UNIVERSITY OF NAIROBI

DEPARTMENT OF CHEMISTRY

DETERMINATION OF SELECTED PHYSICO-CHEMICAL PARAMETERS AND HEAVY METALS IN NGAMIA-5 OIL EXPLORATORY WELL RESERVE (WASTE) PIT IN TURKANA, KENYA

BY

Mutua Elizabeth Mbithe

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A Thesis submitted in partial fulfillment of the requirements for the award of the Degree of Master of Science in Environmental Chemistry.

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DECLARATION

This thesis is my original work and has not been submitted for award of a degree in another university.

MUTUA ELIZABETH MBITHE

REG.NO-I56/69828/2013

SIGNATURE……………………. DATE ………………………………..

This thesis has been submitted for examination with our approval as the official University supervisors.

PROFESSOR GEOFFREY N. KAMAU

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NAIROBI

SIGNATURE…………………………DATE………………………………….

Dr. CHRISTOPHER. NYAMAI

DEPARTMENT OF GEOLOGY

UNIVERSITY OF NAIROBI

SIGNATURE…………………………DATE………………………………….

Mr. DAVID M. MAINA

INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY

UNIVERSITY OF NAIROBI

SIGNATURE…………………………DATE………………………………….

DEDICATION

I sincerely dedicate this work to the Almighty God who has faithfully led me through my academic journey to this level. His mighty power cancelled everything which would delay me from completing my study on time. Glory be to God.

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ABSTRACT

Oil and gas operations produce wastes that are potentially toxic to the environment. The wastes get disposed of into reserve pits which are surface impoundments excavated adjacent to the drilling rigs. Reserve pits can contaminate soil, groundwater, and surface water with heavy metals and other toxic substances if improperly managed. In an attempt to characterize the physical-chemicals and demonstrate the potential environmental impact of the heavy metal content of drill waste generated during the drilling of Ngamia 5 exploratory well in Turkana, Kenya, this study was developed to determine their toxicity and the potential environmental impacts following their disposal. Samples of drilling waste disposed of in a reserve pit were collected at prescribed depths and analyzed for heavy metals using Total x-ray fluorescence. The samples were also analyzed for other physico- chemical parameters (oil and grease, Electrical conductivity and pH), which are the key parameters used when determining disposal of drilling waste.

Results showed that the mean pH values ranged from 8.2 to 8.7 categorizing the drill waste as basic while Electrical conductivity values ranged from 1.28 to 2.16 mmhos cm^{-1}. Most physico- chemical parameters were generally within the limits of guidelines by regulatory authorities save for oil and grease values which were exceedingly very high (41.66 ± 25.74 mgl^{-1}) compared to the established limits. The trend of all the parameters showed that the values increased with depth. Calcium (Ca) had the highest concentration (1192.81 ± 150.73 mgl^{-1}) followed by barium (Ba) (1076.27 ± 147.32 mgl^{-1}) and then iron (Fe) (381.46 ± 62.23 mgl^{-1}) in that order while Arsenic had the lowest concentration (0.08 ± 0.002 mgl^{-1}) followed by nickel (Ni) 0.26 ± 0.03 mgl^{-1}.

The concentration of metals in the mud phase (bottom) was the highest followed by middle then the water phase (top) and was in the order of Bottom > Middle > Top. Generally, the values of most metals were higher than those of the United States Environmental Protection Agency, Federal Environmental Protection Agency and Directorate of Petroleum Resources Standards thereby implying possible negative impacts on the immediate environment. These high levels of some of the physico-chemical parameters such as oil & grease and heavy metals in the drilling waste as seen in this study may be source of environmental pollution. This therefore, underscores the need for due diligence in managing drilling waste discharges from the ongoing exploratory drilling activities in Kenya.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ACCRONYMS

API	American Petroleum Institute
CRM	Certified Reference Material
E&P	Exploration and Production
EPA	Environmental Protection Agency
GDP	Gross Domestic Product
HSE	Health, Safety and Environments
IMF	International Monetary Fund
NAF	Non-Aqueous drilling fluids
NEMA	National Environmental Management Authority
NORM	Naturally Occurring Radioactive Materials
OBF	Oil based drilling fluids
PAHs	Polynuclear Aromatic Hydrocarbons
RBS	Rutherford Backscattering
SBF	Synthetic based drilling fluids
TXRF	Total X-Ray Fluorescence
USEPA	United States Environmental Protection Agency
WBF	Water based drilling fluids
WHO	World Health Organisation

LIST OF ABBREVIATIONS

$BaSO_4$	Barite
BTEX	Benzene, toluene, etheylbenzene, and xylene
dS/m	Decisiemen per metre
mg/l	Milligram per liter
Kg	Kilogram
EC	Electrical conductivity
Mmhos/cm	milli mhos per centimeter
pH	Hydrogen ion concentration

CHAPTER ONE

INTRODUCTION

1.1 Background

Oil exploration and production is associated with many environmental and socio-economic impacts (Baptiste and Nordenstam, 2009). Despite this, many nations throughout the world would still cherish to discover oil and gas within their territories. This is due to the fact that the availability of such natural resource is seen as a point of economic transformation and in fact can determine the development fortunes of such nations. The world economy has been developing with oil as its lifeblood for over a hundred years. Oil is directly responsible for about 2.5% of world GDP and accounts for a third of humanity's primary energy supply (World economic report, 2013). Presence of oil presents a golden opportunity for a country to promote and diversify its economic growth and development.

Kenya is now among the few African nations to have recently discovered oil in commercial quantities. The country is still relying on external supply of crude oil to meet its domestic energy requirement. Energy situation in the country is currently unreliable due to heavy investment involved in oil importation, which the country can hardly afford. Considering the huge spending on oil importation, the oil discovery is seen as a turning point to economic prosperity. The oil find is seen as a blessing by most Kenyans because the certainity of revenues that will be generated from this sector are high and will boost the country's economy several folds. According to World Bank report, Kenya's Gross Domestic Product (GDP) was 5.82% (US$ 46.481 Billion) in 2013 and is projected to improve to around 6% in 2015.

With the current crude oil price, the government has predicted annual oil revenue of US$ 300 million. With a GDP of US$ 40 billion and an annual budget (2014 - 15) of Sh 1,64 trillion (US$ 19.3 billion), an injection of an annual revenue of US$ 300 million from oil exports would be much welcome to the Kenyan economy, which the International Monetary Fund (IMF) termed as a frontier economy. Consequently, the government will have more revenue to finance its budget and take care of infrastructural development, a crucial component for economic growth. Foreign exchange earnings will be higher, which will greatly reduce the import bill, since oil currently accounts for the highest import percentage about 30% of the country's annual import cost.

Oil exploitation comes with its potential dangers which impact the environment at different levels; air, water, soil and consequently all living things on the planet. All the activities involved in the hydrocarbon exploration and production according to Odiete (1999), normally have one impact or the other on the environment. However, the greatest impact arises from the release of wastes into the environment in concentration that is not naturally found in such environment. The wastes generated during petroleum exploration and production can be broadly classified into liquids and solids. These include a wide variety of materials, ranging in volume from the thousands of barrels of fluids ("muds") used to drill a well, to the hundreds of barrels of drill cuttings extracted from the borehole and the much smaller quantities of wastes associated with various additives and chemicals sometimes used to condition drilling fluids (Ferrari et al., 2000).

All of these materials get disposed of in the reserve pit, which is a surface impoundment used for onsite disposal of drilling waste. The pits store these variety of potentially toxic, as well as non-hazardous liquid and solid wastes associated with oil and gas development (Ramirez, 2009). A survey conducted by the U.S. Environmental Protection Agency and the American Petroleum Institute found that pit waste contain toxic substances that could present hazard to human health and the environment if improperly managed (USEPA, 2002). When these toxic substances get discharged into unlined pits, they leach directly into the soil and may contaminate groundwater. Lined pits can also lead to pollution via ruptures in liners or by overflowing the pit area. These events can result in soil, surface and ground water contamination, which can have a negative effect on both human and ecosystem health (Ramirez, 2009).

Prominent among the composition of the exploratory drilling wastes in a reserve pit include: Naturally Occurring Radioactive Materials (NORM) – Radium 226 or 228; salts; volatile organic compounds (VOCs) e.g., benzene, toluene, ethyl benzene, xylene; polycyclic aromatic hydrocarbons (PAHs) e.g., naphthalene; heavy metals e.g., arsenic, barium, cadmium, chromium, lead, mercury, selenium, vanadium, zinc; other hydrocarbons, such as crude oil (Gbadebo et al., 2010). Their environmental effects extend for several kilometers and remain toxic for many years. For example, excess salts can effectively sterilize soils for years while NORM can be taken up by vegetation and pose a health threat to animals that consume the plants. Hazardous and carcinogenic materials like benzene, polycyclic aromatic hydrocarbons (PAH) can contaminate soil and water thereby causing health effects like respiratory ailments, effects on neurologic, cardiac and gastrointestinal systems, and skin disorders. The amount of exposure and how the exposure occurs (e.g., skin contact, ingestion and inhalation) affects the extent of damage to the systems (USEPA, 2003).

Heavy metals, oil and grease introduced into the environment in excessive amounts presents the greatest concerns. They constitute a source of great danger to human beings and other living organisms health (Wild, 1996; Population Reports, 2000). Most of the heavy metals are toxic to plants, animals and invariably man, if absorbed in excessive amounts. Some are carcinogenic in nature and act as enzyme inhibitors that disrupt the metabolic process of organisms. When present in high concentrations in the environment, heavy metals may enter food chain from soils and result in health hazards. Besides, once these metals are present in an environment, they cannot be broken down to non toxic forms; as such, they remain a potential threat for many years (Isirimah, 2000).

The presence of high levels of these toxic substances in drilling reserve pits is usually a phenomenon of great concern. Various studies have established that reserve pits present hazard to human health and the environment (USEPA, 2002). Not only do waste pits contaminate soil and ground water aquifers but they also poison wildlife and livestock directly. For example in Mexico, the New Mexico Environmental Bureau, has recorded more than 6,700 cases of oil and gas pits causing soil and water contamination in the state, with 557 of those cases resulting into groundwater contamination (Anderson, 2003). Similarly, numerous wildlife-related problems associated with oil and gas waste pits have been documented. Animals, especially those found in arid and semi-arid areas get drawn to the pits containing toxic fluids. If the pits are inadequately fenced and netted, wildlife and livestock can access the pit contents and end up dying (US FWS, 2001). Therefore, it is apparent that oil exploration and production reserve pits usually have significant environmental issues which are too conspicuous to be neglected.

Evidently, oil and gas exploitation comes with a huge environmental impact which if not well managed could cost the nation more than the benefits derived. In view of this and with the many exploration drilling taking place in various areas in our country, obviously, the need to examine and analyze the toxicity of the drilling waste in the reserve pits and determine their potential environmental impacts becomes indispensable. Since such wastes have been observed to be of continuously growing concern in the western world due to their numerous negative effects on the health, safety and environments (HSE) (Moseley, 1983), Kenya cannot be an exception in this regard.

Therefore, for this study, the emphasis was on the analysis of drilling waste generated from Ngamia 5 onshore exploratory oil well in order to determine the contaminants present and suggest possible alternative ways of managing the waste.

1.2 Statement of the Problem

Oil and gas operations are known to produce fluids and wastes that are potentially toxic to living organisms and environment. Example of these wastes include: used drilling mud, drill cuttings, produced water and other fluids. These wastes contain an array of toxic substances such as heavy metals, hydrocarbons and Naturally Occurring Radioactive Materials (NORM) at hazardous levels. The wastes get disposed of in reserve pits which are surface impoundments excavated adjacent to drilling rigs. Kenya is now among the few African nations to have recently discovered oil in commercial quantities at Ngamia 5. Unfortunetely, the drilling waste in Ngamia-5 oil exploratory well reserve pit has not been chemically analyzed for potential environmental impacts. Without some level of analytical testing to fully disclose the toxic substances contained in the reserve pit, however, the public has no way of gauging the potential hazards posed by such waste. Drilling companies are known to hide the potentially toxic ingredients they use when drilling from concerned citizens. Besides, the current regulations governing waste materials associated with oil or gas exploration or production activities in the country do not specifically address contaminants found in reserve pits and provide no guidance in determining required regulatory standard levels/limits. The regulations typically focus on operational controls rather than monitoring environmental impact. Specifically, existing regulations focus on site design, drilling procedures, pit design and specifications and handling of materials and wastes. However, they do not consider analytical testing as a critical requirements. Consequently, it became necessary to undertake a study to analyze the drill waste in Ngamia-5 reserve pit with a view to identify the potential contaminants present and based on the findings, determine if the wastes could be harmful to the receiving environment. Study findings are expected to advise the government on appropriate measures in handling and disposal of the generated drilling waste and formulate the necessary appropriate policies and guildlines for future drilling of the oil wells, as the country gears up for greater oil and gas exploration and production in the future.

1.3 Study Objectives

The overall objective was to analyze drilling waste from Ngamia-5 oil exploratory well reserve pit in order to establish its characteristics and determine the potential environmental impact.

The specific objectives were to:

i. Determine some selected physico-chemical parameters of the drilling waste.
ii. Identify and quantify the heavy metals present in the drilling waste.
iii. Project potential environmental impact of the drill waste based on laboratory results.
iv. Recommend appropriate measures in relation to handling and management of the reserve pit.

1.4 Research Questions

The study was seeking to answer the following research questions:

i. Which physico-chemical parameters were exhibited by the drilling waste of Ngamia5 exploratory well reserve pit?
ii. Which heavy metals were present in the drill waste and at what concentrations?
iii. What are the potential environmental impacts of the drill waste based on the laboratory results?
iv. Which measures are appropriate in relation to handling and management of the reserve pit?

1.5 Significance of the Study

The study was being conducted for the first time in Kenya. The findings gathered from this study will serve as a guide for future researchers in assessing the toxicity of waste coming from oil exploration and production activities which started recently in the country. Information from this study is also key to environmental regulatory bodies for it will be used to determine if the waste in the reserve pits could be a potential source of contamination to the surrounding environment in the event of erosion and leaching, hence dictate its handling and disposal remedials. Estimation of environmental risks by any management option cannot be made without such an assessment. The study is also very important to the policy makers for it will guide them in reviewing and implementing new polices which fill the current voids and specifically address waste from oil exploration and production activities. Besides, Kenya is a signatory to the Millennium Development Goals of 2000 and goal number 7 deals with sustainable environmental management for a clean and healthy environment for humanity. Additionally, the Kenya Vision 2030 outlines the importance of sustainable environmental management for a clean and healthy environment. Therefore, the study blends very well with global and national development blue prints for sustainable environment.

1.6 Study Limitations and Assumptions

Instrumental methods of analysis and wet Chemistry techniques used in this study may require to be complimented and confirmed with advanced instruments, which were not available at the time. Again, comparison of concentration levels of parameters investigated in this study to existing regulatory levels was difficult since such regulatory guidelines have not been established here in the country. The study does not make the assumption that all reserve pits contain same contaminants at same concentration. Also, the study does not imply that all exploration wastes are disposed of onsite.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview of drilling operation

Oil exploration involves activities undertaken to identify and access geological formations that contain oil. A common example of such an activity is drilling, or the creation of a wellbore that perforates the ground and reaches the subsurface strata that house an oil reservoir. Drilling of oil is accomplished by use of equipment that can cut through soil and rock. A well is drilled to depths of several hundred to more than 5,000 meters (Shadizadeh and Zoveidavianpoor, 2010). A multi-component structure called the drilling rig (Figures 2.1) is set up and used to control and operate the down hole drilling equipment. Drilling fluids (muds) are pumped down through the hollow drill pipe, through the drill bit nozzles and up the annular space between the drill pipe and the hole (Neff, 2005). Drilling mud mixture is particularly related to site and whole condition; it is used to lubricate and cool the drill bit, maintains pressure control of the well as it is being drilled, and helps to remove the cuttings from the hole to the surface, among other functions. In fact, the technology of mud mixing and treatment has been recognized as a source of pollutants (Shadizadeh and Zoveidavianpoor, 2010).

The mud and the cuttings are separated once they come up to the rig. This is done by various techniques such as shale shakers, sand traps, desanders, desilters, centrifuges and mud cleaners. The mud that is separated from the cuttings is either recycled or disposed of onshore (Cripps et al., 1999). It is always a goal to remove as much cuttings from the fluid that is economically possible, before recirculating the fluid back to the borehole (Joel and Amajuoyu, 2009). As a common practice in drilling of oil and gas wells, when a target depth has been reached according to the drilling plan, the drill string is removed and the exposed section of the borehole is permanently stabilized and lined with casing that is slightly smaller than the diameter of the hole. The main function is to maintain well-bore stability and pressure integrity.

Cement is then pumped into the space between the wall of the drilled hole and the outside of the casing to secure the casing and seal off the upper part of the borehole. Each new portion of casing is smaller in diameter than the previous portion through which it is installed. The final number of casing strings depends on the total depth of the well and the sensitivity of the formations through which the well passes. The process of drilling and adding sections of casing continues until final well depth is reached (Shadizadeh and Zoveidavianpoor, 2010).

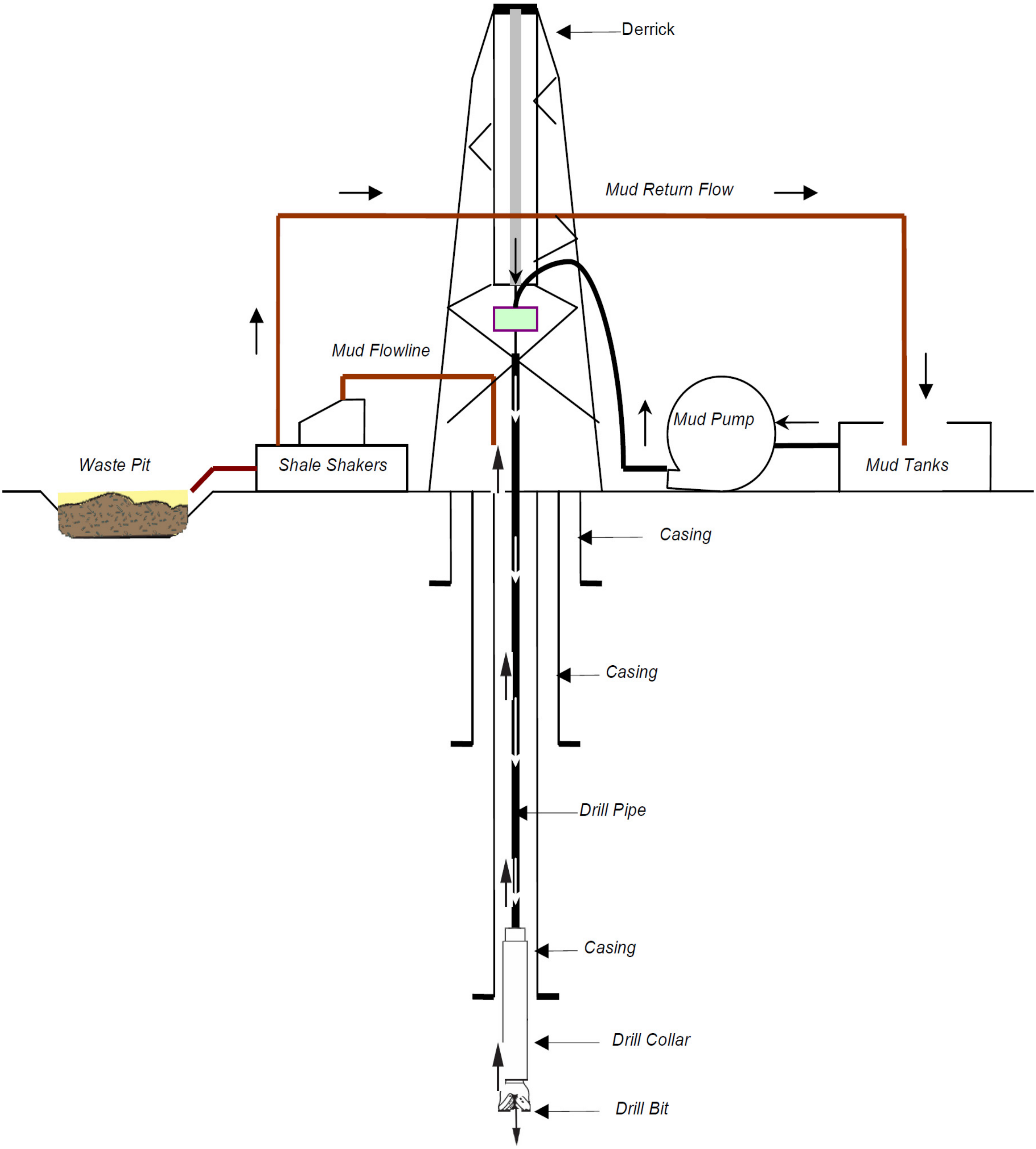

Figure 2.1: Schematic representation of a drilling rig (not to scale).

2.2 Waste Generation

The drilling process generates millions of barrels of drilling waste each year; primarily used drilling fluids, oil-contaminated drill cuttings, produced water and other associated waste (Shadizadeh and Zoveidavianpoor, 2010). The U.S. Environmental Protection Agency estimates that 3.7 billion tons of E&P waste was generated in 1985 (USEPA, 1987). A general description of each waste is presented in broad terms below**.**

2.2.1 Drilling fluids (Muds)

They constitute the largest volume of drilling-related wastes generated. The composition of modern drilling fluids or muds can be quite complex and can vary widely, not only from one geographical area to another but also from one depth to another in a particular well as it is drilled (Shadizadeh and Zoveidavianpoor, 2010). Muds fall into three general categories: water-based muds (WBMs), which can be made with fresh or saline water and are used for most types of drilling. They are typically used in drilling due to their lower cost and are generally used in the drilling the upper sections of the well (Mairs et al., 1999).

Oil-based muds (OBMs), which can be used when water-sensitive formations are drilled, when high temperatures are encountered, or when it is necessary to protect against severe drill string corrosion in hostile down whole environments. Synthetic-based muds (SBMs) use non-aqueous fluids (other than oils) as their base and include internal olefins, esters, linear alpha-olefins, poly alpha-olefins, and linear paraffins. Synthetic-based muds have drilling properties similar to those of oil-based muds but do not have polynuclear aromatic hydrocarbons (PAHs), are less toxic, biodegrade faster, and have a lower bioaccumulation potential (Bell et al., 1998).

Drilling fluid serves several functions for the drilling operations, such as conducting the drill cuttings away from the drill face, balancing the hydrostatic pressure, and providing physical and chemical properties to protect the rock formation that is being drilled. Drilling muds contain four essential parts: (1) liquids, either water or oil; (2) reactive solids, the viscosity- and density-building part of the system, often bentonite clays; (3) inert solids such as barite; and (4) additives to control the chemical, physical, and biological properties of the mud. These basic components perform various functions. For example, clays increase viscosity and density, barium sulfate (barite) acts as a weighting agent to maintain pressure in the well, and lime and caustic soda increase pH and control viscosity. Other conditioning materials include organic polymers, starches, lignitic material, and various other chemicals like emulsifiers, lubricants, wetting agents, corrosion inhibitors, surfactants, detergents and salts (Bell et al., 1998). A typical elemental composition of common constituents of water-based drilling muds is given in Table 2.1 (Bleier et al., 1993). Many of the additives used in drilling fluids can be toxic and must be regulated to lower their potential for environmental impact (Clark, 1994). Drilling fluids account for about 2 to 4 percent of oil and gas wastes (USEPA, 1987).

Table 2.1 Elemental Composition of Drilling Fluid Constituents (ppm) (Bleier et al., 1993).

Elements	**Water**	**Cuttings**	**Barite**	**Clay**	**Chrome-ligno sulfonate**	**Lignite**	**Caustic**
Aluminum	0.3	40,400	40,400	88,600	6,700	6,700	0.013
Arsenic	0.0005	3.9	34	3.9	10.1	10.1	0.039
Barium	0.01	158	590,000	640	230	230	0.26
Cadmium	0.0001	0.08	6	0.5	0.2	0.2	0.0013
Chromium	0.001	183	183	8.02	40,030	65.3	0.00066
Cobalt	0.001	183	183	8.02	40,030	65.3	0.00066
Copper	0.0002	2.9	3.8	2.9	5	5	0.00053
Iron	0.003	22	49	8.18	22.9	22.9	0.039
Lead	0.5	21,900	12,950	37,500	7,220	7,220	0.04
Magnesium	0.003	37	685	27.1	5.4	5.4	0.004
Mercury	4	23,300	3,900	69,800	5,040	5,040	17,800
Nickel	0.0001	0.12	4.1	0.12	0.2	0.2	5
Potassium	0.0005	15	3	15	11.6	11.6	0.09
Silicon	2.2	13,500	660	2,400	3,000	460	51,400
Sodium	7	206,000	70,200	271,000	2,390	2,390	339
Strontium	6	3,040	3,040	11,000	71,000	2,400	500,000

Source: (Courtesy Bleier et al., 1993).

2.2.2 Drill cuttings

Well cuttings include all solid materials produced from the geologic formations encountered during the drilling process that must be managed as part of the content of the waste drilling mud. Drill cuttings consist of small rock fragments produced when the drill bit teeth cuts into the rock and deepens the hole. These fragments are usually asymmetric with aflake structure and they can vary in size and texture, depending on the nature of the rock and the drill bit (Neff, 2005). Drill cuttings have to be removed from the well, and this is done by pumping drilling fluid inside the drill string down the drill pipe. The fluid exits through holes in the drill bit, suspend the cuttings and return to the surface via the annulus (Neff, 2005). These small rock fragments and other heavy materials settle out by gravity in the reserve pit.

2.2.3 Produced waters

Produced waters are mixtures of the naturally occurring (and typically saline) water in the geologic formation being drilled, naturally derived constituents such as benzene and radionuclides. The produced waters must be separated from the oil and gas products before their entry into crude or natural gas pipelines. Produced waters account for 96 to 98 percent of all oil drilling wastes (figure 2.2).

2.2.4 Associated wastes

Associated waste include: well completion, treatment, and stimulation fluids; sediment, water, and other tank bottoms; oily debris; contaminated soils; and produced sands. Waste chemicals used in the course of drilling operations also form part of associated waste. They can include any substances deliberately added to the drilling mud for the various purposes and may be disposed of by placing them in the well's reserve pit. They amount to about 0.1 percent of oil drilling wastes. All of these materials get disposed of in the reserve pit (Nagy, 2002).

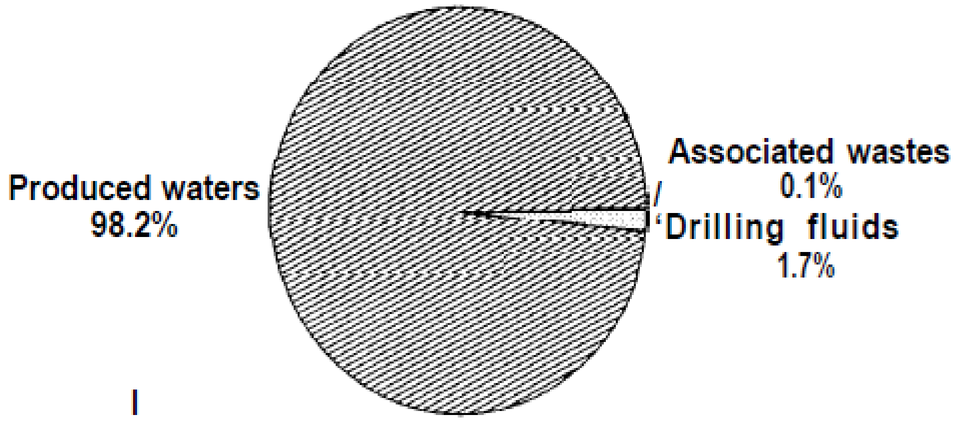

Figure 2.2: Relative amounts of waste generated during drilling operations.

2.3 Unwanted Components in the drill waste posing problems during waste disposal

All wastes from drilling operations generally have a number of unwanted components that can potentially harm the environment. The most common of these are heavy metals, salts and hydrocarbons. The concentration of these materials varies significantly. The primary concern arises when the waste must be disposed of (Reis, 1996).

2.3.1 Heavy metals

Heavy metals in drill waste are important contaminants of concern that can impact the environment (Sheahan et al., 2001). Metals in drill waste come from naturally occurring formations that get incorparated into the waste during drilling; others are added to the drilling fluids as additives used to alter the fluid properties while others come from aeolian input (Breuer et al., 1999).The most commonly found metals have traditionally been barium from barite weighting agents and chromium from chrome-lignosulfonate deflocculants. Drilling fluids typically contain high concentration of barium. Barium is a constituent of barite and barite is used in large amounts in drilling muds as a density control material especially when deep wells are drilled or when geopressured strata is penetrated (Neff, 2005).

Barite consists of barium sulfate ($BaSO_4$) and most of the barite is ground to a small uniform size before it is used as a weighting agent in the mud. Due to the impurities in the barites, other metals will also usually be present. Elevated levels of copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in drill waste have been found relative to the natural occurring metals

(Breuer et al., 1999). Because barite is contaminated with metals to a varying extent, it is considered as the dominant source for metal contamination in the drilling mud. Chromium is also another major constituent of mud additives, particularly chrome-based deflocculants. Chromium in its toxic hexavalent form can be used as a gel inhibitor/thinner, a high-temperature stabilizer, a dispersant, a biocide, and a corrosion inhibitor (Campbell and Akers, 1990).

Other metals are also found in drilling fluid additives, although at lower concentrations. Arsenic is used as a biocide to prevent the growth of bacteria. Cadmium is found in some pipe dopes. The mineral barite, the source for the barium sulfate used for density control, can have relatively high naturally occurring levels of cadmium and mercury (Candler et al., 1990). Mercury has also been used in manometers in the natural gas industry to meter the flow rate of gas. Zinc is occasionally used as inorganic zinc salts for density control or as hydrogen sulfide scavengers to minimize corrosion and maintain human safety (Reis, 1996).

These heavy metals encountered in the drilling waste are usually related to a variety of environmental concerns, depending on the metal and its concentration. An important aspect is that these heavy metals do not stay contained within the drilling waste but they leach out into the soil and underground water column (Deeley, 1990). Concern over their presence in an environment arises from the fact that they cannot be broken down to non–toxic forms and so their contamination in any given ecosystem remains a potential threat more or less permanently (Isirimah, 2000). According to Wild (1996) and UN Population Reports (2000), heavy metals which are most dangerous to health include: lead, mercury, cadmium, arsenic, copper, zinc and chromium. These metals when concentrated in particular areas pose serious health dangers, especially because they enter the food chain.

As reported by Candler et al. (1990), chronic exposure to Mercury causes weakness, fatigue, anorexia and disturbances of gastrointestinal functions. Following high exposures, tremors and spasm of the fingers, eyelids, lips and even the whole body can occur. In severe cases, delirium and hallucinations may occur. Mercury exposure can damage the nervous system, kidney and liver. Prolonged exposure of Lead induces toxic responses in the haemotological, neurological, and renal systems, leading to brain damage, convulsions, behavioral disorders, and death. There is some evidence that some soluble lead salts are carcinogenic in some animals, but there is little evidence of their carcinogenicity in humans. Organometallic derivatives may be concentrated in lipid tissues and cause chromosome damage.

Excess exposure to Cadmium can lead to renal failure, anemia, bone fractures, kidney stones, osteomalacia, retarded growth, pulmonary emphysema and pain in the back and joints. Cadmium has been implicated in respiratory tract cancer. There is little evidence of carcinogenicity for exposure by ingestion. Organometallic derivatives may be concentrated in lipid tissues and cause chromosome damage. Cadmium interferes with the metabolism of zinc and copper in human.

Chromium is considered to be an essential element in humans at low levels. At higher concentrations, hexavalent chromium can be highly toxic, while trivalent chromium is relatively nontoxic. Hexavalent chromium can cause severe irritation to the respiratory system, asthma, and kidney damage. Some hexavalent chromium compounds are carcinogenic. Other effects of chronic exposure at high levers include lung cancer, dermatitis, and alceration of the skin, chronic catarrh and emphysema. Chronic exposure to Arsenic can lead to weakness, anorexia, bronchitis, gastroinstestinal disturbances, peripheral neuropathy, skin disorder and damage to the liver, nerves and kidneys. Exposure to arsenic compounds in drugs, food and water have been causally associated with the development of cancer, primarily of the skin and lung, althogh a direct connection has never been proven.

2.3.2 Salts

Another unwanted component of drilling waste at disposal time is salts. Salts enter the drilling waste via various ways. For example, salts, like sodium or potassium chloride, are often added to drilling fluid to protect sensitive formations from reacting with the drilling fluid. Salts can also enter into the drilling waste if a well is being drilled through a salt dome or a formation having water with a high salt concentration. At concentrations higher than the naturally occurring levels found in a given ecosystem, salts can cause an adverse impact (Reis, 1996).

The discharge of waste having a higher salt content into fresh water bodies can impact aquatic organisms. High concentrations of sodium chloride can affect the development of embryos and fetuses and can cause fetal death (Mount et al., 1993). High salt concentrations can also affect the development of the musculoskeletal system and cause eye, skin, and upper respiratory system irritation. Moreover, because the salinity of wastes from drilling operations is usually greater than that of marine waters, the environmental impact of high salt concentrations is also of concern regarding marine organisms. Highly saline produced water has a higher density than seawater and will segregate to the bottom of any surface waters.

This density gradient inhibits the mixing and dilution of the very salty water. This segregation is only a problem in shallow estuaries and marshes that allow little dilution (St. Pe et al., 1990).

Salts can indirectly impact plant growth by altering the physical properties of soil. When saline drill waste is discharged on land, it can alter the pore structure of the soil by causing compaction, limiting the access of air and water to the plant roots. The impact varies, however, with salinity level and plant type. If the total dissolved solids content are above about 2,800 mg/1, salt can build up in the soil (Vickers, 1990). Excess sodium in soil can also cause clays to disperse, lowering the permeability of the soil. This can form an impenetrable surface crust that hinders the emergence of seedlings and limits the availability of nutrients such as iron, manganese, calcium, and magnesium to the plants (Kaszuba and Buys, 1993).

Another impact of salts arises primarily from an excess salt concentration in the cellular fluids of the plants. Abnormal salt concentration in cellular fluids causes disruption of the fluid chemistry balance within cells. This disruption inhibits cellular growth, water uptake, and the overall health of the plants. Growth of non marine plants is impaired at total dissolved salt concentrations between about 1,500 and 2,500 mg/1, although this threshold level varies significantly with plant type, how the water is applied, and whether the soil is kept saturated. Salt concentrations below about 1,000 mg/1 seem to improve some plant growth (Vickers, 1990). When salt was spread over soil in the form of salty drilling muds, the yield of brome grass was reduced when the concentration of chloride exceeded about 1,000 kg Cl/hectare for potassium and sodium chloride, and about 50 kg Cl/hectare for a freshwater gel.

A number of ways to measure the salinity of soils has been developed. These measurements include:

Electrical conductivity (EC) - is a measure of the total amount of cations and anions dissolved in water. These ions can include sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and

Hydroxide (OH^-). The electrical conductivity is the reciprocal resistance of the solution. Table 2.3 summarizes the effects of different EC values on crops (U.S. Salinity Staff, 1954).

Table 2.2 Effect of Electrical Conductivity on Crops

EC Range (mmhos/cm)	Effect
0-2	Negligible
2-4	Yield of very sensitive crops impacted
4-8	Yield of many crops impacted
8-16	Only tolerant crops still produce
>16	Only very few tolerant crops still produce

Source: U.S. Salinity Staff, 1954.

A level of salinity that will not adversely impact most vegetation, land, or groundwater resources from the one-time discharge is one at which the electrical conductivity of the discharged brine is less than 4 mmho/cm. This level will limit the reduction of crop yields to less than 15% (Deuel, 1990).

Electrical conductivity is related to the *total dissolved solids* (TDS) concentration in the water. The TDS is the weight of residue *after* all of the water has been evaporated. The TDS has units of mass/volume of solution. The relationship between EC and TDS is given as follows:

TDS = A*EC (3-1) …………………………………………..Equation 2.1

Where; A is an empirical constant equal to about 640 (Tchobanoglous and Burton, 1991). The units of the constant are cm-mg/mmho/liter.

Sodium adsorption ratio (SAR) is an empirical mathematical expression used to characterize the detrimental effects of sodium on soils. It is calculated through the following equation:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}}$$ ………………………….………..Equation 2.2

Where the cation concentrations are expressed in milli moles/liter.

Concentrations are determined by direct chemical analysis of reserves pit liquids or aqueous extracts of waste solids or soils. High sodium levels (SAR greater than 12) in soil solutions cause Ca and Mg deficiencies in plants (American Petroleum Institute, 1989b).

2.3.3 Hydrocarbons

Hydrocarbons are normally an undesirable material which pose problem during waste disposal. Hydrocarbons enter the drilling waste when drilling through a hydrocarbon bearing formation or when oil-based muds are used or when oil is used for a spotting fluid when a pipe becomes stuck. In general, the deeper the well, the greater the concentration of hydrocarbon that enter the drilling waste. Different types of hydrocarbon families include alkanes, alkenes, alkynes, cycloparaffins, aromatics, and polyaromatic hydrocarbons (PAHs). Historically, gross analysis of petroleum hydrocarbons within a waste has been reported as oil and grease (O&G), total petroleum hydrocarbon (TPH), or total organic carbon (TOC). Oil & Grease was primarily used as a measure for exploration and a production (E&P) waste prior to the 1990's, with TPH becoming predominant since that time.

Numerous studies have been conducted on potential environmental impacts on hydrocarbon exposure. Impact of oil and grease has been observed in marine animals. Oil at sub lethal concentrations can significantly alter the behavior and development of marine organisms. Behavioral changes from exposure to hydrocarbons are primarily those involving motility, while in higher organisms, changes affect avoidance, burrowing, feeding, and reproductive activities. Behavioral changes in feeding have been observed at hydrocarbon concentrations as low as a few microgram/1. Other measures of sublethal effects include changes in respiration, the ratio of oxygen consumed to nitrogen excreted, biochemical enzyme assays, and cellular activity. The respiratory rate following exposure is usually reduced, although in some cases, it is increased. The level of exposure for respiratory impact for fish and planktonic crustaceans in the laboratory is less than 1 mg/1. Continued hydrocarbon exposure also lowers the growth rate of animals (National Research Council, 1985).

Exposure to hydrocarbons can adversely affect the development of organisms in some species at concentrations below 1 mg/1. Some species (annelids, gastropods, and copepods) show no long-lasting damage, while other species (corals, bivalves, and some crustaceans) can suffer long-term damage at an oiled site (National Research Council, 1985). The impact of hydrocarbon exposure also depends on whether the hydrocarbon is dissolved or dispersed as suspended droplets. For shrimp, the toxicity of dispersed crude oil was found to decrease with decreasing amounts of total aromatic hydrocarbons (benzene, alkyl benzenes, and naphthalenes). For sand lance fish, however, the impact could not be tied directly to the concentration of aromatics in the water. Instead, it was postulated that the oil droplets attached to their eggs and cut off their oxygen supply (American Petroleum Institute, 1985).

One concern with oil is the potential impact on birds by direct contact. Oil coats their feathers, causing them to lose their water-repellance and thermal insulation. The birds then sink and drown or die of hypothermia. Oil can also be ingested by the birds during preening of oiled plumage (National Research Council, 1985). The effect of oil on marine mammals is highly variable. Fur insulated mammals lose their ability to thermally regulate their temperature as their oil-contaminated fur loses its insulating capacity. The loss of thermal insulation creates a higher metabolic activity to regulate body temperature, which results in fat and muscular energy reserves being rapidly exhausted. This can result in the animal's death by hypothermia or drowning (National Research Council, 1985).

The impact of hydrocarbons on human health depends somewhat on whether exposure was from ingestion, inhalation, or dermal (skin) contact and on whether the exposure was acute (short-term) or chronic (long-term). The acute effects of ingestion may include irritation to the mouth, throat, and stomach, and digestive disorders and/or damage. Small amounts of hydrocarbons can be drawn into the lungs, either from swallowing or vomiting, and may cause respiratory impact such as pulmonary edema or bronchopneumonia. The chronic effects of ingestion may include kidney, liver, or gastrointestinal tract damage, or abnormal heart rhythms. Prolonged exposure to aromatics like benzene may cause damage to the blood-producing system and serious blood disorders. The metabolism of aromatic hydrocarbons after ingestion can result in the creation of mutagenic derivatives even if the original hydrocarbon is relatively nontoxic. A number of PAHs have been linked to cancer of the skin, lung, and other sites on the body ((Sheahan et al., 2001).

The acute symptoms of hydrocarbon exposure by inhalation may include irritation of the nose, throat, and lungs, headaches and dizziness, anesthetic effects, and other central nervous system depression effects. These symptoms can occur at air concentrations of 0.5 mg/1 for 30 minutes (Hastings et al., 1984). Chronic effects of inhalation exposure to hydrocarbons containing high concentrations of aromatic compounds can cause muscular weakness and cramps, sporadic electroencephalography irregularities, and possible liver and renal damage. Exposure of eyes and skin to hydrocarbons may result in irritation, mechanical or chemical damage to eye tissue, or dermatitis (Burnham and Bey, 1991; Burnham and Rahman, 1992).

Hydrocarbons also impact plant growth when released on land. Levels of oil and grease above a few percent in soils have shown degradation of plant growth by causing both acute and chronic plant injury. That is, oil and grease causes exclusion of air leading to plant suffocation or exhaustion of oxygen due to increased microbial activity thus leading to poor growth. Oil also interferes with plant-soil-water relationships, and toxicity from sulfides and excess available manganese produced during the decomposition of the hydrocarbon (Baker, 1991). Other effects of oil and grease on plants include damage to cell membranes, reduced transpiration rate, increase in respiration rate, and inhibited translocation, though the severity of the effects depends upon the constituents and amount of oil, on the environmental conditions, and on the species of plant (Baker, 1991).

2.4 Drilling Wastes Disposal

The most recent data on drilling waste disposal by the American Petroleum Institute (API) (2000) shows the oil industry used reserve pits in 68 percent of the oil and conventional natural gas wells drilled in 1995 and closed loop drilling systems in 25 percent of the wells. In 1995, 68 percent of drilling wastes were disposed onsite through evaporation and burial. Approximately 1.2 bbls of drilling waste are produced per foot of well depth drilled (API 2000). In 1995, an estimated 148 million barrels of drilling waste were produced. According to the U.S. Energy Information Administration, a total of 335 million feet were drilled in the exploration and development of oil and natural gas in 2008 (EIA, 2009). Assuming the drilling of those wells resulted in an average of 1.2 bbls of drilling waste per foot of well depth drilled; approximately 402 million bbls of drilling waste were produced in 2008. Several methods of waste disposal include:

i. On-site Disposal of waste in Reserve.

On-site disposal and burial involves allowing reserve pit fluids to dry in the open sun and encapsulating the remaining solids with the reserve pit synthetic liner and burying the wastes in place. Depending on state regulations, oil operators are allowed from 30 days to one year after well completion to close a reserve pit.

ii. Solidification of Drilling Wastes

If reserve pits must be used, cost-effective technology exists to solidify pit fluids immediately following well completion. Solidification can add to the waste volume but prevents mobilization of potential contaminants into the soil and/or groundwater (EPA, 2000). Solidification involves the removal of the free liquid fraction of reserve pit fluids and then adding solidifiers such as commercial cement, fly ash, or lime kiln dust. Removal and off-site disposal of liquids removes most of the water soluble metals, salts, and chemicals from the drilling waste material.

iii. Pit less or Closed Loop Drilling

Pit less drilling or closed-loop drilling reduces the amount of drilling waste, recycles drilling fluids, and reduces drilling costs (Rogers et. al. 2006a and b). Pit less drilling can reduce the volume of waste by 60 to 70 percent (Rogers et. al. 2006b). Pit less drilling also conserves water and prevents soil contamination. Pit less drilling systems are equipped with a “chemically-enhanced” centrifuge that separates drilling mud liquids from solids (Rogers et. al. 2006b). The separated drilling mud solids are stored in a steel tank and then transferred to a synthetically-lined clay pad for drying .The pads are designed to prevent the runoff of any liquids. The drill cuttings are either buried on site or are transferred to an approved commercial disposal facility for disposal (Rogers et. al. 2006b). The drill cuttings can create environmental problems and pose a risk to wildlife if the trench or excavated burial pit collects water from snowmelt or rainfall. Ponded water in the trench or burial pit may become contaminated with hydrocarbons present in the drill cuttings. Immediate burial of drill cuttings and contouring of the site should prevent the ponding of snowmelt or rainwater. Sheens, oil, and sludges in the disposal pit will pose a risk to migratory birds and other wildlife .Additionally, if the pits are not lined, soil and groundwater contamination can occur if the drill cuttings contain leachable concentrations of hydrocarbons and metals.

iv. Treatment and Reuse of Drilling Fluids

Operators in the Jonah natural gas field in southwestern Wyoming are currently using new technology to treat and reuse drilling fluids. Drilling fluids are treated using a patented combination of fluid and thermal dynamics to remove oil and salts. The treatment separates the drilling fluid into fresh water, heavy brine, condensate, and methanol. The condensate is recovered and sold. The methanol and brine are reused in drilling fluids. The fresh water is either reused at other drilling locations or is used for the benefit of livestock or wildlife.

v. Down-hole Disposal of Drilling Fluids

Oil operators in Alaska inject the drill cuttings underground after the solids are finely ground and mixed with a liquid to form slurry (Veil and Dusseault, 2003). This disposal technique is typically used in conjunction with pit less drilling. Open earthen reserve pits are not used to temporarily store the drilling fluids. The elimination of open pits removes the mortality threat to migratory birds and other wildlife. Slurry injection of drilling wastes also poses less environmental impacts when properly managed and monitored as the wastes are disposed deep underground and isolated from aquifers (Veil and Dusseault, 2003).

2.4.1 Disposal of drilling wasted in Reserve pits

Reserve pits, also known as surface impoundments or ponds are the most common method used for onsite disposal of used drilling fluids, well cuttings and other wastes (Reis, 1996). They are an essential component in the great majority of well drilling operations, where they are used to accumulate, store, and, to a large extent, dispose of spent drilling fluids, cuttings, and associated drill site wastes generated during drilling, completion, and testing operations.

Some pits are used for settling/skimming of solids and separation of residual oil; storage of produced waters prior to injection or off-site transport; percolation of liquids via drainage or seepage into surrounding soil; and evaporation (in lined pits) of produced waters into the atmosphere (Davani et al.,1986). Other "special" pits are used for such purposes as flaring natural gas; collecting wastes from the emptying or depressurization of wells (or vessels); and, in emergencies, temporarily storing liquids resulting from process upsets. Therefore, they can be used for final disposal of all or part of the drilling wastes, with or without prior onsite treatment of wastes or for temporary storage prior to offsite disposal.

Reserve pits are usually excavated directly adjacent to the site of the rig and associated drilling equipment. It is usually a requirement for the pits to be excavated from undisturbed, stable subsoil so as to avoid pit wall failure. Where excavation below ground level is impossible, it is required the pit wall be constructed as an earthen dam that prevents runoff of liquid into adjacent areas (USEPA, 1990). Reserve pits, however, may be in continuous use for many years before being closed or may at least be present on-site for use in emergencies.

There is usually one reserve pit per well. The size of the reserve pit is largely a function of well depth (USOTA, 1992). The contents of reserve pits vary depending on the type of formation drilled, the type of drilling mud used and other chemicals added to the mud circulation system during the drilling process (Ramirez, 2009). Other materials may also be added to the pit before closure either deliberately or inadvertently. Such materials include rig wash, diesel fuel, and waste oil from machinery, metal and plastic containers. Of all materials discharged to reserve pits, an estimated 90 percent are drilling fluids (mostly in the form of drilling muds and completion fluids) and drilling cuttings (figure 2.4).

Reserve pits are usually closed following a well completion and liquids in the pits may be evaporated, discharged to land or surface waters, reinjected in underground wells, or trucked off site for disposal (Ramirez, 2009). Reserve pits will, however, continue to be the principal method of drilling fluid storage and management (Nagy, 2002). Although most States have established regulations for siting, operation, and closure of pits, the proper closure of reserve pits and the disposition of their contents are still matters of concern in the environment.

Figure 2.3: A reserve pits Source: (Shadizadeh and Zoveidavianpoor, 2010).

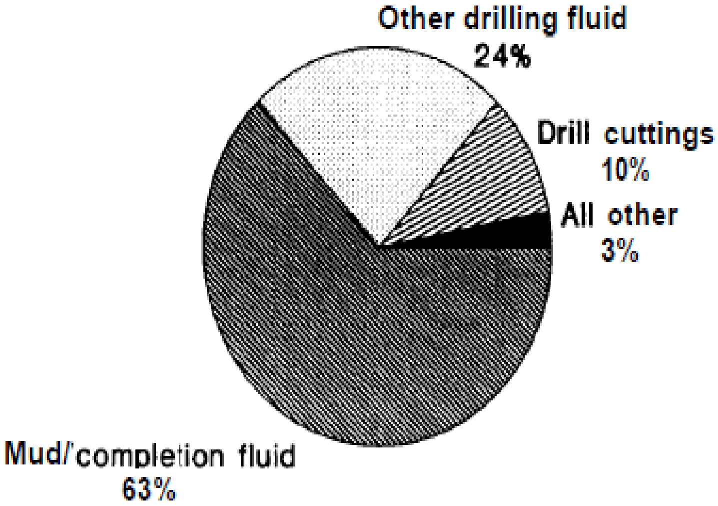

Figure 2.4: Types of Drilling waste Discharged to Reserve Pits.

Sources: (API, 1978).

2.4.2 Environmental impacts of waste pit

Pits store these variety of potentially toxic, as well as non-hazardous liquid and solid wastes associated with oil and gas development. U.S. Environmental Protection Agency acknowledges that pit waste contains toxic substances that could present hazard to human health and the environment if improperly managed (USEPA, 2002). Reserve pits are usually constructed in a simple and straight forward way. They are generally built or excavated into the surface soil zones or into unconsolidated sediments, both of which are commonly highly permeable. They do not require intensive maintenance to ensure proper function, but they may, in certain circumstances, pose environmental hazards during their operational phase (USEPA, 1987).

In a report by EPA on oil and gas environmental assessment effort, one key finding in the report was that almost every reserve pit evaluated had significant environmental issues (US EPA report, 2003). (Reis, 1996) states that “improper reserve pit management practices have created sources of benzene, lead, arsenic, and fluoride, even when these contaminants were not detected or were not present in the drilling mud system.” Contaminants in drill wastes leach out through pit sides and contaminate groundwater aquifers, soils and vegetation;

sterilize soils and prevent vegetative growth. Precipitation and flooding also mobilize these contaminants into adjacent soils and surface waters.

Other times, reserve pit berms rupture and overflow of pit contents occur with consequent discharge to land or surface waters. This happen especially in areas of high rainfall or where soil used for berm construction is particularly unconsolidated soil. In such situations, berms can become saturated and weakened, increasing the potential for failure. Even where the pits are lined, sometimes the liners are often improperly installed, or become torn hence leading to frequent leaks (Ramirez, 2009). Leaching of pollutants after pit closure can also occur and may be a long-term problem especially in areas with highly permeable soils (Beal *et. al*., 1987).

Several cases where reserve pit pollution occurred have been documented (Ramirez, 2009). For example, in Mexico, the New Mexico Environmental Bureau, since its inception in the mid-1980s, has recorded more than 6,700 cases of oil and gas pits causing soil and water contamination in the state, with 557 of those cases resulting into groundwater contamination (Anderson, 2003). Migration of salts from buried drilling wastes from unlined reserve pits has been documented in U.S. Fish and Wildlife Service in northeastern Montana. Similarly, the U.S. Fish and Wildlife Service documented the migration of leachate 400 feet from reserve pits buried in 1959 in north-central North Dakota and reported groundwater contamination 50 feet below the buried reserve pits (U.S. Fish & Wildlife Service, 2002).

Another issue of great concern relating to reserve pits is when the pits contaminate wildlife and livestock directly. Numerous wildlife-related problems associated with oil and gas field waste pits have been documented. Animals, especially those found in arid and semi-arid areas get drawn to the pits containing toxic fluids. If the pits are inadequately fenced and netted, wildlife and livestock can access the pit contents. So many cases where birds, wildlife and livestock mortality occurred from drinking or simply coming in contact with the toxic fluids in pits have been reported (Ramirez, 2009). For instance, the U.S. Fish and Wildlife Service (FWS) have found deer, pronghorn, waterfowl, songbirds and rabbits in oil pits. Even if animals are not killed in the pits, the oil and chemicals in the pits may affect their health by becoming more susceptible to diseases and predation (U.S FWS, 2001).

Waste pits are also fatal attraction to migratory birds, bats and other wildlife (Stephenson, 1997). Birds usually mistake the pits for wetlands where on landing on the waste pit, they get covered with oil which weigh the birds down causing them to drown .Many bird deaths go undetected because the carcasses sink to the bottom of the pits. In addition to that, oil destroys the feathers' ability to insulate the birds resulting in death from heat or cold stress. Even a light sheen on the water surface can be deadly. Oil on the feathers of female birds can be transferred to their eggs back at the nest, killing the embryo. Small amounts of oil applied externally to an egg shell can be extremely toxic to embryos. Some birds become victims of pits when they feed on insects trapped in oil covering the surface of the water. Animals also scavenging on dead birds at these pits often succumb to the toxic effects of oil (U.S. Fish & Wildlife Service, 2002).

2.5 Environmental Regulations

The survival of man and of any nation for that matter depends on their ability to manage their wastes in an environmentally sound manner. This can only be achieved by the establishment and enforcement of appropriate guidelines and standards set to ensure that we do not destroy our environment and indeed the very basis of our existence. Historical environmental practices by the petroleum industry have lead to the loss of public confidence that the industry is able to regulate itself and still protect the environment. Because of this, a large number of environmentally-related laws have been passed, and more are under consideration. Regulations vary significantly from country to country, state to state, and locality to locality. In most areas, there are multiple, overlapping regulatory agencies that govern various aspects of oil and gas exploration and production.

Many environmental regulations impose both civil and criminal penalties, with fines and jail terms for violators. Civil penalties can be imposed on both companies and individuals for violations, regardless of intent. Criminal penalties can be imposed on individuals for deliberate violations of the regulations. It is the individual's responsibility to ensure that their actions are in compliance with all existing regulations.

Good communications between industry, legislators, and regulatory agencies are considered necessary in developing meaningful regulations. Input from industry is important to ensure that new regulations are based on accurate scientific information and that they contribute to real environmental protection without adding a useless burden to industry. Table 2.3 gives a brief overview of many of the laws and regulations impacting drilling and production activities. Regulatory agencies should be contacted prior to initiating any drilling and production activity to ensure that those activities will be conducted in compliance with whatever the current regulations at that time and place may be.

2.5.1 United States Federal Regulations

A number of federal environmental regulations affect the upstream petroleum industry. Environmental regulations are generally broad and can overlap. In some cases, they can be inconsistent. For example, drilling muds are exempt from the Resource Conservation and Recovery Act (RCRA), Subtitle C, and can be legally disposed of in reserve pits. Reserve pits contents such as drilling muds, however, are not exempt from the Comprehensive Environmental Response, Compensation, and Liability Act (Superfund). Although the U.S. Environmental Protection Agency is responsible for promulgating these regulations, individual states can be granted primacy if they adopt regulations that are at least as strict as the federal regulations.

Table 2.3: Some of the Federal Environmental Regulations

Resource Conservation and Recovery Act (RCRA)	Regulates Management, Treatment, and disposal of hazardous wastes.
Safe Drinking Water Act	Regulates injection wells that may contaminate freshwater aquifers
Clean Water Act	Regulates activities that may pollute surface waters.
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)	Regulates cleanups of existing hazardous waste sites
Superfund Amendment and Reauthorization Act (SARA)	Regulates reporting of storage and use of hazardous chemicals.
Clean Air Act	Regulates activities that emit air pollutants.
Oil Pollution Act	Regulates emergency response plans for oil discharges.
Toxic Substance Control Act	Regulates testing of new chemicals.
Endangered Species Act	Regulates actions that jeopardize endanger or threatened species.
Hazard Communication Standard	Regulates the availability of information on chemical hazards to employees
National Environmental Policy Act (NEPA)	Regulates actions of federal government that may result in environmental impacts.

2.5.1.1 Resource Conservation and Recovery Act (RCRA)

The Resource Conservation and Recovery Act (RCRA) was initially enacted in 1976 and amended in 1980 to establish a system for managing hazardous solid wastes. This act specifies criteria for determining whether wastes are hazardous or nonhazardous and promulgated requirements on how each are to be managed. Under RCRA, a waste is any material that is discarded or is intended to be discarded. It is the intent of future use that determines whether it is considered a waste regulated under RCRA. This act also defines solid wastes as any wastes that are either solid, semisolid, liquid, or gases contained in storage vessels. It further defines a hazardous waste as any solid waste that can cause or significantly contribute to an increase in mortality or in serious irreversible or incapacitating reversible illness, or pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, disposed of, or otherwise managed.

Under RCRA, it is a crime to:

1. Knowingly cause hazardous materials to be transported to an unpermitted facility or to knowingly transport hazardous materials without a manifest,
2. Knowingly treat, store, or dispose of hazardous wastes without a permit or in violation of a permit,
3. Knowingly falsify records, labels, manifests, or other documents used for complying with the Act, or
4. Knowingly fail to comply with, or interfere with, record keeping requirements under the Act.

The EPA has established five criteria to determine whether a waste is hazardous or not which include:

- ***Ignitability* -** A waste is considered ignitable if it presents a fire hazard during routine management. A waste is considered ignitable if it is a liquid and has a flash point less than 140°F; if it is not a liquid and is capable of causing fire through friction, absorption of moisture, or spontaneous chemical changes and, when ignited, burns so vigorously that it creates a hazard; or if it is an ignitable compressed gas or an oxidizer as defined under U.S. Department of Transportation regulations.
- ***Corrosivity*** **-** A waste is considered corrosive if it is able to deteriorate standard containers, damage human tissue, and/or dissolve toxic components of other wastes. An aqueous waste is considered corrosive if it has a pH less than or equal to 2 or greater than or equal to 12.5. A nonaqueous liquid is corrosive if it corrodes SAE 1020 steel at a rate greater than 0.25 inches per year at a temperature of 130°F.
- ***Reactivity* -** *A* waste is considered reactive if it has a tendency to become chemically unstable under normal management conditions or react violently when exposed to air or mixed with water, or if it can generate toxic gases. Specific regulatory definitions for reactivity have not been developed. Examples of reactive wastes include cyanide or sulfide solutions, water-reactive metals, and picric acid.

- ***Toxicity*** - A waste is considered toxic if it can leach toxic components in excess of specified regulatory levels upon contact with water. The test procedure to be used, called *toxicity characteristic leaching procedure* (TCLP), is carefully specified under the regulations and is very expensive to conduct.

If a waste is considered to be hazardous under RCRA, "cradle-to grave" management and tracking of the waste is then required, including waste generation, transportation, treatment, storage, and disposal.

After an extensive review of wastes generated by the upstream petroleum industry, it was determined that those were not intrinsically hazardous (U.S. Environmental Protection Agency, 1987; American Petroleum Institute, 1983). Because of this, most of these wastes have been exempted from RCRA. This exemption includes drilling muds, produced water, and other wastes directly associated with drilling and production activities. This exemption gives operators the ability to manage most drilling and production wastes as nonhazardous wastes, although waste management must still be in compliance with the many other existing regulations.

Not all wastes generated during drilling and production is exempt from RCRA. Nonexempt wastes include those that are generated from the maintenance of equipment or that are not unique to exploration and production activities. Furthermore, some exempt wastes can lose their exemption upon custody transfer, e.g., crude oil loses its exemption when it reaches a refinery. Wastes that are sent to certain off-site disposal facilities that are not dedicated to petroleum wastes may also lose their exemption. In addition to the RCRA designation of hazardous wastes, states can also generate their own lists of hazardous and nonhazardous materials.

2.5.2 Kenyan Regulations

Kenya's quest to safeguard the environment is manifested in the establishment of the National Environmental Protection Authority (NEMA) which exercises general supervision and coordination over all matters relating to the environment. It is buttressed by the Environmental (Impact Assessment and Audit) Regulations of 2003. It further establishes the Standards Enforcement and Review Committee whose principal function is to set standards for water quality, air quality, classification of waste for purposes of proper handling, pesticide residues in raw agricultural commodities, noise emissions, noxious smells, and ionizing radiation.

Administratively, the nation's style of environmental governance is more tuned to a top-down approach. As such, the basic policy instrument is 'command and control' approach and that involves compliance to laws (regulations), environmental standards and guidelines. On that ground, NEMA has since its inception been using the Environmental impact assessment and audit procedures as its major tool for achieving compliance with its legislation. Under the procedure: (a) new developments are to register with NEMA, conduct an environmental assessment of their proposals and submit an environmental assessment report to NEMA for review. There are levels of assessment depending upon the type, scale and location of the activity. Environment Permit is granted for the development to start when NEMA is satisfied with the assessment conducted and the mitigation measures (b) industries in existence before the legislation are to conduct an environmental assessment of their facility and propose ways and means of improving the level of performance of their set-ups. These Environmental Management Plans are then submitted to the NEMA for review.

The new industrial set-ups are also required to comply with this procedure after 18 month in operation (c) industries are also requested to submit monthly returns of their environmental parameters monitored to the NEMA. Comments are also expected in cases where values exceed certain limits and what measures are in place to check the discrepancy (d) industries are also requested to submit Annual Environmental Report to NEMA, indicating how they have performed environmentally, what have been achieved, what went wrong and what needs to be done. NEMA then measures environmental compliance based on the number of applications received for environmental permits within a certain time frame. The objectives of these laws are justified and relevant to the needs of the environment and the society as a whole. However, the inputs in terms of human, capacities and financial resources, which are needed to accomplish these objectives, are limited and inadequate.

2.5.2.1 Kenya's Environmental Standards and Guidelines on oil exploration and production waste

The existing environmental guidelines in Kenya have been carefully crafted from major international environmental standards and guidelines making the Kenya standards quite robust. Notably among these international standards include the World Health Organization's (W.H.O) guidelines, US Environmental Protection Agency (EPA) and the MARPOL convention. These guidelines are not explicit and do not specifically address the contaminants found in oil and gas exploration and production waste.

2.6 Theory of Total X-Ray Fluorescence Spectrometry (TXRF)

Total X-ray fluorescence spectrometry (TXRF) is an analytical screening tool that was first used to analyze lead (Pb) in paint in the 1970s during abatement and exposure studies (Kalnicky and Singhvi 2001), and has since been used in environmental testing of alloys, geological materials, sediments, glasses, with very minimal sample preparation and treatment (Sitko 2009; Lawryk et al. 2009). Over the years, the TXRF has gained acceptance from the environmental research community as a viable analytical tool because of the efficiency of the radioisotope source excitation coupled with extremely sensitive detectors and other electronics, hence offering multi-element analysis capability, economy, high speed and simplistic operation, where its advantages and limitations are well comprehended.

The basics of the TXRF lie in the atoms of the receiving sample emitting different energies when they are excited by X-rays. The excited photons enable the qualitative and quantitative analysis of most elements in a given sample (Kalnicky and Singhvi 2001). First the X-rays dislodge an atom from the inner shell. The atom from an outer shell fills the inner shell (K or L). The excited atom releases energy in the X-ray region of the wavelength has it returns to the ground state. The released photons with energy are equivalent to the difference between the two different shells. For instance, the transition from the L-shell to the K-shell results in a spectral line, which is designated Kα, while the transition from the M-shell to the K-shell provides a spectral line, which is designated Kβ (Figure 2.5). Thus, each element possesses different characteristic lines in the spectrum because each type of orbital transition produces a distinct X-ray. Clark et al.(1999) showed that when certain atoms are excited, they release energy in the form of fluorescence as they return to the unexcited state. The photons emitted are then detected by the instrument. Figure 2.6 provides an overview of the basics in theory of the TXRF.

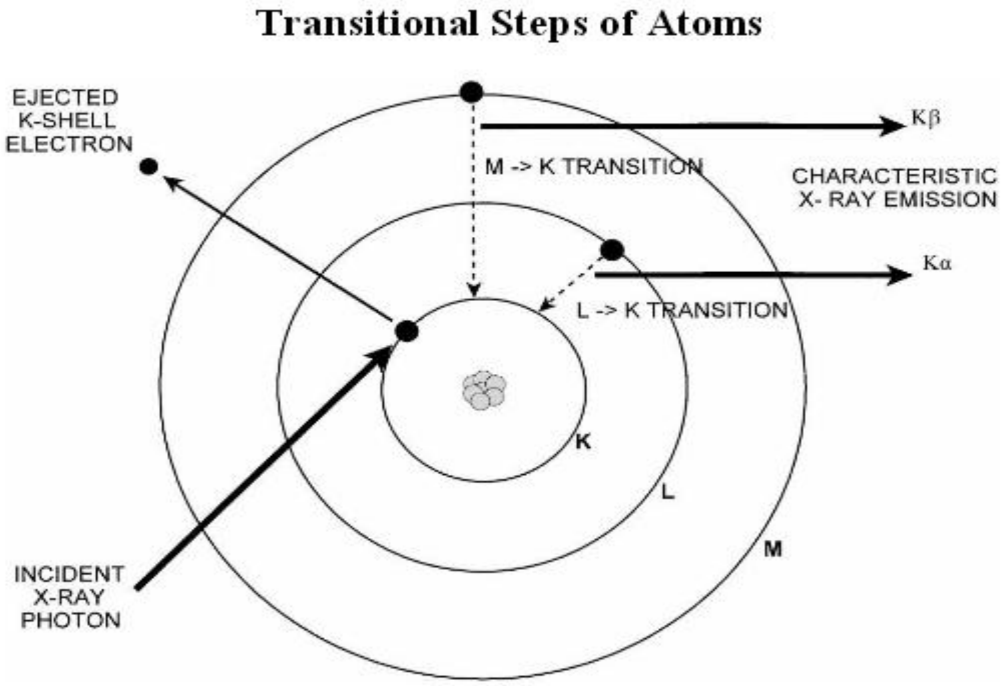

Figure 2.5: The three step process describing x-ray fluorescence.

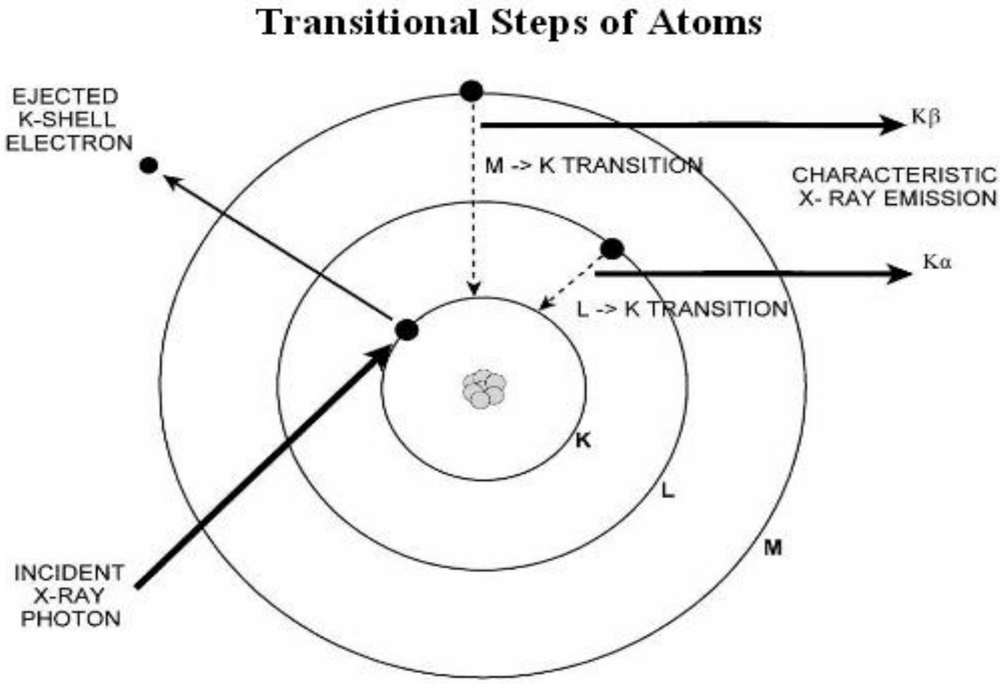

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Figure 2.6: Mechanism of X-ray fluorescence of an atom.

The TXRF can be used to detect most of the elements in the periodic table ranging from Na to U and even higher atomic number (Z) elements, although the detection of low Z elements requires the use of a vacuum or helium purge gas (Palmer et al. 2009). Modern field portable TXRF instruments, however, have improved solid state detectors with sufficient energy resolution for multi-element analysis with few spectral interference problems, and they do not require liquid nitrogen cooling. Many models have been developed and marketed for specific applications such as the analysis of lead in paint (Dost 1996).Under normal circumstances, a positive detection of a sample is confirmed by multiple fluorescence lines with different energy that can be expanded to show limited resolution of the analyzer (Figure2.7). However, the interpretation of the TXRF spectra containing multiple fluorescence line overlaps can be very complicated due to the fundamental limitations of the detector in distinguishing photons with similar energies.

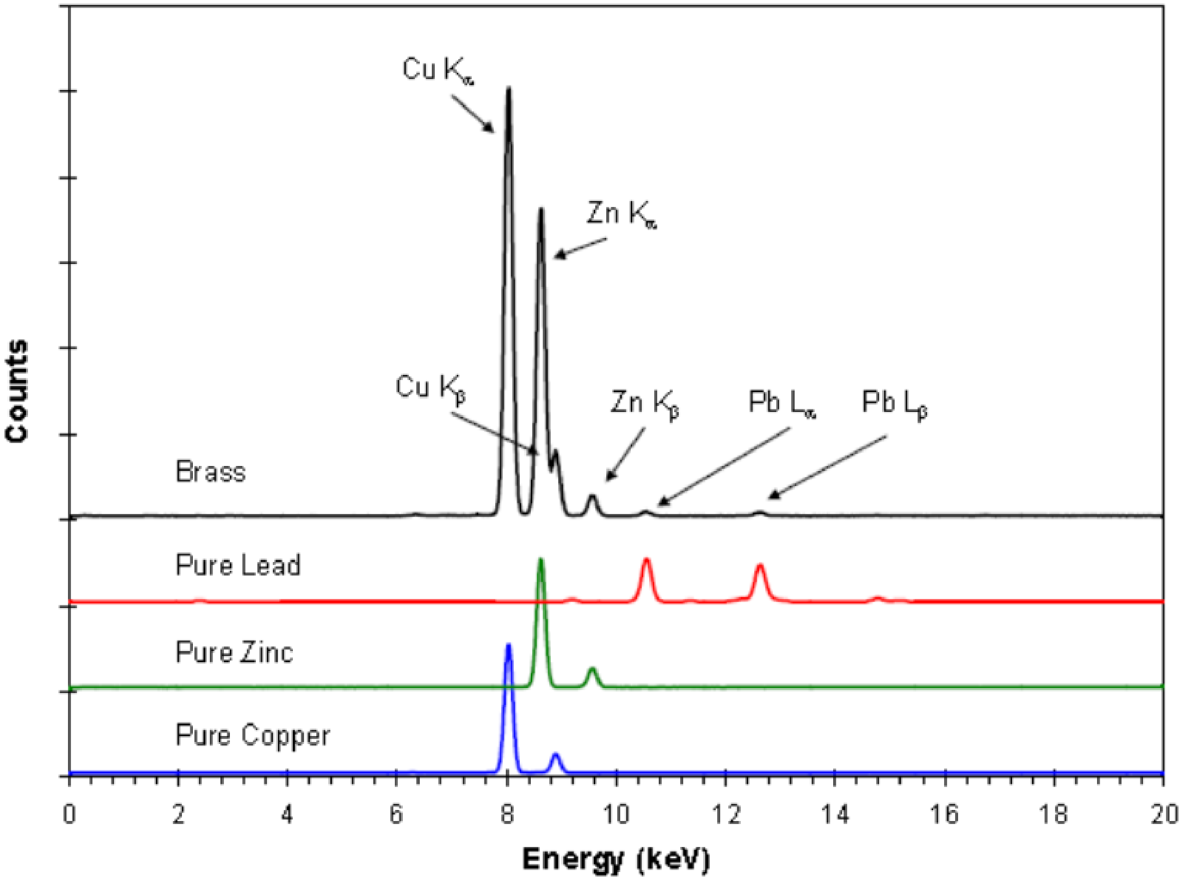

Figure 2.7: Comparison of three pure element spectra and a spectrum taken from a brass sample.

CHAPTER THREE

MATERIALS AND METHODS

3.0. Introduction

In this chapter, the study area and the method of conducting field study are described. The study was based in Turkana County. The county has become an important hub because of oil exploration activities which started recently, and production which is expected to continue for the next 20 years, therefore, becoming a potential area prone to pollution. Sampling procedures, samples preparation, sample analysis and statistical data analysis techniques are also presented.

3.1. Study Area

The study was carried out in Ngamia-5 exploratory well reserve pit. Ngamia-5 (Figure 3.1) is among the wells which were drilled from the Ngamia oil field discovery well pad. It is in the South Lokichar Basin within the Tertiary rift Blocks 10BB in the Northwest part of Kenya. It is located 500 metres northeast of the Ngamia-1 discovery well in a different fault compartment and it encountered 160 to 200 metres net oil pay, which is amongst the highest of all the wells drilled in the basin to date. Ngamia-5 was drilled to a final depth of 2,317 metres and was deviated approximately 500 metres North East of Ngamia-1. A dozen more wells have been drilled in the area most of them being appraisal wells. The choice for Ngamia-5 well reserve pit was based on the fact that it was the only accessible and completed exploratory well at the time sampling was taking place.

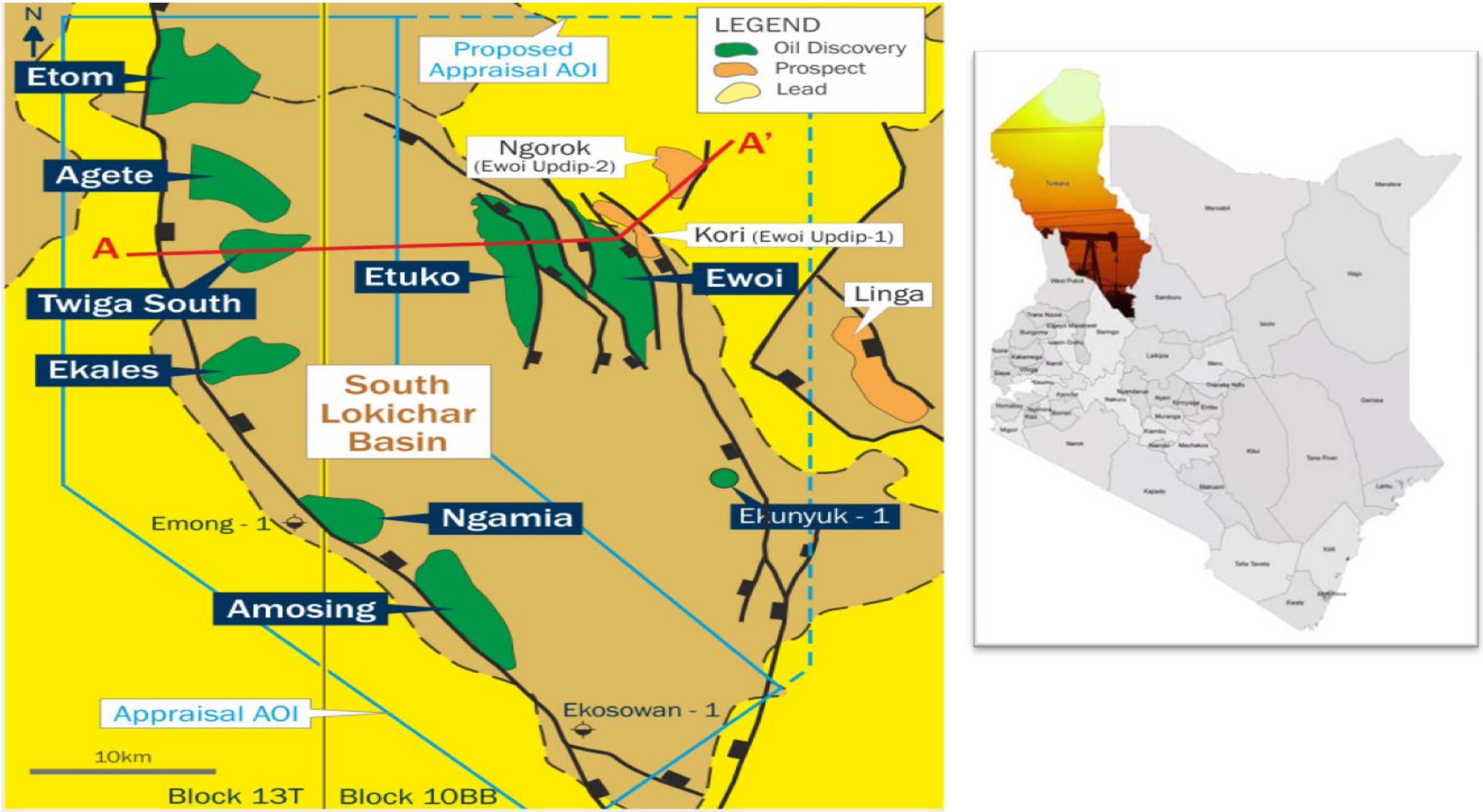

Figure 3.1: Map of the study area-Ngamia Play (Image courtesy of Tullow Oil Kenya).

3.2 Sampling

The sampling method in this study was utilized from a sampling procedure performed on API site 4 (Deuel and Holliday, 1990). The reserve pit is rectangular in shape with dimensions 16 m×9 m×3 m deep (Figure 3.2). The pit was divided into three sections; surface, middle and bottom section. The sampling device was a dredge which was lined with Teflon to avoid sample contamination. This device was preferred because of its ease of use and deeper penetration. Samples were taken along the pit diagonals at three evenly spaced depths between the liquid surface and the thick-supernatant interface. Triplicate samples were taken from each point and then combined to make a single composite sample representative of that point. In total, fifteen composite samples were collected such that, five samples were from the surface, five from middle level and other five from the bottom level of the pit. The samples were well labeled and put in clean 1L plastic sampling bottles and later taken to the laboratory for analysis. Samples were collected in the month of December 2014 two weeks after the completion of the well drilling which was in November 2014.

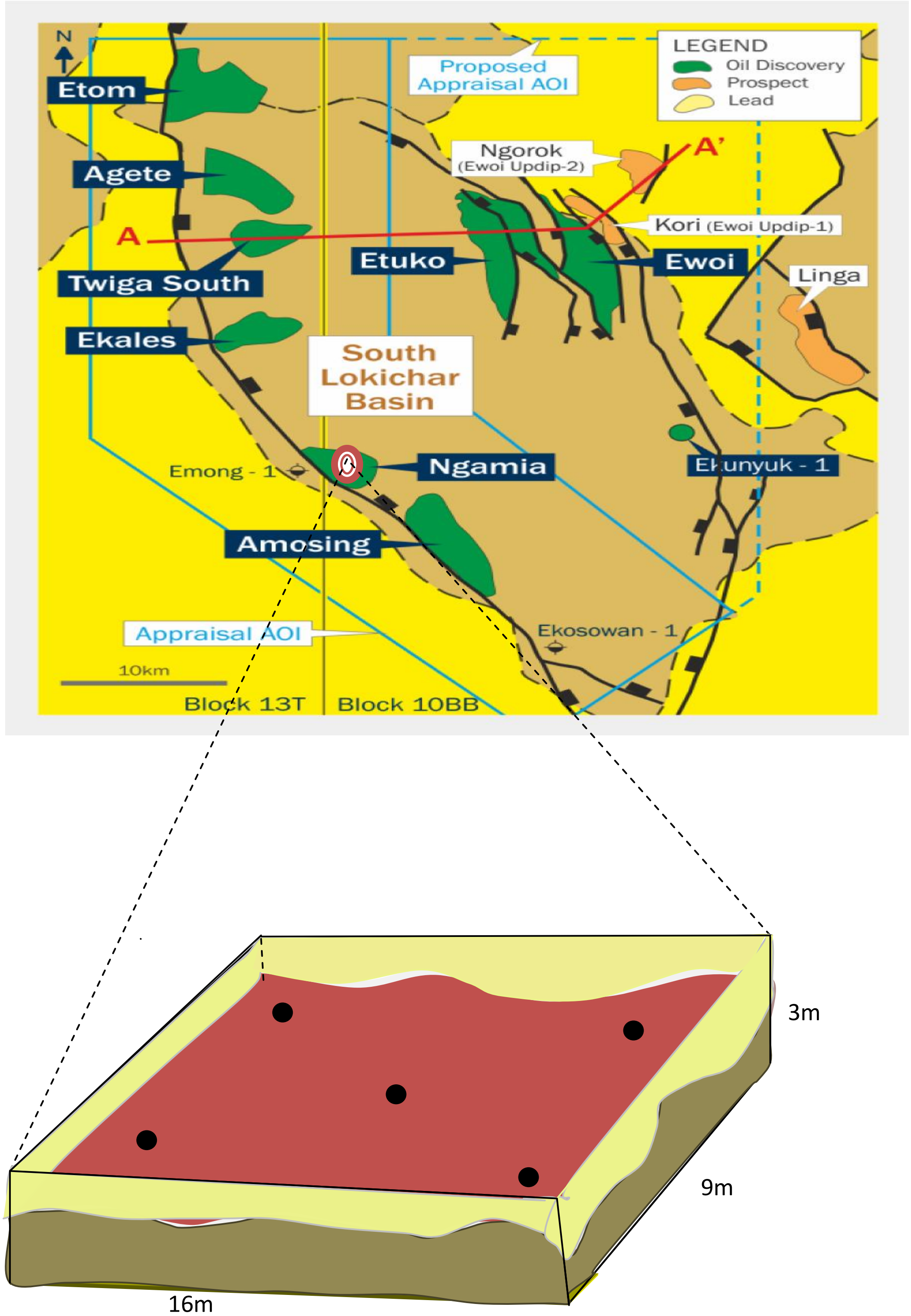

Figure 3.2: Schematic representation of the sampling points of the waste pit.

3.3 Cleaning of apparatus

Using clean apparatus is important to minimize contamination during preparation and analysis. The glassware and plastic containers were soaked overnight in water with detergent. They were washed thoroughly with warm water and soap. They were then rinsed with tap water and finally with double distilled water. They were then put in a rack to dry.

3.4 Electrical Conductivity and pH Determination

The samples were well prepared for Electrical conductivity and pH analysis according to the recommended laboratory procedures. That is, the samples were first clarified through filtration by passing them through a Whatman No. 1 (11 micron) filter paper. The clarified extract was then used for the analysis of:

i. Hydrogen ion concentration (pH)

The pH meter (Model 292 Mk2) was first standardised by use of the electrodes against two reference buffer solution at 25^{o}C. About 25 ml of the filtrate for each sample was poured in to a beaker after which the pH electrode was immersed into the sample and waited for reading to stabilize. The pH for each sample was read and recorded at 25^{o}C. The probes were rinsed with deionised water after each measurement to avoid contamination in accordance to the manufacturer’s instructions.

ii. Electrical Conductivity(EC)

About 25 ml of each extract was poured into a beaker. The electrical conductivity of each sample was determined electrometrically with a calibrated HACH model electrical conductivity meter. The electrical conductivity of the samples were read directly and recorded in mS cm^{-1} units.

3.5 Determination of Oil and grease

i. Liquid phase

All the reagents used were of analytical grade. 30 ml of each sample was acidified using hydrochloric acid to pH 2 and poured into a separatory funnel. 15ml of hexane and few crystals of NaCl were then added to the sample and extraction done by shaking vigorously for 2 minutes. The layers were allowed to separate and the solvent layer filtered into pre-weighed boiling flask through a funnel containing solvent moistened glass wool. Extraction was repeated thrice with addition of fresh solvent and combining all solvent in the boiling flask. The boiling flask was connected to the distilling head and solvent evaporated by immersing the lower half of the flask in water at 70°C with a solvent blank accompanying each sample. The flask was removed from the distilling head when it appeared dry and put into a moisture oven for 1 hour to remove the excess moisture. It was then cooled for 30 minutes in a desiccator and the residue weighed.

To determine the concentration of the oil and grease in mg/l in the liquid samples, calculation was done as shown below:

$$\text{Oil and Grease in mg/l} = \frac{R - B}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 3.1}$$

Where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams.

B = blank determination, residue of equivalent volume of extraction solvent, in milligrams.

V = Volume of sample used

ii. Sludge phase

25g of wet sludge with a known dry-solid content was weighed, placed in a 150 ml beaker and acidified to pH of 2 with approximately 0.3 ml concentrated HCl. Anhydrous sodium sulfate was added to the sample and stirred until the sample appeared dry. The resulting paste was spread on the sides of beaker to facilitate drying and left to stand overnight until the substance solidified. The sample was quantitatively transferred to a paper extraction thimble filled with glass wool (or glass beads) and extraction done in a Soxhlet apparatus using hexane at a rate of 20 cycles/hr until the solvent was colorless.

The extract was filtered into a pre-weighed 250 ml boiling flask using grease-free glass wool, and both the flask and glass wool rinsed with the solvent. The boiling flask was connected to the distilling head and the solvent evaporated by immersing the lower half of the flask in water at 70^{o}C with a solvent blank accompanying each set of samples. The flask was removed from the distilling head when it appeared dry and put into a moisture oven for 1 hour to remove the excess moisture. It was then cooled for 30 minutes in a desiccator and the residue weighed (figure 3.3).

Figure 3.3: Oil and grease in the samples after extraction.

Oil and grease in the sample was calculated as a percentage of the total dry solids as shown below.

% oil and grease = $100 * G / D$

$$D = \frac{(W * 100)}{(100 + (100 * (W - D) / D))} \quad \text{……………………………………..Equation 3.2}$$

Where: G = Gain in weight of the flask

D = Dry weight of sample in grams

W = Wet weight of sample in grams

3.6 Determination of Total metal content using TXRF

3.6.1 Washing sample carriers

The carriers contribute to the achievement of the optical analytical results in TXRF analysis (Marguí *et al.*, 2010). They can influence the concentration of the sample since they are the only link of the sample to the measuring instrument and therefore they should be cleaned before applying the sample. The carriers were first pre-cleaned with a fluff-free cleaning tissue. The washing cassette was mounted with the carriers and transferred in a glass beaker filled with 5% Rutherford Backscattering (RBS) cleaning solution and heated without boiling for five minutes on a hot plate. The carriers were then rinsed with distilled water and the cassette was immersed in 10% nitric acid which was then heated for two hours on a heating plate. The cassette was transferred in a beaker filled with distilled water and heated for five minutes and then rinsed thoroughly with double distilled water and wiped again with acetone. Finally 10µl of silicon solution was applied at the centre of the carriers and the carriers were then dried on a hot plate at 80^{o}C for 30 minutes. The carriers were analysed to ascertain cleanliness using the TXRF technique.

3.6.2 Heavy metal Analysis

The samples were analyzed using S2 Picofox TXRF spectrometer (figure 3.5). In this instrument, an X-Ray beam, generated by the Molybdenum tube, is reflected on a Ni/C-multilayer resulting in a monochromatic X-Ray beam. This beam passes the sample holder carrying the sample at a very small angle (0.3 – 0.6°), causing total reflection of the beam. The characteristic fluorescence radiation emitted by the sample is detected by an energy dispersive detector and the intensity is measured by means of an amplifier coupled to a multi-channel analyzer (Klockenkämper, 1997). The element concentration is calculated using equation 3.3.

$$C_x = \frac{N_x / S_x \times C_{is}}{N_{is} / S_{is}} \qquad \text{…………………………………… } \textit{Equation 3.3}$$

Where,

$\mathbf{C_x}$ is the analyte concentration

$\mathbf{C_{is}}$ is the internal standard concentration

$\mathbf{N_x}$ is the analyte net intensity

$\mathbf{N_{is}}$ is the internal standard net intensity

$\mathbf{S_x}$ is the analyte relative sensitivity

$\mathbf{S_{is}}$ is the internal standard's relative sensitivity

Samples were irradiated for 1000 seconds using a 50 kV and a current of 1000 µA. In-built S2 Picofox software was used for quantification. The software performs the de-convolution of the spectra, where net intensities of the element peaks are calculated with regard to corrections of line overlaps, background factors and escape peak correction (Klockenkamper, 1997). Total element concentrations are calculated using equation 3.3.

Figure 3.4: Using Total X-Ray Fluorescent (TXRF) instrument to determine heavy metals in the samples.

3.6.3 Quality control

Sample carriers were thoroughly cleaned, dried and irradiated for 100 seconds to confirm no elemental peaks other than silicon, argon and molybdenum appear with intensities higher than Ar Kβ- line. Disposable pipette tips were also used to reduce cross contamination.

Prior to commencement of any analysis, resolution, sensitivity and count rate of the TXRF instrument was determined by analyzing 1ng of Mn standard, 1ng of Ni standard and 1μg of As standard, respectively. A multi-element certified reference material from Bernd Kraft was analyzed to determine the accuracy of the instrument (Figure 3.6). This CRM contains ten elements (Mn, Cr, Ca, V, Ti, Fe, Co Ni, Cu and Zn), each at a concentration of 10 ppm (Table 4.6). The experimental observed values were compared to the certified values.

Figure 3.5: Multi-element certified reference material.

3.7 Statistical analyses

The obtained data was subjected to statistical tests using software IBM Statistical Package for Social Sciences (SPSS), version 22. One way ANOVA (analyses of variance) was used to determine whether the mean heavy metal concentrations varied significantly between sampling depths. Tables and graphs were used to present the results.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 Introduction

In this chapter, the results of the physico-chemical parameters which include pH, Electrical Conductivity, Oil and grease are first presented, analyzed and discussed; they are then followed by results of heavy metals. All other relevant data are also presented in Appendix 1-Appendix 6.

4.1 Drill Waste pH

pH results for each of the sampling points are tabulated as shown in table 4.1 below. They were all recorded at 25^oC . The mean pH of the samples from the reserve pit was 8.48 ± 0.22. The drilling waste had a basic pH. This mean implied the pH was within the range reported by Ayad and Salih (2011) of 8.5 and slightly below 9.25, a value reported by USEPA (1987) (Table 4.2).

Table 4.1: pH results of the reserve pit samples.

POINT	SURFACE	MIDDLE	BOTTOM
1	8.2	8.5	8.8
2	8.3	8.4	8.7
3	8.2	8.5	8.8
4	8.3	8.5	8.7
5	8.2	8.4	8.7
MEAN	**8.24 ± 0.05**	**8.46±0.05**	**8.74±0.05**
AVG. MEAN	**8.48 ± 0.22.**		

Table 4.2: Comparisons of pH values obtained from the present study and pH data obtained from other studies.

STUDY	**pH range**		**Standard range (FEPA,1991)**
	Top	**Bottom**	
Present Study	8.2	8.7	6 - 9
Ayad and Salih (2011).	8.2	9.7	6 - 9
Kinigoma (2001)	6.00	6.8	6 - 9
USEPA (1987)	8.9	9.5	6 - 9

The pH of drill waste increased slightly with depth (Table 4.1). Samples obtained from the bottom part of the pit (sludge) had a higher pH (8.74) compared to the samples obtained from the top (8.24), (figure 4.1), whereby a significant difference was observed between the sampling depths ($p<0.05$). This observation conformed to the findings of USEPA (1987),which showed that the bottom sludge phase of the drilling waste in a reserve pit tends to be more basic than the liquid phases because of the hydroxyl ions which get trapped in the solid particles which settle at the bottom. The basic nature of the drill waste may be due to the addition of lime, caustic soda, soda ash and/or sodium bicarbonates which are the most common additives of drilling mud and they form alkaline solutions (Reis, 1996). Generally, pH values were within the recommended range by regulatory authorities of between 6 and 9 (Table 4.2) (FEPA, 1991). The drill waste can be categorized as non-hazardous. A waste is considered hazardous under RCRA if its aqueous phase has a pH less than or equal to 2 or greater than or equal to 12.5 (USEPA, 1987). pH affects the solubility of many divalent metal ions such as calcium and magnesium as well as solubility of other components of drill waste; thus it greatly affects the mobility of these inorganic and organic constituents in the environment (USEPA, 1987). pH is important for it is an intergral parameter in determining the method of drill waste disposal.

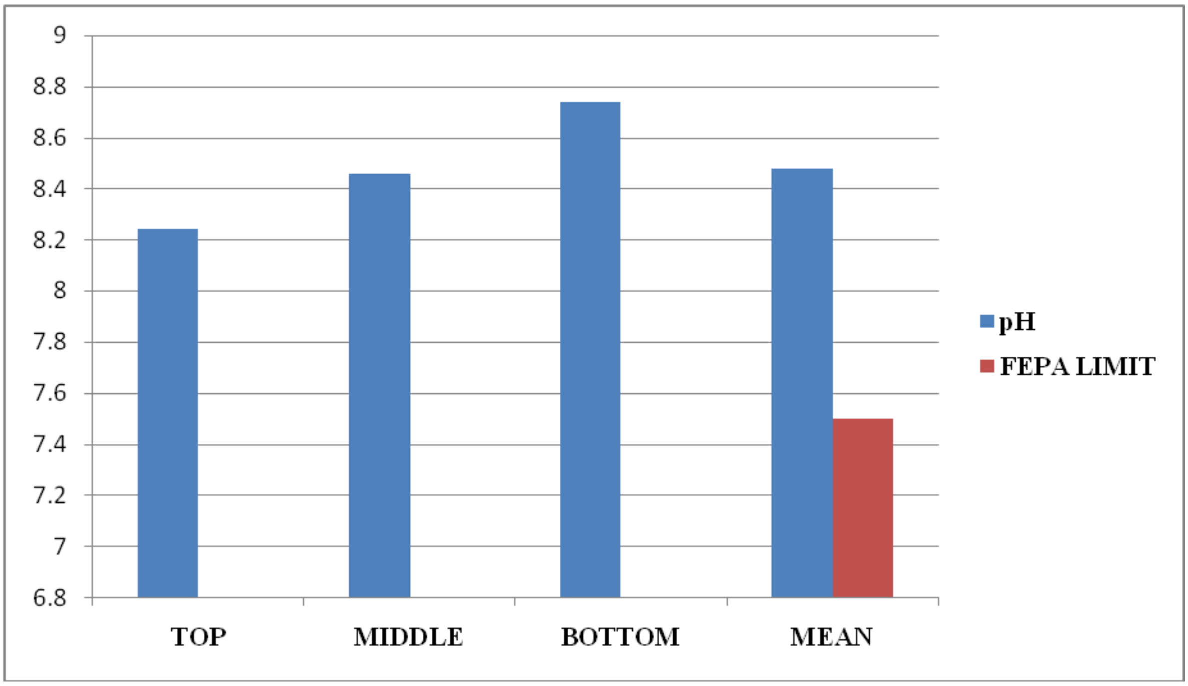

Figure 4.1: Variation of pH between the sampling depths.

4.2 Electrical Conductivity

Electrical conductivity values of the drill waste are reported in Table 4.3. The mean Electrical Conductivity of the samples was 1.67 ± 0.38 mmhos/cm ,a value which was very low. The low EC of the drill waste may be attributed to low use of salt based additives in the drilling muds and may also be attributed to drilling through non-saline geological formation. The values increased down the waste pit with the samples obtained from the bottom having the highest mean value (2.17 ± 0.08 mmhos/cm) followed by middle samples (1.58 ± 0.06 mmhos/cm) then the top samples (1.28 ± 0.10 mmhos/cm). They were in the order of Bottom > Middle > Top and a high significant difference was observed between the sampling depths ($p < 0.05$). This increase of EC down the pit may be associated with the increase in the number of salt ions bound to the settling solid particles of the waste. Figure 4.2 show the graphical presentation of the mean EC values and the recommended regulatory limit levels.

Table 4.3: Results of Electrical Conductivity in mmhos/cm.

POINT	SURFACE	MIDDLE POINT	DEEP
1	1.22	1.59	2.10
2	1.24	1.49	2.25
3	1.18	1.66	2.23
4	1.33	1.58	2.14
5	1.44	1.58	2.07
MEAN	**1.28 ± 0.10**	**1.58 ± 0.06**	**2.17 ± 0.08**
AVG. MEAN	**1.67 ± 0.38**		

According to table 4.4, the extent of pollution by ions for Ngamia -5 reserve pit is much less compared to the ion pollution reported by Ayad and Salih (2011), who reported EC values of drill waste in a reserve pit which ranged from 7.98 to 9.90 mmhos cm^{-1}. Salinity of the drilling waste is usually caused by use of salt based additives which are added to the drilling fluids to obtain certain desired properties such as shale inhibition. Table 4.4 demonstrates that the mean value of EC obtained from this work was less than half of that reported in the literature and was within the recommended regulatory level of 4 mmhos cm^{-1} which approximates a TDS of 2560 mg l^{-1} (USEPA, 1987).

Electrical conductivity (EC) is an indicator of salt content in a given substance and is one of the typical criteria for measuring salinity. Electrical conductivity is a very key parameter that dictates the environmental performance of the drilling waste and is a parameter used by local government to regulate and decide on the disposal method for the drilling waste (Gbadebo et al., 2010). Electrical conductivity thus plays a pivotal role in determining subsequent cost and the disposal method of drill waste (Reis, 1996).

Table 4.4: Comparisons of Electrical conductivity values obtained from the present study and EC data obtained from other studies.

STUDY	**EC range(mmhos/cm)**		**Standard limits**
	Top	**Bottom**	
Present Study	1.28	2.16	4.0
Ayad and Salih (2011).	7.98	9.90	4.0
EPA (1987)			4.0

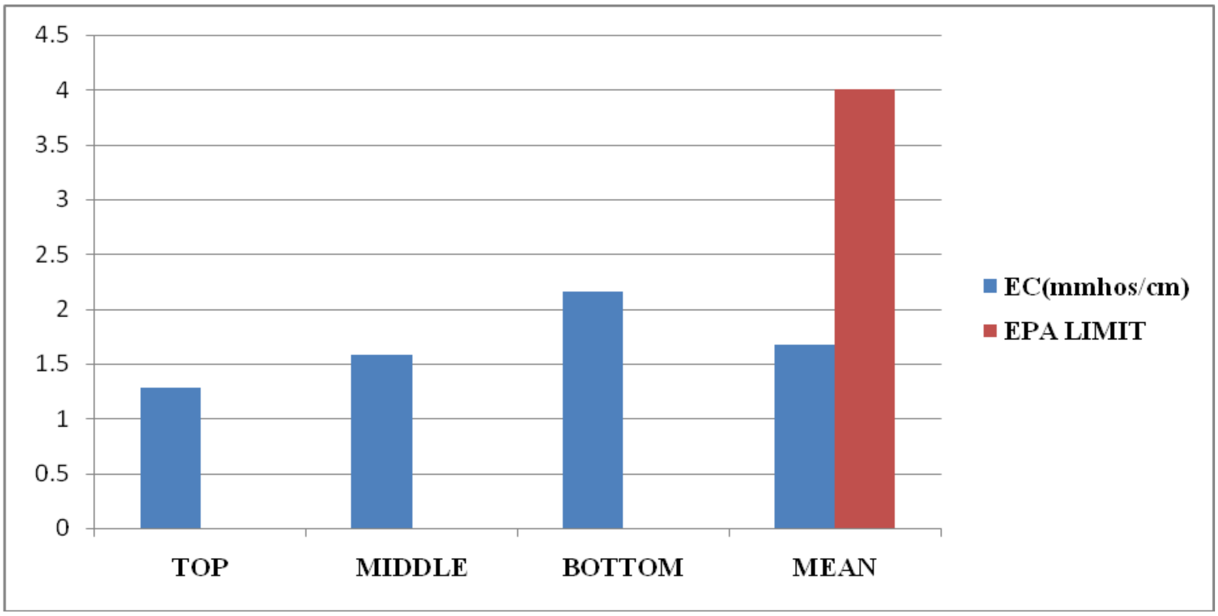

Figure 4.2: Variation of Electrical conductivity in mmhos/cm between the sampling depths and the accepted regulatory limit.

4.3 Oil and Grease

Oil and grease results were recorded in Table 4.5 below. The mean oil and grease value of the drill waste samples in the reserve pit was 41.66 ± 25.74 mg/l. The values increased down the reserve pit with the samples obtained from the bottom having the highest mean values (72.02 ± 2.94 mg/l), followed by middle samples (41.66 ± 2.26 mg/l) then the top samples (11.3 ± 1.17 mg/l). They were in the order of Bottom > Middle > Top and a high significant difference was observed between the sampling depths ($p<0.05$).

Table 4.5: Results of Oil and Grease in mg/l.

POINT	TOP	MIDDLE	BOTTOM
1	11.23	44.82	69.41
2	9.84	40.94	72.35
3	12.05	38.56	68.74
4	12.81	41.75	73.92
5	10.57	42.25	75.66
MEAN	**11.30 ± 1.17**	**41.66 ± 2.26**	**72.02 ± 2.94**
AVG. MEAN	**41.66 ± 25.74**		

The high content of oil and grease in the drill waste may have entered into drill waste while drilling through the hydrocarbon bearing formation or when oil used for spotting fluid became stuck or when diesel was added to oil-based drilling mud (Duel and Holiday, 1990). Usually, the deeper the well, the greater the concentration of oil that enters in the drilling waste (Reis, 1996).

The increase of oil and grease down the pit was because oil and grease have a tendency of attaching onto the soil and clay particles which are dense and were settling downwards. This may also be associated with the tendency of oil to redistribute itself as a result of exposure to a multiphase environment, i.e., soil phase, vapor phase, water phase, and the oil phase itself.

Thus, the higher molecular weight compounds are generally less mobile and stay near the surface, while the lighter weight compounds migrate deeper into the subsurface because of greater aqueous solubility (Saterbak et al., 1999). Figure 4.3 demonstrates that oil and grease values in this research work were far much higher than the recommended 10 mg/l by FEPA (1991) and the established threshold level of 15 mg/l by USEPA (1993). At such high concentrations, oil and grease can seriously threaten the life of edaphic systems as well as people and animals if it permeates through the soil and reach the underground water aquifers or get into surface water bodies through run-off (Odokuma and Ikpe, 2003).

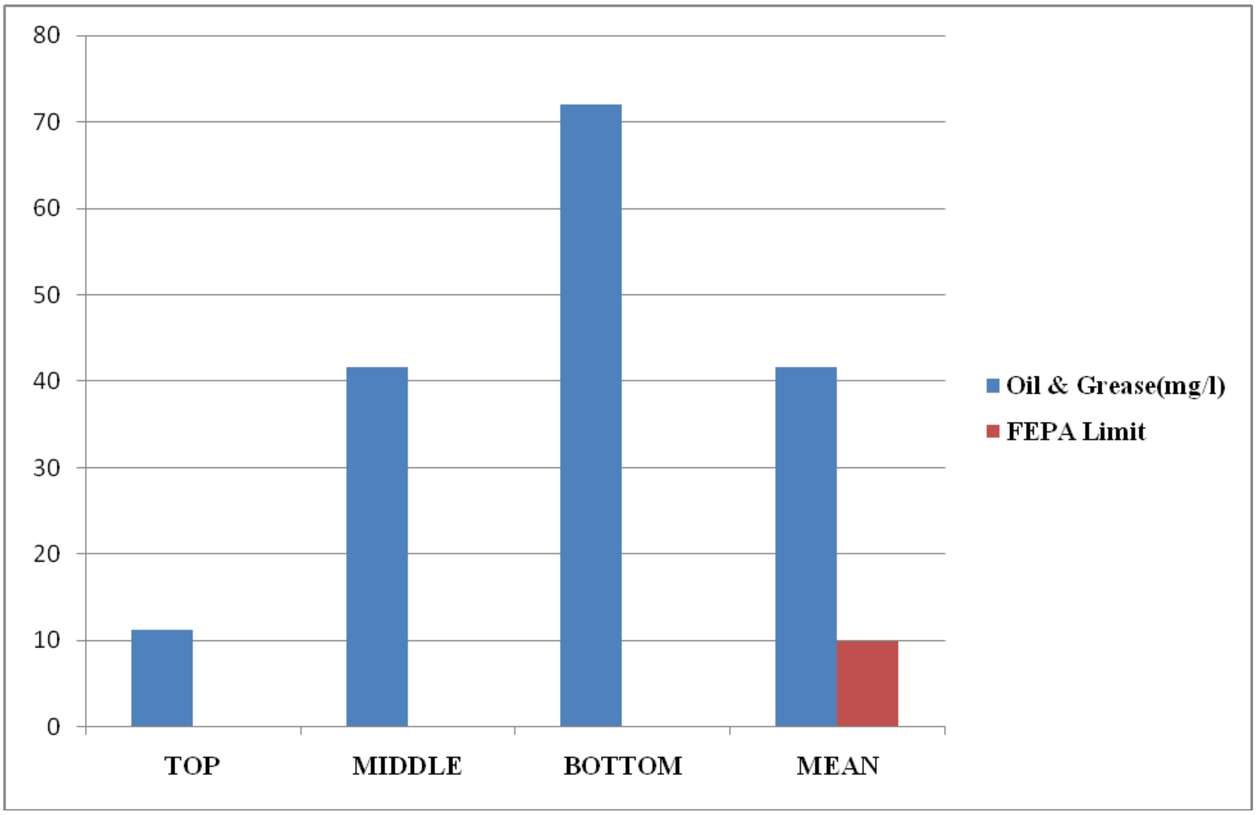

Figure 4.3: Variation of Oil & Grease in mg/l between the sampling depths and the accepted regulatory limit.

4.4 Total Metal content

4.4.1 Evaluation of the analytical method

Heavy metal concentration in reserve pit samples were analyzed using TXRF spectrometer. The accuracy of the analytical procedure was evaluated by analyzing multi-element Certified Reference Material (CRM) using TXRF (table 4.6). A one tailed paired sample t-test showed that the experimental values (m = 9.85, s = 0.07) and the certified values (m = 10.0, s = 0.03) were statistically similar, t (9)= -0.595, p> 0.05.

Table 4.6 Results of analysis of multi-element certified reference material using TXRF spectroscopy.

Element	**Experimental value (ppm)**	**Certified value (ppm)**
Ca	10.74 ± 0.03	10 ± 0.03
Ti	9.05 ± 0.06	10 ± 0.03
V	8.93 ± 0.04	10 ± 0.03
Cr	9.52 ± 0.07	10 ± 0.03
Mn	9.89 ± 0.05	10 ± 0.03
Fe	9.29 ± 0.06	10 ± 0.03
Ni	11.02 ± 0.07	10 ± 0.03
Cu	10.00 ± 0.05	10 ± 0.03
Zn	10.28 ± 0.03	10 ± 0.03

4.4.2 Total metal content

The results for metal analysis in Ngamia 5 reserve pit are summarized in table 4.7. These are the mean concentration in mg/l for different depths. Table 4.8 shows the comparison of metals' concentrations obtained in this study with other studies.

Table 4.7: Total elemental content of drill waste samples (mg/l).

	SURFACE	MIDDLE	DEEP
K	144.75 ± 6.65	378.05 ± 17.55	636.8 ± 55.07
Ca	320.55 ± 14.26	760.85 ± 33.65	2497.02 ± 208.88
Cr	1.12 ± 0.2	1.82 ± 0.13	4.28 ± 0.23
Mn	1.67 ± 0.18	2.33±0.2	12.74 ± 1.27
Fe	131.24 ± 5.55	216.29 ± 9.65	796.84 ± 67.61
Ni	0.03 ± 0.01	0.14 ± 0.03	0.6 ± 0.1
Cu	0.28 ± 0.03	0.68 ± 0.06	2.49 ± 0.26
Zn	0.56 ± 0.05	0.98 ± 0.07	4.06 ± 0.4
As	0.06 ± 0.01	0.08 ± 0.02	0.09 ± 0.03
Rb	0.14 ± 0.02	0.3 ± 0.03	0.91 ± 0.11
Sr	1.76 ± 0.1	5.74 ± 0.28	12.11 ± 1.1
Ba	234.11 ± 10.74	1293.33 ± 57.95	1701.36 ± 149.45
Pb	0.13 ± 0.02	0.6 ± 0.05	4.51 ± 0.47

Key: Results were presented as mean ± standard deviation of triplicate analysis.

From the results, it can be observed that the drill waste in Ngamia 5 reserve pit contained appreciable contents of Fe, Ba, base metals (Ca & K,), and toxic elements (Mn, Pb, Zn, Ni & Cr); an observation which was also made by Veritas (2000) who found high concentrations of barium, lead, chromium, copper and zinc in the analysed drill waste. The mean concentration range for K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Ba, Pb in the reserve pit in mg/l was (145 - 637), (320 - 2497), (1.12 - 4.28), (2.33 - 12.74), (131 - 796), (0.03 - 0.6), (0.28 - 2.49), (0.56 - 4.06), (0.06 - 0.09), (0.14 - 0.91), (1.76 - 12.1), (234 - 1701), (0.13 - 4.51), respectfully. The results indicated that Ca, Ba, Fe and K were relatively higher in concentration than all the other metals and their distribution profile is shown graphically in figure 4.4 - 4.6. They were of the order Fe < K < Ba < Ca and these results were similar to the ones reported by Ayad et al. (2013), who found that Ca had the highest concentration followed by Ba and Fe (Ca > Ba > Fe). Similarly, As, Ni and Rb had the lowest mean concentration in the reserve pit and they were of the order As < Ni < Rb (figure 4.5).

The concentration of some heavy metals obtained in this study were in good agreement with values obtained in other studies while others differed as demonstrated in table 4.9. For example, the mean zinc value (1.869 mg/l) obtained in this study was three times higher than the value reported by Kinigoma (2001) of 0.604 mg/l. Similarly, barium, calcium, zinc, iron, chromium, lead and arsenic values of this study were much lower when compared to results obtained by American Petroleum Institute (API) (1989a) and US Environmental Protection Agency (EPA), (1987).

Heavy metals were not uniformly distributed in the pit. The concentrations (mg/l) of K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As , Rb, Ba, Sr Ba and Pb at the bottom (636.8 ± 55.07 , 2497.02 ± 208.88 , 4.28 ± 0.23, 12.74 ± 1.27 , 796.84 ± 67.61 , 0.6 ± 0.1, 2.49 ± 0.26, 4.06 ± 0.4, 0.09 ± 0.03, 0.91 ± 0.11, 12.11 ± 1.1, 1701.36 ± 149.45 and 4.51 ± 0.47), respectively was higher than the concentration at the top (144.75 ± 6.65, 320.55 ± 14.26 , 1.12 ± 0.2 , 2.33 ± 0.2 , 131.24 ± 5.55, 0.03 ± 0.01 , 0.28 ± 0.03 , 0.56 ± 0.05, 0.06 ± 0.01, 0.14 ± 0.02, 1.76 ± 0.1, 234.11 ± 10.74, 0.13 ± 0.02) respectively; a trend that conforms to the previous findings of Leuterman et al. (1988), who also observed that metal concentrations in the mud phase were generally higher than in the water phase. In general, the trend in the three levels of the pit was of the order Surface < Middle < Bottom and the ratio of the three levels is shown in table 4.8

This non uniform distribution of metals with the mud phase having higher concentration of metals than water phase can be ascribed to the fact that heavy metals are often bound to the organic and coarse clay particulates and tend to accumulate at the bottom of the pit (Deuel and Holliday, 1990). While other studies have revealed no preferential distribution of metals in reserves pits (Wojtanowicz et al., 1989), Deuel and Holliday (1990) affirms that non uniform distribution of metals in a pit needs to be considered when sampling the pit for metal concentration. The concentrations of most were far much higher than the recommended levels by regulatory bodies (table 4.9).

Table 4.8: Ratios of the three depths; Surface: Middle: Bottom.

HEAVY METALS	**SURFACE**	**MIDDLE**	**BOTTOM**
Cr	1	2	4
Fe	1	2	6
Mn	1	2	7
Ni	1	4	20
Cu	1	2	9
Zn	1	2	7
Rb	1	1	6
Sr	1	3	7
As	1	1	2

Table 4.9: Recommended concentration levels by regulatory bodies.

Metal	**Mean Conc.(mg/l) (Present study)**	**FEPA(mg/l)**	**WHO(mg/l)**	**USEPA(mg/l)**
Fe	381.46	0.1	0.5	0.3
Cu	1.15	1.5	2.0	1.3
Zn	1.86	1.0	3.0	5.0
Pb	1.74	0.05	0.01	0.0
Ni	0.26	0.05	0.5	0.05
Cr	2.41	0.05	0.05	0.1
Ca	1192.81	200		
Mn	5.58		0.5	0.05
As	0.8	0.05		
Ba	1076.27	100		

Table 4.10: Comparisons of Metal content Data obtained from the present study and Data obtained from other studies.

STUDY	Ba	Ca	Zn	Fe	Cr	Pb	As	Cu
Present study in ppm	1076.3	1193	1.869	381.464	2.4078	1.749	0.0811	1.15
Kinigoma(2001)		169.60	0.604	20.0	0.081	<0.000		0.029
EPA (1987)	10119	71700	683	56800	81	446	29	
API (1989)	29200	47200	189	21200	17	59	8	

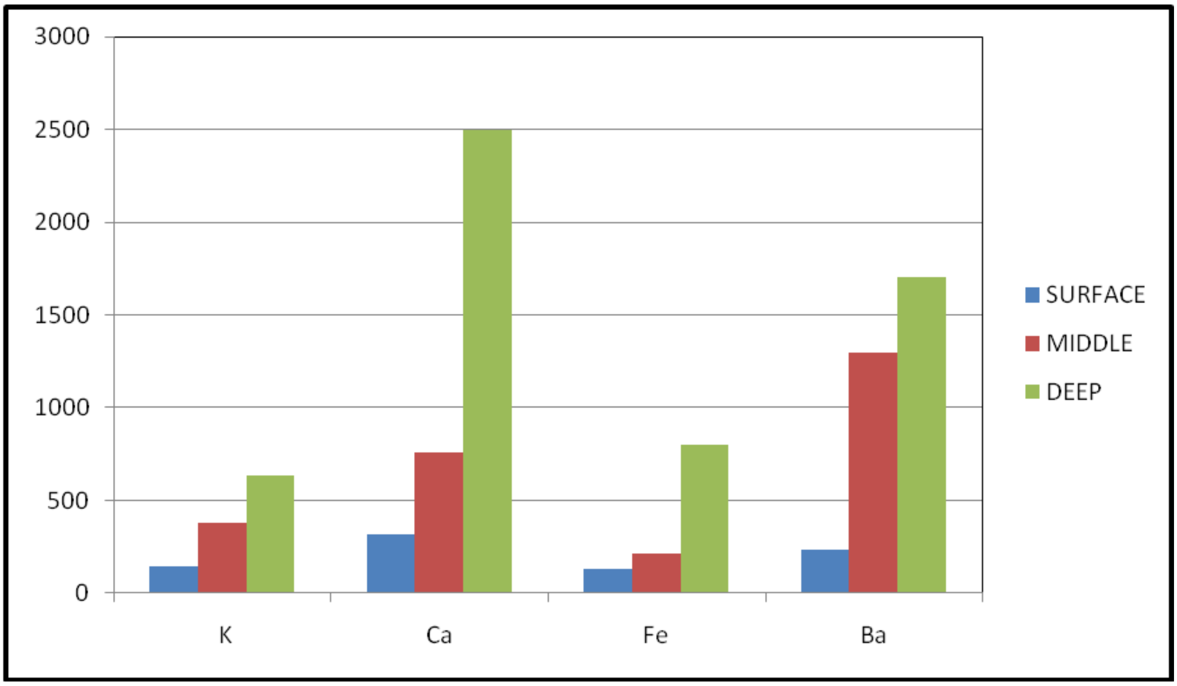

Figure 4.4: Distribution of the metals with the highest concentration in mg l^{-1} (K, Ca, Fe and Ba) in the three levels of the reserve pit.

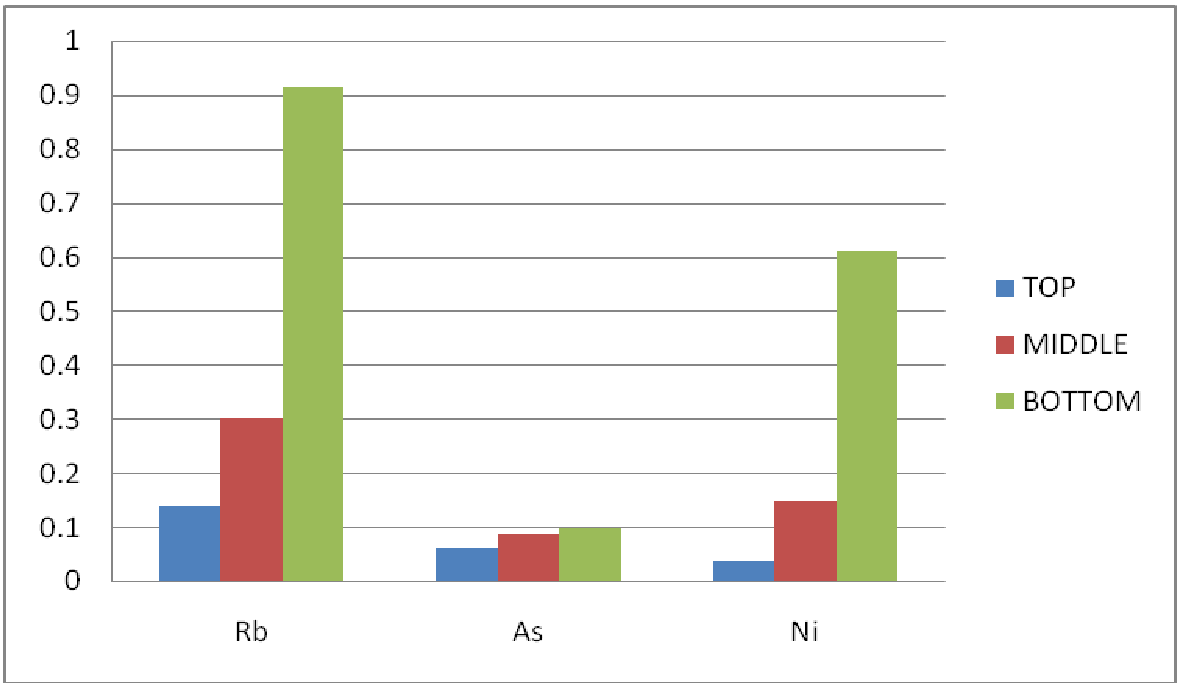

Figure 4.5: Distribution of the metals with the lowest concentration in mg l^{-1} (Rb, As and Ni) in the three levels of the reserve pit.

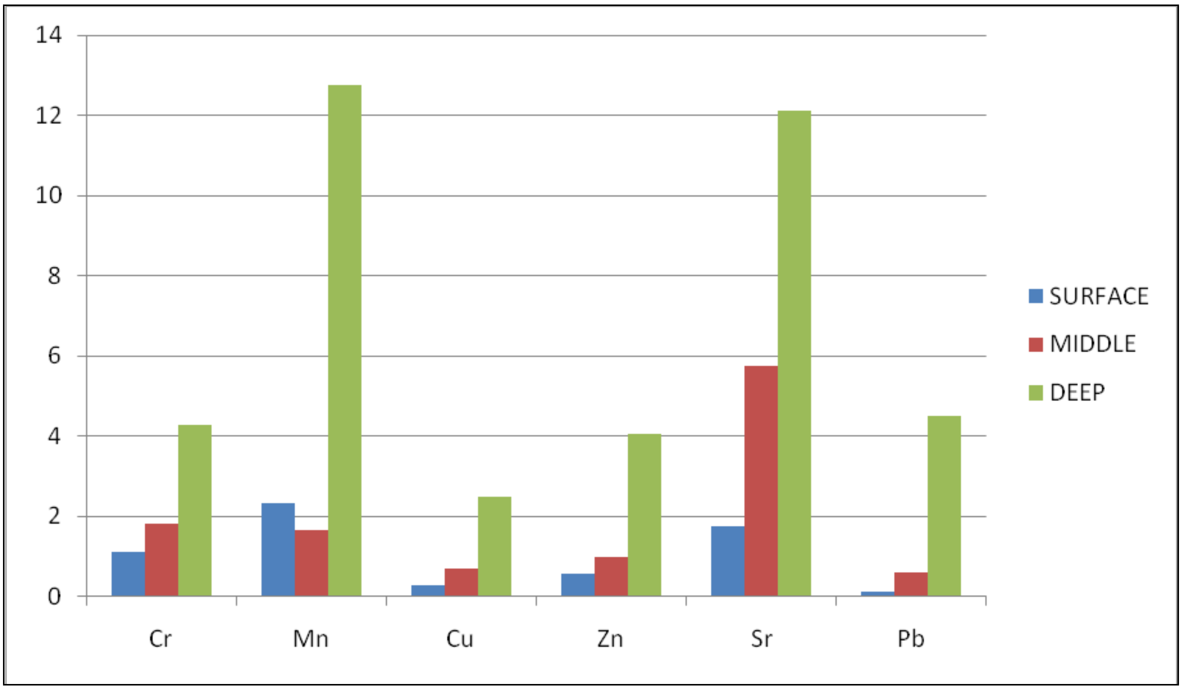

Figure 4.6: Distribution of Cr, Mn, Ni, Cu, Zn, Sr and Pb in mg l^{-1} in the three levels of the reserve pit.

4.5 Concentration of selected metals in the reserve pit

4.5.1 Barium

The mean concentration of barium in the reserve pit was 1076.27 mg/l. Samples obtained from the bottom part of the pit had the highest barium concentration (1701.36 ± 149.45 mg/l), followed by middle samples (1293.33 ± 57.95 mg/l), while the top samples had the lowest concentration (234.11 ± 10.74 mg/l) (figure 4.7). The obtained values of barium were much lower compared to the ones reported by Ayad et al. (2013) of 26000 mg/l and Deuel and Holliday (1990) of 29200 mg/l. However, the values were far much higher than the recommended 100 mg/l by USEPA (1990). Barium is considered hazardous if its concentration in the drilling reserve pit is above 100 mg/l.

The high levels of barium in the reserve pit could have originated from the drilling mud. Barium is a constituent of barite, which is used as a density control material in the drilling mud. Drilling fluids typically contain high concentration of barium and the most commonly used form of barium, however, is barium sulfate, which is highly insoluble (Candler et al.,1990). High content of barium in drill waste imposes toxicity in the reserve pits. Barium sulfate which is the most commonly found form of barium is insoluble in geochemical conditions and is not taken up by plants. Though soluble Ba can leach out to contaminate underground water, it is not absorbed by animals or humans if ingested (Reis, 1996).

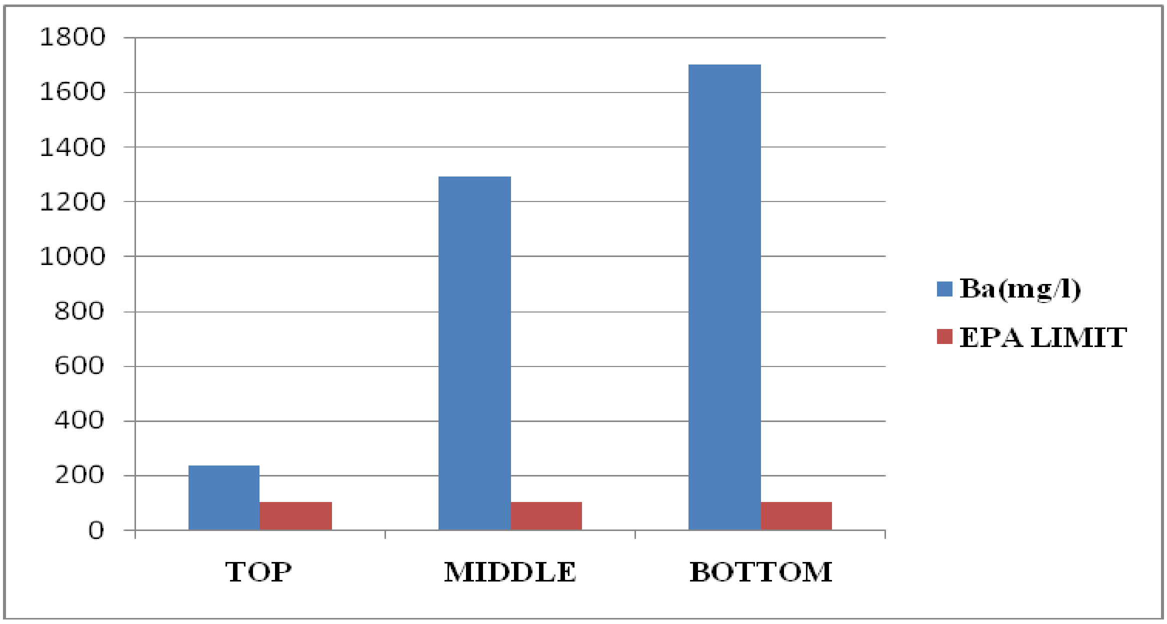

Figure 4.7: Variation of barium in mg/l within the sampling depths and EPA limit.

4.5.2 Lead

The mean concentration of lead in the reserve pit was 1.74 ± 0.4 mg/l (Figure 4.8). Generally, the values increased down the pit with the mud phase having a higher concentration of 4.51 ± 0.47 mg/l than the water phase 0.13 ± 0.02 mg/l. These concentration levels were much lower compared to results reported by Leuterman et al. (1988) for lead in both mud 24.46 mg/l and water phase 3.36 mg/l, respectfully. Lead levels in the reserve pit were higher than the recommended 0.005 mg/l by FEPA (1991) and the threshold levels of 0.05 mg/l for reserve pits.

The presence of lead in the reserve pit may have come from the contaminants in the drilling mud mostly barite. Analysis of barite has shown to have lead concentrations in the range of 1000 μg/kg (Stig et al., 2002). The other source of lead in drill waste may have come from pipe dopes which help in preventing the seizure of the joint from galling at high stresses and prevents fluid flow along the threads. Lead has the ability to leach out of the pipe dope and contaminate the drilling fluid then end up in the drill waste (McDonald, 1993).

There is a possibility of future increase of lead concentration in the surrounding environment from continuous discharge of lead containing drill wastes. Lead can be mobilized from the reserve pits to adjacent soils and surface waters by precipitation. It can also leach out to the underground water causing serious contamination. Prolonged exposure to lead induces toxic responses in the hematological, neurological, and renal systems, leading to brain damage, convulsions, behavioral disorders, and death. Some plants show retarded growth at 10 ppm. Subtoxic effects have been observed in micro flora at 0.1 ppm (Reis, 1996).

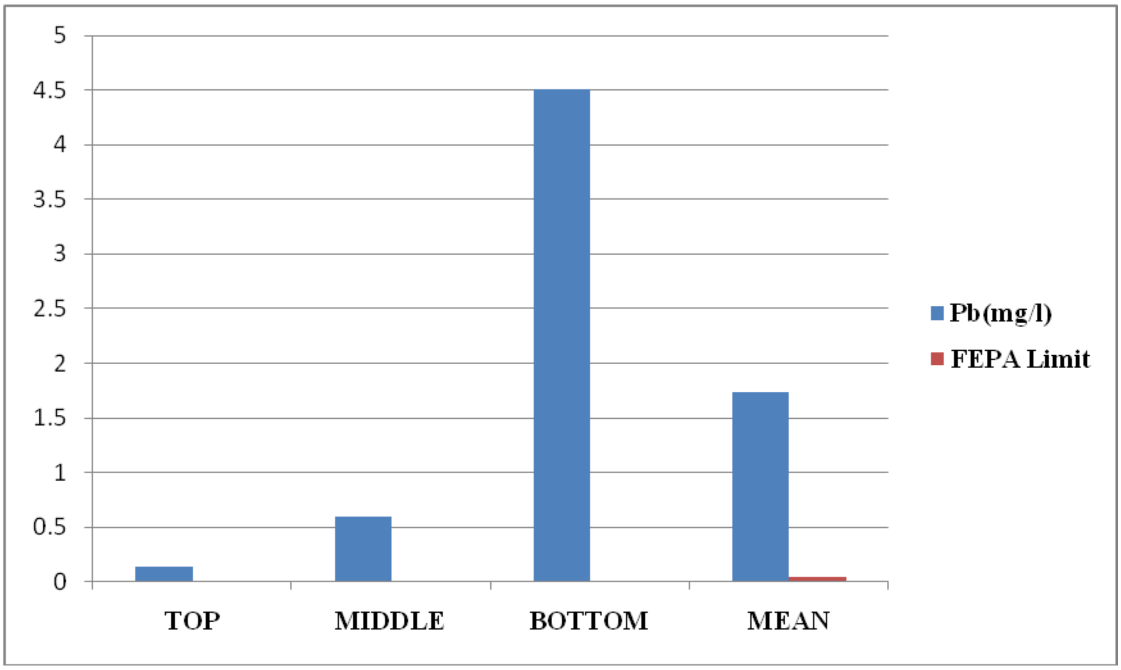

Figure 4.8: Variation of lead in mg/l within the sampling depths and FEPA limit.

4.5.3 Chromium

The mean chromium concentration in the reserve pit was 2.41 ± 0.23 mg/l. Chromium concentration showed an increasing tread down the pit with the mud phase having 4.28 ± 0.23 mg/l higher than the water phase 1.12 ± 0.2 mg/l. These values were higher compared to the values reported by Shadizadeh and Zoveidavianpoor (2010) for chromium of 0.006mg/l and 0.08mg/l for water phase and mud phase, respectively. However, the values were similar to the results reported by Leuterman et al. (1988) of 3.97 mg/l for mud phase and 2.09mg/l for water phase. These concentration levels of chromium are very high when compared to the established threshold levels of 0.1mg/l by USEPA (1990) (figure 4.9).

Chromium may have entered the reserve pits through drilling mud. Chromium is a major constituent of many mud additives, particularly chrome-based deflocculants. Chromium in its toxic hexavalent form can be used as a gel inhibitor- thinner, a dispersant, a biocide, a corrosion inhibitor and a high temperature stabilizer (Campbell and Akers, 1990). Typical chromium levels in drilling muds are between 100 and 1,000 mg/l (Bleier et al., 1993).

Chromium can be mobilized from the reserve pits to adjacent soils and surface waters by precipitation. It can also leach out to the underground water causing serious contamination

(Beal et al., 1987). The toxicity of chromium in the environment depends primarily on its chemical valence state and its concentration. Chromium is considered to be an essential element in humans at low levels. At higher concentrations, hexavalent chromium can be highly toxic, while trivalent chromium is relatively nontoxic. Hexavalent chromium can cause severe kidney damage. Some hexavalent chromium compounds are very carcinogenic. Other effects of chronic exposure at high levels include lung cancer, dermatitis, alceration of the skin, chronic catarrh, and emphysema (Reis, 1996).

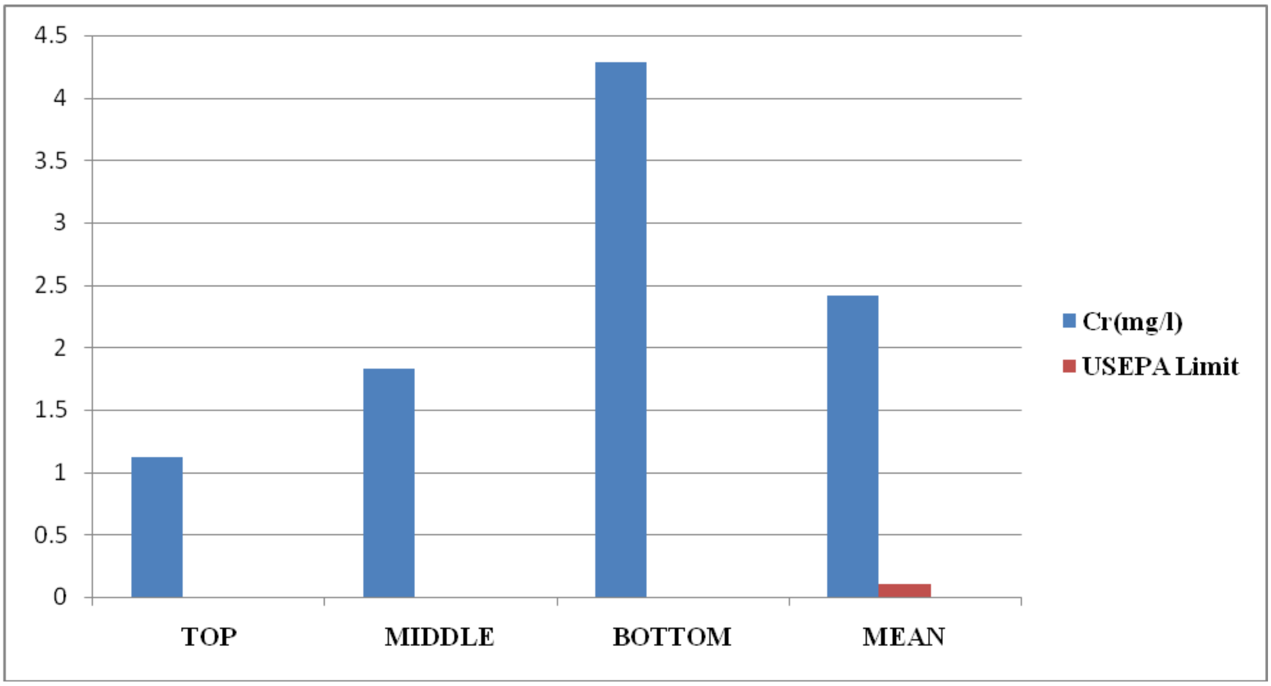

Figure 4.9: Variation of Chromium in mg/l within the sampling depths and USEPA limit.

4.5.4 Zinc

The mean zinc concentration in the reserve pit was 1.86 ± 0.2 mg/l (figure 4.10). The surface samples had the lowest concentration of 0.56 ± 0.05 mg/l while bottom had the highest concentration of 4.06 ± 0.4 mg/l. These concentrations were however, higher than that reported by Leuterman et al. (1988) of 0.21mg/l and 0.07 mg/l for both mud and water phase respectively. In general, the mean concentration of zinc in the reserve pit was much lower than the recommended 5.0 mg/l by USEPA (1990).

Presence of zinc may be ascribed to pipe doping for it is used in formulating much of pipe dope and has the ability to leach out and contaminate the drilling fluid. At different concentrations, zinc is also occasionally added as inorganic zinc salts for density control or as hydrogen sulfide scavengers to minimize corrosion (Candler et al., 1990).

Zinc in the drill waste can be mobilized into the environment via leaching, precipitation and flooding. Zinc is an essential element in the human metabolism and is required in low concentrations. It is toxic to plants at above 400 ppm and lethal to fish and other aquatic animals at 1.0 ppm. Since zinc concentration in the reserve pit was very low, the reserve pit may not be a source of zinc contamination to the surrounding environment in events of leaching and flooding.

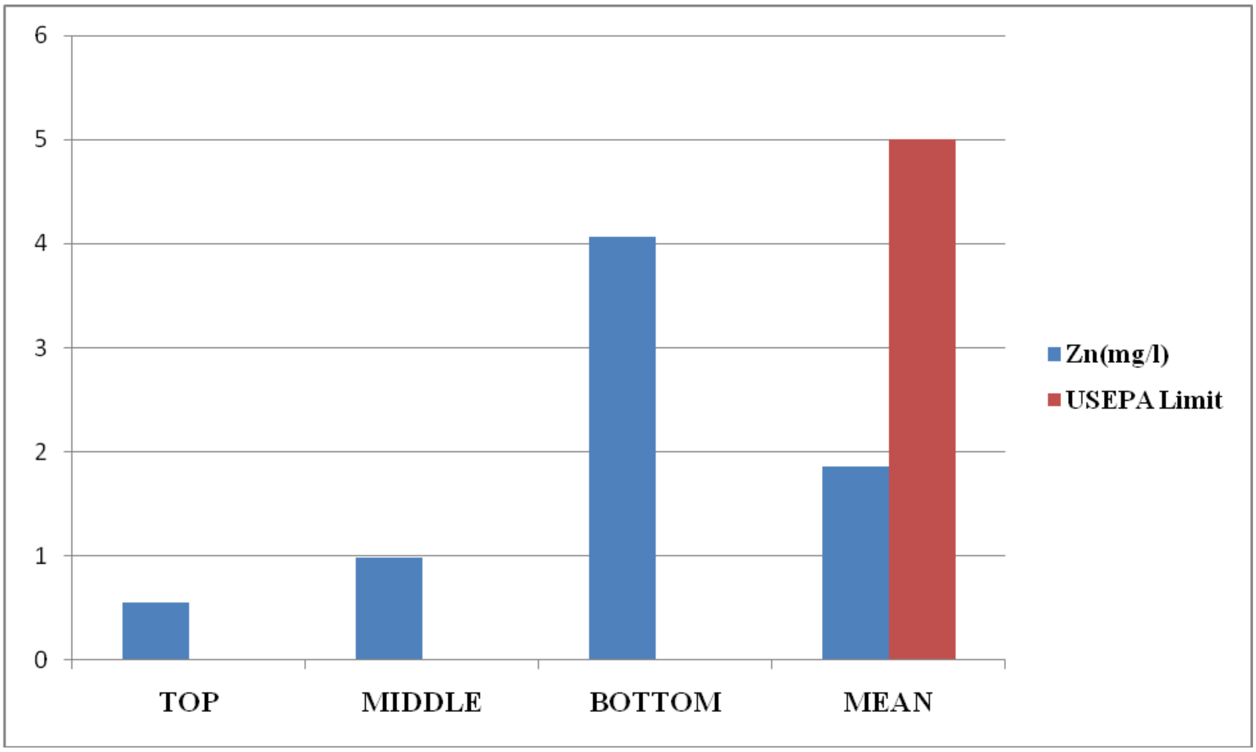

Figure 4.10: Variation of Zinc in mg/l within the sampling depths and EPA limit.

4.5.5 Arsenic

Arsenic was one of the heavy metals with the lowest concentration in the reserve pit. The mean concentration was 0.08 ± 0.02 mg/l (figure 4.11). This concentration increased with depth with the mud phase having higher concentration (0.09 ± 0.03 mg/l) than that of water phase (0.06 ± 0.01mg/l). Arsenic concentration in the reserve pit was slightly higher than the recommended standards by FEPA (1991) of 0.05 mg/l.

Presence of arsenic in the reserve pit may have come from the drilling mud. Arsenic is usually found in low concentrations in the drilling fluids because it used as a biocide to prevent the growth of bacteria (Reis, 1996). Arsenic in the drill waste can be mobilized from the reserve pit into the environment via precipitation, flooding or leaching into underground water aquifers. Chronic exposure to arsenic can lead to weakness, anorexia, bronchitis, gastrointestinal disturbances, peripheral neuropathy, skin disorders and damage to the liver, heart, nerves, and kidneys. When it gets into water bodies, arsenic may impact embryo and larval states of fish and benthic invertebrates.

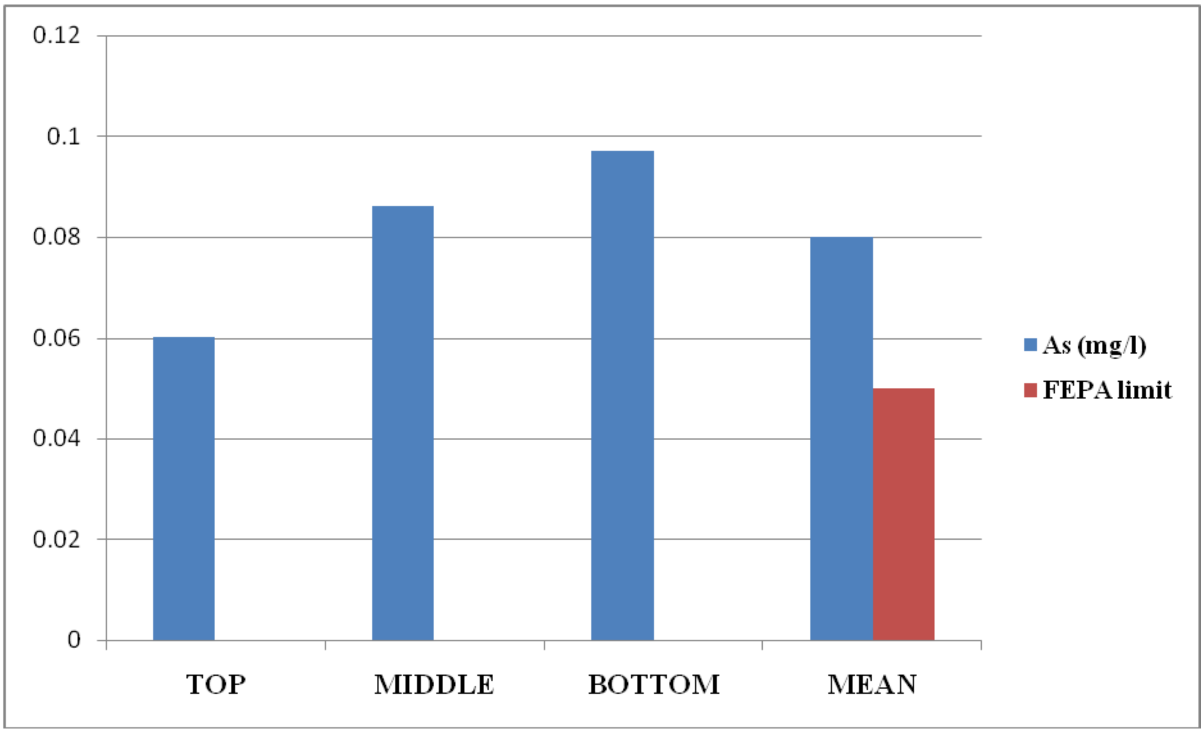

Figure 4.11: Variation of Arsenic in mg/l within the sampling depths and FEPA limit.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The study sought to investigate and analyze drilling waste from Ngamia-5 oil exploratory well reserve pit in order to identify and quantify the contaminants present and determine their potential environmental impact. Based on the obtained results, it is evident that Ngamia-5 reserve pit has a negative impact on Turkana County environment. The generated exploratory wastes which include: used drilling fluids, drilling cuttings and wash-down fluids are directly discharged into the reserve pit of this well site. These wastes contain an array of toxic substances such as heavy metals and hydrocarbons at hazardous levels. The mean concentration of oil and grease quantified was four times higher than the recommended levels by FEPA. Additionally, the concentration of heavy metals such as lead, chromium, arsenic and barium were 34, 24, 2 and 10 times higher than the set regulatory standards by USEPA.

The contaminants also increased with the depth of the pit, where the bottom part of the pit was having the highest concentration of contaminants. This tendency of the contaminants to settle at the bottom of the pit implies that they can easily leach downwards resulting into contamination. These contaminants, especially the heavy metals, do not stay contained within the waste, they leach out and contaminate the groundwater aquifers. They also get mobilized out of the pit by precipitation and flooding thus end up causing soil and surface water pollution hence posing a significant threat to human health and ecological systems. An important aspect of these contaminants is that they initially give rise to first order impacts and with time the second and third order becomes manifested. Humans, birds, sheep, cows and related wildlife are now directly exposed to the contaminants in the reserve pit. This means, people drinking water from Turkana or consuming sheep, cows, birds, and even fish from this area could be at risk of health problems because the pollutants build up in the food chain by bioaccumulation and biomagnifications.

Additionally, the existing environmental guidelines and standards in Kenya are inadequate to cope with the upcoming environmental threats forced by the oil and gas exploration and production. Despite the potential negative environmental impacts from the oil and gas development, this study revealed that although Kenya has the appropriate legislation framework, there is still an existing problem of implementation with regard to monitoring and enforcement. Up to date, Kenya has not been able to properly enforce environmental compliance due to the associated cost in terms of capacity establishment, resource and logistic demand. Morever, the current regulations governing waste materials associated with oil and gas exploration and production activities in the country are not explicit and do not specifically address contaminants found in reserve pits and provides no guideline in determining required regulatory standard limits since the regulations typically focus on operational controls rather than monitoring environmental impacts. The absence of such provisions has serious repercussions on environmental monitoring which could be easily exploited to the advantage of the oil and gas companies and should therefore be developed and enforced to guide future oil and gas exploration and production in Kenya.

5.2 Recommendation

Considering the above results and conclusions it is therefore recommended that:

- ✓ As Kenya goes forward with oil exploration which will be followed by production, it is imperative that we obtain better knowledge of the quantity and quality of the contaminants being generated from these drilling processes.

- ✓ Proper explicit regulatory standards and guidelines for oil and gas exploration and production waste should be established to protect soil, surface and groundwater from contamination.

- ✓ Wastes resulting from oil drilling activities (cuttings & muds) should be properly treated before being disposed of into the environment by oil exploration companies. The new trend is that waste materials from the oil industries should be seen as raw materials for re-use. The solid wastes (drilling muds & cuttings) if properly treated can serve as raw materials for cement producing plants, bricks and expanded clay producing plants and can also be used in land restoration projects.

- ✓ The drilling company needs to perform recovery process on its waste so that the amount of oil and grease is reduced in the reserve pits.

5.3 Further research work

There is need for studies to be conducted to identify and quantify other contaminants found in drilling waste like Naturally Occurring Radioactive Materials (NORMS), Polycyclic aromatic hydrocarbons (PAHs), Total hydrocarbons (TPHs) and aliphatic hydrocarbons (AHs).

Further studies of the same work should be conducted using advanced techniques of analyses and characterization to compliment the data so far obtained in the current study.

More studies should be conducted on other reserve pits found within the study area to ascertain the level of heavy metals and other contaminants present.

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APPENDICES

APPENDIX 1

ANOVA RESULTS: PH

Descriptives

PH

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	5	8.2400	.05477	.02449	8.1720	8.3080	8.20	8.30
2	5	8.4600	.05477	.02449	8.3920	8.5280	8.40	8.50
3	5	8.7400	.05477	.02449	8.6720	8.8080	8.70	8.80
Total	15	8.4800	.21778	.05623	8.3594	8.6006	8.20	8.80

ANOVA

PH

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.628	2	.314	104.667	.000
Within Groups	.036	12	.003		
Total	.664	14			

Multiple Comparisons

Dependent Variable: PH

Tukey HSD

(I) DEPTH	(J) DEPTH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.22000*	.03464	.000	-.3124	-.1276
	3	-.50000*	.03464	.000	-.5924	-.4076
2	1	.22000*	.03464	.000	.1276	.3124
	3	-.28000*	.03464	.000	-.3724	-.1876
3	1	.50000*	.03464	.000	.4076	.5924
	2	.28000*	.03464	.000	.1876	.3724

*. The mean difference is significant at the 0.05 level.

APPENDIX 2: ANOVA RESULTS - ELECTRICAL CONDUCTIVITY

Descriptives

ELECTRICAL CONDUCTIVITY

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	5	1.2826	.10205	.04564	1.1559	1.4093	1.19	1.44
2	5	1.5802	.06167	.02758	1.5036	1.6568	1.49	1.66
3	5	2.1580	.07918	.03541	2.0597	2.2563	2.07	2.25
Total	15	1.6736	.38389	.09912	1.4610	1.8862	1.19	2.25

ANOVA

ELECTRICAL CONDUCTIVITY

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	1.981	2	.991	145.061	.000
Within Groups	.082	12	.007		
Total	2.063	14			

Multiple Comparisons

Dependent Variable: ELECTRICAL CONDUCTIVITY

Tukey HSD

(I) DEPTH	(J) DEPTH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.29760*	.05226	.000	-.4370	-.1582
	3	-.87540*	.05226	.000	-1.0148	-.7360
2	1	.29760*	.05226	.000	.1582	.4370
	3	-.57780*	.05226	.000	-.7172	-.4384
3	1	.87540*	.05226	.000	.7360	1.0148
	2	.57780*	.05226	.000	.4384	.7172

*. The mean difference is significant at the 0.05 level.

APPENDIX 3

ANOVA RESULTS - OIL AND GREASE

Descriptives

OIL AND GREASE

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	5	11.3000	1.17388	.52498	9.8424	12.7576	9.84	12.81
2	5	41.6640	2.26220	1.01168	38.8551	44.4729	38.56	44.82
3	5	72.0160	2.93849	1.31413	68.3674	75.6646	68.74	75.66
Total	15	41.6600	25.74130	6.64637	27.4049	55.9151	9.84	75.66

ANOVA

OIL AND GREASE

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9216.082	2	4608.041	913.674	.000
Within Groups	60.521	12	5.043		
Total	9276.603	14			

Post Hoc Tests

Multiple Comparisons

Dependent Variable: OIL AND GREASE

Tukey HSD

(I) DEPTH	(J) DEPTH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-30.36400*	1.42034	.000	-34.1533	-26.5747
	3	-60.71600*	1.42034	.000	-64.5053	-56.9267
2	1	30.36400*	1.42034	.000	26.5747	34.1533
	3	-30.35200*	1.42034	.000	-34.1413	-26.5627
3	1	60.71600*	1.42034	.000	56.9267	64.5053
	2	30.35200*	1.42034	.000	26.5627	34.1413

*. The mean difference is significant at the 0.05 level.

APPENDIX 4

DEFINITIONS OF TERMS AS USED IN THIS THESIS

Drilling mud	A suspension, usually in water but sometimes in oil (diesel), used in rotary drilling, consisting of various substances in a finely divided state (commonly bentonitic clays and chemical additives), introduced continuously down the drill pipe under pressure and through openings in the drill bit, and transported back up in the annular space between the pipe and the walls of the hole to a surface pit, where it is conditioned and reintroduced into the wellbore. It is used to lubricate and cool the bit, carry the cuttings up from the bottom, and prevent blowouts and cave-ins. Also see “mud systems.”
Oil and Grease	A group of organic substance soluble in an organic solvent.
Requirement	A rule that industry has an obligation to meet and under which the EUB may take enforcement action in cases of noncompliance
Drilling waste clear liquids	Liquids separating from water-based drilling wastes. The liquids appear nonturbid when sampled from the discharge point and qualify for pump-off. The clear liquids may be colorless or may have natural colour or staining.
Drilling waste fluids	A mixture of water, drilling muds, additives, and various other wastes that specifically relate to the drilling activity.
Composite sample	A sample consisting of a number of thoroughly mixed subsamples representative of the whole.
pH	The degree of acidity or alkalinity of a substance, as measured by the concentration of hydrogen ions. On this scale, pH 1 is a strong acid, pH 14 is a strong alkali, and pH 7 is the point of neutrality.
Electrical conductivity	The ability of a solution to carry an electrical current. Refers to the specific electrical conductance of the water, which is a function of the total dissolved solids. High salinity (high EC) affects plant growth and soil quality.

Environment:	All components of the earth, including air, land, and water; all layers of the atmosphere; all organic and inorganic matter and living organisms; and all interacting natural systems.
Drilling waste fluids	A mixture of water, drilling muds, additives, and various other wastes that specifically relate to the drilling activity.
Drilling waste total waste	The entire contents of a sump or drilling waste storage system, which is considered a single waste for sampling, treatment, and disposal.
Drilling waste clear liquids	Liquids separating from water-based drilling wastes. The liquids appear nonturbid when sampled from the discharge point and qualify for pump-off. The clear liquids may be colorless or may have natural colour or staining.
Drilling waste fluids	A mixture of water, drilling muds, additives, and various other wastes that specifically relate to the drilling activity.
Dissolved hydrocarbons	Hydrocarbons partitioned into the water phase of drilling wastes.

APPENDIX 5

pH Values for Exploration, Development and Production Waste (EPA Samples, 1987)

	Midpoint	Tank bottom	Endpoint	Influent	Tank	Effluent	Central pit	Tank bottom	Pit
Production									
Sludge		7.0;7.0;7.0							
Liquid	6.4;6.6;8.0		2.7;7.6;8.1						
Central Treatment									
Sludge				8.8;8.8;8.8	2.0;3.9;5.8	6.7;8.2;10.0			
Liquid				5.7;6.5;7.3		7.0;8.2;10.1			
Central Pit									
Sludge							7.2;8.0;9.2		
Liquid							5.7;7.5;8.5		
Drilling									
Sludge									6.8; 9.0;12.8
Liquid								7.1;7.1;7.1	6.5;7.7;12.7

APPENDIX 6

Average Elemental Composition of Reserves Pits (EPA samples,1987).

Metal	Phase	Concentration (mg/l)
Calcium	Mud	207
	Water	156
Chromium(Soluble)	Mud	3.97
	Water	2.09
Chromium (Total)	Mud	56.05
	Water	14.47
Lead (Soluble)	Mud	6.51
	Water	0.08
Lead (Total)	Mud	24.46
	Water	3.36
Magnesium (Total)	Mud	17.21
	Water	65.47
Manganese (Soluble)	Mud	0.29
	Water	0.19
Manganese (Total)	Mud	77.67
	Water	4.74
Potassium	Mud	313
	Water	750
Sodium	Mud	1,819
	Water	2,125
Zinc (Soluble)	Mud	0.21
	Water	0.07
Zinc (Total)	Mud	52.54
	Water	5.07
pH	Mud	8.79
	Water	8.10

Average Elemental Composition of Reserves Pits(API samples,1987).

Chromium	**Pit 1 (mg/g)**	**Pit 2 (mg/g)**	**Pit 3 (mg/g)**	**Pit 4 (mg/g)**
Chromium	**10.119**	**8.906**	**11.088**	**7.085**
Barium (Total)	**0.071**	**0.024**	**0.179**	**0.056**
Lead	**0.044**	**0.354**	**0.057**	**0.037**
Zinc	**0.170**	**0.256**	**0.148**	**0.162**

Average Elemental Composition of Res. Pits (private study,API&EPA samples,1987).

Metal	**Private study (mg/g)**	**API (mg/g)**	**EPA (mg/g)**
Arsenic	**0.003**	**0.008**	**0.029**
Calcium	**31.0**	**47.2**	**71.7**
Chromium	**0.016**	**0.017**	**0.081**
Barium (Total)	**29.2**	**N/A**	**N/A**
Iron	**15.1**	**21.2**	**56.8**
Lead	**0.064**	**0.059**	**0.446**
Magnesium	**3.72**	**4.72**	**8.10**
Manganese	**0.273**	**0.393**	**0.940**
Potassium	**2.61**	**1.85**	**N/A**
Sodium	**2.36**	**3.78**	**5.62**
Zinc	**0.120**	**0.189**	**0.683**

Source : From Deuel and Holliday 1990.