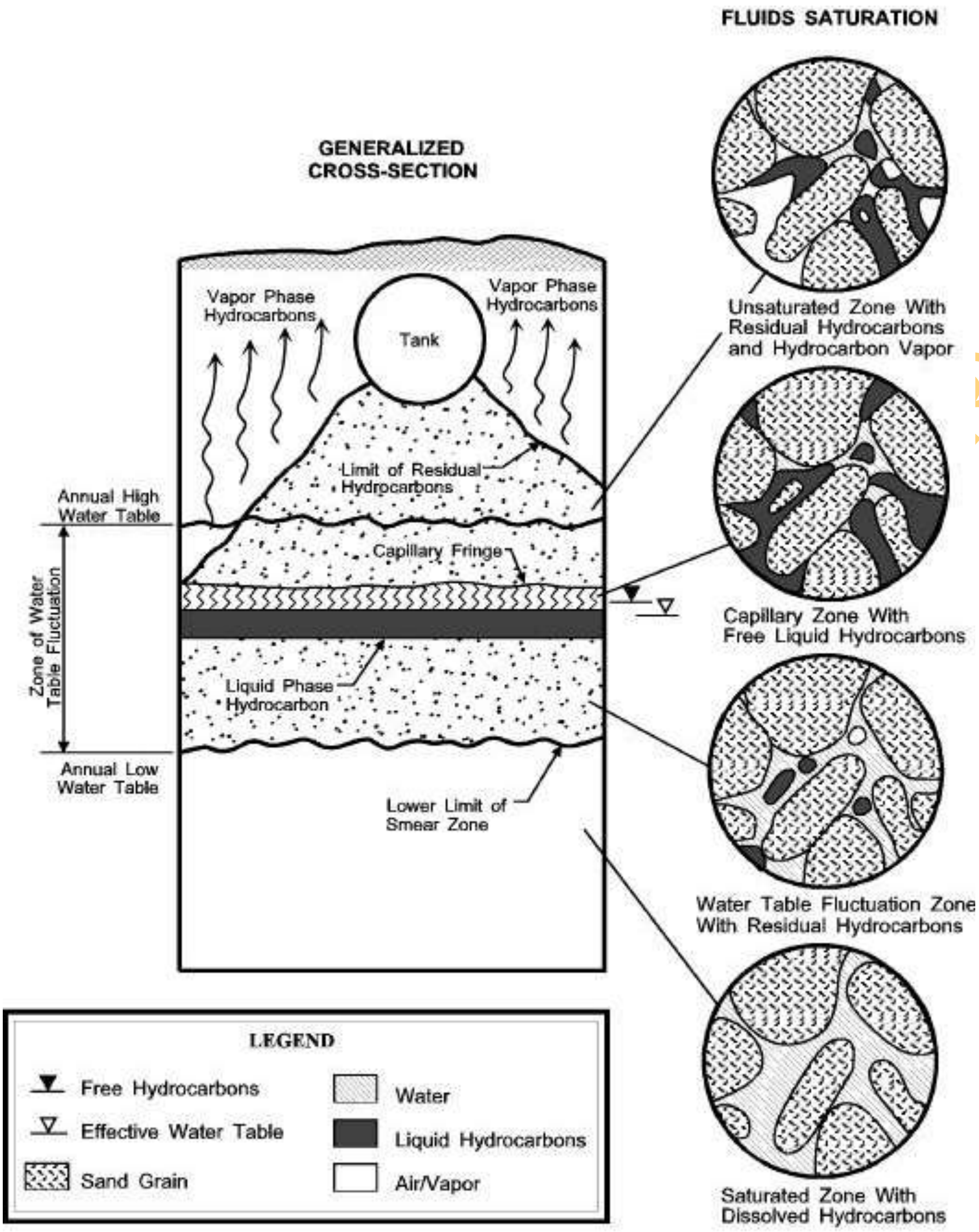


Fig 1.3: Vertical distribution of hydrocarbon phases (source: Modified from Lundy and Gogel, 1988).

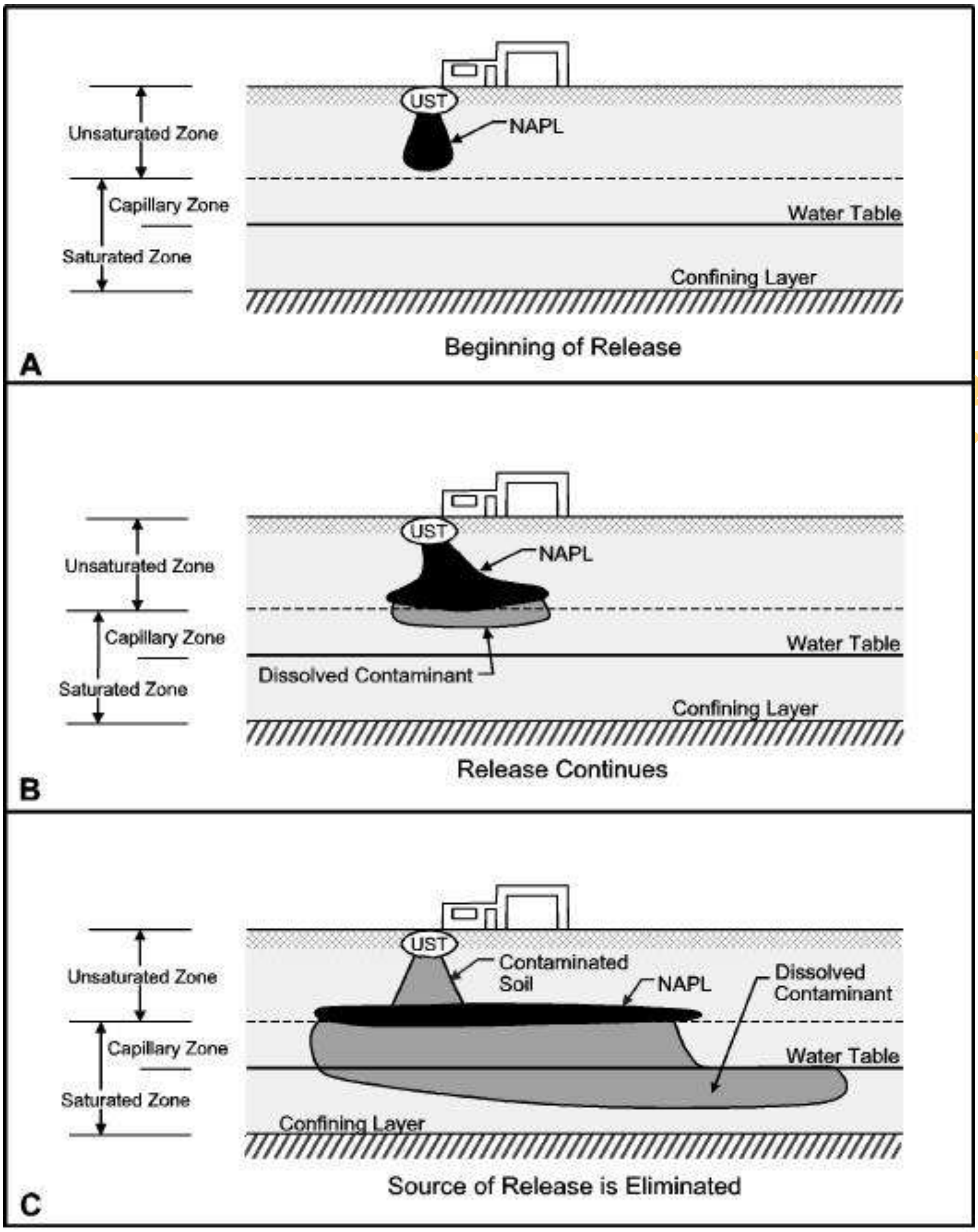


Fig.1.4: Progression of a typical petroleum product release from an underground storage tank (source: EPA, 1990)

1.2.3 Properties of Geologic Media

The extent and rate of petroleum hydrocarbon migration depends in part on the properties of the subsurface medium in which it is released. The subsurface medium may be naturally occurring geologic materials (*e.g.*, sedimentary, metamorphic, or igneous rock or sediments) or artificial fill that has been imported to the site by human activity. In order to design effective and efficient free product recovery systems, you need to characterize both the type and the distribution of geologic media (or fill material) so that you can determine the likely migration routes and travel times.

In the context of fluid flow in the subsurface, geologic media can be classified on the basis of the dominant characteristics of pore space, fractures, or channels through which fluids move. In porous media, fluids move through the interconnected voids between solid grains of soil. Fractured media are those in which fluids migrate readily through fractures rather than the adjacent soil or rock matrix. Fracturing is usually associated with consolidated materials, but it can also occur in unconsolidated clays due to desiccation. Karst media are those in which fluids flow through solution features and channels (*e.g.*, caves associated with carbonate rocks such as limestone).

Porosity and permeability are the two most important media-specific properties of a natural geologic material. Porosity characterizes the ability of media to store fluids, and permeability characterizes the ability of the media to transport fluids. Exhibit III-5 summarizes the significance of geologic properties and their relevance to free product recovery.

1.2.3.1 Porosity

Porosity, or more specifically effective (“drainable”) porosity, is an important factor to be considered in the evaluation of a free product recovery system. Calculation of the amount of free and immobile product in the subsurface requires a value or estimate of effective porosity. Porosity defines the storage capacity of a subsurface media. All rocks and unconsolidated media contain pore spaces. The percentage of the total volume of an unconsolidated material or rock that consists of pores is called porosity. Porosity is classified as either primary or secondary. Primary porosity, which is created when sediments are deposited (or crystalline rocks are formed), depends on the shape, sorting, and packing of grains. Primary porosity is greatest when grains are nearly equal in size (i.e., are well graded or sorted) and non spherical in shape. Unconsolidated sediments that contain a wide range of grain sizes (*i.e.*, are poorly graded or sorted) tend to have a low primary porosity because smaller grains fill the pore spaces between the larger grains. Secondary porosity develops after rocks have been formed or sediments deposited.

Examples are joints, foliations, fractures, and solution openings. Also included in this category are animal burrows, root holes, and desiccation cracks in clay soils. While the latter examples typically facilitate free product migration only very locally, the former examples can exert a much more regional influence. Characterization of the flow of groundwater and free product through solution channels, fractures, and joints can be especially problematic. Wells completed at sites underlain by these features may not accurately (or completely) define flow directions or rates.

The flow of groundwater and free product through the larger openings can sometimes even be under conditions of open channel flow. Once free product enters these larger openings, it can migrate undetected over relatively great distances (miles in some cases) in a matter of weeks or months. Although it would potentially be easier to recover free product in such a setting, it is much more difficult (and in many cases impossible) to locate recoverable accumulations.
Total porosity is based on the volume of all voids (primary and secondary), whether or not the pores are connected. When pores are not connected and dead-end pores exist, groundwater cannot move through the rock or sediments. Effective porosity is the term that characterizes the ratio of the volume of interconnected pores to the total volume of unconsolidated materials or rock.

There is no direct correlation between effective and total porosity. Effective porosity is approximated by drainable porosity and can be significantly less than total porosity. In general, the smaller the grains in the rock, the smaller the effective porosity (and the greater the retention capacity or residual saturation). For example, clays and limestone can have an upper range of total porosity that is in excess of 55 percent (see Exhibit III-6), but a lower range of drainable porosity of 1 percent or less.

1.2.3.2 Permeability

Permeability is one of the most critical properties to be considered in the design of any recovery system for free product recovery. The rates of groundwater flow and free product migration are related directly to permeability. The rate of free product migration also depends on other parameters, but permeability exhibits the greatest range in values (varying over 5 or 6 orders of magnitude for common geologic media). The intrinsic permeability of the geologic media is independent of the nature of the fluid flowing through the media. Intrinsic permeability is related to hydraulic conductivity, which is a measure of the ability of the geologic medium to transmit water, but the terms are not interchangeable. Hydraulic conductivity is a function of properties of both the media and the fluid. Although confusing, hydraulic conductivity is often referred to as simply “permeability”.

Geologic media with high hydraulic conductivities are highly permeable and can easily transmit non-viscous fluids, especially water and many types of petroleum products. Various geologic media tend to have hydraulic conductivity values within predictable ranges. A geologic medium is described as “isotropic” if the measured permeability is the same in all directions. Flow through an isotropic medium is parallel to the hydraulic gradient. This condition might exist in uniform, well-graded sand. The permeability of a geologic medium is often observed to vary depending upon the direction in which it is measured. Known as “anisotropy”, this condition can cause the flow of groundwater and free product to occur in a direction that is not necessarily the same as the principle direction of the hydraulic gradient. Because of anisotropy, a cone-of-depression formed around a pumping well may be asymmetrical (*e.g.*, elliptical) rather than circular. Sediments that are comprised of a high proportion of flat, plate-like particles (*e.g.*, silt, clay) which can pack tightly together and foliated metamorphic rocks (*e.g.*, schist) often exhibit anisotropy. Anisotropy may occur in three dimensions. For example, in flat-lying sedimentary units, horizontal permeability is usually much greater than vertical permeability.

1.3 PREVIOUS WORK DONE

The nature of geologic processes results in the non-uniform deposition and formation of rocks and sediments. Geologic media often are characterized by the degree of uniformity in grain size and properties such as permeability. Geologic media with uniform properties over a large area are referred to as being homogeneous. By contrast, geologic media that vary in grain size from place to place are called heterogeneous. In nature, heterogeneity is much more common than homogeneity. Soil properties (*e.g.*, permeability, texture, composition) can be dramatically different over short distances. These changes strongly influence the direction and rate of the flow of groundwater, free product, and vapor through the subsurface. For example, free product may migrate farther and faster than it would in homogeneous media because hydrocarbons tend to move through the most permeable pathways and bypass extremely low permeability zones. Fine grained fractured media are heterogeneous in the extreme. Migration distances in fractured media can be large because of the very small storage capacity of the fractures. Ehinola *et al.*, 2008 focussed on the use of GIS, hydrochemical and Geophysical technique to delineate polluted zone in parts of Lagos aquifers and to suggest possible remedial measures.

Ehinola *et al.*, also in 2008 carried out a study on the prediction of overburden and underground water quality assessment in parts of Lagos southwestern Nigeria. Ojuri *et al.*, 2009 carried out a study which will provide basic experimental data on porous media material which would be widely useful to geotechnical/ environmental researchers and engineers who are involved in contaminated site assessment and remediation in Nigeria. Thomas and Delfino (1991) used a Gas chromatographic/chemical indicator approach to assess groundwater contamination by petroluem product. They used it to note the likely types of petroleum contamination. Oteri 1987 did a groundwater pollution monitoring in environmental investigation.

Geophysical methods are widely employed in numerous domains related to environment and engineering (Auken et al., 2006).The electrical resistivity method is very effective in delineating contaminated zones of ground water and is capable of clarifying subsurface structure distinctly. It has been utilized in the investigation of contaminants in waste disposal sites (Kaya et al, 2007). Ayolabi and Folashade (2005) used the geoelectric method and hydrochemical analysis to assess pollution due to a dumpsite in Lagos. It has also proven to be useful for the characterization of oil contaminated soils (Modin et al., 1997; Sauck, 1998, 2000; Shevnin et al., 2003; 2005).

In 1985, the American Petroleum Institute conducted a study on solubilities of petroleum hydrocarbons in groundwater. In a simple laboratory experiment, one part gasoline with 10 parts water was placed in a sealed vessel and the mixture was rotated for 96 h. Concentrations of BTEX in the mixture were determined with aliquots taken from the aqueous phase and subsequent measurements with aGCrMSD. The reported solubilities of some gasoline components as the average of five experiments and their pure phase solubilities are detected. (American Petroleum Institute, 1985.).

In parts of Warri, Delta State, Ogoni in Rivers State, the water is heavily polluted. The United Nations Environment Programme (UNEP) carried out studies that confirmed the contamination of groundwater in Ogoni area as well as the soil. The UNEP recommended the need to clean up the region and the federal government had noted that the clean-up of contaminated soil will take decades. Leaking pipelines have also been reported to have contaminated the groundwater in Kaduna.

Adeniyi and Afolabi (2002) have reported total petroleum hydrocarbon in vicinity of facilities handling refined petroleum product in Lagos metropolis, Nigeria. They determined TPH in three locations in the vicinity namely: a Petrol station, a Mechanic workshop and the Nigeria Electricity Power Authority (NEPA) station, respectively. They compared the results of the three stations with the result of the control station. The values of TPH obtained at the three stations were higher than the values obtained at control station.

Okonkwo et al. (2006) reported the level of TPH in dusts from petroleum handling facilities such as gasoline stations, selected high traffic density roads and residential areas within the Tshwane metropolitan area in South Africa. They reported high TPH values in gasoline stations than other two stations studied. It has been reported (Adeniyi and Owoade, 2010) that road side soil samples obtained along Lagos Badagry express way in Nigeria were contaminated with TPH. Two sampling stations along the express way namely Lagos State University Bus stops and Adeniran Ogunsanya College of Education Bus Stop was studied for TPH contamination of soil samples.

Near surface aquifers are susceptible to pollution from a variety of sources especially in the urban environment (Foster et al., 1988; Akpoborie et al., 2000). Specifically, Asiwaju- Bello (2007), Longe and Balogun (2010) have confirmed the presence of coliform and BOD contamination resulting from dump site leachates into near surface aquifer in the Ikeja area of Lagos. Unfortunately, this shallow aquifer is tapped by hundreds of shallow wells that in many cases are the only reliable sources of domestic water supply in parts of Lagos. Deeper and more expensive boreholes that obtain water from lower horizons would have been are preferred because groundwater from these deeper boreholes is generally assumed to be free from contamination and thus considered safe for drinking purposes usually without prior treatment.

Oil spillage is one of the major sources of pollution in environment, including soil, surface and groundwater. The top soil is the first component of the ecosystem that receive the load of contaminant and which is usually greater than in the surrounding sub-urban or rural areas, therefore, soil is an important sink for contaminants (Alloway 1990). Toxic chemicals, both organics and inorganics including trace metals are the main contaminants in soil. These toxic chemicals are often absorbed by plants or trees. Chemical composition deposition of metals, and Competition for free cation exchange sites are some of the factors that guide the uptake efficiency of metals by plants (Majolagbe et al., 2010).

The use of tree bark as herbs, eating raw fruits without thorough washing is a common practice particularly in Africa, these constitute direct route of metals to metabolic pathway of man. Trace metals indeed play important roles in biochemical processes, being essential component of molecular structure therefore participate in processes such as enzyme regulation and gene expression. However, the concentrations of contaminant may be high enough to be of risk to human health and /or ecosystem. The plume of contaminant can also percolate the sub soil and affect the surrounding aquifer. Various other major sources of pollution in groundwater include leachate from municipal refuse dumpsite, industrial discharge (liquid waste), domestic waste, salt water intrusion, application of agricultural chemicals, pipeline vandalisation and geological formations

(Adegbola et al., 2012). Organic pollution of groundwater limits its use, causes economic loss, environmental problems, and decreases the agricultural productivity of the soil(Wang et al., 2008).

Oil spillage occurs due to a number of causes including corrosion of pipelines and tanks, sabotage and production operation (Nwankwo and Emujakporue, 2012). Recent hydrocarbon contamination produces high resistivity anomalies while matured oil contamination produces low resistivity anomalies, several months after the spill has occurred; oil contamination creates a low resistivity zone (Atekwana et al., 2001).Application of the resistivity method for the geological characterization of polluted zones was made in different types of geological environment and industrial enterprises has been reported by Shevnin et al., (2003) and Delgado-Rodriguez, et al., (2006). The resistivity contrast between an oil polluted area and surrounding rock depends on the spill age, therefore the age of spill influences the selection and optimization of the applied technology (Shevnin et al.,2003). Leakages from both underground and surface storage tanks of petroleum products constitute a notable source of pollution within Lagos metropolis (Malomo and Wint,2003).

Baruwa oil pollution was noticed in 1994, which has spread over an area of 81.44 hectares. The spillage of petroleum products occurred from the valve pit on the Atlas Cove to Mosimi depot pipeline. These pipelines are dedicated to individual products such as petrol, kerosene and diesel oil (Onabowale, 2010).

1.4 JUSTIFICATION/ MOTIVATION/ STATEMENT OF PROBLEM

This study showed that people in other areas outside the Niger Delta particularly in Lagos where there are ageing tanks and pipelines are vulnerable to impact of massive oil contaminants in their ground water and subsequently the source of their drinking water. While oil has accounted for over 90 per cent of Nigeria's foreign exchange earnings over the years, local consumption in Lagos accounts for about 60 percent of total gasoline consumption in the country.

Investigations confirmed that many people in areas where oil pipelines and tank cross both within and outside the Lagos where oil production takes place are ingesting high and dangerous levels of hydrocarbons. We personally drilled two boreholes; one control and one in contaminated area and took water samples in the presence of the community leader and also from other wells and boreholes in areas where pollution of the drinking water was suspected to have been taking place in Baruwa and its environs in Lagos and the water samples were sent for laboratory analysis in the course of this research work.

1.5 AIM AND OBJECTIVES

This study is designed to provide baseline data as an aspect of environmental impact assessments that will assist in determining the level of remediation that the Baruwa water sources may require overtime..

The objectives of the study are as follow

1. To create base maps at scale 1:10,000.

2. To determine hydrogeological sequences (delineate aquiferous units) and lithologic profile beneath the area.

3. Understand the sedimentological and hydrological properties of the study area.

4. Analyze water samples for heavy metals, cations, anions and hydrocarbon content.

5. The study was also carried out to estimate and delineate areas that require immediate remediation in the groundwater resources.

1.6 LOCATION OF THE STUDY AREA.

The city of Lagos lies in south-western Nigeria, on the Atlantic coast in the Gulf of Guinea, west of the Niger River delta, located on longitude 3° 24' E and latitude 6° 27' N. On this stretch of the high-rainfall West African coast, rivers flowing to the sea form swampy lagoons like Lagos Lagoon behind long coastal sand spits or sand bars. Some rivers, like Badagry Creek flow parallel to the coast for some distance before finding an exit through the sand bars to the sea. The two major urban islands of Lagos in Lagos Lagoon are Lagos Island and Victoria Island. These islands are separated from the mainland by the main channel draining the lagoon into the Atlantic Ocean, which forms Lagos Harbour. The islands are separated from each other by creeks of varying sizes and are connected to Lagos Island by bridges. However the smaller sections of some creeks have been sand filled and built over.

Baruwa community is located in the Alimosho local government of Lagos state. It lies between latitudes 6^{o}36’12"N and longitude 3^{o}16'X”E. It is drained by Lagos lagoon, Badagry creek and Lekki lagoon which run into the lagoon. Geographically the, state lies on a poorly sorted coastal sedimentary plain and recent alluvial deposit in Nigeria. The Local Council is richly blessed with arable landmass of about 57.621 km^{2} and it is surrounded by rivers Owa and Oponu (Fig.9), which are suitable for navigation, fishing and tourism purposes. The location map of Baruwa and its environs is shown in Fig 1.5 and 1.6.

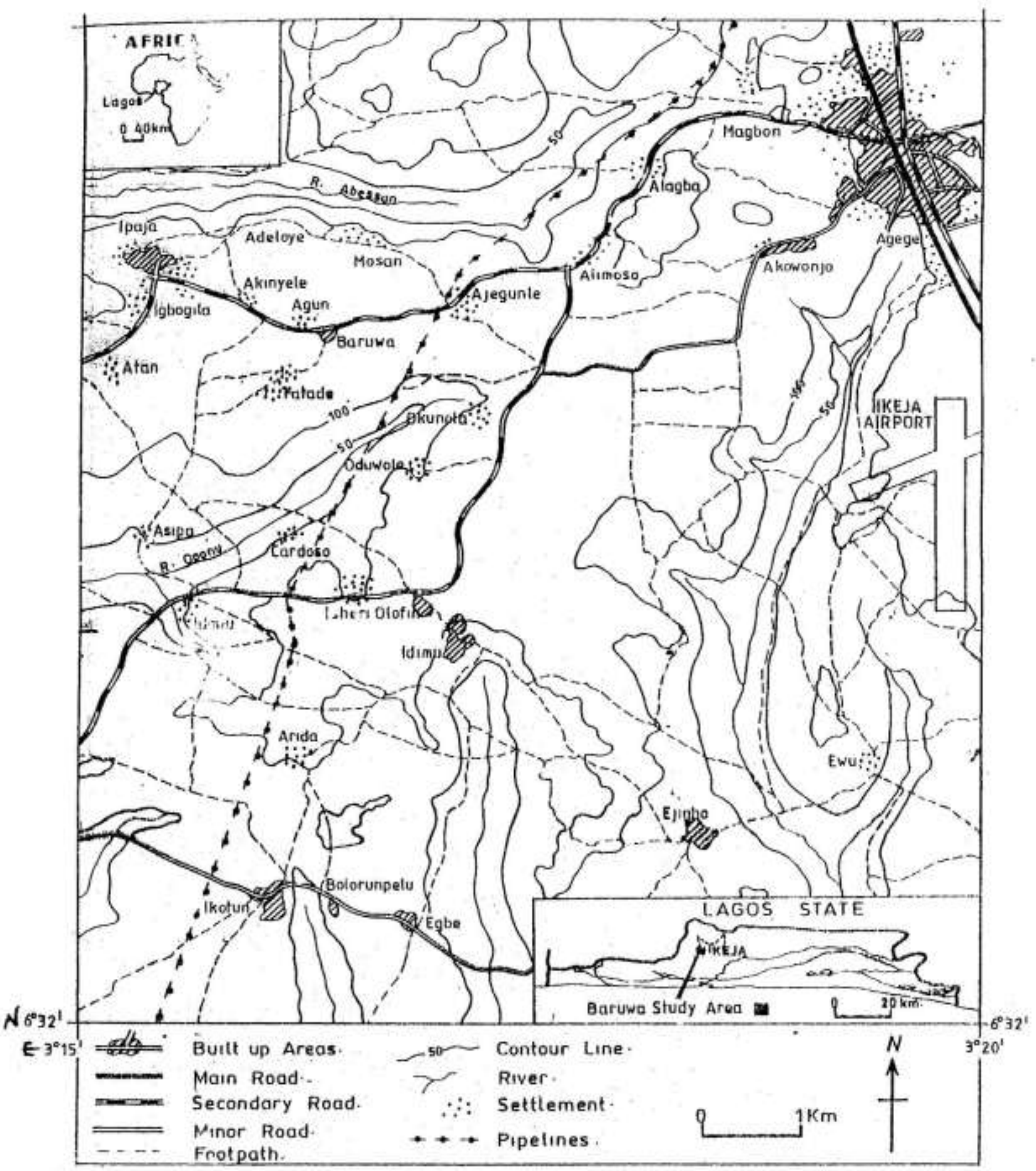


Fig 1.5: Previous location map showing the study area

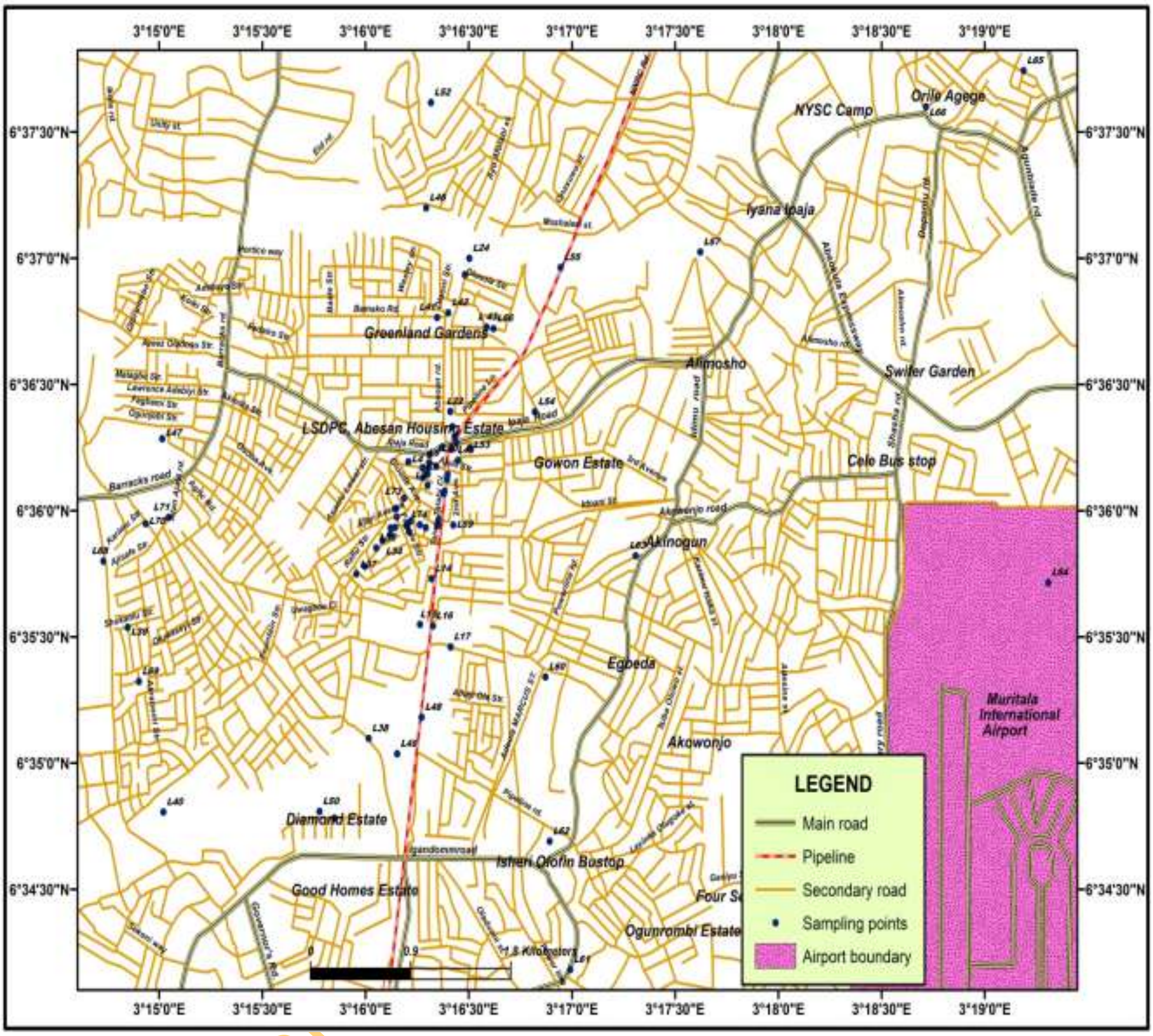


Fig 1.6: Newly created map of the study area

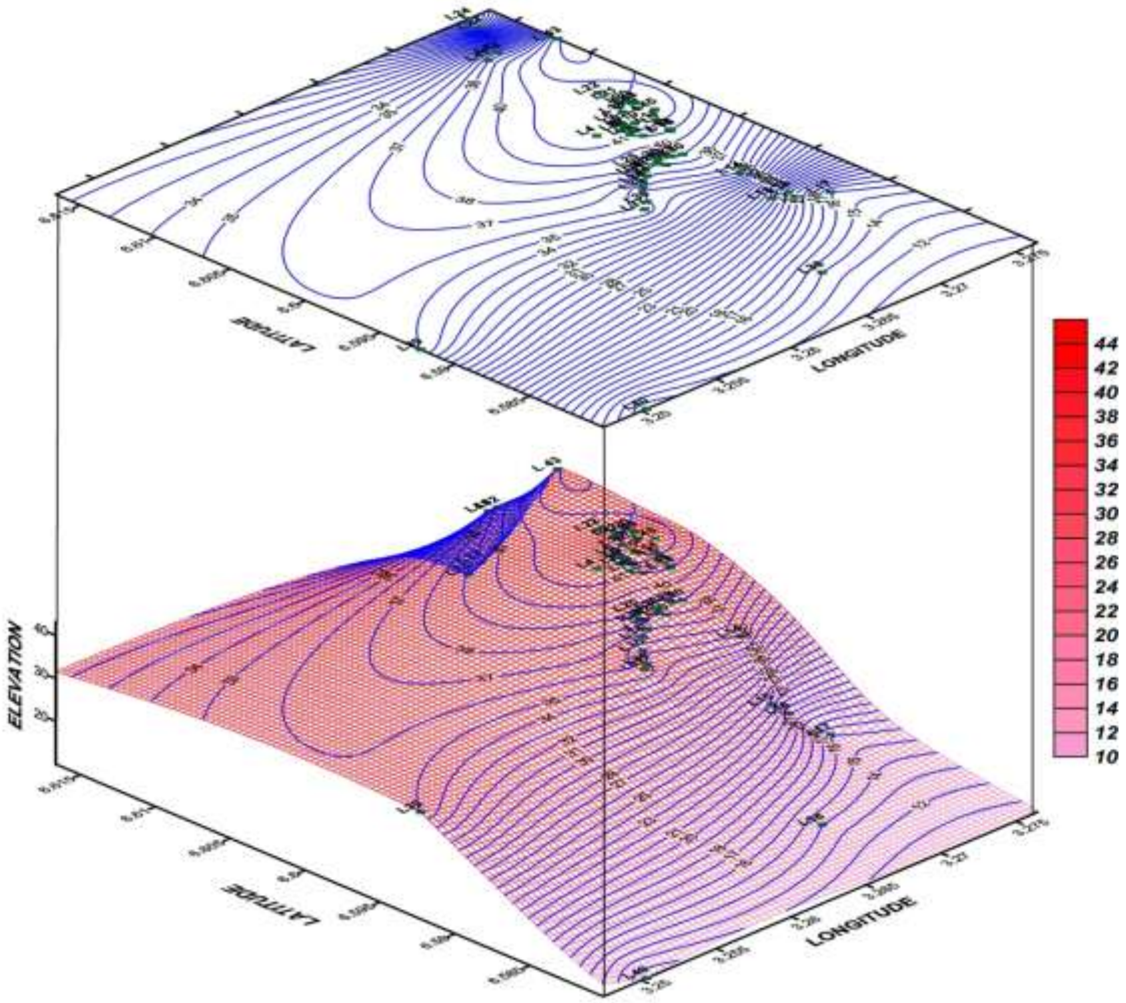


Fig. 1.7: Three dimensional view of the sampling points

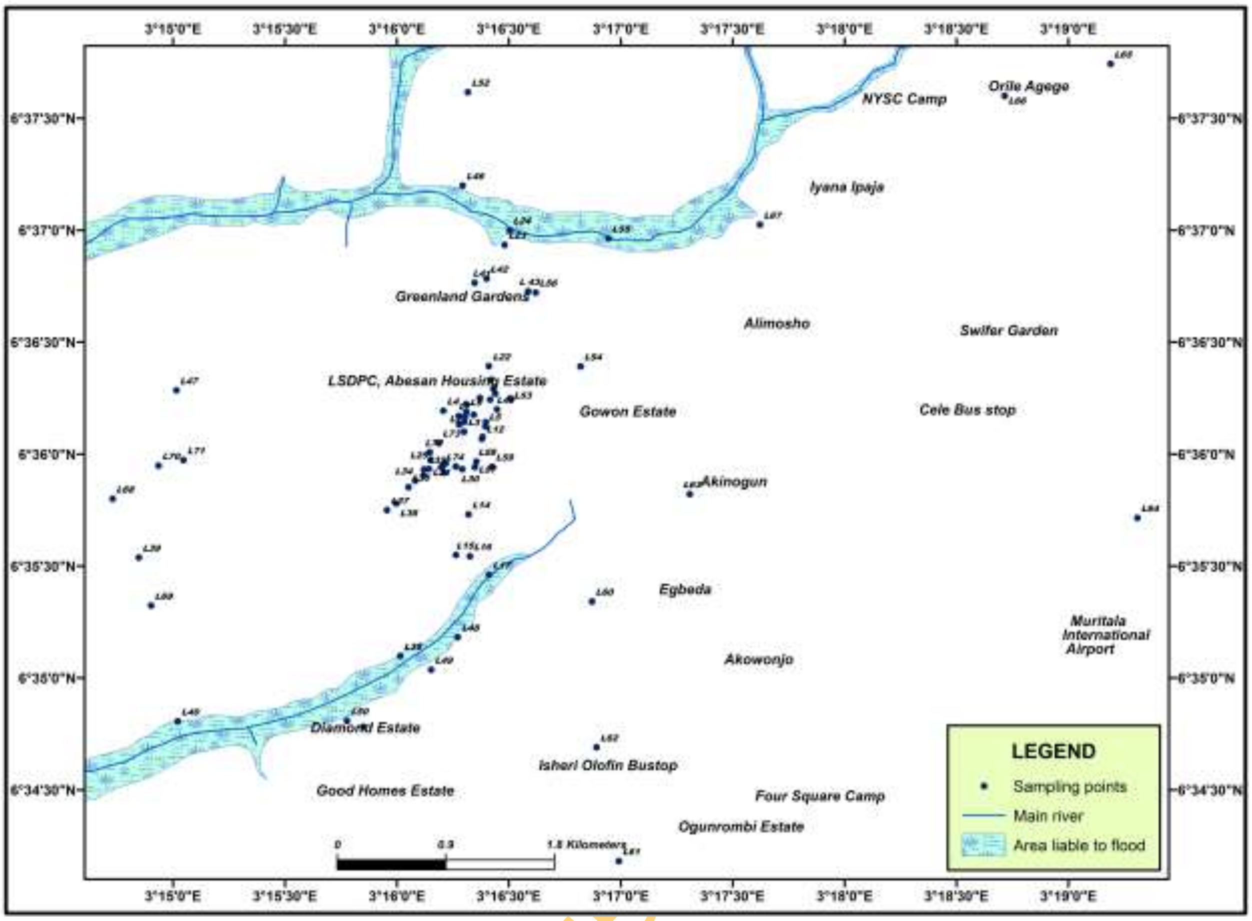


Fig.1.8: Drainage map of the study area

Fig. 1.9: Picture showing river Ponu flowing through the study area.

Fig. 1.10: Picture showing vandalized pipeline at Baruwa

Fig. 1.11: Picture showing exposed vandalized pipeline at Baruwa

Fig. 1.12: Pictures showing some replaced vandalized pipeline at baruwa

1.7 CONTROL AND REMEDIATION OF GROUNDWATER CONTAMINATION

The control and remediation of groundwater is basically the methods employed in the attempt to clean up contaminated groundwater. Several steps are normally taken to clean up a site once contamination has been discovered. Initially a remedial investigation is conducted to determine the nature and extent of the contamination. In the risk assessment phase, scientists evaluate if site contaminants might harm human health or the environment. If the risks are high, then all the various ways the site might be cleaned up are evaluated during the feasibility study. The record of decision is a public document that explains which of the alternatives presented in the feasibility study will be used to clean up a site.

Usually, the most protective, lowest cost, and most feasible cleanup alternative is chosen as the preferred cleanup method. The selected cleanup method is designed and constructed during the remedial design or remedial action phase. The operations and maintenance phase then follows. Periodically the remedial action is evaluated to see if it is meeting expectations outlined in the record of decision.

The various ways to respond to site contamination can be grouped into the following categories:

1. Containing the contaminants to prevent them from migrating from their source;
2. Removing the contaminants from the aquifer;
3. Remediating the aquifer by either immobilizing or detoxifying the contaminants while they are still in the aquifer;
4. Treating the groundwater at its point of use;
5. Abandoning the use of the aquifer and finding an alternative source of water.

Several ways are available to contain groundwater contamination: physically, by using an underground barrier of clay, cement, or steel; hydraulically, by pumping wells to keep contaminants from moving past the wells; or chemically, by using a reactive substance to either immobilize or detoxify the contaminant. When buried in an aquifer, zero-valent iron (iron metal filings) can be used to turn chlorinated solvents into harmless carbon dioxide and water.

The most common way of removing a full range of contaminants (including metals, volatile organic chemicals, and pesticides) from an aquifer is by capturing the contamination with groundwater extraction wells. After it has been removed from the aquifer, the contaminated water is treated above ground, and the resulting clean water is discharged back into the ground or to a river. Pump-and-treat, as this cleanup technology is known, can take a long time, but can be successful at removing the majority of contamination from an aquifer.

Another way of removing volatile chemicals from groundwater is by using a process known as air-sparging. Small-diameter wells are used to pump air into the aquifer. As the air moves through the aquifer, it evaporates the volatile chemicals. The contaminated air that rises to the top of the aquifer is then collected using vapor extraction wells.

Common groundwater remediation techniques include;

1.7.1 Permeable Reactive Barrier Wall Technologies

A permeable reactive barrier wall or In situ Chemical Reduction (ISCR) is a technology that remediates contaminated groundwater and soil without mass excavation, disposal or conventional "pump and treat" methods. Usually, a treatment media, or reactive barrier, is buried in a narrow trench beneath the ground surface so that contaminated groundwater passes through the media, and it emerges 'clean' because contaminates are treated and/or removed by the reactive barrier. Typical treatment media used as a permeable reactive barrier wall include granular iron, activated carbon, engineered bacteria, chemicals, and special clays. Often, slurry walls are used to funnel the groundwater toward a reactive media gate; this type of installation is called a "funnel and gate". Special construction considerations are needed for installing reactive barrier walls to ensure the design life of the media and to be cost-effective. Since any permeable reactive barrier wall must be buried deep underground and below the groundwater table, geotechnical methods are quite useful in minimizing excavation volumes, eliminating dewatering, and reducing costs.

In most cases, the least expensive method for installing funnel and gate is a slurry trench method. A slurry wall can provide the funnel to direct groundwater toward the reactive barrier materials.

A Bio-poiymer slurry trench drain can provide the gate of the permeable reactive barrier wall for the installation of the reactive media. The savings from this combination of methods are considerable including savings in excavation volumes, disposals costs, mobilization, and construction time. Slurry trenching methods have been proven to permit the installation of reactive iron (ZVI), engineered bacteria, compost, carbon and other materials without significantly affecting the reactive potential of the reactive barrier walls. In some cases, i.e. bio-treatment schemes, the Bio-Polymer slurry can actually promote the reactivity of the media. The installation of the reactive iron using the bio-polymer slurry method requires special equipment, materials and methods that have been developed, in part, by Geo-Solutions ®.

On some sites, the reactive media can be applied directly to the contamination instead of through a funnel and gate. Usually, these sites have lower groundwater flows and the contamination is less mobile. For these sites, in situ soil mixing with ISCR provides an ideal method for applying the reactive materials directly without excavation or dewatering. In-situ treatment using soil mixing is usually much less expensive than off-site disposal and completely avoids excavation and transportation costs.

With proper design and construction, PRBs can be effective for many years without requiring material replacement or maintenance. In contrast, adsorption treatment processes are limited by the loading capacity of the adsorbent material. However, PRBs are an effective solution for many groundwater contamination problems. In addition, special construction techniques such as British-Petroleum trenches and soil mixing can be used to make PRBs more attractive.

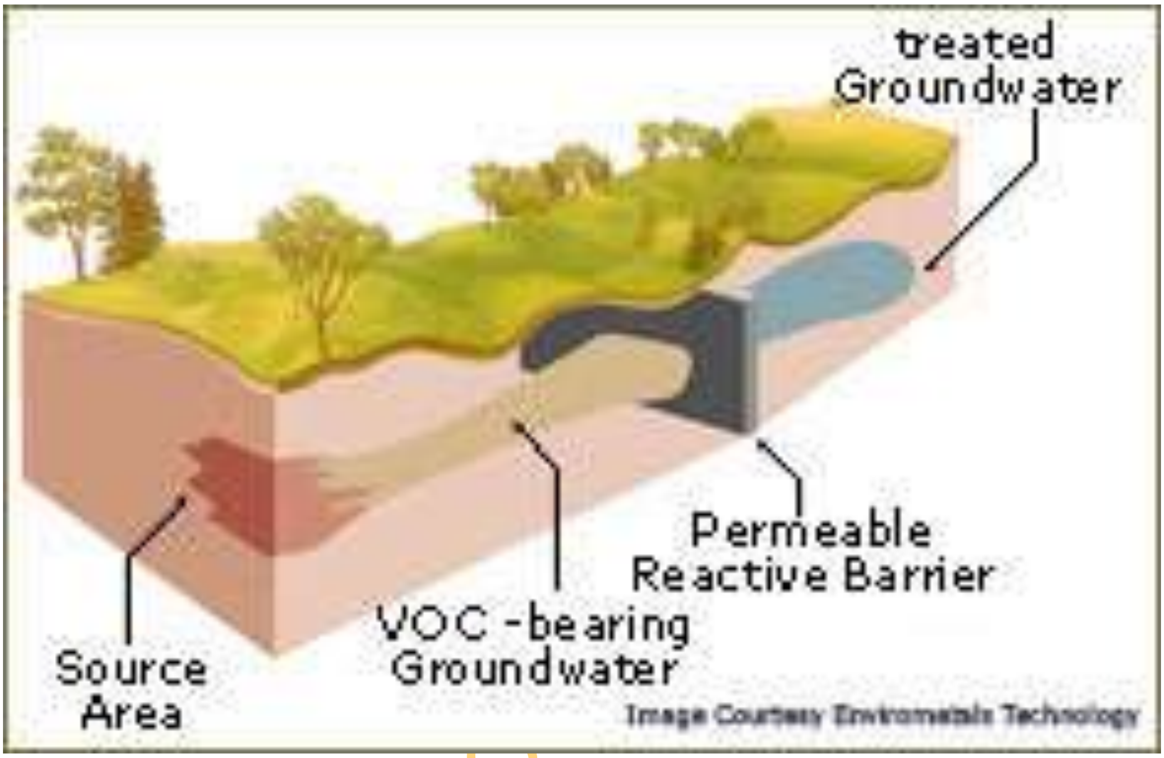


Fig. 1.13: Permeable Reactive Barrier Wall Illustration

1.7.2 Horizontal Wells

Horizontal wells are used in conjunction with a variety of treatment technologies to deliver or remove liquids and gases to or from the subsurface. Horizontal wells may be used to enhance other technologies such as Bio-venting, Soil Vapour Extraction, Air Sparging, In-well Air Stripping, and Sub-Structure Vapour Depressurization. Horizontal wells are sometimes preferable to vertical wells because they provide greater access to contamination that is moving horizontally, or reach subsurface areas without damaging surface structures. Where land reuse is anticipated, horizontal wells reduce constraints by minimizing the treatment footprint. Horizontal or directionally drilled wells are positioned horizontally or at an angle. Directional wells can either be double-ended (surface to surface) or single-ended (blind sided). Each type of well has advantages and disadvantages. During well installation, a navigation tool is located close to the drill bit. Slow rotation of the drill head removes and compacts the soil into the borehole wall. In some cases, cuttings are brought to the surface as is done with vertical drilling. Directional drilling equipment is capable of starting a borehole, steering the drill bit down to a desired horizontal depth, continuing at that depth, and then steering back to the surface. Installation of the well takes place after drilling activities are completed.

As opposed to vertical wells, horizontal wells may have a greater potential to collapse. For example, special drilling strategies are needed for wet sands because they are difficult to stabilize. Borehole collapse is also more likely in single-ended drilling since the hole is left unprotected between drilling and reaming and between reaming and casing installation. Double-ended holes may be easier to install since reaming tools and well casing can be pulled backward from the opposite opening, and the hole does not have to be left open. (Fig. 1.14).

Wells have been difficult to position precisely. It is reported that new guidance technology has limited this concern. Single-ended completion also involves the precise steering of reaming tools required to match the original borehole path. Currently, the technology is limited by depth. Most installed horizontal wells are less than 50 vertical feet. However there are a few wells that have been completed deeper, the deepest reported at 230 feet. This is because the mechanism for tracking the direction of the well generally decreases with increasing depth of installation, and it may be influenced by site-specific hydrogeologic conditions.

If gas or liquid is going to be injected, lateral movement of contaminants should be monitored. Each potential site must be assessed for the utility of horizontal wells. Heterogeneous soils with rocks and cobbles may limit the ability to drill.

Directional well technology is used for a range of applications, including groundwater removal, air sparging, free product recovery, in-situ bioremediation, soil vapour extraction, in-situ soil flushing, and leachate containment/collection. It is especially useful when a contaminant plume covers a large area or when surface obstructions are present. The technology is applicable to the complete range of contaminant groups. Recently, this technology has been used to install Sub-Structure Vapour Depressurization system under existing buildings, replacing the conventional method of drilling vertically through floors.

The use of horizontal wells can be effective in treating contaminated site. It was modified for the environmental remediation industry in the late 1980s and early 1990s. Contaminants that are less dense than water (like petrol) will float on the water table while those that are heavier will sink to the bottom. In both cases, a horizontal well can be precisely positioned within the water table to provide maximum contaminant extraction.

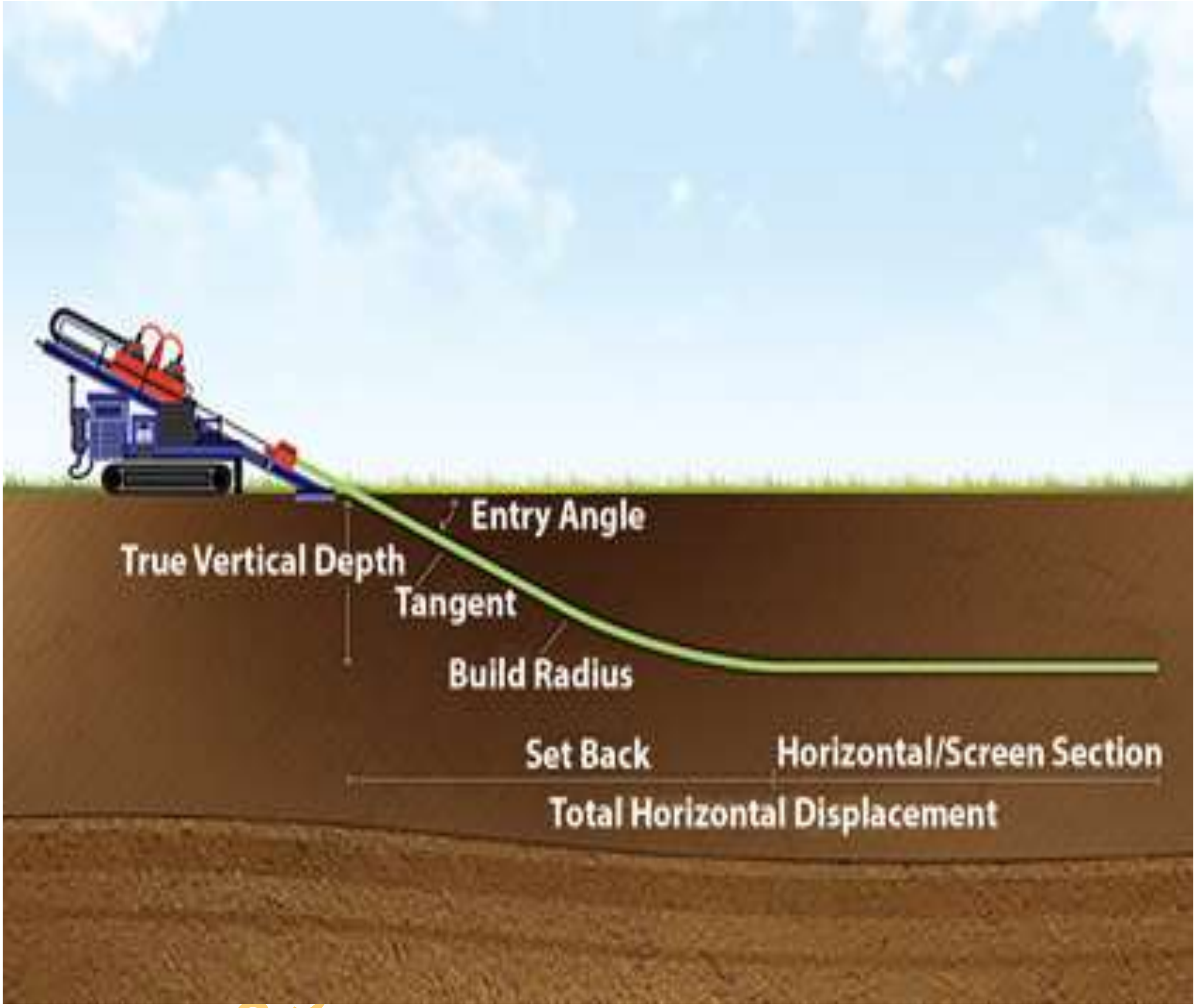


Fig. 1.14: Horizontal wells

1.7.3 Bioremediation technique

Bioremediation is a treatment process that uses naturally occurring micro-organisms to break down some forms of contamination into less toxic or non-toxic substances. By adding nutrients or oxygen, this process can be enhanced and used to effectively clean up a contaminated aquifer. Because bioremediation relies mostly on nature, involves minimal construction or disturbance, and is comparatively inexpensive, it is becoming an increasingly popular cleanup option.

Some of the newest cleanup technologies use surfactants (similar to dishwashing detergent), oxidizing solutions, steam, or hot water to remove contaminants from aquifers. These technologies have been researched for a number of years, and are just now coming into widespread use. These and other innovative technologies are most often used to increase the effectiveness of a pump-and-treat cleanup.

In addition a horizontally drilled well can also provide an excellent conduit for placing organisms in the groundwater and sustaining them with air, water and nutrients i.e. combination of two techniques - horizontal well and bioremediation technique.

Depending on the complexity of the aquifer and the types of contamination, some groundwater cannot be restored to a safe drinking quality. Under these circumstances, the only way to regain use of the aquifer is to treat the water at its point of use. For large water providers, this may mean installing costly treatment units consisting of special filters or evaporative towers called air strippers. Domestic well owners may need to install an expensive whole-house carbon filter or a **reverse osmosis** filter, depending on the type of contaminant.

1.7.4 Pile Biodegradation

Pile biodegradation technology is used to decontaminate soils polluted with light hydrocarbons (gasoline, diesel fuel, heating oil, light crude oils). Soils are excavated, transported and placed on a waterproof platform equipped with facilities that allow for forced aeration of soil, capture and treatment of leached water, and filtration of the contaminated air through activated carbon or peat filters. Soil may be covered to reduce the spread of VOCs and heat loss. Heavy metals such as lead and mercury and presence of chlorinated hydrocarbons can limit the efficiency of pile biodegradation methodology (GSI, 1995).

1.7.5 Phytoremediation

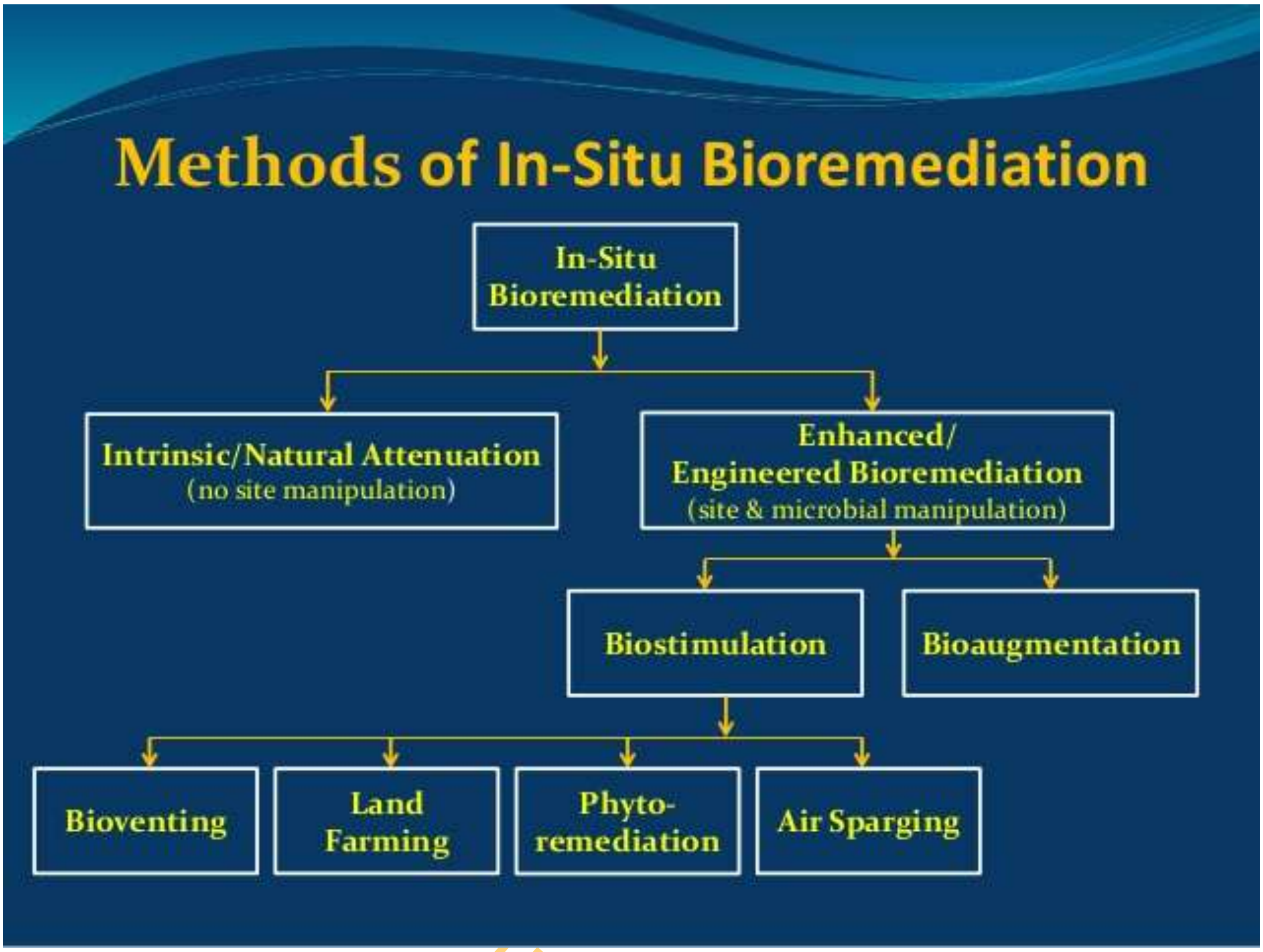
Phytoremediation is a process that uses actively growing plant roots to stimulate a diverse population of soil microorganisms, some of which have the capability to metabolize hydrocarbon contaminants. A research at Purdue University in Indiana has pioneered the use of plants to help clean up soil contaminated with petroleum products (Lazaroff, 2000). The team states that due to slow mobility of petroleum compounds in soil, phytoremediation becomes an effective method for the top portion of soil contamination (~1.8m or 6ft). Based on their theory, plant roots accelerate the microbial activities in soil by providing oxygen and nutrients in soil. Soil microbes then break down the petroleum contaminants. Phytoremediation may not be a feasible technique for leaking Underground storage tanks (UST) sites where petroleum contamination is usually deeper than the plant's root zone and plantation may not be possible at such sites.

1.7.6 Natural Attenuation

Natural attenuation is a strategy of allowing natural processes to reduce contaminant concentrations over time. This process involves physical, chemical and biological processes which act to reduce the mass, toxicity, and mobility of subsurface contamination. Natural attenuation should be accompanied with continuous monitoring to assure that the degradation process is progressing at a desired rate. Light hydrocarbons (aromatics) in gasoline will biodegrade relatively quickly. The heavier hydrocarbons found in gasoline and diesel fuel are less degradable and also less soluble in ground water. When ethanol blended gasoline leaks, ethanol in gasoline can compete for bacteria with other hydrocarbons therefore extending the plumes of more toxic hydrocarbons.

1.7.7 Air Sparging

Air sparging is a method of site remediation that introduces air (or other gases) into the saturated zone contaminated with VOCs. In addition to volatilization of VOCs, air sparging promotes the growth of aerobic bacteria in saturated zones and may oxidize reduced chemical species. Soil vapor extraction wells are placed in sites where air sparging is applied and they extract the volatilized contaminants that are transported to the unsaturated zone by air sparging (Hoag et al., 1996). Hinchee, 1994, categorizes air sparging as two distinct technologies, in-well aeration and the injection of air into the saturated zone. In-well aeration is the injection of air below the water table in a well, producing a physical change in the



Methods of In-Situ Bioremediation

In-Situ Bioremediation

Intrinsic/Natural Attenuation (no site manipulation)

Enhanced/ Engineered Bioremediation (site & microbial manipulation)

Biostimulation

Bioaugmentation

Bioventing

Land Farming

Phyto-remediation

Air Sparging

Fig. 1.15: Flowchart showing bioremediation techniques

ground water system known as the “airlift pump effect”. As air bobbles move upward in the well and reach the water surface, they create a relative vacuum behind in their flow paths. This pressure difference causes the ground water to move into the well from the bottom screens and return to the aquifer from the shallower portion of the screens. This movement of ground water into the bottom of the well results in VOCs entering the well as they are stripped from solution with the sparging gas. A major draw back in this system is the gradual build up of bacteria and inorganic precipitation in the vicinity of the well screens that can significantly reduce the circulation of water and the sparging efficiency. The objective of the second air sparging technique is to inject pressurized air into the aquifer material through the well screens or diffusers. It has been reported that the injected air into the aquifer migrates in stable channels and only the contaminated soil within these channels are exposed to the injected air. If stable air channels form in the aquifer by air injection, the only removal process of the contaminants not in direct contact with the airflow paths would be liquid phase diffusion (Hoag et al., 1996).

Equilibrium partitioning of the contaminants at the gas/water interface can be written as: Cg=CaqH, where Cg is the gaseous concentration in terms of mg/L, Caq is the aqueous concentration in mg/L, and H is the dimensionless Henry's law constant. This relation can be used to describe the partitioning of gas and water in the sparging system. The efficiency with which air sparging transfers oxygen to water is measured by determining the rate at which the dissolved oxygen concentration of ground water increases. Increase in oxygen concentration depends on the partial pressure of oxygen in the sparging gas, which in part depends on the gauge pressure of the air pump. In a study conducted by Hoag (1994) a gauge pressure of 0.96 atmosphere was required to induce air sparging, eight meters below the water table in an aquifer formation of silt and sand.

1.7.8 Glass Reinforced Plastic

An innovation to curb groundwater contamination through leaking pipes is the evolution of the Glass Reinforced Plastic (GRP). The Glass Reinforced Plastic (GRP) is produced by impregnating glass fibers with compatible polymeric binder materials and finally cured according to desired specifications. It is known to be a non-conductive material. It has added advantage over mild steel underground tank by not requiring the impregnation of concrete in order to prevent corrosion problems. As practiced in many industrialized countries, the replacement of mild steel in the construction of pipes, tanks and petroleum product pipelines should be pursued vigorously as this will help to prevent the incidence of spills from corroded storage tanks and pipelines.

GRP PIPING

PART OF A GRP WATER SLIDE FOR A SWIMMING POOL

Fig.1.16 and 1.17: Picture showing Glass Reinforced Plastic (GRP).

1.7.9 Pump and Treat

Pump and treat is a technique that extracts contaminated ground water from the subsurface with the use of extraction wells. Contaminated ground water is treated by air stripping, passage through activated carbon or bioremediation. This treatment technique is usually accompanied with in situ vapor extraction to enhance the removal of residual volatile hydrocarbon from the zone of fluctuating ground water. This technique is not effective for low permeable aquifers that may require long-term pumping and treating and discharge permits (USEPA, 1993). Once the contaminated ground water is pumped out of the aquifer through a series of extraction wells, the extracted ground water can be treated at the surface level and return to the aquifer. Granulated activated carbon is usually used to treat contaminated ground water at the surface.

CHAPTER TWO

LITERATURE REVIEW

2.0 GEOLOGIC SETTING AND BASIN EVOLUTION

2.1 REGIONAL GEOLOGY AND TECTONIC FRAMEWORK

The Dahomey Basin is one of the seven sedimentary basins in Nigeria. It is also called the Dahomey Embayment or West Nigerian basin in older literature. It is a very extensive basin; it extends from Southeastern Ghana in the west through Southern Togo and Southern Benin Republic to the western flank of Niger Delta. The eastern half of the basin occurs within the Nigeria territory. (Fig. 2.1). (Jones and Hockey, 1964; Ogbe, 1972; Omatsola and Adegoke, 1981). It is a marginal pull apart basin (Klemme, 1975) or marginal sag basin (Kingston *et al.*, 1983) which developed in the Mesozoic when the African and South American lithospheric plates separated and the continental margin foundered (Burke *et al.*, 1971; Whiteman, 1982). The axis of the basin and the thickest sediment occurs slightly west of the border between Nigeria and the Republic of Benin (Slansky, 1962; Antolini, 1968; Billman, 1976) (Fig. 2.2).

The Dahomey Basin is bounded on the west by fault and other tectonic structures associated with the landward extension of the Romanche Fracture Zone and its eastern limit is similarly marked by the Benin Hinge Line, a major fault structure marking the western limit of the Niger Delta Basin. The latter is also a landward extension of the Chain Fracture Zone (Fig.1.14). To the east of the Benin Hinge Line is the Okitipupa Ridge (Adegoke, 1969).

The Dahomey Basin was created during the first stage of rifting. In such rift basin, it is common to observe a first stage of initial continental crust thinning, arching and faulting probably around Middle Jurassic times. A series of Graben and half Graben were rapidly filled with lacustrine and alluvial sediments blanketed in the Albian times with transgressive marine sediments, marking the first penetration of the continent as observed during the lower Cretaceous times. By the Cretaceous times, Africa and South America plates were totally split with a spreading ridge and oceanic crust separating the continent. At this stage, the Dahomey Basin was simply a passive margin with marine sediments derived from northerly direction prograding southwards over a gently sagging basin. This process still persists through the Tertiary to Recent. During the Early to Late Cretaceous, probably Santonian, there was another episode of major tectonic activity, probably associated with the closure and folding of the Benue Trough. The granites, gneisses, and associated pegmatites as well as the sediments in the Dahomey Basin were tilted and block faulted, forming a series of Horst and Graben (Fig. 2.5). Considerable erosional activity accompanied the uplift and block faulting. The extensive Lower Cretaceous pre drift sediments were almost completely eroded from the Horst. e.g. Bodashe horst. During the Maastrichtian the basin became quiescent and has experienced only gentle subsidence since then.

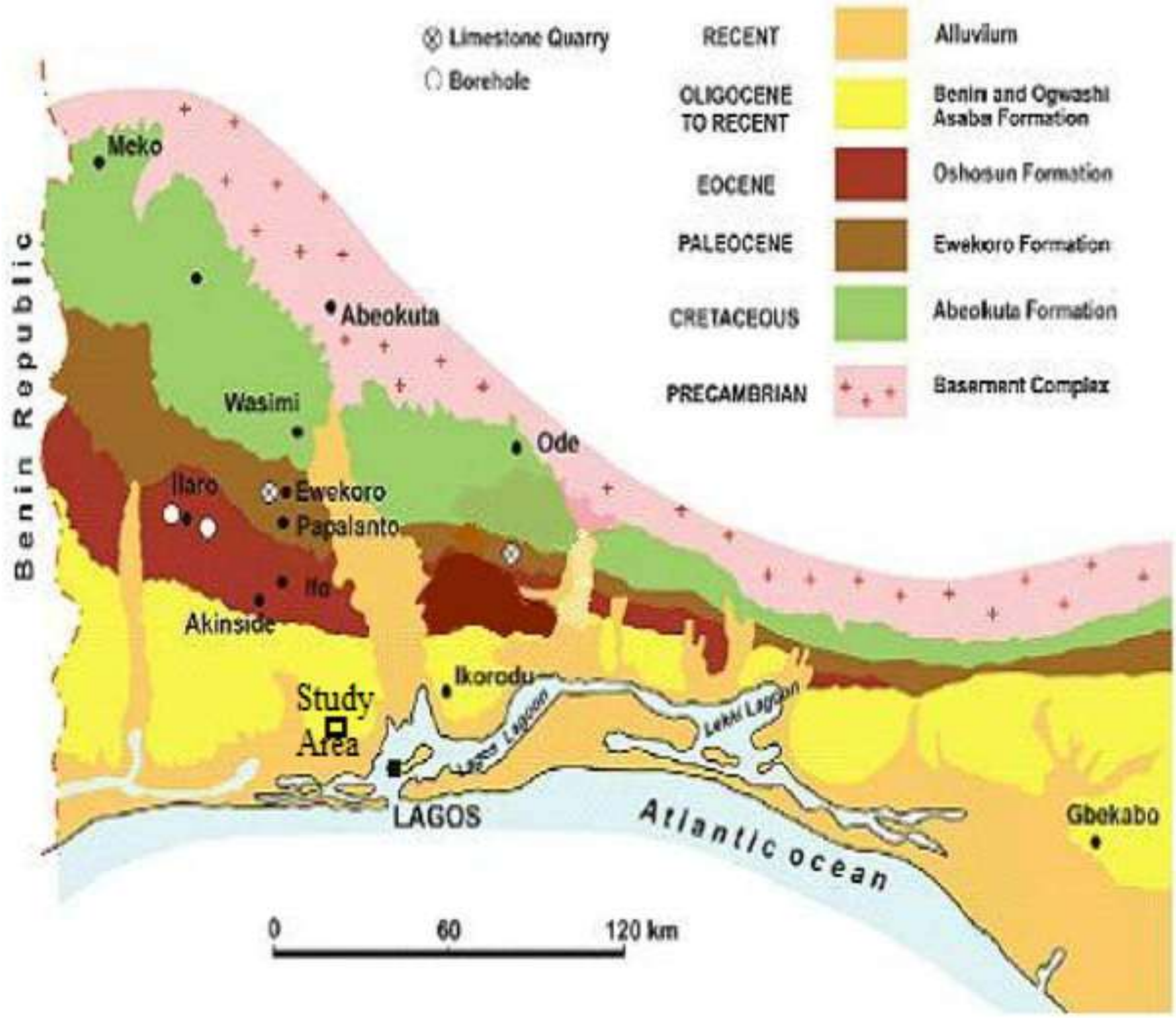


Fig. 2.1: Geological Map of the Lagos Area

(Source: Billman, 1976).

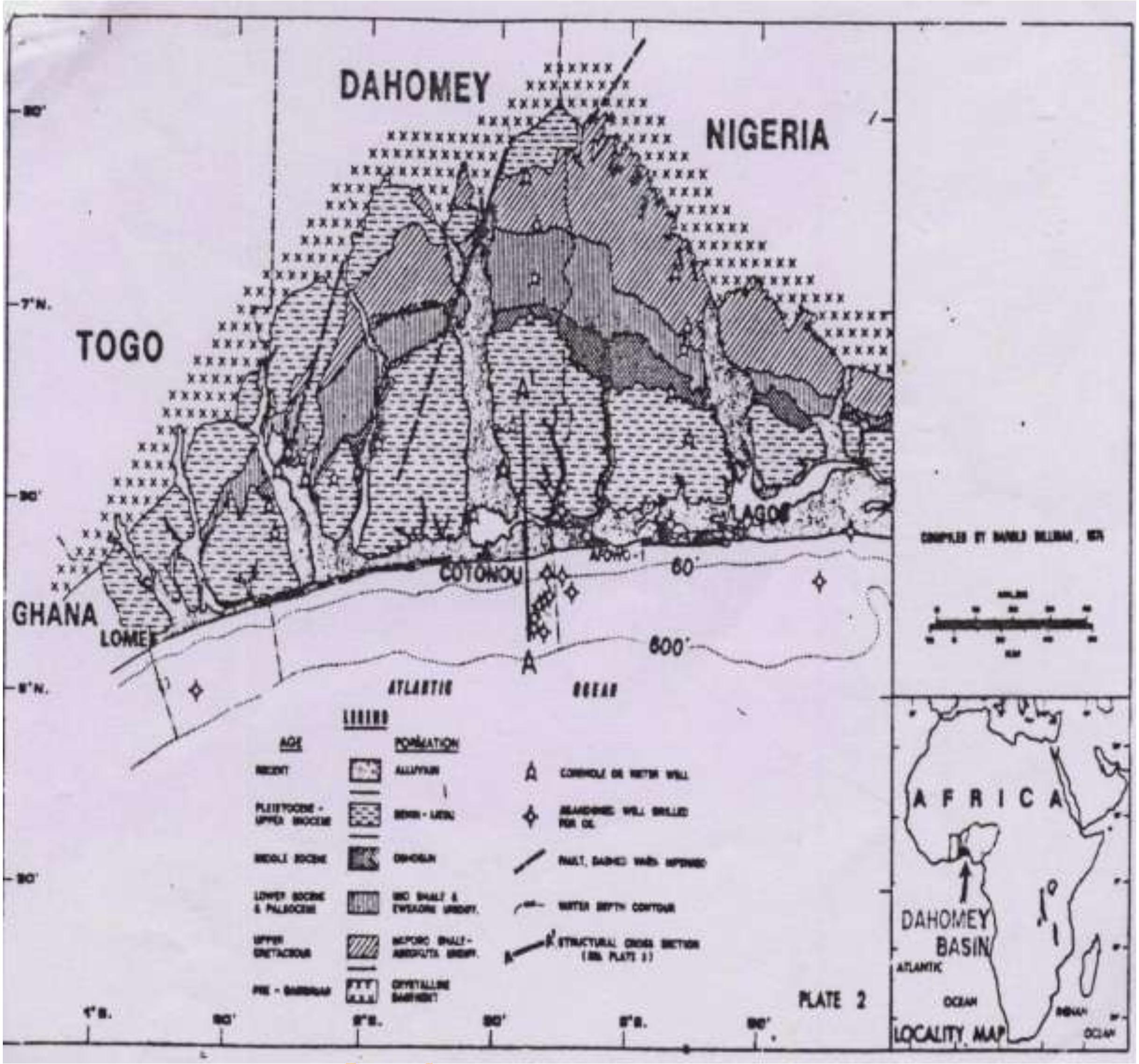


Fig. 2.2: Generalized geological map of the Dahomey Basin

Source: Billman 1976.

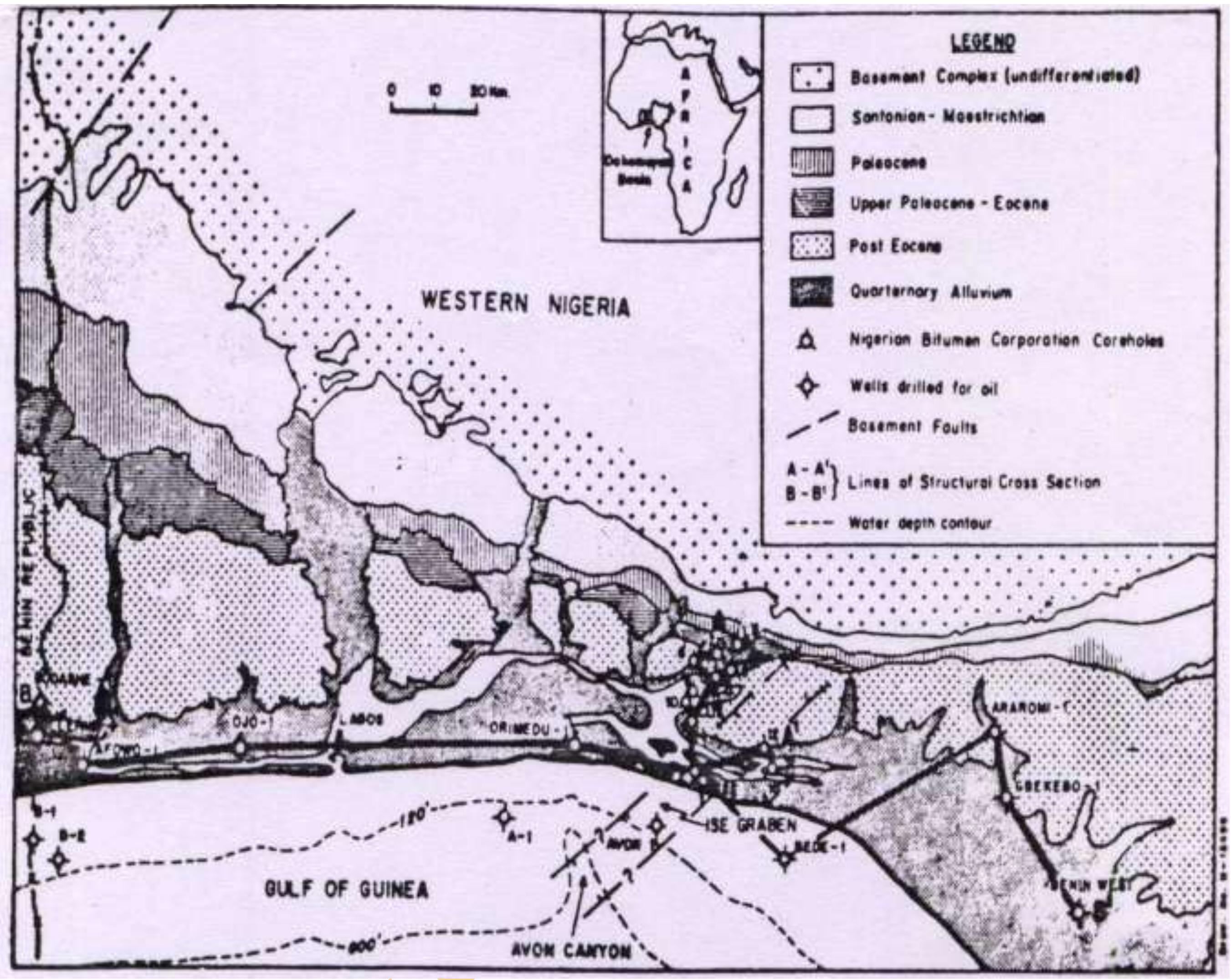


Fig.2.3: Geological map of the eastern Dahomey Basin

Source: Omatsola and Adegoke, 1981.

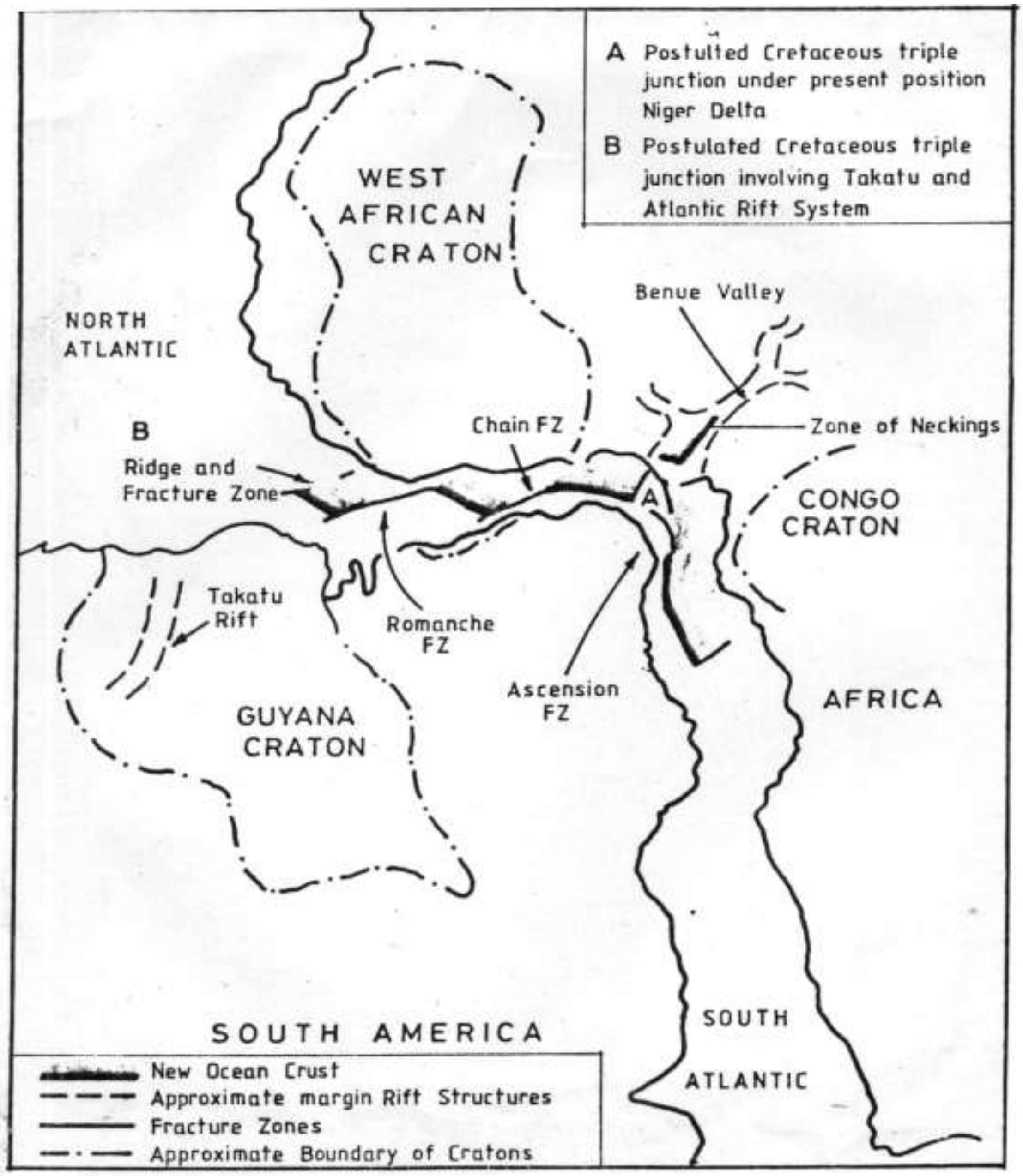


Fig. 2.4: Opening of the South Atlantic about a triple junction during the early Cretaceous (Source: Burke *et al*. 1972).

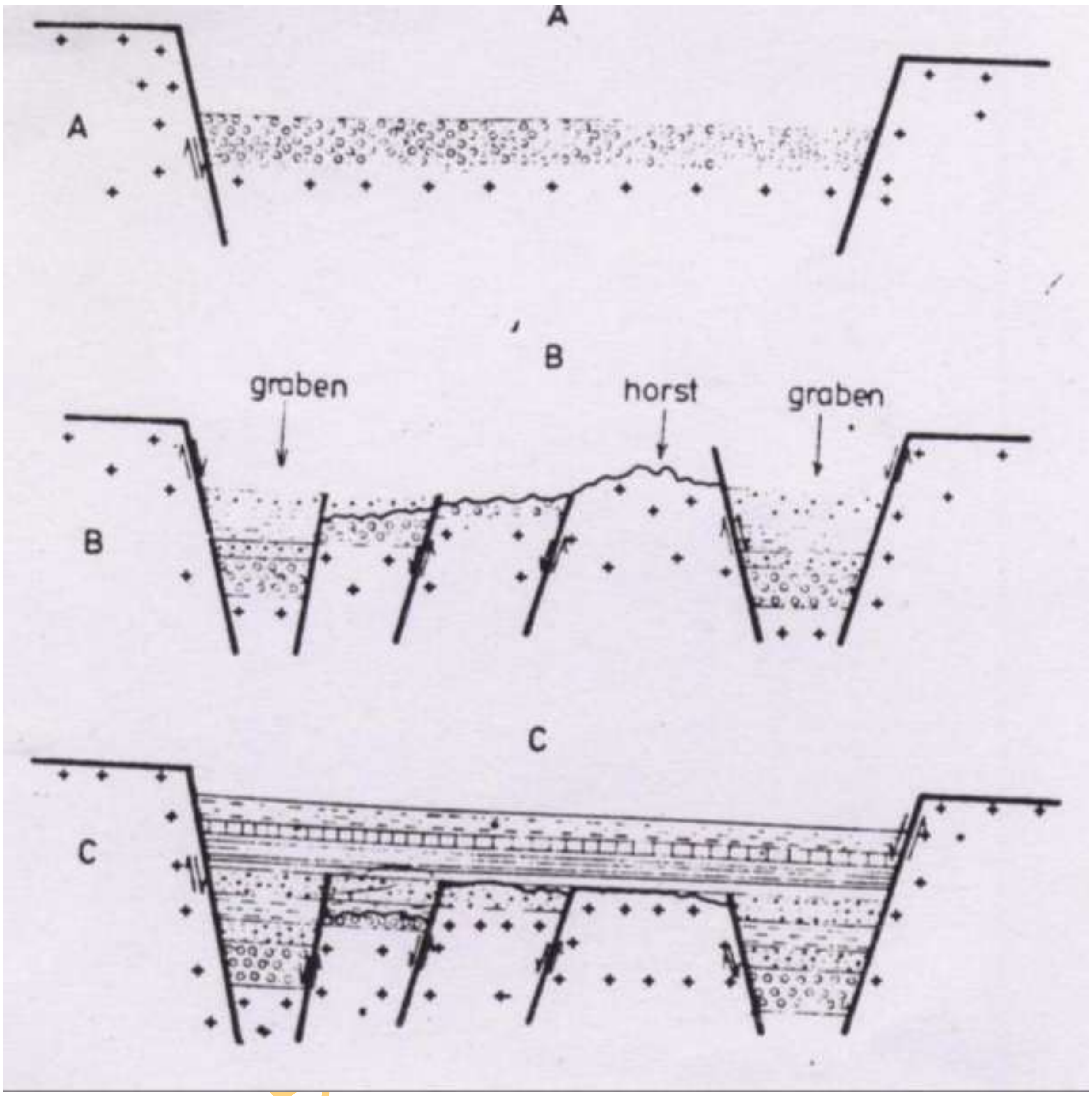


Fig.2.5: Tectonic model for the evolution of the Dahomey Basin

(Source: Omatsola and Adegoke 1981).

2.2 GENERAL STRATIGRAPHY OF DAHOMEY BASIN

Various authors using both surface and subsurface information have described the stratigraphic setting of the eastern Dahomey Basin, and they include Jones and Hockey, (1964), Adegoke (1969), Ogbe (1970), Kogbe (1974), Billman (1976), Ako*et al.*(1980), Omatsola and Adegoke (1981), Reyment (1981), Whiteman (1982), Agagu (1985) Nwachukwu and Adebayo (1987), Ekweozor and Nwachukwu (1989), Hack *et al.*(1997), Nton (2001)among others.

The succession from the oldest to the youngest include Abeokuta Group (which comprises of Ise Formation, Afowo Formation and Araromi Formation all formed in the Cretaceous), Ewekoro Formation (Paleocene), Akinbo Formation (Late Paleocene to Early Eocene), Oshoshun Formation (Eocene) and Ilaro Formation which is also Eocene. The earliest documented marine transgression in Nigeria took place during the Mid - Albian, but this was limited to the Benue Valley and the Southeastern Nigeria (Kogbe, 1976). The end of the Albian marked the regressive phase during which the pre drift continental sand, grits, and siltstones of the Ise Formation and especially, the basal conglomerates overlying the basement complex were deposited (Adeleye, 1975, Omatsola and Adegoke, 1981).

The ***Ise Formation*** consists of conglomerates and grits at the base and is overlain by coarse to medium grained loose sands with interbedded kaolinite. The conglomerates are unimbricated and at some locations, ironstones occur. Both the cross bedding azimuth of the sandstones and the pebble alignment point to a NE paleocurrent system (Nton, 2001). The age range is from Neocomian to Albian.

The ***Afowo Formation*** which overlies the Ise Formation is mostly composed of coarse to medium grained sandstones, with variable but thick interbedded shales, siltstones and clays. The shale component increases progressively from bottom to top, the lower part of the formation is transitional with mixed brackish to marginal horizons alternating with well sorted, sub rounded , clean, loose fluviatile sands. (Billman, 1976). This indicates a littoral or estuarine near shore environment of deposition in which water level flunctuated fairly rapidly. The medium grained loose sands, sandstone sand grits with interbeds of kaolinitic clay of the Afowo formation were deposited during Turonian to Maastrichtian, (Omatsola and Adegoke, 1981).

The ***Araromi Formation***is the youngest formation in the Abeokuta Group and is composed of fine to medium grained sands at the base and overlain by shales and siltstone beds with thin interbedded limestones and marls (Ogbe, 1972, Okosun, 1990). Lignitic sands are also common in the sequence. The shales are very fossiliferous bearing abundant planktonic and benthonic foraminifera and ostracods (Billman, 1976). The Araromi Formation was deposited by the marine transgression that started at the end of the Maastrichtian which continued through the Paleocene (Adegoke, 1969). This formation together with the underlying Afowo and Ise Formation constitutes what Omatsola and Adegoke (1981) proposed as the Abeokuta Group.

The ***Ewekoro Formation*** overlies the Abeokuta Group conformably, consisting of highly fossiliferous limestones (Adegoke, 1969, Adegoke et.al., 1970, Adegoke et.al., 1980). The formation turns to marl and its arenaceous content increases towards the base and grades into the underlying predominantly sandy Abeokuta Group. According to Ogbe (1972), the Ewekoro Formation is partly brackish water, partly marine and partly fresh water in origin. The Ewekoro Formation is an extensive limestone body which is traceable over a distance of about 320km continuously from Ghana eastward toward the eastern margin of the Dahomey Basin in Nigeria. The limestone is exposed both at the Ewekoro and Shagamu quarry. It is thickly bedded and colour banded. Apart from the quarry exposures, there are very rare outcrops except those intercepted in several boreholes. It's shallow marine origin is manifested by abundant coralline algae, gastropods, pelecypods, echinoids fragments and other skeletal debris (Nton, 2001). The age is Paleocene.

The ***Akinbo Formation*** (Ogbe, 1972) overlies the Ewekoro Formation and consists of shales, clayey sequence. The base is defined by the presence of glauconitic band. The type locality is at Ewekoro quarry. East of Ijebu Ode, the formation replaces the Ewekoro Formation which thins out here. Westward, the formation extends into the Republic of Benin and Togo (Slansky, 1962). The age of the formation ranges from Paleocene to Eocene.

The ***Oshoshun Formation*** overlies the Akinbo Formation and is composed of greenish – grey or beige clay and unconsolidated clayey shale with interbed of sandstone. The shale is thickly laminated and glauconitic (Okosun, 1998). The basal bed consists of any of the following facies: sandstone, mudstone, claystone, and shales. This formation is compositionally phosphorite (Nton, 2001). Thin beds of limestone or marl are locally present in this formation. The shales found in this formation were deposited in well oxygenated deep marine environment. The age is Paleocene to Eocene.

IlaroFormation: which directly overlying the Oshosun formation was formed during the Middle to Late Eocene regression (Adegoke, 1967; Kogbe, 1976; Ako et. al., 1980). It consist of predominantly coarse sands of estuarine, deltaic and continental environments which display rapid lateral facies change (Slansky, 1962; Jones and Hockey,1964) . the sands are generally white and mineralogically composed of pure quartz grains.

Coastal Plain sands / Benin Formation: The Benin Formation is the youngest stratigraphic sequence in the eastern Dahomey Basin. it consists of poorly sorted sands with lenses of claystones. The sands are partly cross bedded and show transitional to continental characteristics. The age ranges from Oligocene to Recent (Reyment 1965). Thickness as much as 400m has been reported towards the coast (Agagu, 1985).

2.3 GEOLOGY OF LAGOS

The geology of the Lagos area is dominated by a continuous and monotonous repetition of clayey and sandy horizons. These horizons show some discernable lateral continuation and are made up of successions of sandy-clay, sands, clayey sands and gravely sands sequences. The sandy layers which are fine silty-sands to very coarse gravely sands range from reddish-brown to pinkish in colour while the clay units vary from whitish through pinkish, reddish to brown and dark–brown in colour. The sands and clay sequences are intercalated with isolated andsometimes discontinuous bands of dark-brown to black peat and lignite.

Table 2.1: Summary of Geology of the Eastern Dahomey Basin

Age	Lithology	Description	Authors
Recent	Recent lithoral alluvial deposit	Poorly sorted loose sediments ranging from silt clay and fine to coarse grained	Jones and Hockey (1964), Omatshola and Adegoke (1981), Agagu (1985), Enu (1990), Nton (2001).
Oligocene to Pleistocene	Coastal plain sands	Poorly sorted clayey sand and pebbly sands	Jones and Hockey (1964)
Eocene	Ilaro formation	Massive yellowish and poorly consolidated cross bedded sandstone	Agagu (1985), Omatshola and Adegoke (1981)
Eocene	Oshoshun formation	Sequence of mostly pale greenish grey laminated phosphatic marl, light grey to purple clay with interbedded sandstone	Agagu (1985)
Paleocene	Imo group		Ogbe (1972)
	Akinbo formation	Shale glauconitic rock and gritty sand to pure grey and little clay	
	Ewekoro formation	Shaly limestone which is sandy and highly fossiliferous	
Necomian to Maastrician	Abeokuta group		Omatshola and Adegoke (1981)
	Araromi formation	Sand overlain by dark grey shale, siltstone and interbeded limestone, marl and occasional lignite band	
	Afowo formation	Coarse to medium sandstone with interbeds of shale, siltstone and clay	
	Ise formation	Continental sand grits and siltstone	

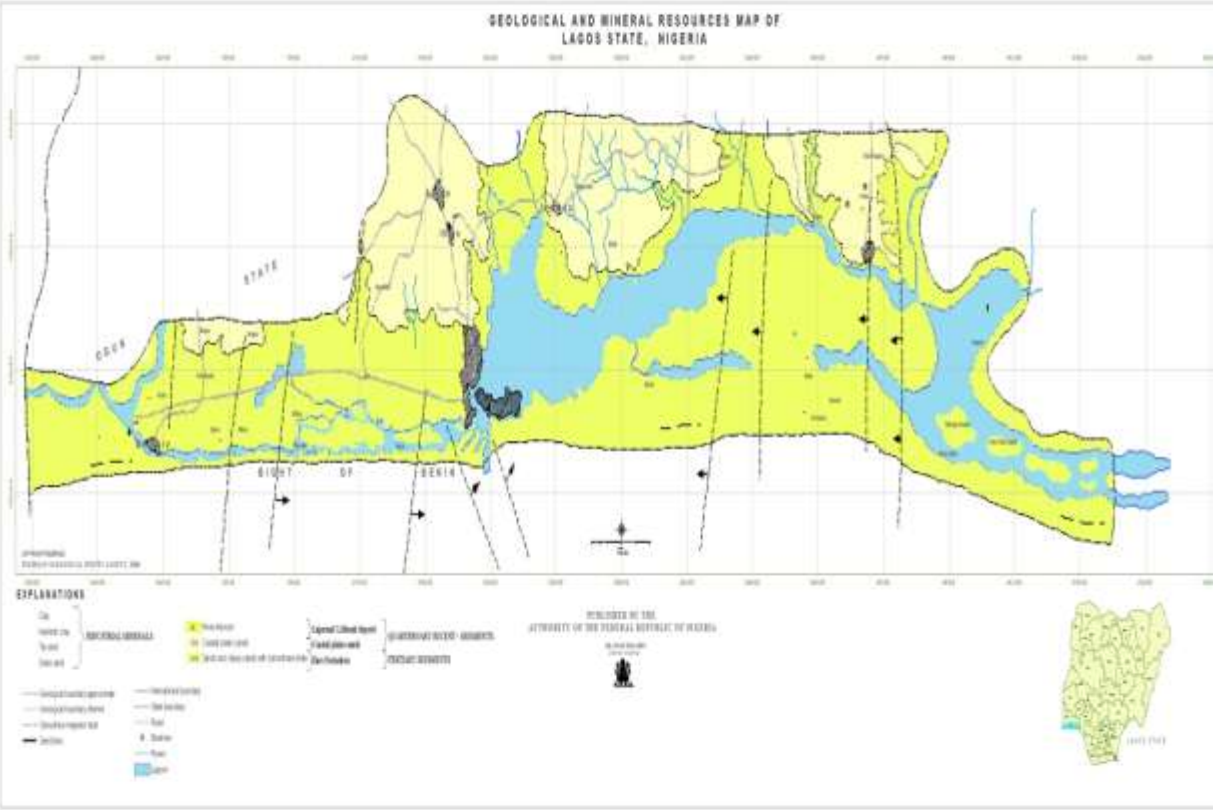


Fig. 2.6: Geological Map of the Lagos Area

(Source: NGSA, 2009)

2.4 HYDROGEOLOGY, HYDROGEOPHYSICS AND HYDROGEOCHEMISTRY OF LAGOS

Borehole data revealed that most of the domestic boreholes and hand-dug wells have depths ranging from 20m to 60m while industries and the water corporation have boreholes with depths ranging from 100m to 300m with some having a depth of 700m (Olatunji, 2006). Geophysical results obtained from the metropolis revealed a plethora of apparent resistivity curves. These include the Q, K, QH, QQHA, KQHA, HKQQ, QQQ, HKQHK, HAKHK, HQKHK, KHKQK and the KHKHA types depending on the depth of penetration of the soundings. However the multi - layered curves are more dominant, an indication of the chaotic depositional sequences that were responsible for the lithology. Groundwater chemistry revealed that the water samples are generally potable except for some of the shallow boreholes that have been impacted by surface run-offs, saline water intrusions from the lagoons as well as iron contamination.

The water types in the area are mainly Na–HCO^3 and Ca–(Na)–HCO^3water types (Olatunji et al., 2005; Tijani et al., 2005).

2.4.1 Local Geology and Hydrogeology of study area

The study area is located within the Nigerian Coastal Zone, being a zone of coastal creeks and lagoons Fig.2.6, (Pugh, 1954). Three aquifer horizons have been delineated in the Lagos metropolis subsurface;

These are categorized to first aquifer horizon thought to belong to the Recent lithoral / alluvial deposit and the Benin formation (Longe *et al*., 1987). The second aquifer horizon is made up of sands and clay thought to be the coarse sandy estuarine deltaic and continental beds of Ilaro formation (Jones & Hockey, 1964; Longe *et al*., 1987) Third aquifer layer consists of alternating sequences of clayey and sandy strata. Locally, the study area is underlain by the Benin Formation. Longe et al. (1987) and Longe and Enekwechi (2007) describe a succession of a 4m thick lateritic cover that is underlain by alternating thin sands and clays for this part of Oregun ,Ikeja. The first aquifer of loose, medium to coarse sands with an average thickness of about 10m underlies this sequence. This water table aquifer is tapped by shallow boreholes and dug wells for domestic water supplies and is highly vulnerable to contamination. A semi- permeable silty clay layer which attains a maximum thickness of 10m separates the first aquifer horizon from the second sandy aquiferous zone. The second aquifer zone is a more important ground water source for private, commercial and industrial supplies and exists between 20 to 70m (Longe et al. 1987). This aquifer is confined and average values of transmissivity and storage coefficient of 1120 m2/day and 3.77 x 10-4 respectively for this aquifer zone have been reported (Longe, 2011).

The third major aquifer zone, ranging from 15 to 30m in thickness, occurs at greater depth in the Benin Formation. Encountered in central Lagos metropolis at depths ranging from 118m to 166m below sea level, this aquifer underlies much of Lagos State and dips towards the coast (Longe et al. 1987). The Abeokuta Group aquifer is thick, extensive, contains water with recorded temperatures of up to 700 C (Onwuka and Amadi, 1989) and so relatively deep that it is exploited only by very few industrial boreholes.

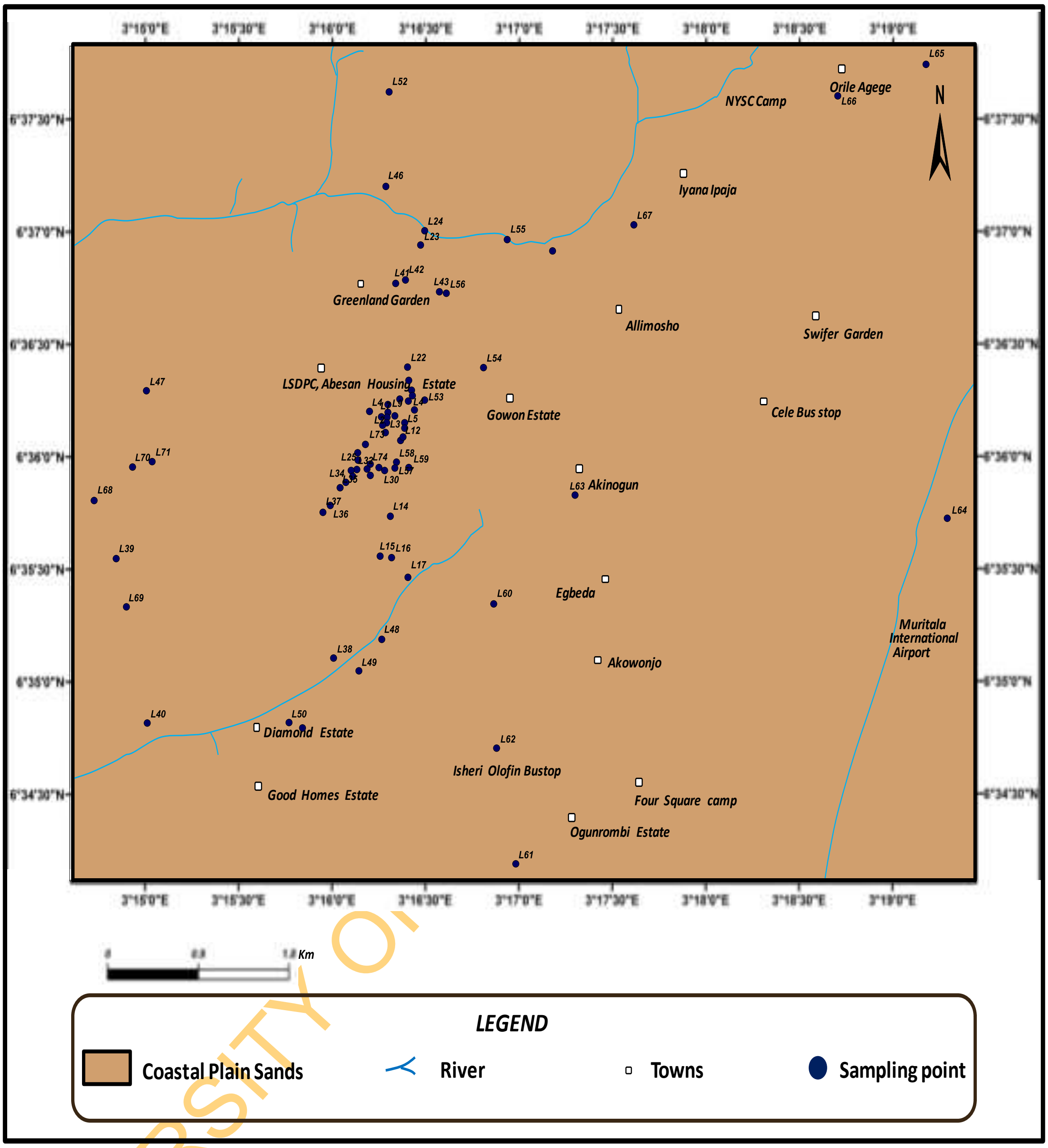


Fig. 2.7: Newly created Geological map of the study area

CHAPTER THREE

RESEARCH METHODOLOGY

3.0 MATERIALS AND METHODOLOGY

Reconnaisance survey of the study area was carried out with the aid of garmin e trex global positioning system (GPS) and a topographic map revealing the main roads, secondary roads, built up areas stream channels and petroleum product pipeline networks was used to generate a new base map. Seventy four points were sampled for this study. This comprises of hand dug well and borehole water samples (Fig. 3.2)

Based on preliminary studies two boreholes (depth>35m), one each in uncontaminated and contaminated area were drilled with hang auger to determine hydrogeological sequences beneath the area (Fig.3.4). Thirty groundwater samples were collected purposively from the two drilled and other available boreholes and were analysed for heavy metals, cation/anions and the hydrocarbon content using Atomic Absorption Spectrophotometric AAS, Colorimetric and Gas Chromatography- Mass Spectrometric methods, respectively. The analysis was carried out at the **Basel Centre** University of Ibadan (Fig. 3.3).

Twenty four sediment samples representing aquiferous units were purposively selected from the boreholes for sedimentological analysis and determination of some hydraulic properties using standard methods (Fig.3.5).

All sample locations were determined using the GPS. Various thematic maps were developed using the appropriate software. The area of contaminated land and volume of water that would require remediation were estimated hydrogeologically from the thematic maps.

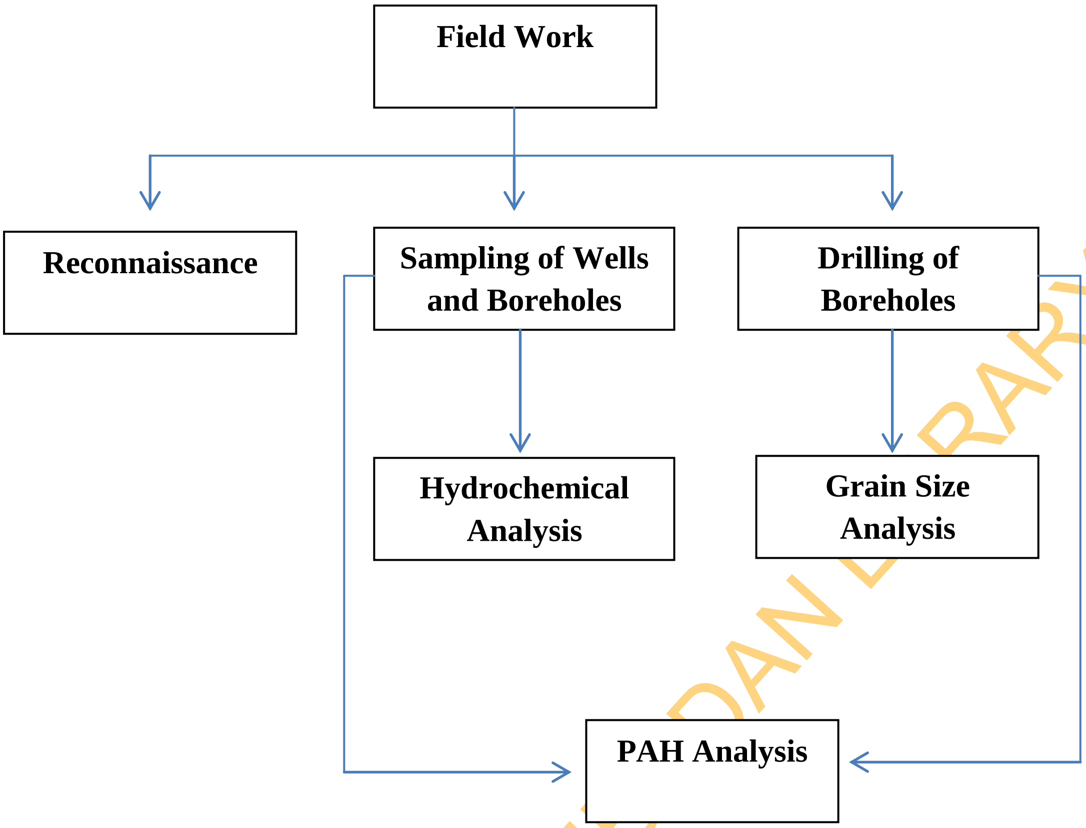


Fig. 3.1: Flowchart showing methods and methodology

Fig.3.2: Underground well polluted with petroleum at Baruwa.

Fig. 3.3: Preliminary hydrochemical analysis before going to the lab.

Fig. 3.4: Drilling of borehole to collect sample at different intervals

Fig. 3.5: Some of the sediment samples collected at different depth.

3.1 PHYSICOCHEMICAL ANALYSES OF GROUNDWATER

Dug well and borehole groundwater samples were collected in plastic containers, which were previously cleaned with distilled water. As a part of the quality control measures, containers were rinsed with sampled groundwater before filling. Samples for the heavy metals analyses were collected in one liter polyethylene bottles, and preserved using 2 ml concentrated HNO3. Separate samples were collected for major cation and anion analyses. All samples were preserved at 25ºC and transported to the laboratory for analysis. Physicochemical parameters of the samples were analyzed following standard analytical procedure (APHA, 1995). On site measurement of pH and electrical conductivity (EC) were carried out using pH and electrical conductivity meters.

The physico-chemical parameters of that was analysed includes;

3.1.1 Temperature; Water temperature is an important property that determines water suitability for human use, industrial applications and aquatic ecosystem functioning. Water temperature can affect the dissolved oxygen content, an important water characteristic that strongly affects many aquatic organisms. Temperature of water is controlled primarily by climate. Groundwater temperatures below 10 m (33 ft) are quite stable in a given location relative to surface waters. Temperature is moderated by the thermal mass of the earth, so groundwater tends to have a relatively minor seasonal temperature change. Groundwater varies with latitude, being warmer near the equator and colder away from the equator. In general, the average annual temperature of groundwater is a degree or two (°C) higher than the mean annual air temperature. In addition, groundwater temperature increases 1-5 °C (average about 2.5'C) per 100 m depth. The increase in temperature may be due to local geothermal activity. If the groundwater is in proximity to volcanic activity, then it may be naturally heated by a geothermal source. The temperature of the contaminated water samples was determined by 'Orion 3 star Bench-top meter '. The contaminated water samples were poured into a clean 250ml beaker and the probe of the equipment was inserted into the beaker containing the water sample.

3.1.2 pH: this is a measure of how acidic or basic water is. pH is important because it controls many chemical and biological processes that occur in the water. pH is measured on a scale that ranges from 0 to 14, with 7 considered neutral. Values of pH less than 7 are acidic, while values higher than 7 are basic. pH can be used as a proxy of water quality conditions since water pH is easily changed by chemical alteration. The pH scale is reported in "logarithmic units," with each number representing a 10-fold change in the acid or basic content of water. On this scale, a decrease in the pH by 1.0 unit is equivalent to a 10-fold increase in acidity. A water sample with a pH of 5.0 is 10 times as acidic as one with a pH of 6.0, and water with a pH 4.0 is 100 times as acidic as one with a pH of 6.0. Low-pH water will corrode or dissolve metals and other substances. A ‘pH 211 Microprocessor’ pH meter was used to analyse for pH of the water sample. The water samples were collected in a 250ml beaker, the probe of the pH meter was inserted into the beaker containing the contaminated water sample and the proceures boldly written on the equipment is followed to take readings.

Thirty (30) active wells and boreholes were sampled in a way to ensure true representation of the study area. Samples were drawn with the aid of locally made plastic drawer which has been prewashed with acid and soaked in deionised water. 0.75 L samples, acidified with 1.5mL concentrated HNO_3 (analar), are used for metal analyses (APHA, 1998). The plastic bottle were previously washed and soaked overnight with 5% HNO_3 solution (Protano,2000). Samples were preserved at 4^oC till the time of analyses. Blanks were treated the same way as sample.

3.2 DETERMINATION OF TOTAL HARDNESS

Hardness; the total hardness of water represents primarily the total concentration of Calcium and Magnesium ions. Water described as ‘hard’ is high in dissolved minerals, specifically calcium and magnesium. The degree of hardness becomes greater as the calcium and magnesium content increases and is related to the concentration of multivalent cations dissolved in the water. Hardwater is not a health risk, but a nuisance because of mineral build up on fixtures and poor soap and or detergent performance. Hard water interferes with almost every cleaning task from laundering and dishwashing to bathing and personal grooming. Clothes laundered in hard water may look dingy and feel harsh and scratchy. Dishes and glasses may be spotted when dry. Hard water may cause a film on glass shower doors, shower walls, bathtubs, sinks, faucets, etc. Hair washed in hard water may feel sticky and look dull. Water flow may be reduced by deposits in pipes.

Total hardness of the water sample was determined with the use of an atomic absorption spectrophotometer. 50 mL of the water sample was digested with 5 mL of concentrated nitric acid. This was then filtered through a filter paper into a 25 mL volumetric flask, the filtrate was made up to mark with distilled water. This was then read with the AAS, for calcium and magnesium. A combination of both form of hardness is equivalent to the total hardness. The value which is obtained in mg/L

3.3 DESCRIPTION AND OCCURRENCE OF HEAVY METALS ANALYSED

3.3.1 Chromium:

Chromium does not occur freely in nature. The main chromium mineral is chromite. As was mentioned earlier, chromium compounds can be found in waters only in trace amounts. The element and its compounds can be discharged in surface water through various industries. It is applied for example for metal surface refinery and in alloys. Stainless steel consists of 12-15% chromium. Chromium metal is applied worldwide in amounts of approximately 20,000 tons per year. It may be polished and it does not oxidize when it comes in contact with air. The metal industry mainly discharged trivalent chromium. Hexavalent chromium in industrial wastewaters mainly originates from tanning and painting. Chromium compounds are applied as pigments, and 90% of the leather is tanned by means of chromium compounds. Wastewater usually contains about 5 ppm of chromium. Chromium may be applied as a catalyser, in wood impregnation, in audio and video production and in lasers. Chromite is the starting product for inflammable material and chemical production.

Chromium may be present in domestic waste from various synthetic materials. Through waste incineration it may spread to the environment when protection is insufficient. In nuclear fission the ^{51}Cr isotope is released, and this can be applied for medical purposes.

3.3.2 Iron:

Elementary iron dissolves in water under normal conditions. Many iron compounds share this characteristic. Naturally occurring iron oxide, iron hydroxide, iron carbide and iron penta carbonyl are water insoluble. The water solubility of some iron compounds increases at lower pH values. Other iron compounds may be more water soluble than the examples mentioned above. Iron carbonate has a water solubility of 60 mg/L, iron sulphide of 6 mg/L, and iron vitriol even of 295 g/L. Many iron chelation complexes are water soluble. Usually there is a difference between water soluble Fe^{2+} compounds and generally water insoluble Fe^{3+} compounds. The latter are only water soluble in strongly acidic solutions, but water solubility increases when these are reduced to Fe^{2+} under certain conditions.

3.3.3 Lead

Elementary lead does not dissolve in water under normal conditions (20°C, and pressure = 1 bar). It may however occur dissolved in water as $PbCO_3$ or $Pb(CO_3)_2^{2-}$. A well-known example of a water soluble lead compound is lead sugar (lead(II)acetate), which derived its name from its sweet nature. Lead frequently binds to sulphur in sulphide form (S^{2-}), or to phosphor in phosphate form (PO_4^{3-}). In these forms lead is extremely insoluble, and is present as immobile compounds in the environment. Lead compounds are generally soluble in soft, slightly acidic water. Most industrially processed lead is applied for fabricating computer and TV screens. The lead compound tetra-ethyl lead is applied as an additive in fuels. This organic lead compounds is quickly converted to inorganic lead, and ends up in water, sometimes even in drinking water. Fortunately, this form of release of lead is less and less abundant.

3.3.4 Nickel

Elementary nickel is water insoluble at T=20°C pressure = 1 bar. However, nickel compounds may be water soluble. Nickel chloride is most water soluble; 553 g/L at 20°C, to 880 g/L at 99.9°C. Nickel carbonate has a water solubility of 90 mg/L, whereas other nickel compounds, such as nickel oxide, nickel sulphide and nickel tetra carbonyl are water insoluble. Nickel may be found in slate, sandstone, clay minerals and basalt. The main nickel source is pentlandite. The element accumulates in sediments and is a part of various biological cycles. Nickel may end up in water from both point and non-point sources. Diffuse nickel emissions may stem from power plants, waste incinerators and metal industries. Nickel is directly emitted from various industries through discharge on surface waters. It is applied in alloys for treatment of heavy metal polluted surface water, in nickel-cadmium batteries, as a catalyzer and as a pigment. Pure nickel is often applied as a protective coating on steel and copper objects. Nickel-copper alloys have been applied in coins for a very long time. Other alloys are applied for kitchen ware, jewelry and turbine production. Nickel may be applied as an anti-corrosive. Nickel acetate is applied as a mordant in textile printing, and nickel

carbonate is applied as a catalyzer for fat hardening and for ceramic paint production, as is nickel chloride. Nickel tetra carbonyl is a by-product of nickel cleansing and is applied in various production processes.
Nickel compounds are also applied in agriculture. Phosphate fertilizers contain traces of nickel. Nickel is often present in agricultural soils situated near fossil fuel industries. Organic matter often adsorbs nickel, causing coal and oil to contain traces of the element. Nickel compounds may also be found in sludge, and in slags and fly ashes from waste incinerators. Better waste separation would prove useful, because nickel is up to 60% recyclable.

3.3.5 Zinc

Elementary zinc does not react with water molecules. The ion does form a protective, water insoluble zinc hydroxide ($Zn(OH)_2$) layer with dissolved hydroxide ions, according to the following reaction mechanism:

$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2(s)$

Zinc reacts with H+ ions, according to the following reaction mechanism:

$Zn(s) + 2H^{+} \rightarrow Zn^{2+}(aq) + H_2(g)$

This reaction releases hydrogen, which reacts with oxygen explosively.

Zinc salts cause a milky turbidity in water in higher concentrations. Additionally, zinc may add an unwanted flavour to water. This occurs at concentrations of about 2 mg Zn^{2+}/ L. About three-quarters of the total zinc supply is used in metal form. The remainder is applied as various zinc compounds in various industries. Industrial wastewaters containing zinc stem from galvanic industries, battery production, etc. Zinc compounds are applied for many different purposes. Zinc chloride is applied for parchment production, zinc oxide is a constituent of salves, paints and catalysers, zinc vitriol is applied as a fertilizer, and zinc bacitracine is applied as a growth stimulant in animal husbandry.
The larger part of zinc in wastewater does not stem from point sources. It stems from larger surface waters containing the element. Zinc leaks from zinc pipes and rain pipes, consequential to circulation of carbon rich water. Car tires containing zinc and motor oil from

zinc tanks release zinc compounds on roads. Zinc compounds are present in fungicides and insecticides, and consequently end up in water.

3.3.6 Manganese

Manganese is a pinkinsh-gray, chemically active element. It is a hard metal and is very brittle. It is hard to melt, but easily oxidized. Manganese is reactive when pure, and as a powder it will burn in oxygen, it reacts with water (it rusts like iron) and dissolves in dilute acids. Manganese is essential to iron and steel production. At present steel making accounts 85% to 90% of the total demand, most of the total demand. Manganese is a key component of low-cost stainless steel formulations and certain widely used alumimum alloys. Manganese dioxide is also used as a catalyst. Manganese is used to decolorize glass and make violet coloured glass. Potassium permanganate is a potent oxidizer and used as a disinfectant. Other compound that find application are Manganese oxide (MnO) and manganese carbonate ($MnCO_3$): the first goes into fertilizers and ceramics, the second is the starting material for making other manganese compounds.

3.3.7 Cadmium

Cadmium is a lustrous, silver-white, ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis. It is similar in many respects to zinc but it forms more complex compounds. About three-fourths of cadmium is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission.

3.4 DIGESTION OF METALS

50 mL of water samples were put in 250 mL beakers and about 5 mL of concentrated nitric acid was used for digestion on hot plate until digestion was complete. Also 50 mL of distilled water was digested with 5 mL of nitric acid as a method blank sample. The digests were allowed to cool and then filtered. The extracts were made up to mark in a 25 mL standard flask with distilled water. The extract was then subjected to Buck Scientific 210 VGP model Atomic Absorption Spectrophotometer analysis for Pb, Cd, Cu, Cr, Mn, Zn.

Calculation

The metal concentration in water sample was determined using the formula;

$$\text{Metal concentration, mg/L} = \frac{A \times B}{C}$$

Where,

A= Concentration of metal (instrument reading) in the digested solution (mg/L)
B= Final volume of digested solution after making up to mark (25 mL)
C= Volume of water sample (mg/L)

3.5 DETERMINATION OF PHOSPHATE

Reagents:

Ammonium molybdate solution: 4g of ammonium molybdate salt was dissolved in a minimum quantity of water in a clean beaker; it was then transferred into a 100ml volumetric flask and made up to mark with distilled water.

Ascorbic acid solution: 1.796g of ascorbic acid was dissolved in 100ml of distilled water.

5M of sulphuric acid: 35ml of concentrated sulphuric acid was dissolved in little quantity of water and made up to 250ml mark in a volumetric flask with distilled water.

Potassium antimonyltatarate solution: 0.6858g of potassium antimonyltatarate was dissolved in little quantity of distilled water in a clean beaker. This was then quantitatively transferred into a 250ml volumetric flask and made up to mark with distilled water.

Reducing agent: 15ml of ammonium molybdate solution was dissolved in 50ml of H2SO4, 75ml of ascorbic acid and 12.5ml of potassium antimonyltatarate were added to the already existing mixture. The resulting solution was then thoroughly mixed until turbidity disappears.

Phosphate standard solution: 21.95mg of potassium dihydrogen phosphate was dissolved in a little quantity of distilled water. It was then transferred into a 100ml volumetric flask and made up to mark with distilled water.

Procedure

Phosphate was determined by measuring 40ml of sample into a 50ml volumetric flask, followed by the addition of 8ml of reducing agent. The solution was then made up with distilled water and allowed to stand for 10 minutes to allow for adequate Colour development. The absorbance of the solution was then read aat a wave length of 880nm.

Furthermore, a calibration was obtained by pipeting into a series of stoppered 50ml volumetric flask appropriate amount of phosphate working/ solution to cover the range up to 15um P(3ml, 6ml, 9ml, 12ml and 15ml). 8ml of the reducing agent was added and the solution was made up to mark with distilled water. The absorbance of the standard were also run atn880nm and phosphate concentration was then read by extrapolating from the calibration curve, the level of phosphate was calculated using the expression below.

Calculation

$$PO_4^{3-} ug/ml = \frac{\text{no of ug phosphate from calibration}}{\text{Volume of sample in (ml)}}$$

3.6 DETERMINATION OF SULPHATE

Reagents:

Buffer solution: Dissolve 30g of $MgCl.6H_2O$, 5g of $CH_3COONa.3H_2O$, 1.0g of KNO_3 and 20ml acetic acid, CH_3COOH (99%) in 500 mL distilled water and make up to 1000 mL

Barium chloride: crystals, 20-30mesh.

Standard sulphate solution: Dissolve 0.1479g anhydrous sodium sulphate, Na_2SO_4 in distilled water and dilute to 1000mL. 1L = 100 µg SO_4^{2-}

Calibration

Standard curve was prepared by carrying standard sulphate solution through entire procedure. Standards were spaced at 5mg/L increment in the 0 to 40 mg/L range.

Procedure

50 mL of sample was taken into a 250mL Erlenmeyer flask. 5 mL buffer solution was added and mixed well. 1-spatula $BaCl_2$ crystals was added with stirring. Stirring continued for 1 minute after addition of $BaCl_2$. Suspension was poured into an absorption cell of photometer and turbidity was measure at 5±0.5 min at a wavelength of 420 nm.

Calculation

mg SO_4^{2-}/L = {mg (SO_4^{2-}) x 1000} / {mL of sample}

3.7 DETERMINATION OF NITRATE

Reagents and standards

Standard silver sulphate: 4.40g Ag_2SO_4 was dissolved in distilled water and dilute to 1000mL, 1mL = 1mg Cl.

Phenol disulfonic acid (PDA): 25g white phenol was dissolved in 150 mL conc. H_2SO_4. Additional 85mL conc. H2SO4 was added to the 150mL H_2SO_4, stir well and heat for 2h.

Ammonium hydroxide NH_4OH conc.

Stock nitrate solution: 0.7216g potassium nitrate dried in an oven at 105^0C for 24hr was dissolve in little quantity of distilled water and dilute to 1000mL with distilled water. 1mL = µg N.

Calibration

Prepare nitrate calibration standards in the range 0 to 350µg N by diluting 1, 2, 4, 7…..35mL of the standard nitrate solution to 50mL. Treat the nitrate standards in the same manner as the samples.

Procedure

50ml of the leachate sample was filtered into a crucible. 2ml of silver sulphate solution was added and the resulting solution was evaporated to dryness. The residue scrubbed with 1ml of phenoldisulphonic acid by means of a stirring rod. 10ml distilled water and 10ml concentrated ammonia solution was added. The solution was quantitatively transferred into a 25ml volumetric flask and it was made up to mark with distilled water. The absorbance of the solution was then measured at a wavelength of 410nm.

Calculation

$$NO_3^- \text{ mg/L} = \frac{\text{No of nitrate from calibration extraction extrapolation}}{\text{Volume of sample}}$$

3.8 DETERMINATION OF ALKALINITY

Reagents and standards

a. **Standard H_2SO_4, 0.05 M**: Prepare 0.05 M H_2SO_4 by diluting 3mL conc. H_2SO_4 to 1000mL. Standardise it against standard 0.05 M Na_2CO_3 solution.

b. **Phenolphthalein indicator:** Dissolved 0.5g in 500mL 95% ethyl alcohol. Add 500mL distilled water. Add dropwise 0.02 M NaOH till faint pink colour appears (pH 8.3).

c. **Methyl orange indicator:** Dissolve 0.5g and dilute to 1000mL with CO2 free distilled water (pH 4.3-4.5).

Standardization of H_2SO_4 solution

25 mL of Na_2SO_4 solution was pipette into a conical flask. 3 drops of methyl orange indicator was added and the resulting solution was then titrated with H_2SO_4 to indicator end point. The titration process was repeated three times and the average titre value was obtained. The molarity of H_2SO_4 was then determined.

Procedure

a. 25 mL of the sample was measured into a conical flask and add 2-3 drops of phenolphthalein indicator. If pink colour develops titrate with 0.05 M H2SO4 till disappears or pH is 8.3. Note the volume of H_2SO_4 required.

c. Add 2-3 drops of methyl orange to the same flask, and continue titration till yellow colour changes to orange. Note the volumes of H_2SO_4 required.

d. In case pink colour does not appear after addition of phenolphthalein continue as above.

Calculation

$$\text{Total alkalinity, as mg CaCO3/L} = \frac{\text{volume of } 0.05 \times 1000}{\text{volume of sample (mL)}}$$

3.9 DETERMINATION OF CHLORIDE

Reagents

0.014M Silver nitrate solution: 2.4g of silver nitrate salt was measured, dissolved with the addition of little amount of distilled water and made to mark of 1L.

0.0141M Sodium chloride solution: 0.842g of dried sodium chloride salt was dissolved in distilled water and made to the mark in 1L standard flask with distilled water.

Potassium dichromate (K_2CrO_7): 5g of dried potassium dichromate (K_2CrO_7) was dissolved in distilled water and made to mark in 100ml standard flask.

Standardization of $AgNO_3$ solution:

Few drops of the K_2CrO_7 indicator was added to about 25ml of standard 0.014M sodium chloride solution to indicator end point (reddish brown) using freshly prepared $AgNO_3$

solution. The titration was repeated severally and the average titre value taken. Also, method blank was carried out using distilled water. The actual concentration of the $AgNO_3$ solution was calculated as follows:

$$M_{AgNO3} = \frac{0.0141 \times 25}{Vx - Vy}$$

Where;

M_{AgNO3} = actual concentration of freshly prepared $AgNO_3$ solution
Vx = average titre value of NaCl solution
Vy = titre value for blank

Procedure: 25 mL of samples was titrated to indicator end point (reddish- brown) with freshly standardized $AgNO_3$ solution using K_2CrO_7 solution as indicator. Distilled water was used for method blank. The chloride concentration was calculated using the formula;

$$Cl^- (mg/L) = \frac{35453 \times M \times (Vt - Vb)}{Vs}$$

Where;

M = molarity of standardized $AgNO_3$ solution
Vt = average volume of $AgNO_3$ solution used sample in mL
Vb = average volume of $AgNO_3$ solution used for blank in mL
Vs = volume of sample titrated in mL

3.10 PAHs DETERMINATION

Liquid-liquid extraction procedure was used. 100 mL of sample was extracted in a glass separating funnel fitted with a glass stopper using 3 ml hexane as extractant. The separating funnel was shaken vigorously for at least 3 minutes and the organic layer was allowed to separate clearly from the aqueous phase for a minimum of 5 minutes, after which, the organic layer was collected into a separate glass bottle. The extraction was repeated thrice for each sample. Water residues were expelled from the organic layer by passing extracts through funnels containing anhydrous sodium sulphate. Clean-up of the extracts was achieved with a glass syringe loaded with silica gel, glass wool and anhydrous sodium sulphate and then eluted with about 10 mL of hexane. The syringe was first conditioned by soaking in hexane before and after packing. Extracts were concentrated using rotary evaporators. Concentrated extracts was re-dissolved in dichloromethane (DCM) and the solution of extract was transferred to the bottle in which 10 ml of hexane had been added. Samples were analysed by a GC System coupled to a quadrupole mass spectrometer. The system was operated in electron impact mode (EI, 70 eV). The separation was achieved with a 30 m × 0.25 mm i.d. HP-5ms column coated with 5% diphenyl–polydimethylsiloxane (film thickness 0.25m). The oven temperature was programmed from 60 ◦C (holding time 1 min) to 175 ^{O}C at 6 ^{O}C/min (holding time 4 min) to 235 ^{O}C at 3 ^{O}C/min and finally to 300 ^{O}C at 8 ^{O}C/min, keeping the final temperature for 5 min. Injection was performed in the splitless mode. Helium was the carrier gas (50 cm/s). Injector, transfer line and ion source temperatures were 280, 250 and 200 ^{O}C, respectively.

3.11 GRAIN-SIZE ANALYSIS

Grain size analysis was conducted on 3 selected sandstone samples. The analysis was carried out in the sedimentological laboratory of the Department of Geology, University of Ibadan. The analysis was aimed at measuring the individual grain sizes of the sandstone samples. About 100 g of each sample were disaggregated using a porcelain mortar and pestle. The disaggregated samples were thoroughly mixed and split into quarters. This was weighed in a meter balance (P20 model) of a precision 0.011g. Then each sample was poured into a set of US mesh sieves comprising of 2.00, 1.18, 0.85, 0.60, 0.425, 0.30, 0.025, 0.5, 0.10, 0.075 and 0.063 mm and a receiving pan. The fraction retained in each sieve and the pan was weighed in a balance and its weight recorded and tabulated. The percentage aggregate was visually estimated and expressed in percentage.

The individual weight percentage was calculated and also the cumulative weight percentage. The grain size (in phi) was then plotted on the ordinated while the individual sample weight (in %) was plotted on the abscissa, thus forming a pictorial chart showing grain size distribution (histogram) and frequency curve for each sample. The cumulative frequency curve (ogive) is plotted on a probability graph paper by plotting the grain size (in phi scale). The phi values of the following percentile; 5%, 10%, 25%, 50%, 75%, 84% and 95% were read off from the ogive curve. These were used to calculate the statistical parameters of standard deviation, skewness, kurtosis, mean and median.

The statistical parameters obtained from grain size analysis (granulometric analysis) for 3 sandstone samples were used for plotting the cumulative frequency and histogram. From this graphical plotting, statistical size frequency parameters such as the graphic mean (mean size), sorting, skewness and kurtosis were calculated using various percentile values.

3.12 METHODOLOGY FOR POROSITY

The dried pulverized samples were poured into a container. The sample is filled up to 80% mark of the container. Water of 100ml is measured and gradually poured into the sample in the container. Adequate care is taken so as not to clog the sandstone samples in other not to make it water logged. When the sample is saturated the remaining water in the beaker is measured with a cylinder and the percentage of the porosity is deduced.

The formula used:

Bulk volume = V = $h\#r^2$

Pour Volume = Vp

Porosity(%) = $\frac{Vp}{Vb} \times 100$

Where Vb is the bulk volume

h = Height of the container

\# = 3.14

r^2 = radius of ½ of diameter of container

Vp = Pour Volume: which is the volume of water used up.

3.13 PEMEABILITY ANALYSIS DETERMINATION IN THE LABORATORY

The test was carried out to determine the ease with which water flows through rocks and soils. The co-efficient of permeability is a constant of proportionality relating to the ease with which a fluid passes through a porous medium. Falling head permeameter was used to carry out the permeability test for the samples.

APPARATUS; Permeability cell, stop watch, thermometer, a stand pipe panel, De-airing tank, stop cock.

PROCEDURE: The permeability cell was assembled to place soil in it for the test, the tube was fitted with a metal disc at each and also, the cell top was filled with steel wool. The assembled cell was placed in the soaking tank and slowly the soaking tank was filled with De-aired water. While the tank is being filled, a glass tee piece was attached to the top connection on the cell using the rubber tubing supplied. The relevant standpipe tube was filled up with de-aired water and the tube was connected to the tee piece which was connected to the cell.

The apparatus was filled with water up to a mark on the standpipe. The stop cock is turned on and the water is allowed to percolated through into the container at the base simultaneously until the level has dropped to a second mark. The time taken for the water level to fall to this height is observed and recorded.

The co-efficient of permeability is obtained from the formula:

$K = 2.303a.l/A \times (\log H_1 - \log H_2) / t_2\text{-}t_1$

Where,

$H_{1=}$ initial height of the water in the standpipe above that which is in the container.

$H_{2\,=}$ final height of the water in the standpipe above that which is in the container.

$A_{2\,=}$ cross sectional area of sample

a = cross sectional area of the standpipe

I = height of the sample

The falling head method can provide a reliable value or the co-efficient of permeability of the samples but the same time has limitations.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 LITHOLOGIC DESCRIPTION OF DRILLED BOREHOLE

The drilled borehole encountered the first, second and third aquifer. These are categorized to first aquifer horizon thought to belong to the Recent lithoral / alluvial deposit and the Benin formation (Longe *et al*., 1987). The second aquifer horizon is made up of sands and clay thought to be the coarse sandy estuarine deltaic and continental beds of Ilaro formation (Jones & Hockey, 1964; Longe *et al*., 1987) Third aquifer layer consists of alternating sequences of clayey and sandy strata. The first aquifer encountered in borehole 2 is reddish brown fine grained friable sandstone with thickness of about 3m underlain by a sequence of clay and sand. This water table aquifer is tapped by shallow boreholes and dug wells for domestic water supplies and is highly vulnerable to contamination. A semi- permeable silty clay layer which attains a maximum thickness of 10m separates the first aquifer horizon from the second sandy aquiferous zone. The second aquifer zone is a more important ground water source for private, commercial and industrial supplies and exists between 18 to 21m. This aquifer is confined and average values of transmissivity and storage coefficient of 1120 m2/day and 3.77 x 10-4 respectively for this aquifer zone have been reported (Longe, 2011).

The third major aquifer zone, ranging from 27 to 30m in thickness (Table 4.1, Table 4.2), occurs at greater depth in the Benin Formation, this aquifer underlies much of Lagos State and dips towards the coast (Longe et al. 1987). The Abeokuta Group aquifer is thick, extensive, contains water with recorded temperatures of up to 700 C (Onwuka and Amadi, 1989) and so relatively deep that it is exploited only by very few industrial boreholes.
drilled borehole encountered. (Fig. 3.4, Fig. 3.5, Fig. 4.1 and Fig. 4.2)

Table 4.1: Borehole 1(Control) Lithologic Description

Depth (ft)	Depth (m)	Lithologic Description
0-10	0-3	Reddish brown topsoil
10-20	3-6	Reddish brown clay
20-30	6-9	Reddish brown fine grained sandstone
30-40	9-12	Reddish brown fine grained sandstone
40-50	12-18	Brownish very coarse grained clayey sandstone
50-60	18-21	Reddish brown coarse grained sandstone
60-70	21-24	Reddish brown elastic sandy clay
70-80	24-27	Light brown clay
80-90	27-30	Light brown fine grained sandstone
90-100	30-33	Light brown clay
100-110	33-36	Light brown fine grained sandstone
110-120	36-39	Light brown fine grained sandstone
120-130	39-42	Brownish white fine grained sandstone

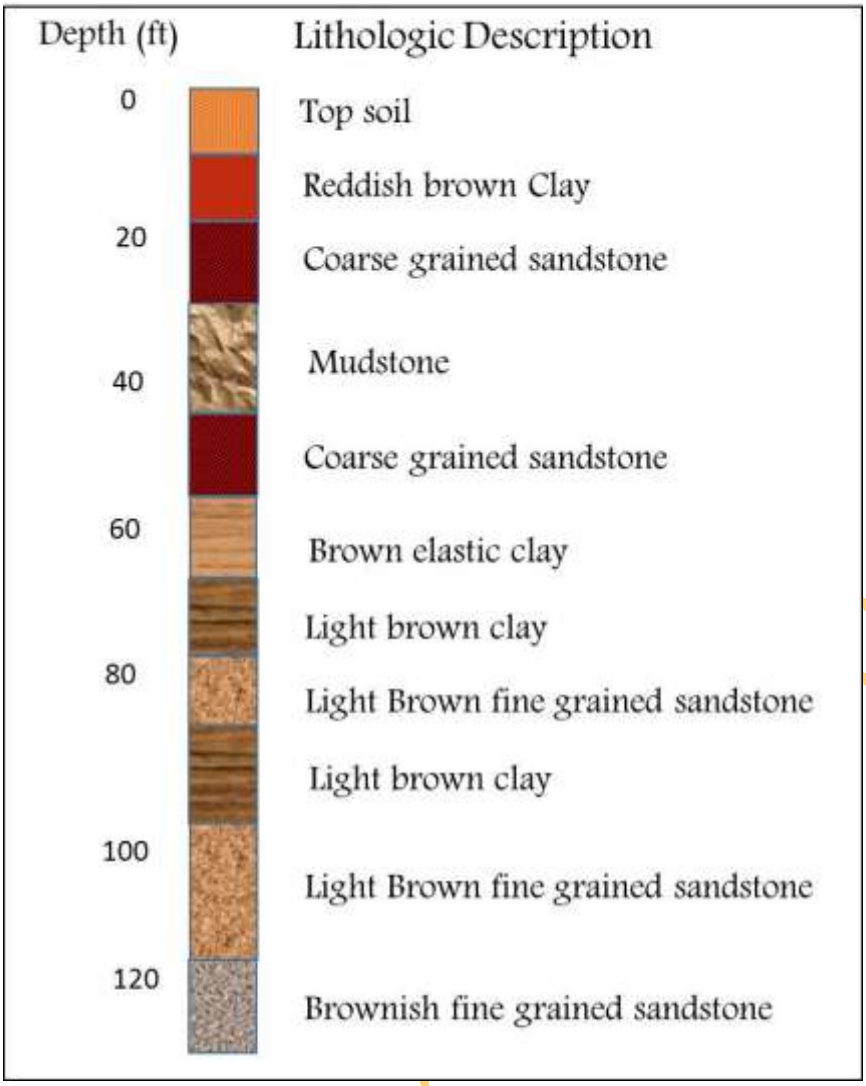


Fig. 4.1: Litholog Produced For Borehole 1 (Control)

Table 4.2: Borehole 2 (Contaminated) Lithologic Description

Depth (ft)	Depth (m)	Lithologic Description
0-10	0-3	Brown topsoil
10-20	3-6	Reddish brown clay
20-30	6-9	Reddish brown fine grained sandstone ***1st Aquifer***
30-40	9-12	Reddish brown fine grained sandstone
40-50	12-18	Light brown clay
50-60	18-21	Light brown fine sandstone ***2nd Aquifer***
60-70	21-24	Brownish sandy clay
70-80	24-27	Brownish sand and conglomerate
80-90	27-30	Brownish sand and conglomerate ***3rd Aquifer***
90-100	30-33	Brownish sand and conglomerate
100-110	33-36	Light brown fine grained sandstone

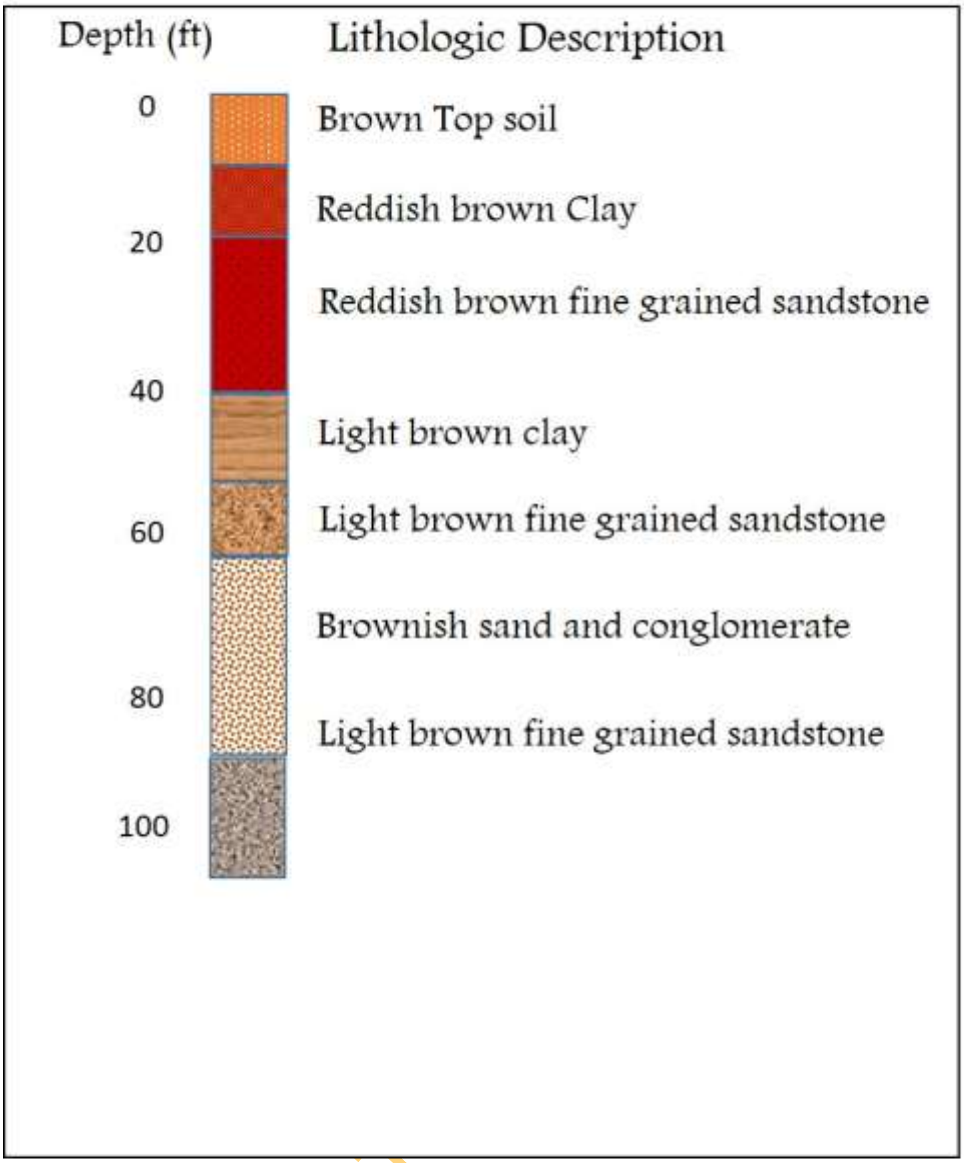


Fig. 4.2: Litholog produced for borehole 2 (contaminated)

4.2 GRAIN SIZE ANALYSIS

The statistical parameters obtained from grain size analysis (granulometric analysis) for 3 sandstone samples were used for plotting the cumulative frequency and histogram. From this graphical plotting, statistical size frequency parameters such as the graphic mean (mean size), sorting, skewness and kurtosis were calculated using various percentile values (Table 13), shows the result of the sieve analysis carried out on 3 sandstone samples. Other parameters such as mean grain size, modal size, median, sorting, skewness and kurtosis were deduced from graphic representation (frequency curve and histogram of the data).The curves and histogram shows the frequency of grains in each size class and usefully give an immediate impression of the grain size distribution. Most of the sediments being considered are unimodal except for few ones that are nearly bimodal.

4.2.1 Graphic Mean

Mean size is a function of:

The size range of available materials and amount of energy impacted to the sediment which depends on current velocity or turbulence of the transporting medium.

The mean value for the grain size distribution within the analysed sediments is 1.64. Graphic means distribution for this sediments ranges from 1.27 to 1.67 (Table 4.9). This is indicative of coarse to medium grained sands.

This suggests that the sediments were deposited under low energy condition – sediments usually become finer with decrease in energy of the transporting medium (Folk, 1974).

4.2.2 Sorting

This is a measure of the standard deviation which is the spread of the grain size distribution with the value range of 0.94 to 1.26 and a mean value of 0.97. Sorting is the most useful grain size data since it gives an indication of the effectiveness of the depositional medium in separating grains of different classes. According to Friedman, 1962, the various ranges of sorting in sandstones indicates the various environments of the sand (Table 4.10) From Table 4.10, most of the samples are moderate to poorly sorted with only a few, which are moderately well sorted. This is indicative of low to fairly high energy current and consequently super mature sediments (Pamella, 2003).

4.2.3 Skewness

This is a reflection of the depositional process. It is simply a measure of the symmetry of the distribution. Skewness is useful in environmental diagnosis because it is directly related to the fine and coarse tails of the size distribution, and hence suggestive of energy of deposition. The skewness values of the samples ranges from 0.18 to 0.26, thus indicating the presence of fine fraction and coarse fraction in population of particles. The positive values indicate skewness towards the finer grain sizes and the negative values indicating skewness towards the coarser grain sizes. River sediments are often fine skewed.

4.2.4 Kurtosis

This is a measure of the peakedness of the curves towards the coarser grain sizes. The samples are predominantly leptokurtic, that is, the central portions are better sorted at the tails. (Table 4.11). In numerical terms, the range of kurtosis is between 0.58 to 1.40 typifying that 50% of the samples are leptokurtic, 29% are very leptokurtic, 14% are mesokurtic and 7% is very platykurtic. This strongly suggests a fluvial or tidal environment and hence the sands are river deposited.

Table 4.3: Grain Size Analysis Data for 30ft

Sieve {mm}	Phi {ø}	Raw wt or individual {gm.}	Corrected wt {g}	Cum wt {g}	Cum wt {%}	Indwt {%}
2.00	-1.00	1.34	1.34	1.34	1.34	1.34
1.18	-0.25	3.78	3.79	5.13	5.13	3.79
0.85	0.25	9.97	9.96	15.09	15.09	9.97
0.60	0.75	13.63	13.63	28.72	28.73	13.63
0.425	1.25	22.36	22.37	51.09	51.10	22.37
0. 30	1.75	19.73	19.75	70.84	70.85	19.75
0.25	2.00	8.98	8.9	79.80	79.82	8.96
0.15	2.75	11.95	11.96	91.76	91.78	11.96
0.10	3.25	3.80	3.80	95.56	95.58	3.80
0.075	3.75	1.52	1.52	97.08	97.10	1.52
0.063	4.00	2.80	2.80	99.88	99.90	2.80
Pan	-	0.10	0.10	99.98	100.00	0.10

Sample No:	30ft
Raw Wt:	100 grammes
Total Wt:	99.92 grammes
Loss (grammes):	0.08 grammes

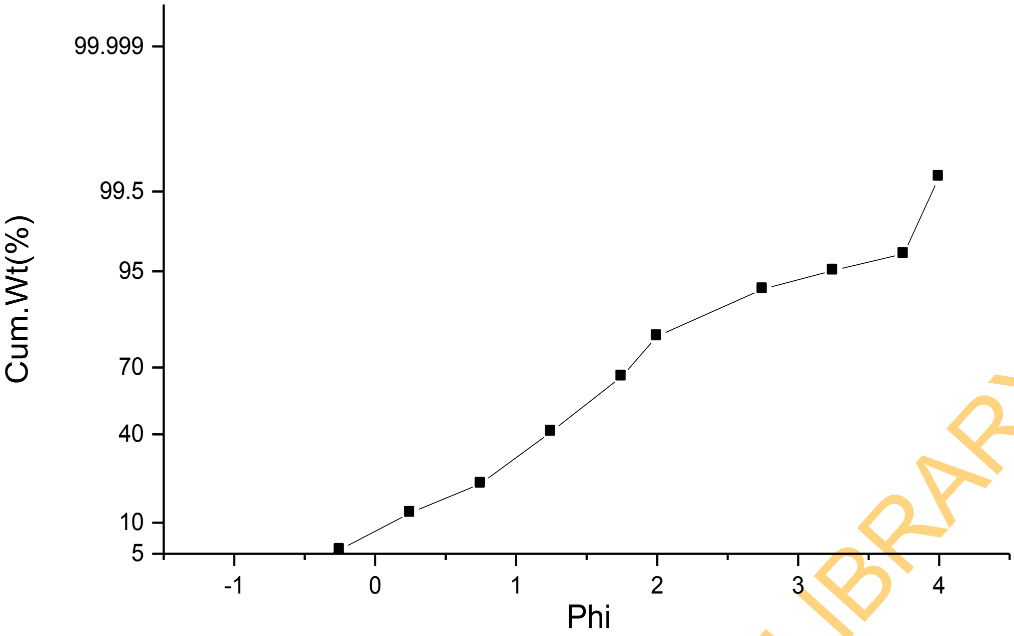


Fig. 4.3: cumulative weight percentage curve

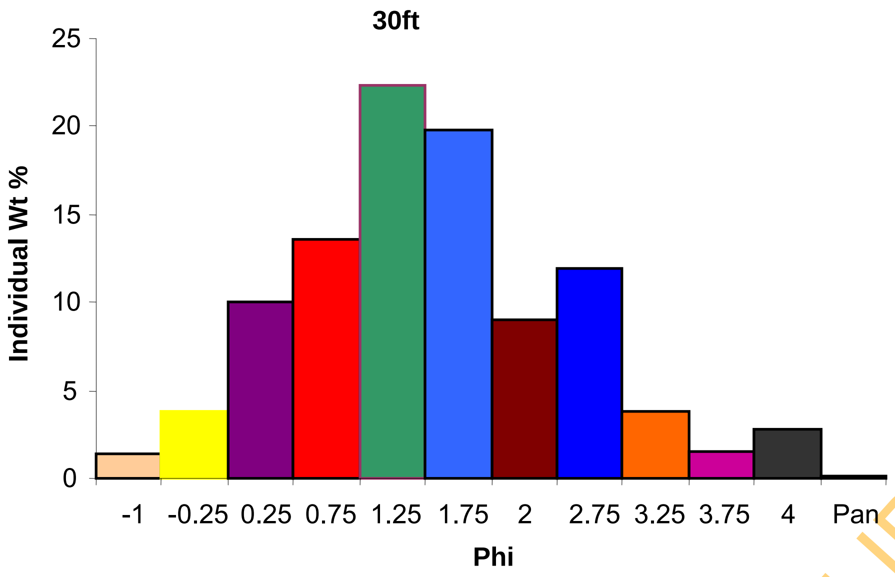


Fig. 4.4: Individual weight percentage curve at 30ft

Table 4.4: Grain Size Analysis Data for 60ft

Sieve {mm}	Phi {ø}	Raw wt or individual {gm.}	Corrected wt {g}	Cum wt {g}	Cum wt {%}	Indwt {%}
2.00	-1.00	0.10	0.10	0.10	0.10	0.10
1.18	-0.25	0.20	0.21	0.31	0.31	0.21
0.85	0.25	1.10	1.10	1.41	1.41	1.10
0.60	0.75	4.63	4.64	6.05	6.05	4.64
0.425	1.25	20.06	20.05	26.10	26.12	20.06
0. 30	1.75	33.12	33.10	59.20	59.24	33.12
0.25	2.00	16.10	16.11	75.31	75.36	16.12
0.15	2.75	16.83	16.84	92.15	92.21	16.85
0.10	3.25	2.91	2.91	95.06	95.13	2.91
0.075	3.75	0.95	0.95	96.01	96.08	0.95
0.063	4.00	3.12	3.12	99.13	99.20	3.12
Pan	-	0.80	0.80	99.93	100.00	0.80

Sample No:	60ft
Raw Wt:	100 grammes
Total Wt:	99.93 grammes
Loss (grammes):	0.07 grammes

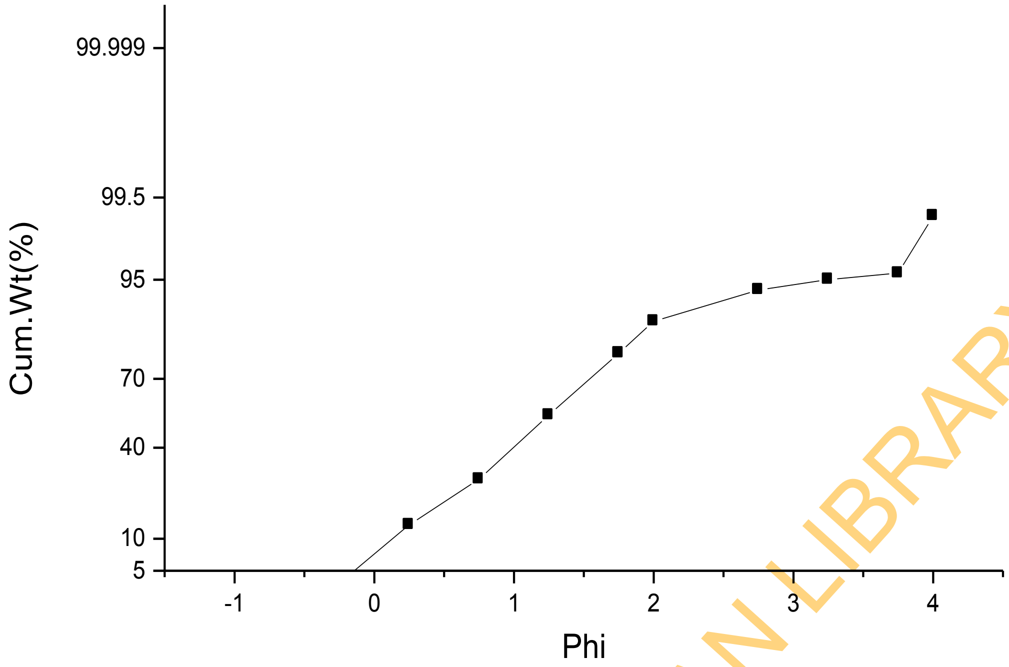


Fig. 4.5: cumulative weight percentage curve at 60ft

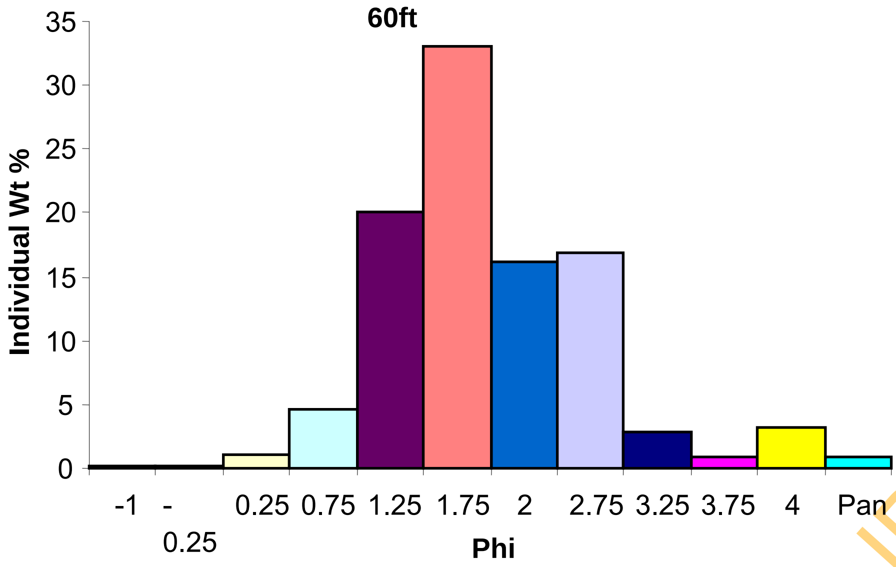


Fig. 4.6: Individual weight percentage curve at 60ft

Table 4.5: Grain Size Analysis Data for 120ft

Sieve {mm}	Phi {ø}	Raw wt or individual {gm.}	Corrected wt {g}	Cum wt {g}	Cum wt {%}	Indwt {%}
2.00	-1.00	0.80	0.80	0.80	0.80	0.80
1.18	-0.25	2.74	2.74	3.54	3.54	2.74
0.85	0.25	6.87	6.88	10.42	10.43	6.88
0.60	0.75	9.88	9.87	20.29	20.30	9.88
0.425	1.25	20.34	20.32	40.61	40.63	20.33
0. 30	1.75	11.66	11.67	52.28	52.31	11.68
0.25	2.00	15.75	15.73	68.01	68.05	15.74
0.15	2.75	4.29	4.29	72.30	72.34	4.30
0.10	3.25	1.15	1.15	73.45	73.50	1.15
0.075	3.75	0.70	0.70	74.15	74.20	0.70
0.063	4.00	24.90	24.89	99.04	99.10	24.90
Pan	-	0.90	0.90	99.94	100.00	0.90

Sample No:	120ft
Raw Wt:	100 grammes
Total Wt:	99.94 grammes
Loss (grammes):	0.06 grammes

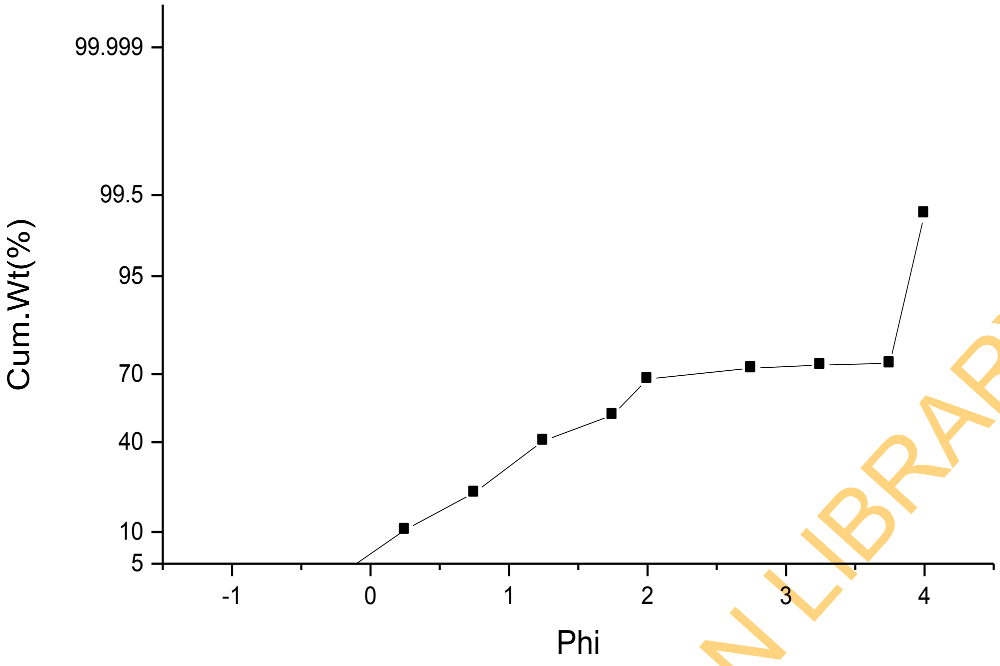


Fig. 4.7: cumulative weight percentage curve at 120ft

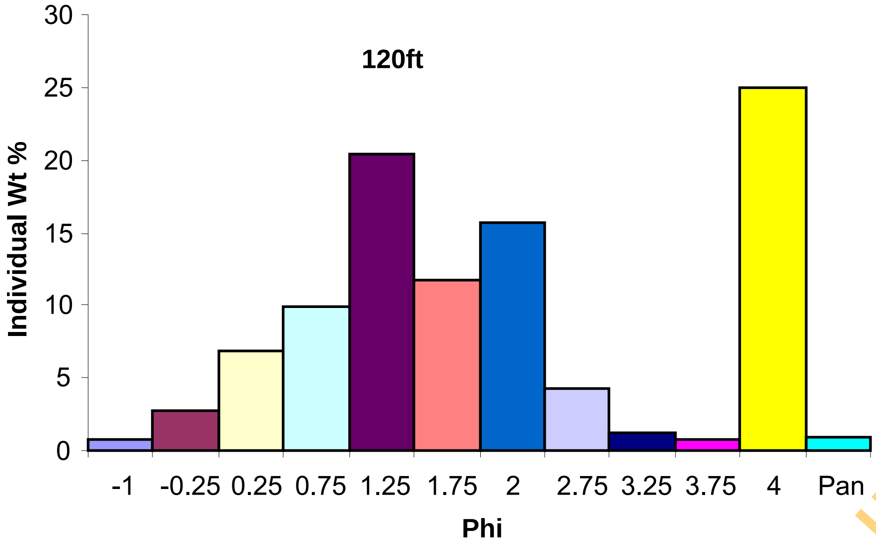


Fig. 4.8: individual weight percentage curve at 120ft

Table 4.6: Percentile Values for Grain Size Analysis.

Sample No	ϕ5	ϕ16	ϕ25	ϕ50	ϕ 75	ϕ84	ϕ 95
30ft	0.26	0.32	0.65	1.27	1.86	2.27	3.29
60ft	0.77	1.08	1.24	1.67	2.03	2.33	3.48
120ft	-0.02	0.58	0.98	1.64	3.78	3.87	3.91

Table 4.7: Classification of sands

Ranges of values of standard deviation (ϕ units)	Sorting class	Environments of sandstones
<0.35	Very well sorted	Coastal and lake dunes; many beaches (foreshore), common on shallow marine shelf.
0.35-0.50	Well sorted	Most beaches(foreshore); shallow marine shelf, many inland dunes
0.50 – 0.80	Moderately well sorted	Most inland dunes; most rivers; most lagoons, distal marine shelf
0.80 – 1.40	Moderately sorted	Many glacio-fluvial settings; many rivers; some lagoons; some distal marine shelf.
1.40 – 2.00	Poorly sorted	Many glacio-fluvial settings
2.00-2.60	Very poorly sorted	Many glacio-fluvial settings
>2.60	Extremely poorly sorted	Some glacio-fluvial settings

(Source: Friedman G.M. 1962)

Table 4.8: Summary of Results obtained from Grain Size Analysis and its Interpretation.

Sample	Median, ϕ	Mean, ϕ	Mode, ϕ	S.D, ϕ	Skewness, ϕ	Kurtosis ϕ	Interpretation
30ft	1.27	1.29	1.25	0.95	0.18	1.03	Moderately sorted, Fine skewed and mesokurtic.
60ft	1.67	1.69	1.75	0.72	0.20	1.40	Moderately sorted, Fine skewed and leptokurtic
120ft	1.64	2.03	4.00	1.42	0.26	0.58	Poorly sorted, Fine skewed and very platykurtic.

Statistical Parameters and Formulas for Grain Size Parameters (After Folk and Ward, 1957).

Median: The diameter corresponding to the 50% mark on the cumulative curve

Graphic mean

$$Mz = \o \frac{(16+ 50+84)}{3}$$

Inclusive graphic standard deviation

$$= \o \frac{(84-16)}{4} + \o \frac{(95-5)}{6.6}$$

<ø 0.35	Very well sorted
ø 0.35 to ø 0.5	Well sorted
ø 0.50 to ø 0.71	Moderately well sorted
ø 0.71 to ø 1.0	Moderately sorted
ø 1.0 to ø 2.0	Poorly sorted
ø 2.0 to ø 4.0	Very poorly sorted
>ø 4.0	Extremely poorly sorted

Inclusive graphic skewness

$$S_{KI} = \frac{\o 16 + \o 84 - 2\o 50}{2(\o 84 - \o 16)} + \frac{\o 5 + \o 95 - 2\o 50}{2(\o 95 - \o 5)}$$

ø 1.0 to ø 0.3	Very fine skewed
ø 0.3 to ø 0.1	Fine skewed
ø 0.1 to ø -0.1	Near symmetrical
ø -0.1 to ø -0.3	Coarse-skewed
ø -0.3 to ø -1.0	Very coarse skewed

Graphic Kurtosis

$$K_G = \frac{\o 95 - \o 5}{2.44(\o 75 - \o 25)}$$

<ø 0.67	Very Platykurtic
ø 0.67 to ø 0.90	Platykurtic
ø 0.90 to ø 1.11	Mesokurtic
ø 1.11 to ø 1.50	Leptokurtic
ø 1.50 to ø 3.00	Very leptokurtic
>ø 3.00	Extremely leptokurtic.

4.3 POROSITY AND PERMEABILTY

The results of permeability test on the undisturbed samples from the 3 locations are shown in (Tables 4.10 – 4.12). The values of peameability co-efficient range from 9.469 x 10^{-5} to 9.469 x 10^{-5} mm/sec (average: 9.469 x 10^{-5}mm/sec) for samples location 1 (30ft) table 4.10, those of location 2 (60ft) ranges from 4.103 x 10^{-5}mm/sec to 4.108 x 10^{-5}mm/sec (average: 4.105 x 10^{-5}mm/sec) table 4.11, while those of location 3 (120ft) ranges from 5.090 x 10^{-5}mm/sec to 5.102 x 10^{-5}mm/sec (average: 5.102 x 10^{-5}mm/sec). (table 4.12). The peameability co-efficient of the soils differ appreciably within short distance with the co-efficient of variation. Therefore, the result obtained at a point cannot be used to generalize a large area.

Clayton and Huie (1973) recommended a maximum permeability co-efficient of 1 x 10mm/sec for recompacted or natural silty clay. The values of the permeability co-efficient obtained for the three soils were significantly higher than the above specified values. Therefore, this will increase the pollution of groundwater by petroleum products from the spill site in the area.

The sample analysed have fairly high porosity and permeability judging from their friability. Friability in sandstone is largely due to a relatively lack of cement. Cementation in sandstone must have started soon after deposition when the grains were still very loose. The grain size parameters of the sandstone were compared with the combined standard chart for porosity (Table 4.9), permeability, grain size and sorting for unconsolidated sand (Beard and Weyl, 1973) and were extrapolated in order to obtain the porosity and permeability range for the sandstone. The values of porosity and permeability suggest a good storage capacity for the sediments. which is the characteristics of a good reservoir for hydrocarbon and or groundwater.

Table 4.9: Presentation of result for Porosity

S/No	Sample ID	Vb	Vp	Porosity(%)
1.	30ft	50.24	10	19.9
2.	60ft	50.24	8	15.9
3.	120ft	50.24	9	17.9

The formula used:

Bulk volume = V = $h\#r^2$

Pour Volume = Vp

Porosity(%) = Vpx 100
Vb

Where Vb is the bulk volume
h = Height of the container
# = 3.14
r^2 = radius of ½ of diameter of container
Vp = Pour Volume: which is the volume of water used up.

Table 4.10: Presentation of result for Permeability at 30ft

Sample No	**Length of sample (cm)**	**Elapsed Time (mins)**	**H_1 (cm)**	**H_2 (cm)**	**H (H_1-H_2) (cm)**	**Permeability K (mm/sec)**
30ft	13	3.30	135	115	20	9.469×10^{-5}
30ft	13	3.30	135	115	20	9.469×10^{-5}
30ft	13	3.30	135	115	20	9.469×10^{-5}

Average = 9.469×10^{-5}

Table 4.11: Presentation of result for Permeability at 60ft

Sample No	**Length of sample (cm)**	**Elapsed Time (mins)**	**H_1 (cm)**	**H_2 (cm)**	**H (H_1-H_2) (cm)**	**Permeability K (mm/sec)**
60ft	13	8.35	155	130	25	4.108×10^{-5}
60ft	13	8.36	155	130	25	4.103×10^{-5}
60ft	13	8.36	155	130	25	4.103×10^{-5}

Average = 4.105×10^{-5}

Table 4.12: Presentation of result for Permeability at 120ft

Sample No	**Length of sample (cm)**	**Elapsed Time (mins)**	**H_1 (cm)**	**H_2 (cm)**	**H (H_1-H_2) (cm)**	**Permeability K (mm/sec)**
120ft	13	4.17	145	130	30	$5.114 X 10^{-5}$
120ft	13	4.18	145	130	30	$5.102 X 10^{-5}$
120ft	13	4.19	145	130	30	$5.090 X 10^{-5}$

Average = $5.102 X 10^{-5}$

4.4 PHYSICO-CHEMICAL PARAMETERS OF WATER SAMPLES:

The result of the physicochemical parameters of the water sampled from the Baruwa community and its environs presented in Table 4.13,

PH

The pH value recorded ranges from 4.36 to 6.67 which falls less than the WHO standard (6.5-8-5). The lowest value of 4.36 was recorded at location 15, at locations 5,8,9,10,12,17,18,25,27,28, the value ranges from 4.56 to 4.95 (Fig. 4.10) which is indicative of an acidic water regime. It can be deduced from this result that varieties of contamination may be attributed to the spilling of petroleum product in the vicinity of pipeline vandalization, these may include acidic gases which in solution slightly increased the acidity of both surface and ground water. It may be an indication of the acidic nature of the groundwater in the study area too. PH less than 7 can impart taste of water or lead to corrosion of plumbing (Ano and Okwunodulu, 2008).

Temperature

The temperature of water samples analysed ranged 26.3^{o}C to 28.8^{o}C (Fig. 4.9)

Colour

The presence of petroleum products gives water a light brownish yellow colour which is aesthetically unattractive and may be harmful.

Hardness

Hardness is a property of water derived mainly from the presence of calcium and magnesium. Although other divalent metallic cations may also contribute hardness to water. Values obtained for hardness in the study area range from 2.59mg/l to 248.57. (Fig. 4.19).

4.5 HYDROCHEMICAL PARAMETERS OF WATER SAMPLES

Chloride: The chloride concentration from Table 4.13 and Table 4.14 Ranged from 24.54 mg/L in (location 3) to 286.34 mg/L in (location 15). The permissible limit for chloride in potable water is 250 mg/L, according to WHO, EU and NIS (Table 4.14) most of the water samples from different sources in the study area falls within the permissible chloride limit with exception of location 15 (286.34 mg/L), in Fig. 4.12 the high chloride concentration in this area may be due in parts to the discharge of chloride bearing effluents into the stream by industries, ingress of saline water from back water and presence of soluble chloride salt bearing rock (Geetha et al., 2008; George et al., 2010). According to Adewuyi et al., (2010), chloride is not considered harmful to human but imparts a salty taste to water above the permissible limit.

Sulphate: The concentration of sulphate ranged from 1.4 mg/L in (location 6) to 88.24mg/l in (location 22), Fig. 4.17. The permissible limit for sulphate in potable water is 500mg/l (WHO), 250 mg/L (EU), 100 mg/L (NIS), (Table 4.14) and this value fall below these limits.

Nitrates: The concentration of nitrates ranged from 0.07 mg/L (location 11) and 1.16 mg/L (location 22) (Fig. 4.16). The permissible limits for nitrate by WHO, EU and NIS is 50 mg/L. (Table 4.14) the nitrate concentration I location 22 is slightly increased. High concentration of nitrate in drinking water is debilitating on human health. Nitrate is a strong oxidizing agent and NO_2 can react with secondary amines present human body to form nitrosamine (George et al., 2010). The major adverse effect associated with human exposure to nitrate is ***methaemoglobinema.*** Nitrate converts haemoglobin to methaemoglobinema by oxidizing the Fe^{2+} in haemoglobin to Fe^{3+}which cannot transport oxygen. High levels of Fe^{3+} -haemoglobin in human blood can cause cyanosis characterized by bluish skin and lips (Al-Dabbagh et al., 1986).

Calcium: Calcium concentration ranged from 0.25 mg/L (location 2) to 13.20 mg/L (location 5) (Fig. 4.11). The concentration obtained for all the water samples were lower than the maximum permissible limit (75 mg/L) as set by WHO, EU, AND NIS (Table 4.14), hence the water is suitable for human consumption and industrial use with respect to Calcium.

Magnesium: Magnesium concentration range from 0.4 mg/L (location 23) to 77.78 mg/L (location 5) (Fig. 4.15). The Mg concentration for all the water sampled is above the 0.2 mg/L maximum permissible limit as set by NIS (Table 4.14). Mg is a beneficial metal but toxic at high concentration and can cause water hardness and also exert a cathartic and diuretic action (APHA, 1985). Magnesium is not uniformly distributed in water and it is also influenced by human activities on the environment (Ishaya and Abaje, 2009 a,b).

4.6 HEAVY METALS

Chromium: Chromium concentration in the study area falls below detection limit of the equipment used except for location 1 which has value of 0.86 mg/L that is significantly higher than the permissible limits set by WHO EU and NIS. This may be as a result of industrial and anthropogenic activities which led to increase in the Cr level in the environment. Ingestion of water with chromium concentration above 0.05 mg/L can lead to cancer or allergic dermatitis (NIS, 2007).

Zinc: Zinc concentration range from 0.03 mg/L (location 4)to 0.38 mg/L (location 21) (Fig.4.20). The maximum permissible limit set by WHO and NIS for Zinc concentration is 0.3mg/l (Table 4.14) .the Zinc concentration of most water sampled falls below this limit except for sample collected at location 21. Although Zn is not a human carcinogen, but excessive intake of zinc through contaminated food chain could lead to vomiting, dehydration, abdominal pain, lethargy and dizziness (ATSDR, 1994).

Iron: The concentration of Iron ranged from 0.05 mg/L to 2.58 mg/L (Fig. 4.13). Most of the samples have values below the maximum permissible limit (0.3 mg/L) set by WHO (Table 4.14) and NIS and 0.2 mg/L set by EU except locations 1, 3, 5, 6, 7, 10, 13, 29 (Fig. 4.13).

Manganese: Manganese range from 0.05 mg/L -1-64 mg/L (Fig. 4.14). From literature both Fe and Mn are metals that occur frequently in deeper water in varying concentration. Prolonged exposure of human to manganese is associated with toxicity to nervous system, producing a syndrome that resembles parkinsonism.

The range of values of trace metals in groundwater analysed is presented in Table 4.14. not all the trace metals analysed in groundwater samples were found present. The element Iron is the most abundant element in earth crust. Probably, this explains the high value of Fe (2.58 mg/L) in the groundwater. The breakdown of casing and pump often lead to unnecessary high level of iron “red water”. Other major sources of iron include nature of rock which houses the groundwater, leachates from refuse dump, industrial waste, and seepage from septic tank. Amadi et al. (1989) pointed out that pH is an important factor that could influence the solubility and resultant concentration of iron. The geology of the area could also be additional source of the element iron (Majolagbe et al 2011). Iron is an essential element in human nutrient; it helps in formation of haemoglobin. It also helps during pregnancy and lactation. However the toxicological study has established a link between accidental exposure or and iron overload and idiopathic hemochromatosis as well as excess dietary iron (Jacob and Wordwood, 1981).

Table 4.13 Range of pH, water level and temperature from all locations sampled

Location	**PH**	**Waterlevel(m)**	**temperature ^{0}c**
L1	5.21	23.11	28.2
L2	5.51	30	27.2
L3	6.67	**STREAM**	27.5
L4	6.45	23	26.6
L5	4.87	**STREAM**	26.8
L6	5.15	29.05	27.1
L7	5.4	25.92	26.6
L8	4.84	23.13	27.3
L9	4.98	25.35	27.9
L10	4.95	**RIVER**	27.8
L11	5.6	22.2	26.6
L12	4.8	25.91	27.3
L13	5.2	22.92	26.6
L14	5.4	23	27.1
L15	4.36	20.68	27.1
L16	5.51	23.02	27.3
L17	4.77	25.05	26.3
L18	4.82	23.02	27.2
L19	5.08	33.12	26.8
L20	5.21	25.38	26.7
L21	5.18	25.9	28.2
L22	6.25	18	27.4
L23	6.52	14.62	27.2
L24	5.52	22.5	28.2
L25	4.9	23.05	28.8
L26	5.36	21.7	28.1
L27	4.56	22.6	27.7
L28	4.89	22.2	26.5
L29	5.61	19.56	26.4
L30	6.3	23.13	27.2

Table 4.14: Summary Of Hydrochemical Parameters Analysed

Hydrochemical parameters	Range (mg/l)	WHO standards (mg/l)
Chloride	24.54 - 286.34	250
Nitrate	0.07 - 1.16	10
Sulphate	1.40 - 88.24	250
Phosphate	0.001 - 0.236	5
Magnesium (hardness)	0.41 - 77.78	-
Calcium (hardness)	0.25 - 13.20	-
Total hardness	2.59 - 248.57	100
Ph	4.36 - 6.67	6.5 – 8.5
Zn	0.03 – 0.38	2.00
Mn	0.05 – 1.64	0.05
Fe	0.05 – 2.58	0.3

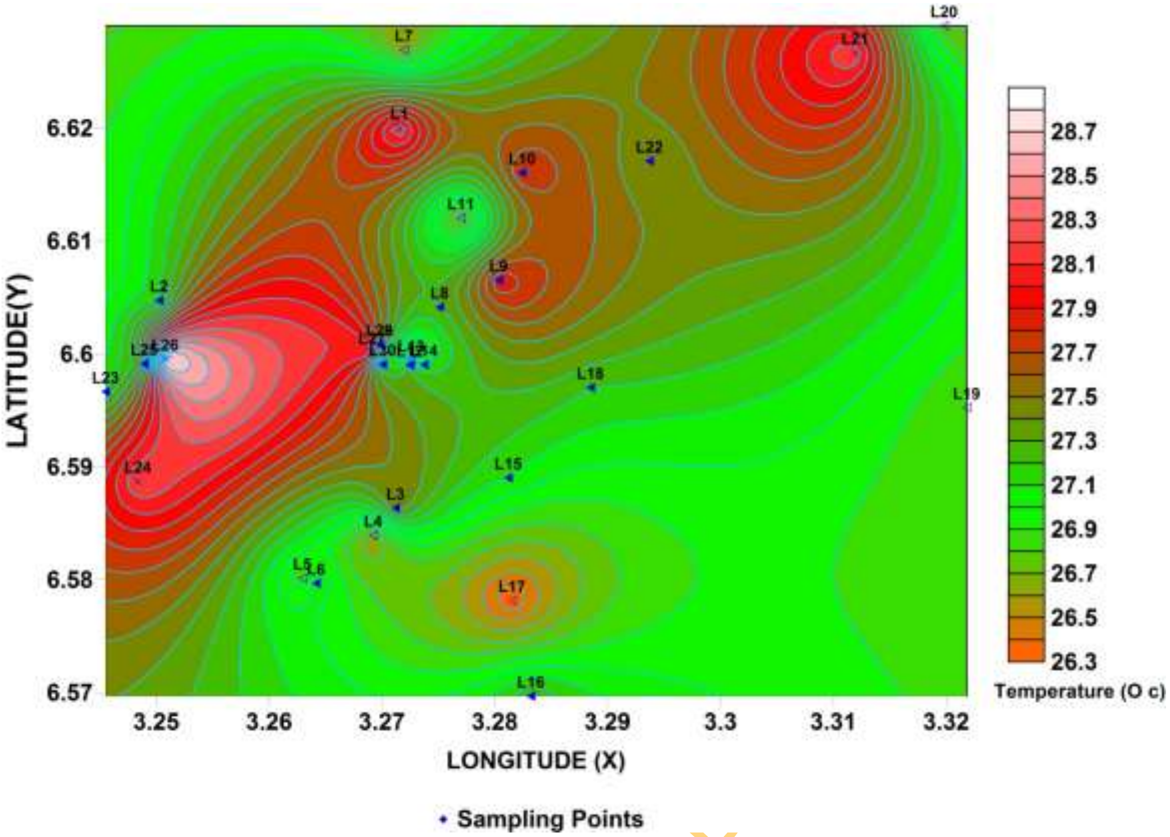


Fig. 4.9: Variation in Temperature in Each Location Sampled

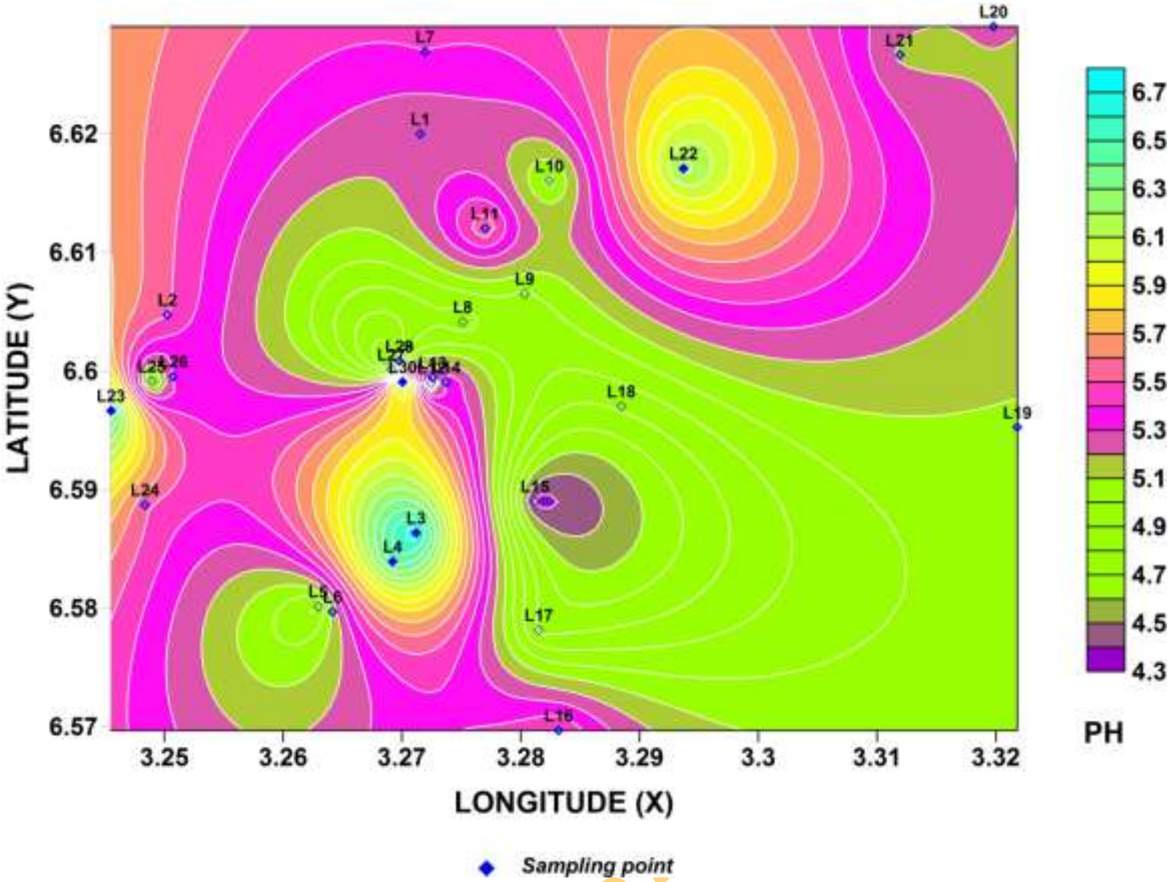


Fig. 4.10: Variation in PH in each Location Sampled

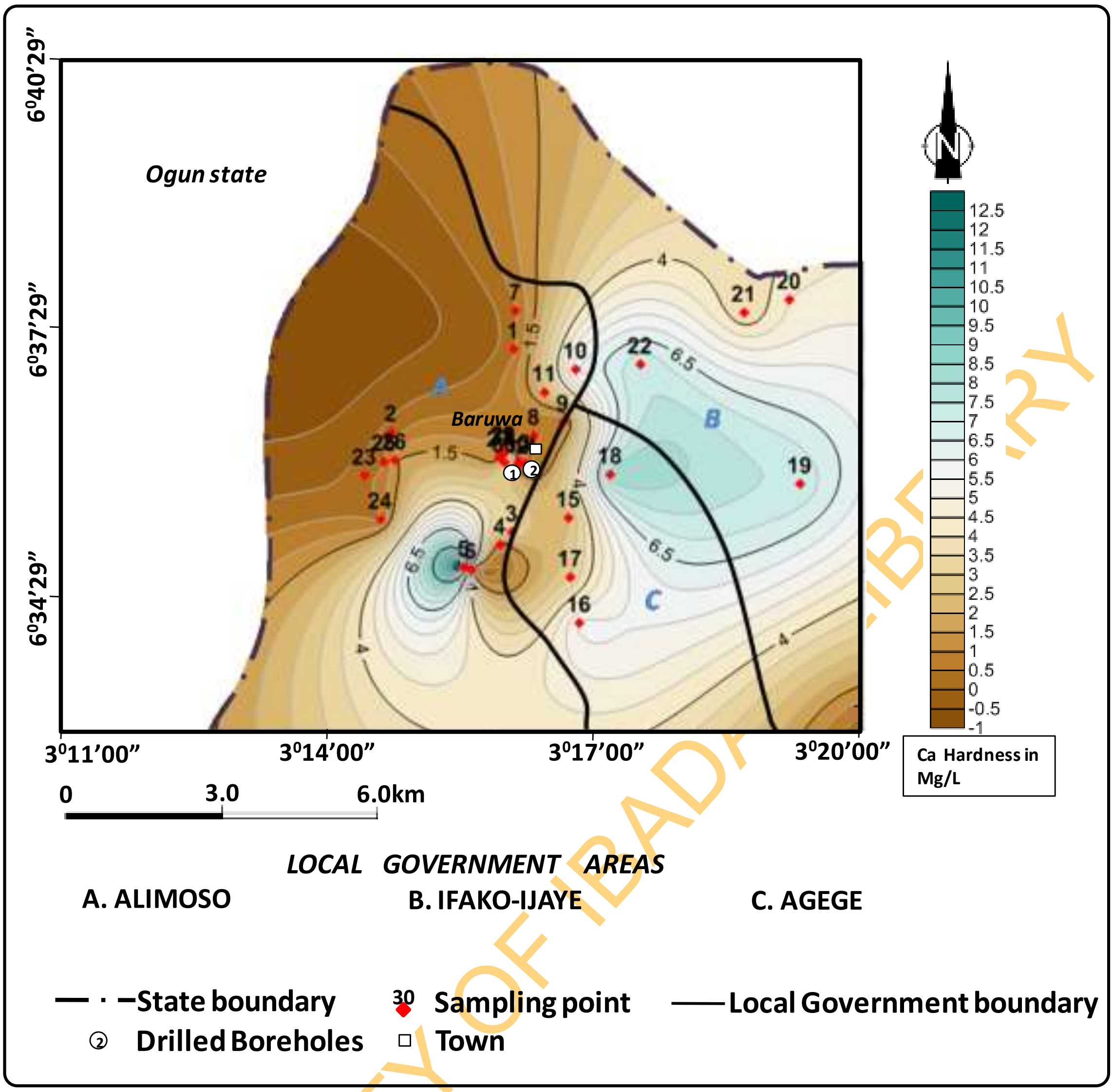


Fig. 4.11: Variation in Ca Hardness in each Location Sampled

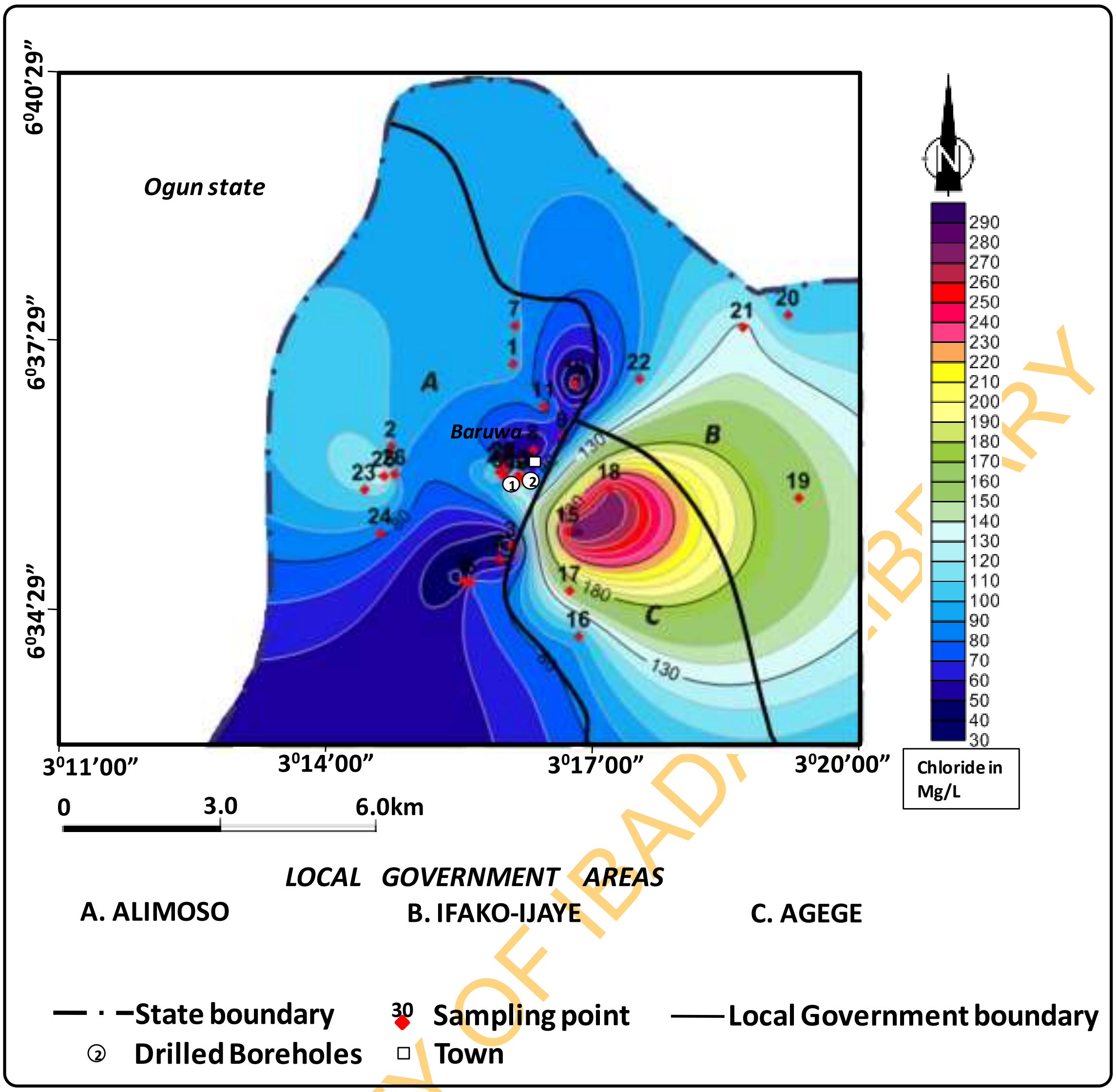


Fig. 4.12: Variation in Chloride in each Location Sampled

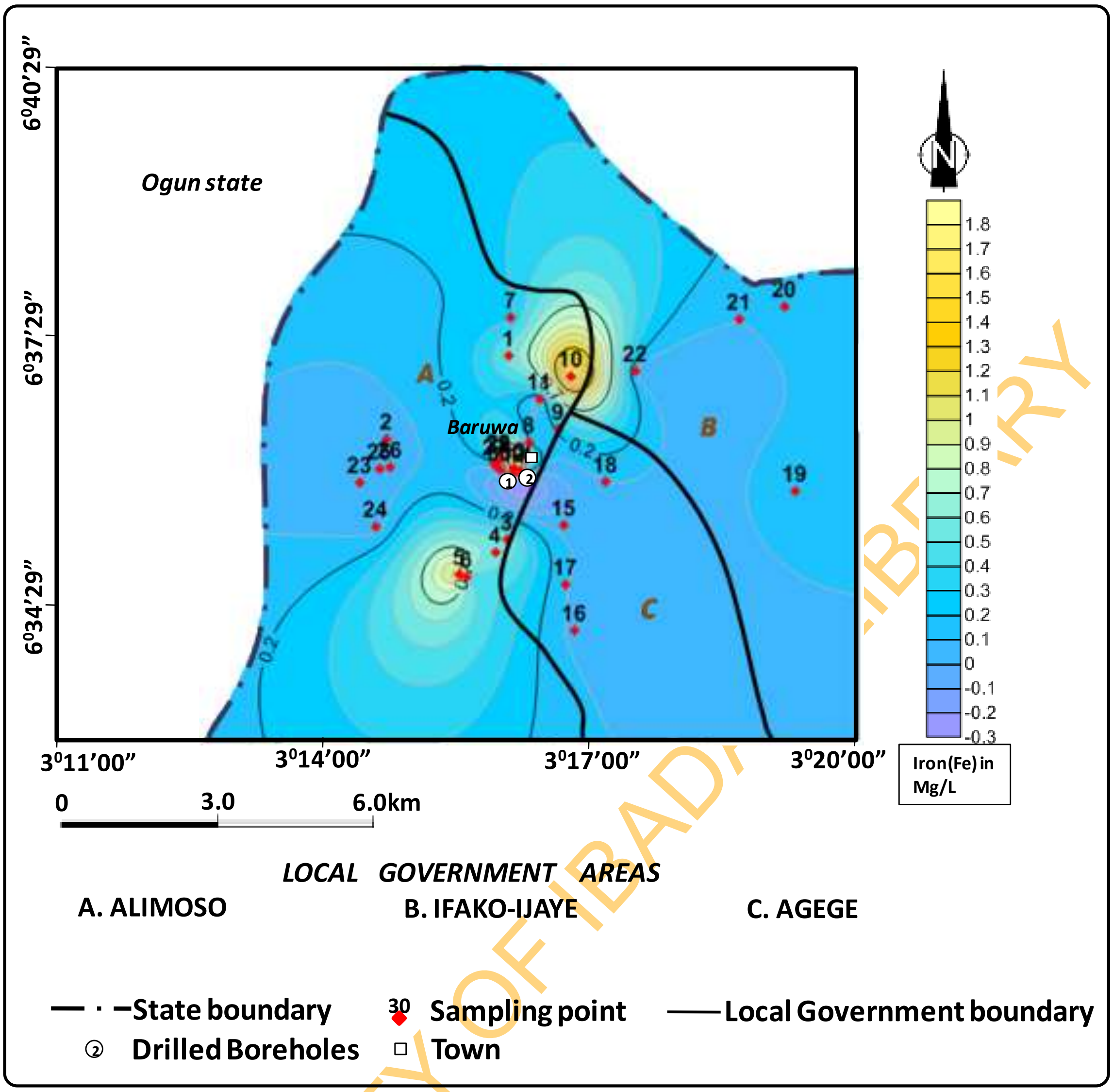


Fig. 4.13: Variation in Iron in each Location Sampled

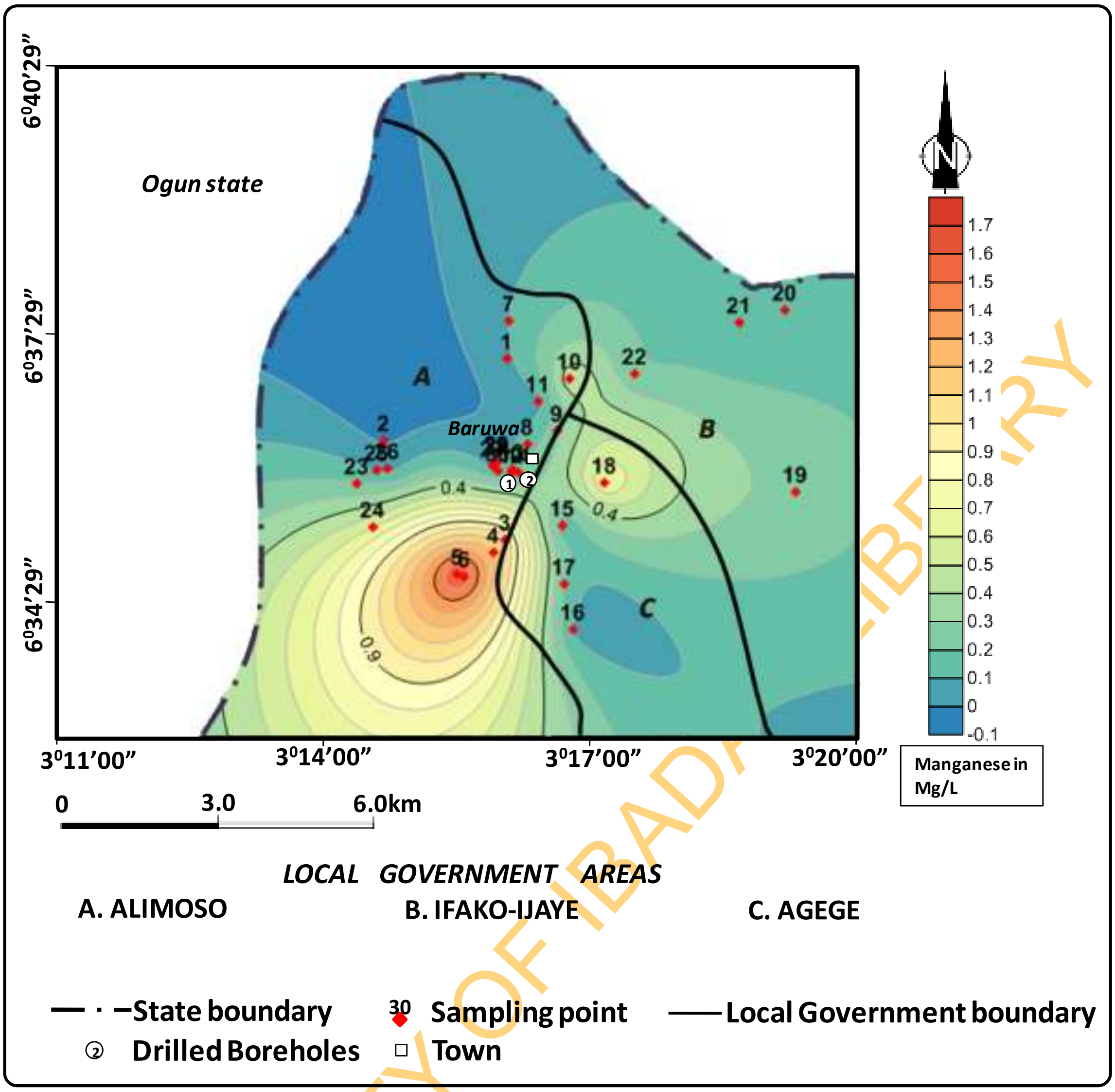


Fig. 4.14: Variation in Manganese in each Location Sampled

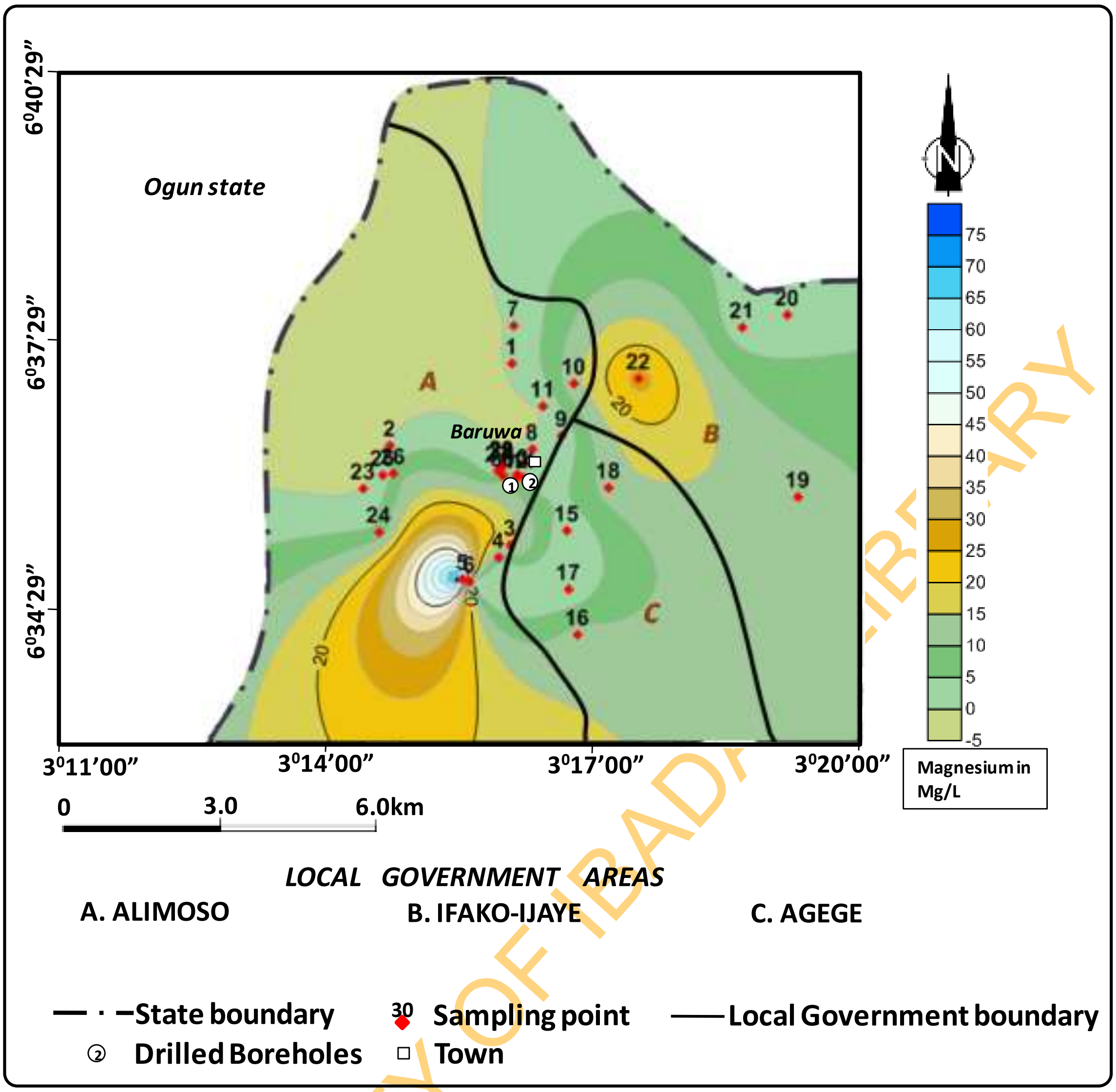


Fig. 4.15: Variation in Mg Hardness in each Location Sampled

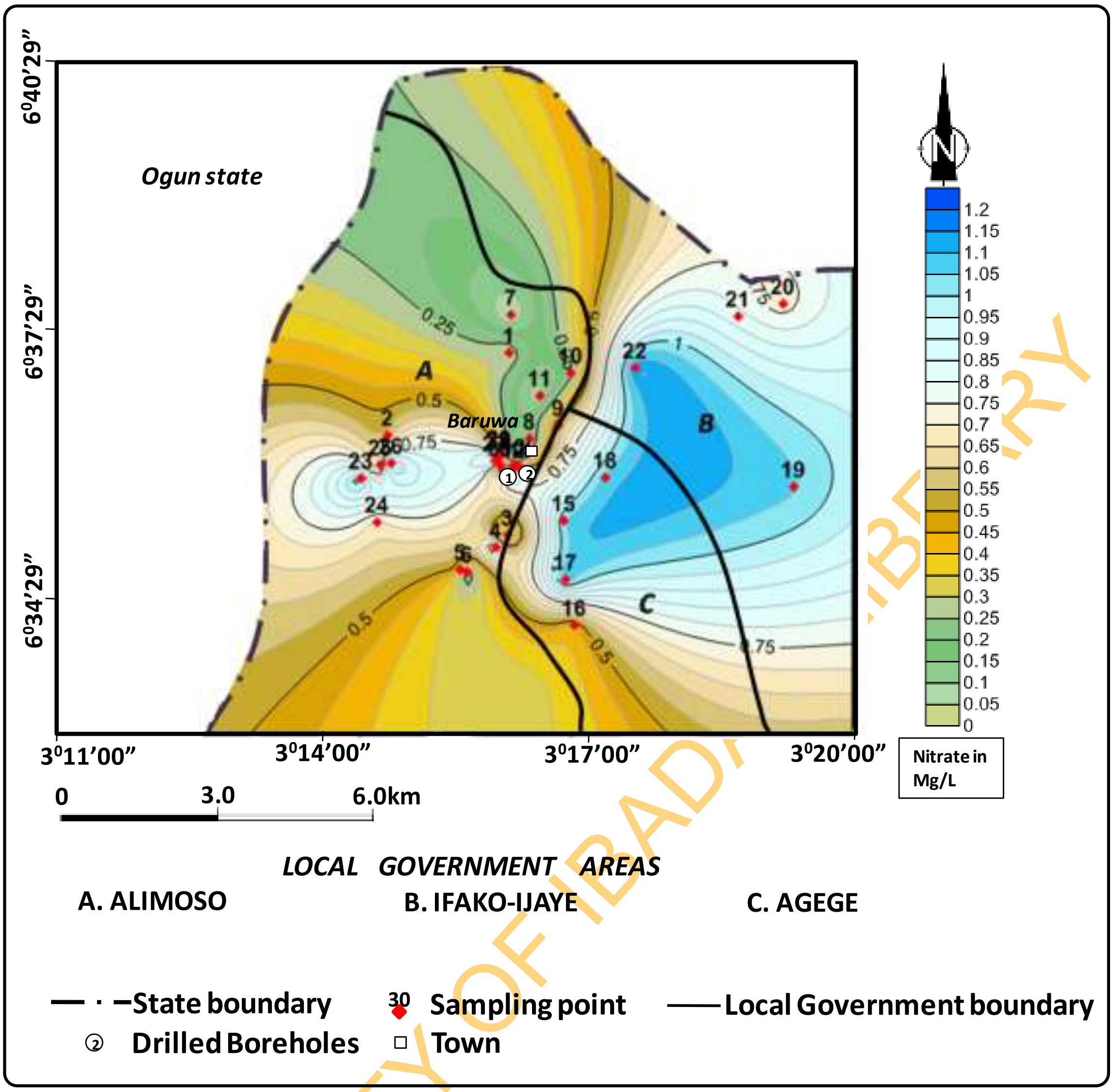


Fig. 4.16: Variation in Nitrate in each Location Sampled

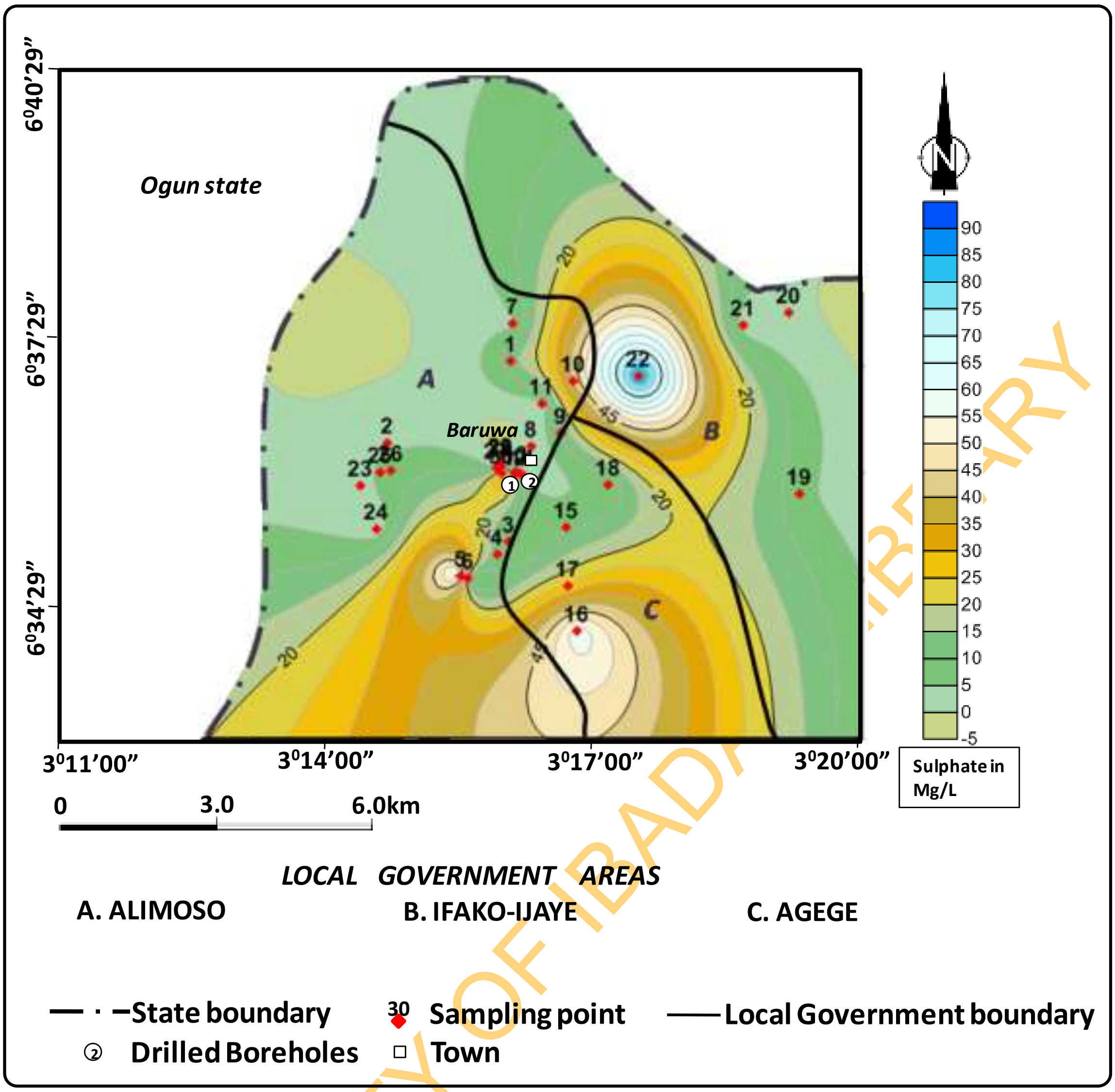


Fig. 4.17: Variation in sulphate in each Location Sampled

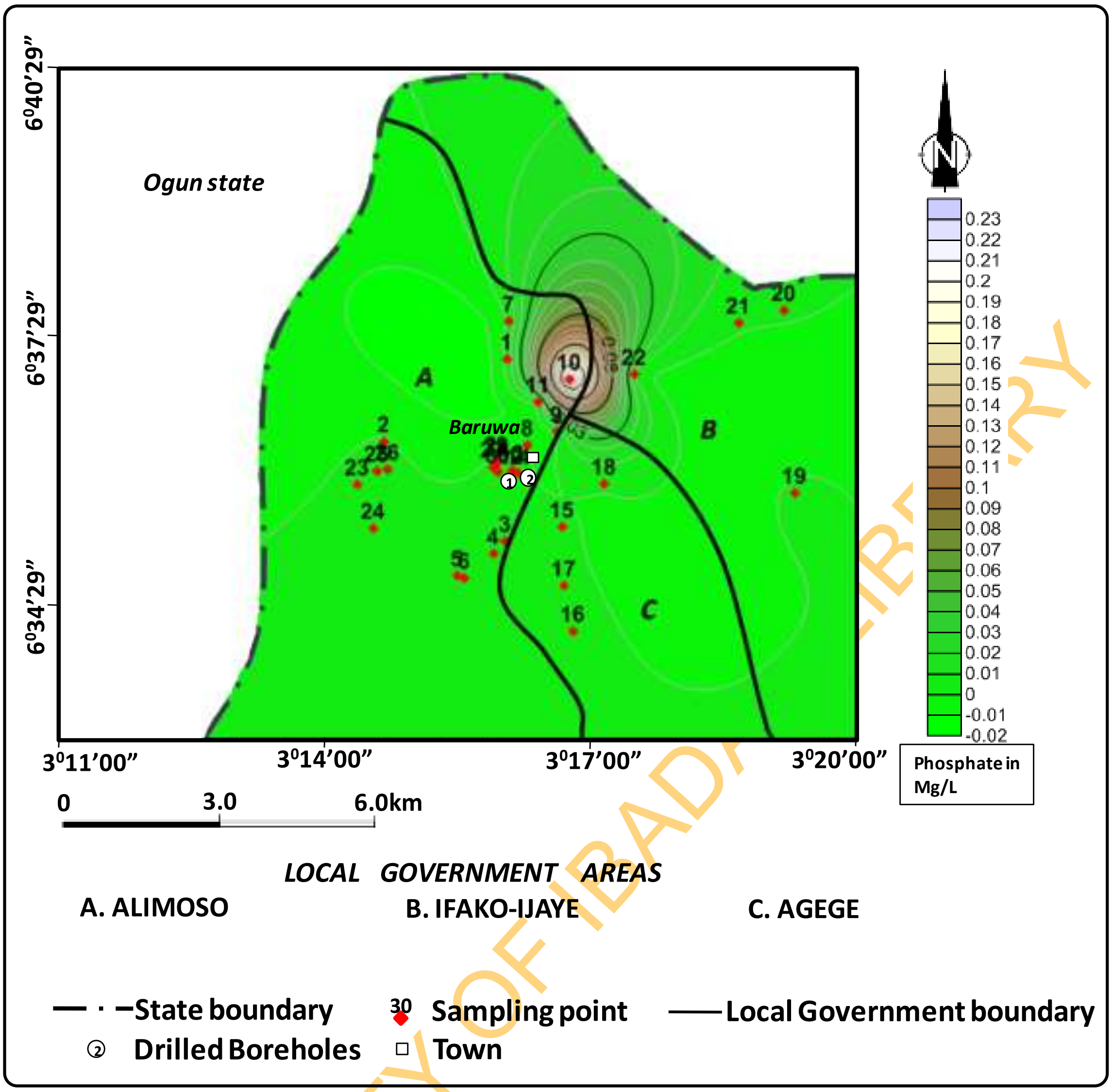


Fig. 4.18: Variation in phosphate in each Location Sampled

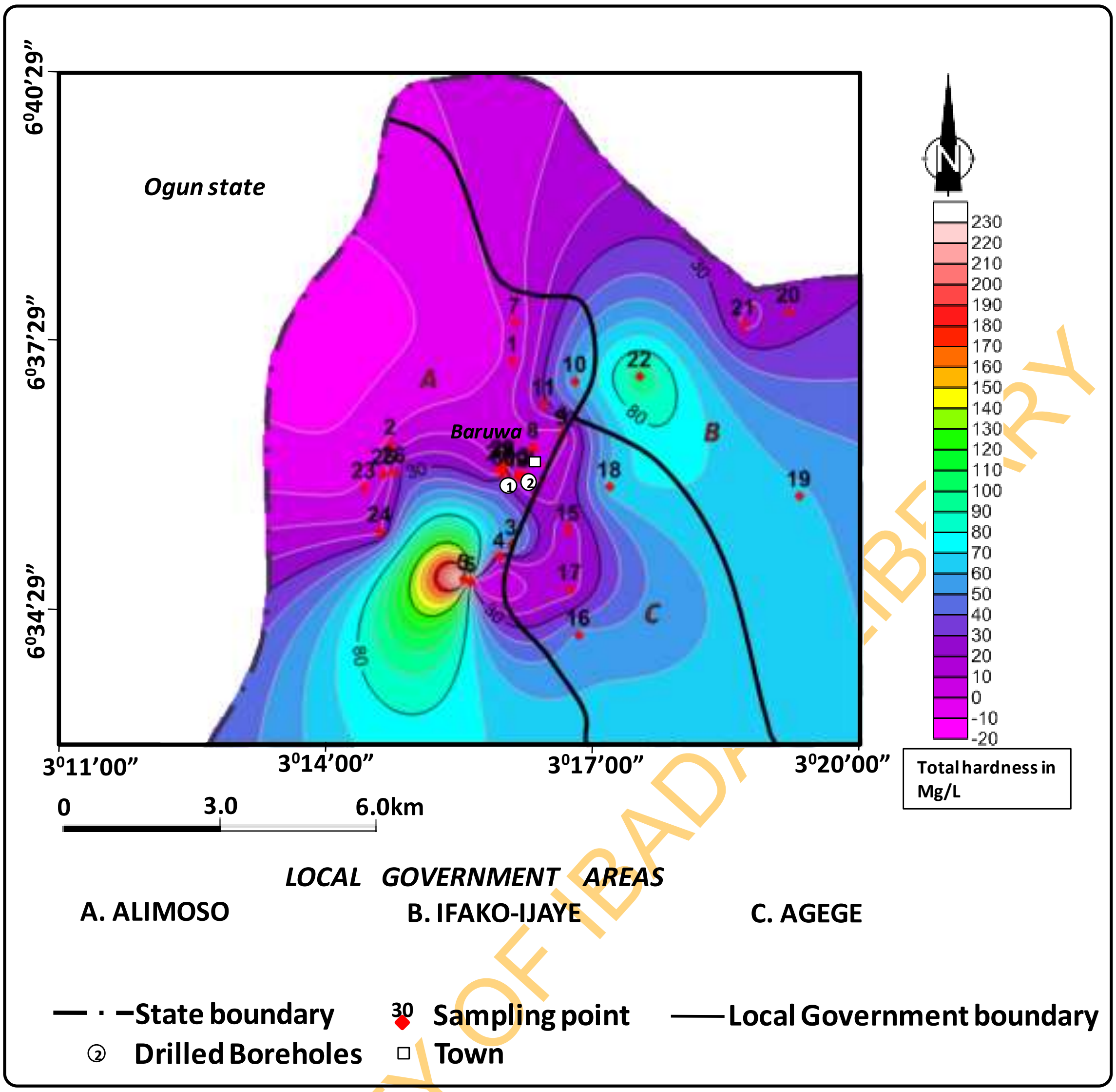


Fig. 4.19: Variation in Total hardness in each Location Sampled

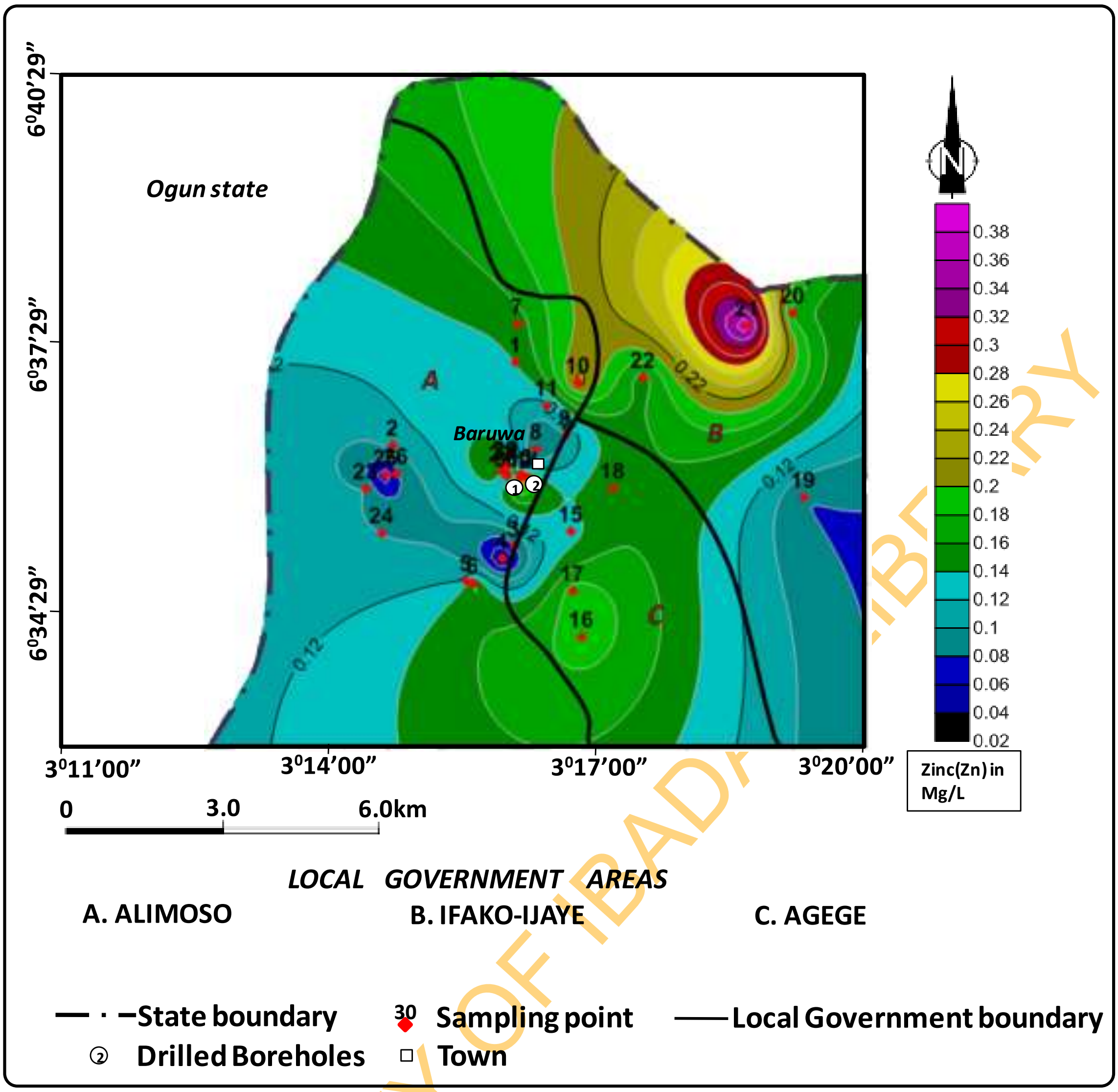


Fig. 4.20: Variation in Zinc in each Location Sampled

4.7 PETROLEUM HYDROCARBONS

4.71 PAH and TPH .

From the result of the GC - MS it was observed that the hydrocarbons identified in the samples are C24-C30 and C26-C44. With reference to (Fig.1) this falls within the range of lubricating oil and fuel oil. The lubricating oil ranges from C22-C31 while the fuel oil ranges from C14-C26 (Senn and Johnson 1985). TPH which is a term used a large family of several hundreds of chemical compounds that originally come from crude oil. Individual hydrocarbons present in petroleum product are as follows Gasoline C6- C12, diesel C8-C26 kerosene C8-C18, fuel oil C17-C26 and lubricating oils C15-C50. The fate and transport of liquid petroleum products in the subsurface is determined primarily by the properties of the liquid and the characteristics of the geologic media into which the product has been released. Soil properties that influence the movement of petroleum hydrocarbon include porosity and permeability which has been discussed earlier in the chapter. Pure phase liquids that do not readily dissolve in water are called non aqueous phase liquids (NAPL). In general they are subdivided into two classes those that are lighter than water (LNAPLs) and those with a density greater than water (DNAPLs). Hydrocarbon fuels such as gasoline, heating fuel, kerosene, jet fuel and aviation fuel are LNAPL. The category into which the hydrocarbon found in our samples falls into. Despite the large number of hydrocarbons found in petroleum products, only a relatively small number of them have been characterized for toxicity (Research Triangle 1999). The health effects of some fractions can be fully characterized based on their components or representative compounds (e.g., light aromatic BTEX fraction (benzene, toluene, ethylbenzene, and xylenes) and naphthalene. The Agency for Toxic Substances and Disease Registry (ATSDR) does not assess cancer potency for TPH components, and only for some components toxicological information is provided, e.g., minimal risk level (MRL) (ASDR, 1996). Health effects that are common to the BTEX are of neurological nature. Benzene has hematological effect and is classified in EPA Group A (human carcinogen). The inhalation minimal risk level for each of the BTEX compounds (acute MRL) was determined: benzene 0.05 ppm, toluene 3.0 ppm, o-, m-, and p-xylene 1.0 ppm , and ethylbenzene 0.2 ppm (Research Triangle, 1999). For gasoline, kerosene, and jet fuels, commonly selected hydrocarbon chemicals of concern are benzene, toluene, ethylbenzene, and (BTEX). Additional chemicals of concern for kerosene and jet fuels are polycyclic aromatic hydrocarbons (PAHs). For diesel fuel, light fuel oils, and heavy fuel oils, the commonly selected hydrocarbon chemicals of concern are PAHs.

It should be stressed that the results obtained using TPH methods other than gas chromatography (GC) must be interpreted with caution because the potential risk posed by BTEX compounds may not be adequately addressed. The gas chromatography-flame ionization detector (GC-FID) methods appear to offer the best hope for standard TPH tests in soil and groundwater verification of site cleanup. The (GC-MS) is currently the most advanced and comprehensive technique for evaluation of petroleum compounds in the environment. The increased solubility of the BTEX chemical components from gasoline mixtures can thus more likely result in groundwater contamination. High TPH test results may require action on the

4.8 CONTRIBUTION TO KNOWLEDGE

From this study,

The hydrogeological sequences comprising of three aquiferous units have been identified and the second aquifer layer discovered to be contaminated by petroleum products.

Porosity and permeability results revealed the area is underlain by very porous and permeable sediments making infiltration of contaminant high.

It has been observed that groundwater sources in this area have been heavily contaminated with petroleum products which have serious health implications to users.

The areas to be remediated have been delineated from the thematic maps and the area of contaminated land that needs remediation has been calculated as 9,900,000m$^{2;}$ the volume of water that needs to be remediated is also calculated as 89,100,000m^{3} from the study. (Fig. 4.21).

Heavy oil and metals identified in Baruwa and its environs can have long term environmental effect like bioaccumulation. To remediate this problem, the use of proximate modern or latest remedial technique such as the use of permeable reactive Barriers (PBRs), Glass Reinforced Plastic (GRP), Horizontal wells and Bioremedial technique should be encouraged. More research work is needed in these areas especially in the technology of PRBs and Bioremediation technique.

Delineation of contaminated areas from thematic maps

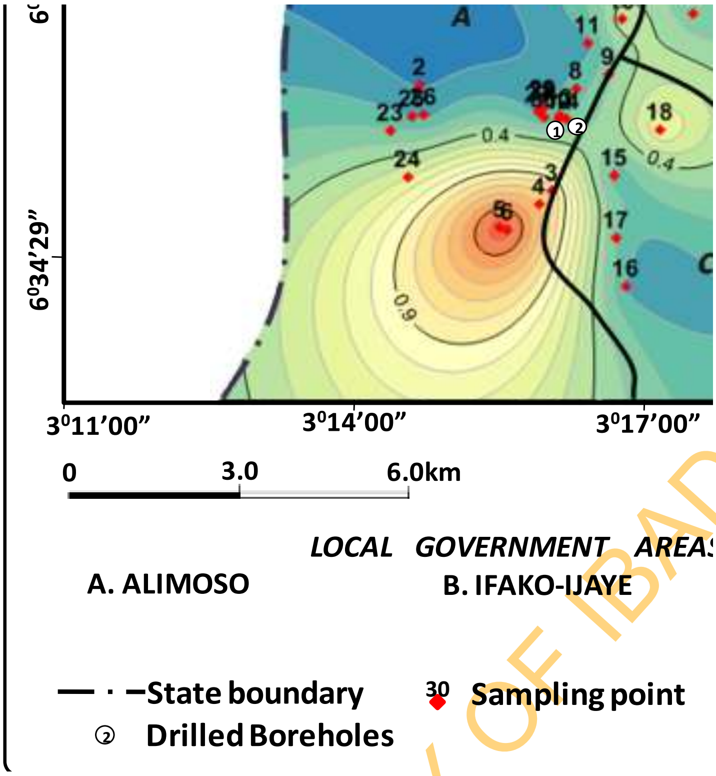


Fig 4.21: Map showing area to be remediated

Area = Length x Breadth = 2200 x 4500 = 9,900,000 m^2

Volume = Length x Breadth x height = 2200 x 4500 x 9 m^3

Volume = 89,100,000 m^3

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Hydrocarbon releases to soil and groundwater are problematic because the effects of those releases are really not known with certainty. This is especially true if the hydrocarbon contains the environmentally mobile carcinogen benzene and is generally true with regards to the cumulative effects of many small and widely distributed hydrocarbon contaminated sites. An important yet unanswered question is where the substantial amount of benzene that has presumably leaked from pipelines in baruwa now located. Both theoretical and empirical evidence suggests that bacterial biodegradation may act to hold small release effectivelyin check and eventually transform hydrocarbons. However the development of science based mechanistic models to predict hydrocarbon fate and transport is complicated by micro and macro scale subsurface heterogeneities, the complexity of hydrocarbon mixtures and a variety of difficult to estimate coefficients and other model input parameters including biotransformation rates. These circumstances make the search for health based soil clean up criteria an uncertain and controversial process. The situation is similar for shallow groundwater in low permeability formation.

Groundwater contamination in Baruwa community of Lagos Southwestern Nigeria is mainly due to the leakage of pipeline traversing the area. Continuous monitoring of the pipeline using remote sensing devices (such as the use of infrared video and photography from airborne platform, airborne laser fluourosensors, air-borne and space-borne optical sensors, as well as air-borne and space-borne Synthetic-Aperture-Radar imageries) to provide early warnings as to the presence of potential leakage is recommended.

There is need for launching public awareness campaigns and convincing the relevant authorities in government and oil industries as to the need to undertake groundwater protection measures. The public should be educated and encouraged to avoid vandalization of pipeline by the use of signpost with inscriptions boldly written in different languages of the ethnic groups present in the environment in which the petroleum pipeline is traversing.

Due to lack of equipments and time constraint, the various groundwater aquifers and confining unit could not be determined. However, deeper wells are recommended to residents of Baruwa community. It is suggested that highly contaminated hand-dug wells in the area should be closed down while boreholes should be re-drilled to a deeper and uncontaminated aquifer or confining unit. The re-drilled well should be properly cased and gravel-packed to avoid intrusion of water from the contaminated aquifer.

Water quality management is an issue that must be given top priority and urgent attention. To remediate the problem of groundwater contamination by petroleum-product spillage or seepage, the use of proximate modern or latest remedial technique such as the use of permeable reactive Barriers (PBRs), Glass Reinforced Plastic (GRP), Horizontal wells and Bioremedial technique should be encouraged. More research work is needed in these areas especially in the technology of PRBs and Bioremediation technique.

In addition, the government and environmental parastatals concerned should make and endeavour to maintain three boreholes in strategic parts of the affected community.

Finally, groundwater contamination is particularly insidious because of the slow movement of water through aquifers. Contamination introduced into an aquifer can show up years later at a site far from the original source. Groundwater through wells is the source of more than 80% of the country’s water supply; it is up to the individual owner to test and assure himself of the safety of his water. If your drinking and household water is supplied by a private well, it is vitally important that you are aware of the contaminants in water that you should test for, and the well filter systems that will remove them.

5.2 RECOMMENDATION

Even though many technologies are available for the treatment of contaminated sites, the selection depends on contaminant and site characteristics, regulatory requirements, costs, and time constraints (Riser-Roberts, 1998; Reddy et al., 1999). Since most remediation technologies are site-specific, the selection of appropriate technologies is often a difficult, but extremely important, step in the successful remediation of a contaminated site. Therefore, the successful treatment of a contaminated site depends on proper selection, design, and adjustment of the remediation technology’s operations based on the proper- ties of the contaminants and soils and on the performance of the system.

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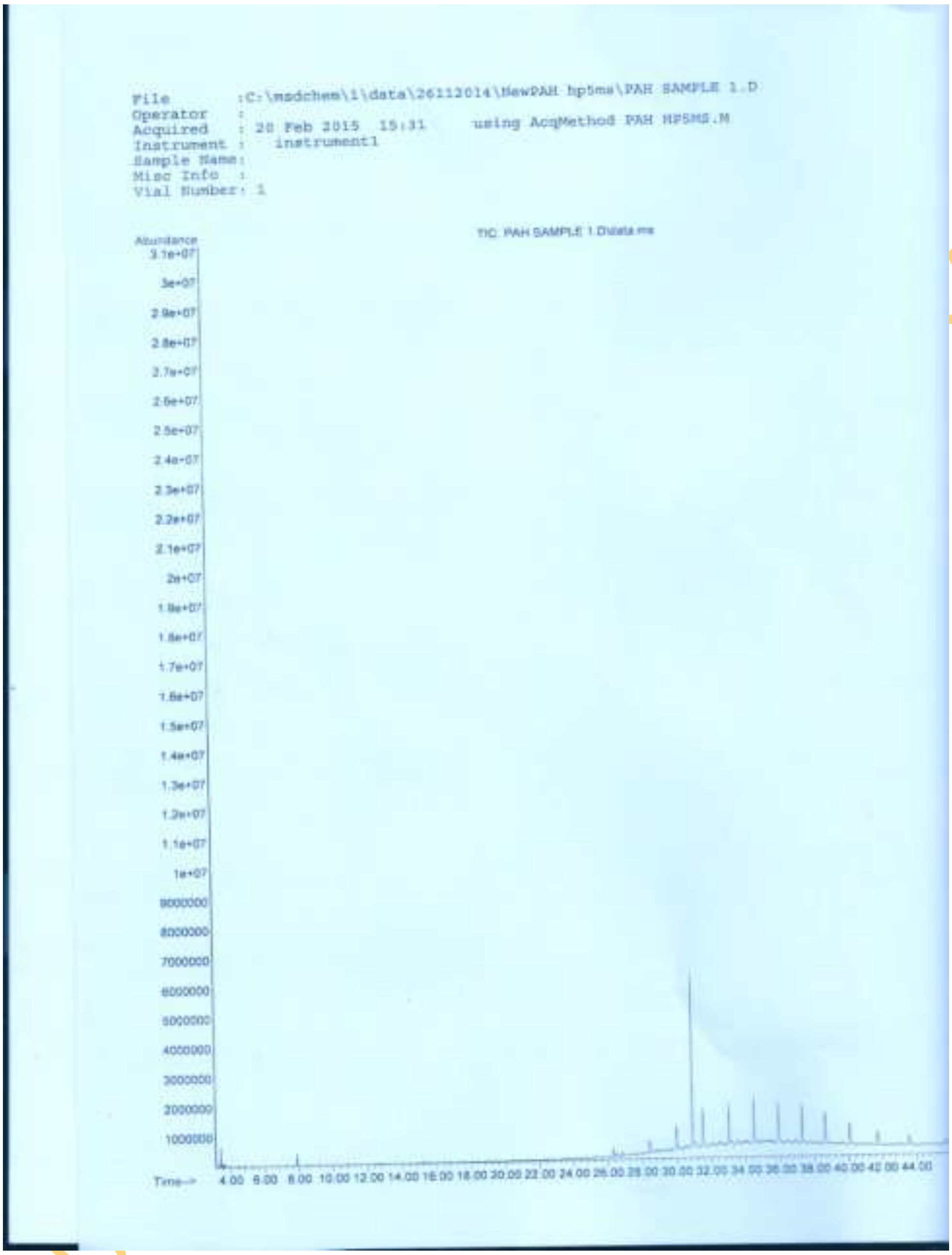
APPENDIX

Chromatogram for sample 1



```
File        :C:\msdchem\1\data\26112014\NewPAH hp5ms\PAH SAMPLE 1.D
Operator    :
Acquired    : 20 Feb 2015  15:31     using AcqMethod PAH HP5MS.M
Instrument  :   instrument1
Sample Name:
Misc Info   :
Vial Number: 1
```

Chromatogram for sample 2

File :C:\msdchem\1\data\26112014\NewPAH hp5ms\PAH SAMPLE 2.D
Operator :
Acquired : 20 Feb 2015 16:39 using AcqMethod PAH HP5MS.M
Instrument : instrument1
Sample Name:
Misc Info :
Vial Number: 2

RESULTS OF WATER PHYSICO-CHEMICAL PARAMETERS

Sample Code	Parameters						
	Chloride (mg/L)	Nitrate (mg/L)	Sulphate (mg/L)	Phosphate (mg/L)	Mg hardness (mg/L)	Ca hardness (mg/L)	Total hardness
L1	95.45	0.32	14.71	0.001	0.86	0.35	3.59
L2	98.17	0.55	3.5	0.001	0.87	0.25	3.2
L3	24.54	0.19	4.2	0.002	18.8	3.23	60.24
L4	51.81	0.86	13.31	0.001	5.5	0.92	17.52
L5	35.45	0.49	60.92	0.004	77.78	13.2	248.57
L6	76.36	0.14	1.4	0.001	0.61	0.28	2.68
L7	92.72	0.05	4.2	0.001	0.72	0.42	3.53
L8	49.09	0.12	2.1	0.001	1.32	0.48	5.27
L9	65.45	0.56	BDL	0.001	1.28	0.52	5.34
L10	30	0.19	42.02	0.236	13.91	6.08	59.77
L11	87.26	0.07	3.5	0.002	0.45	2.42	29.44
L12	204.53	1.09	5.6	0.001	7.8	1.09	5.61
L13	128.17	0.03	9.8	0.001	0.76	0.37	3.42
L14	59.99	0.57	2.8	0.001	1.05	0.46	4.52
L15	286.34	1.04	9.8	0.001	1.84	2.32	14.15
L16	95.45	0.43	58.82	0.001	12.37	5.69	54.32
L17	158.17	1.09	25.91	0.001	1.27	3.02	15.61
L18	272.7	1.06	4.9	0.001	12.72	8.47	66.64
L19	158.17	1.06	6.3	0.001	12.36	7.42	61.42
L20	100.9	0.72	1.4	0.001	2.68	4.54	25.39
L21	133.62	0.82	1.4	0.001	1.27	3.43	17.3
L22	100.9	1.16	88.24	0.003	27.61	7.44	99.58
L23	111.81	1.05	BDL	0.001	0.41	0.38	2.59
L24	81.81	0.68	1.4	0.001	6.06	0.44	16.94
L25	136.35	0.51	6.3	0.002	1.27	0.32	4.49

L26	87.26	1.04	7.7	0.002	8.98	1.57	28.89
L27	136.35	1.06	5.6	0.002	0.95	0.71	5.3
L28	136.35	1.06	11.2	0.002	3.83	4.24	27.02
L29	54.54	0.52	4.9	0.001	3	2.6	18.2
L30	57.27	0.17	46.22	0.001	10.66	4.08	43.42

RESULTS OF HEAVY METALS IN WATER

Samples				Metal Concentrations (mg/L)			
	Pb	Cr	Cd	Ni	Zn	Mn	Fe
L1	BDL	0.86	BDL	BDL	0.14	BDL	0.56
L2	BDL	BDL	BDL	BDL	0.11	BDL	0.05
L3	BDL	BDL	BDL	BDL	0.08	1.08	0.61
L4	BDL	BDL	BDL	BDL	0.03	BDL	BDL
L5	BDL	BDL	BDL	BDL	0.12	1.64	1.12
L6	BDL	BDL	BDL	BDL	0.17	BDL	0.46
L7	BDL	BDL	BDL	BDL	0.15	BDL	0.27
L8	BDL	BDL	BDL	BDL	0.08	BDL	0.12
L9	BDL	BDL	BDL	BDL	0.1	BDL	BDL
L10	BDL	BDL	BDL	BDL	0.23	0.49	1.82
L11	BDL	BDL	BDL	BDL	0.11	0.06	0.05
L12	BDL	BDL	BDL	BDL	0.26	BDL	0.21
L13	BDL	BDL	BDL	BDL	0.14	BDL	2.58
L14	BDL	BDL	BDL	BDL	0.17	BDL	0.06
L15	BDL	BDL	BDL	BDL	0.13	0.11	0.06
L16	BDL	BDL	BDL	BDL	0.19	0.07	0.06
L17	BDL	BDL	BDL	BDL	0.19	0.17	0.1
L18	BDL	BDL	BDL	BDL	0.16	0.71	0.1
L19	BDL	BDL	BDL	BDL	0.08	0.28	0.16
L20	BDL	BDL	BDL	BDL	0.17	0.12	0.15
L21	BDL	BDL	BDL	BDL	0.38	0.1	0.1
L22	BDL	BDL	BDL	BDL	0.15	0.21	0.05
L23	BDL	BDL	BDL	BDL	0.1	BDL	0.05

L24	BDL	BDL	BDL	BDL	0.1	BDL	0.05
L25	BDL	BDL	BDL	BDL	0.04	BDL	0.05
L26	BDL	BDL	BDL	BDL	0.08	0.05	0.05
L27	BDL	BDL	BDL	BDL	0.16	0.05	0.16
L28	BDL	BDL	BDL	BDL	0.06	0.06	0.05
L29	BDL	BDL	BDL	BDL	0.17	0.11	0.56
L30	BDL	BDL	BDL	BDL	0.08	0.12	0.15