ASSESSMENT OF HEAVY METALS IN THE WATER, SEDIMENT, *CLARIAS GARIEPINUS* (BURCHELL, 1822) AND *OREOCHROMIS NILOTICUS* (LINNAEUS, 1758) IN KUBANNI RESERVOIR IN KADUNA STATE, NIGERIA

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MARCH, 2020

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BY

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A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN FISHERIES

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MARCH, 2020

DECLARATION

I declare that the work in this dissertation entitled "**ASSESSMENT OF HEAVY METALS IN THE WATER, SEDIMENT, *CLARIAS GARIEPINUS* (BURCHELL, 1822) AND *OREOCHROMIS NILOTICUS* (LINNAEUS, 1758) IN KUBANNI RESERVOIR IN KADUNA STATE, NIGERIA**" has been carried out by me in the Department of Biology. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Abbas Olagunju JELILI _____ _____

Signature Date

CERTIFICATION

This Dissertation "ASSESSMENT OF HEAVY METALS IN THE WATER, SEDIMENT, *CLARIAS GARIEPINUS* (BURCHELL, 1822) AND *OREOCHROMIS NILOTICUS* (LINNAEUS, 1758) IN KUBANNI RESERVOIR IN KADUNA STATE, NIGERIA" by Abbas Olagunju JELILI meets the regulations governing the award of the degree of Master of Science degree in Fisheries of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research work is dedicated to GOD Almighty for His guidance and protection throughout this programme and to all my family members, friends, relatives and the entire family.

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I am grateful to God Almighty for His abundant mercies who has given me this great opportunity because it is not by might or by my power but the grace of God that sustain me throughout this programme.

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ABSTRACT

This study was aimed at assessing the water quality, concentration of selected heavy metals in the water, sediment and fish species in Kubanni Reservior for 12 months. Purposive and standard methods of experimental analyses were adopted for the research. Three (3) sampling stations were established for collection of water, sediment and fish species. Thirty six (36) samples each were collected for water and sediment as well as seventy (72) samples for fish. Atomic Absorption Spectroscopy (AAS) was used for measurement of the levels of elements. The results shows that Temperature, pH, DO_2, BOD, turbidity, COD, alkalinity, hardness, NO_3-N, PO_4-P, TDS and EC, ranged between within 23.30 -27.57ºC, 6.9 – 8.22H^+, 8.68 – 6.40mg/l, 1.18 - 1.72mg/l, 41.01 – 64.73mg/l, 46.30 – 160.55mg/l, 30.00 – 77.10mg/l($CaCO_3$), 62.80 – 67.63mg/l($CaCO_3$), 0.31 – 0.49mg/l, 0.19 – 0.37mg/l, 89.00 – 197.00mg/l and 117.67 – 261.33µhoms/cm respectively. The physico-chemical parameters varied significantly ($P<0.05$) between the months in the three sampling stations. The mean concentration range of Pb, Mn and Zn in water were 0.00 – 0.24, 0.12 – 0.73 and 0.00 – 0.14mg/l, respectively, while in sediments it ranged from 16.05 – 87.35, 194.40 – 378.21and 155.07 – 259.36mg/kg respectively. Pb in sediments significantly varied between the stations. The mean concentration of Pb in the gill, liver and muscle was 0.35 – 2.15, 0.44 – 1.77 and 0.81 – 1.55mg/kg, respectively in *Oreochromis niloticus* and in *Clarias gariepinus* it was 0.62 – 1.37, 0.29 – 1.68 and 0.37 – 2.58mg/kg respectively. Mn in the gills, liver and muscle of *Orechromis niloticus* were between 43.93 – 90.09, 7.60 – 26.46 and 7.67 – 40.37 mg/kg respectively; Mn in muscle of *Orechromis niloticus* varied significantly ($P<0.05$) between the station. In *Clarias garieinus,* Mn concentration were 26.04 – 69.51, 2.98 – 9.40 and 2.52 – 6.83mg/kg in gills, liver and muscle respectively. The mean concentration of Zn in the gills, liver and muscle of *Orechromis niloticus* ranged between 29.10 – 82.67, 1.98 – 6.40 and 15.33 – 44.14mg/kg respectively. Zn in gills of

Orechromis niloticus varied significantly ($P<0.05$) between the stations. Zn in bt5he gills, liver and muscle of *Clarias gariepinus* were 15.82 – 30.99, 1.30 – 18.21 and 8.18 – 24.10 mg/kg respectively. The levels of Pb in water, Mn in gills of *Clarias gariepinus*, gills, liver and muscle of *Orechromis niloticus* were above the World Health Organization (WHO). limit. The results showed evidence of bioaccumulation of heavy metals in the fish with levels that are higher than WHO limits. There pose a potential health risk for inhabitants that depend on the reservoir for fish consumption and water for domestic use. Constant monitoring of the levels of contamination to assess the impact of the heavy metals is hereby recommended.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information of the Study

Since the dawn of industrial revolution, mankind has been introducing numerous hazardous compounds into the environment at an exponential rate. These hazardous pollutants consist of a variety of chemical substances including heavy metals, which pose a serious threat to fish and human health (Wuana and Okieimen (2011). Metals are introduced into the environment through both anthropogenic and natural processes. The natural processes result from weathering of rock, soil and volcanic eruptions. The anthropogenic source includes several human activities involving mining, processing use of metals, disposal of industrial and domestic wastes. Heavy metals are primarily a concern because they cannot be destroyed by degradation. Frequently, the remediation of contaminated soils, ground water and surface water requires the removal of toxic metal from contaminated areas (Wuana and Okieimen (2011). In most developing countries, water resources remain the main reservoirs of industrial, domestic and agricultural wastes. Hence, streams, coastal environments, including banks of the rivers suffer from metallic pollutants due to increased industrialization arising from urbanization (Wuana and Okieimen (2011).

Generally, reports of heavy metal accumulation in aquatic ecosystem shows that they are either in aquatic organisms or in sediments (Babukutly and Chacko, 1992). Others such as mercury and Lead are not required even in small amounts by living organisms. All heavy metals produce toxic materials if the exposure levels are sufficiently high enough to exceed the maximum allowable concentration or tolerable maximum permissible levels. The concentration of heavy metals in the

environment is associated with biological and geochemical cycles and is influenced by anthropogenic activities such as waste disposal.

In sediment, their occurrence may be of crustal or lithological origin or are added through anthropogenic activities (Asaolu, 1998; Oyakhilome *et al*., 2013). The occurrence of these heavy metals in the environment has brought about the attention of scientists around the world due to their toxic effect at some levels and their possible accumulation in the ecological system. It is now possible to determine the level of contamination of sediments by pollutants and the eventual effect on ecological system can be measured (Muller *et al.,* 1994). However, there is a growing realization to identify the total concentration and the form in which these elements exist in order to modify their toxicity. To assess the environmental impact of polluted sediments, the determination of total trace metal is not sufficient, because it is the chemical form of the metal in the sediment that determines its behavior in the environment and its mobilization capacity. It is well known that metals are present in soil sediment in different chemical forms, which influence their reactivity and hence their mobility and bioavailability (Aiyesanmi *et al.*, 2010; Oyakhilome *et al.*, 2013).

Heavy metals are elements with specific gravity greater than 5.0mg and are metals which can be toxic in small concentrations (Van Nevel *et al.*, 2014). Metals are non-biodegradable and are considered as major environmental pollutants causing cytotoxic, mutagenic and carcinogenic effects in animals (Yunus *et al.*, 2010). Heavy metals such as copper (Cu) and Zinc (Zn) are essential for fish metabolism while some others such as Lead (P) and Cadmium have no known role in biological system (Srikanth *et al.*, 2013). However, in high concentration, these metals tend to accumulate in fish body and later form threat to human health through food chain.

Metals are introduced into the aquatic system through several modes that include weathering of rocks and soils, dissolution of aerosol particles in the atmosphere and through industrial activities such as mining, canning and electroplating which produce metal-rich effluents (Lippmann *et al*., 2003; Kamal 2008; Hingley 2013; Farooq 2014). With increased diversification in industrialization and extensive use of metal-based fertilizer in Nigeria, the concentration of heavy metal pollutants would continue to rise through natural run-off (Palaniappan and Muthulingam 2016).

The presence of heavy metal pollutants in fresh water is known to disturb the delicate balance of the aquatic ecosystem and this has been noticed (Zhou *et al.,* 2008) to manifest in the presence of some irregularities in the fish physicology as fish tends to concentrate some metals in their body tissue (Whitfield and Elliott 2002; Campbell *et al*., 2003; Amoo *et al.,* 2005; Omoigberale and Ikponmwosa-Eweka 2010; Farooq 2014). Aquatic organisms have the ability to accumulate heavy metals from various sources including sediments, soil erosion and runoff, air deposition of dust and aerosol, and discharges of waste water (Asaolu, 1998). Therefore, accumulation of heavy metals in aquatic organisms can pose a long lasting effect on biogeochemical cycling in the ecosphere. Heavy metals can also adversely affect the growth rate in major carps (Rauf *et al.,* 2009). Multiple factors including season, physical and chemical properties of water can play a significant role in metal accumulation in different fish tissues (Ashraf *et al.*, 2012).

Bioaccumulation of heavy metals in fresh water ecosystem is of global importance in the environment it stems from the persistence toxicity. Metals generally enter the aquatic environment through atmospheric activities caused by industrial effluents, domestic sewage and

mining wastes. The metal contaminants in aquatic system usually remain either in soluble or suspension form and finally tend to settle down to the bottom or are taken by the organisms (Linnik and Zubenko 2000; Ruwali 2016).

According to Phillips and Rainbow (2013), heavy metals are partitioned between water, sediments, suspended solids and aquatic biota in water bodies. Knowledge of the chemistry of any water body is very important in the distribution pattern of aquatic animals and the effect on the life of the aquatic organisms. The chemical speciation of heavy metals in aquatic system biodiversity depends on the specific physical/chemical factors that prevail in the local environments such as salinity, dissolved organics; pH, hardness and sedimentary load all influence the prevailing chemical forms of heavy metals in the aquatic systems. These in turn influence the metal-availability and toxicity (ERNST 2012).

1.2 STATEMENT OF RESEARCH PROBLEM

The increasing rate of human activities on Kubanni Reservoir called for the needs to know the resent status of the water body after dredging activities, fish and sediment risk exposure of heavy metals from untreated agricultural, urban and industrial effluents. Metals are non-biodegradable and are considered as major environmental pollutants causing cytotoxic, mutagenic and carcinogenic effects in man and animals (Wasi *et al*., 2013). This may results in bio-accumulation of heavy metals in man using water and consuming fish caught from this Reservoir since its tributaries pass through populated residential areas, towns and agricultural sites (Sikder *et al*., 2013). There are scanty report of heavy metal pollution in Kubanni Reservior in Kaduna State.

1.3. JUSTIFICATION

Kubanni Reservior is a veritable source of fishery to Zaria community but surprisingly, it has received little or no attention on heavy metals assessment with respect to recent dredging activities carried out. Therefore the need to carry out research with the aim of establishing baseline information and the actual status and potentials of the reservoir. Recent studies have shown for instance that human activities have created ecological pressure on the natural habitat of fish organism over time. There is an upsurge of interest in water pollution as a result of this deleterious effect.

Aquatic organisms such as fish have the ability to accumulate heavy metals from various sources including sediments, soil erosion and runoff, air dust and aerosol, and waste water (Labonne *et al*., 2001; Goodwin *et al*., 2003). Therefore, accumulation of heavy metals in aquatic organisms can pose a long lasting effect on biogeochemical cycling in the ecosphere. Heavy metals can also adversely affect the growth rate in fish species (Rauf *et al*., 2009) Fish are often at the top of aquatic food chain and may accumulate large amounts of metals from the water (Mansour and Sidky, 2007). Metal bioaccumulation is largely attributed to differences in uptake and depuration period for various metals in different fish species (Tawari-Fufeyin and Ekaye, 2007). Multiple factors including season, physical and chemical properties of water Kargin, (1996) as cited by Adefemi and Awokunmi (2010) can play a significant role in metal accumulation in different fish tissues. The gills are directly in contact with water. In view of that, the concentration of metals in gills reflects their concentration in water where the fish lives, whereas the concentrations in liver represent storage of metals in the water (Romeo *et al*., 1999).

The quality of aquatic environment depends on a multiple of physical, chemical and biological interactions Adefemi *et al*., (2008) as cited by Olowu *et al* (2010). Fish distribution generally follows environment quality parameters (Bamidele and Fasakin 2016). This is demonstrated by

continuous circulation, transformation and accumulation of energy and matter through the medium of living things and their activities which upset the dynamic balance in the ecosystem Adefemi and Awokunmi (2010) as cited by Olowu *et al*., (2010).

Sediments have been reported to form the major repository of heavy metal in aquatic system while both allochthonous and autochthonous influences could make a concentration of heavy metals in the water high enough to be of ecological significance Atta *et al*., (1997); Ikem and Egiebor 2005; Adeniyi and Yusuf, 2007; Nwoko and Egonwa 2015) as cited by Olowu *et al*., (2010). Bioaccumulation and biomagnification is capable of leading to toxic level of these metals in fish, even when the exposure is low. The presence of metal pollutant in fresh water is known to disturb the delicate balance of the aquatic ecosystem. Fishes are notorious for their ability to concentrate heavy metals in their muscles and since they play important role in human nutrition, they need to be carefully screened to ensure that unnecessary high level of some toxic trace metals are not being transfer to man through fish consumption (Adeniyi and Yusuf, 2007; Charis and Abbasi, 2005).

1.4 AIM

To investigate some physico-chemical parameters of the water and concentration of heavy metals in water, sediment and some selected fish species in Kubanni Reservior in Kaduna State.

1.5 OBJECTIVES OF THE STUDY

The objectives of the study are to:

I. determine the Physico-chemical parameters of the Kubanni Reservoir;
II. investigate the concentration of Pb, Mn and Zn in the water and sediment of the Kubanni Reservoir.

III. investigate the concentration of Pb, Mn and Zn in *Clarias gariepinus* and *Orechromis niloticus* caught from Kubanni Reservoir of Kaduna State.

1.6 HYPOTHESES

I. There are no significant difference in the physico-chemical parameters of water in Kubanni Reservoir;

II. The concentration of heavy metals in water and sediment of Kubanni Reservoir does not differ significantly at $P < 0.05$;

III. The concentration of heavy metals of the gill, liver and muscle (tissues) of *Clarias gariepinus* and *Orechromis niloticus* does not differ significantly at $P < 0.05$.

CHAPTER TWO

2.0 Heavy Metals Pollution

Heavy metals refer to any metallic chemical element that has relatively high density that is at least 5 times higher than of water (Lars, 2003). Aquatic ecosystems are receiving continuously increasing levels of heavy metals with anthropogenic sources having been identified as the major sources of heavy metal pollutants in aquatic systems (Linnik and Zubenko, 2000; Farkas, 2000; WHO, 2000). In fish, gills are considered to be the dominant site for contaminant uptake because of their anatomical and physiological properties that maximize absorption efficiency from water (Tawari-Fufeyin and Ekaye, 2007). Sediments are important sinks for various pollutants such as pesticides and herbicides while, heavy metals in surface water may exist as simple hydrated ions as well as inorganic and organic complexes (Linnila, 2000; Rashed, 2001).

Some heavy metals such as copper (Cu), zinc (Zn), iron (Fe), chromium (Cr), manganese (Mn) and nickel (Ni) though essential to human body, are toxic at elevated levels, whereas cadmium (Cd) and lead (Pb) are non-essential metals and are toxic even in trace amounts. Toxicity is highly aggravated by their non-degradability and tendency to bio-accumulate to toxic levels (Tuzen, 2003).Heavy metal toxicity can result in lower energy levels and damage blood composition, lungs, liver, kidneys and other vital organs, damaged or reduced mental and central nervous function or even cause cancer (Canly and Atly, 2003; Tuzen, 2003;Fernandes *et al*., 2008). Heavy metal poisoning is more likely to result from inhalation, ingestion, skin contact with the metals or compounds from dust, fumes or materials from work place, or in residential settings, especially homes with lead paints or old plumbing (Mtanga and Machiwa, 2007).

Human activities affect the natural geological and biological distribution of heavy metals through pollution of air, water, and soil. Humans are also responsible for altering the chemical forms of heavy metals released to the environment. Such alterations often affect a heavy metal's toxicity by allowing it to bioaccumulate in plants and animals, bioconcentrate in the food chain, or attack specific organs of the body. Bioaccumulation refers to an increase in the concentration of a metal in a biological organism over time, compared to the normal concentration in the environment Many metals and other chemicals accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted (Verma and Dwivedi (2013).

Some heavy metals such as mercury and lead are toxic metals that have no known vital or beneficial effect to organisms, and their accumulation over time in the bodies of an animals can cause serious illness. Certain elements that are normally toxic are, for certain organisms or under certain conditions, may be beneficial. Examples include vanadium, tungsten, and even cadmium. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Therefore, they tend to accumulate in the soil, seawater, freshwater, and sediments (Siddique *et al.,* 2009).

In small quantities, certain heavy metals are nutritionally essential for a healthy life (e.g., iron, copper, manganese, and zinc). Some of these are referred to as the trace elements (Fraga, 2005).

These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products (Vanek, 2012).

2.1.0. The Occurrence of Heavy Metals in Nature

Metals in the environment may be present in the solid, liquid or gaseous state. They may be present as individual elements, and as organic and inorganic compounds. The movement of metals between environmental reservoirs may or may not involve changes of state.

The geosphere is the original source of all metals (except those that enter the atmosphere from space in the form of meteorites and cosmic dust). Within the geosphere, metals may be present in minerals, glasses, and melts. In the hydrosphere, metals occur as dissolved ions and complexes, colloids, and suspended solids (Laskar, 2010).

In the atmosphere, metals may be present as gaseous elements and compounds and as particulates and aerosols (Nriagu; 1989). Gaseous and particulate metals may be inhaled and solid and liquid (aqueous-phase) metals may be ingested or absorbed, thereby entering the biosphere. In addition to being the original source of all terrestrial metals, the geosphere may represent a sink for metals. The atmosphere and hydrosphere also constitute sinks for metals; however, from a geological perspective, they are more likely to be considered as agents of transport.

The movement of metals from one site to another depends on the linear and temporal scales of observation. For example, the oceans are a vast reservoir for a variety of chemical elements. They also serve as a conduit for elements derived from weathering of rocks to return to the geosphere through sedimentation. A reservoir may act as a catalyst for changes of state of metals and metal compounds, without actually having incorporated those metals, as in the case of some biologically mediated reactions (Schalk *et al*., 2011).

2.1.1. Behaviour of Heavy Metals in the Environment

The main source for metal input to plants and soils is atmospheric deposition. Volatile metalloids such as As, Hg, Se, and Sb can be transported over long distances in gaseous forms or enriched in particles, while trace metals such as Cu, Pb, and Zn are transported in particulate phases (Adriano, 2001; Fairbrother *et al.*, 2007). In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the major sink for metals (Sparks, 2005). Freshwater systems are contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids (Adriano 2001).

A number of biogeochemical processes take place at the heterogeneous interface between the rock, soil, water, air and living organisms (Spark, 2005). These processes or interactions in turn control the solubility, mobility, bioavailability and toxicity of metals (Sparks, 2005). Metals are found in soil solution as free ions or complexes to inorganic or organic ligands.

Both die free ions and the metal-ligand complexes can be

(i) taken up by plaints,

(ii) retained on mineral surfaces, natural organic matter, and microbes,

(iii) transported through the soil profile into groundwater via leaching or by colloid-facilitated transport,

(iv) precipitated as solid phases, and

(v) diffused in porous media such as soils.

Microorganisms can transform metals such as Hg, Se, Sn, As and Cr by means of oxidation-reduction and methylation (the process of replacing an atom, usually a H atom, with a methyl

group) mechanisms and dimethylation reactions. These processes affect transport or mobility and solubility or toxicity of metals (Adriano 2001; Sparks 2005). For example, methylated (organic) forms of Hg are more toxic than inorganic forms of the element and they bio-accumulate in organisms. Methylation is favoured in environments characterized by low oxygen levels, low pH, and high soil organic matter (SOM) contents. Heavy metal contamination of soil is a far more serious problem than air or water pollution because heavy metals are usually tightly bound by the organic components in the surface layers of the soil. Consequently, the soil is an important geochemical sink which accumulates heavy metals quickly and usually depletes them very slowly by leaching into groundwater aquifers or bio-accumulating into plants (Singo 2013).

Heavy metals can also be very quickly translocate through the environment by erosion of the sediment particles to which they am adsorbed or bound and re-deposited elsewhere (Saha *et a*l 2017).

The transport, cycling, fate, bioavailability and toxicity of heavy metals are markedly influenced by their physico-chemical forms in water, sediments and soil. Whenever a heavy metal or its compound is introduced into an aquatic environment, it is subjected to a wide variety of physical, chemical and biological processes. These include hydrolysis, chelation, complexation, redox, biomethylation, precipitation and adsorption reactions. Often, heavy metals experience a change in the chemical form as a result of these processes and so their distribution, bioavailability and other interactions in the environment are also affected. They can leach into living systems from natural ore deposits and other sources such as waste disposal of heavy metal containing waste. In fact, waste disposal accounts for higher percentage of most heavy metals including manganese in the environment (Fu *et al.,* 2008)

2.1.2. Uses of Heavy Metals

Heavy metals are important components of building materials, vehicles, appliances, tools and computers; and are essential in the infrastructure including highways, bridges, railroads, airports, electrical utilities and food production and distribution (Sparks, 2005).

Civilization was founded upon the metals of antiquity, gold, copper, silver, lead, tin, iron and mercury (Sparks, 2005). Natural and consumer products contain small concentrations of different heavy metals. For example, cadmium is mainly used in batteries, plastics and it is also found in cigarette smoke, in shellfish and vegetables (ATSDR, 1999).

Mercury is found in batteries, dental amalgam, vacuum pumps and valves. Airborne mercury comes from the combustion of diesel, jet fuel and heating oil. Arsenic is high in seafood and may also be found as a contaminant in animal feeds. It is also present in wood preservatives, herbicides, corrosion inhibitors, in lead and copper alloys (Pandey and Madhuri 2014).

Cadmium is used industrially as an anti-friction agent, as a rust-proofer, in plastics manufacture, in alloys and in alkaline storage batteries. Chromium is found in fresh foods, copy machine toner and nickel in coins, kitchen utensils and milk (Zheng *et al*., 2013). Copper is essential to all living organisms and has a wide range of effects depending on concentration and chemical formulation. It is used in the electrical industry in alloys such as brass, in chemical catalysts and in wood-preservatives. Lead has been used in batteries, electronic equipment, in petrol, toys, paint, etc. Lead has been used as fuel additive in many countries for several years, although this practice has since stopped in most of the countries of the world, because of the health implications of lead (Gorospe and Gerstenberger 2008)

Manganese compounds are used in manufacturing of products such as batteries, steel and unleaded petrol. Manganese dioxide is commonly used in the production of dry-cell batteries,

matches, fireworks, porcelain and glass-bonding materials. It is also used as the starting material for the production of other manganese compounds (Howe *et al*., 2004).

Manganese chloride is a precursor of other manganese compounds. It is used as a catalyst in the chlorination of organic compounds, in animal feed to supply essential trace minerals and in dry-cell batteries (US EPA, 1984). Manganese sulfate is used as a fertilizer, livestock nutritional supplement and in ceramics (US EPA, 1986). As potassium permanganate, it is used as a oxidizing agent and disinfectant in water purification and in waste-treatment plants. It is used in metal cleaning, bleaching and as a preservative for fresh flowers and fruits (Lawton and Robertson 1999)

Currently, methylcyelo-pentadienyl manganese tricarbonyl (MMT) is the most popular lead replacement compound due to its lower production costs (Graboski *et al.,* 2001). The manganese based additive is added in smaller amounts than TEL (tetraethyllead), with a maximum concentration of 18 mg/L (Gooseff, 2003).

2.1.3. The Anthropogenic Sources of Heavy Metals

Much research has been conducted on heavy metal contamination in soil from various anthropogenic sources such as industrial wastes (Nicholson *et al.,* 2003; Olajire *et al*., 2003; Iwegbue *et al*., 2006; Lone *et al.,* 2008; Wuana and Okieimen, 2011; Alloway, 2013), automobile emissions (Lagerwerff and Specht, 1970; Fergusson and Ryan 1984; Garcia-Miragaya, 1984), mining activity (Davies and Ginnever, 1979; Culbard and Johnson, 1984), and agricultural practices (Colboum and Thornton, 1978).

The anthropogenic heavy metals are believed to easily accumulate in the top soil, causing potential problems such as toxicity to plants and animals, accumulation in food chain, perturbation of the ecosystem and adverse health effects (Nagajyoti *et al.,* 2010).

2.1.4. Toxicity of Heavy Metals

Heavy metals are dangerous because they tend to accumulate. Compounds accumulate is living things any time they are taken up and stored faster than they are broken down or extracted (metabolized).heavy metals can enter the water supply by industrial or consumer waste or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and ground waters (Lenntech, 2005). Heavy metals toxins contribute to a variety of adverse health effects. These exit over than 20 different heavy metals toxins that have impacts on human health and each toxin will produce different behavioral physiological and cognitive changes in an exposed individuals. The degree to which a system organ tissue or cell is affected by a heavy metal toxin depends on the toxin its self and the individuals degree of exposure to the toxin (Extreme health USA., 2005). The toxicity of heavy metals can be listed in order of decreasing toxicity as Hg>Cd>Cu>Zn>Ni>Pb>Cr>Al>Co, also this is only approximate as the vulnerability of species to individual metals varies (Gomes *et al* 2001).

2.1.5. Human Exposure and Health Hazards Associated with Heavy Metals

Humans are always exposed to the natural levels of trace elements. Under normal circumstances; the body is able to control some of these amounts. However, continuous exposure to elevated levels of metals could cause serious illness or deaths (Okonkwo and Mothiba 2005; Rollin *et al*., 2005; Moja and Mnisi, 2013). Increased exposure may occur through inhalation of airborne

particles or through ingestion of contaminated soil by children or by absorption through the skin (WHO, 1984).

Metals and their compounds can accumulate in the body's tissues, such as bones or nerves. They can cross the placenta and harm an unborn child in pregnant women. Children are the most susceptible to health problems caused by heavy metals, because their bodies are smaller and still developing (Fergusson and Kim 1991; Thomson 2005). The health hazards presented by heavy metals depend on the level and the length of exposure (Thomson *et al*., 2005). In some cases, the health effects are immediately apparent; in others, the effects are delayed. High levels of toxic metals deposited in body tissues and subsequently in the brain, may cause significant developmental and neurological damage, including depression, increased irritability, anxiety, insomnia, hallucination, memory loss, aggression and many other disorders (Flora, 2014).

2.1.6. MANGANESE

Manganese is considered an essential trace element for plants and animals. Manganese makes up about 1000 ppm (0.1%) of the Earth's crust, thus making it the 12th most abundant element (Emsley, 2001). Manganese occurs principally as pyrolusite (MnO_2), psilomelane (BaH_2O) $2Mn5O_{10}$, and to a lesser extent as rhodochrosite ($MnCO_3$). Manganese compounds are powerful oxidizing agents with various oxidation states (+4, and +7,) and can directly combine with boron, carbon, sulphur, silicon and phosphorous (Emsley, 2001). Dust and smoke containing manganese oxides result from mining, crushing and smelting of ores. Mn (from dust deposits and rainfall) usually accumulates in the upper layers of the soil (Wuana and Okieimen, 2011).

Among the several oxidation states, the +2 oxidation state is the most stable state and the one used in living organisms for essential functions while other states are toxic for the human body.

Depending on their oxidation state, Mn ions have various colours and are used industrially as pigments while MnO_2 is used as the cathode material in standard and alkaline disposable dry cells and batteries.

As a free element, it is a metal with important industrial metal alloy uses, particularly in stainless steels and Mn phosphating used as a treatment for rust and corrosion prevention on steel (Zhang and Cheng, 2007).

Though it is a required trace mineral for all known living organisms, in larger amounts, and apparently with far greater activity by inhalation, Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible (ATSDR, 2002). Mn-related complications also include psychiatric and motor disturbances, termed manganism which has occurred in people employed in the production and processing of Mn alloys (Nussey *et al*., 2000). People exposed to high levels of environmental pollution by Mn suffer from cerebella dysfunctions, neurological damage as was once observed in inhabitants of Groote Eylandt off the North coast of Australia (Reilly, 2002).

Manganese is involved in many enzyme systems and in electron transport. In solution, it occurs as the Mn^{2+} ion. Under oxidizing conditions, most of the manganese precipitates as insoluble $Mn0_2$. Mn in soil exists in three valence states, Mn^{2+}, Mn^{3+} and Mn^{4+}. The Mn^{2+} is considered to be the easily accessible form to the plant, while Mn^{3+} is accessible depending upon the soil conditions. The tetravalent manganese (Mn^{4+}) is considered as inaccessible to the plant. These three forms exist in a state of dynamic equilibrium. Organic matter decomposition aids manganese solubility. Toxic concentration of manganese is more likely than that for Zn, Fe or Cu. Toxic levels occur only in strongly acidic soils.

Prolonged inhalation of high levels of manganese negatively affects the central nervous system, visual reaction time, hand steadiness and eye-hand coordination (EPA, 2003).

Studies in fish for Mn have been recorded in fish from different rivers (Oguzie and Izvebigie 2009; Obasohan, 2008). Mn mean levels in fish from Ogba River ranged from 0.0 to 0.75mg/kg, and also Mn concentration of 17.37 mg/kg in fish gills from River Nile have been reported (Oguzie and Izvebigie 2009; Obasohan, 2008; Alaa and Osman, 2010). The high concentrations of Mn are attributed to the gills being the dominant site for contaminant uptake because of their anatomical and/or physiological properties that maximize absorption efficiency from water (Alaa and Osman, 2010).

Kage, (2003) Mn reported that ranged from 1598.33 to 4322.83 mg/kg in Nairobi river. Mn concentration in sediments from River Nile ranged from 139.8 to 351.8 mg/kg (WHO, 2003; Alaa and Osman, 2010).

Various levels of Mn limit in river water recommended by WHO is 0.4 mg/l (WHO, 2003); Mn levels from River Nile that was within the recommended limits fluctuated between 0.033 and 0.14mg/l while higher levels of 2.5 mg/l and 0.423 mg/l were recorded from Nairobi River and River Ganga respectively (FAO, 2003a; Wachira, 2007; Kar *et al*., 2008; Alaa and Osman, 2010). The higher levels than the recommended limit of 0.4 mg/l was attributed to a sudden rainfall followed by high river discharge from upstream environment, industrial effluents and municipal wastes, geology of river bed and catchment area (Wachira, 2007; Kar *et al*., 2008).Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the river water quality (Kar *et al*., 2008).

2.1.7. Lead and it toxicity implication

Lead has a density of 11.3g/cm^3 atomic number 82 and is obtained from its sulphide mineral galena, carbonate cerussite, and sulphate anglesite. The ores are frequently found in combination with other recoverable metals such as Cu, Zn and Cd. Lead exists in various oxidation states (O, I, II and IV), which are of environmental importance with oxidation +2, the form in which most Pb is bio-accumulated by aquatic organisms (Ibemenuga, 2013).

Lead was placed position 2 on the Agency for Toxic Substances and Disease Registry's (ATSDR) top 20 list of most dangerous heavy metals and it accounts for most of the cases of pediatric heavy metal poisoning (ATSDR, 2002).Lead has been used in pipe making, drains and soldering materials as well as battery manufacture, plumbing, ammunition, fuel additives, paint pigments and pesticides (ATSDR, 2005).

Metallic lead does not dissolve in water and does not bum, however, lead can combine with other chemicals to form lead compounds or lead salts. Some lead salts dissolve in water better than others. Although lead itself cannot be broken down, lead compounds in water may combine with different chemicals depending on the acidity and temperature of the water.

Most of the lead used by industry comes from mined ores (primary) or from recycled scrap metal or batteries (secondary). The main sources of lead pollution are lead smelters, battery manufacturers, paper and pulp industries, boat and ship fuels and ammunition industries. In addition, the production of television picture tubes, pigments, petroleum fuels, printing, glass industries, photographic materials, etc., also adds Pb (II) to the environment (Kiff, 1987). People living near hazardous waste sites may be exposed to lead by breathing air, drinking water, eating foods, or swallowing or touching dust or dirt that contains lead (ATSDR, 1999a). For others (people who do not live near hazardous waste sites), exposure to lead may occur by eating foods

or drinking water that contain lead, by spending time in areas where leaded paints have been used, by working in jobs where lead is used, by having hobbies in which lead may be used such as sculpturing (lead solder) and staining glass.

Cigarette smoke also contains small amounts of lead. Lead may enter foods if they are put into improperly glazed pottery or ceramic dishes and from leaded-crystal glassware.

The effects of lead exposure are the same whether it is breathed or swallowed. Low levels of lead have been identified with anemia as it causes injury to the blood forming systems while high levels cause severe dysfunction of the kidneys, liver, the central and peripheral nervous system (Jain *et al*., 1989), and high blood pressure (ATSDR, 1999a).

Hypertension has also been associated with lead exposure in the general population. At the typical levels to which individuals are exposed, lead can cross the placenta and damage developing fatal nervous systems. High level exposure to lead may cause miscarriage in pregnant woman and can also damage the organs responsible for sperm production in male (Martin and Griswold, 2009).

The most severe neurological effect of lead in humans is lead encephalopathy, which is a general term to describe various diseases that affect brain function. Lead exposure may cause weakness in fingers, wrists, or ankles (Martin and Griswold, 2009).

Children are more sensitive to the effects of lead than adults (Linton *et al*., 1980). A child who swallows large amounts of lead may develop blood anemia, kidney damage, severe stomachache, muscle weakness, and brain damage (Thornton *et al*., 1989). The lower intellectual quality levels and other neuropsychological deficiencies among the children exposed to higher lead levels have been well documented (Kotok *et al*., 1977). Lead acetate and lead phosphate have been shown to

be potential carcinogens based on studies in animals. However, there is inadequate evidence to clearly determine lead's carcinogenicity in humans (Jarup, 2003).

Lead poisoning damages the nervous system, kidneys, liver and cause sterility, growth inhibition, developmental retardation (Von Schimding & Fuggle, 1996). Lead is toxic at all levels, hence lead based petrol, toys and paints have been banned (Moja and Mnisi, 2013).

Lead has been of particular concern due to its toxicity and ability to bio-accumulate in aquatic ecosystems, as well as persistence in the natural environment (Miller *et al*., 2002; Anim *et al*., 2010). Lead is known to accumulate in fish tissues such as bones, gills, liver, kidneys and scales, while gaseous exchange across the gills to the blood stream is reported to be the major uptake mechanism (Oguzie and izvebigie, 2009; Tawari-Fufeyin and Ekaye, 2007). Some effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anemia due to reduction of enzymes concerned with synthesis of red blood cells (Lars, 2003).

Lead also leads to decreased fertility, causes cancer and other minor effects like vomiting, nausea, and headache (Lars, 2003; WHO, 2008). Exposure to high Pb levels can severely damage the brain and kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men and it may ultimately cause death (ATSDR, 2002).

Since fish have ability to bio-accumulate metals for a long time, the level of metal ions at a particular time may not give accurate information on concentration at that particular time. Pb levels recorded in Ogba, Warri and Ikpoba Rivers were lower than WHO and FEPA standard limit of 2.0mg/kg for food fish which implied that the consumption of these river’s fish as far as

Pb contamination is concerned were safe (Oguzie and izvebigie, 2009;Obasohan, 2008). High concentrations in fish of over 2.0 mg/kg during dry season were attributed to the high water temperatures associated with the dry season (Obasohan, 2008). Higher temperatures can result in higher activity and ventilation rates in fish and tend to lower oxygen affinity of the blood and thus increase the rate of pollutant accumulation (Nussey *et al*., 2000; Obasohan, 2008). A higher temperature could also lead to higher metabolic rates, which could induce more feeding and in turn result in increased metal concentration, if the metals are taken up via food chain (Nussey *et al*., 2000); meaning that, Nile river was polluted and needed constant control and assessment (Awofolu *et al*., 2005; WHO, 2008;Alaa and Osman, 2010). Elevated levels of Pb could be directly detrimental to the health of the aquatic ecosystem and indirectly to man. The sediments could be a contributing source of these heavy metals in water, hence continual assessment was highly essential (Awofolu *et al*., 2005). Also, Agatha (2010) recorded Pb mean levels of 9.43 mg/kg from Forcados River in sediment samples that were lower than the WHO recommended limit of 35mg/kg. Decreasing concentrations of Pb metal away from pollution point has been recorded which was attributed to dilution effect as a result of runoff or rain water with a big part of heavy metals in sediments being released back to water compartment in the process of remobilization (Kar *et al*., 2008; Öztürk *et al*., 2009; Agatha, 2010).

Studies from Ikpoba River recorded Pb mean concentration of 0.035mg/l in water and also Pb mean levels of 0.1 mg/l was obtained from Nairobi river which surpassed the recommended limit of 0.01mg/l for drinking water set by WHO (WHO, 2003; Kithiia, 2006; Oguzie and Izevbigie, 2009). Oguzie and Izevbigie, (2009) reported that the level of Pb in the water though lower than <1 mg/l value recommended for portable drinking water by the Federal Ministry of Environment and the World Health Organization requires that caution be taken in the discharge of effluents

without treatment into Nigeria's in-land water bodies. This was because anthropogenic sources have been implicated as the major cause of pollution in aquatic environment (Kithiia, 2006; Oguzie and Izevbigie, 2009). Kithiia, (2006) recommended use of riverine vegetation as useful in absorbing heavy metals as a means of purification.

2.1.8. Zinc

Zinc makes up about 75 ppm of the Earth's crust, making it the 24th most abundant element with a density of 7.14g/cm^3. Zn is normally found in association with other base metals such as Cu and Pb in ores and has a low affinity for oxygen and prefers to bond with sulphur and occurs as ores such as sphalerite (ZnS), calamite ($ZnCO_3$) and zincite (ZnO). Zn forms alloys such as brass and bronze and has been used in construction of buildings, roofing and cladding (Emsley, 2001).

Other uses of Zn include making circuit boards, photocopiers, dry cell batteries and its compounds are used in chemical and pharmaceutical industries such as paints, medicines and nutritional supplements (Reilly, 2002).

Zinc is an essential trace element it plays a role in humans, carbohydrate, lipid and protein metabolism and in the synthesis and breakdown of DNA. Because of these functions, zinc deficiency in the fetus will result in retarded growth malformation of body, and chromosomal abnormalities. A zinc deficiency after birth may result in dwarfism, poor appetite, mental lethargy, etc (Prasad, 1991).

Its deficiency as well as excess is harmful. Recent research has shown that zinc is extremely important especially in fetal development and the nutrition of infants. The adult human body contains about 2.3 g of zinc which occurs mostly in over 100 enzymes. The normal daily requirement for zinc is 15 mg for adult and 5 mg for children (Maret and Sandstead, 2006).

The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption while free Zn^2+ion in solution is highly toxic to plants, invertebrates, and even fish (FAO/WHO, 2003). Excess Zinc salts can cause nausea, abdominal pain or stomach cramps, vomiting, central nervous system disorder (ATSDR, 2002) on the other hands prolonged exposure to high intakes of Zn results in copper deficiency and subsequent anemia (Reilly, 2002); It has been reported that zinc is able to damage nerve receptors in the nose, which can cause anosmia and recommended that consumers should stop using zinc-based intranasal cold products and ordered their removal from store shelves (Johnson *et al*., 2007; Safty *et al*., 2008). There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed Zn oxide formed during the welding of galvanized materials (Sihag and Wadhwa, 2017).

Nriagu (1980) stated that zinc is toxic also for aquatic biota. Most of the rocks in the earth's crust contain zinc in varying concentrations. Depending on the type of the rock, highest concentration is found in basic eruptive rocks (e.g. basalt, 70-130 mg/kg). An average concentration of 50-60 mg/kg is generally found in acid eruptive (granite' rhyolite) rocks. Zinc is found in relatively high concentration in soils (50mg/kg on an average) (Aubert and Pinta, 1980). Zn content in soil is much higher in the vicinity of ore deposits and smelters. Atmospheric deposition increases Zn concentration in surface soil in Zn2+ form and in complexes. The concentration is low in the surface soil, but increases in greater depth. Zn is an essential growth element for plants and animals, but at elevated levels, it is toxic to some aquatic species (APHA, 1995). Excessive Zn in soil may cause damage to plants and at lower pH, the yield is reduced (Aubert and Pinta, 1980).

Various Zn mean levels from fish have been recorded from different rivers that have been lower than the 75 mg/kg recommended limit for fish and fish products. Zn mean levels of 9.67 mg/kg

from Forcados River and 1.26 to 2.38 mg/kg Zn in the fish gills from Ikpoba River for the dry and wet seasons respectively, were all within the WHO set limits of 75 mg/kg Zn in fish and fishery products and did not constitute immediate hazards (FAO, 2003; Oguzie and Izevbigie, 2009; Agatha, 2010).

River sediments have been found to have levels of Zn in a number of rivers with values that vary from the recommended limit of 123 mg/kg (Kage, 2003; WHO, 2003; Alaa and Osman, 2010; Agatha, 2010). Zinc concentrations of 91.5 to 307 mg/kg have been recorded in sediments from Nile River during the dry season. 34.61mg/kg from Forcados River's sediments and 126.33-307.00 mg/kg from Nairobi River's sediments were obtained where some did not constitute immediate hazard to aquatic fauna and human consumers (Kage, 2003; Alaa and Osman, 2010;Agatha, 2010). A concentration of 0.60 mg/kg from Nairobi River was found to be below the recommended limit of 123 mg/kg for Zn in sediment (Wachira, 2007). Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was, however, recommended (Wachira 2007; Agatha, 2010).

Levels of Zn in rivers flowing through industrial or mining areas can be as high as 20 mg/l while soils contaminated with Zn through the mining of zinc-containing ores, refining, or where zinc-containing sludge is used as fertilizer, can contain several grams of zinc per kilogram of dry soil (Emsley, 2001). A higher Zn mean level of 76.25 mg/l than the 3 mg/l recommended limits was recorded from Forcados River while lower mean levels of 0.085 mg/l during dry season and 0.716 mg/l during wet season from River Ganga's water and 1.0 mg/l from Nairobi River's water were recorded (WHO, 2003; Kithiia, 2006; Kar *et al*., 2008; Agatha, 2010). This level was attributed to land use activities such as agriculture system and effluent from residential and industrial area. Downstream decrease in water pollutants was observed and was attributed to the

dilution effect and self-purification. Constant monitoring of the levels of contamination to assess the impact of the heavy metal in the aquatic system and use of riverine vegetation was recommended as useful in absorbing heavy metals as a means of purification (Kithiia, 2006; Agatha, 2010).

2.1.9. Heavy Metals in Sediments

Sediments represent an important sink for trace metals in aquatic systems. Concentrations of heavy metals in sediment can be greater than the overlying water. More than 90% of the heavy metal load in aquatic systems is bound to the suspended particulate matter and sediments (Calmano *et al*., 1993). The distribution of heavy metals in sediment closest to populated areas can provide researchers with evidence of the anthropogenic impact on ecosystems and help to assess the risks associated with discharged human waste. Because of their large adsorption capabilities, fine-grained sediments represent a major repository for trace metal and a record of the temporal changes in contamination. Thus, sediments can be used for historical reconstruction. Sediment core studies have been used as pollution records over the last decades. The core studies has shown to be a great tool for establishing effects of anthropogenic and natural processes on depositional environments.

The accumulation of heavy metals in mangrove sediments has been reported for a number of countries including Hong Kong, Brazil and Nigeria (Machado *et al*., 2002; Liang *et al*., 2003; Essien *et al*., 2009). Although there have been investigations on the levels of heavy metals in marine sediments of Malaysia (Yap *et al*., 2002), heavy metal data for local mangrove habitants are lacking. The metal contents in sediments are often used to describe the contamination of metals in different environment. For instance Li *et al*. (2007) studied on heavy metals in coastal wetland sediments of the Pearl River Estuary, China. The total concentrations of heavy metals

such as Zn, Ni, Cr, Cu, Pb and Cd, and their chemical speciation were investigated. The results showed that the sediments were significantly contaminated by Cd, Zn and Ni. Pb, Cd and Zn that was strongly associated to with exchangeable fractions, while Cu, Ni and Cr were predominantly associated with organic fractions. The results found Cd and Zn would be the main potential risk and the sediment quality is no longer meeting the demand of the current wetland utilization strategies (Li *et al*., 2007). Zheng *et al*. (2008) have investigated the distribution and sources of Hg, Pb, Cd, Zn and Cu in the surface sediments of Wuli River, Cishan River and Lianshan River. They also assessed heavy metal toxicity risk with the application of two different sets of Sediment Quality Guideline (SQG) indices. The results showed that Hg contamination in the sediments of Wuli River was originated from the previous sediment contamination of the chlor-alkali producing industry, whereas Pb, Cd, Zn and Cu contaminations were mainly derived from atmospheric deposition and unknown small pollution sources. The heavy metal contamination to Cishan River sediments was mainly derived from zinc plant while sewage wastewater was the main primary source for Lianshan River. Hg is the major toxicity contributor to Wuli River and Lianshan River followed by cadmium. In Cishan River, Cd is the major sediment toxicity (Zheng *et al*., 2008).

Analyses of heavy metals from sediment samples from 59 stations spread throughout the Yangtze River intertidal zone indicated that the metal concentrations showed significant spatial variation. The results from statistical analyses have suggested that the concentrations of Cd were closely related to total organic carbon content whereas Cu, Cr, Ni, Pb and Zn had a close association with Mn. This study also suggests that the metal contamination cannot be simply evaluated by examining metal concentrations alone. A complementary approach that integrates sediment standard criteria, enrichment factor and geoaccumulation index should be considered in

order to provide a more accurate appraisal of the fate and transport of metals from anthropogenic sources and the resultant environmental impact of these materials on intertidal sediments (Zhang *et al*., 2009).

Fractionation of heavy metals in sediments can help in understanding potential hazards of heavy metals. Study done by Li *et al*., (2007) analyzed total concentrations and fractions of selected heavy metals (Cd, Cr, Cu, Pb, and Zn) in surface sediments from Dianchi Lake, Yunnan Province, China, in addition to factors that may affect distributions of the various heavy metal fractions. Total concentrations of the heavy metals decreased in the order Zn > Cu > Pb > Cr > Cd. These heavy metals, except Cr were much higher than their background levels, showing that the Dianchi Lake was polluted with Cd, Zn, Pb, and Cu. Cadmium and Zn occurred mainly as the non-residual fraction. In contrast most of the Cr, Pb and Cu occurred in the residual fraction. Correlation analysis showed that total heavy metal concentrations, organic matter and reducible Fe were the main factors affecting the distributions of the various heavy metal fractions. In the Waihai section of Dianchi Lake, the concentrations of Cd, Zn, Pb, and Cu in the non-residual fraction were significantly lower than those of the Caohai section. This indicated that potential heavy metal hazards in the Caohai section were greater than the Waihai section.

Morillo *et al*., (2002) analyzed seventeen sediment samples from the Odiel and its main tributaries. The chemical partitioning of metals (Cu, Zn, Cd, Pb, Fe, Ni, Cr and Co) in each sample was determined in four fractions (acid-soluble, reducible, oxidizable and residual). The total content of each of the metals was also determined. The results revealed high concentrations of Fe, Cu, Zn, Pb and Cd, as a result of contamination from the mining and industrial activity. Based on the chemical distribution of metals, Cd, Zn and Cu were the most mobile metals. Cd is the metal that showed the highest percentages in the acid-soluble fraction and the lowest in the

residual fraction. However, Pb, Fe, Cr and Ni are present in the greatest percentages in the residual fraction, which implies that these metals are strongly bound to the sediments.

Another study done by Yap *et al*., (2002) had focused on concentrations of Cu and Pb in the offshore and intertidal sediments of the west coast of Peninsular Malaysia. It was found that total Cu and Pb from the west coast of Peninsular Malaysia were generally low and similar to those already reported in other Malaysian localities. For the offshore sediment, the higher metal levels indicated that the offshore area of the Straits of Malacca had started to receive impact from the sea-based activities. The elevated levels of metals found in the intertidal sediments could be due to land-based activities in general (Yap *et al*., 2002).

2.1.10. Heavy Metals in Aquatic Organisms

Fish and marine products contain many elements which are essential for human life at low concentration. Nevertheless, they can become toxic at high concentrations. However, certain heavy metals such as mercury, cadmium and lead do no show essential functions in life and are toxic even at low concentration when ingested over long period. These metals were present in the aquatic environment long before human being existed. The proportion between the natural background concentration of heavy metals and anthropogenic heavy metals in fish varies from element to element. In unpolluted areas, fish normally carry natural burden of heavy metal concentration. In heavily polluted areas, the heavy metal concentrations actually found are exceeding the natural concentration (Kalay *et al*., 1999).

Fish and other aquatic animals take up heavy metals from their food and water that passes through their gills. The uptake of metals is often dependent on the amount of food ingested and on the heavy metal content of the food. Accumulation takes a long time and may result in high concentrations in aged organisms. Some species, which are relatively long lived, are known for

storing higher amounts of heavy metals in different organs. The main organs which are used in fish for storage and detoxification of heavy metals are liver, kidney and bones. These organs are normally not used for human consumption in Europe and America. In Asia, however, smaller fish are consumed completely and other gut contents often are used in fermented sauce or salted. There is a vast literature on the content of heavy metals in fish, mollusk and crustaceans. Majority of these papers have reported high concentrations of heavy metals which are due to anthropogenic activities. The parts that are mostly investigated for heavy metal concentration are organs and tissues which normally accumulate and store heavy metals (Dural *et al*., 2007).

Less information is available about the heavy metal content in the edible part consumed by humans. Abdullah, (2007) found that mollusk has a potential to be used as bio-indicator for the contamination of Cd and Zn in water and sediment of an estuarine environment, as indicated by its high concentration factors (BCFs) values. The species seemed to accumulate certain metals in its tissue and resisted the entry of others from its surrounding environment. Study done by Mohammad and co-workers (2002) on heavy metal concentrations in water and tiger prawn (Penaeus monodon) from Sabah, East Malaysia had shown that there was no general correlation between metal levels in water and in the prawn tissue. The data suggested complexities in uptake and retention of metals in tiger prawns. The animal seemed to resist the build-up of certain metals whereas it allowed the entry of others to the extent of exceeding the proportion that occurred in the environment. Some of the controlling factors include the nature of the metals, environmental factors, the body's reaction, physiological tolerance, tissue thresholds and regulatory mechanisms (Mohammad *et al*., 2002). Ahmad *et al*., (1995) had studied the level of heavy metals in ten species of marine prawns along the coastal areas of Peninsular Malaysia. It was found that the levels of trace metals in most of the samples studied were below the

maximum permissible limit of the Food Regulations in Malaysia, with the exception of a few samples collected from the coasts of Melaka and Matang, which contained higher levels of Pb and Cd. However, there was no clear evidence on the relationships of heavy metals in sediments and prawns (Ahmad *et al*., 1995).

In the southern part of the Korean Peninsula, concentrations of trace elements in the tissue of Mytillus galloprovincaialis varied with size of mussels, season, depending on many factors like sexual development, and seawater temperature. The levels of some trace metals in seawater were correlated significantly with those in soft tissue and byssal threads. There were spatial variations in metal concentrations in the soft tissue and byssus attributed to different sources of trace elements located near the sampling sites. Significant relationships were found between heavy metals in mussel soft tissues and byssal threads and suspended matter (Wang *et al*., 2005).

2.1.11. Distribution Pattern of Heavy Metals in Tissues and Organs

The difference in the accumulation of trace metals in various organs of fishes may be attributed to the proximity to the tissues to the availability of the metals. The age, size and feeding habits of fish or aquatic animals as well as their retention time in polluted waters may affect the heavy metals accumulation in these organisms. For fish, the gills, skin and digestion tract are potential sites of absorption of water borne chemicals. There may be variations in the bioaccumulation of different metals in fish. Kidneys and liver tend to accumulate maximum heavy metals concentrations due to their capacity to accumulate trace metals brought by blood from other parts including gills and muscles. This will induce the binding protein, metallothionein that is believed to play a crucial role against the trace metals by binding them. (Adhikari *et al*., 2009).

Adhikari *et al*., (2009) found that muscle of various fish species from Kolleru Lake, India contained the lowest concentrations of trace metals among all the tissues investigated. Muscle

does not come into direct contact with the metals as it is totally covered externally by the skin that in many ways help the fish to ward off the penetration of the trace metals (Adhikari *et al.*, 2009). Since it is not an active site for detoxification and therefore transport of trace metals from other tissues to muscle does not seem to arise.

Liver tissues in fish are more often recommended as environmental indicator organisms of water pollution compared to any other fish organs. This is possibly because liver tend to accumulate pollutants of various kinds at higher levels from their environment as reported by Tanee *et al*., (2013). The accumulation of the tested metals in liver could be based on the greater tendency of the elements to react with the oxygen carboxylate, amino group, nitrogen or sulphur of the mercapto group in the metalothionein protein (Kendrick *et al*., 1992).

Papagiannis *et al*., (2004) have evaluated the level of contamination of two heavy metals appearing at high concentrations in lake water in four fish species (*Cyprinus carpio, Silurus aristotelis, Rutilus ylikiensis,* and *Carassius gibelio*) caught in the lake. The metal concentrations were determined in three different tissues, namely muscle, liver and gonad in order to assess the metal contamination in these tissues. The study showed that *Cyprinus carpio* and *Rutilus ylikiensis* were contaminated with the highest metal content. Tissue analysis revealed that liver and gonads have accumulated the highest levels of Cu and Zn. Metal concentrations in the edible part of the examined fish such as muscle were at the safety permissible levels for human consumption (Papagiannis *et al*., 2004).

2.1.12. Bioaccumulation

Bioaccumulation is a general term describing a process by which chemical substances accumulate in aquatic organisms, with the term bio concentration referring to concentrations greater than those present in the external environment. Bioaccumulation integrates the overall process of chemical uptake and retention, and has been described by various authors through studies on uptake kinetics, metabolism and excretion/depuration, tissue distribution and compartmentalization, complexation, storage and bio-concentration. Bio-concentration is a consequence of exposure, but cannot be considered a true response, since few data exist that provide direct cause and effect evidence between tissue residue levels and chronic or sub lethal effects. For most components of AMD, a given concentration has unknown consequences for the organism or the population, or on other species through community interactions (Van der Oost, 2003).

This discussion of bioaccumulation is restricted to its suitability as an indicator of field exposure to contaminants. Therefore, little effort is spent to describe the uptake kinetics, depuration or metabolism of these metals associated with acid mine drainage. The discussion concentrates on the potential use of whole body, tissue and blood metal levels to indicate ambient metal levels (Phillips, 2017).

2.2.0 Sources of heavy metals

2.2.1 Waste Disposal

Many metals specially Cu, Cd, Pb, Sn and Zn are dispersed into the environment in leachates from landfills. Which pollute soils and ground waters, and in fumes from incinerators.

2.2.2 Agriculture Material

Agriculture constitutes one of the most important non-point sources of metals pollutants. The main sources are:

a. Impurities in fertilizers: Cd, Cr, Pb, Mo, U, V, Zn, (eg Cd and U in the phosphatic fertilizer);

b. Pesticides: Cu, As, Hg, Pb, Mn, Zn (eg Cu, Zn and Mn – based fungicides, Hg seed dressings and historical Pb-As orchad sprays);

c. Disscants: As for cottons

d. Wood preservative: As, Cu;

e. Wastes from intensive Pig and poulty productions: As, Cu;

f. Composts and manures: Cd, Cu, Ni, Pb, Zn, As;

g. Sewage sludge: specially: Cd, Ni, Pb, Zn, As (also many other elements);

h. Corrosion of metal objects (e.g. galvanized metal roofs and wire fences (Zn, Cd) (Hassaan *et al.*, (2016).

2.2.3 Geochemical Sources

In geological terms, heavy metals are included in the group of elements referred to as (trace metals) which together constitute less than 1% of the rocks in the earth crust; the macro elements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, P and S) comprise 99% of the earth crust. The natural enrichment of metals in the soils may still give rise to harmful effect to living organisms (Hassaan *et al.*, (2016).

• Lead (Pb) lead acid batteries, paints, E-waste, smelting operations, coal- based thermal power plants, ceramics, and bangle industry

• Mercury (Hg) Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste (damaged thermometers, barometers, sphygmomanometers), electrical appliances etc.

• Arsenic (As) Geogenic/natural processes, smelting operations, thermal power plants, fuel

• Copper (Cu) Mining, electroplating, smelting operations

• Vanadium (Va) Spent catalyst, sulphuric acid plant

• Nickel (Ni) Smelting operations, thermal power plants, battery industry

• Cadmium (Cd) Zinc smelting, waste batteries, e-waste, paint sludge, incinerations & fuel combustion

• Molybdenum (Mo) Spent catalyst

• Zinc (Zn) Smelting, electroplating (Hassaan *et al.*, (2016)

2.2.4 Other sources of heavy metals pollution include:

i. Batteries – Pb, Sb, Zn, Cd

ii. Pigments and paints - Pb, Sb, As, Cd, Mo, Si, Co, Zn

iii. Catalysts – Ni, Mo, I, Co, Rh

iv. Polymer stabilizers- Pb, Sn, Zn, Cd (for incineration of plastic)

v. Printing and graphics- Se-(Xerox process), Pb, Zn, Cd

vi. Medical use-dental alloys- Ag, Sn, Hg, Cu, Zn

vii. Drugs/medicinal preparation – AS, Sb, Bi, Ba, Se, Li, Ta

viii. Additive in fuels and lubricants- Pb, Se, Te, Mo, Li, Recent Research in Science and Technology (2013).

2.3.0 BIOLOGICAL PARAMETERS

2.3.1. Fish

Fish play a vital role in the circulation and recirculation of nutrient in aquatic environment. It was recognized by Wetzel (2001) that the composition, abundance and diversity of benthos can

be modified overtime by continuous and or increased artificial eutrophication of an aquatic ecosystem. As a result, these organisms have been found useful and reliable as biological indicators of the quality of the water.

Composition and abundance of fish vary spatially due to several factors among which the most important are the physicochemical characteristics of the sediment associated with depth and the speed of water current (Wetzel, 2001). Morgan *et al*., (1988) suggests that water speed in excess of 2-3m/s inhibit the development of benthos in any water channel. The role of benthos as fish food is well known.

Gill tissues play an important role in interface with the environment in performing its functions in gas exchange, ion regulation, acid balance, and waste excretion while muscle on the other hand is not an active tissue in bioaccumulation (Filazi *et al.,* 2003, Bajc *et al.,* 2005, and Shukla *et al.,* 2007). Gills have been reported as metabolically active site and can accumulate heavy metals in higher level (Murtala *et al.,* 2012). This is evidenced by the position that the gills occupied in the accumulation pattern for the heavy metals. Furthermore, the adsorption of metals onto the gills surface as the first target for pollutants in water could also be a significant influence in the total metal levels of the gill. Target organs such as gills, liver, heart, kidney, and intestine are metabolically active parts that can accumulate heavy metals in higher levels as shown in the works of (Eneji *et al*., 2011, Murtala *et al.,* 2012) and also in the present study. Deb *et al*., (1999) reported that metal may be in high concentrations in gill, lung, and digestive gland because of relatively high potential for metal accumulation.

2.3.2. Description and Classification of the Experimental fish

The African catfish (*Clarias gariepinus* Burchell, 1822) locally referred to as mudfish belongs to the Phylum Chordata; Class Osteichytes; Order Siluriformes; Family Clariidae and Genus Clarias. In Africa, more than one hundred different species (100) have been identified for which about nines species features prominently in African aquatic ecology. There are nine (9) common Clarias species 5 *gariepinus, Clarias anguillaris, Clarias pachynema, Clarias macromystax, Clarias agbonyiensis, Clarias buthupogon, Clarias lazera, Clarias macracanthus and Clarias tsanensis* (Graaf *et al*., 1995 and Teugels, 1982).

Ecologically, Tuegels (1982) confirmed that the *Clariidae* can be found in stagnant water, lake, pool, and running water body. They are hardy such that they can survive wide range of extreme aquatic conditions Tuegels (1982). This distinct characteristic is traced to their accessory breathing lungs that complement their gills which enable them to live several hours outside water body. The fish is very active at night, a bottom feeder and omnivorous in its feeding pattern. However, they also exhibit predatory behaviour mostly at night hence they are mostly referred to as nocturnal fish and do not reproduce in captivity. Naturally therefore, they are involved in migratory breeding during the onset of rains where they move from deep water to shallow water especially with running water. In captivity in pond, they often wriggle out of the body of water to carry out land excursion for a long distance.

The *Oreochromis niloticus,* is an African freshwater Cichlid and one of the world's most important food fishes it belongs to the Domain: Eukaryota, Kingdom: Metazoa, Phylum: Chordata, Subphylum: Vertebrata, Class: Actinopterygii, Order: Perciformes, Family: Cichlidae, Genus: *Oreochromis*, Species: *Oreochromis niloticus*. Owing to its hardy nature, and its wide range of trophic and ecological adaptations, it has been widely introduced for aquaculture,

augmentation of capture fisheries and sport fishing (Trewavas, 1983; Welcomme, 1988), and is now found in every country in the tropics. The Nile tilapia is often described as 'pioneer' species, meaning it thrives in disturbed habitats, opportunistically migrating and reproducing. These traits mean that Nile tilapia often outcompetes native species in areas where it has been introduced.

2.3.3. Tissue Levels of Fish

There have been many attempts to use tissue metal levels to monitor the impacts of contaminated environments. Muscle metal burdens are used as an integrator of contaminant levels over long time periods. Limits on fish tissue levels of metal contaminants have been set to protect human health, and non-lethal methods have been described for sampling muscle (Skurdal *et al*., 1986). However, total metal levels in axial muscle may not be reflective of exposure concentrations. Variation between tissues in the tendency to accumulate metals has been widely documented and, despite elevated metal levels commonly found in metabolic tissues, levels in axial muscle may, in fact, be significantly higher in unexposed fish (Miller *et al*., 1989a). Within the range of tolerance for nutritionally essential metals such as Mn, Fe, Zn and Cu, normal homeostatic mechanisms allow isolation of the muscular compartment from environmental elevations (Murphy *et al*., 1978; Giesy *et al*., 1980; Wilson, 1980; Miller *et al.*, 1989a,b). Levels of metals in bone are relatively conservative, and elevations have been found to closely parallel the environmental concentrations (Bendell-Young *et al*., 1986; MilIer *et al*., 1989b). Bendell-Young *et al*. (1986) caution that growth rates have to be taken into account for some metals.

For fish, not all tissues will show elevations after exposure to acid mine drainage. In a study of Cu and Zn contamination, white sucker (Catostomus commersoni) from contaminated sites showed significant increases in levels of both Cu and Zn in liver, kidney and gill tissue, but not in muscle and some other peripheral tissues (Miller *et al.*, 1989a). Similar increases in levels of

Cu and Zn in metabolic tissues have been reported for other species of fish taken from contaminated environments (Wilson, 1980; Roth and McCarter, 1984a). In juvenile rainbow trout, the highest concentration of Hg was found in the kidney or spleen, liver and kidney, while the largest relative increases were in the brain, muscle and kidney (Baatrup *et al*., 1986; Baatrup and Danscher, 1987). Cell injuries were closely related to the Hg tissue burden (Baatrup *et al*., 1986).

2.4.0. Methods of Analysis of Lead, Manganese and Zinc

2.4.1. Analysis of Lead, Manganese and Zinc

Elements including lead, manganese and zinc have been analyzed by various methods which include flame atomic absorption spectrometry (FAAS), graphite furnace absorption spectrometry (GF-AS) and inductively coupled plasma – atomic emission spectroscopy (ICP-AES) (Aceto *et al*., 2002; Bingol and Akcay, 2005). Atomic absorption spectrometry is commonly used for it has the advantage of being highly specific, availability and selectivity (Garcia and Baez, 2012).

2.4.2. Atomic Absorption Spectroscopy

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires a standard with known analyte content to establish the relation between the measured and the analyte concentrations and relies on Beer Lambert's law (Skoog *et al*., 2005; Christian, 2005).

The sample is converted into atomic vapors by a process known as atomization. The precision and accuracy of this method depends on the atomization step and therefore a good choice of the atomization method is required. The two types of atomizers are continuous and discreet atomizers. In continuous atomizers the sample is fed into the atomizer continuously at a constant

rate giving a spectral signal which is constant with time. Atomization methods that are of continuous type are flame, inductively coupled argon plasma and direct current argon plasma (Nakahara, 1983).

With the discrete atomizers, a measured quantity of a sample is introduced as a plug of liquid or solid. The spectral signal in this case rises to a maximum and then decreases to zero. An electro thermal atomizer is one of the discrete types. The atoms then absorb radiations of characteristic wavelengths from an external source. The atoms of lead, nickel, manganese, zinc, cadmium and chromium, absorb radiations of wavelengths of 217.0nm, 232.0nm, 279.5nm, 213.9 nm 228.8nm and 357.9nm, respectively from an external source which is usually a hollow cathode lamp (Eser *et al*., 2004).

This technique has been widely employed for elemental analysis in a number of matrices such as soils, water, nuts wine and wine products (Navin *et al*., 2000; Tuzen, 2003). The two sources of radiation are continuous source which makes use of deuterium and mercury lamps and a hollow lamp which consists of an anode made of either tungsten wire or wink and a hollow cathode made of either the element of interest or its own salt. Flame atomization method consists mainly of a fuel and oxidant. Their temperatures are determined by flow rate and ratio of oxidant and fuel while the electro thermal atomizer is basically made of carbon rods. The free atoms are vaporized from the carbon atomizer into the optical light path to a monochromator which presents a monochromatic radiation to the detector. The radiations from the monochromators are received by detectors which converts them to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes.

2.5.0. Physico-Chemical Parameters in Kubanni Reservoir

2.5.1. Water Temperature

Jonasson *et al*., (1990) reported that the main abiotic factors which determine the suitability of an environment where temperature and dissolved oxygen. Most fishes got their bulky food from planktons and temperature fluctuations affect plankton's distribution. Ridly (2002) reported that respiration, photosynthesis and nutrient uptake are temperature dependent. Temperature can also influence egg development time, growth rate, size and mortality of zooplankton (Orchutt and Porter, 1983). Fish adjust their body temperature and metabolic rate by moving into cooler or warmer water.

2.5.2. Water pH

pH is the measure of the acidity or alkalinity of water. Low pH creates a stress situation in most organisms resulting in a decrease in metabolism. Oladipo *et al.,* (2006) opined that a pH range of 6.5-9.0 is suitable for maximum growth and abundance of phytoplankton.

Kemdirim (2000) also showed that maximum pH values coincided with period of high phytoplankton activity as a result of depletion of carbon dioxide by photosynthetic activity of the phytoplankton. Godfrey (1978) stated that increase in acidity, decrease species diversity.

Temperature and solar radiation accelerates photosynthesis, which in turn increase carbon dioxide absorption altering the bicarbonate equilibrium and producing OH^- thus raising the pH (Chapman and Kimstach, 1996).

2.5.3. Dissolved Oxygen (DO)

Dissolved oxygen is essential for the metabolism in all aquatic organism that possess aerobic biochemistry and it is commonly taken as indicator of potential production of primary production (Wade, 1985).

The high level of oxygen in water is a positive sign for the health and stability of the aquatic ecosystem, while its absence is a signal of severe pollution. Volume of oxygen increases as temperature decreases. Decrease in oxygen concentration can be attributed mostly to respiration by plants, animals and abiotic bacterial decay (Cole, 1979). Concentration below 5mg/l may adversely affect the functions and survival of biological communities and below 2mg/l can lead to death of most fishes (Chapman and Kimstach, 1996).

2.5.4. Biochemical Oxygen Demand

Biochemical oxygen demand (BOD) measure the level of organic pollution. It show biochemically degradable organic matter present in a sample (Deas and Orlob, 1999).

Microorganisms use oxygen dissolved in water which is their source of carbon for biochemical oxidation of organic matter. Where there is high pollution, most of the dissolved oxygen is used with the resultant effect on the living biota.

2.5.5. Turbidity

The amount of dispersed suspended solids in natural water bodies is an important indicator of water quality. These solids (such as silt, clay, algae, and organic matter) obstruct the transmittance of light through water and create a qualitative characteristic known as turbidity. Turbidity is often closely correlated to climatological or surface water conditions, and therefore indicates changes in environmental conditions of lakes, rivers and streams. For example, high

levels of suspended sediment can interfere with photosynthesis by blocking light from reaching aquatic plants. This not only damages vegetation but also results in reduced levels of dissolved oxygen because of the reduction in photosynthesis. Moreover, waters with high levels of suspended solids absorb more light, which can cause an increase in water temperature, creating even lower dissolved oxygen. This stresses aerobic aquatic organisms and could ultimately lead to fish kills (Kemdirim, 2000)

2.5.6. Chemical Oxygen Demand (COD)

Chemical oxygen demand is an indicator of organics in the water, usually used in conjunction with biological oxygen demand (BOD). COD is a measure of the oxygen equivalent of the organic matter content if a sample that is susceptible to oxidation by a strong chemical oxidant (APHA, 1995). The COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and in the effluents from sewage and industrial plants (Chapman and Kimstach 1996). Thus the COD is a reliable parameter for judging the extent of pollution in water. The COD of water increases with increasing concentration of organic matter and inorganic matter (Boyd and Weissman 1981). Garg *et al*., (2010) reported that COD ranged from 3.60 to 17.40 mg/l in Ramsagar Reservoir.

2.5.7. Total Alkalinity

Alkalinity is a measure of the acid-neutralizing or buffering capacity of a solution. The properties of water are easily influenced by alkalinity, making it an important and widely used test. If any changes are made to a solution which could impact pH, alkalinity acts a buffer, this ability to neutralize acid (H+ ions) is what makes alkalinity so important, Chapman and Kimstach (1996) reported that the presence of carbonates (CO_3^{-2}) and bicarbonates (HCO_3^-)

influence the hardness and alkalinity of water. Alkalinity in excess of 300mg/l does not adversely affect fishes but interferes with actions of certain commonly used chemicals, e.g. copper, sulphate (Buttner *et al*., 1993). Water with low alkalinity (<24mg-^{1} of $CaCO_3$) have low buffering capacity and can therefore be susceptible to alteration in pH, Therefore, a sample with high alkalinity will have a greater resistance to changes in pH (Chapman and Kimstach 1996).

2.5.8. Water Hardness

Hardness generally indicate water type, buffering capacity and productivity. Buttner *et al*., (1993) reported that soft water has low buffering action while hard water has high buffering action. Soft water is mostly neutral to acidic while hard water is alkaline.

Hardness is important in fish culture because it allow fishes to grow well. Some fish species such as cat fish do not grow well in water deficient of hardness (Buttner *et al*., 1993).

Betram and Balance (1996) also noted that seasonal variation in water hardness often occur, reaching the highest level during low flow conditions and lowest value during flood.

2.5.9 Nitrate-Nitrogen (NO_3-N)

Nitrate is formed through nitrification process, i.e. oxidation of combined nitrogen and oxygenated systems by the action of aerobic bacteria, the nitrite ion (NO_2−) contains nitrogen in a relatively unstable oxidation state. Nitrate not taken up directly by aquatic plants is denitrified in anaerobic sediments (Furnas *et al*., 1992). Boyd (1998) reported the desired nitrate concentration for the aquaculture is 0.2 to 10 mg/l. Surface water can also be contaminated by sewage and other wastes rich in nitrates. Higher concentration of nitrate in drinking water is toxic (Umavathi *et al*., 2007). As per the Environmental Protection Agency (EPA), the maximum contaminant level (MCL) of nitrate concentration is 10mg/l for drinking water (Self and

Waskom, 2008). Runoff from refuse dumping sited and farming activities affect nitrate concentration greatly in receiving waters. The fertilizer used on farms, through leaching and surface runoff into the stream during heavy rainfall could also contributed to the high levels of nitrate in receiving streams (Rao, 2000).

2.5.10. Phosphate – Phosphorus

Phosphorus stimulates growth of aquatic organisms (Wade, 1985). Phosphorus is one of the essential elements of living organisms because it is associated with energy transfer. Eutrophication of the lake is attributed to the external input of phosphate which is the most important factor in the regulation of phytoplankton production (Vollenweider *et al*., 1974).

Hsieh *et al*., (2007) noted that the sum of all the forms of phosphorus is a renewable measure of the fertility of a lake.

2.5.11. Total Dissolved Solids (TDS)

Total dissolved solids are the solids present in the water in the dissolved state. It consists of inorganic salts and dissolved materials. Garg *et al*. (2010) reported that TDS value from 166.37 to 239 mg/l in Ramsagar reservoir in Madhya Pradesh. Sawant and Chavan (2013) recorded the maximum total dissolved solid values of 172.66 mg/l during summer season owing to loss of water due to evaporation and concentration of salts in the water.

2.5.12. Electrical Conductivity

This is the measure of the amount of ions present in a water body and this can be used to measure the productivity and fisheries potential of water body. Conductivity is a general indicator of water quality (Thomas *et al*., 1996).

Ashton and Schoeman (1983) showed that electrical conductivity and ion concentration in lakes increase with depth. Chapman and Kimstsach (1996) report that conductivity of most freshwater range from 10-1000µscm-1 but may exceed 1,000µscm-1 especially in polluted waters or those receiving large quantities of land run-off.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study Area

The study was carried out in Kubanni Reservior Zaria, one of the largest cities in Kaduna State, Nigeria. The Reservior is located between latitude $11^0$8, $11^0$10'N and longitude $07^0$41'E at an elevation of 2,200m above sea level and approximately 122m in width and a depth of 6m. It is located within the premises of Ahmadu Bello University, The Reservior tributaries are the Samaru and Kampagi Streams. Kampagi stream, which originates from a rural settlement, has a seasonal flow whereas Samaru stream that originates from a semi-urban settlement has an all-year-round flow due to its sustenance by urban runoffs and seepages.

3.2.0 Sampling Stations

3.2.1 Experimental Design

Three samples stations were established within an approximately 600 meters section in respect to the reservoir water inlet and fish landing stations and more than 200m distance between each locations (Figure 3.1).

3.2.2 Description of sampling stations on Kubanni Reservior

Station one (1) was located adjacent to Postgraduate School ABU Zaria where activities such as Fish landing, buying and selling takes place, station two (2) was located along the tributaries and fishing point from Samaru where agricultural farming, emptying of sewage and other effluents takes place around it, while station three (3) was located on the catchment area or fishing point and agricultural activities also takes place around it.

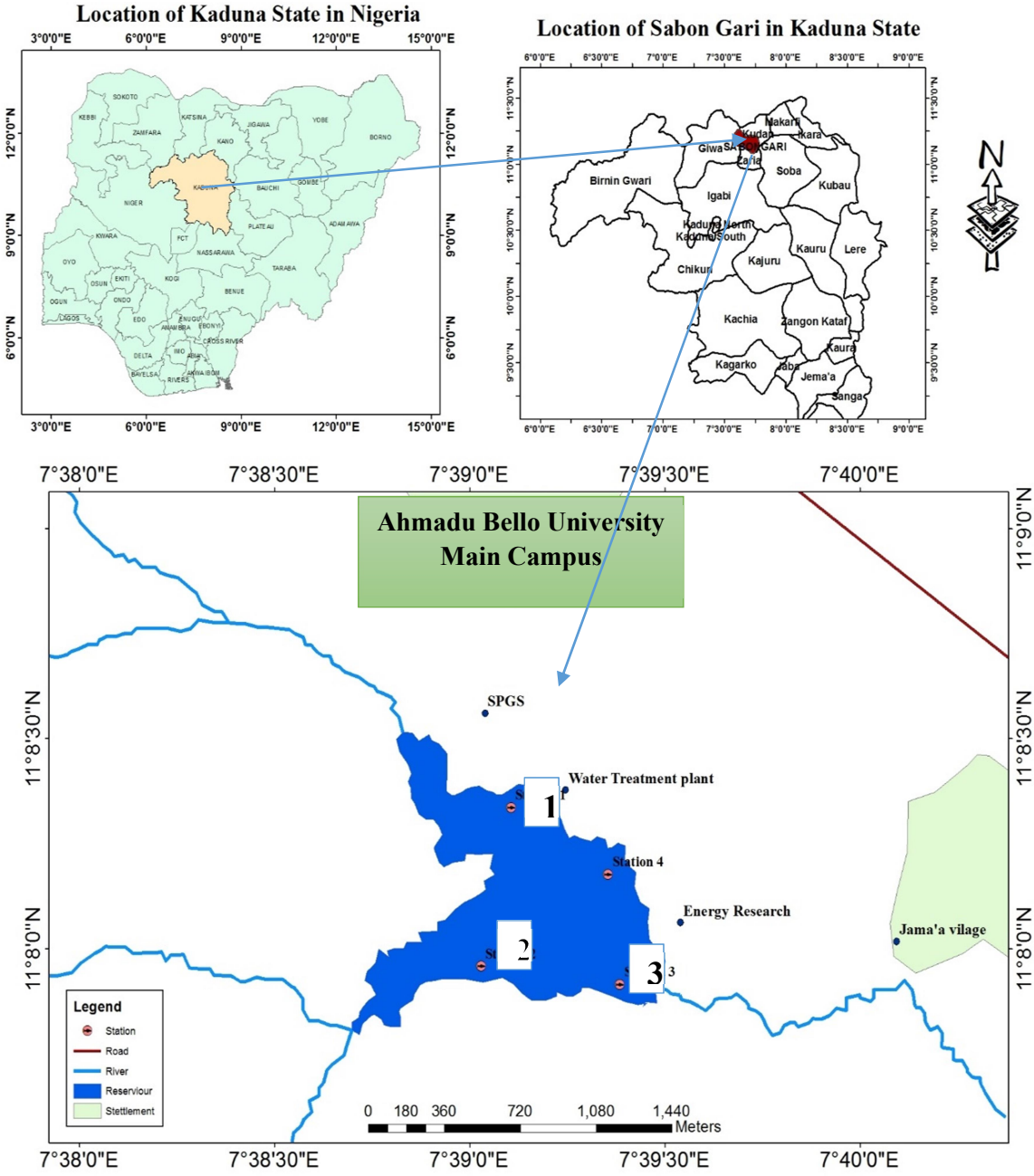

Figure 3.1: Location Kubanni Reservior Zaria, Kaduna State.
Source: *Department of Geography* (2017).

3.3 Collection of Fish Samples

Fish samples were collected monthly for the period of twelve (12) months, for both dry wet seasons (April, 2017 to March, 2018) from each of the sampling stations using gill nets and Malian traps.

Fishes captured were injected with 5% formalin in the abdominal region in order to arrest spoilage during transportation of specimens. The specimens were immediately preserved in cooled box with ice and immediately transferred to the Hydrobiology laboratory at the Department Biological Sciences, A.B.U. Zaria for collection of gills, liver and muscles, thereafter fish samples were transported to multiuser laboratory at the Department of Chemistry, Ahmadu Bello University Zaria for Pb, Zn and Mn determination in gills, livers and muscles.

3.4 Collection of Sediment

The sediment were collected from each of the three sampling stations using a labelled and retreated Poly Venyle Chloride tube of 1meter long 25mm in diameter and 2mm thick.

The PVC tube was inserted into the sediment under the water as deeply as possible turning it clock wisely until it reached the harder substratum and could not penetrate further. The pipe was the turned anti clock wisely until the PVC pipe could be detached from the harder substratum. The detached PVC was inverted upside down to allow the water out. The sediments in the PVC was manually extruded with a re-treated wood into clean polythene sack.

3.5 Collections of Water Samples

Water samples were collected once in a month for the period of twelve months for both dry wet seasons (April, 2017 and March, 2018) from each sampling stations using plastics bottles. The water samples were conveyed to Hydrobiology laboratory for AAS anyalsis.

3.6 Preservation of Fish and Sediment Samples

The samples (fish and sediments) were dried until there was no further change in weight, wet digested and then analyzed using atomic absorption spectroscopy for Pb, Mn, and Zn.

3.7.0 Determination of Some Physico-Chemical Parameter

3.7.1 Temperature

Temperature of the water was measured in degree Celsius (^{0}C) on site using mercury-in-glass thermometer by lowering the thermometer in an inclined position in water for about 5minutes for stabilization before taking the reading (APHA, 1995).

3.7.2 Biological Oxygen Demand

Duplicate 300ml of sampled water were placed in 300ml BOD bottles and was covered carefully to exude air bubbles, the bottles were incubated in the dark for 5days at 20^{0}C, after 5 days in the incubator, this was immediately followed by the addition manganese sulphate solution ($MnSO_4$) and 1ml alkaline iodide azide reagent, the bottles were stoppered carefully to exude air bubbles and then mixed thoroughly by inverting the bottle several times to mix the content.

The precipitates were allowed to settle for two minutes leaving clear supernatant, after which 2ml conc. H_2SO_4 was added by allowing the acid run down the neck of the bottle, then stoppered again and mixed by gentle inversion of the bottle several times until dissolution was complete and a clear supernatant was obtained. Thereafter 100ml of the prepared solution was transferred into conical flask and 2ml of freshly reared starch indicator was added, the solution was titrated with 0.0125N of sodium thiosulphate solution ($Na_2S_2O_3.5H_2O$) until the disappearance of the blue color (APHA, 2005).

BOD was then calculated using the following formula:

$(BOD)_5$ in mg/l $=DO_1-DO_5$

Where BOD = Biological Oxygen Demand,

DO = Dissolved oxygen

3.7.3 Dissolved Oxygen, Total Dissolved Solids

Water samples were collected twice into 300ml BOD stopper bottles, and fixed with 2ml Manganous sulphate. 2ml alkaline-iodide 2ml concentrated H_2SO_4 was added. Hundred ml was measured and was titrated against 0.012M sodium thiosulphate until it turns to pale yellow. The 1.00ml starch solution was added which turned the sample into blue colour. The titration was continued until the blue colour disappeared and repeated twice. The average volume of the thiosulphate titrate used were taken as equivalent to miligram of dissolved oxygen per liter (APHA 1985).

3.7.4 Electrical Conductivity

Hannan instrument (Model: Hi-9828) was used to measure electrical conductivity in the hydrobiology laboratory 28. The electrode was rinsed using distilled water and re-rinsed again, and set at zero. The electrode was then dipped into the Plastic beakers containing the water sample and allowed to equilibrate for about three minutes before reading the electrical conductivity. The reading was expressed in Sμ/cm (APHA 1985).

3.7.5 Turbidity

The turbidity was recorded using Hanna Multi-parameter (Model: Hi-9828). The electrode was re-rinsed and set at zero. The electrode was then dipped into the water sample and was allowed to equilibrate or about three minutes before reading the turbidity. Reading were expressed in centimeter.

3.7.6 Total Alkalinity

The alkalinity of the water samples were measured using Hanna Multi-parameter (Model: Hi-9828). The electrode was rinsed and set at zero. The electrode was then dipped into the water sample and was allowed to equilibrate for about three minutes before reading the electrical conductivity. Readings were expressed in part per million (APHA 1985).

3.7.7 pH

The pH was measured by using a pH meter. The pH probe was placed into the sample and allowed it to equilibrate for about three minutes before taking the reading.

3.7.8. Total Dissolved Solid and Electrical Conductivity

Total dissolved solid and Electrical conductivity were determined using Hanna instrument portable pH/EC/DS/T^0 (Mode No. HI991, 300, Hanna)

3.7.9. Total Hardness

Twenty five milliliters (25ml) was added to 25ml of water sampled and a quantity of two milliters of buffer solution of pH 0.14, and 0.1g of Errochrome black T dye was added, the mixture was the titrate with EDTA titrant (0.01M), then total hardness was estimated by multiplying the titrate value by 40, as $CaCo_3$/L (APHA 2005).

3.7.10. Nitrate-Nitrogen

The NO_3–N was determined using the spectrophotometer, hatch model:2010 (United States Environmental Protection agency, 1987). One hundred ml of water samples were filtered by suction to remove turbidity (APHA, 1995). Two test tubes were then placed on a metal rack, each to which 7.0ml of the filtered water sample whose pH has been adjusted to 7+02 was added,

another two separated test tubes were each allotted with 7.0ml of similarly tested solution of 100mg/l potassium nitrate as standard. Then two test tubes were also treated but with 1.00mg/l potassium nitrate as the standard B. A pair of test tubes were used as a reagents blank.

3.7.11. Phosphate-Phosphorus

One hundred ml of water sample was poured into conical flask then, one milliliter of Ammonium molybdate reagent and a drop of stannous chloride was added at interval of 12 minutes was given before taking readings at 600nm

3.8.0. Dry Ashing of Fish

One gram of each samples was weighed and transferred to a crucible, then dry at 105^{o}C in an oven to remove all residual moisture before ashing. The vessels was then placed in the muffle furnace and gradually heated at 50^{o}C every 30mins to 550^{o}C and ashed for 2 hours. After cooling, the residual ash was dissolved in 8ml of HNO_3 and the digests were then solubilized and filtered. (Abbruzzini *et al*., 2014).

3.8.1. Digestion of Collected Samples

The aqua regia method, involving concentrated HNO_3 and HCI at 1:3 proportion (EPA-ROC, 1994) was applied using a conical beaker heated on a plate as the standard method to digest the samples for the total analysis of the heavy metals prior to digestion by the aqua regia, organic matter was destroyed by concentrated (H_2O_2).

3.8.2. Water Digestion

The water sample bottles were shaken thoroughly in their plastic containers manually. One hundred milliliters of the sample was measured using a 100ml volumetric flask and put in a

conical flask, 5ml of concentrated nitric acid was then added. The mixture was heated slowly on a hot plate and evaporated to about 20ml ensuring that the water did not boil. A further 5ml of concentrated nitric acid was added and the beaker was covered with a watch glass while heating continued. Nitric acid continued to be added until the solution appeared light colored and clear. Lastly, 2ml of concentrated hydrochloric acid was added and heated slightly to dissolve any remaining residue. Few drops of hydrogen peroxide were then added to ensure complete digestion had taken place. The solution was filtered and the filtrate was transferred to a 100ml volumetric flask to cool and the filtrate was made up to the mark with distilled water (Radojovenic and Bashkin, 2006).

3.8.3. Digestion of Sediments

Well mixed samples of 1 g each were weighed using a Sartorius AG Gottingen electronic balance model CP8201. The samples were put into 250 ml glass beaker and digested with 24 ml of aqua regia and then evaporated to near dryness. The sediments samples were then dissolved in 10 ml of 2% nitric acid, filtered and then diluted to 100 ml with distilled water (Begum *et al*., 2009).

3.8.4 Digestion of Fish

The digestion methods that was been used in this study are acid digestion and dry ashing, at the hydrobiology laboratory, Biology Department, Ahmadu Bello University Zaria, Kaduna state. Under the acid, nitric-hydrochloric acid (HNO_3 + HCI) an aqua regia solution. In dry ashing, sample was been heated in a muffle furnace and the residual ash was dissolved in HNO_3.

Nitric acid (HNO_3) digestion Fish sample (1.0g was placed in a 25ml beaker, afterwards, about 10ml of concentrated HNO_3 (analytical grade, 69%w/w) was poured into the beaker. A watch

glass was placed at the mouth of the beaker which was placed on a magnetic stirrer/hotplate. Initially, the temperature was kept at about 40 ^{o}C for one hour to prevent vigorous reactions. Then the temperature was maintained at 140^{o}C for another three hours. when the digestion was completed all tissue samples were dissolved in the acid. Then the mixture was allowed to cool to room temperature. Distilled water was added into the vessel to dilute the mixture for Atomic Absorption Spectrophotometer (AAS) detection of heavy metals. The sample was been filtered using filter paper (whatman No.1 grade). The filtrates was stored iny a refrigerator set at four degrees Celsius until the metal determination by AAS (Plessis and Adriaan, 2015).

3.9.0 Preparation of stock solutions and standards

3.9.1 Lead stock solution and standards

Lead stock solution (100mg/l) was prepared by dissolving 1.59g of lead (ii) nitrate in 500 ml of distilled water and then made up to 1 litre of solution using distilled water. Through serial dilutions, standard working solutions of lead of 1, 2, 3, 4 and 5mg/l were made which were used to generate a calibration curve for lead.

3.9.2 Zinc stock solution and standards

Zinc stock solution (100mg/l) was prepared by dissolving 0.289g of zinc nitrate salt in 300ml of distilled water and then made up to 1 litre of solution using distilled water. A working zinc standard solution (20mg/l) was made by diluting 20 ml of the stock solution to 100ml of solution. The calibration graph was made using solutions with the following concentrations; 0.5, 1, 1.5, 2, and 2.5mg/l of zinc.

3.9.3 Manganese stock solution and standards

Manganese stock solution (100mg/l) was prepared by dissolving 0.10g of manganese metal powder in 10ml of concentrated hydrochloric acid mixed with 1 ml of concentrated nitric acid.

A 10ml of nitric acid was then added and the solution finally diluted to 1000ml with distilled water. A working manganese standard solution (20mg/l) was made by diluting 20ml of the stock solution to 100ml of solution using distilled water. The calibration graph was made using solutions with the following concentrations; 0.5, 1, 1.5, 2 and 2.5mg/l of manganese.

Table 3.1. Selected Heavy Metals and Condition of Analysis

Elements analyzed	Wave length of the analysis(nm)
Lead (Pb)	283.3
Manganese (Mn)	278.5
Zinc (Zn)	213.8

3.9.4. Determination of Lead, Manganese and Zinc in Sediments and organs of *Oreochromis niloticus* and *Clarias gariepinus.*

Regression equations established from a plot of absorbance readings of standards against their concentration were used to determine the concentration of Pb, Mn and Zn in triplicates.

The actual concentration of Pb, Mn and Zn values was displayed by AAS.

$$\text{Actual concentration (mg/kg)} = \frac{\text{digested concentration (mg/L)} \times \text{Volume digested (L)}}{\text{Weight of dried sample digested (kg)}}$$

The actual weight of Mn, Pb and Zn in *Oreochromis niloticus* and *Clarias gariepinus*, water and sediments, were estimated by multiplying the values displayed by the AAS read and the dilution factor.

3.10.0. Sample Analysis

Lead, Manganese and Zinc were determined using Atomic Absorption Spectrophotometer (Buck 211 Model) at the multi-user laboratory, Department of Chemistry, Ahmadu Bello University, Zaria.

3.10.1. Data Analysis

Data obtained were subjected to one way analysis of variance (ANOVA). The differences between the mean values were determined using Duncan's Multiple Range Tests (DMRT) at 95% confidence level ($P < 0.05$). T-test was used to compare the seasonal variation of physico-chemical parameters in Kubanni Reservoir t-test was used to separate means between seasons. Pearson's correlation coefficient was used on the data using SPSS 17.0 for windows to determine significant relationships between the physico-chemical parameters.

CHAPTER FOUR

4.0 RESULTS

4.1 Water Quality Parameters of Kubanni Reservoir

4.2 Water Temperature

Water temperature of the three stations in Kubanni Reservoir ranged between 23.30±0.04 to 27.57±0.17°C (Table 4.1a and 4.1b). High temperatures between March (27.57°C) – June (26.40°C). The lowest temperature (23.30 °C) was recorded in January in station 2 and low temperatures were recorded between August (24.07 °C) to January (23.03°C), while the highest temperature (27.90 (°C) was recorded in May in station 1 (Table 4.1a, and 4.1b). Analysis of variance in Table 4.1a shows significant difference ($P < 0.05$) between months, while Table 4.2 and 4.3 shows no significant difference ($P > 0.05$) between seasons and stations respectively. Drop of temperature in all the three stations in January.

4.2 Water pH

The monthly variation of water pH of Kubanni Reservoir ranges from 6.97±0.18 to 8.22±0.28 as shown in Table 4.1a and 4.1b. The Kubanni Reservoir is neutral during rainy season and dry season months (Table 4.1a and 4.1b.). Stations 1 and 2 shows highest pH values (8.77 and 8.26 H^+) in May and September respectively than station 3 while low pH values were recorded in March in station 2 and 3 (6.81 and 6.77 H^+) respectively). Analysis of variance in Table 4.1a and 4.1b shows significant difference between the stations and season ($P < 0.05$), while Table 4.2 and 4.3 shows no significant difference ($P > 0.05$) between seasons and stations respectively.

Table 4.1a: Mean ±SE Monthly Physico-chemical Parameters of Kubanni Reservoir, Zaria, Kaduna State

Months	Stations	Temp(ºC)	pH(H+)	DO(mg/l)	BOD(mg/l)	Tur(cm)	COD(mg/l)	Alk(mg/l)	Hard(mg/l)	NO_3 (mg/l)	PO_4 (mg/l)	TDS(mg/l)	EC(µs/cm)
April, 2017	1	26.32	7.32	6.72	2	48.3	156.01	95	192.4	0.48	0.25	112	393
	2	26.93	6.81	8.14	1.14	27.11	175.32	53.8	174	0.47	0.28	132	209
	3	27	6.77	7.22	1.23	47.63	150.33	54.1	188.4	0.49	0.3	113	182
		26.75±0.22^{b}	6.97±0.18^{e}	7.36±0.42^{bc}	1.45±0.23^{abc}	41.01±1.03^{c}	160.55±7.56^{a}	67.63±13.68^{ab}	184.93±5.59^{a}	0.48±0.01^{ab}	0.28±0.02^{abc}	119.00±6.51^{bc}	261.33±66.29^{a}
May	1	27.9	7.03	6.79	1.81	42.22	60.23	71	140.48	0.46	0.23	113	226
	2	27.32	7.12	8.09	1.61	39.15	75.42	60.9	152.8	0.41	0.25	92	185
	3	27.5	7.02	7.2	1.75	41.66	56.32	60.1	152.8	0.45	0.1	88	177
		27.57±0.17^{a}	7.06±0.03^{de}	7.36±0.38^{bc}	1.72±0.06^{a}	41.13±0.19^{c}	63.99±5.83^{cd}	64.00±3.51^{ab}	148.69±4.11^{b}	0.44±0.02^{abcd}	0.19±0.05^{c}	97.67±7.75^{bc}	196.00±15.18^{ab}
June	1	26.09	8.77	6.67	1.59	40.8	52.4	60.1	110	0.42	0.25	192	223
	2	26.4	8.05	8.12	1.37	40.6	55.31	65.1	90	0.42	0.23	104	188
	3	26.1	7.85	7.33	1.48	41.1	40.71	63.3	100	0.45	0.29	92	112
		26.20±0.10^{c}	8.22±0.28^{a}	7.37±0.42^{bc}	1.48±0.06^{abc}	44.83±0.37^{b}	49.47±4.46^{cd}	62.83±1.46^{ab}	100.00±5.77^{de}	0.43±0.01^{abcd}	0.26±0.02^{bc}	195.00±1.00^{a}	172.67±10.09^{b}
July	1	25.93	7.01	7.32	1.24	45.2	59.8	50	90	0.43	0.21	190	126
	2	25.74	7	8.1	1.43	45.2	60.01	53	95	0.49	0.34	190	115
	3	25.72	7.21	7.32	1.57	44.1	51.95	69	80	0.47	0.22	194	112
		25.80±0.07^{d}	7.07±0.07^{de}	7.58±0.26^{bc}	1.41±0.10^{abc}	41.01±0.94^{c}	57.25±2.65^{cd}	57.33±5.90^{b}	88.33±4.41^{f}	0.46±0.02^{abc}	0.26±0.04^{bc}	191.33±1.33^{a}	117.67±4.26^{b}
August	1	24.8	7.5	8.55	1.29	64.8	40.88	30	70	0.32	0.31	196	168
	2	25.2	7.9	8.81	1.17	64.3	49.02	40	72.4	0.34	0.42	196	158
	3	24.92	7.5	8.67	1.08	65.1	49	32	73	0.29	0.37	193	192
		24.97±0.12^{e}	7.63±0.13^{bcd}	6.88±0.03^{cd}	1.18±0.06^{c}	64.73±0.23^{a}	46.30±2.71^{d}	34.00±3.06^{c}	71.80±0.92^{g}	0.32±0.02^{ef}	0.24±0.02^{bc}	129.33±31.52^{b}	174.33±32.76^{b}
eptember	1	24.32	7.72	7.3	1.21	65.1	54.55	24	76.8	0.3	0.21	192	149
	2	24.29	8.11	8.28	1.12	64.5	54.85	32	55.6	0.31	0.39	199	157
	3	24.5	7.83	8.23	1.32	64.6	60.12	34	56	0.33	0.33	198	155
		24.37±0.07^{f}	7.89±0.12^{ab}	7.94±0.32^{ab}	1.22±0.06^{bc}	64.73±0.19^{a}	56.51±1.81^{cd}	30.00±3.06^{c}	62.80±7.00^{h}	0.31±0.01^{f}	0.22±0.01^{bc}	196.33±2.19^{a}	153.67±2.40^{b}

Means with same superscript along the column are not significantly different at $P > 0.05$.

Table 4.1b: Mean ±SE Monthly Physico-chemical Parameters of Kubanni Reservoir, Zaria, Kaduna State

Months	Stations	Temp(ºC)	pH(H+)	DO(mg/l)	BOD(mg/l)	Tur(cm)	COD(mg/l)	Alk(mg/l)	Hard(mg/l)	NH3 (mg/l)	PO4 (mg/l)	TDS(mg/l)	EC(µs/cm)
Oct	1	24.03	7.32	7.52	1.21	40.1	56.04	81	84	0.39	0.2	194	169
	2	24.03	8.26	8.3	1.22	38.2	60.02	69.4	75	0.41	0.29	199	171
	3	24.14	7.32	8.39	1.22	45.3	40.02	80.9	90	0.37	0.22	198	173
		24.07 ± 0.04^{f}	7.63 ± 0.31^{bcd}	8.07 ± 0.28^{ab}	1.22 ± 0.00^{bc}	41.20 ± 0.64^{c}	52.03 ± 6.11^{cd}	77.10 ± 3.85^{a}	83.00 ± 4.366^{f}	0.39 ± 0.01^{cdef}	0.24 ± 0.03^{bc}	197.00 ± 1.53^{a}	171.00 ± 1.16^{b}
Nov	1	24.11	7.19	7.3	1.31	41.22	70.08	67.1	122.8	0.39	0.26	190	166
	2	24.19	7.2	7.2	1.23	40.22	40.84	69.5	102	0.39	0.28	189	162
	3	24.23	7.29	7.11	1.41	42.72	42.95	62.3	99	0.4	0.21	187	169
		23.81 ± 0.05^{g}	7.23 ± 0.03^{cde}	7.20 ± 0.06^{bcd}	1.32 ± 0.05^{bc}	41.39 ± 0.73^{c}	51.29 ± 9.41^{cd}	66.30 ± 2.12^{ab}	107.93 ± 7.48^{d}	0.39 ± 0.00^{cdef}	0.25 ± 0.02^{bc}	188.67 ± 0.88^{a}	165.67 ± 2.03^{b}
Dec	1	23.9	7.81	8.5	1.23	41.31	50.67	64.2	132.8	0.35	0.21	185	161
	2	23.82	7.91	7.9	1.33	42.3	42.59	65	122.4	0.38	0.22	192	162
	3	23.72	7.33	7.42	1.25	43.3	41.75	66.6	132	0.4	0.24	193	161
		24.18 ± 0.04^{g}	7.68 ± 0.18^{abc}	7.94 ± 0.31^{ab}	6.40 ± 0.06^{e}	42.30 ± 0.57^{c}	45.00 ± 2.84^{d}	65.27 ± 0.71^{ab}	129.07 ± 3.34^{c}	0.38 ± 0.02^{edf}	0.22 ± 0.01^{bc}	190.00 ± 2.52^{a}	161.33 ± 0.33^{b}
Jan, 2018	1	23.39	7.32	7.3	1.32	41.52	79.04	63.4	151.2	0.43	0.2	109	159
	2	23.25	8	7.4	1.52	41.49	84.19	65.5	161.6	0.52	0.21	152	152
	3	23.27	7.24	7	1.42	41.5	50.73	69.2	154	0.52	0.24	95	172
		23.30 ± 0.04^{h}	7.52 ± 0.24^{bcde}	8.68 ± 0.08^{a}	1.42 ± 0.06^{abc}	41.50 ± 0.01^{c}	71.32 ± 10.40^{c}	66.30 ± 2.12^{ab}	155.60 ± 3.11^{b}	0.49 ± 0.03^{a}	0.31 ± 0.05^{ab}	118.67 ± 17.15^{bc}	161.00 ± 5.86^{b}
Feb	1	26.2	7.32	6.4	1.71	42.12	112.01	63	188.4	0.39	0.27	102	134
	2	26.33	7.3	6.5	1.69	42.31	104	64.2	192.4	0.29	0.23	100	153
	3	26.9	7.7	6.31	1.22	40.43	84.95	65	180	0.52	0.21	100	121
		26.42 ± 0.16^{bc}	7.44 ± 0.13^{bcde}	7.23 ± 0.12^{bcd}	1.54 ± 0.16^{ab}	41.62 ± 0.60^{c}	100.32 ± 8.03^{b}	64.07 ± 0.58^{ab}	186.93 ± 3.65^{a}	0.40 ± 0.07^{bcd}	0.37 ± 0.03^{a}	100.67 ± 0.67^{bc}	136.00 ± 9.29^{b}
Mar	1	26.73	7.5	6.9	1.72	41.5	134.01	68	185.6	0.43	0.32	92	183
	2	26.22	7.53	6.83	1.25	35.88	170.03	65.2	168	0.42	0.29	85	115
	3	26.32	8	6.91	1.41	46.01	130.56	68.8	174.4	0.5	0.21	90	112
		26.48 ± 0.22^{bc}	7.68 ± 0.16^{abc}	1.46 ± 0.14^{abc}	1.27 ± 0.03^{bc}	40.83 ± 0.15^{c}	144.87 ± 12.62^{a}	67.33 ± 1.09^{ab}	176.00 ± 5.14^{a}	0.45 ± 0.03^{abcd}	0.27 ± 0.03^{bc}	89.00 ± 2.08^{c}	136.67 ± 23.18^{b}
Monthly Mean		25.33±0.18	7.50±0.15	7.08±0.23	1.80±0.07	45.52±0.47	74.90±6.20	60.18±3.42	124.59±4.57	0.14±0.02	0.25±0.02	151.05±6.26	167.27±14.40
P-value		0	0.001	0.01	0.038	0	0	0	0	0	0.004	0	0.34

Means with same superscript along the column are not significantly different at $p > 0.05$.

Table 4.2: Seasonal Variation for Physico-chemical Parameters of Kubanni Reservoir

Physicochemical	Seasons	
	Wet	**Dry**
Temperature (°C)	24.98±0.32[a]	25.67±0.31[a]
pH	7.57±0.13[a]	7.43±0.08[a]
DO (mg/l)	7.83±0.15[a]	7.17±0.14[b]
BOD (mg/l)	1.43±0.06[a]	1.35±0.03[b]
Turbidity (cm)	45.71±2.09 [a]	45.34±2.12[b]
COD (mg/l)	54.26±2.02[b]	95.56±11.18[a]
Alkalinity	6.76±0.21[a]	6.41±0.11[a]
Hardness (mg/l in $CaCo_3$)	1.44±0.21[b]	1.89±0.37[a]
NH_3-N (mg/l)	0.39±0.06[a]	0.43±0.07[a]
PO_4-P (mg/l)	0.23±0.05[b]	0.28±0.06[a]
TDS (mg/l)	167.78±45.02[a]	134.33±42.87[a]
EC (µs/cm)	178.72±60.99[a]	155.83±28.89[a]

Means with same superscript along the row are not significantly different at $p > 0.05$. Keys: pH= Potential Hydrogen, DO= Dissolved Oxygen, BOD= Biological Oxygen Demand, COD= Chemical Oxygen Demand, NO_3-N= Nitrate Nitrogen, PO_4-P= Phosphate Phosphorus, TDS= Total Dissolved Solids, EC= Electrical Conductivity.

Table 4.3: Mean ±SE of Physico-Chemical Parameters by Stations in Kubanni Reservoir

Physicochemical	Stations		
	1	2	3
Temperature(°C)	25.31±0.40[a]	25.31±0.39[a]	25.36±0.41[a]
pH	7.48±0.14[a]	7.60±0.14[a]	7.42±0.11[a]
DO (mg/l)	7.27±0.20[a]	7.81±0.20[a]	7.43±0.20[a]
BOD (mg/l)	1.44±0.07[a]	1.39±0.06[a]	1.35±0.05[a]
Turbidity (cm)	45.60±2.63[a]	45.40±2.60[a]	45.58±2.63[a]
COD (mg/l)	77.14±10.62[a]	80.97±13.41[a]	66.62±10.63[a]
Alkalinity	6.65±0.26[a]	6.52±0.13[a]	6.58±0.22[a]
Hardness (mg/l)	1.71±0.12[a]	1.63±0.09[a]	1.65±0.12[a]
NH_3-N (mg/l)	0.40±0.02[a]	0.40±0.02[a]	0.43±0.02[a]
PO_4-P (mg/l)	0.24±0.01[a]	0.29±0.02[a]	0.25±0.02[a]
TDS (mg/l)	155.58±12.85[a]	152.50±13.56[a]	145.08±14.83[a]
EC (µohms/cm)	188.08±20.56[a]	160.58±7.84[a]	153.17±8.74[a]

Means with same superscript along the row are not significantly different at $p>0.05$. Keys: pH= Potential Hydrogen, DO= Dissolved Oxygen, BOD= Biological Oxygen Demand, COD= Chemical Oxygen Demand, NH_3-N= Nitrate Nitrogen, PO_4-P= Phosphate Phosphorus, TDS= Total Dissolved Solids, EC= Electrical Conductivity.

4.3. Dissolved Oxygen Concentration

The dissolved oxygen concentration ranges from 6.40±0.06 to 8.68±0.08mg/l (Table 4.1a and 4.1b) higher dissolved oxygen concentrations (8.55, 8.81 and 8.67mg/l). Higher concentration were obtained across all the three stations. Lowest value was recorded in March (6.40mg/l) as revealed in Table 4.1a and 4.1b. Significant variation ($p < 0.05$) was observed between the months and the seasons (Table 4.1a, 4.1b and 4.2 respectively) while Table 4.3 shows no significant difference ($P > 0.05$) in between the stations.

4.4 Biological Oxygen Demand in Water

Biochemical oxygen demand (BOD) of Kubanni Reservoir showed mean seasonal values of 1.18±0.06 to 1.72±0.06mg/l (Table 4.1a and 4.1b). Higher BOD values of 2.00 and 1.81mg/l were recorded in April and May in station 1, while the lowest value 1.08mg/l was recorded in August from station 3 (Table 4.1a and 4.1b). Significant variation ($p < 0.05$) was observed between the months, while there is no significant difference ($P > 0.05$) in between seasons and stations respectively (Table 4.2 and 4.3).

4.5. Turbidity

The mean monthly variation for Turbidity in the three stations were presented in Table 4.1a and b. The lowest Turbidity of 27.11mg/l was recorded in station 2 in April while in the months of August and September recorded the highest value (65.10mg/l) in station 3 and 1, there was a progressive increase in turbidity from May to September (Table 4.1a and 4.1b). Significant variation ($p < 0.05$) occurred between the months (Table 4.1a and 4.1b) while Table 4.2, and 4.3 shows no significant difference between seasons and stations respectively ($p > 0.05$).

4.6. Chemical Oxygen Demand

Chemical Oxygen Demand (COD) ranged from 46.30±2.71 to 160.55±7.56mg/l (Table 4.1a and 4.1b). The highest concentration was recorded in station 2 in March and April with concentration value of 170.03 and 175.32 mg/l, while the lowest COD was 40.02mg/l recorded in station 3 in the months of October (Table 4.1a and b). There was significant variation ($p < 0.05$) in BOD concentration between month and seasons (Table 4.1a, and 4.1b and 4.2 respectively) while Table 4.3 shows no significant variation ($p > 0.05$) between the stations.

4.7. Total Alkalinity

Alkalinity mean values ranges from 30.00±3.06 to 77.10±3.85 (Table 4.1a and 4.1b). Higher values of alkalinity were recorded in station 1, in April and October respectively. The months of July and august showed gradual increase of alkalinity in all the three stations, while lower values were obtained in September and August in stations 2 and 3 as shown in Table 4.1a and 4.1b. Significant variation ($P < 0.05$) was observed between the months (Table 4.1a and 4.1b) while Table 4.2 and 4.3 shows no significant difference ($P > 0.05$) in between seasons and stations respectively.

4.8. Total Water Hardness

The mean monthly variation in water hardness are presented in Table 4.1a and 4.1b. The mean values ranged from 62.80±7.00 to 67.63±13.68 (mg/l. $CaCO_3$), the high concentration of (192.4mg/l) were obtained in February and April in stations 1 and 2. Low concentrations values were obtained in stations 2 and 3 of 55.6 and 56 mg/l respectively (Table 4.1a and 4.1b). There was significant variation ($P < 0.05$) in water hardness between the months and seasons (Table

4.1a, 4.1b and 4.2 respectively) while Table 4.3 shows no significant difference ($P > 0.05$) in between stations.

4.9 Nitrate-Nitrogen

The mean values of Nitrate-Nitrogen obtained in Kubanni Reservoir during the sampling period were found to range from 0.31±0.01 to 0.49±0.03mg/l (Table 4.1a and 4.1b). Lowest concentration of 0.29mg/l was recorded in station 2 and 3 in August, while the highest concentration of 0.52mg/l was recorded in station 2 and 3 in February (Table 4.1a and 4.1b). Significant variation ($P < 0.05$) was observed between the months (Table 4.1a and b) while Table 4.2 and 4.3 shows no significant difference ($P > 0.05$) in between seasons and stations respectively.

4.10 Phosphate-Phosphorus

The monthly mean value variation of phosphate-phosphorus was represented in Table 4.1a and b, which ranged between 0.19±0.05 to 0.37±0.03mg/l. The maximum phosphate-phosphorus concentration was obtained in August and September (0.42 and 0.39mg/l respectively) in station 2 while a minimum value of 0.10mg/l was recorded in May. Station 2 showed maximum phosphate-phosphorus concentration than stations 1 and 3 (Table 4.1a and 4.1b). There was significant variation ($p < 0.05$) between the months and seasons (Table 4.1a, 4.1b and 4.2 respectively) while and 4.3 shows no significant difference ($P > 0.05$) in between stations.

4.11 Total Dissolved Solid

The mean level recorded in this study for TDS ranged from 89.00±2.08 to 197.00±1.53mg/l (Table 4.1a and 4.1b). The highest concentration of 199mg/l was recorded in station 2 in September. The lowest value of 85mg/l was recorded in station 2 in May (Table 4.1a and 4.1b).

Significant variation ($P < 0.05$) was observed among the months (Table 4.1a and b) while Table 4.2 and 4.3 shows no significant difference ($P > 0.05$) in between seasons and stations respectively.

4.12. Electrical Conductivity

The mean monthly electrical conductivity in Table 4.1a and b showed a little variation in all the months which ranged from 117.67±4.26 to 261.33±66.29µs/cm. The conductivity of the Kubanni Reservoir was lower during the rainy season. The lowest conductance of 112µs/cm was recorded in station 3 in June, July and March, while the highest conductance of 393µs/cm in station 1 in April as shown in Figure 4.1a and b. Significant variation ($P < 0.05$) was observed between the months (Table 4.1a and 4.1b) while Table 4.2 and 4.3 shows no significant difference ($P > 0.05$) in between seasons and stations respectively.

4.13 Concentration of Lead Manganese and Zinc in Water and Sediments of Kubanni Reservoir

Table 4.4 shows the lead, manganese and zinc Concentration of Kubanni Reservior

4.14 Lead in Water

Table 4.4a and 4.4b shows the concentration of lead in Kubanni Reservior. The low concentration of lead in water were recorded in all the three stations (1, 2 and 3) while the highest concentration value of 0.5mg/l was recorded in November in station 2. The mean value obtained for the period of 12 months with respect to the stations is between 0.00±0.00 to 0.24±0.03 with a monthly mean value of 0.12±0.03 (Table 4.4a and 4.4b). Table 4.3a, and b shows no significant difference ($P < 0.05$) between the months for lead in water, Table 4.5 and 4.6 shows no significant variation ($P > 0.05$) between the seasons and stations respectively. Correlation coefficient analysis of lead in water highly correlate with Pb in liver of *Clarias gariepinus* (Table 4.13).

4.15 Lead in Sediment

Table 4.4a and 4.4b shows the result of lead concentration in the Kubanni Reservoir. The mean of lead concentration ranges between 16.05±2.93 to 87.35±8.7mg/kg, with a monthly mean value of 40.05±.40. Low lead concentration in sediments were recorded in station 2 and 3 between the month of May and February, while the highest concentration of lead was observed in March in station 1 (Table 4.4a and 4.4b). There was significant difference ($p < 0.05$) between Pb values of sediments among the months. However, no significant variation ($p > 0.05$) between the seasonal Pb values across the entire stations (Table 4.5 and 6). Lead in sediments correlate with Zinc in

muscle of *Clarias gariepinus*, Zinc in gills and muscle of *Oreochromis niloticus*, Mn in the gills of *Clarias gariepinus* and Pb in muscles of *Clarias gariepinus* (Table 4.13).

Table 4.4a: Monthly (±S.E.) Variation of Heavy Metals in Sediments (mg/kg) and Water (mg/l) in Kubanni, Reservoir

		Heavy Metal					
		Pb		Mn		Zn	
Months	Stations	Water	Sediments	Water	Sediments	Water	Sediments
April, 2017	1	0.057	45.81	0.605	389.42	0.2	116.98
	2	0.25	34.08	0.098	397.52	0.1	361.33
	3	0.08	49.26	0.124	347.68	0	178.76
		0.13 ± 0.06^{abc}	43.05 ± 4.59^{b}	0.28 ± 0.17^{a}	378.21 ± 15.44^{a}	0.10 ± 0.06^{a}	219.02 ± 73.35^{a}
May	1	0.109	22.56	0.139	338.8	0.2	183.82
	2	0.1	65.7	0.124	241.5	0.228	128.65
	3	0.07	37	0.092	222.9	0	265.8
		0.09 ± 0.02^{abc}	41.75 ± 12.67^{b}	0.12 ± 0.01^{a}	267.73 ± 35.94^{ab}	0.14 ± 0.07^{a}	192.76 ± 39.84^{a}
June	1	0.197	23.47	0.912	299.6	0	145.71
	2	0	56.98	0.563	234.4	0.05	260.19
	3	0	28.3	0.436	245.3	0	290.24
		0.07 ± 0.05^{abc}	36.25 ± 10.46^{b}	0.64 ± 0.14^{a}	259.77 ± 20.16^{ab}	0.02 ± 0.01^{a}	232.05 ± 44.03^{a}
July	1	0	14.73	0	213.8	0	218.21
	2	0.031	27.83	0.564	238.1	0	293.72
	3	0.021	32.8	0.583	190.5	0.216	147.08
		0.02 ± 0.01^{bc}	25.12 ± 5.39^{b}	0.38 ± 0.19^{a}	214.13 ± 13.74^{ab}	0.07 ± 0.02^{a}	219.67 ± 42.34^{a}
August	1	0	21.6	0.03	260.9	0	202.16
	2	0	20.23	0	352.8	0	317.56
	3	0	58.6	0.35	278.8	0	212.73
		0.00 ± 0.00^{c}	33.48 ± 12.57^{b}	0.13 ± 0.11^{a}	297.50 ± 28.12^{ab}	0.00 ± 0.00^{a}	244.15 ± 36.83^{a}
September	1	0	97.03	0	246.2	0	163.89
	2	0	20.9	0.492	208.8	0	268.44
	3	0	18.67	0.481	173.7	0	132.14
		0.00 ± 0.00^{c}	45.53 ± 25.76^{b}	0.32 ± 0.16^{a}	209.57 ± 20.93^{b}	0.00 ± 0.00^{a}	188.16 ± 41.18^{a}

Means with same superscript along the column are not significantly different at $P > 0.05$

Table 4.4b: Monthly (±S.E.) Variation of Heavy Metals in Sediments (mg/kg) and Water (mg/l) in Kubanni, Reservoir

		Heavy Metal					
		Pb		Mn		Zn	
Months	Stations	Water	Sediments	Water	Sediments	Water	Sediments
Oct	1	0.073	18.31	0.025	262.7	0	199.31
	2	0	19.68	0.364	205.6	0.04	301.91
	3	0.106	11.96	0.349	114.9	0	208.4
		0.06±0.03^{abc}	16.65±2.38^{b}	0.25±0.11^{a}	194.40±43.03^{b}	0.01±0.00^{a}	236.54±32.79^{a}
Nov	1	0.072	89.67	0.937	298.4	0.02	102.37
	2	0.51	12.21	0.22	335.3	0.1	231.64
	3	0	67.11	0	233.9	0.07	214.85
		0.19±0.16^{ab}	56.33±23.00^{ab}	0.39±0.28^{a}	255.87±21.27^{ab}	0.06±0.02^{a}	182.95±40.58^{a}
Dec	1	0	22.8	0.219	369.4	0	208.18
	2	0.09	20.6	0.507	367.5	0	127.23
	3	0	22.34	0.404	250.4	0	129.81
		0.03±0.01^{bc}	21.91±0.67^{b}	0.38±0.08^{a}	329.10±39.35^{ab}	0.00±0.00^{a}	155.07±26.56^{a}
Jan, 2018	1	0	21.7	0.501	255.8	0.16	288.02
	2	0.1	11.89	0.028	330.2	0	351.07
	3	0.06	14.56	0.855	226.9	0.1	139
		0.05±0.03^{abc}	16.05±2.93^{b}	0.46±0.24^{a}	304.30±39.40^{ab}	0.09±0.05^{a}	259.36±62.87^{a}
Feb	1	0.103	49.87	0.475	375.8	0.237	167.53
	2	0.098	54.4	0.036	115.6	0.01	298.21
	3	0.067	67.12	0	123.6	0.103	166.89
		0.09±0.01^{abc}	57.13±5.16^{ab}	0.17±0.15^{a}	205.00±85.43^{b}	0.12±0.07^{a}	210.88±43.67^{a}
Mar	1	0.238	96.92	0.144	358	0	198.3
	2	0.199	69.8	0.201	247.1	0	234.18
	3	0.286	95.33	0.197	142.2	0	139.82
		0.24±0.03^{a}	87.35±8.79^{a}	0.18±0.02^{a}	249.00±62.30^{ab}	0.00±0.00^{a}	190.77±27.50^{a}
Mean		0.12±0.03	40.05±4.40	0.31±0.05	263.72±13.27	0.05±0.01	210.95±11.69
P-value		0.105	**0.017**	0.534	0.097	0.18	0.915

Means with same superscript along the column are not significantly different at $P > 0.05$

Table 4.5: Seasonal Mean (±S.E.) Variation of Selected Heavy Metals in Sediments and water in Kubanni Reservior

	Heavy metals	Lead(Pb)	Manganese(Mn)	Zinc(Zn)
Water	Dry	0.13±0.03[a]	0.31±0.06[a]	0.06±0.02[a]
	Wet	0.10±0.14[b]	0.31±0.06[a]	0.04±0.02[a]
	P-value	0.056	0.980	0.476
Sediments	Dry	46.97±6.82[a]	286.93±22.02[a]	203.01±18.54[a]
	Wet	33.13±5.26[a]	240.52±13.31[b]	218.89±14.57[a]
	P-value	0.089	**0.028**	0.486

Means with same superscript along the column are not significantly different at $P > 0.05$

Table 4.6: Mean (±S.E.) Variation of Selected Heavy Metals in Sediments and water between the Established Stations

SEDIMENTS				
Metals	**Station 1**	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	43.70±9.37[a]	34.53±6.14[a]	41.92±4.40[a]	0.068
Manganese (Mn)	31.06±16.84[c]	264.51±23.43[a]	212.57±13.27[b]	0.005
Zinc (Zn)	182.87±14.20[c]	264.51±21.74[a]	185.46±15.48[b]	0.003
WATER				
Metals	**Station 1**	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	0.10±0.03[a]	0.15±0.02[a]	0.11±0.01[a]	0.831
Manganese (Mn)	0.33±0.09[a]	0.27±0.06[a]	0.31±0.21[a]	0.664
Zinc (Zn)	0.03±0.02[a]	0.09±0.04[a]	0.04±0.02[a]	0.418

Means with same superscript along the row are not significantly different at $P > 0.05$

4.16 Manganese in Water

The concentration of Manganese in the water of Kubanni Reservoir of Kaduna state (Table 4.4a and 4.4b) has a low value of 0.00mg/l across all the sampling stations, while higher values of 0.91 and 0.93mg/l were recorded in station 1 in June and November respectively. Table 4.4a and b shows the mean values ranges from 0.12±0.01 to 0.73±0.38mg/l, a monthly mean value of 0.31±0.05. There was no significant difference ($P > 0.05$) between the months seasons and stations and for Manganese in water (Table 4.4a, 4.4b, 4.5 and 4.6 respectively). Correlation coefficient analysis shows that Manganese in water positively correlate with Mn in muscles of *Clarias gariepinus*, Pb in gills of *Oreochromis niloticus* and Zn in liver of *Clarias gariepinus* (Table 4.13).

4.17 Manganese in Sediments

Table 4.4a and 4.4b shows the mean levels of Manganese recorded in Kubanni Reservoir of Kaduna State, with range of 194.40±43.63 to 378.21±15.44mg/kg and a monthly mean value of 263.72±13.27. The high concentration values were observed in station 1 with concentration values of 34.80 and 36.90mg/kg for the month of May and December while the lowest concentration values was obtained in station 2 in May with concentration value of 0.105 mg/kg (Table 4.4a and 4.4b). There was no significant difference between the months for sediments water ($p > 0.05$) as shown in Table 4.4.4a and 4.4b but a significant variation ($p < 0.05$) was observed between the seasons and stations (Table 4.5 and 4.6 respectively). Correlation coefficient analysis shows that Manganese in sediments positively correlate Mn in (gills, liver and muscles) of *Clarias gariepinus*, Pb in muscles of *Oreochromis niloticus* and Zn in liver of *Oreochromis niloticus* (Table 4.13).

4.18 Zinc in Water

Table 4.4a and 4.4b presents the result for mean concentrations from 0.00±0.00 to 0.14±0.07 and a monthly mean value of 0.05±0.01 of zinc in Kubanni Reservoir of Kaduna State for the period of twelve months in three sampling stations. Lowest concentration values 0.00mg/l were recorded for all the three stations. In Table 4.4a and 4.4b, 0.23, 0.22 and 0.21 mg/l were the higher concentration values recorded for station 1, 2 and 3 in February, May and July respectively. Table 4.4 shows the mean values for zinc in water ranging (Table 4.4a and 4.4b). Analysis of variance shows no significant difference ($P > 0.05$) between the months, seasons and stations respectively for zinc in water Table 4.4a, 4.4b, 4.5 and 4.6 respectively). Correlation coefficient analysis shows Zinc in water positively correlate with lead in (gills, liver and muscle of) *Clarias gariepinus*, Pb in Gills of *Oreochromis niloticus* and Zn in Gill of *Clarias gariepinus* (Table 4.9).

4.19 Zinc in Sediments

Zinc concentration values recorded in the three sample station are shown in Table 4.4a and 4.4b. The lowest values of 0.00mg/l was obtained in stations 2 and 3, highest value recorded was 0.83mg/l in Station 3 in the month March. Table 4.3a and b. shows the mean values between 155.07±26.56 to 259.36±62.87 and a monthly mean value of 210.95±11.69 (Table 4.4a and 44b) There is no significant difference between the months and seasons for sediments ($p > 0.05$) as shown in Tables 4.4a, 4.4b and 4.5 respectively, however significant difference ($p < 0.05$) occurred between the stations (Table 4.6).Correlation coefficient analysis showed that Zinc in sediments positively correlate Zn in (muscle, liver and gills) *Orechromis niloticus*, Zn in muscle of *Clarias gariepinus* and Manganese in muscle of *Clarias gariepinus* (Table 4.13).

4.20 Lead Concentration in Gills of *Oreochromis niloticus*

High concentration values of Pb were observed on the gills of *Oreochromis niloticus* were recorded across all the sampled stations, while low values were also recorded across the three sampling stations (1, 2 and 3) with concentration value of 0.00mg/kg (Table 4.7a and 4.7b). The mean values ranges from 0.35±0.29 to 2.15±0.17 as showed in Table 4.7a and b, with a monthly mean value of 1.15±0.13 (Table 4.7a and 4.7b). There was no significant difference between months and stations for lead in gills of *Oreochromis niloticus* ($p > 0.05$) as shown in Table 4.7a, b and 4.9 respectively but a significant variation ($p < 0.05$) was observed between the seasons (Table 4.8). Correlation coefficient analysis showed that lead in gills of *Oreochromis niloticus* was found to positively correlate with lead in sediments, lead in water, Manganese in water and Zinc in water while it negatively correlated with Manganese in sediments and Zinc in sediments (Table 4.13).

4.21 Lead Concentration in Liver of *Oreochromis niloticus*

The concentration of Lead in liver of *Oreochromis niloticus* for the three sampled stations in Kubanni Reservoir is illustrated in Table 4.7a and 4.7b, the high concentration of Lead in the liver of *Oreochromis niloticus* was recorded in April in station 2 and 3 with concentration values of 2.72 and 2.321mg/kg. The mean values of lead in liver ranges from 0.29±0.15 to 1.68±0.85 and a monthly mean value of 0.93±0.13 (Table 4.7a and 4.7b) was recorded. Analysis of variance in Table 4.7a, 4.7b, 4.8, 4.9 showed no significant difference ($p > 0.05$) between months, seasons and stations respectively for lead in liver of *Oreochromis niloticus*. Correlation coefficient analysis showed that lead in liver of *Oreochromis niloticus* was found to positively correlate with Lead in sediments and lead in water, while it negatively correlated with Manganese in sediments and water and Zinc in sediments and water (Table 4.13).

Table 4.7a: Mean (±S.E.) Lead, Manganese and Zinc in *Oreochromis niloticus* (mg/kg) caught from Kubanni Reservior

		Oreochromis niloticus								
		Gills			Liver			Muscles		
Months	Stations	Pb	Mn	Zn	Pb	Mn	Zn	Pb	Mn	Zn
April, 2017	1	2	77.27	31.23	0	19.21	6.46	0	4.81	24.38
	2	2.12	98.01	28.87	0.451	18.97	3.03	1.24	2.21	21.18
	3	2.31	16.02	14.5	0.421	19.24	3.46	1.22	3.89	20.16
		2.14±0.09^{a}	63.77±24.61^{a}	24.87±5.23^{a}	0.29±0.15^{a}	19.14±0.09^{ab}	4.32±1.08^{a}	0.82±0.41^{a}	3.64±0.76^{ab}	21.91±1.27^{a}
May	1	1.21	43.31	32.53	1.231	21.35	3.86	1.24	3.67	23.01
	2	2.41	56.67	23.53	0.352	2.36	8.01	0	2.21	23.98
	3	1.21	31.81	31	0	15.78	7.32	1.53	9.23	0
		1.61±0.40^{ab}	43.93±7.18^{a}	29.02±2.78^{a}	0.53±0.37^{a}	13.16±5.64^{ab}	6.40±1.28^{a}	0.92±0.47^{a}	5.03±2.13^{ab}	15.66±7.84^{a}
June	1	1.2	51.24	12.8	0	0	7.96	0	2.67	19.58
	2	1.41	31.04	34.64	1.321	11.9	5.31	1.213	3.09	30.91
	3	0	65.18	0	0.143	10.9	5.02	1.32	2.93	21.82
		0.87±0.44^{ab}	49.15±9.91^{a}	15.82±10.11^{a}	0.49±0.42^{a}	7.60±3.81^{b}	6.09±0.94^{a}	0.84±0.42^{a}	2.90±0.12^{ab}	24.10±3.46^{a}
July	1	1.7	71.85	22.93	1.313	9.26	5.65	1.18	6.23	17.17
	2	1.21	96	28.58	0.91	14.62	5	0.124	6.06	0
	3	0.31	102.43	20.28	0	23.12	5.31	1.421	6.46	17.85
		1.07±0.41^{ab}	90.09±9.31^{a}	23.92±2.45^{a}	0.74±0.39^{a}	15.67±4.04^{ab}	5.32±0.19^{a}	0.91±0.40^{a}	6.25±0.12^{ab}	11.67±5.84^{a}
August	1	1.19	54.72	32.21	0	13.47	7.86	1.91	2.28	7.28
	2	0	81.89	21.11	1.21	19.04	5.11	1.3	3.12	21.69
	3	1.2	74.51	31.2	1.71	11.9	4.21	1.121	3.86	23.68
		0.80±0.40^{ab}	70.37±8.11^{a}	28.17±3.54^{a}	0.97±0.51^{a}	14.80±2.17^{ab}	5.73±1.09^{a}	1.44±0.24^{a}	3.09±0.46^{ab}	17.55±5.17^{a}
September	1	0.92	25.91	30.29	0	13.03	0	1.22	2.12	29.15
	2	0.123	77.32	34.03	1.21	32.11	3.15	1.321	2.34	21.68
	3	0	82.1	24.61	1.201	34.23	5.11	1.12	7.96	19.49
		0.35±0.29^{b}	61.78±17.99^{a}	29.64±2.74^{a}	0.85±0.40^{a}	26.46±6.74^{a}	2.75±1.49^{a}	1.22±0.06^{a}	4.14±1.91^{ab}	23.44±2.92^{a}
Oct	1	0	66.16	34.48	0.81	34.92	5.24	1.271	3.1	0
	2	0.9	10.98	23.51	0	12.91	3.12	1.15	2.02	24.54
	3	1.35	86.23	33.21	1.21	12.87	4.31	0	5.65	0
		0.75±0.40^{ab}	54.46±22.50^{a}	30.40±3.46^{a}	0.67±0.35^{a}	20.23±7.34^{ab}	4.22±0.61^{a}	0.81±0.41^{a}	3.59±1.08^{ab}	8.18±2.18^{a}

Means with same superscript along the column are not significantly different at $p>0.05$

Table 4.7b: Mean (±S.E.) Lead, Manganese and Zinc in *Oreochromis niloticus* (mg/kg) caught from Kubanni Reservior

		Oreochromis niloticus								
		Gills			Liver			Muscles		
Months	Stations	Pb	Mn	Zn	Pb	Mn	Zn	Pb	Mn	Zn
Nov	1	1.21	0	26.81	0.703	27.86	8.39	0.61	9.21	9.89
	2	1.32	91.23	18.29	2.321	19.81	3.12	1.15	3.41	26.75
	3	0	82.22	9.12	1.421	14.97	5.31	0.93	7.86	27.72
		0.84±0.42^{ab}	57.82±29.03^{a}	18.07±5.11^{a}	1.48±0.47^{a}	20.88±7.34^{ab}	5.60±1.53^{a}	0.90±0.16^{a}	6.83±1.75^{a}	21.45±5.79^{a}
Dec	1	0	0	12.44	1.29	22.76	1.69	1.13	2.49	11.62
	2	1.39	96.39	31.21	1.231	18.91	3.94	0	5.31	15.87
	3	1.42	102.5	23.28	0	34.88	0.312	0	3.11	20.84
		0.94±0.47^{ab}	66.30±33.20^{a}	22.31±5.44^{a}	0.84±0.42^{a}	25.52±4.82^{a}	1.98±1.11^{a}	0.38±0.18^{a}	3.64±0.85^{ab}	16.11±2.66^{a}
Jan, 2018	1	1.66	45.8	31.61	1.321	12.47	0	1.35	0	13.43
	2	0	107	21.43	0.3	17.91	8.31	0.49	5.24	22.89
	3	1.39	15.42	31.7	1.624	12.97	9.02	1.92	2.31	18.62
		1.02±0.51^{ab}	56.07±26.93^{a}	28.25±3.41^{a}	1.38±0.40^{a}	14.45±1.74^{ab}	5.78±2.90^{a}	1.25±0.42^{a}	2.52±1.52^{b}	18.31±2.74^{a}
Feb	1	0	3.41	18.3	0	18.34	4.39	0	4.73	18.48
	2	2.35	54.72	34.12	2.72	21.02	4.31	1.21	8.39	19.94
	3	1.63	14.94	30.31	2.31	12.14	3.14	1.42	4.31	28.94
		1.32±0.69^{ab}	88.58±42.62^{a}	27.58±4.77^{a}	1.68±0.85^{a}	17.17±2.63^{ab}	3.95±0.40^{a}	0.88±0.44^{a}	5.81±1.30^{ab}	22.45±3.27^{a}
Mar	1	2.34	134.25	37.93	0.337	19.51	2.33	1.82	5.25	12.86
	2	2.29	54.3	31.45	2.043	13.21	4.22	1.32	7.69	24.05
	3	1.82	72.62	23.61	1.213	14.33	7.12	1.52	6.22	27.91
		2.15±0.17^{a}	47.29±17.02^{a}	30.99±4.14^{a}	1.25±0.49^{a}	15.68±1.94^{ab}	4.56±1.39^{a}	1.55±0.15^{a}	6.39±0.71^{ab}	21.91±4.51^{a}
P-value		0.118	0.941	0.46	0.649	0.181	0.447	0.619	0.205	0.466
Mean	`	1.15±0.13	62.47±6.06	25.75±1.41	0.93±0.13	17.56±1.33	4.73±0.39	0.99±0.01	4.48±0.57	18.26±1.69
WHO		2	5	40	2	5	40	2	5	40

Means with same superscript along the column are not significantly different at $p>0.05$

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Table 4.8: Seasonal Mean (±S.E.) Variation of Pb, Mn, and Zn in *Clarias gariepinus* and *Oreochromis niloticus* caught in Kubanni Reservoir

Fish Organs	Seasons	Lead(Pb)	Manganese(Mn)	Zinc(Zn)
***O. niloticus* gill**	Dry	1..40±0.14[b]	63.30±10.73[a]	25.35±1.92[a]
	Wet	0.90±0.10[a]	61.63±6.00[a]	26.16±2.01[a]
	Mean±S.E	1.15±0.13	62.47±6.06	25.75±1.41
	P-value	0.011	0.889	0.785
***O. niloticus* liver**	Dry	1.1±0.14[a]	18.81±1.34[a]	4.36±0.62[a]
	Wet	0.75±0.13[a]	16.32±2.30[a]	5.09±0.47[a]
	Mean±S.E	0.93±0.07	17.56±1.33	4.73±0.39
	P-value	0.797	0.379	0.312
***O. niloticus* muscle**	Dry	0.96±0.15[a]	4.80±0.57[a]	20.31±1.38[a]
	Wet	0.64±0.12[a]	4.17±0.52[a]	16.77±2.46[a]
	Mean±S.E	1.15±0.13	4.48±0.57	18.26±2.69
	P-value	0.103	0.416	0.232

Means with same superscript along the column are not significantly different at $p>0.05$

Table 4.9: Mean (±S.E.) Variation of Selected Heavy Metals in organs of *Oreochromis niloticus* for the Stations

Heavy metals	***Oreochromis n.***	**Gills**		
	Station 1	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	1.19±0.22[a]	1.29±0.26[a]	1.05±1.34[a]	0.764
Manganese (Mn)	58.27±12.35[a]	71.29±8.62[a]	62.16±9.67[a]	0.661
Zinc (Zn)	27.46±2.58[a]	27.56±1.66[a]	23.28±3.16[a]	0.402
Heavy metals	***Oreochromis n.***	**Livers**		
	Station 1	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	0.58±0.17[a]	1.16±0.21[a]	1.07±0.24[a]	0.135
Manganese (Mn)	16.27±2.93[a]	18.22±2.52[a]	17.11±1.97[a]	0.855
Zinc (Zn)	4.66±1.03[a]	4.96±0.58[a]	4.88±0.60[a]	0.950
Heavy metals	***Oreochromis n.***	**Muscles**		
	Station 1	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	0.87±0.16[a]	0.86±0.15[a]	1.15±0.17[a]	0.424
Manganese (Mn)	3.28±0.49[a]	4.85±0.72[a]	5.23±0.60[a]	0.073
Zinc (Zn)	15.57±2.32[a]	21.81±2.26[a]	19.08±2.82[a]	0.221

Means with same superscript along the rows are not significantly different at $p>0.05$.

4.22 Lead Concentration in Muscles of *Oreochromis niloticus*

Table 4.7a and 4.7b shows the result of lead concentration in muscles of *Oreochromis niloticus* for the three sampled stations in Kubanni Reservoir, the mean values of lead in muscles ranges from 0.81±0.41 to 1.55±0.15mg/kg, while a monthly mean value of 0.99±0.10 was recorded. Low lead concentration in muscles of *Oreochromis niloticus* were recorded in station 1, 2 and 3 for different Months, although lead wasn't detected in some Months across the three sampled stations, while the high concentration of lead in muscles was recorded in February and July in station 3 with concentration values of 1.92 and 1.91mg/kg, as shown in Table 4.7a and 4.7b. No significant difference between months, seasons and stations (Table 4.7a, 4.7b, 4.8 and 4.9 respectively) for lead in muscles of *Oreochromis niloticus* ($p > 0.05$). Correlation coefficient analysis showed that Lead in Muscles of *Oreochromis niloticus* was found to positively correlate with Lead in sediments, Manganese in sediments and Zinc in sediments while it negatively correlated with Lead in water, Manganese in water, and Zinc in water (Table 4.13).

4.23. Manganese (Mn) Concentration in Gills of *Oreochromis niloticus*

Mean values for Manganese in gills of *Oreochromis niloticus* ranges in the three sampled stations in Kubanni Reservoir from 43.93±7.18 to 90.09±9.13mg/kg, while a monthly mean value of 62.47±6.06 (Table 4.7a, and 4.7b) was recorded. Low concentration of Manganese in gills was recorded as 0.00mg/kg in station 1 in October, while higher concentration values of Manganese in gills were recorded in station 1 in the months of March and August with concentration values of 134.25 and 134.05mg/kg respectively (Table 4.7a, and 4.7b). No significant difference between months, seasons and stations (Table 4.7a, 4.7b, 4.8 and 4.9 respectively) for Manganese in *Oreochromis niloticus* ($p > 0.05$). Correlation coefficient analysis shows that Manganese in gills of *Oreochromis niloticus* was found to positively correlate with

lead in sediments, lead in water and Zinc in sediments while it negatively correlated with Manganese in sediments, Manganese in water and Zinc in water (Table 4.13).

4.24 Manganese Concentration in Liver of *Oreochromis niloticus*

Table 4.7a, and 4.7b illustrate concentrations of Manganese (Mn) in *Oreochromis niloticus* liver with 0.00mg/kg as the lowest concentration value in station 1 in months of January and September while higher concentration values of 34.88, 34.92 and 34.23mg/kg were recorded in station 1, 2 and 3 in December for station 1 and April for both station 2 and 3. Table 4.7a, and 4.7b shows mean manganese concentration on *Oreochromis niloticus*, to range from 7.60±3.81 to 26.46±6.74 and a monthly mean value of 17.56±1.33 was recorded. There is no significant difference between the months, seasons and stations for Manganese liver of *Oreochromis niloticus* ($p > 0.05$) as shown in Table 4.7a, 4.7b, 4.8 and 4.9 respectively. Correlation coefficient analysis of Manganese in liver of *Oreochromis niloticus* was found to positively correlate with Lead in water, while it negatively correlated with Lead in sediments, Manganese in sediments, Manganese in water, Zinc in sediments and Zinc in water (Table 4.13)

4.25. Manganese Concentration in Muscles of *Oreochromis niloticus*

Manganese (Mn) Concentration in muscles of *Oreochromis niloticus* for the three sampled stations in Kubanni Reservoir ranged between 2.52±1.52 to 6.83±1.75mg/kg. The monthly mean value of muscles (4.48±0.38mg/kg) was recorded. No Manganese was observed in Muscles of *Oreochromis niloticus* observed in January. However, high Concentration (9.21mg/kg) of Manganese in muscles of *Oreochromis niloticus* was observed in October in station 2 (Table 4.7a, and 4.7b). There was no significant variation ($P > 0.05$) between the manganese values observed monthly, compared to those observed in (Table 4.7a, 4.7b, 4.8 and 4.9 respectively). Correlation coefficient analysis of Manganese in Muscles of *Oreochromis niloticus* was found to

positively correlate with Lead in water, Lead in sediments and Zinc in sediments while it negatively correlated with Manganese in sediments, Manganese in water, and Zinc in water (Table 4.13).

4.26. Zinc Concentration in Gills of *Oreochromis niloticus*

Table 4.7a, and 4.7b represents the variations of zinc concentration in the gills of *Oreochromis niloticus* in Kubanni Reservoir in respect to the months, no Zinc (0.00mg/kg) in the gills of *Oreochromis niloticus* was recorded in stations 3 in June while some of the analysis obtained with negative values were regarded as zero values. A higher concentration value of 37.93, 37.82 and 37.81mg/kg for zinc concentration in the gills of *Oreochromis niloticus* were recorded in May and August in the three sampled stations. The mean value obtained for the period of 12 months in respect to the stations ranges between 15.82±10.11 to 30.99±4.14 and a monthly mean value of 25.75±1.41mg/kg (Table 4.7a, and 4.7b) was recorded. No significant difference between the months, seasons and stations for Zinc in gills of *Oreochromis niloticus* ($p > 0.05$) as shown in Table 4.7a, 4.7b, 4.8 and 4.9 respectively. Correlation coefficient analysis of Zinc in gills of *Oreochromis niloticus* was found to positively correlate with lead in sediments, lead in water, Zinc in sediments and Zinc in water while it negatively correlated with Manganese in sediments and Manganese in water (Table 4.13).

4.27. Zinc Concentration in Liver of *Oreochromis niloticus*

Table 4.7a, and 4.7b shows the mean values for Zinc in liver of *Orechromis niloticus*, which ranges between 1.98±1.11 to 6.40±1.28 mg/kg and a monthly mean value of 4.73±0.39 mg/kg was recorded. Table 4.7a, and 4.7b shows the higher and lower concentration values (0.00mg/kg) recorded, was recorded in stations 1 in June and July as the lowest concentration value, while higher concentration (9.02mg/kg) were recorded in station 1 as well in March and September

respectively, negative values were considered as Zero values . Table 4.7a, 4.7b, 4.8 and 4.9 shows no significant difference between the months, seasons and stations respectively for Zinc in liver of *Oreochromis niloticus* ($p > 0.05$). Correlation coefficient analysis shows that Zinc in liver of *Oreochromis niloticus* was found to positively correlate with Lead in water, Lead in sediments, Manganese in sediments and Zinc in sediments while it negatively correlated with Manganese in water, and Zinc in water (Table 4.13).

4.28. Zinc Concentration in Muscles of *Oreochromis niloticus*

Table 4.7a and 4.7b shows the mean Zinc concentration in fish value obtained for the period of 12 months across the three sampled stations which ranged from 8.18±2.18 to 24.10±3.46 mg/kg, while a monthly mean value of 18.54±1.42 mg/kg was recorded. The highest concentration value (30.21 and 30.91mg/kg) for Zinc in the muscle of *Oreochromis niloticus* was recorded in February in station 2 and 3, while no zinc concentration was observed in the muscle of *Oreochromis niloticus* caught from Kubanni Reservoir, though Zinc wasn't detected in some stations during the sampling period while some of the data that were obtained from the analysis with negative values were regarded as zero values (Table 4.7a and 4.7b). Table 4.7a, 4.7b, 4.8 and 4.9 showed no significant difference ($p > 0.05$) between the months, seasons and stations respectively for Zinc in muscle of *Oreochromis niloticus*. Correlation coefficient analysis shows that Zinc in Muscles of *Oreochromis niloticus* was found to positively correlate with Lead in water, Lead in sediments and Zinc in sediments while it negatively correlated with Manganese in sediments, Manganese in water, and Zinc in water (Table 4.13).

4.29. Lead Concentration in Gills of *Clarias gariepinus*

Table 4.10a and 10b shows the lead concentration in the gills of *Clarias gariepinus* caught from Kubanni Reservoir of Kaduna State. The monthly lead ranged between 0.62±0.38 to 1.37±0.06

mg/kg, while a monthly mean value of 0.97±0.08 was recorded. High concentration values (1.40.mg/kg) were recorded across the three sampled stations in different months, while 0.00mg/kg concentration values was observed across the three sampled stations. Table 4.11 and 10b shows significant difference ($p < 0.05$) between the seasons for lead in gills *Clarias gariepinus* ($p < 0.05$) but no significant variation ($p > 0.05$) was observed between the months and stations (Table 4.10a, 10b and 4.12 respectively). Correlation coefficient analysis shows that Lead in gills of *Clarias gariepinus* was found to positively correlate with Lead in sediments and Zinc in water while it negatively correlated with Lead in water, Manganese in sediments, Manganese in water and Zinc in sediments (Table 4.14).

4.30. Lead Concentration in Liver of *Clarias gariepinus*

Table 4.10a and 10b shows the mean values for lead in liver of *Clarias gariepinus*, which is between 0.44±0.34 to 1.77±0.17 while a monthly mean value of 1.08±0.13 was recorded. Table 4.10a and 10b shows the higher and 0.00mg/kg concentration values was recorded, across all the sampled stations (1, 2 and 3) as the lowest concentration in different months, while higher concentration (1.94, 1.94 and 1.92mg/kg) were recorded in station 1, 2 and 3 in April, April and May respectively. There was no significant difference ($p > 0.05$) between the months, seasons and stations for lead in liver of *Clarias gariepinus* as shown in Table 4.10a, 10b 4.11 and 4.12 respectively. Correlation coefficient analysis shows that Lead in Liver of *Clarias gariepinus* was found to negatively correlate with Manganese in sediments and Manganese in water while it positively correlate with Lead in sediments, Lead in water, Zinc in water and Zinc in sediments

(Table 4.13).

Table 4.10a: Mean (±S.E.) Zinc concentration in organs of *Clarias gariepinus* (mg/kg) caught from Kubanni Reservior

		Clarias *gariepinus*								
		Gills			Liver			Muscles		
Months	Stations	Pb	Mn	Zn	Pb	Mn	Zn	Pb	Mn	Zn
April, 2017	1	1.43	33.9	42.3	1.94	14.84	16.9	2.68	5.24	39.56
	2	1.434	32	43.1	1.94	22.03	17.64	2.721	3.12	42.06
	3	1.251	12.23	31.9	1.43	31.18	15.28	2.34	3.89	11.31
		1.37±0.06^{a}	26.04±6.92^{c}	39.10±3.61^{c}	1.77±0.17^{a}	22.68±4.73^{abcde}	16.61±0.70^{ab}	2.58±0.12^{a}	4.08±0.62^{a}	30.98±9.86^{a}
May	1	0	25.2	44.97	0	21.2	13.1	1.21	8.39	0
	2	1.312	31.65	44.01	1.51	10.9	10.75	2.72	3.12	31
	3	1.441	41	42.1	1.21	14.98	12.4	1.12	9.23	15
		0.92±0.46^{a}	32.62±4.59^{bc}	43.69±0.84^{bc}	0.91±0.46^{ab}	15.69±2.99^{cde}	12.08±0.70^{ab}	1.68±0.52^{ab}	6.91±1.91^{a}	15.33±8.95^{a}
June	1	1.219	38.4	79.8	1.25	0	10.25	0	1.69	41.09
	2	1.353	31.05	31.2	1.92	12.1	13.08	1.49	3.94	21.44
	3	1.345	41.1	78.1	1.4	10.9	19.8	0	3.3	12.23
		1.31±0.04^{a}	36.85±3.00^{bc}	63.03±15.92^{ab}	1.52±0.20^{ab}	7.67±3.85^{e}	14.38±2.83^{ab}	0.50±0.26^{b}	2.98±0.67^{a}	24.92±8.51^{a}
July	1	1.026	81.01	77.73	1.32	17	9.14	2.41	0	25
	2	1.081	41.32	81.5	1.42	9.05	15.23	0	8.31	51
	3	1.252	39.1	51.1	0	8.29	11.22	1.31	3.65	21.31
		1.12±0.07^{a}	53.81±13.62^{abc}	70.11±9.57^{a}	0.91±0.46^{ab}	11.45±2.79^{de}	11.86±1.79^{ab}	1.24±0.70^{ab}	3.97±2.41^{a}	32.44±9.34^{a}
August	1	0.831	72.7	68.7	0	16.7	13.78	1.12	3.15	48.3
	2	0.512	39.2	92.1	1.45	38.51	12.87	0	5.11	21.2
	3	0.841	53.1	87.2	1.25	29.82	12.87	0	2.11	25.21
		0.73±0.11^{a}	55.00±9.72^{abc}	82.67±7.13^{a}	0.90±0.45^{ab}	28.34±6.34^{abcd}	13.17±0.30^{ab}	0.37±0.12^{b}	3.46±0.88^{a}	31.57±8.44^{a}
September	1	1.32	69.03	28.5	1.31	53.36	7.23	0	3.12	35.9
	2	0	90.1	29.3	0	48.28	18.32	1.72	4.31	23.1
	3	0.551	52.61	30.1	0	19.47	0.074	1.112	3.11	21.24
		0.62±0.38^{a}	70.58±10.85^{a}	29.30±0.46^{c}	0.44±0.34^{b}	40.37±10.55^{a}	8.54±5.31^{b}	0.94±0.50^{b}	3.51±0.40^{a}	26.75±4.61^{a}
Oct	1	1.182	81.8	34.6	1.21	7.29	19.68	0	3.12	78.15
	2	0.725	32.1	21.6	1.24	22.34	12.31	1.121	5.31	22.96
	3	0.249	63.12	31.1	1.31	21.89	9.71	1.31	3.31	31.32
		0.72±0.27^{a}	59.01±14.93^{ab}	29.10±3.88^{c}	1.25±0.03^{ab}	17.17±4.94^{cde}	13.90±2.99^{ab}	0.81±0.41^{b}	3.91±0.70^{a}	44.14±17.17^{a}

Means with same superscript along the column are not significantly different at $p>0.05$

Table 4.10b: Mean (±S.E.) Zinc concentration in organs of *Clarias gariepinus* (mg/kg) caught from Kubanni Reservior

			Clarias *gariepinus*								
			Gills			Liver			Muscles		
Months	Stations	Pb	Mn	Zn	Pb	Mn	Zn	Pb	Mn	Zn
Nov	1	1.057	74.49	26.5	1.31	0.037	12.19	0	3.94	62.17
	2	0.901	49.1	32.3	1.21	38.71	18.22	1.31	0.312	32.2
	3	1.312	51.3	34.2	1.34	18.4	12.81	1.21	6.31	31.32
		1.09±0.12^{a}	58.30±8.12^{ab}	31.00±2.32^{c}	1.29±0.04^{ab}	19.05±11.17^{bcde}	14.41±1.92^{ab}	0.84±0.42^{b}	3.52±1.74^{a}	41.90±10.14^{a}
Dec	1	1.051	59.22	40.3	1.45	16	11.23	2.24	5.25	4.95
	2	2	83.12	43.1	1.51	18.85	11.81	1.21	3.65	25.12
	3	0.72	43.13	42.3	0	19	10.85	0	6.01	32.83
		1.26±0.38^{a}	61.82±11.61^{ab}	41.90±0.83^{c}	0.99±0.49^{ab}	17.95±0.98^{cde}	11.30±0.28^{ab}	1.15±0.64^{ab}	4.97±0.70^{a}	20.97±8.31^{a}
Jan, 2018	1	0.811	67.8	23.3	1.24	16.67	16.22	0.54	4.81	0
	2	1.15	54.1	43.1	1.31	29.1	2.38	0.1	2.34	52.83
	3	0	61.21	45.36	1.21	34.11	17.26	1.21	3.22	31.41
		0.65±0.34^{a}	61.04±3.96^{ab}	37.25±7.01^{c}	1.25±0.03^{ab}	26.63±5.18^{abcde}	11.95±4.80^{ab}	0.62±0.32^{b}	3.46±0.72^{a}	28.08±15.34^{a}
Feb	1	1.151	42.2	33.65	0	23.96	17.44	2.188	7.96	16.23
	2	0.913	53.31	45.02	0.42	31.05	17.05	1.39	5.31	23.61
	3	1.051	63.12	43.31	0.954	41.18	17.62	1.42	5.02	32.71
		1.04±0.07^{a}	52.88±6.04^{abc}	40.66±3.54^{c}	0.46±0.28^{b}	32.06±5.00^{abc}	17.37±0.17^{b}	1.67±0.26^{ab}	6.10±0.94^{a}	24.18±4.77^{a}
Mar	1	1.392	64.3	77	0.705	50.65	18.22	1.37	21.67	34.12
	2	0	93.1	53.4	1.92	32.26	18.17	2.25	3.41	31.4
	3	1.15	51.12	67	1.31	32.13	18.24	1.31	3.12	23.21
		0.85±0.43^{a}	69.51±12.40^{a}	65.80±6.83^{a}	1.31±0.35^{ab}	38.35±6.15^{ab}	18.21±0.02^{a}	1.64±0.30^{ab}	9.40±6.13^{a}	29.58±3.28^{a}
P-value		0.556	0.052	0	0.23	0.016	0.329	0.079	0.646	0.753
Mean		0.97±0.08	53.12±3.23	29.23±1.42	1.08±0.13	23.12±2.21	12.82±0.75	1.17±0.14	4.48±0.38	29.23±1.42
WHO		2	5	40	2	5	40	2	5	40

Means with same superscript along the column are not significantly different at $p>0.05$

Table 4.11: Seasonal Mean (±S.E.) Variation of Pb, Mn, and Zn in *Clarias gariepinus* caught in Kubanni Reservoir

Fish Organs	Seasons	Lead(Pb)	Manganese(Mn)	Zinc(Zn)
***C. gariepinus* gills**	Dry	0.65±0.20[b]	54.93±4.49[a]	42.62±2.09 [a]
	Wet	0.90±0.15[a]	51.31±4.73[a]	52.98±5.70 [a]
	Mean±S.E	0.97±0.08	53.12±3.23	47.80±1.41
	P-value	**0.015**	0.612	0.086
***C. gariepinus* liver**	Dry	1.18±0.20[a]	26.12±2.78[a]	13.31±0.97[a]
	Wet	0.99±0.17[a]	20.12±3.36[a]	12.32±1.08[a]
	Mean±S.E	1.08±0.13	23.12±2.21	12.82±0.75
	P-value	0.778	0.241	0.051
***C. gariepinus* muscle**	Dry	1.42±0.20[a]	5.26±1.05[a]	29.28±3.62[a]
	Wet	0.92±0.19[b]	4.13±0.57[a]	29.19±4.10[a]
	Mean±S.E	1.17±0.14	4.68±0.38	29.23±1.42
	P-value	**0.043**	0.438	0.987

Means with same superscript along the column are not significantly different at $p>0.05$

Table 4.12: Variation of Selected Heavy Metals in organs of *Clarias gariepinus* for the Stations

Heavy metals	***C. gariepinus***	**Gills**		
	Station 1	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	1.08±0.13 [a]	0.88±0.16 [a]	1.02±0.15 [a]	0.612
Manganese (Mn)	61.99±6.25 [a]	47.44±6.28 [a]	47.67±4.06 [a]	0.127
Zinc (Zn)	43.80±8.73 [a]	45.39±5.21 [a]	48.64±5.47 [a]	0.877
Heavy metals	***C. gariepinus***	**Liver**		
	Station 1	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	0.97±0.18 [a]	1.27±0.16 [a]	0.99±0.18 [a]	0.436
Manganese (Mn)	22.40±5.56 [a]	25.05±3.57 [a]	23.44±2.92 [a]	0.902
Zinc (Zn)	12.84±1.29 [a]	13.79±1.58 [a]	12.17±1.52 [a]	0.731
Heavy metals	***C. gariepinus***	**Muscle**		
	Station 1	**Station 2**	**Station 3**	**P-values**
Lead (Pb)	1.29±0.31[a]	1.24±0.24[a]	1.06±0.22[a]	0.801
Manganese (Mn)	4.57±0.81[a]	4.02±0.56[a]	3.84±0.36[a]	0.672
Zinc (Zn)	38.39±8.43[a]	31.49±3.25[a]	24.40±2.32[a]	0.187

Means with same superscript along the rows are not significantly different at $p>0.05$.

4.31. Lead Concentration in Muscles of *Clarias gariepinus*

The concentration of lead in the muscles of *Clarias gariepinus* of Kubanni Reservoir is presented in Table 4.10a and 10b, showing low concentration of Lead (0.00mg/kg) in the gills of *Clarias gariepinus* recorded in all the three sampled stations in June, July, August September October and December, though lead wasn't detected in some stations during the sampling period while some of the analysis that was obtained with negative values were regarded as zero values. Higher concentration values (2.70 and 2.721mg/kg) for lead in the muscles of *Clarias gariepinus* were recorded in the months of March and April in station 1, 2 and 3. The mean values obtained for the period of 12 months in respect to the stations ranges between 0.37±0.12 to 2.58±0.12, while a monthly mean value of 1.17±0.14 was recorded (Table 4.10a and 10b). There was significant difference ($p < 0.05$) between the seasonal lead value for lead in muscles of *Clarias gariepinus* as shown in Table 4.11 however no significant difference ($p > 0.05$) between the months and stations (Table 4.10a and 10b and 4.12 respectively). Correlation coefficient analysis shows that Lead in Muscles of *Clarias gariepinus* was found to negatively correlate with Manganese in water and Manganese in sediments while it positively correlate with Lead in sediments, Lead in water, Zinc in water and Zinc in sediments which (Table 4.13).

4.32. Manganese Concentration in Gills of *Clarias gariepinus*

Low Manganese concentration (12.21 and 12.23mg/kg) in Gills of *Clarias gariepinus* were recorded in station 2 and 3 in the month April, while a high concentration value of 83.12mg/kg was recorded in December in station 1 (Table 4.10a and 10b). Table 4.8 shows the mean values of Manganese in Gills of *Clarias gariepinus* ranging from 26.04±6.92 to 69.51±12.40 and a monthly mean value of 53.12±3.23 was recorded. Analysis of variance showed no significant difference ($p > 0.05$) between the months, seasons and stations for Manganese in gills of *Clarias*

gariepinus as shown in Table 4.10a, 10b, 4.11 and 4.12 respectively. Correlation coefficient analysis shows that Manganese in gills of *Clarias gariepinus* was found to positively correlate with Lead in sediments, Lead in water, Manganese in sediments, Manganese in water and Zinc in sediments except for Zinc in water which it negatively correlate (Table 4.13).

4.33. Manganese Concentration in Liver of *Clarias gariepinus*

The Manganese concentration in Liver of *Clarias gariepinus* for the three sampled stations in Kubanni Reservoir is illustrated in Table 4.10a and 10b, no Manganese concentration (0.00mg/kg) was recorded in Liver in station 1 in the months of January and May, while the higher concentration of Manganese in liver was recorded in November, December and March in station 2 and 3 with concentration values of 53.37 and 53.34mg/kg. The mean values of Manganese in Liver ranges from 7.67±3.82 to 40.37±10.55) as showed in Table 4.10a and 10b while a monthly mean value of 23.12±2.21 was recorded. Analysis of variance in Table 4.10a and 10b shows significant difference ($p < 0.05$) between the months, no significant difference ($p > 0.05$) between the seasons and stations for Manganese in liver of *Clarias gariepinus* (Table 4.11 and 4.12). Correlation coefficient analysis shows that Manganese in Liver of *Clarias gariepinus* was found to negatively correlate with Zinc in water and Manganese in water while it positively correlate with Lead in sediments, Lead in water, Manganese in sediments and Zinc in sediments (Table 4.13).

4.34. Manganese Concentration in Muscles of *Clarias gariepinus*

Table 4.10a and 10b shows the mean values obtained for the period of 12 months across the three sampled stations which ranged from 2.98±0.67 to 9.40±6.13, while a monthly mean value of 4.68±0.38 was recorded. A high concentration value of 9.23mg/kg for Manganese in the muscle

of *Clarias gariepinus* was recorded in the month October in station 1, while low concentration of Mn (0.00mg/kg) in the muscle of *Clarias gariepinus* was recorded in station 1 in month of July, though Manganese wasn't detected in some stations during the sampling period. Analysis of variance in Table 4.10a, 4.10b, 4.11 and 4.12 showed no significant difference between the months, seasons and stations respectively for Manganese in muscles of *Clarias gariepinus* ($p > 0.05$). Correlation coefficient analysis shows that Manganese in Muscles of *Clarias gariepinus* was found to positively correlate with Lead in water, Manganese in water, Zinc in sediments, Manganese in sediments and while it negatively correlate with, Lead in sediments and Zinc in water (Table 4.13).

4.35. Zinc Concentration in Gills of *Clarias gariepinus*

The mean value obtained for the period of 12 months in respect to the sampled stations ranges between 29.10±3.88 to 82.67±7.13 (Table 4.10a and 10b) while a monthly mean value of 47.80±3.31 was recorded. The concentration of zinc in the gills of *Clarias gariepinus* of Kubanni Reservoir is presented in Table 4.10a and 10b which shows the variations in different stations in respect to months. Zinc wasn't detected in the gills of *Clarias gariepinus* in station 1 in November and December, while some of the analysis that was obtained with negative values were regarded as zero values, the highest concentration value of 92.1mg/kg for zinc in the gills of *Clarias gariepinus* was recorded in March in station 1.

There was significant difference ($p < 0.05$) between the months as shown in Table 4.10a and 4.10b however no significant difference ($p > 0.05$) between seasons and stations for Zinc in gills of *Clarias gariepinus* as showed in Table 4.11 and 4.12 respectively.

Correlation coefficient analysis shows that Zincs in gills of *Clarias gariepinus* was found to positively correlate with Manganese in sediments and Zinc in water while it negatively correlate with Lead in sediments, Lead in water, Manganese in water and Zinc in sediments (Table 4.13).

4.36. Zinc Concentration in liver of *Clarias gariepinus*

The mean level for the months across the three sampled stations ranges between 1.30±0.28 to 18.21±0.02 mg/kg and a monthly mean value of 12.82±0.75 was observed, Table 4.10a and 10b shows the concentration levels of Zinc in the Liver of *Clarias gariepinus* recorded in Kubanni Reservoir of Kaduna State during the study. Low concentration values were recorded in the three sampled stations with concentration level of 0.70smg/kg, for the month of November, while high concentration values were recorded in station 2, in March, September and December (19.68, 19.52 and 19.81mg/kg respectively). There is no significant difference ($p > 0.05$) between the months, seasons and stations for Zinc in liver of *Clarias gariepinus* as showed in (Table 4.10a and 10b), 4.11 and 4.12 respectively. Correlation coefficient analysis shows that Zinc in Liver of *Clarias gariepinus* was found to negatively correlate with Zinc in water and Manganese in sediments while it positively correlate with Lead in sediments, Lead in water, Manganese in water and Zinc in sediments (Table 4.13).

4.37. Zinc Concentration in Muscle of *Clarias gariepinus*

Mean values for Zinc in muscles of *Clarias gariepinus* in the three sampled stations in Kubanni Reservoir ranges from 15.33±8.95 to 44.14±17.17, and a monthly mean value of 29.23±1.42 was recorded. Lowest concentration of Zinc in muscles (0.00 mg/kg) was recorded in station 1 in June, while the higher concentration values for Zinc in Muscles was recorded in station 1 as well in March and September with concentration values of 78.15mg/kg respectively (Table 4.10a and

10b). Analysis of variance in (Table 4.10a , 10b, 4.11 and 4.12 shows no significant difference ($p > 0.05$) between the months, seasons and stations respectively for Zinc in muscles of *Clarias gariepinus*. Correlation coefficient analysis shows that Zinc in Muscles of *Clarias gariepinus* was found to negatively correlate with Manganese in water, Manganese in sediments and Zinc in water while it positively correlate with, , Lead in water, Lead in sediments and Zinc in sediments (Table 4.13).

Table 4.13: Correlation Matrix of Selected Heavy Metals in Water, Sediments and Some Fish Organs

Variables	PbS	PbW	MnS	MnW	ZnS	ZnW
PGC	0.104	-0.033	-0.401*	-0.134	-0.006	0.039
PLC	0.319	0.401*	-0.225	-0.166	0.130	0.006
PMC	0.365*	0.156	-0.128	-0.242	0.090	0.284
PGO	0.270	0.042	-0.116	0.258	-0.005	0.193
PLO	0.216	0.253	-0.374*	-0.070	-0.81	-0.133
PMO	0.098	-0.256	0.127	-0.038	0.202	-0.027
MGC	0.330*	0.028	0.291	0.016	0.410*	-0.326
MLC	0.138	0.097	0.067	-0.153	0.270	-0.403*
MMC	-0.089	0.157	0.067	0.046	0.035	-0.319
MGO	0.301	0.005	-0.187	-0.127	0.072	-0.236
MLO	-0.035	0.064	-0.164	-0.068	-0.226	-0.192
MMO	0.101	0.195	-0.115	-0.167	0.166	-0.459**
ZGC	-0.171	-0.174	0.115	-0.265	0.231	0.127
ZLC	0.175	0.045	-0.037	0.075	0.133	-0.177
ZMC	0.352*	0.064	-0.208	-0.244	0.450**	-0.178
ZGO	0.515**	0.242	-0.135	-0.078	0.406*	0.019
ZLO	0.288	0.007	0.028	-0.252	0.486**	-0.088
ZMO	0.369*	0.094	-0.132	-0.294	0.511**	-0.058

Keys:*=Significant,**=Highly Significant, PbS=Lead in Sediments, PbW=Lead in Water, MnW=Manganese in Sediments, MnW=Manganese in Water, ZnS=Zinc in Sediments, ZnW=Zinc in Water, PGC=Lead in gills of *Clarias gariepinus,* PLC=Lead in liver of *Clarias gariepinus*, PMC=Lead in muscles of *Clarias gariepinus*, PGO=Lead in the gills of *Oreochromis niloticus*, PLO=Lead in liver of *Clarias gariepinus*, PMO=Lead in muscles of *Clarias gariepinus*, MGO=Manganese in gills of *Clarias gariepinus*, MLC=Manganese in liver of

Oreochromis niloticus, MMC=Manganese in muscles of *Clarias gariepinus*, MGO=Manganese in gills of *Oreochromis niloticus*, MLO=Manganese in liver of *Oreochromis niloticus*, MMO=Manganese in Muscles of *Oreochromis niloticus*, ZGC=Zinc in gills of *C. gariepinus*, ZLC=zinc in Liver of *Clarias gariepinus*, ZMC=Zinic in muscle of *Clarias gariepinus*, ZGO=Zinc in gills of *Oreochromis niloticus*, ZLO=Zinc in liver of *Oreochromis niloticus*, ZMO=Zinc in muscles of *Oreochromis niloticus*.

Relationship among the water quality parameters in Kubanni Reservoir

4.38. Temperature

Correlation coefficient analysis shows that temperatures was found to correlate positively with turbidity and electrical conductivity in January, April May and June, While in September it also positively correlate with Alkalinity and pH (Figure 4.1).

4.39. Water pH

Figure 4.1, shows that water pH was found to correlate positively with alkalinity, Phosphate Phosphorus and hardness chemical oxygen demand in September and March, while in January, April, May and June it also positively correlate with temperature, turbidity, nitrogen nitrate and electrical conductivity.

4.40. Dissolved Oxygen

Correlation coefficient analysis showed that there was negative and significant correlation between Dissolved Oxygen and Biological Oxygen Demand, Total Dissolved Solid in July, October, November and December while in March DO_2 positively correlate with water hardness and phosphate phosphorus (Figure 4.1).

4.41. Biological Oxygen Demand

A negative and significant correlation was observed between Biological Oxygen Demand, Total Dissolved Solid and Dissolved Oxygen in July, October, November and December, while in month of March BOD positively correlate with water hardness and phosphate phosphorus (Figure 4.1).

4.42. Turbidity

Positive correlations occur between turbidity, electrical conductivity and temperature in January, April, May and June while in September it also correlate with alkalinity and pH (Figure 4.1).

4.43. Chemical Oxygen Demand

Correlation coefficient analysis in Figure 4.1 showed positive correlation between Chemical Oxygen Demand, phosphate phosphorous and water hardness in March. A negative correlation also exist between water hardness and Biological Oxygen Demand, Dissolved and Total Dissolved Solid in July, August, October, November and December.

4.44. Alkalinity

Correlation coefficient analysis in Figure 4.19 revealed positive correlation between Alkalinity and pH in September, water pH was also found to correlate positively with Turbidity and electrical conductivity in January.

4.45. Water Hardness

Correlation coefficient analysis in Figure 4.1 showed positive correlation between water hardness with phosphate phosphorous in March. A negative correlation also exist between water hardness and Biological Oxygen Demand, Dissolved and Total Dissolved Solid in July, August, October, November and December.

4.46. Nitrate-Nitrogen

Correlation coefficient analysis between nitrate-nitrogen with pH, hardness, alkalinity, conductivity and dissolved oxygen negatively correlate with BOD (Figure 4.1).

4.47. Phosphate-Phosphorus

There was negative and significant correlation between phosphate phosphorus and water hardness in March while in July, August October November and December they negatively correlate with Phosphate-Phosphorus (Figure 4.1).

4.48. Total Dissolved Solid

Correlation coefficient analysis revealed that there was negative and significant correlation between Total Dissolved Solid, Biological Oxygen Demand and Dissolved Oxygen in July, October, November and December, while in month of March TDS positively correlate with water hardness and phosphate phosphorus (Figure 4.1).

4.49. Electrical Conductivity

Correlation coefficient between electrical conductivity and other parameters showed significant positive correlation (Figure 4.1), water temperature and Turbidity in January, April, May and June and also correlate positively with Alkalinity and water pH in September.

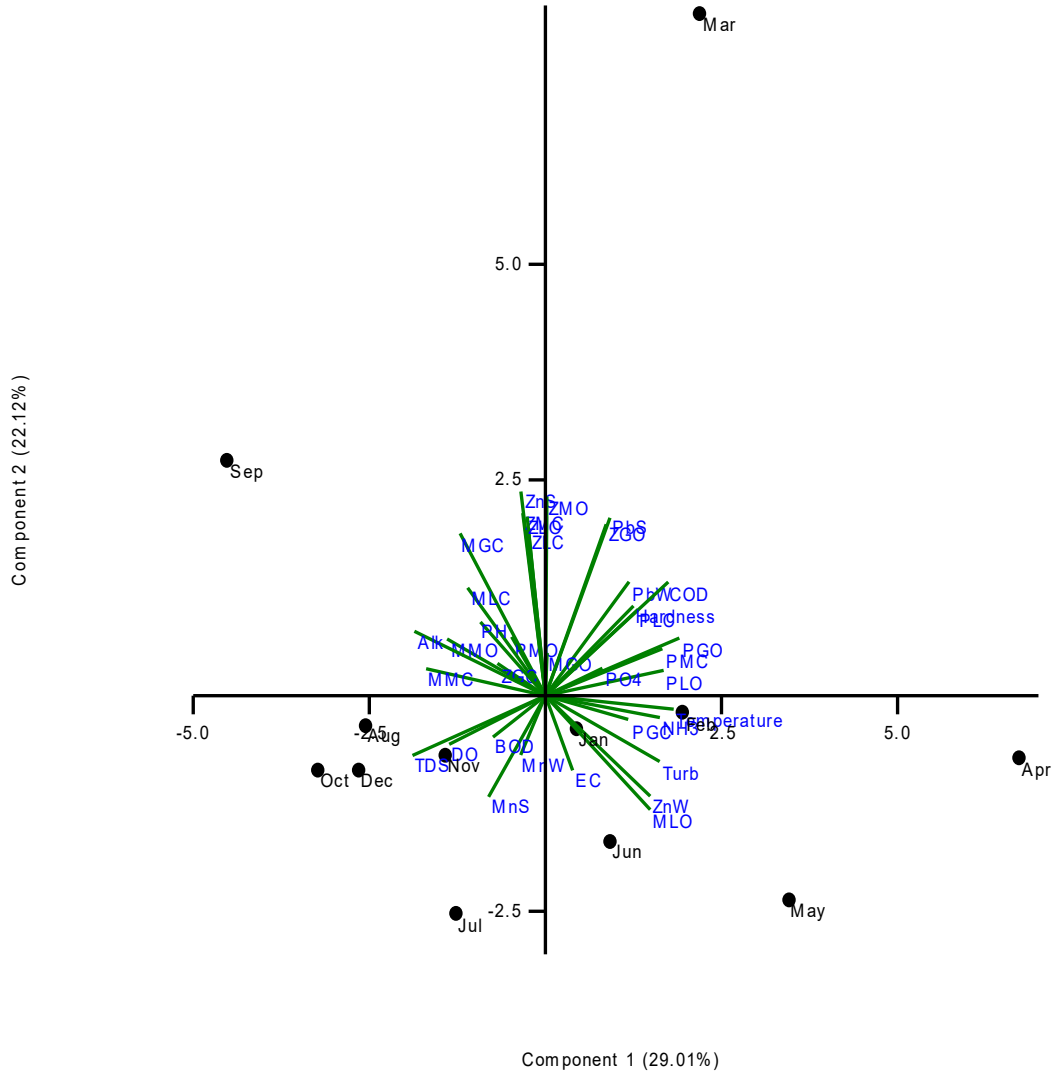

Figure 4.1: Relationship between Physicochemical Parameter, with Heavy Metal in Water, Sediments and Fish Organs.

Keys: PbS=Lead in Sediments, PbW=Lead in Water, MnW=Manganese in Sediments, MnW=Manganese in Water, ZnS=Zinc in Sediments, ZnW=Zinc in Water, PGC=Lead in gills of *Clarias gariepinus,* PLC=Lead in liver of *Clarias gariepinus*, PMC=Lead in muscles of *Clarias gariepinus*, PGO=Lead in the gills of *Oreochromis niloticus*, PLO=Lead in liver of *Clarias*

gariepinus, PMO=Lead in muscles of *Clarias gariepinus*, MGO=Manganese in gills of *Clarias gariepinus*, MLC=Manganese in liver of *Oreochromis niloticus*, MMC=Manganese in muscles of *Clarias gariepinus*, MGO=Manganese in gills of *Oreochromis niloticus*, MLO=Manganese in liver of *Oreochromis niloticus*, MMO=Manganese in Muscles of *Oreochromis niloticus*, ZGC=Zinc in gills of *C. gariepinus*, ZLC=zinc in Liver of *Clarias gariepinus*, ZMC=Zinic in muscle of *Clarias gariepinus*, ZGO=Zinc in gills of *Oreochromis niloticus*, ZLO=Zinc in liver of *Oreochromis niloticus*, ZMO=Zinc in muscles of *Oreochromis niloticus*.

CHAPTER FIVE

5.0. DISCUSSIONS

5.1. Physico-Chemical Parameters of Water

The physico-chemical parameters of the water samples from Kubanni Reservoir were found within beneficial levels which support both human and aquatic animals' usage.

The lower temperature in January could be due to the prevailing North-East trade wind called Harmattan, as suggested by Adakole (2000), Oniye *et al*. (2002), Tukura (2005), and Adakole *et al*. (2008) reported that water temperatures were low during this harmattan period of the year in their studies on related aspects of some water bodies of Northern Nigeria. This findings is in accordance with observations of Kemdirim (1990), Kolo and Oladimeji (2001) in Shiroro dam, whoever Adakole *et al.* (2003) and Abolude (2007) recorded similar results in same study area.

The monthly variation of pH in Kubanni Reservoir during this study were neutral and moderate across all the stations compared to the National Watercourses Standards and WHO. The low pH indicates acidity, this might be due to the presence of CO_2, nitrate and sulphate ions in water. The pH range obtained in this study falls within the recommended range 6.5-9 by Boyd and Tucker, (1998) which supports aquatic life including fish. This results corroborate with Olaniyan (1968), who reported that level of pH are closely related to the amount of carbonates present in solution. Similar observation was made by Adakole *et al*. (2003) and Abolude (2007) in the same study area.

The lower DO recorded during rainy season could be attributed to the peak time of biochemical oxygen demand due to presences of bacteria and other decomposers resulting to stress of aquatic animals, when DO changes rapidly there will be no enough time for physiological adaptation

(Ibrahim *et al*., 2009). The higher the temperature, the lower the dissolved oxygen and vice versa, could be due to the increased solubility of DO_2 at lower temperature or organic materials which use up oxygen as they are degraded: reducing agents that deplete oxygen resources as they are chemically oxidized (Adakole *et al*., 2008). The high DO_2 in dry season that coincided with maximum water temperature, this might be due to the prevailing North-East trade wind called Harmattan. These findings agrees with Oladimeji (2001), Adakole (2000) and Tukura (2005) who reported that dissolved oxygen concentration are high during the harmattan period. Similar observations has also been made by Adakole *et al*. (2008), and Abolude *et al.* (2007) in same study area.

The Biological Oxygen Demand (BOD) in Kubanni Reservoir increases during dry season which contributes to oxygen depletion this may be attributed to the presences of organic waste in the water (Awanda, 1987). When BOD levels are high, Dissolved Oxygen (DO) levels decrease because the oxygen that is available in water is being consumed by bacteria, since less dissolved oxygen is available in the water, fish and other aquatic organism may not survive (Bhatti and latif, 2011). Limnologist has also utilized the demand for oxygen by oxidizable organic matter as a means of comparing water quality, especially those thought to be affected by organic pollution (Adakole *et al*., 1999). This results varied with the observation of Adakole *et al.* (2003) who recorded higher values than the recommended limit by World Health Organization, however Chapman and Kimstach, 1996, stated that "unpolluted waters have BOD values of 2mg/l or less". This study is similar to Abolude (2007) who recorded a lower value in same study area.

Highest turbidity recorded during wet season could be due to high water volume favoring surface run-off from the catchment area and increase in siltation as well re-suspension of dissolved materials and flooding. Low turbidity experienced as dry season progressed could also be due to

dilution as a result of low water level and absence of flooding. Increase in total dissolved solid may result in increased turbidity. This observation is supported by the results Adakole (1995).

The highest concentration of Chemical Oxygen Demand (COD) observed in this study was above the maximum allowable limit (50mg/l) by National Watercourse. This indicates that the water might be polluted, this might be attributed to the inflow of sewage water coming from the upstream (Kampagi and Samaru Stream). However this finding agrees with Abolude (2007), who also observed a higher COD value in the same study area.

The high value of Alkalinity may be due to the reduced water volume and dilution. This is similar to the findings of Ufodike *et al*, (2001) who reported similar observation in "Dokoma Lake", also Adakole *et al*. (2008) in "Man-Made Lake in Zaria".

Increase of water hardness observed might probably be as a result of low water level and the concentration of ions, while low concentration values recorded could be due to dilution as a result of wind action and light intensity which improves evaporation in turn increases hardness (Ufodike *et al*., 2001) and (Kolo and Oladimeji, 2001), this results is similar to Adakole *et al*. (2003) and Abolude (2007) who worked in same study area.

The high concentration of Nitrate-Nitrogen (NO_3-N) recorded could be due to residual effects from runoff from farmlands around Kubanni Reservoir and also the application of fertilizers by farmers from catchment area. Another reason could be as a result of nitrates released from sediments during decomposition of organic matter. The low concentration of NO_3-N values recorded during extreme dry season indicate presences of aquatic algae which utilized NO_3-N. Similar findings were report by Adeniji (1987), Kennedy and Hain (2002) who reported that NO_3-N increase with surface runoff and deeper depths.

The maximum Phosphate-Phosphorus (PO_4-P) concentration was observed during dry season than wet season this might be due to residual effect of phosphate fertilizer application which is common around the catchment area, effect of reduction in water volume or climatic change, this findings is supported by Wetzel (2001), Karikari *et al.* (2007), that the rate of phosphorus released into the water can double when sediment are frequently disturbed.

Lower concentrations of Total Dissolved Solid (TDS) observed during the dry season could be due to low water volume favoring settling of suspended materials as well as the absence of flood water and evaporation due to high temperature, higher concentration during rainy season could be due to dilution as a result of high water level and flooding resulting to increase in total dissolved solid/turbidity which may further leds to decrease in benthic fauna and increase in the algal bloom similar observation was made by Adakole *et al.* (2003) in same study area, Kemdirim (1990), also reported that TDS decreases as the rainy season progressed . This observation conformed Abolude (2007) who recorded a significant low value (34.42mg/l) in same study area.

There was a slight variation of Electrical Conductivity (EC) in the rainy season but slightly high during dry season. According to Chapman and Krammer (1991); Akin-Oriola (2003) who stated that the gradual decrease in conductivity during dry season could be due to dilutions of the reservoir during the rainy season and possibly the precipitation of the metallic ions during this period coupled with the low water level in the dry season period. Also, Increase in total dissolved organic matter result to increase in conductivity (Adakole, 2000). This observation was in line with the observation of Anwi and Ofori-Danson (1993) who repoeted that the dilution as a result of rain have a moderate effect in Lake Volta. Similar result were reported Adakole *et al*., (2003) who recorded a higher value of 256.80µhoms/cm, however this findings also contradict

the findings of Abolude (2007) who recorded a significantly low value of 69.20µhoms/cm in the same study Area.

5.2. Concentration of Heavy Metals in Water and Sediments

Water and Sediments samples from Kubanni Reservior of Zaria, Kaduna State were analysed for a period of twelve (12) months for selected heavy metals from April, 2017 to March, 2018 and the results were discussed.

High value of lead (Pb) in water observed in this study may be attributed to the discharge of untreated municipal, agricultural and urban effluent to the Reservoir, while the low concentrations of Pb observed could be as a result of dilution effect from runoff water as well as absorption by plants and sediments in the Reservoir. Similar observation was reported by Kithiia, 2006; Kar *et al.* 2008, this findings is in line with Abolude (2007) who also recorded higher value of (1.22 mg/l) in the same study area that also exceeded the recommended limit by WHO for Pb in drinking water, these might be that the Reservoir is polluted which makes the water unsuitable for human consumption, as Pb is known to be toxic even at low levels with resultant ill-health effects as chronic exposure has been linked to growth retardation in children (Awofolu *et al.,* 2005; WHO, 2008).

The wide ranges of Pb concentration in sediments could be attributed to variations in presence of mud, high soil organic matter content and urban effluents draining into the Reservoir. This soil component could possibly be responsible for higher soil lead retention (Mico *et al.,* 2006). Lead could also be from the application of agrochemical and fertilizers in the agricultural area (Mico *et al*., 2006) e.g urea and superphosphate. This is in line with Alaa and Osman, 2010. Awofolu *et al.,* (2005) who reported that the sediment could be an influential factor on the level of Pb in

river water. The value of lead (Pb) observed in the Sediments during the study were below the recommended limits (35 mg/kg) by WHO, lead is toxic even at low Levels as it is non degradable and has a tendency to bio-accumulate to toxic levels (Tuzen, 2003; WHO, 2008). Some of the effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anemia due to reduction of enzymes concerned with synthesis of red blood cells (Lars, 2003;WHO, 2008).

The high concentration of Manganese(Mn) in water might be attributed to dissolution from impending rocks, application of fertilizer, insecticides/herbicides, discharge of effluents, municipal wastes as well as runoff from Kamagi, Samaru Stream other residential effluents all directing their effluents to streams (Ibrahim and Tayel, 2005; Alaa and Osman, 2010). This result agrees with Adakole *et al*., 2008 on Man Made Lake in Zaria Nigeria. This is also in line with the findings of Wachira, 2007; Kar *et al.,* 2008; Alaa and Osman, 2010. Similar observation was reported by Baldantoni *et al.,* (2005); and Abolude (2007) who also work in the same study area recorded a higher value (1.00mg/l) above the WHO recommended limit. Mean concentrations of

Low concentrations of Mn in sediments observed in this study could be attributed to anthropogenic activities emanating from fishermen and geology of river bed and catchment area. This findings is in line with the observation of Abolude (2007) who work in the same study area and recorded a higher value (371.58mg/kg), Though the limit of Mn in sediments is not documented, in larger amounts, and apparently with far greater activity by inhalation, Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible (ATSDR, 2002). Victims of Mn poisoning suffer from cerebella dysfunctions as well as awkward high-stepping gait (Reilly, 2002).

Higher concentration values recorded for Zn in water in this study could be attributed to a big part of heavy metals in sediments being released back to water compartment in the process of remobilization this is in line with report of Kar *et al.,* 2008, WHO, 2008. The mean level was below maximum permissible limit (3mg/l) for Zn in drinking water as recommended by WHO, the result is in line with observation of Adakole *et al*., (2008) and Abolude (2007) who work on same study area and recorded a significant lower values (0.44mg/l).

The mean value of Zinc (Zn) in sediments sampled from all the sampling stations exceed the recommended limit of 123 mg/kg (WHO/USEPA). Sediments are, however, known to accumulate more heavy metals with time that might be remobilized back to the water and to the food chain (Kar *et al.,* 2008; WHO, 2008). While Zn is an essential element to plants and living organisms including human beings, prolonged exposure to high intakes of zinc results in copper and iron deficiency and subsequent by anemia (Reilly, 2002). The significantly low concentration in this study could have resulted in remobilization of heavy metals back to the water and uptake by plants along the Reservoir. This results agrees with findings of Abolude (2007) who work in the same study area and also recorded a higher value of 147.58mg/kg, which is above the recommended limit.

5.3. Concentration of Heavy Metals in Organs of *Orechromis niloticus* and *Clarias gariepinus.*

Exposure of fish to elevated levels of heavy metals in an aquatic environment leads to absorption of bioavailable metals directly from their immediate environment via gills and skin or through ingestion of contamination water and food (Nussey *et al*., 2000). Gills, liver and muscles of *Orechromis niloticus* and *Clarias gariepinus* fishes gotten from Kubanni Reservior of Zaria,

Kaduna State were analysed for a period of twelve (12) months for selected heavy metals from April, 2017 to March, 2018 and the results were discussed.

Lead (Pb) mean value for analysis of gills of *Orechromis niloticus* were below 2.0 mg/kg of the WHO recommended limit for Pb in fish and fish products. Higher concentration values of Pb in the *Orechromis niloticus* gills could be attributed to gills being the first point of contact with water exchange in their environment, Ikem and Egiebor (2005). This results is in line with the findings of Kar *et al.,* (2008). Pb is known to be toxic even at low levels with resultant ill-health effects as chronic exposure has been linked to growth retardation in children (Awofolu *et al.,* 2005; WHO, 2008).

The stated limit of Lead **(**Pb**)** is 2.0mg/kg as recommended by WHO, 2003 for fish and fish products, concentration of Lead in liver of *Oreochromis* was observed to be within the limit this may be attributed to liver being a detoxifying organs in the body, Obasoham (2008). Higher concentration of Lead in liver may be attributed to discharge of effluents, municipal wastes and the inability of the liver to detoxify accumulated leads Ikem and Egiebor (2005). The case of Mina Mata (organic mercury poisoning) and Ita-Ita (cadmium poisoning) in human beings is enough to drive home the serious health hazards due to these metals (Aliyu *et al.,* 2015). The effects of lead exposure are the same whether it is breathed or swallowed. Low levels of lead have been identified with anemia as it causes injury to the blood forming systems while high levels cause severe dysfunction of the kidneys, liver, the central and peripheral nervous system (Jain *et al.,* 1989), and high blood pressure (ATSDR, 1999a).

The concentration of lead (Pb) in the muscles of *Orechromis niloticus* were below the WHO's recommended limit of 0.40mg/kg for fish and fish products (FAO/WHO, 1984), high concentration of lead in muscles could be attributed to residential effluent, while the lower lead

concentration in muscles which could be attributed to dilution and uptake by plants and sediments. Low concentration of lead in fish muscles may not pose immediate hazard to people consuming it the fish found in this area FAO/WHO, 2011. This study agrees with the findings of Kithiia (2006).

The high concentration of Mn in fish gills could be attributed to the gills being the dominant site for contaminant uptake because of their anatomical or physiological properties that maximize absorption efficiency from water (Ikem and Egiebor, 2005). Manganese **(**Mn**)** Concentration in the gills of *Orechromis niloticus* was found above WHO recommended limit for fish and fish products of 2.0mg/kg (WHO, 2003), This report is in line with Abolude (2007) who also recorded higher value (91.54mg/kg) above the recommended limit in same study Area. However lower concentration of Mn than the current study but also higher than the recommended limit has been recorded in fish gills from other larger water bodies (Alaa and Osman, 2010).

Mean concentrations of Manganese **(**Mn**)** recorded after analyzing the liver of *Orechromis niloticus* were above the WHO recommended limit for fish and fish products of 2.0mg/kg (WHO, 2003), High concentration of Mn in liver of *Orechromis niloticus* could be attributed to residential effluent (FAO/WHO, 2011), this might not constitute or pose immediate hazard to people consuming the fish found in this area. Similar observation was made by Abolude (2007) who recorded higher value (53.99mg/kg) above the recommended limit in same study Area. The significantly lower could be attributed to dilution and uptake by plants and sediments (Kithiia, 2006).

Manganese (Mn) Concentration in Muscles of *Oreochromis niloticus* was found to be below recommended limit 2.0mg/kg (WHO, 2003) for Mn in fish and fish products. The low concentration of Manganese in Muscles of *Oreochromis niloticus* this could be attributed to

lesser or non-Agricultural activities around the Kubanni Reservoir during the dry season, this might not pose immediate hazard to people consuming the fish found in this area, while the highest concentration of Manganese in Muscles of *Oreochromis niloticus* wet season could be due to application of fertilizer, insecticides and herbicides on the farm lands around the Reservoir (Kithiia, 2006). this observation is supported by the findings of Obasohan (2008) titled "The use of heavy metals load as an indicator of the suitability of the water and fish of Ibiekuma stream for domestic and consumption purposes".

Manganese can lead to a variety of psychiatric and motor disturbances, termed manganese which has occurred in people employed in the production and processing of manganese alloys (Nussey *et al.,* 2000). Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the aquatic ecosystem quality (Kar *et al.,* 2008).

Mean concentrations of Zinc **(**Zn**)** recorded after analysing the *Orechromis niloticus* gills were found below recommended limit (40 mg/kg) for Zn in fish and fish products. This might not pose immediate hazard to people consuming the fish found in this area. High concentration could be attributed to residential effluent (FAO/W.HO, 2011), while low concentration recorded could be attributed to dilution and uptake by plants and sediments, this is similar to the findings of Kithiia (2006).

Concentrations of Zinc (Zn) in *Orechromis niloticus* liver recorded in this study was below the maximum acceptable limit (40mg/kg) by WHO for Zn in fish and fish products, though it may not pose immediate effect to people consuming the fish found in this area. Low concentration value could be attributed to dilution and uptake by plants and sediments (Kithiia, 2006), while

the high concentrations is attributed to industrial and/or residential effluent (FAO/WHO, 2011), this results agrees with the finding of Obasohan (2008).

The concentrations of Zinc (Zn) recorded after analysing the muscles of *Oreochromis niloticus* samples are found below the allowable limit of (40mg/kg) recommended by WHO for Zn in fish and fish products. The highest concentration of Zinc in the muscle of *Oreochromis niloticus* could be attributed to the decrease in water level and increase in the activities of fishermen at the landing site, where painted materials such as metallic bowls are been used to collect the catches, this study conformed with the finding of Obasohan (2008) titled "The use of heavy metals load as an indicator of the suitability of the water and fish of Ibiekuma stream for domestic and consumption purposes". Accumulation of Zn in fish may result in several dysfunctions, Exerts adverse effects by accruing structural damage which affects the growth, development and survival (Kori-Siakpere *et al*., 2008).

Lower concentration levels of Lead **(**Pb**)** in the Gills of *Clarias gariepinus* recorded in Kubanni Reservoir of Kaduna State were below the WHO's recommended limit of 0.40mg/kg for fish and fish products (FAO/WHO, 1984). The highest concentration recorded during dry season this may be due releases of industrial effluent, landfill and soil leaching and underground injection (EPA, 2004), this observation is similar to the findings of Kithiia (2006).

The mean values for lead (Pb) in liver of *Clarias gariepinus*, which is below the 0.40mg/kg recommended limit for Zn in fish and fish products. Higher concentration values recorded could be attributed to human activities in the environment include; combustion of coal, residential combustion of wood, iron and steel painting and batteries waste (Calkins, 2009), this result agrees with the observations of Kithiia (2006).

Mean concentrations of Lead **(**Pb**)** recorded in muscles of *Clarias gariepinus* in this study was also lower than the permissible limit 0.4 mg/kg by WHO for Pb in fish and fish products. Higher concentration of Lead was recorded in the muscles of *Clarias gariepinus* during the dry season could be related to factors such as the parent rock, climate and anthropogenic activities around the reservoir (Jia *et al*., 2010). It resultant effect in adult is severe neurological encephalopathy, which is a general term to describe various diseases that affect brain function. Lead exposure may cause weakness in fingers, wrists, or ankles, Children are more sensitive to the effects of lead than adults (Linton *et al.,* 1980). A child who swallows large amounts of lead may develop blood anemia, kidney damage, severe stomachache, muscle weakness, and brain damage (Thornton *et al.,* 1987) this studies agrees with observation of Obasoham (2008) and Kar *et al.* (2008).

The concentration of Manganese (Mn) detected in the gills of *Clarias gariepinus* from this study was above the recommended limit for fish and fish products of 2.0mg/kg (WHO, 2003), WHO/FAO 2011, maximum permissible limit of 2.5mg/kg. The higher concentration values of Manganese in Gills of *Clarias gariepinus* recorded, this could be attributed to the activities of fishermen at the catchment area, discharge of effluents and municipal wastes, geology of Reservoir bed and catchment area, this findings is supported by the results of Obasoham (2008) and Kar *et al.* (2008). Accumulation of Mn over time can lead to a variety of psychiatric and motor disturbances, termed manganese which has occurred in people employed in the production and processing of manganese alloys (Nussey *et al.,* 2000).

Mean concentrations of Manganese **(**Mn**)** recorded in the Liver of *Clarias gariepinus* in Kubanni Reservoir was found below the WHO recommended limit for fish and fish products of 2.0mg/kg (WHO, 2003), Manganese can lead to a variety of psychiatric and motor disturbances, termed

manganese which has occurred in people employed in the production and processing of manganese alloys (Nussey *et al.,* 2000). Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the aquatic ecosystem quality (Kar *et al.,* 2008).The higher concentrations of Manganese in liver could be attributed to Discharge of sewages into the reservoir or other aquatic environment which can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behaviour (Al-Weher, 2008), similar result was recorded by Obasoham (2008).

According to The National Research Council of Canada (NRC) the safe and adequate daily intake levels for manganese recommended range from 0.3 to 1 mg d^{-1} for children up to 1 year, 1–2 mg d^{-1} for children up to age 10, and 2–5 mg d^{-1} for children 10 and older, but our recent data are unsafe for these aged groups (Institute of Medicine, 2003).The mean value for Manganese (Mn) Concentration in Muscle of *Clarias gariepinus* obtained for the period of 12 months across the three sampled stations are above the permissible limit for children of age ten and below, however, the stated limit 2.0mg/kg (WHO, 2003) is still safe for children age 10 and older. The highest concentration value for Manganese in the muscle of *Clarias gariepinus* was recorded may be attributed to the farming activities (use of chemicals e.g insecticides and application of fertilizer) around Kubanni Reservoir and other activities happening upstream disposal of municipal waste into the water body (Al-Weher, 2008), similar findings was made by Kar *et al.* (2008).

The mean concentration recorded for Zinc **(**Zn**)** in the gills of *Clarias gariepinus* of Kubanni Reservoir were below the 40 mg/kg recommended limit for Zn in fish and fish products, this might not pose immediate hazard to people consuming the fish found in this area. The high

concentration could be attributed to anthropogenic sources arising from human activities such as municipal effluents, as well as non-point source run off are the main sources of metals in rivers (Sonayei *et al*., 2009). This findings is in accordance with observation of Kithiia (2006).

Higher concentration of Zinc (Zn) in Liver of *Clarias gariepinus* may be attributed to larger quantity of heavy metals in sediments being released back to water compartment in the process of remobilization come in contact with the fish, while the lowest concentration observed during the wet season could be attributed to dilution and uptake by plants and sediments this observation conformed with the findings of Kithiia (2006). Generally, the mean concentrations of Zn recorded in the livers of *Clarias gariepinus* were below the maximum acceptable limit of 5.0mg/kg and allowable limit of 15.0mg/kg recommended by WHO for Zn in fish and fish products.

Mean concentrations of Zinc **(**Zn**)** recorded in the muscle of *Clarias gariepinus* are below the WHO recommended limit for fish and fish products of 40 mg/kg (WHO, 2003), the higher concentration values for Zinc in Muscles recorded could be attributed to residential effluent (FAO/WHO, 2011). Lowest concentration of Zinc in muscles could be attributed to dilution and uptake by plants and sediments, this findings is supported by observation of Kithiia (2006).

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATION

6.1 Conclusions

i. This study shows that the physico-chemical parameter of Kubanni Reservoir water is within favorable range for survival of fish.

ii. There were more heavy metals in sediments than water of Kubanni Reservior, the metal concentrations obtained from the sediment samples were compared with Sediment Quality Guideline which showed that these concentrations did not exceed the probable effect concentration (PEC) levels

iii. Based on the result of this study, the levels of metals bio-accumulated in tissues of *Oreochronmis niloticus* and *Clarias gariepinus* did not exceeds the permissible limits set for heavy metals by FAO, FEPA and WHO). The highest levels of all the metals in the present study were observed in gills and liver of the two fish species, while muscle shows the lowest value.

Therefore these fishes in this area of study did not pose any threat to human upon their consumption.

6.2 Recommendations

The followings recommendation are hereby made

i. It is recommended that steps should be taken to control heavy metals inflow into the Reservoir, considering is a source of drinking water to Ahmadu Bello University communities and habitat to fish and other aquatic organism.

ii. ii. The samples of selected fish species (*Clarias gariepinus* and *Oreochromis niloticus*) organs (gills, liver, muscles) obtained from the 3 stations during 12 months sampling period were found to contain all the analyzed heavy metals (Pb, Mn and Zn) at different levels in Kubanni, though they are still safe for consumption, steps should be taken to protect fish species.

ii. The current management practice of safeguarding the Reservoir from pollutants should be maintained.

iii. A further study should be done to include other heavy metals and fish species to determine their contamination rate. This is because their anthropogenic activities such as chemicals lack dumpsites.

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APPENDIX

Appendix 1a: Past and Present Studies Mean Values Comparison of Heavy Metal in Sediments and Water.

	present	**Previous** Abolude, (2007)	**present**	**Previous** Abolude, (2007)
Months	Sediment (mg/kg)		Water(mg/l)	
Pb	40.05±4.40	-------	0.12±0.03	1.22
Mn	263.72±13.27	371.58	0.31±0.05	1.00
Zn	210.95	147.58	0.05±0.01	0.44

Appendix 1b: Past And Present Studies Mean Values Comparison of Heavy Metal in Organs *Oreochromis niloticus*.

		Oreochromis niloticus				
	Present	**Previous** Abolude, (2007)	**present**	**previous** Abolude, (2007)	**present**	**previous** Abolude, (2007)
Months	Gill		Liver		Muscle	
Pb	1.11±0.07	---------	1.13±0.13	--------	1.21±0.14	---------
Mn	53.12±3.23	91.54	4.69±0.59	53.99	4.48±0.38	--------
Zn	25.75±1.41	----------	13.65±0.75	----------	18.54±1.42	---------

ABBREVIATIONS

* - Significant

** - Highly Significant

< - less than

> - greater than

±S.E – Mean Standard Error

µS/cm – MicroSeconds Per Centimeter

A.B.U - Ahmadu Bello University Zaria

AAS - Atomic Absorption Spectrometry/Spectrophotometer

Al – Aluminum

ANOVA - Analysis of Variance

APHA- American Public Health Association

As - Arsenic

ATSDR - Agency for Toxic Substances and Disease Registry's

BaH_2O – Manganese psilomelane

BCFs - Bio-indicator concentration factors

BOD - Biochemical Oxygen Demand

$CaCO_3$ – Calcium Carbonate

Cd - Cadmium

Co – cobalt

CO_3^{-2} - Carbonates

COD - Chemical Oxygen Demand

Cr - chromium

Cu - copper

DMRT - Duncan's Multiple Range Tests

DNA –Deoxyribo Nucleic Acid

DO - Dissolved Oxygen

EC – Electrical Conductivity

EDTA –Ethylenediaminetetraacetic acid

EPA – Environmental Protection Agency

FAAS - Flame Atomic Absorption Spectrometry

FAO – Food and Agricultural Organization

Fe - iron

FEPA – Federal Environmental Protection Agency

GF-AS - Graphite Furnace Absorption Spectrometry

H+ - Ions

H_2O_2 - Hydrogen peroxide

H_2SO_4 – Tetraoxosulphate (vi) acid

HCI – Hydrochloric acid

HCO_3^- - Bicarbonates

Hg – Mercury

HNO_3 – Nitric Acid

ICP-AES - Inductively Coupled Plasma – Atomic Emission Spectroscopy

MCL - Maximum Contaminant Level

Mg/kg – Milligram Per Kilogram

Mg/L – Milligram Per Litre

MGC - Manganese in gills of *Clarias gariepinus*

MGO - Manganese in gills of *Oreochromis niloticus*

MLC - Manganese in liver of *Oreochromis niloticus*

MLO - Manganese in liver of *Oreochromis niloticus*

MMC - Manganese in muscles of *Clarias gariepinus*

MMO - Manganese in Muscles of *Oreochromis niloticus*

MMT - Methylcyelo-pentadienyl Manganese Tricarbonyl

Mn - manganese

$Mn0_2$ - Manganese oxide

Mn^{2+} - Manganese ion

Mn^{3+}- trivalent manganese

Mn^{4} - tetravalent manganese

MnCO3 – rhodochrosite

MnO_2 – Manganese pyrolusite

$MnSO_4$ - Manganese Sulphate Solution

MnW - Manganese in Sediments

MnW - Manganese in Water

Mo - Molybdenum

$Na_2S_2O_3.5H_2O$ - Sodium Thiosulphate Solution

Ni - nickel

Nm – Nanometer

NO_3-N - Nitrate Nitrogen

NO_3-N - Nitrate-Nitrogen

$^{\circ}C$ – Degree Celsius

OH^{-} - hydrogen oxide (ion)

Pb – lead

PbS - Lead in Sediments

PbW - Lead in Water

PEC - Probable Effect Concentration (levels)

PGC - Lead in gills of *Clarias gariepinus*

PGO - Lead in the gills of *Oreochromis niloticus*

pH – Potential Hydrogen (ion)

PLC - Lead in liver of *Clarias gariepinus*

PLO - Lead in liver of *Oreochromis niloticus*

PMC - Lead in muscles of *Clarias gariepinus*

PMO - Lead in muscles of *Clarias gariepinus*

PO_4-P – Phosphate Phosphorus

PVC - Poly Venyle Chloride

Sb – Stitium

Se – Selenium

Sn – Stannium

SOM - Soil Organic Matter

SPSS - Statistical Package for the Social Sciences

SQG - Sediment Quality Guideline

TDS - Total Dissolved Solids

TDS – Total Dissolved Solids

TEL – Tetraethyllead

Tur. – Turbidity

USEPA – United State of Environmental Protection Agency

Va - Vanadium

WHO – World Health Organization

ZGC - Zinc in gills of *Clarias gariepinus*

ZGO - Zinc in gills of *Oreochromis niloticus*

ZLC - zinc in Liver of *Clarias gariepinus*

ZLO - Zinc in liver of *Oreochromis niloticus*

ZMC - Zinic in muscle of *Clarias gariepinus*

ZMO - Zinc in muscles of *Oreochromis niloticus*

Zn - Zinc,

$ZnCO_3$ - Calamite

ZnO - zincite

ZnS – Sphalerite

ZnS - Zinc in Sediments

ZnW - Zinc in Water