ASSESSMENT OF HEAVY METALS IN WILD AND FARMED AFRICAN CATFISH *CLARIAS GARIEPINUS* (BURCHELL, 1822) IN SELECTED RIVERS AND FISHFARMS IN KADUNA STATE, NIGERIA

BY

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AHMADUBELLO UNIVERSITY,
ZARIA

JULY, 2017

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ZARIA, NIGERIA

JULY, 2017

DECLARATION

I hereby declared that this dissertation entitled "**Assessment of Heavy Metals in Wild and Farmed African Catfish *Clarias gariepinus* (Burchell, 1822) in Selected Rivers and Fishfarms in Kaduna State, Nigeria"** has been performed by me,Henry Eric Onyidoh in the Department of Biology under the Supervision of Professor P.I. Bolorunduro and Dr. D.M.Shehu. The information derived from the literature has been duly acknowledged in the text and in the references. No part of this thesis was previously presented for another degree at any other institution.

Henry Eric, ONYIDOH ----------

Signature **Date**

CERTIFICATION

This dissertation entitled "**Assessment of Heavy Metals in Wild and Farmed African Catfish *Clarias gariepinus* (Burchell, 1822) in Selected Rivers And Fishfarms in Kaduna State, Nigeria"**by Henry Eric Onyidoh meets the regulations governing the award of the Degree of Master of Science in Educational Biology of Ahmadu Bello University, Zaria and approved for its contribution to knowledge and literary presentation.

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DEDICATION

This thesis is dedicated to my mumMrs Eunice TitiUchenna Onyidoh (U-Nicey)who gave me wings disguised as Education. Only God will reward her.

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ABSTRACT

The presence and bioaccumulation pattern of some heavy metal concentrations in wild and farmed African catfish, *Clarias gariepinus* (Burchell, 1822) muscles collected from selected rivers and fish farms in Kaduna State, Nigeria, were assessed. Fish and water samples used for the assessment were collected during the wet and dry seasons from River Kaduna, River Galma in Zaria; and from two fish farms in Sabon Tasha, Kaduna and Dakace, Zaria. Physico-chemical parameters, such as Puissance Hydrogen (pH), temperature, Turbidity etc., were also analysed. The analyses of heavy metals, Iron (Fe), Lead (Pb), Nickel (Ni), Cadmium (Cd) and Mercury (Hg), in all water and *Clarias gariepinus* muscle samples was carried out in the Multi-User Science Research Laboratory, Department of Chemistry, Ahmadu Bello University, Zaria, using Thermo-element Solar S4 Atomic Absorption Spectrophotometer (AAS), while the Varian Generation Accessory (VGA 77) with closed end cell was used for Hg determination. The results obtained were subjected to t-test analysis to determine the level of significance ($p < 0.05$) between the means, while Pearson correlation coefficient was employed to determine the relationships. pH was highest in River Kaduna during the wet season, in the upstream (7.04), while there was a dip in the downstream (6.67) during the dry season. Seasonal variations in temperature were evident, as the ranges obtained in the rivers were from 27.03°C – 30.68°C and the farms ranged from 23.76°C – 27.42°C, which were within World Health Organization (WHO) recommended threshold (30°C – 36°C). Dissolved Oxygen (DO) varied widely in the rivers (5.11mg/l – 7.04mg/l) as well as in the farms (9.29mg/l – 10.74mg/l). Total dissolved solids (TDS)obtained in this study were all very high (Rivers: 54.91mg/l – 82.09mg/l, Farms: 28.43mg/l – 42.03mg/l), but were all lower than the WHO standardindicativeofportability (1000 – 1600mg/l). Heavy metal concentrations in water samples and heavy metal bio-accumulation in both wild and farmed *C. gariepinus* muscles showed irregular distributions with descending order of:Fe >Pb>Hg>Ni > Cd. Fe

levels were the highest in both rivers water samples (3.23mg/l), closely followed by Pb (0.78) and Hg (0.69mg/l), while the farms also had Fe as the dominant element (1.31mg/l), with Pb (0.26mg/l) and Hg (0.09mg/l), respectively. Both water bodies had Ni concentration (0.2mg/l) higher than the WHO limits of 0.02mg/l, while the farms' concentration (0.03mg/l) was slightly higher than WHO threshold limit. In the muscle of *C. gariepinus*, Fe concentrations were also high in rivers (3.53mg/kg), while the Farms was 1.44mg/kg, all above the FAO recommended limit (0.5mg/kg) in fish. Generally, only Cd didnot exceed the maximum permissible limits in the tissues of*C. gariepinus*. However, with Fe, Hg, Pb and Ni all higher than the acceptable limits, most especially in the rivers, this could pose a serioushealth risk to consumers. Thus, a close periodical and regular monitoring of heavy metal pollution in the water bodies is strongly advocated.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

In recent years the concentrations of toxic metals in many ecosystems are reaching unprecedented levels. The increasing use of metals in industry and mining activities have led to serious environmental pollution through effluents and emanations (Güven *et al.*, 1999). Under certain environmental conditions, heavy metals may accumulate and cause serious ecological damage. The aquatic ecosystem is often seen as the ultimate recipient of almost everything including heavy metals (Ogoyi *et al.*, 2011). Pollution of heavy metals in aquatic environment is a growing problem worldwide and currently it has reached an alarming rate. There are various sources of heavy metals; some originates from anthropogenic activities like draining of sewage, dumping of hospital wastes and recreational activities. Conversely, metals also occur in small amounts naturally and may enter into aquatic system through leaching of rocks, airborne dust, forest fires and vegetation (Fernandez and Olalla, 2000). As heavy metals cannot be degraded, they are continuously being deposited and incorporated in water, sediment and aquatic organisms (Linnik and Zubenko, 2000), thus causing heavy metal pollution in water bodies.

Heavy metal is any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations (Ngumbu, 2014). Examples of heavy metal include mercury, cadmium, arsenic chromium, thallium and lead. As trace elements, some heavy metals (e.g. copper, iron, zinc, manganese and selenium) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning (Lenntech, 2014). Heavy metals can enter the human food through water, air, soil, plants and animals. The pollution of the environment by heavy metals is viewed as an international problem because

of its effects. In recent years, the pollution of aquatic environment with heavy metals has become a worldwide problem because of their potential toxic effect and also most of them accumulate in tissues and organs of aquatic organism (Goldstein and Hewitt, 1990andGledhill *et al.,* 1997). However, the amount of absorption and bioaccumulation of the heavy metals depends on ecological, physical, chemical and biological condition and the kind of element and physiology of organisms (Jaffer *et al.,* 1988). Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms (Eletta *et al.,* 2003; Malik, 2004; Obasohan *et al.,* 2006 and Igwemmar *et al.,* 2013). There is increasing concern about the quality of foods in several parts of the world. The determination of toxic elements in food has prompted studies on toxicological effect of these elements in food. Fish as an important component of the human diet, is generally appreciated as one of the healthiest and often times referred to as the "cheapest" source of protein, as its amino acid compositions are richer in Cysteine than most of the other sources of protein (Eletta *et al.,* 2003).

In Nigeria, limited surveys on heavy metals in fish have been reported. Tawari-Fufeyin (1998) working on whole body tissues of fishes from Ikpoba reservoir in Benin-City reported the concentration of vast amounts of Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Nickel (Ni) and Zinc (Zn). Also Nwaedozie (1998) noted that heavy metals such as Hg, Cd, Pb, Cr, Zn and Fe were identified in appreciable quantities in the fish samples from Kaduna River. Obasohan *et al.* (2006) examined the concentrations of Cu, Mn, Zn, Pb, Cr, Ni and Cd in fish tissues of two tropical fish species from Ogba River, Nigeria.While Alinnor and Obiji (2010) investigated the level of heavy metals – Pb, Fe, Cd, Mn, Hg, Cu and Zn in fish samples from Nworie River in Imo State.

Specifically, aquatic systems are more sensitive to heavy metal pollutants and the gradual increase in the levels of such metals in the aquatic environment, mainly due to anthropogenic

sources have now become a problem of primary concern (Oluyemi and Olabanji, 2011). This is due to their persistence as they are not usually eliminated either by biodegradation or by chemical means, in contrast to most organic pollutants. Moreover, the decay of organic materials in aquatic systems together with detritus formed by natural weathering processes and uncontrolled mining activities provides a rich source of nutrients in both the bottom sediments and overlaying water body (Jafari and Gunale, 2006and Wade *et al.*, 2008), with microorganisms, microflora and algae capable of incorporating and accumulating these metal species into their living cells from the various supply sources (Jaffar *et al.*, 1988).

Consequently, fishes become enriched with the accumulated substances, and eventually man, consuming these fishes inevitably suffers from the results of an enrichment process which have taken place at different trophic levels (Zhuang *et al.*, 2013). However, it has been noted that heavy metal concentrations vary according to demographic climates. Heavy metals concentration are reported in industrialized nations such as China, United States of America (USA), Germany, Russia and Japan, where most imported fishes are cultured before sold to Nigeria(Huang, 2003; USEPA, 2009; Molina, 2011; FAO, 2012; WHO, 2012;Zhuang *et al.*, 2013 and Abubakar *et al.*, 2015). For instance, Huang (2003) reports that heavy metals entering the aquatic ecosystems in the coastal waters of Eastern Taiwan, are deposited in aquatic organisms continually, which through the effects of bioaccumulation via the food chain becomes potentially toxic to humans as the accumulation can reach substantially high levels, with resultant lethal effects such as renal failure, autism in children, premature births, heart failures etc.

1.2 Statement of Research Problem

Although, Kaduna State is not a heavily industrialized city (Nnaji *et al*., 2011), it still has its fair share of pollutants within her surrounding, due to the presence of several cottage

industries and activities of the Nigerian Bottling Company, Nigeria Breweries, Sunseed Oil Mill, Zaria Industries Limited and the Kaduna Refinery, whose effluents, containing heavy and trace metals are continually being discharged into River Kaduna, River Kubanni, River Galma and other surrounding water bodies (Nwaedozie, 1998; Uzairu *et al.*, 2009; Nnaji *et al.*, 2011; Abubakar *et al.*, 2012). Thus, it is pertinent to examine the levels of heavy metals concentrations in wild fish species in river bodies used for aquaculture in Kaduna state, in order to determine the contamination levels.

Also because of the growing aquaculture practice in Nigeria, Kaduna inclusive,farmers are constantly seeking ways to improve and manage fish farms despite water shortages, especially in the northern part of Nigeria (FAO, 2007; Galadima *et al.*, 2011; WHO, 2012) there's is a growing concern that the water sourced from hand dug wells and boreholes contain heavy metals as a result of sustained practice of illegal mining of solid minerals, urban sewage runoff and inadequate waste management practices (Sakai *et al.*, 1996; Dimuna, 2004; Dan-Azumi and Bichi, 2010; Galadima *et al.*, 2011; Galadima and Garba, 2012; Agwu, 2012). These locally cultured fish speciesmay often contain contaminants, including heavy metals, above acceptable levels. Thus, there is a need to analyse heavy metal concentrations in both wild and locally farmed fishes in Kaduna State, to establish their suitability for human consumption.

1.3 Justification of the Study

Although many studies have been done on the levels of heavy metals in fish samples along theWest African Sub-region (Sodomou *et al.*, 2005; Voegborlo *et al*., 2006; Christopher *et al.*,2009; Voegborlo and Adimado, 2010and Kwaansa-Ansah, 2012), very little work has beenconducted in Kaduna, Nigeria, especially in relation to an analysis of heavy metals in wild and locally farmed fish species.

Heavy metals are persistent environmental contaminants, and are at least five times denser than water, and as such they cannot be metabolized by the body and thus becomes bio-accumulative (Es'haghi, 2011), thus heavy metal contamination of water bodies has been of major concern regarding their toxicity, persistence and non-degradability in the environment (Onianwa, 2001; Butu, 2013; Iguisi*et al.*, 2001; Udiba *et al.,* 2014).

Also, the role of aquaculture and fisheries to the Nigerian economy is significant but consumers' safety must not be toyed with, but for now it has not reached any appreciable level, primarily due to improper management, inadequate quality control measures and inadequate waste management systems. These have been highlighted as some of the major problems of fish consumption in Nigeria(Kudi*et al.,* 2008; Adewuyi *et al.,* 2010; Galadima and Garba, 2012 andOforka *et al*, 2012).

1.4 Aim and Objectivesof the Study

This study is aimed at investigating the presence andbioaccumulation pattern of heavy metals in wild and farmed *Clarias gariepinus* inKaduna to establish theirsuitability for human consumption.

The specific objectives of this study are as follows:

i. To analyse the water quality parameters of the selected rivers and fish farms.
ii. To determine the concentration levels of heavy metals in the selected rivers and fish farms.
iii. To determine the concentration levels of heavy metals in wild and farmed *C. gariepinus* in the selected rivers and fish farms.

1.5 Hypotheses

The following null hypotheses would be used in this study:

i. There is no significant difference in water quality parameters of the selected rivers and fish farms.

ii. There is no significant difference in heavy metals concentrations in the selected rivers and fish farms.

iii. There is no significant difference in heavy metal concentrations in wild and farmed *C. gariepinus* in the selected rivers and fish farms.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Water Pollution

According to Tariq *et al.*(2006), there is a global concern about the rapidly deteriorating state ofrivers with respect to heavy metal pollution. Serious metal pollution could result from thedischarge of unregulated effluents into natural freshwater bodies (Spiegel and Farmer, 1985).Surface and ground water pollution describes the introduction by manof foreign substances capable of causing harm to man, hazard to other living organisms (Oze *et al*., 2006). Population explosion,rapidurbanization, industrial and technological expansion,energy utilization and wastesgeneration from domesticand industrial sources have rendered many waterresources unwholesome and hazardous to man andotherliving resources, making water pollutionnow asignificantglobal problem (Anetor*et al.*, 2003). Industrial, agricultural and domestic effluents are amain source of directand often continuous input ofpollutants into aquatic ecosystems with long-termimplications on ecosystem functioning including changesin food availability and an extreme threat to theself-purification capacity of the surface water bodies (Udiba *et al*., 2014).Theseindustrial discharge or wastes include heavy metals,pesticides, polychlorinated biphenyls (PCBs), dioxins,poly-aromatichydrocarbons(PAHs),petrochemicals,phenolic compounds and microorganisms (Davies and Gasse,1988; Vesiland *et al*.,1990; Botkin and Kelly, 1998; Fakayode,2005; Nubi *et al*, 2008).

While most people in urban cities of the developing countries have access to pipedwater, several others still rely on borehole and river waterfor domestic use. Most of the rivers in the urban areas ofthe developing world are receptacles for effluentsdischarged from the industries (Olayinka, 2004; Mumba, *et al.,* 2005). Aquatic contamination by heavy metalsis

very harmful since these elements are not degradablein the environment and may accumulate in livingorganisms (Udiba *et* al., 2014). Some heavy metals cancontinue to accumulate in thetissue of organisms untilthey reach intolerable levels resulting in morbidity ormortality(Offem and Ayotunde, 2008). In the humanbody, they may undergo biotransformation,metabolismandexcretedwithouttheriskoftoxicitydependingon thechemicalcharacteristics of themetal and thedose.However, some of the metals resist chemical andbiological transformation and accumulate in thetissues to cause toxic effects (Oze *et al*.,2006). Man being higher in the food chain stands the risk of higherbioaccumulation.Theadverseeffects of these pollutantson the nerves give rise to neurotoxicity. Some heavymetalsare neurotoxic. For instance lead, mercury, nickel,zinc, cadmium, chromium and manganese (Oze *et al*.,2006). Environmental data concerning the levels andprevalence of heavy metals in inland water used extensively as a source of aquaculture water supply is of utmost importance in view of the danger associated with it.

2.2 Health – Environment Nexus

The link between health and environment explicitly recognizes that althoughexposure to a pollutant or other environmentally mediated health hazard may be theimmediate cause of ill health (Akinbamijo, 2000; Dimuna, 2004; Agwu, 2012; Abubakar *et al*., 2015); the "driving force" and "pressures" leading to environmental degradation may be the most effective points of control of the hazard (Molina, 2011). However, the relationship between human health and environment is complex. Environmental health hazards are associated with a variety of aspects of economic and social development. In response to environmental pressures, the state of the environment is often modified (Annalee *et al.*, 1998), the changes involved may becomplex and far-reaching, affecting almost all aspects of the environment and all environmental media. Many changes are intense and localized, and often concentrated close to the source of pressure (Molina, 2011). Due to the complex

interactions which characterize the environment, almost all these changes have extensive secondary effects (Criselda, 2009).

Driving forces include policies that determine trends in economic development, technologydevelopment, consumption patterns, andpopulation growth. Thedriving forces in turn generate different kinds of pressures on the environment, in such forms aswaste from humansettlements and depletion of natural resources or emission ofpollutantsfrom human activities (Annalee *et al.*, 1998; Criselda, 2009; Molina, 2011). These pressures can lead to changes in the state ofthe environment, as seen when land use is changed or when discharges of toxic chemicals or other forms of waste increaseconcentrations of pollutants in theenvironmental compartments (Molina, 2011).

2.3 Sources of Heavy Metals

Apart from natural background geochemical sources, heavy metals are emitted from a variety ofanthropogenic sources. Heavy metals emissions occur through a wide range of processes andpathways; including the air (via combustion, extraction and processing), the surface waters (viarunoffs and releases from storage and transport) and the soil and ground waters through leaching.Of the three (air, water and soil), atmospheric emissions tend to be of greatest concern health-wisebecause of the quantities involved and the widespread dispersion and potential for exposurethat often ensues (Ayandiran *et al*., 2009).

The amounts of most heavy metals deposited to the earth surface from human activities are fargreater than depositions from natural background sources. Possible sources include miningactivities, disposal of metal-containing industrial effluents (Kyoung, 2010), wastewaterarising from shanties (Wade*et al.,* 2008), effluents from municipal and industriallandfill sites (Zhuang*et al.,* 2013), municipal wastewater, dry docking companies and petrolfilling stations (Mumba*et al.*,2005). Combustion processes are the main sources of

heavy metalsespecially smelting, internal combustion engine, power generation and incineration (Sakai*et al.*, 1996).

2.4 Distribution Pathways and Fate of Heavy Metals in Aquatic Biomes

Once in the aquatic environment, metals are unevenly dispersed among the various aquatic niches. The metals in theaquatic environment may occur either in dissolved, particulate or complex form. The mainprocesses governing distribution and partition are dilution, dispersion, sedimentation andadsorption/desorption (Wade*et al.*,2008). Nonetheless, some chemical processes could alsooccur depending on the Physico-chemical properties of the water (pH, dissolved ions andtemperature). Adsorption could be the first step in the ultimate removal of metals from water.Inthe course of distribution, permanent or temporary storage of metals takes place in the sedimentsof both freshwater and marine environments. Microbial activity and redox processes may changethe properties of sediments and affect the composition of interstitial water. As a result, Iron andMagnesium oxides may be converted to carbonates or sulphides, leading to a decrease in theabsorption capacity of the sediments. Reworking of the sediments by aquatic organisms willbring sediments to the surface, where a significant fraction of the metal may be released(Sakai *et al.*, 1996).

2.5 Bio-Magnifications and Bioaccumulations of Heavy Metals in Fish

The easiest way to understand how bioaccumulation and bio-magnifications work is to use them ina food chain scenario. Bioaccumulation begins at the first level of a food chain where there is anincrease in the concentration of a pollutant from the environment to the first consumer (i.e.pollutants to plankton to filter feeder) (Ngumbu, 2014). It can also refer to the amount of toxins in individualanimals because as a top predator consumes multiple, contaminated food sources, it will“accumulate” more toxins. Bio-magnifications occurs when the concentration of a pollutantincreases from one link in the food chain to another (i.e.

polluted fish will contaminate the nextconsumer and continues up a tropic food web as each level consumes another) and results in thetop predator containing the highest concentration levels (FAO, 2007). In order for bio-magnifications to occur, apollutant must be long-lived, mobile, soluble in fats and biologically active (Ngumbu, 2014), examples of thesetypes of pollutants include dichloro-diphenyl-trichloroethane (DDT), polychlorinated biphenyls(PCBs), heavy metals (Hg, Pb, Cd, etc.) and β-methylamino-L-alanine (BMAA). In high enoughconcentrations, these toxins can lead to serious health issues for marine fauna and humans(USEPA, 2005).

2.6 Selected Heavy Metals and their Toxicity

2.6.1 Mercury

Mercury has very wide applications in science, agriculture, industry and dentistry and medicaldiagnostics. Common uses of mercury include thermometers and compact fluorescent light bulbsand control systems (ATSDR, 2007). The abundance of mercury in the earth's crust is about 0.08ppm, it occurs mainly as native mercury and as cinnabar (HgS). Natural mercury arises fromthe earth's crust through volcanic eruptions, coal burning, smelting, chlor-alkali productionplants and evaporation from oceans. Approximately 10,000 tons of natural mercury originatesfrom degassing of earth's crust; to this amount approximately 20,000 tons/year is added byanthropogenic activity (Botkin and Kelly, 1998). Mercury emissions from industries are themain source of anthropogenic discharge and mercury pollution in atmosphere. It is estimated thatthe mercury emissions will increase at a rate of 5% a year (Zhuang *et al.,* 2013). According toMurray and Holmes (2004), the major contributors to Hg emission in the USA included coalfiredelectric utilities (52.7%), municipal wastes combustion (5.6%), mercury-cell chlor-alkaliplants and hazardous-waste incinerators (4% each), stationary internal combustion engines(ICEs) (3.5%), industrial, commercial and

institutional (ICI) boilers (3.3%), lime manufacturing(3.0%) and medical waste incineration (1%). Informal gold mining has used mercury sinceantiquity. High contamination of Brazilian Amazon (Brazil is world's second largest producer ofgold) is indicated by the strong presence of mercury in its biota (Bradi,2005).

The emitted mercury both natural and anthropogenic is in an inorganic form, predominantlymetallic vapour, which is carried off to great distances by winds and eventually falls in waterbodies. In aquatic environments, inorganic mercury is microbiologically transformed intolipophilic organic compound, methyl mercury. This transformation makes mercury moreproneto biomagnifications in food chains (Botkin and Kelly, 1998). Consequently,populations withtraditionally high dietary intake of food originating from fresh or marine environment havehighest dietary exposure to Hg. Extensive research done on locals across the globe have alreadyestablished this for instance polar Eskimos. Persons who routinely consume fish or a particularspecies of fish are at an increased risk of methyl mercury poisoning (Botkin and Kelly, 1998).

Since mercury intake is expressed on a per kilogram body weight basis, exposure of childrenunder age 14 is two to three times high because of higher food intake per kilogram body weight.After measuring total mercury in the edible portions of 244 selected fish and shellfish purchasedin Canada at the retail level, the Canadian advisee to children and women of child-bearing age isto limit their consumption of fresh and frozen tuna, swordfish and shark to not more than onemeal per month (Nussey*et al.,* 2000).

Extensive evidence has shown that neural development extends from the embryonic periodthrough adolescence and that different behavioural domains (e.g. sensory, motor and variouscognitive functions) are sub served by different brain areas. Of prime concern, however, isthepossibility that developmental exposure to neuro-toxicants may result in an

acceleration of age - relatedfunctional decline. This concern is compounded by the fact that developmentalneurotoxicity that results in small effects can have a profound societal impact when amortizedacross the entire population and across the life span of humans (Rice and Barone, 2000). Thedifference in sensitivity between foetus and adult organism is between 2 and 5 with foetus beingmore susceptible to methyl mercury toxicity (Snyder, 1990). Maternal consumption duringpregnancy of methyl mercury contaminated fish in Japan and of methyl mercury contaminatedbread in Iraq caused psychomotor retardation in the offspring. Studies in Iraq suggested adversefetal effects when maternal hair mercury concentrations were as low as 20 ppm. This raises apossibility that mothers consuming diet containing mercury could pass the toxicant to foetus and to infants through breast milk (Bradi, 2005).

Mercury toxicity is also potentially linked to autism (a disorder that can lead to lifelongdisability) in children (Billard, 2003). Subtle neurological disorders in children due to mercuryexposure have been documented (Lim *et al.,* 2008). Neuropathological examination of the brainsof children prenatally exposed to organic mercury revealed dysplasia of cerebral and cerebellarcortexes, neuronal ectopia and several other developmental disturbances (Criselda, 2009).In another survey of fish eating population with low hair Hg levels <10 ppm, it was found thatneurological symptoms particularly sensory disturbances such as glove and stocking type occurred at a very high rate (Hajeb*et al.,* 2009). The adult population of Amazonian ecosystemwith hair mercury below 50µg/g demonstrated near visual contrast sensitivity, decreased manualdexterity, tendency for increased muscular fatigue, decreased muscular strength among womensignificantly in a dose dependent manner (Bradi,2005). Similarly disruption of attention,fine motor function and verbal memory was also found in adults of fish eating populations onexposure to low mercury levels (Yilmaz, 2003).

2.6.2 Lead

Lead is found in small amounts in the earth's crust. It can be found in all parts of ourenvironment and it is emitted from human activities like mining, manufacturing and the burningof fossil fuels. Airborne lead can be deposited on soil and water, thus reaching humans via thefood chain.

The principal source of Pb in the marine environment appears to be the exhaust of vehiclesrunwith leaded fuels that reaches the sea water by way of run-off and wind-blown dust (Fernandez and Olalla, 2000). Lead is found at high concentration in muscles and organs of fish. Whenaccumulated in the human body, it replaces calcium in bones. Lead exposure has beenmainlyrelated to retardation of neurobehavioral development, especially Autism in children (Oforka *et al.,* 2012). The EU maximum residue limits permitted in fish is 0.3µg/g for Pb (Eletta *et al.*,2003).

In human, the toxic effects of Pb have been demonstrated at very low levels, and somestudieshave even suggested that there may be no level of exposure below which Pb is harmless. Leadtoxicity involves several organs and can result to a variety of biochemical defects (WHO, 2012).Lead is particularly toxic to the brain, kidneys, lungs, heart and reproductive system. Exposurescan cause impairments in intellectual functioning, kidney damage, miscarriage, increased bloodpressure and hypertension (Obasohan, 2008). Data from European Food Safety Authority(EFSA) have related exposure to Pb to effects like neurotoxicity, nephrotoxicity, carcinogenicityand endocrine and reproductive failures in adults (Elett*aet al.,* 2003). Moderate exposure toPb can also significantly reduce human semen quality and is related to damage to DNA inchildren and impairment of the reproductive function in adults (Elett*aet al.,* 2003).

Several studies have shown that Pb exposures can significantly reduce the Intelligent Quotient(IQ) of school- aged children; some estimates suggest that every 10-microgram-per

decilitre increase in Pb levels in the blood is associated with a 1-to-5-point decrease in the IntelligentQuotient (IQ) of exposed children (Offem and Ayotunde, 2010). Lead exposures have also been associated withaggressive behaviour, delinquency and attention disorders in boys between the ages of 7 and 11(Offem*et al.*,2010).The Joint FAO/ WHO Expert Committee on Food Additives provisionally recommend that theweekly intake of Pb should not exceed 25µg/kg or 0.025mg/kg body weight for infants, children and adults (FAO, 2003).

2.6.3 Cadmium

Cadmium is a natural element in the earth's crust and it is usually found as a mineral with otherelements. All soils and rocks, including coal and mineral fertilizer, have some levels of cadmiumin them. In industry and consumer products, it is used for batteries (Ni-Cd batteries of mobilephones), pigments, metal coatings and plastics. It also forms alloys with some other metals.

Cadmium enters air from mining, industry, and burning of coal and household wastes. Itsparticles can travel long distance in air before falling to the ground or in water (Nnaji *et al.*, 2007).Cadmium is widely distributed at low levels in the environment and is not an essential elementfor humans, animals and plants. WHO/FAO has determined a maximum tolerable weeklyintake of 7µg/kg body weight for human (USFDA, 1993). The EU maximum residue limit(MRL) permitted in fish is 0.1-0.3 µg/g (El-Ghasham*et al.*, 2008).

Over the last century, the human body burden of Cd has increased dramatically due to increasingenvironmental, industrial and anthropogenic activities (Nnaji *et al.*, 2007). Humans normally absorbCd into the body either by ingestion or inhalation (Oforka *et al.*,2012). Cadmium is moreefficiently absorbed from the lungs than from the gastrointestinal tract (ATSDR, 2007). Thelatter usually reflects the toxic action of a high body burden on the kidney and possibly theskeleton. The absorption efficiency is a function of solubility of the

specific cadmium compoundas well as its exposure, concentration and route. According to an FAO report (2003), about 2-6%of the Cd ingested is actually taken up into the human body during the digestion process or through dermal absorption.

Cadmium retention in body tissues is related to the formation of Cd-metallothionein, a Cdprotein complex of low molecular weight. Cadmium accumulates in the human body;particularly in the liver and kidney cortex (El-Ghasham*et al.*,2008). It has anelimination half-life of 10-30 years (El-Ghasham*et al.*,2008).The effects of Cd on the kidney take the form of renal dysfunction and excessive urinary loss of calcium. The former is reflected by failure to reabsorb substances normally, and often results inaminoaciduria, proteinuria, glucosuria and decrease renal tubular absorption of phosphate.

Cadmium excretion and low molecular weight proteinuria are early symptoms of renaltubularCd damage (WHO, 2012). Other toxicity symptoms induced by cadmium include gastrointestinaldisorders and hypertension. It is also reported that intoxication with Cd in pregnant women hasbeen related to reduced pregnancy length and new-born weight and, recently, to disorders of theendocrine and/or immune system in children (El-Ghasham*et al.*, 2008).People with severe Cd nephropathy may exhibit excessive urinary loss of calcium.With chronicCd exposure, urinary calcium may eventually decline to become less than normal. Associatedskeletal changes probably related to calcium loss to Cd exposure include osteoporosis (Nnaji *et al.*,2007) and osteomalacia (bone changes ordisorders associated to intense skeletal pains). These metabolic disorders were common featuresof a Cd poisoning syndrome nicknamed “itai-itai” observed in Japan around the end of theSecond World War. Current estimate suggest that more than 200 million people worldwide haveosteoporosis and that the prevalence of this disease is escalating (Guven *et al.*, 1999).

Inhalation of Cd causes acute inflammatory reaction of the lungs. Long term exposureproduceschronic bronchitis and increased susceptibility to infections like bronchiectasis andemphysema.Other pulmonary irritants, particularly cigarette smoke, a significant source of Cd, mayexacerbate its toxic effects (WHO, 2012). U.S. EPA (2005) has determined that there is sufficient evidence that Cd is carcinogenic to humans. USEPA derivedan inhalation potency factor based on inhalation studies in humans, but no oral studies in humansor animals were identified that were judged suitable for developing oral cancer potency for Cd.

The most significant measure of excessive Cd exposure is increased Cd excretion in urine.Increased urinary Cd reflects recent exposure, increased body burden and elevation of renal Cd.Urinary Cd measurement thus provides a good index of excessive Cd exposure (Nnaji *et al.,* 2007).

2.6.4 Nickel

Nickel isasilverywhite,hardandmalleablemetal.Itbelongstotheso-calledironcobaltgroup(Group VIII)oftheperiodictable;Nihasatomicweightof58.71,withspecific gravity of 8.9. It isveryabundant element. It is found in all soils and is emittedfromvolcanoes (Hussain, 1991).Itnormallyoccursinoxidationstates 0 andII.Nickelisusedasanalloy in the steel industry, electroplating, Ni/Cd batteries, arc-welding, rods, pigmentsfor paints and ceramics, surgical and dental prosthesis, molds for ceramic and glasscontainers, computer components, and catalysts (Bradi, 2005).At very trace levels, Ni is considered as an essential trace element (Hussain, 1991 and Sivaperumal *et al.,* 2007). It actsasan activator of some enzyme systems but its toxicity at higher levels is more prominent.High levels of Ni can cause respiratory problemsand it is carcinogenic (Ikema and Egieborb, 2005; ATSDR, 2007 and Sivaperumal *et al.*, 2007).

The general population can be exposed to nickel via inhalation, oral, and dermal routes of exposure. Based on occupational exposure studies, reports of allergic contact dermatitis, and animal exposure studies, the various routes of nickel toxicity in the human body is the respiratory tract following inhalation exposure, the immune system following inhalation, oral, or dermal exposure, and possibly the reproductive system and the developing organism following oral exposure (Duda-Chodak and Blaszezyk, 2008). The most commonly reported adverse health effect associated with nickel exposure is contact dermatitis (Cangul *et al.,* 2002). Contact dermatitis is the result of an allergic reaction to nickel that has been reported in the general population and workers exposed via dermal contact with airborne nickel, liquid nickel solution, or prolonged contact with metal items such as jewellery and prosthetic devices that contain nickel (Cangul *et al.,* 2002). After an individual becomes sensitized to nickel, dermal contact with a small amount of nickel or oral exposure to fairly low doses of nickel can result in dermatitis (Denkhaus and Salnikow, 2002). They affirmed that, approximately 10–20% of the general population in the world is sensitized to nickel.

Adverse respiratory effects have been reported in humans and animals exposed to nickel compounds at concentrations much higher than typically found in the environment (Duda-Chodak and Blaszezyk, 2008). The available data on noncancerous respiratory effects in humans are limited (Cangul *et al.,* 2002). They further reported that, in nickelworkers, exposure to nickel did not result in increases in the risk of death from non-malignant respiratory system disease, and studies examining potential nonlethal respiratory effects have not found consistent results.

Animal data provide strong evidence that nickel is a respiratory toxicant; lung inflammation is the predominant effect. Evidence of lung inflammation has been observed following acute-, intermediate-, and chronic-duration exposure of rats to nickel sulfate, nickel subsulfide, or nickel oxide (Cangul *et al.,* 2002). Nickel sulfate was the most toxic of the three compounds

and nickel oxide was the least toxic. For all three compounds, the threshold for lung effects decreased as the duration of exposure increased. Exposure to nickel sulfate or nickel subsulfide also produced damage to the nasal olfactory epithelium. Human and animal data provide strong evidence that inhalation exposure to some nickel compounds can induce lung cancer. Carcinogenic responses have been observed following inhalation exposure to nickel subsulfide and nickel oxide; in the absence of exposure to other carcinogenic agents, nickel sulfate does not appear to be carcinogenic following inhalation exposure (Cangul *et al.*, 2002). The potential for nickel compounds to induce reproductive effects has not been firmly established. Several animal studies have reported adverse effects in the male reproductive system following oral exposure to nickel sulphate, nickel chloride, or nickel nitrate. The observed effects included histological alterations in the epididymis and seminal vesicles, decreases in sperm concentration, motility, and abnormalities, and decreases in fertility following male exposure, but not female only exposure (Denkhaus and Salnikow, 2002). However, the poor reporting of study results, particularly incidence data and statistical analysis, limits the interpretation of these studies (Cangul *et al.*, 2002; Duda-Chodak and Blaszezyk, 2008). Additionally, other studies have not found histological alterations in the male reproductive system following long-term oral exposure or impaired fertility following oral exposure (Duda-Chodak and Blaszezyk, 2008). A number of studies have reported decreases in survival of the offspring of laboratory animals exposed prior to mating and during the gestation and lactation periods.

2.6.5 Iron

Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5%.Elemental iron is rarely found in nature, as the iron ions $Fe^{2+}$and Fe^{3+}readily combine withoxygen – and sulphur – containing compounds to form oxides, hydroxides, carbonates, andsulphides (Phippen *et al.*, 2008). Iron is most commonly found in nature in the form of its

oxides (WHO, 2012). It has a melting point of 1535 °C and specific gravity of 7.86 at 25 °C (Phippen *et al.,* 2008).

The major source of atmospheric contamination is from the iron and steel industry, electric arcfurnaces, welding, incineration and the burning of fossil fuels (Ayres and Hellier, 1998).Iron and its alloys are used mainly in the transportation, construction, machine and energy industries. Iron is essential for healthy growth of all living things. It is needed for a variety of biochemical reactions, DNA synthesis, formation of haemoglobin, oxygen transport, electron transfer and catalytic effects. In the human body, there are 3 – 4g of iron, most of which is involved in theformation of red blood cells.Mostof the remaining iron is stored inthe liver and spleen as ferritin and hemosiderin. Iron in excess is potentially toxic to all forms of life and by all routes of exposure: toxic to plants at concentrations of 200 mg of Fe per dayand toxicto human at concentrations of200mg of Fe per day.Irondust, usually in the form of the oxides can cause conjunctivitis,choroiditis,retinitis and siderosis of tissues, pulmonary fibrosis and increased risk of lung cancer(Sunderman, 1993).

Iron occurs as a natural constituent in plants and animals. Liver, kidney, fish, and greenvegetables contain 20–150 mg/kg, whereas red meats and egg yolks contain 10–20 mg/kg.Rice and many fruits and vegetables have low iron contents (1–10 mg/kg). It is one of the vital components of algae and of enzymes such as catalase and cytochromes (Vuori, 1995). The abundance of species such as periphyton, benthic invertebrates and fish diversity are greatly affected by the direct and indirect effects of Iron contamination (Vuori, 1995). The Iron precipitate causes considerable damage by means of clogging action and frequently hinders the respiration of fishes (EPA, 1993; Jaishankar *et al.,* 2014). A wide range of free radicals are formed when the absorbed iron fails to bind to proteins, which in turn severely affects the concentration of iron in fish and mammalian cells and biological fluids. This circulating unbound iron results in corrosive effect of gastrointestinal tract and biological

fluids. An extremely higher level of iron enters into the body crossing the rate limiting absorption step and becomes saturated (Jaishankar *et al.,* 2014). This free iron penetrates into the cells of the heart, liver, muscles and brain of aquatic animals. Due to this disruption of oxidative phosphorylation by free iron, the ferrous iron is converted to ferric iron that releases hydrogen ions, thus increasing metabolic acidity. The free iron can also lead to lipid peroxidation, which results in severe damage to mitochondria, microsomes and other cellular organelles (Albretsen, 2006). The toxicity of iron in aquactic organisms' cells has led to iron mediated tissue damage involving cellular oxidizing and reducing mechanisms and their toxicity towards intracellular organelles such as mitochondria and lysosomes. A wide range of free radicals that are believed to cause potential cellular damage are produced by excess intake of iron. The iron produced hydrogen free radicals attack DNA, resulting in cellular damage, mutation and malignant transformations which in turn cause an array of diseases in both aquatic and terrestrial animals (Grazuleviciene *et al.,* 2009)

Iron isregulatedprimarilybyabsorptionsincehumanshavenophysiologicalmechanismbywhichexcess iron is excreted (Abubakar *et al*., 2015), thus, excess body iron can be highly toxic.This toxicity involves many organs leading to a variety of serious diseases such as liver disease, heart disease, diabetesmellitus,hormonal abnormalities, dysfunctionalimmunesystem,etc. (Ladigbolu and Balogun, 2011). The tissuedamageassociated with iron overload is believed to result primarily from free radical reactions mediated by iron (Fraga and Oteiza, 2002).

Thebodynormallyabsorbslessironifitsstoresarefull,but some individuals are poorlydefendedagainstirontoxicity.Onceconsidered rare, iron overload has emerged as animportantdisorder of iron metabolism.Ironoverload is known as *hemochromatosis* and isusuallycausedby agenethat enhances iron absorption (Dural *et*

al.,2007).Othercausesofironoverloadinclude repeated blood transfusions, massive doses of dietary iron, and rare metabolic disorders. Additionally,longtermoverconsumption ofironmaycause*hemosiderosis*,aconditioncharacterizedbylargedeposits of the ironstorageproteinhemosiderin in the liver and othertissues.Ironoverload is mostoftendiagnosed when tissuedamageoccurs,especiallyinironstoringorgans, such as the liver infections are likely to develop because bacteria thrive on ironrich blood.Ironically,someof thesignsofiron overloadareanalogous to those ofirondeficiency: fatigue, headache, irritability,and lowered work performance (Bury*et al.*,2003;Dural*et al*.,2007). Othercommon symptoms of iron overload include enlarged liver,skinpigmentation, lethargy, joint diseases, loss of body hair, amenorrhea, and impotence.Untreated hemochromatosis aggravates the risks of diabetes, liver cancer, heart diseaseand arthritis(Franchini, 2006).

2.7 Heavy Metal Contamination of Fish in Nigeria

River basins in Nigeriaare enhancing crop farming areasduring both the dryand rainy seasons.Fertilizers,herbicides and insecticides are used on these crops and areeventually washed intothe rivervia surface runoff (Annune, 1992; Gbem *et al.*, 2001; Nnaji *et al.*, 2007; Etim and Adie, 2012; Butu, 2013). Butu (2013) reports that petrol powered water pumps are used toirrigate the farmlands in thedryseason and this enables petroleum wastes to get into theRiver, while Nnaji *et al.* (2007) stated that most of the industries(tobacco, metal smelting, electricity meter manufacturing,ginnery, textile, vegetable oil mill etc.) located in Zaria discharge their wastes directly into rivers and adjacent tributaries.Trade wastes (from auto-mechanics, metal fabrication/finishing, abattoirs, local tanneries etc.)are also directly orindirectly discharged into rivers (Etim and Adie, 2012). Domestic sewage andrefuse also find their way intotheriver from the many settlements along the river vialeaching, direct discharge and surface runoff (Amin, 2006). Thus, there is every possibility of contamination

of water, sediments and fish of most rivers by heavy metals since industrial effluents and municipal wastewaters are known to contain high amounts of heavy metals (Abdul and Singh, 1999).

According to Dougherty*et al.,* (2000), fish consumption is a major route of chemical exposure to man, and heavy metal pollutants are potentially harmful to man when fish and water contaminatedwith heavy metals are consumed (Jobling, 1994 and Ellis *et al.,* 1989). It has been copiously established that fishes are an important aspect of human life, such that its demand for nutrition has led to its capture and rearing in both the wild and aquaculture mediums. However, irrespective of their economical and nutritional benefits, fishes respond to various environmental changes and can be used as a bio-indicator for pollution indication studies. Of the over 32,800 species of fishes, the Catfish (*Clarias gariepinus*) is among the most popular in Nigeria's wild waters and aquaculture media (Amos and Bolorunduro, 2000), this is primarily due to their fast growth, hardiness, resistance to diseases, ease to breed both in captivity and wild. However, with these merits come some drawbacks, as several studies have shown that wild captured fishes with a potential of being hardy, bio-accumulate heavy metals to a large extent that has far-reaching health risks (Brown and Walls, 1997; Gbem *et al.,* 2001; Yilmaz, 2003; Hajeb *et al.,* 2009; Olaifa *et al.,* 2010; Mieiro *et al.,* 2012; Bashir *et al.,* 2013). For instance Gbem *et al*., (2001) reported that the gills and gut of *Clarias gariepinus* are the main sites of heavy metal uptake by fish, while the liver, muscle and kidney are also knownto accumulate high amounts of metals. Uzairu *et al.* (2009) studying River Kubanni in Zaria, Nigeria reported that Cadmium mean concentrations in wild *Clarias gariepinus* ranged from 0.019 and 0.267mg/kg, for brain and kidney tissues, respectively, while Olaifa *et al.,* (2010) reports that locally farmed *Clarias gariepinus* showed mean concentrations of0.002 and 0.037 mg/kg of Cadmium concentrations in the intestine and muscle tissues. Furthermore, they revealed that the concentrations of heavy metals in *Clarias*

gariepinus inhabiting a lake and fish farm in Ibadan, Nigeria had ranges of Nickel, Chromium, Manganese and Lead varying from 0.213 – 0.924 mg/kg, which have been known to cause gastrointestinal burns, haemorrhage, generalized oedema, pulmonary oedema, liver damage, kidney damage and ultimately death when ingested. Igwemmar *et al.*, (2013) while studying local sold fishes in Gwagwalada market in Abuja, Nigeria, observed that heavy metals in *Clarias gariepinus*, namely; Copper, Zinc, manganese, iron and lead had very high concentration levels of 0.12, 2.93, 0.07, 3.65 and 0.01 ppm, respectively. They added that with subsequent increase in the level ofthese toxicants they could pose a potential human health hazard.

With the growing awareness of eating "white meat" to lower cholesterol levels, there has been a rising consumption of both wild and locally farmed fish meat in Nigeria; however, there has been no corresponding awareness of consumer safety control in place. This has been reported by Eletta *et al*., 2003; Obasohan *et al.*, 2006; Nnaji *et* al., 2007; Alinnor and Obiji, 2010; Igwemmar *et al*., 2013; Abubakar *et al.*, 2015). For example Obasohan *et al.*, (2006) reports that despite confirmations of heavy metal concentrations of Cu, Mn, Zn, Pb, Cr, Ni and Cd in farmed *Malapterurus electricus* and *Chrysichthys nigrodigitatus* in Benin City, there has been no concerted effort by health or government officials to curb the trend in the ancient city, neither has there been any resolution to monitor and/or screen the farms from where these fishes are farmed to ensure health compliance. Nnaji *et* al., (2007) noted that due to the failure of proper monitoring, administration, regulations and guidelines in fish production, the concentration of heavy metals such as cadmium, chromium, zinc, lead, and copper in *Oerochromis niloticus* and *Synodontis schall* in Nigeria has been on the increase in recent years, yet there has been no measure in place to moderate the drift.

2.8 Ecological Distribution of *Clarias gariepinus* (Burchell, 1866)

Of the over 33,500 species of fishes (Froese and Pauly, 2017), the Catfish (*Clarias gariepinus*) is among the most popular in Nigeria's wild waters and aquaculture media (Amos and Bolorunduro, 2000), this is primarily due to their fast growth, hardiness, resistance to diseases, ease to breeding both in captivity and wild. The African catfishhave almost pan-African distribution (but are naturally absent from the Maghreb, Upper and Lower Guinea and Cape provinces) (Isyagi *et al*., 2009). They are equally present in Jordan, Lebanon, Israel and Turkey. *Clarias gariepinus* has also been introduced into most other countries in Africa, as well as several in Europe, Asia and South America. Similar to other species like common carp, crucian carp, bighead, European crucian carp, mirror carp, , loach, rain bow trout, *Xenocyprinus* and snakehead (*Ophicephalus argus*), China has also adopted *Clarias gariepinus* within its rice-fields and is currently among the main producing countries (Billard, 2003).

This species is found in lakes, streams, rivers, swamps and floodplains, many of which are subject to seasonal drying. The most common habitats are floodplain swamps and pools where they can survive during the dry season(s) due to their accessory air breathing organs (FAO, 2007). *Clarias gariepinus* undertake lateral migrations from the larger water bodies, in which they feed and mature at about the age of 12 months, to temporarily flooded marginal areas in order to breed. These reproductive migrations typically take place shortly after the onset of the rainy season(s). The final gonadal maturation is associated with rising water levels. Under stable environmental conditions, adult *C. gariepinus* have mature gonads year-round. Under ideal conditions, a ripe female may lay about 60,000 eggs/kg (FAO, 2014) and as flooded marginal areas dry up with the end of the rains, juveniles and adults make their

way back to deeper water. In areas with two rainy seasons (especially Brazil), there are usually two reproductive peaks during the year, corresponding in intensity to the magnitude of the rains (FAO, 2007).

Most species of *Clarias* are slow foraging predators and approximately 70 percent of feeding activity takes place at night. Growth is relatively rapid, approaching maximum size within a couple of years. Their culture in modern times follows a similar trend to that of *tilapias*: first domestication trials by the year 1950 and adoption of the African catfish *Clarias gariepinus* as the most desirable catfish for aquaculture in the mid-1970s. However, under culture conditions, it is difficult for the fish to spawn spontaneously. Protocols for artificial propagation based on hormonal stimulation were therefore developed from the 1980s. Research on the development of farming technology has been conducted in Europe (Belgium and the Netherlands) as well as in Africa (e.g. Central African Republic, South Africa, Côte d'Ivoire, and Nigeria) (FAO, 2014).

For many reasons, including the current availability of this species in almost all its water bodies, a huge expanding population with increasing demand for fish and its superior technical skill and infrastructures compared to other African countries, Nigeria has certainly benefited by far the most from research studies (FAO, 2014). However, *Clarias gariepinus* has mostly been used as 'police-fish' to control over-breeding in mixed-sex tilapia culture in earthen ponds in Uganda (Isyagi *et* al., 2009) and also as a control in rice paddies in China and Thailand (Little and Edwards, 1999). In Uganda, the development of *Clarias* culture is more related to its use as baits for fishing in Lake Victoria.More recently, with the development of balanced extruded feed, there has been a huge diversification of culture environment in most African countries where this catfish is reared, including the use of concrete or fibreglass tanks and water recirculation systems. Thus, the main producers or farmers of the African catfish are Netherlands, Brazil, Syria, Italy, Hungary, Kenya,

Cameroun, Ghana, Mali and South Africa, with Nigeria being the largest producer (FAO, 2014).

The success obtained in Nigeria is predicated upon the judicious application of research works, market demand (where prices averages USD3.5/kg), local and foreign fish production campaigns, waivers and subsidies of fish meal and equipment since 1950, and less on the environmental suitability for catfish production (Offem *et al*., 2010).

However, with these merits comes some drawbacks, as several studies have shown that wild captured fishes with potential of being hardy, bio-accumulate heavy metals to a large extent that has far-reaching health risks (Brown and Walls, 1997; Yilmaz, 2003; Hajeb *et al.,* 2009; Olaifa *et al.,* 2010; Mieiro *et al.,* 2012; Bashir *et al.,* 2013). With the growing awareness of eating healthy, there has been a rising consumption of both wild and locally farmed fish in Nigeria, this is in addition to the very low level of consumer safety control in place.

It is in the light of this that this study was carried out, to add to the awareness on the implications of heavy metals risk that could arise from the consumption of catfish - *Clarias gariepinus*from both farmed and non-farmed sources that have been contaminated by heavy metals.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study Area

The global position of Kaduna State is between longitude 6° 6′36″ E to 8° 48′36″ E and latitude 8° 58′12″ N to 11° 29′23″N(KASUPDA, 2013). The State occupies an area of approximately 48,473.2 square kilometres and has a population of more than 6 million according to the 2006 census (NPC, 2006). The entire land structure consists of an undulating plateau with major rivers in the State including River Kaduna, River Wonderful in Kafanchan, River Kagom, River Kubanni, River Gurara and River Galma (KASUPDA, 2013). River Kaduna and River Gurara are the two largest river systems in the State, while River Galma is the main drainage channel in Zaria, thus they all sustain the agricultural, horticultural and aquaculture practices in the State, which has an average rainfall of 750 mm per annum and is concentrated in the 6 months of rainfall – May to September (Samaila *et al.*, 2011).

Using GPS coordinates the samples used in this research work was obtained from four different sampled sites as shown in Table 3.1.

Table 3.1 Sample Water Sources and GPS Coordinates

	Coordinates	
Location	River Kaduna	River Galma
Upstream	N 10° 36' 1.296□ – N 10°36' 1.4814□	N 11°7'10.3116□ – N 11°7'10.3705□
	E 7°30' 9.9648" – E 7° 30' 10.0039"	E 7°44'27.2616" – E 7°44' 27.3013"
Midstream	N 10°29' 9.906□ – N 10°29' 9.9920□	N 11°4'29.6616□ – N 11°4'29.7124□
	E 7°23'9.9276" – E 7°23' 9.9845"	E 7°44'28.3920" – E 7°44'28.4622"
Downstream	N10°28' 41.0124□ – N 10°28' 41.1106□	N 11°2'8.1276□ – N 11°2'8.1884□
	E 7° 16' 30.5544" – E 7° 16' 30.6124"	E 7°44'49.9236" – E 7°44' 50.0003"
Location	Godiya Fish Farm - (Farm 1)	Duniya Farms - (Farm 2)
	N 10° 28' 27.0552□	N 11° 2' 6.7848□
	E 7° 22' 15.3192"	E 7°44' 32.1468"

3.1.1 River Kaduna, Kaduna

River Kaduna in particular has several tributaries emptying into it among which are Kaduna, Kangimi, Romi and Rigasa rivers (Amin, 2006), the area is also drained by a number of man-made drains which were initially constructed to manage urban storm runoff and have been converted to municipal wastewater and industrial effluents disposal conduits such as Kawa, Golf course, Bundum-bundum Sardauna Crescent, Tudun-Wada, Abattoir, Barnawa, Abakpa, Kakuri, Makera and Rafin Dai drains (Samaila *et al.*, 2011). In addition, KEPA (1998) states that due to the rapid urbanization in Kaduna, the capital has one of the largest concentrations of industries in Nigeria, including the Kaduna Petrochemical Refinery. These industries discharges effluents, and together with municipal wastes containing pollutants, they are emptied into River Kaduna (KEPA, 1998).

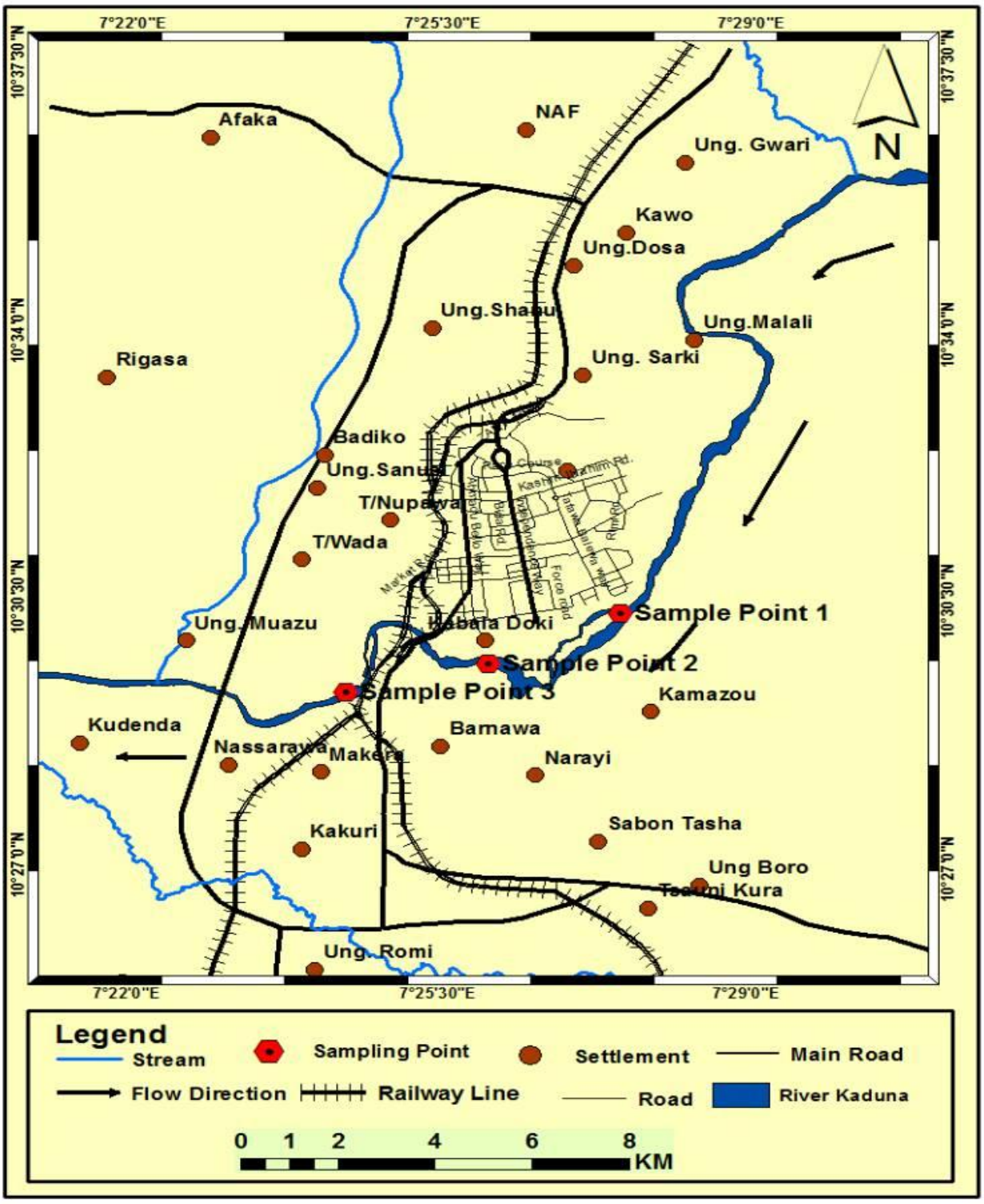


Fig. 3.1 River Kaduna Showing Sampling Points (Source: Department of Geography, A.B.U, Zaria, Kaduna State)

3.1.2 River Galma, Zaria

River Galma is the main drainage channel in Zaria since other rivers and streams discharge into it (Udiba *et al.,* 2014), and it is located at latitude 11º 2″ N and longitude 7º 40″ E (Nnaji *et al.,* 2011). River Galma is located at the south-eastern part of Zaria and its source is the Jos Plateau. The Zaria dam is located on River Galma (Nnaji *et al*., 2007). Dakace industrial area harbours a number of wet industries, such as oil mills, packaging, food and beverages industries. Effluents from these industries are discharged through drains and canal that empties into the River (Udiba *et al.,* 2014). The Galma river basin is a booming agricultural area. Crops are planted on both sides of the riverbank throughout the year. Fertilizers, herbicides and insecticides are used on these crops and are eventually washed into the river via surface runoff (Nnaji *et al.,* 2011). The river is a major source of water supply to a number of communities located along its course and is also used for irrigation, fishing, bathing and even drinking (Udiba *et al.,* 2014).

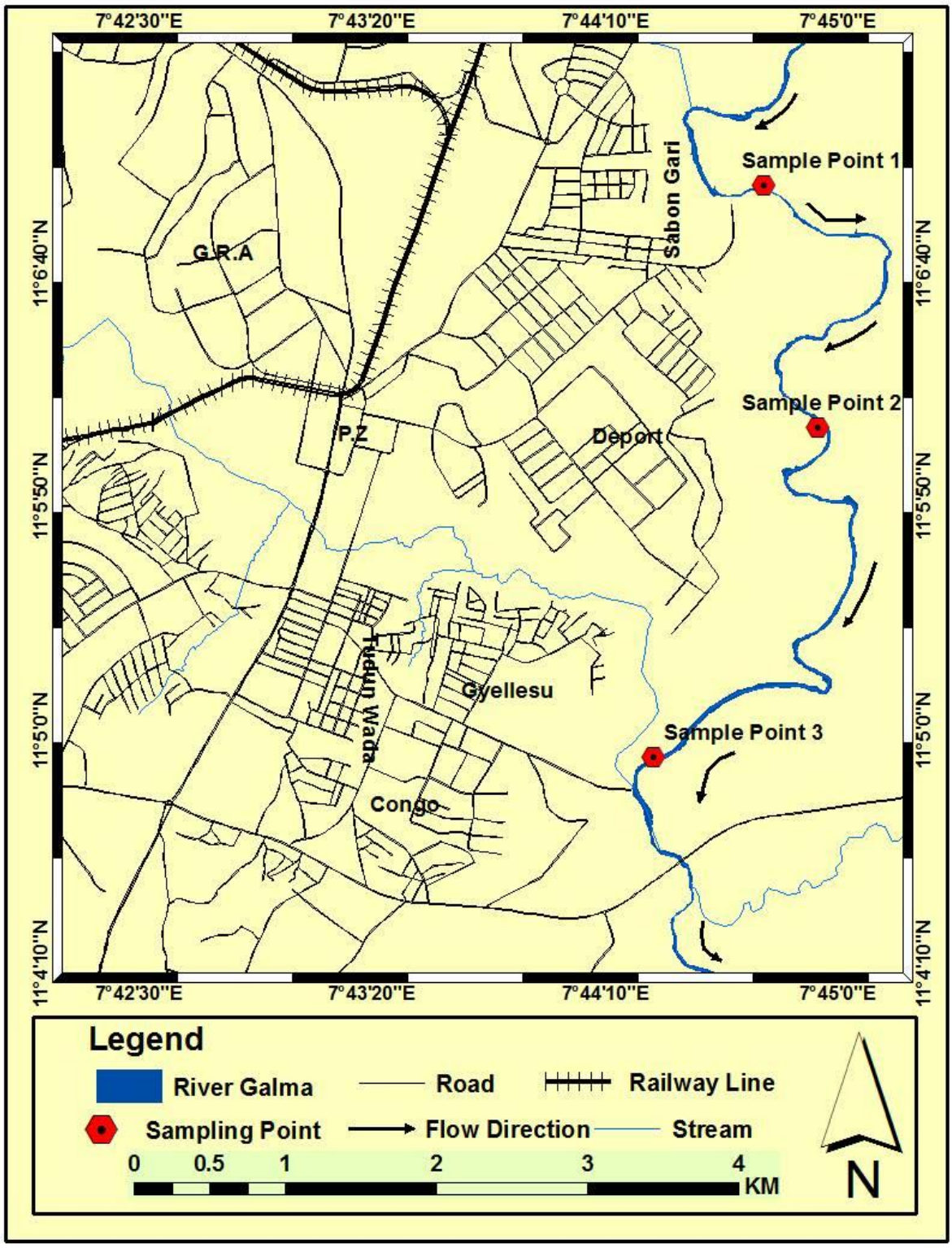


Fig. 3.2 River Galma Showing Sampling Points (Source: Department of Geography, A.B.U, Zaria, Kaduna State)

3.2 Sample Collection

3.2.1 Water Collection

Water samples from the four sampled sites – Rivers Kaduna and Galma, and two farms from Kaduna (Farm 1) and Zaria (Farm 2) were collected for the purpose of determining the accumulation factor in the wild and farmed fish species. The heavy metals that were analysed in the fish samples were also measured in the water samples.

Water samples from Rivers Kaduna and Galma and source of groundwater used for raising the freshwater species *C. gariepinus* in the two sampled farms were collected for analyses. A total of four litres of water sample was collected from the sampling sites as follows:

a. 4 samples (250ml each) was collected from three sampling points (Upstream, Midstream and Downstream) which was established along River Kaduna after identifying the first effluent discharge source (point source) from the industries, in line with Nnaji *et al* (2011). Sample point A (Upstream) was the first point source, followed by Sample point B (Midstream) and Sample point C(Downstream).

   Field survey was performed throughout the study area using Google Earth Global Positioning System (GPS). This survey was performed in order to obtain accurate location point data for each of the sampled sites.

b. Furthermore, another 4 samples of 250ml each was collected from three sampling points which was established along River Galma after identifying the first effluent discharge source (point source) from the industries, in line with Nnaji *et al* (2011). Sample point A (Upstream) was the first point source, followed by Sample point B (Midstream) and Sample point C(Downstream).

c. In addition to the river samples, 2 samples (250 ml each) was collected from three concrete ponds where *C. gariepinus* is reared and another 2 water samples (250 ml each) from the source of water used in the two sampled fish farms.

   All samples were collected in 500 ml plastic bottles, which were pre-washed with 10% nitric acid and de-ionized water. Before sample collection, the bottles were immersed to about 20cm below the water surface to prevent contamination of heavy metals from air. All water samples were then immediately brought to the laboratory where they were filtered through Whatman No.41 (0.45µm pore size) filter paper. The samples were then acidified with 2ml nitric acid to prevent precipitation of metals, reduce absorption of the analytes onto the walls of containers and to avoid microbial activity, after which the water samples were stored at 4^0C until its analysis.

d. **Reagents –** De-ionized water was used to prepare all aqueous solutions. All plastic and glassware used were rinsed and soaked in 10% (v/v) HNO_3 overnight. They were also rinsed with de-ionized water and dried prior to using, as carried out by Voegborlo and Adimado (2010). All acids (Nitric - HNO_3; Sulphuric Acid - H_2SO_4; Hydrochloric Acid - HCl and Percholoric Acid - $HClO_4$), $MnSO_4$, $Na_2S_2O_3.5H_2O$ and oxidants (Hydrogen peroxide, H_2O_2) were of the highest quality from Merck, Germany.

It is imperative to note that fish and water samples were collected for both wet and dry season months.

3.2.2 Fish Collection

a. **Wild Fish Collection** – A total of twenty (20) wild fish samples of *C. gariepinus* were used in this study to investigate the concentration of heavy metals in the rivers. Ten (10) samples of *C. gariepinus* were collected from each of the sampled rivers of River Kaduna and River Galma all in Kaduna State. Five (5) fish samples were collected in the wet season and another five (5) samples were collected in the dry season months, from each of the two river sites.

b. **Farmed Fish Collection** – Another total of twenty (20) farmed fish samples of *C. gariepinus* were used in this study to investigate the concentration of heavy metals in the farms.Ten (10) samples of *C. gariepinus*each was collected from the two fish farms; namely Duniya Farms, Dakace, Zaria and Godiya Farms, Sabon – Tasha, Kaduna all in Kaduna State. In similar fashion five (5) fish samples of *C. gariepinus* were collected in the wet season months and another five (5) samples were also collected in the dry season.

All specimens when collected were placed immediately in polyethylene bags, put into isolated container of polystyrene icebox and then taken to the Fisheries laboratory, Department of Biological Sciences, Ahmadu Bello University, Zaria for identification and morphometric parameters measurement.

100 grams of fish muscle was extracted using surgical blade and weighed from each of the forty (40) fish samples, after which the fish muscle samples were transferred to the Multi-User Science Research Laboratory – MSRL, Ahmadu Bello University, Zaria where they were washed clean with deionised water and later stored at -10^{o}C in the refrigerator prior to use for chemical analysis.

3.2.3 Digestion Procedures

a. Digestion of fish samples

In the present study fish digestion procedure was modified from Manutsewee *et al.,* (2007) who used the same mixture for digestion but they follow ultra sound assisted acid leaching procedure after fish drying for twenty hours. The present study would follow the wet digestion process with different concentrations and volumes of acids. A digestion plate was used for heating.

Before analysis, the fish was thawed and dissected. The muscular tissues on the dorsal surface of each fish taken out and homogenized and about 4 grams of the surface of the homogenized muscles (without skin) of each specimen was taken and placed in a 300ml digestion tube. A digestion mixture containing 6.0ml of high purity HNO_3 (Merck) plus 2ml of HCL (10M) and 4ml of H_20_2 (35%) was then added to each tube. The samples were at that point heated at 130^0C by a heating digester with air condenser until a clear solution was obtained. After cooling, the samples were filtered through Whatman filter paper and the digested portion was diluted to a final volume of 50ml using de-ionized water. Blank reagents without fish samples were also digested using the same method.

b. Analysis of water samples

4ml of concentrated HCl (10M) was added to 250ml of each water sample placed in 600ml beaker, and evaporated to 25ml. The concentrate was then transferred to a 50ml volumetric flask and diluted to mark with deionised water. Prior to this process and further analysis, the solutions were filtered through Whatmannumber 42 filter paper in accordance with Olowu *et al.,* (2010).

c. Blank Preparation

At each step of the digestion processes of the samples acid blanks (laboratory blank) were done using an identical procedure to ensure that the samples and chemicals used were not contaminated. They all contained the same digestion reagents as the real samples with the same acid ratios but without fish samples. After digestion, acid blanks were treated as samples and diluted with the same factor. They were analysed by atomic absorption spectrophotometry before real samples and their values were subtracted to check the equipment to read only the exact values of heavy metals in real samples. Each set of digested samples had its own acid blank and was corrected by using its blank sample.

3.3 Analytical Technique

Trace elements relate to the very small amounts of the analytes found in the sample which require special instrumental techniques to be determined. On the other hand, one element at a high concentration in a sample can be considered as a trace in another.

The analytical technique that was used in determining heavy metals levels in all samples was the Thermo-element Solar S4 Atomic Absorption Spectroscopy (International Equipment Trading Ltd, USA) it is a standard laboratory analytical tool for metal analysis and is based on the absorption wavelength and detections limits for the heavy metals which vary.

The key feature is the production of free, ground state atoms from samples, which pass through the light beam from the hallow cathode lamb. For many conditions the absorption of radiation follows Beer's law:

$$A = abc$$

Where,

A – Absorbance,

a – Absorptivity,

b – Bath-length of absorption and,

c – Concentration of the absorbing species.

Beer's law shows a relation between absorption and concentration of analytes, so calibration of the instrument is needed.

3.3.1 Calibration of Instrument

Calibration requires the establishment of a relationship between signal response and known set of standards. The standards in atomic absorption spectrometry refer to the production of a series of aqueous solutions of varying concentrations (working standards) of the analytes of interest. By measuring the signals for a series of working solutions of known concentrations it is possible to construct a suitable graph. Then, by presenting a solution of unknown concentration to the instrument, a signal is obtained which can be interpreted from the graph, thereby determining the concentrations of the element in the unknown.

The actual concentration of each metal was calculated using the formula:

Actual concentration of metal in sample = (µg/g) *R* x dilution factor

Where:

(ug/g) *R* = AAS Reading of digest

Dilution Factor = Volume of digest used/Weight of digested sample

3.3.2 Validation of Analytical Methodology (Recovery Test)

In the present study a modified method was employed for digestion process. To check the accuracy of the digestion method and the subsequent validity of analytical technique, homogenous mixtures of five samples of fish muscles was spiked with standard solutions of all metals considered in this present study. The concentration of each metal in its standard solutions was calibrated to 1000 µg/g. The first three samples were spiked with 0.1ml of the standard solution of each metal. The other three samples were then spiked with 0.3ml.

A mixture with fish muscles, but without any metal spiking was used as control. All mixtures were then subjected to the digestion procedure used in present study, after which the digested samples were transferred to a 100ml volumetric flask and diluted to mark with deionised water. The resulting solutions were analysed five times for metal concentration. After which the error percentage between the five readings was calculated.

The amount of spiked metal recovered after the digestion of the spiked samples was used to calculate percentage recovery as follows:

$$\% \text{ Recovery} = (T - C)/T \times 100$$

Where:

T = Concentration of metal in treatment sample.

C = Concentration of a metal in control sample

3.3.3 Precautions Followed to Prevent Contamination

One of the main problems in the sample preparation is the contamination of the sample during sample pre-treatment (weighing, cutting and digestion). Therefore, several precautions was taken in order to prevent contamination, such as using acidic solution 10% (v/v) and

deionised water to clean all bottles and glassware prior to using. Water samples were acidified at time of collection in order to reduce adsorption of the analytes onto the walls of containers, to prevent the precipitation of metals and to avoid microbial activity.

Fish samples were also washed with deionised water prior cutting to remove adsorbed metals on skin.

Contamination may also occur from acid mixture used for digestion or from atmospheric air or lab. To check whether any error is being introduced into measurements from any of the mentioned possible sources acid blank was prepared in each set.

3.4 Techniques for Determining Physico-chemical Parameters

3.4.1 pH Measurement

The pH was measured using a digital pH meter (Hachsens-ION+ pH31 GLP lab pH meter LPV2110T.97.002Model). The meter was switched on and was allowed to warm for 5 minutes. It was then standardized with a buffer solution. The meter was then immediately introduced into the water sample and a stable reading was taken.The electrode was then rinsed with deionized water before another measurement was taken (APHA, 1998).All determinations were done in triplicates and the mean values recorded.

3.4.2 Temperature Measurement

Water temperature at various sites was determined using mercury-in-glass thermometer which was immersed in water 6 cm below the water surface and left to stabilize for about five minutes before it was read and recorded. The ambient temperature was determined with the thermometer at each location. The temperature was also determined in the laboratory using Hanna instrument (HI98129 Model).

3.4.3 Dissolved Oxygen Measurement

Water samples were transferred into a 300ml BOD bottle that is calibrated in millilitre (ml). 2ml $MnSO_4$ solution and 2ml alkali-iodide azide reagents were added, which was then stoppered with care to exclude air bubbles. It was then mixed gently by inverting thebottle a number of times until a clear supernatant was obtained. It was allowed to settle for two minutes after which 2ml concentrated H_2SO_4 was added by allowing the acid run-down the neck of the bottle. It was stoppered again and mixed by gentle inversion several times until dissolution was complete. 100ml of the prepared solution was transferred into a conical flask and titrated with 0.0125 of Sodium Thiosulphate($Na_2S_2O_3.5H_2O$) solution to a pale straw/yellow colour. Prior to this, 2ml of freshly prepared starch solution was added and the colour changed to blue. Titration was continued by adding thiosulphate drop-wise until the blue colour disappeared. Dissolved oxygen was determined by modified Winkler-azide method, and determined using the formula:

$$DO = V \times N \times E \div SV$$

Where: V = Volume of $Na_2S_2O_3.5H_2O$

N = Normality of $Na_2S_2O_3.5H_2O$ (0.025ml)

E = Oxygen Volume per 100ml of H20 Sample (0.008)

SV = Sample Volume

This was done in triplicate for each site of the sampling period.

3.4.4 Turbidity Measurement

The turbidity of the water samples were measured using a digital turbidity meter (2100AN Hach Model). The meter was standardized with clean deionized water,and this was then introduced into the water samples. The turbidity reading of each sample was then recorded in triplicates in each site samples, in accordance with NRCC (2011).

3.4.5 Biological Oxygen Demand (BOD)

The (BOD) was determined by measuring the DO of the samples contained in a BODbottlebeforeand after five days at incubation of 20°C.According to APHA-51210B, BODwas calculated using the formula:

$$(S_1\text{-}S_2) - (B_1\text{-}B_2) \times \% \text{ dilution.}$$

Where;

S_1 = DO for the sample,

S_2 = DO after incubation of sample,

B_1 = DO for the first day for blank,

B_2 = DO after incubation for blank.

3.4.6 Determination of Total Dissolved Solid

The total dissolved solid was determined using a Conductivity meter, the programme menu of the Conductivity meter was switched to total dissolved solid, 100 cm^3 of the sample was measured into the beaker and the electrode was introduced into the sample. The results of total dissolved solid were displayed and recorded, in accordance with procedures set out by APHA (1998) and DeZuane (1997).

3.4.7 Electrical ConductivityMeasurement

Conductivities of the water samples were measured using a digital conductivity meter (Hach Sens-Ion+ E7 Basic Conductivity Benchtop Meter Model). The meter was switched on and then standardized using 0.1N KCl at 25°C. The electrode was then immersed into the water sample and conductivity reading of each sample was recorded (Sachchida *et al.,* 2011).

3.5 Data Analysis

The data obtained was subjected to descriptive statistics, using Microsoft Excel (Windows 8 – 2011). The data was further subjected to t-test to determine the level of significant differences between the means, while Pearson Correlation Coefficient was employed to determine the relationships between heavy metals and Physico-chemical parameters analysed. Level of significance set at $p<0.05$. All statistical analysis was carried out using the statistical software package (IBM SPSS version 20).

CHAPTER FOUR

4.0 RESULTS

4.1 Physico-Chemical Parameters of Water Samples

In this study, the pH value in the upstream (6.78) in River Kaduna during the dry season differed significantly ($p>0.05$) from values obtained in the midstream (6.69) and downstream (6.67). However, pH values in the upstream (7.04), midstream (6.95) and downstream (6.93) during the wet season did not show any significant difference ($p>0.05$) as shown in Table 4.1.

Temperature in River Kaduna indicated close variations across the sampled sites, the upstream (28.47°C) showing significant difference ($p<0.05$) from the midstream (27.03°C) and the downstream (27.31°C). The wet season had an upstream value of 29.03°C, which differed significantly from the midstream (27.59°C) and the downstream (27.87°C).

Dissolved Oxygen during the dry season of River Kaduna showed significant differences ($p>0.05$) in three different sections of River Kaduna with the upstream having 6.73mg/l, midstream (5.90mg/l) and downstream (5.62mg/l), while the wet season also showed significant differences across the three sites (Upstream – 7.69mg/l, Midstream – 6.86mg/l and Downstream – 6.58mg/l) at $p<0.05$.

The Turbidity varied slightly in the dry seasons with the upstream (NTU 56.5) and downstream (NTU 55.5) showing no significant difference at $p>0.05$, but the midstream recorded a NTU value of 49.67 which differed significantly from the two prior mentioned sites. During the wet season the upstream (NTU 57.56) and downstream (NTU 56.98) areas did not show any significant difference between them, but differed significantly with that of the midstream (NTU 50.73) at $p>0.05$ (Table 4.1).

Table 4.1 Physico-chemical characteristic of River Kaduna

Parameters	Dry Season			Wet Season		
	Upstream	Midstream	Downstream	Upstream	Midstream	Downstream
pH	6.78 ± 0.04[a]	6.69 ± 0.03[b]	6.67 ± 0.05[b]	7.04 ± 0.03[a]	6.95 ± 0.06[a]	6.93 ± 0.04[a]
Temperature (°C)	28.47 ± 0.08[a]	27.03 ± 0.05[b]	27.31 ± 0.03[b]	29.03 ± 0.08[a]	27.59 ± 0.09[b]	27.87 ± 0.72[b]
DO (mg/l)	6.73 ± 0.02[a]	5.9 ± 0.04[b]	5.62 ± 0.04[c]	7.69 ± 0.05[a]	6.86 ± 0.04[b]	6.58 ± 0.04[c]
Turbidity (NTU)	56.5 ± 0.53[a]	49.67 ± 0.08[b]	55.5 ± 0.53[a]	57.56 ± 0.45[a]	50.73 ± 0.18[b]	56.98 ± 0.52[a]
BOD (mg/l)	2.33 ± 0.05[a]	2.19 ± 0.14[b]	2.25 ± 0.09[a]	3.88 ± 0.07[a]	3.61 ± 0.03[b]	3.44 ± 0.08[b]
TDS (mg/l)	80.39 ± 0.47[a]	79.95 ± 0.16[a]	78.82 ± 0.96[b]	70.01 ± 0.41[a]	68.33 ± 0.85[b]	65.75 ± 0.67[c]
EC (µs/cm)	135.61 ± 3.81[b]	136.61 ± 0.78[a]	130.61 ± 4.11[c]	120.60 ± 0.44[a]	118.44 ± 1.17[b]	116.21 ± 0.87[c]

Means with the same superscripts on same rows were not significantly different (p≥0.05).

The BOD recorded for River Kaduna during the dry season was 2.33mg/l in the upstream, 2.19mg/l in the midstream, and 2.25mg/l at the downstream, however the upstream and downstream did not differ, with only the midstream differing significantly at $p<0.05$. During the wet season the upstream (3.88mg/l) differed significantly from the midstream (3.61mg/l) and downstream (3.44mg/l).

Total dissolved solids (TDS) in River Kaduna did not show any significant differences ($p<0.05$) in the dry season for the upstream (80.39mg/l) and the midstream (79.95mg/l), but differed in the downstream (78.82mg/l). During the wet season there was significant differences in the three sections analysed; with the upstream having a value of 70.01mg/l, while the midstream and downstream sections had values of 68.33mg/l and 65.75mg/l, respectively as shown in Table 4.1.

However, there were fluctuations in electrical conductivity of the water in the dry season, as the upstream had an EC value of 135.61µs/cm, which differed significantly at $p<0.05$ in the midstream (136.61µs/cm) and 130.61µs/cm in the downstream area of the river (Table 4.1). In the wet season, River Kaduna showed variations in all three sections, the upstream registering an EC level of 120.60µs/cm, differing significantly from the midstream (118.44µs/cm) and the downstream (116.21µs/cm) areas ($p<0.05$).

In River Galma, pH value in the midstream (6.44) during the dry season differed significantly from the upstream (6.63) and downstream (6.54) at $p>0.05$. However, pH values in the upstream (6.89), midstream (6.72) and downstream (6.83) during the wet season significantly differed from each other at $p<0.05$ (Table 4.2).

Table 4.2 Physico-chemical Parameters of River Galma

Seasons / Parameters	Dry Season			Wet Season		
	Upstream	Midstream	Downstream	Upstream	Midstream	Downstream
pH	6.63 ± 0.04[a]	6.44 ± 0.05[b]	6.54 ± 0.09[a]	6.89 ± 0.04[a]	6.72 ± 0.05[c]	6.83 ± 0.08[b]
Temperature (°C)	28.26 ± 0.12[a]	28.16 ± 0.08[a]	28.18 ± 0.09[a]	30.61 ± 0.13[a]	30.68 ± 0.07[a]	30.66 ± 0.09[a]
DO (mg/l)	6.62 ± 0.06[a]	4.25 ± 0.04[b]	4.48 ±0.05[b]	7.38 ± 0.04[a]	5.11 ± 0.03[c]	5.26 ± 0.04[b]
Turbidity (NTU)	55.8 ± 0.46[a]	52.7 ± 0.66[b]	52.4 ± 0.69[b]	57.04 ± 0.45[a]	53.96 ± 0.64[b]	53.72 ± 0.70[b]
BOD (mg/l)	2.79 ± 0.15[a]	2.68 ± 0.02[a]	2.68 ± 0.02[a]	4.62 ± 0.38[a]	4.18 ± 0.11[b]	3.39 ± 0.42[c]
TDS (mg/l)	84.97 ± 0.78[a]	81.58 ± 0.41[b]	79.72 ± 0.67[c]	55.92 ± 0.09[a]	54.96 ± 0.35[a]	53.84 ± 0.15[b]
EC (µs/cm)	168.09[a] ± 0.48	165.07 ± 0.52[b]	162.02 ± 0.87[c]	110.95 ± 0.31[a]	109.39 ± 0.42[a]	108.81 ± 0.49[b]

Means with the same superscripts on same rows were not significantly different (p≥0.05).

During the dry season as shown in Table 4.2, River Galma's temperature indicated close variations across the sampled sites.The Upstream had a temperature of 28.26°C, and didn't differ significantly from the midstream (28.16°C) and the downstream (28.18°C). In the wet season, the temperature of the upstream area had a temperature of 30.61°C, and did not differ significantly from the midstream (30.68°C) and the downstream (30.66°C) at $p>0.05$.

In the dry season Dissolved Oxygen showed significant difference ($p<0.05$) in the upstream 6.62mg/l, while between midstream (4.25mg/l) and downstream (4.48mg/l) showed no significant difference. However, during the wet season the river showed significant differences across the three sites with the upstream having a DO level of 7.38mg/l, while the midstream and downstream had DO values of 5.11mg/l and 5.26mg/l, respectively.

The Turbidity varied slightly in the dry seasons in the midstream (52.7 NTU) and downstream (52.4 NTU) showing no significant difference at $p>0.05$, but the upstream recorded an NTU value of 55.8, differing significantly from the two prior mentioned sites. During the wet season the midstream (53.96 NTU) and downstream (53.72 NTU) areas did not show any significant difference, but differed significantly with the upstream which had a turbidity level of 57.04 NTU.

The BOD values of River Galma in the dry season were 2.79mg/l in the upstream, 2.68mg/l in the midstream, and 2.68mg/l at the downstream area. This shows no significant difference at $p>0.05$. In the wet season BOD differed significantly, with the upstream (4.62mg/l) differing significantly from the midstream (4.18mg/l) and downstream (3.39mg/l) at $p>0.05$.

Total dissolved solids (TDS) in River Galma showed significant differences ($p>0.05$) in the dry season for the upstream (84.97mg/l), midstream (81.58mg/l) and the downstream (79.72mg/l) area. During the wet season there was significant difference in the downstream

having a value of 53.84mg/l and differing significantly from the upstream and midstream with values of 55.92mg/l and 54.96mg/l, respectively (Table 4.2).

There were fluctuations in electrical conductivity in the dry season, with an upstream value of 168.09µs/cm, which differed significantly ($p<0.05$) from the midstream (165.07µs/cm) and 162.02µs/cm in the downstream (Table 4.2). In the wet season, River Galma showed variations in the upstream (110.95µs/cm), which did not differ from that of the midstream (109.39µs/cm), but differed significantly from that of the downstream area (108.81µs/cm) at $p<0.05$.

In Table 4.3 pH values in the dry and wet seasons for River Kaduna differed significantly, as the wet season had a mean value of 6.97, while the dry season stood at 6.71. However, temperature between the two seasons did not differ, with the dry season having a value of 27.6°C, while the wet had 28.16°C. Dissolved Oxygen (DO) showed significant difference between the dry (6.08mg/l) and wet (7.04mg/l) seasons, while turbidity showed no significant differences ($p>0.05$) between the dry (53.89) and wet (54.96) seasons. BOD, TDS and EC, showed significant differences ($p<0.05$) as shown in Table 4.3

Table 4.3 Mean Physico-chemical Parameters of River Kaduna and River Galma

Parameters	River Kaduna Dry season	Wet season	River Galma Dry season	Wet season
pH	6.71 ± 0.03^{b}	6.97 ± 0.03^{a}	6.53 ± 0.04^{b}	6.81 ± 0.04^{a}
Temp (^{o}C)	27.60 ± 0.23^{a}	28.16 ± 0.23^{a}	28.20 ± 0.04^{b}	30.65 ± 0.04^{a}
DO (mg/l)	6.08 ± 0.18^{b}	7.04 ± 0.18^{a}	5.11 ± 0.39^{b}	5.92 ± 0.38^{a}
Turbidity (NTU)	53.89 ± 1.08^{a}	54.96 ± 1.07^{a}	53.63 ± 0.58^{b}	54.91 ± 0.57^{a}
BOD (mg/l)	2.26 ± 0.07^{b}	3.65 ± 0.24^{a}	2.71 ± 0.41^{b}	4.07 ± 0.73^{a}
TDS (mg/l)	79.72 ± 13.09^{a}	68.05 ± 4.24^{b}	82.09 ± 5.12^{a}	54.91 ± 2.57^{b}
EC (µs/cm)	134.28 ± 16.32^{a}	118.42 ± 12.57^{b}	165.06 ± 13.54^{a}	109.72 ± 10.33^{b}

Means with the same superscripts on same rows were not significantly different ($p \geq 0.05$).

River Galma's pH differed significantly between the wet season (6.81) and dry season (6.53). Temperature between the two seasons also differed significantly ($p<0.05$), with the dry season having a value of 28.20°C, while the wet season had 30.65°C. Dissolved Oxygen (DO) also showed significant difference between the dry (5.11mg/l) and wet (5.92mg/l) seasons, while turbidity also showed same trend with significant differences at $p>0.05$ between the dry (53.63) and wet (54.91) seasons. BOD, TDS and EC also showed significant differences between the two seasons, with BOD in the dry season having 2.71mg/l as against 4.07mg/l in the wet season. A TDS value of 82.09mg/l was obtained in the dry season as opposed to 54.91mg/l in the wet season, while EC in the dry season had a value of 165.06µs/cm, with the wet season having 109.72mg/l as presented in Table 4.3.

In Table 4.4, a comparison of the physico-chemical analysis between River Kaduna and River Galma revealed the pH during the dry season to be different from River Kaduna (6.71) and River Galma (6.53), temperature and turbidity did not show any significant difference ($p>0.05$). However, there were significant differences between the two rivers for DO, BOD, TDS and Electrical Conductivity values in the dry season. In the wet season, however, rivers Kaduna and Galma only differed significantly in temperature, DO, BOD, TDS and EC, while pH and turbidity did not show any significant difference ($p>0.05$).

Means of both seasons showed that values of pH (River Kaduna 6.84 and River Galma 6.67) did not show any significant difference ($p>0.05$). Turbidity values were also 54.42 NTU for River Kaduna as against River Galma's 54.27 NTU. However, temperature, DO, BOD, TDS and EC did differ significantly between both rivers (Table 4.4).

Table 4.4 Mean Physico-chemical Parameters between Rivers Kaduna and Galma

Parameters	Dry season		Wet Season		River Kaduna	River Galma
	River Kaduna	River Galma	River Kaduna	River Galma	Mean	Mean
pH	6.71 ± 0.03^{a}	6.53 ± 0.04^{b}	6.97 ± 0.03^{a}	6.81 ± 0.04^{a}	6.84 ± 0.18^{a}	6.67 ± 0.19^{a}
Temp (^{o}C)	27.60 ± 0.23^{a}	28.20 ± 0.04^{a}	28.16 ± 0.23^{b}	30.65 ± 0.04^{a}	27.88 ± 0.39^{b}	29.43 ± 1.73^{a}
DO (mg/l)	6.08 ± 0.18^{a}	5.11 ± 0.39^{b}	7.04 ± 0.18^{a}	5.92 ± 0.38^{b}	6.56 ± 0.68^{a}	5.51 ± 0.57^{b}
Turbidity (NTU)	53.89 ± 1.08^{a}	53.63 ± 0.58^{a}	54.96 ± 1.07^{a}	54.91 ± 0.57^{a}	54.42 ± 0.76^{a}	54.27 ± 0.91^{a}
BOD (mg/l)	2.26 ± 0.07^{b}	2.71 ± 0.41^{a}	3.65 ± 0.24^{b}	4.07 ± 0.73^{a}	2.95 ± 0.98^{b}	3.39 ± 0.96^{a}
TDS (mg/l)	79.72 ± 13.09^{b}	82.09 ± 5.12^{a}	68.05 ± 4.24^{a}	54.91 ± 2.57^{b}	73.88 ± 8.25^{a}	68.5 ± 19.22^{b}
EC (µs/cm)	134.28 ± 16.32^{b}	165.06 ± 13.54^{a}	118.42 ± 12.57^{a}	109.72 ± 10.33^{b}	126.35 ± 11.22^{b}	137.39 ± 39.13a

Means with the same superscripts on same rows were not significantly different ($p \geq 0.05$).

The pH value in Farm 1 during the dry season was 6.54 which differed significantly ($p<0.05$) from the wet season (6.80) as presented in Table 4.5. pH values obtained in the dry season in Farm 2 (6.72) showed a significant difference at $p<0.05$ from the wet season (7.18). Table 4.5 also shows that during the dry season, Farm 1 temperature showed mean value of 25.06°C, differing significantly with that of the wet season (27.42°C) as $p<0.05$. In Farm 2, the dry season had a temperature of 23.76°C, which differed significantly from the wet season (26.12°C) at $p<0.05$.

In the dry season, Dissolved Oxygen in Farm 1 (9.29mg/l) showed a significant difference ($p>0.05$) from during the wet season (11.05). In Farm 2, DO levels were significantly different across both seasons (Dry Season – 8.98mg/l and Wet Season – 10.74mg/l). The turbidity did differ significantly ($p<0.05$) in Farm 1 during the dry season (8.55 NTU) with the wet season (9.79 NTU). In Farm 2 the dry season recorded a turbidityvalueof 8.81 which differed significantly from the wet season (10.07 NTU) was obtained. The BOD of Farm 1 recorded a value of 5.99mg/l during the dry season, as against, 3.87mg/l in the wet season, which was significantly different. Farm 2 also showed a significant difference between the dry season (6.23mg/l) and the wet season (3.17mg/l).

The TDS indry season (42.03mg/l) differed significantly from the wet season (32.93mg/l). In addition, Total dissolved solids (TDS) in Farm 2 did show asignificant difference ($p<0.05$) in the dry season (38.33mg/l) as against the wet season (28.43mg/l). However, there were fluctuations in electrical conductivity of Farm 1 water, as EC value obtained in the dry season (96.17µs/cm) was significantly higher at $p<0.05$ than the wet season (63.18µs/cm) as shown in Table 4.5. In Farm 2, the wet season (58.53µs/cm) differed significantly from that of the dry season with EC value of 88.50µs/cm ($p<0.05$).

Table 4.5 Physico-chemical Parameters of Water in Farms 1 and 2

Parameters	Farm 1		Farm 2	
	Dry season	Wet season	Dry season	Wet season
PH	6.54 ± 0.03^{b}	6.80 ± 0.03^{a}	6.72 ± 0.02^{b}	7.18 ± 0.02^{a}
Temp (^{o}C)	25.06 ± 0.10^{b}	27.42 ± 0.10^{a}	23.76 ± 0.09^{b}	26.12 ± 0.09^{a}
DO (mg/l)	9.29 ± 0.02^{b}	11.05 ± 0.02^{a}	8.98 ± 0.02^{b}	10.74 ± 0.02^{a}
Turbidity (NTU)	8.55 ± 0.06^{b}	9.79 ± 0.06^{a}	8.81 ± 0.02^{b}	10.07 ± 0.02^{a}
BOD (mg/l)	5.99 ± 0.38^{a}	3.87 ± 0.24^{b}	6.23 ± 0.45^{a}	3.17 ± 0.65^{b}
TDS (mg/l)	42.03 ± 2.77^{a}	32.93 ± 1.34^{b}	38.33 ± 2.41^{a}	28.43 ± 2.12^{b}
EC (µs/cm)	96.17 ± 4.36^{a}	63.18 ± 3.05^{b}	88.50 ± 3.98^{a}	58.53 ± 4.37^{b}

Means with the same superscripts on same rows were not significantly different ($p \geq 0.05$).

Table 4.6 the pH during the dry season showed significant difference between Farm 2 (6.72) and Farm 1 (6.54), while temperature in Farm 1 (25.06^{o}C) was also significantly differentfrom Farm 2 (23.76^{o}C). TheDO between Farm 1 (9.29mg/l) and Farm 2 (8.98mg/l), turbidity values between Farm 1 (8.55mg/l) and Farm 2 (8.81mg/l) and BOD means between Farm 1 (5.99mg/l) and Farm 2 (6.23mg/l) did not showed any significant differences between the two farm waters at $p>0.05$ during the dry season as presented in Table 4.6. However, there were significant differences between TDS and Electrical Conductivity values during the dry season, as Farm 1 had a TDS mean of 42.03mg/l and an EC value of 96.17µs/cm compared with that of Farm 2 which reported 38.33mg/l and 88.50µs/cm, respectively.

In the wet season, however, Farms 1 and 2 differed significantly, as the pH during the wet season showed significant difference between Farm 1 (6.80) and Farm 2 (7.18), while temperature in Farm 1 (27.42^{o}C) was also significantly different from Farm 2 (26.12^{o}C). However, DO between Farm 1 (11.05mg/l) and Farm 2 (10.74mg/l) did not showed any significant differences between the two farm waters at $p<0.05$ during the dry season as presented in Table 4.6.

Conversely, there were significant differences between the two farms in Turbidity, BOD, TDS and Electrical Conductivity values during the dry season, as Turbidity value in Farm 1 (9.79) was significantly different from the mean value of Farm 2 (10.07). The BOD values between Farm 1 (5.99mg/l) and Farm 2 (6.23mg/l), TDS values between Farm 1 (32.93mg/l) and Farm 2 (28.43mg/l) and EC values of 63.18µs/cm and 58.53µs/cm, for Farm 1and Farm 2, respectively, differed significantly ($p<0.05$).

Table 4.6 Physico-chemical Parameters of Water between Farms 1 and 2

Parameters	Dry season		Wet season		Mean	
	Farm 1	Farm 2	Farm 1	Farm 2	Farm 1	Farm 2
pH	6.54 ± 0.03^{b}	6.72 ± 0.02^{a}	6.80 ± 0.03^{b}	7.18 ± 0.02^{a}	6.67 ± 0.18^{b}	6.95 ± 0.33^{a}
Temp (^{o}C)	25.06 ± 0.10^{a}	23.76 ± 0.09^{b}	27.42 ± 0.10^{a}	26.12 ± 0.09^{b}	26.24 ± 1.67^{a}	24.94 ± 1.66^{b}
DO (mg/l)	9.29 ± 0.02^{a}	8.98 ± 0.02^{a}	11.05 ± 0.02^{a}	10.74 ± 0.02^{a}	10.17 ± 1.24^{a}	9.86 ± 1.25^{b}
Turbidity (NTU)	8.55 ± 0.06^{a}	8.81 ± 0.02^{a}	9.79 ± 0.06^{b}	10.07 ± 0.02^{a}	9.17 ± 0.88^{a}	9.44 ± 0.89^{a}
BOD (mg/l)	5.99 ± 0.38^{a}	6.23 ± 0.45^{a}	3.87 ± 0.24^{a}	3.17 ± 0.65^{b}	4.93 ± 1.49^{a}	4.7 ± 2.16^{b}
TDS (mg/l)	42.03 ± 2.77^{a}	38.33 ± 2.41^{b}	32.93 ± 1.34^{a}	28.43 ± 2.12^{b}	37.48 ± 6.43^{a}	33.38 ± 7.00^{b}
EC (µs/cm)	96.17 ± 4.36^{a}	88.50 ± 3.98^{b}	63.18 ± 3.05^{a}	58.53 ± 4.37^{b}	79.68 ± 23.33^{a}	73.52 ± 21.19^{b}

Means with the same superscripts on same rows were not significantly different ($p \geq 0.05$).

Consequently, in both seasons, only turbidity did not show any significant difference, as turbidity mean values for Farm 1 was 9.17, while that of Farm 2 was 9.44. However, pH (Farm 1 – 6.67 and Farm 2 – 6.95), temperature (Farm 1 – 26.24 and Farm 2 – 24.94), DO (Farm 1 – 10.17mg/l and Farm 2 – 9.86mg/l), BOD (Farm 1 – 4.93mg/l and Farm 2 – 4.70mg/l), TDS (Farm 1 – 37.48mg/l and Farm 2 – 33.38mg/l) and EC (Farm 1 – 79.68µs/cm and Farm 2 – 73.52µs/cm), all did differ significantly between the both farms (Table 4.6).

4.2 Analysis of Heavy Metals in Water Samples

4.2.1 Analysis of Heavy Metals in Water Samples from River Kaduna

Figure 4.1 and 4.2 shows the various distributions in River Kaduna during dry and wet seasons. In Figure 4.1, thePb levels vary from0.988mg/l from samples taken in the midstream in the dry season to 0.748mg/l downstream during the wet season in River Kaduna. On the average, Pb levels during the wet and dry seasons were 0.958mg/l and 0.718mg/l, respectively. In addition, the lowest Lead (Pb) level was recorded for the upstream during the wet season at 0.688mg/l, while the highest was recorded in the downstream (0.748mg/l), followed by midstream (0.717mg/l).

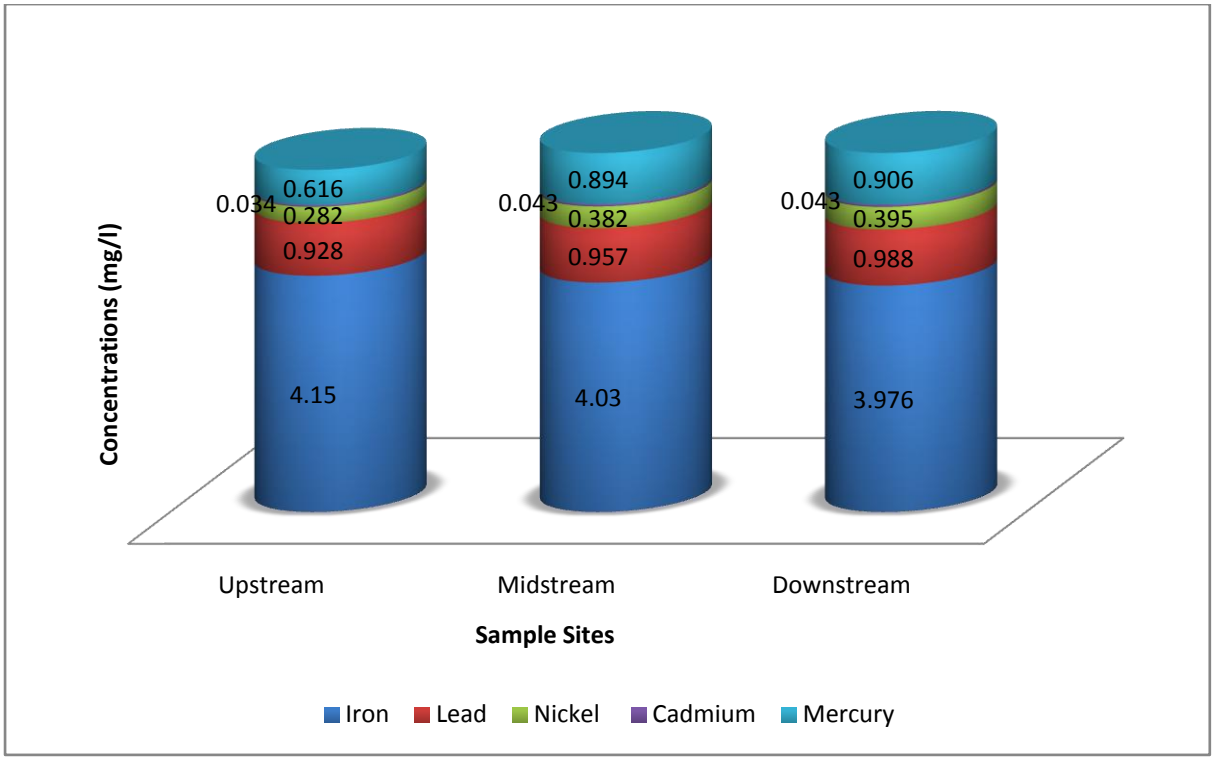


Fig. 4.1 Means of Selected Heavy Metals Obtained in River Kaduna – Dry Season

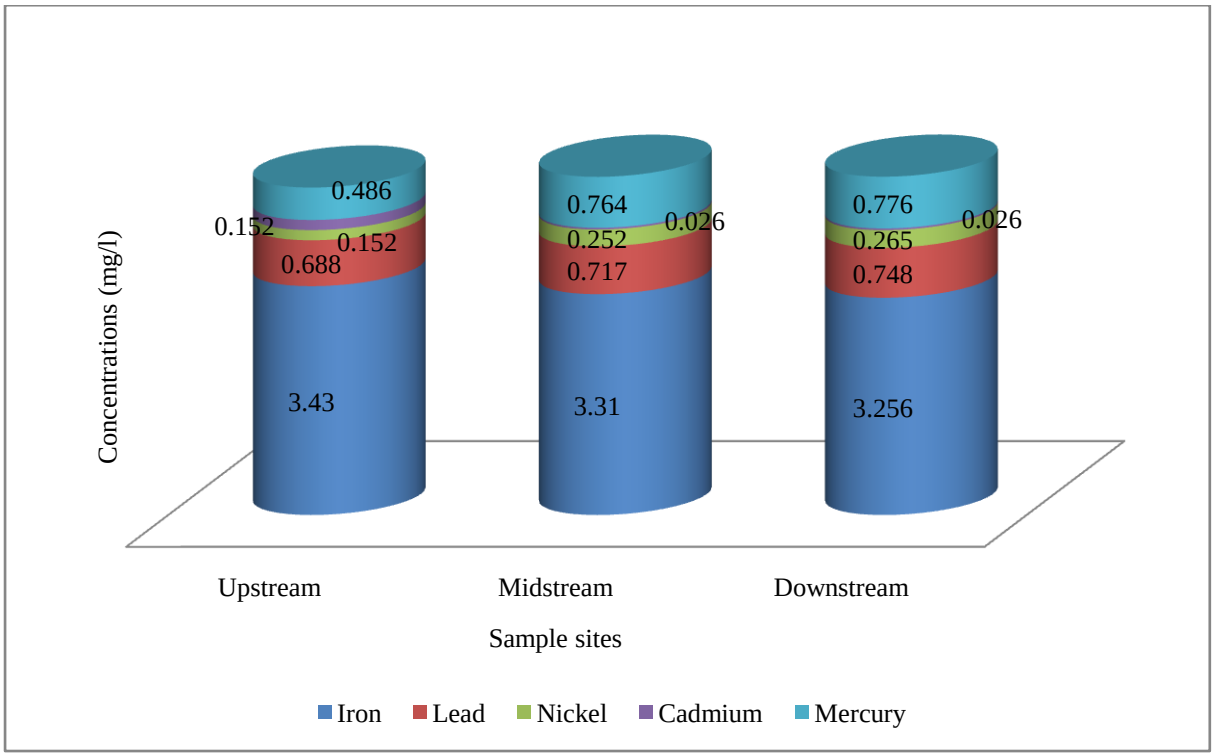


Fig. 4.2 Means of Selected Heavy Metals Obtained in River Kaduna – Wet Season

The Nickel (Ni) content in water samples from the downstream in the dry season (0.395mg/l) was high, while the midstream and upstream were 0.382mg/l and 0.282mg/l, respectively. However, Ni concentrations for the wet season were 0.265mg/l, 0.252mg/l, and 0.152mg/l, for the downstream, midstream and upstream, respectively.

Cadmium also showed varying differences in concentration in the 3 sites during the wet and dry seasons. For instance, the downstream and midstream both in the dry season had the highest value of 0.043 mg/l each; with the upstream (dry season) having the least with 0.034 mg/l, while inwet season the upstream, midstream and downstream had 0.017 mg/l, 0.026 mg/l, 0.026 mg/l, respectively.

However, Mercury was very high in River Kaduna; the highestHg value obtainedwas in the downstream part of the river with 0.906mg/l, midstream (0.894mg/l) and the upstream (0.616mg/l) all in the dry season. Relatively high levels of Iron (Fe) were found in all sections of River Kaduna, with the upstream area accounting for the highest with 4.15mg/l. The downstream area in the dry season was the lowest with 3.976mg/l, while the midstream had a concentration level of 4.03mg/l. Results in the wet season showed that the Fe concentration was highest in the upstream with 3.43 mg/l, midstream (3.31mg/l) and downstream (3.256mg/l).

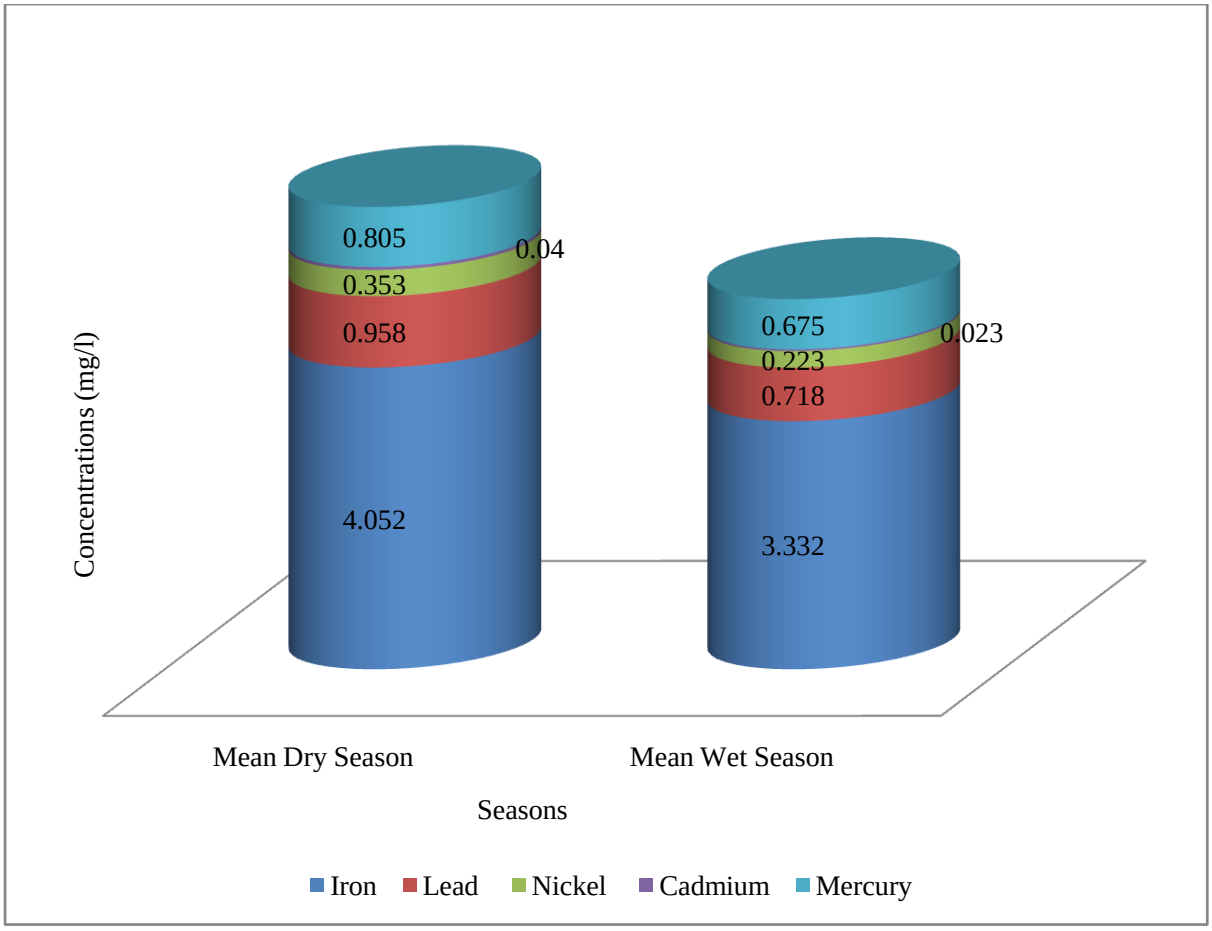


Fig.4.3 Mean Concentrations of Selected Heavy Metals in River Kaduna

On the overall, the maximum concentration for the heavy metals in water samples taken from River Kaduna sample site was Iron (3.69mg/l) and the minimum value being Cadmium (0.0313mg/l). The heavy metals in water samples from River Kaduna had mean concentrations for Lead, Mercuryand Nickel as 0.837mg/l, 0.740mg/l, and 0.288mg/l, respectively (See Figure 4.3).

4.2.2 Analysis of Heavy Metals in Water Samples from River Galma

The results shown in Figure 4.4 indicates that Lead (Pb) concentrations in water samples collected during the dry season from River Galma indicated 0.872mg/l in the upstream, while the midstream and downstream had 0.865mg/l and 0.816mg/l, respectively.

Nickel levels are very high in all sampled sites in River Galma, with the downstream area during the dry season having the highest concentration level of 0.188mg/l, while the midstream has 0.186mμg.l^{-1} and upstream with the least in the dry season with 0.175mg/l.

Also in River Galma, the highest Fe levels measured was in the upstream (3.30mg/l) during the dry season. In addition the midstream and downstream accounted for 3.112mg/l and 2.994mg/l, respectively. When Fe during the wet season was analysed it showed a marked drop in concentration levels, with the highest being the upstream at 2.58mg/land lowest being the downstream with 2.274mg/l, while the midstream Fe level was 2.392mg/l.

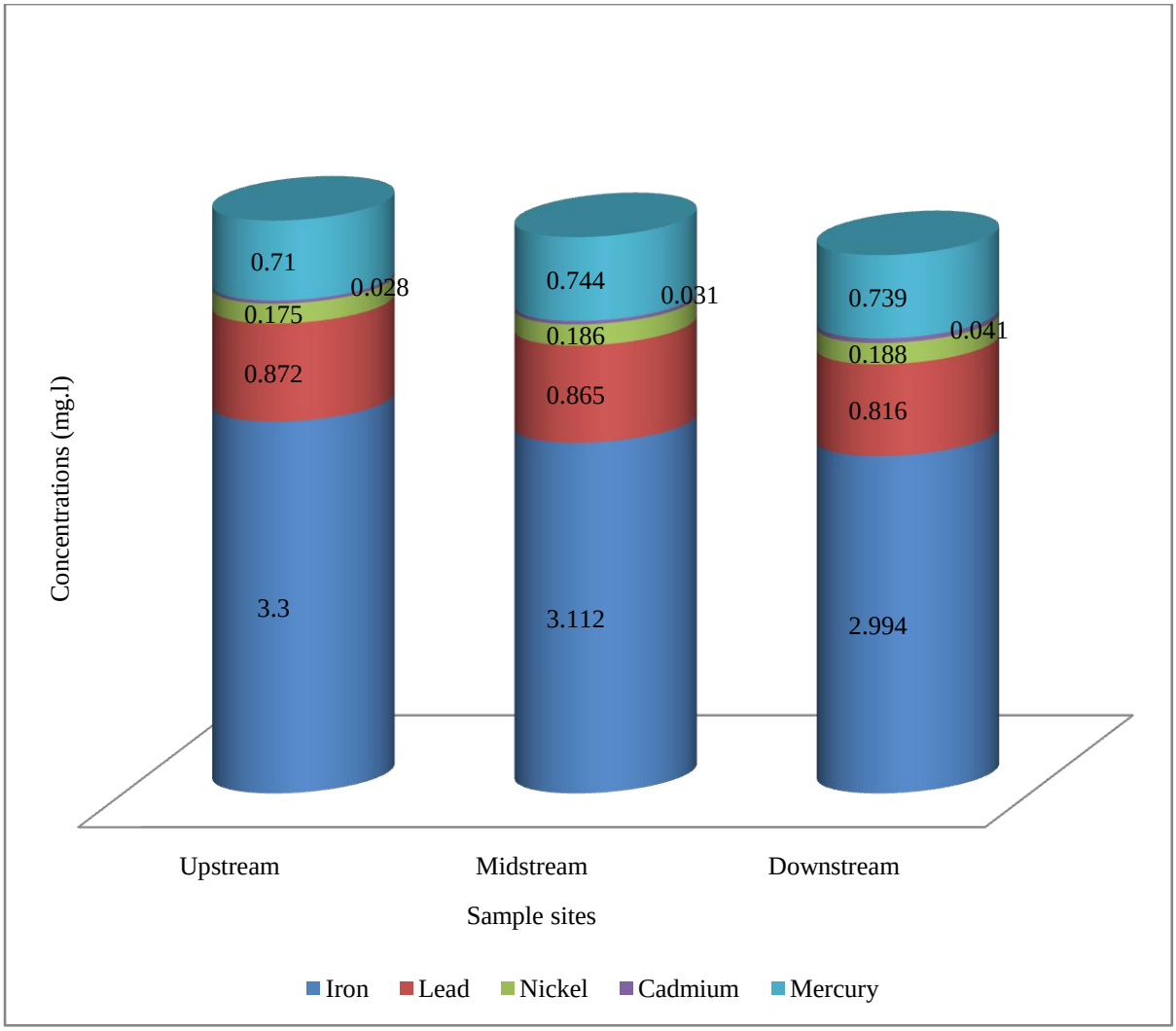


Fig. 4.4 Means of Selected Heavy Metals Obtained in River Galma – Dry Season

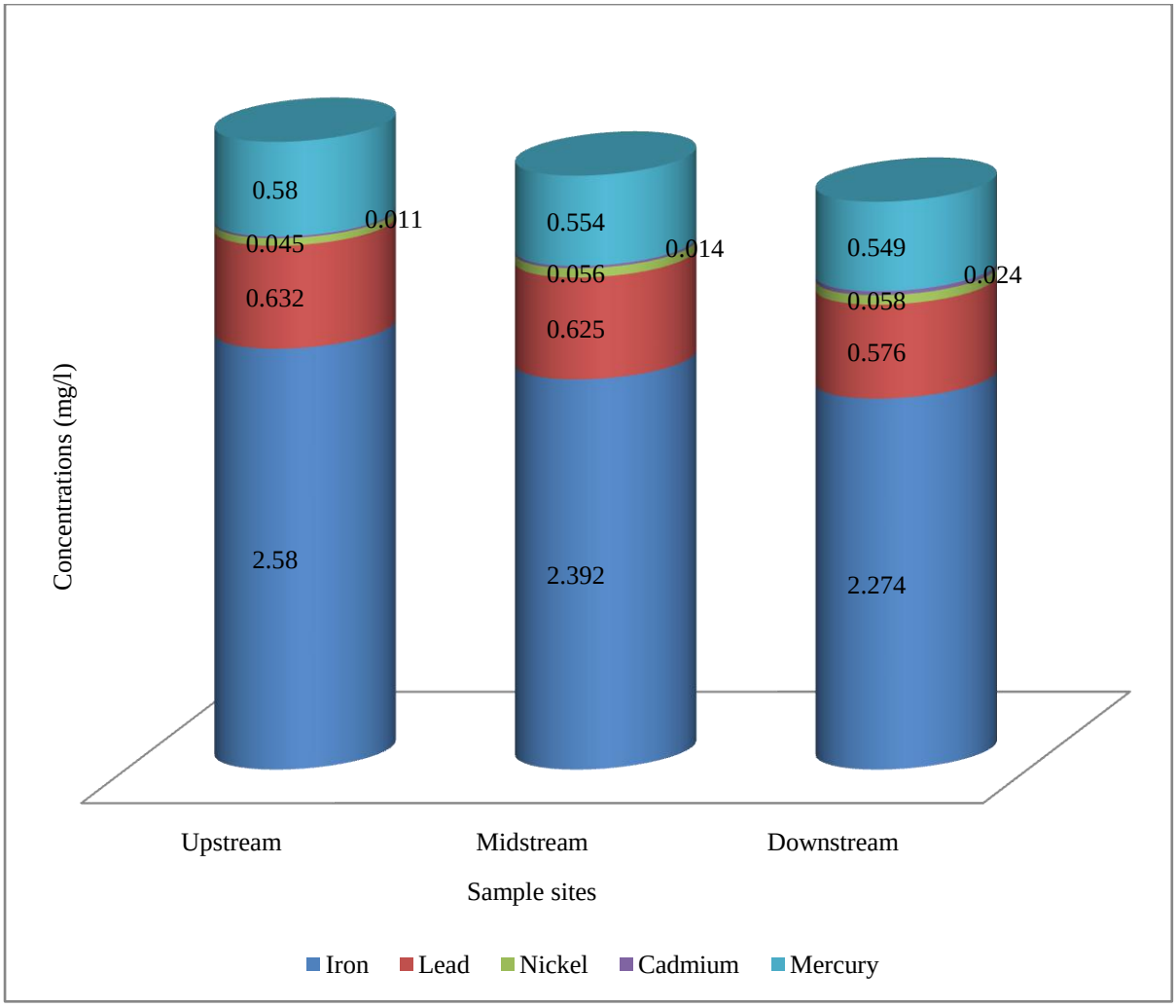


Fig. 4.5 Means of Selected Heavy Metals Obtained in River Galma – Wet Season

However, Cadmium showed slightly high levels in water samples obtained from River Galma during the dry season, as the highest recorded was in the downstream area (0.041mg/l), midstream (0.031mg/l) and upstream (0.028mg/l) as presented in Figure 4.4. In addition, Cadmium showed fairly low levels in water samples obtained from River Galma during the wet season, as the highest recorded was in the downstream area (0.024mg/l), while the midstream (0.014mg/l) and upstream (0.011mg/l) as presented in Figure 4.5. There were also high concentrations of Mercury in the midstream (0.744mg/l), downstream (0.739mg/l), and upstream (0.710mg/l) in the dry season (See Figure 4.4) and wet seasons (upstream – 0.58mg/l, midstream – 0.554mg/l and downstream – 0.549mg/l) which is graphically illustrated in Figure 4.5.

The overall mean concentration of heavy metals in water samples from River Galma, varied from 0.016mg/l to 3.135mg/l as presented in Figure 4.6. In the dry season Fe level was 3.135mg/land the wet season was 2.415, while the average of both seasons was 2.775mg/l from water samples obtained from River Galma. Lead (Pb) in the three sample sites in the dry season averaged 0.851 mg/l, while the wet season stood at 0.611mg/l and the average of both seasons was 0.731mg/l. Nickel was however low with 0.053mg/l in the wet season, while dry season concentration of Niwas 0.183mg/lin water samples, accounting for an average of 0.118mg/l for both seasons. Figure 4.6 shows the various mean distributions.

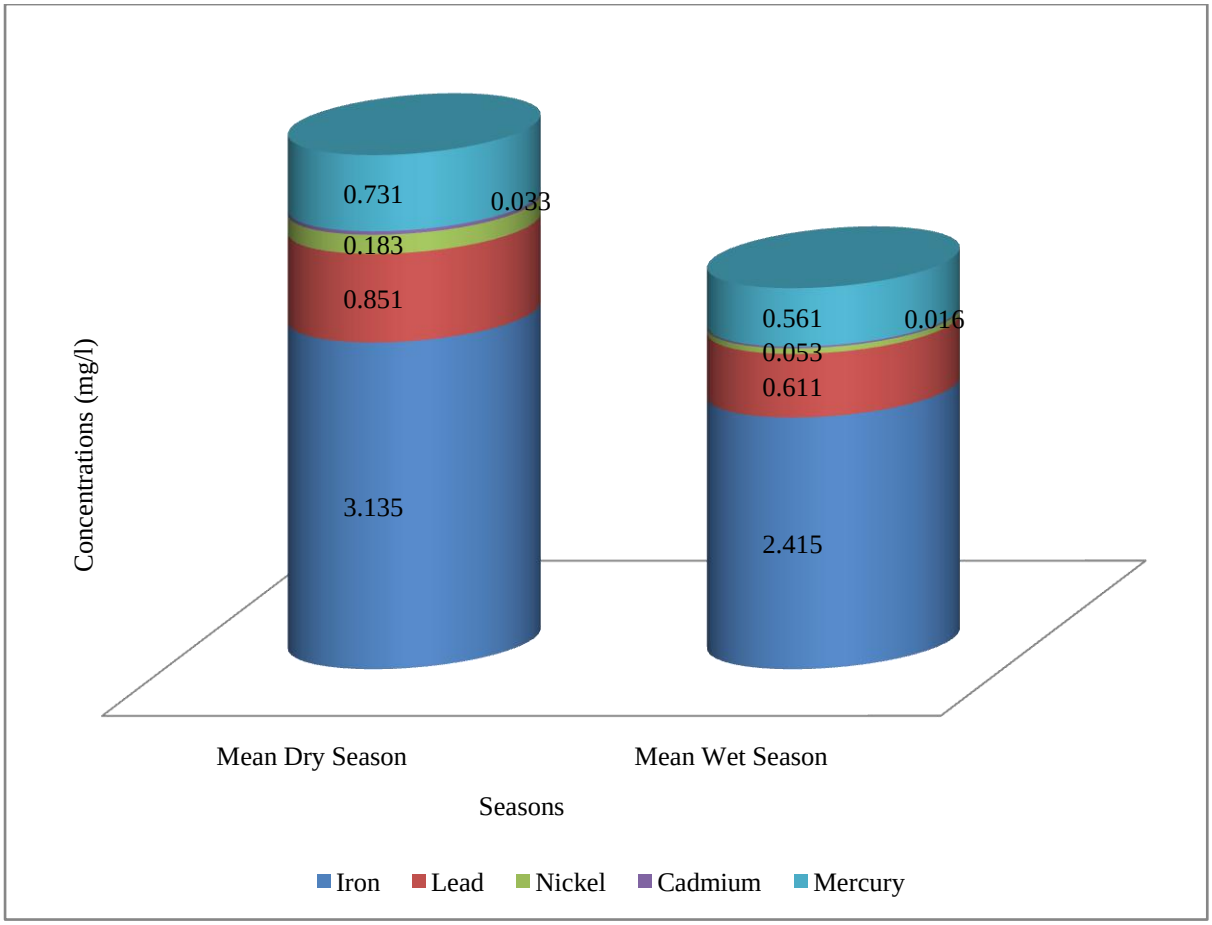


Fig.4.6 Average Concentration of Heavy Metals in River Galma

4.2.3 Analysis of Heavy Metals in Water Samples from Farm 1

Water samples from three concrete ponds of uniform sizes with a length, width and depth of 8feet, 4feet and 8feet respectively, code named Farm 1 (precisely from Godiya Farms in Sabon Tasha Area of Kaduna, Kaduna State) had different concentration levels of heavy metals. Heavy metals levels differ significantlywith seasons and were considerably high as Lead (Pb) was 0.1792mg/lduring the wet season and 0.419mg/l in the dry season, with a mean of 0.299mg/l for both seasons.

On this farm, Iron (Fe) levels were also high in the wet season at 1.062mg/l) and 1.782mg/l in the dry season, the average was 1.422mg/l.During the wet season Nickel concentrations was fairly low at 0.028mg/land a bit higher during the dry season at 0.0413mg/l, the average was 0.035mg/l, as graphically represented in Figure 4.7.

Results for Cadmium during both the dry and wet seasons were comparatively lower in Farm 1 than in both Rivers Kaduna and Galma, with 0.0004mg/l in the wet season and 0.0016mg/lin the dry season and an average of 0.001mg/l for both seasons. Furthermore, Mercury (Hg) levels were also low for both the wet and dry seasons at 0.034mg/land 0.154mg/l, respectively, with the average for both seasons at 0.094mg/l.

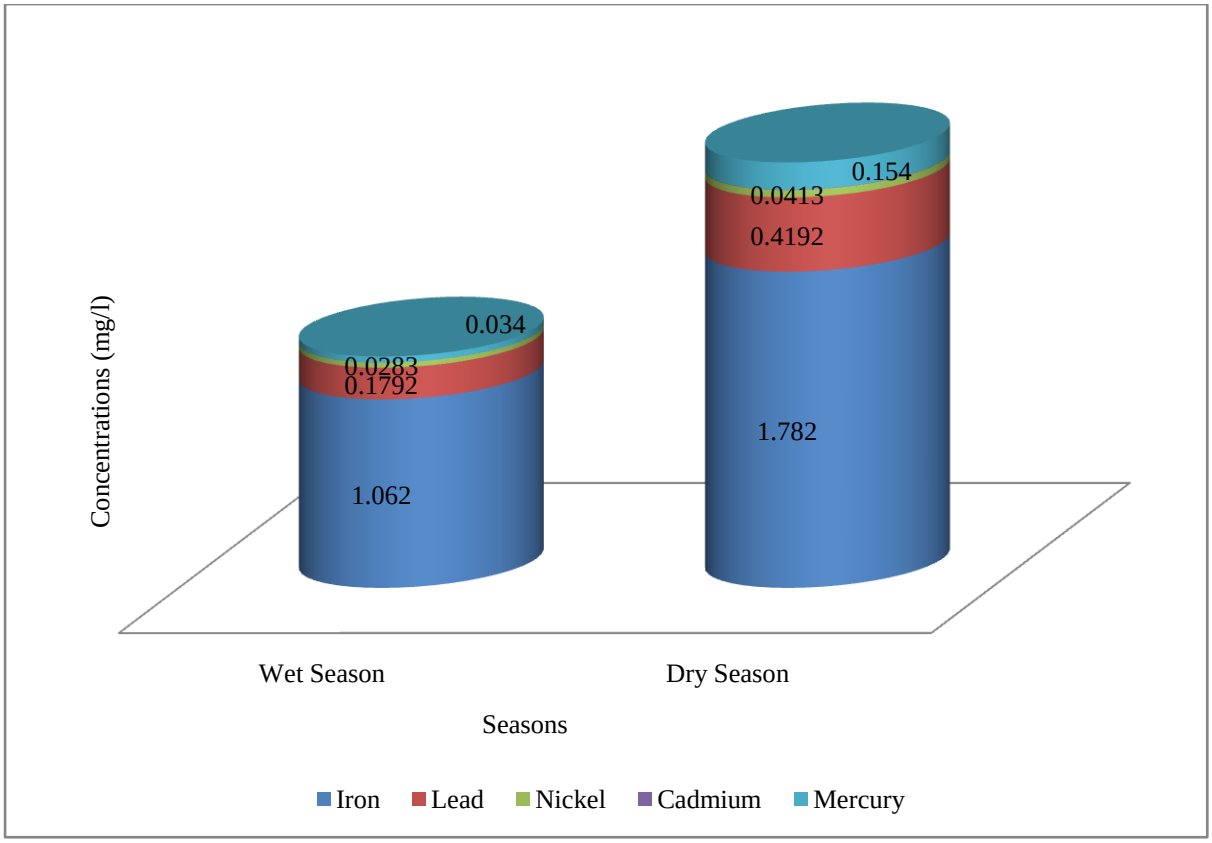


Fig.4.7 Heavy Metals Concentration in Farm 1

4.2.4 Analysis of Heavy Metals in Water Samples from Farm 2

Figure 4.8 displays the various mean concentrations. Farm 2 is Duniya Farms in Zaria, from which water samples were taken from three concrete ponds. Water used as the culture media for rearing *C. gariepinus* was sourced from groundwater using submersible pumps in boreholes. Iron (Fe) concentration in the dry season was 1.56mg/l, which almost doubled that of the wet season at 0.84mg/l, the average for both seasons was 1.2mg/l.

Additionally, Lead (Pb) levels were also significantly high at 0.1mg/l in the wet season and 0.343mg/l in the dry, giving an average of 0.223mg/l. The results for Cadmium (Cd) for both wet and dry season were fairly low at 0.0002mg/l and 0.0014mg/l, respectively.

In addition, Mercury level was also below WHO limit of 0.5mg/l, where the wet season accounts for 0.026mg/l and the dry season was 0.146mg/l, an average of 0.086mg/l was reported for both seasons. Nickel in the wet season had a value of 0.028mg/land the dry season – 0.042mg/l.

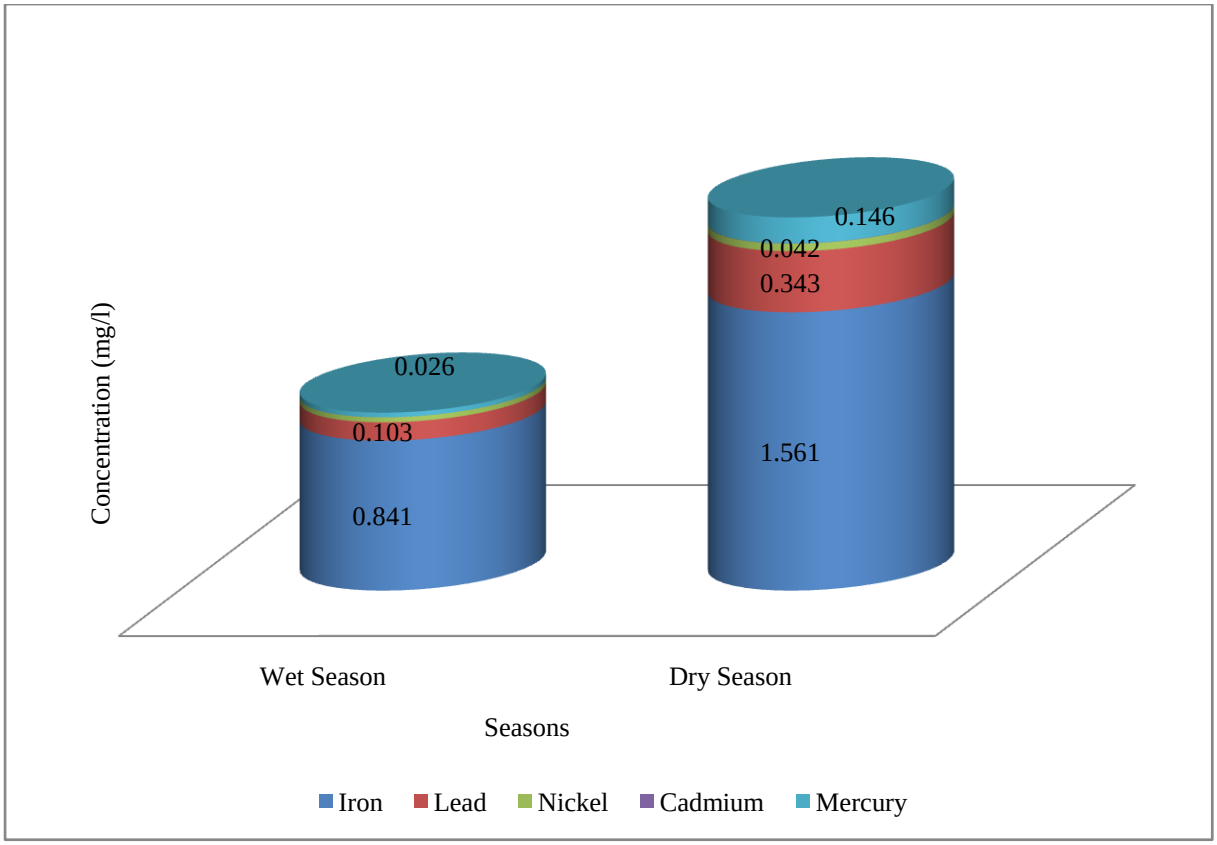


Fig.4.8 Heavy Metals Concentration in Farm 2

4.3 Analysis of Heavy Metals in Fish Samples

Theheavy metals examined in the fish samples include Mercury, Nickel, Iron, Cadmium, and Lead.

4.3.1 Morphometric Parameters of Fish Specimen

Prior to the analyses ofheavy metal concentrations in the sampled fishes, their body parameters were measured. Table 4.7 show the morphometric parameters, i.e. length (standard and total) and body weight (wet) of *C. gariepinus* obtained during the dry and wet seasons at the two selected rivers. Table 4.8 represents the recorded weights and lengths for the fish in the dry and wet seasons of both farms.

The fish (*Clarias gariepinus*) samples collected in the dry season in River Kaduna had weights which ranged from 0.56 kg – 0.79 kg, while their standard length ranged between 29.90 cm to 34.20 cm and the total length ranged from 32.40 cm to 37.70 cm.

Table 4.7 Morphometric Parameters of *C. gariepinus* Collected in River Kaduna and River Galma

	River Kaduna						River Galma					
Seasons	Dry season			Wet season			Dry season			Wet season		
S/No	Weight (kg)	Standard Length (cm)	Total Length (cm)	Weight (kg)	Standard Length (cm)	Total Length (cm)	Weight (kg)	Standard Length (cm)	Total Length (cm)	Weight (kg)	Standard Length (cm)	Total Length (cm)
1	0.68	31.40	34.60	0.46	26.80	29.00	0.49	29.60	32.40	0.41	27.20	29.50
2	0.56	29.90	32.40	0.48	27.40	29.60	0.63	37.30	41.40	0.45	29.90	32.20
3	0.79	34.20	37.70	0.68	29.20	31.40	0.42	31.50	34.30	0.37	23.10	25.40
4	0.63	31.60	34.80	0.57	28.60	30.80	0.53	36.20	41.80	0.49	26.80	29.10
5	0.61	30.80	34.20	0.49	23.90	26.10	0.57	34.10	38.90	0.52	30.70	33.00
Average	0.66	31.58	34.74	0.54	27.18	29.38	0.53	33.74	37.76	0.45	27.54	29.84

Table 4.8 Morphometric Parameters of *C. gariepinus* Collected in Farm 1 and Farm 2

	Farm 1						Farm 2					
Seasons	Dry season			Wet season			Dry season			Wet season		
S/No	Weight (kg)	Standard Length (cm)	Total Length (cm)	Weight (kg)	Standard Length (cm)	Total Length (cm)	Weight (kg)	Standard Length (cm)	Total Length (cm)	Weight (kg)	Standard Length (cm)	Total Length (cm)
1	0.51	28.30	31.10	0.54	28.70	30.90	0.47	27.40	29.80	0.50	28.60	30.50
2	0.53	29.60	32.40	0.55	23.00	32.20	0.49	29.30	32.40	0.52	30.50	32.40
3	0.68	32.40	33.90	0.71	32.80	35.00	0.60	32.40	35.30	0.63	33.60	35.50
4	0.63	32.10	35.30	0.66	32.50	34.70	0.65	33.20	35.40	0.69	34.40	36.30
5	0.65	31.80	33.70	0.67	32.20	34.40	0.72	34.80	36.50	0.75	36.00	37.90
Average	0.60	30.84	33.28	0.63	31.24	33.44	0.59	31.42	33.88	0.50	28.60	30.50

Fishes obtained during the wet season in River Kaduna had an average weight of 0.54 kg, and average total length of 29.38 cm. However, the weight varied between 0.46 kg and 0.68 kg and total lengths between 26.10 cm – 31.40 cm. At River Galma, during the wet season the average weight recorded was 0.45kg (varying from 0.37 kg to 0.52kg).

Farmed *Clarias gariepinus* samples obtained from farms in Kaduna and Zaria had weights ranging from 0.51kg to 0.68kg and 0.47kg to 0.72 kg, respectively, while their average weight was 0.60 kg and 0.59 kg, respectively. Their standard length varied from 28.30 cm to 32.40 cm, while the total length also ranged from 32.40cm to 37.70cm.

4.3.2 Analysis of Heavy Metals in Fish Samples from River Kaduna

Fish specimens obtained from the River Kaduna in the wet and dry seasons had different concentrations of heavy metals ranging from as low as 0.007mg/kg in Cadmium to over 3.60mg/kg for Iron (Figure. 4.9). Samples of fish muscle collected from five fish specimen of *C. gariepinus* showed a mean of very high Iron (Fe) concentrations, just as in the water samples. During the dry season, mean Iron concentrations were 4.06mg/kg, while in the wet season it dropped to 3.20mg/kg, with an average of 3.63mg/kg for both seasons. Lead (Pb) was also high at 0.84mg/kg for the dry season and 0.58mg/kg for the wet.

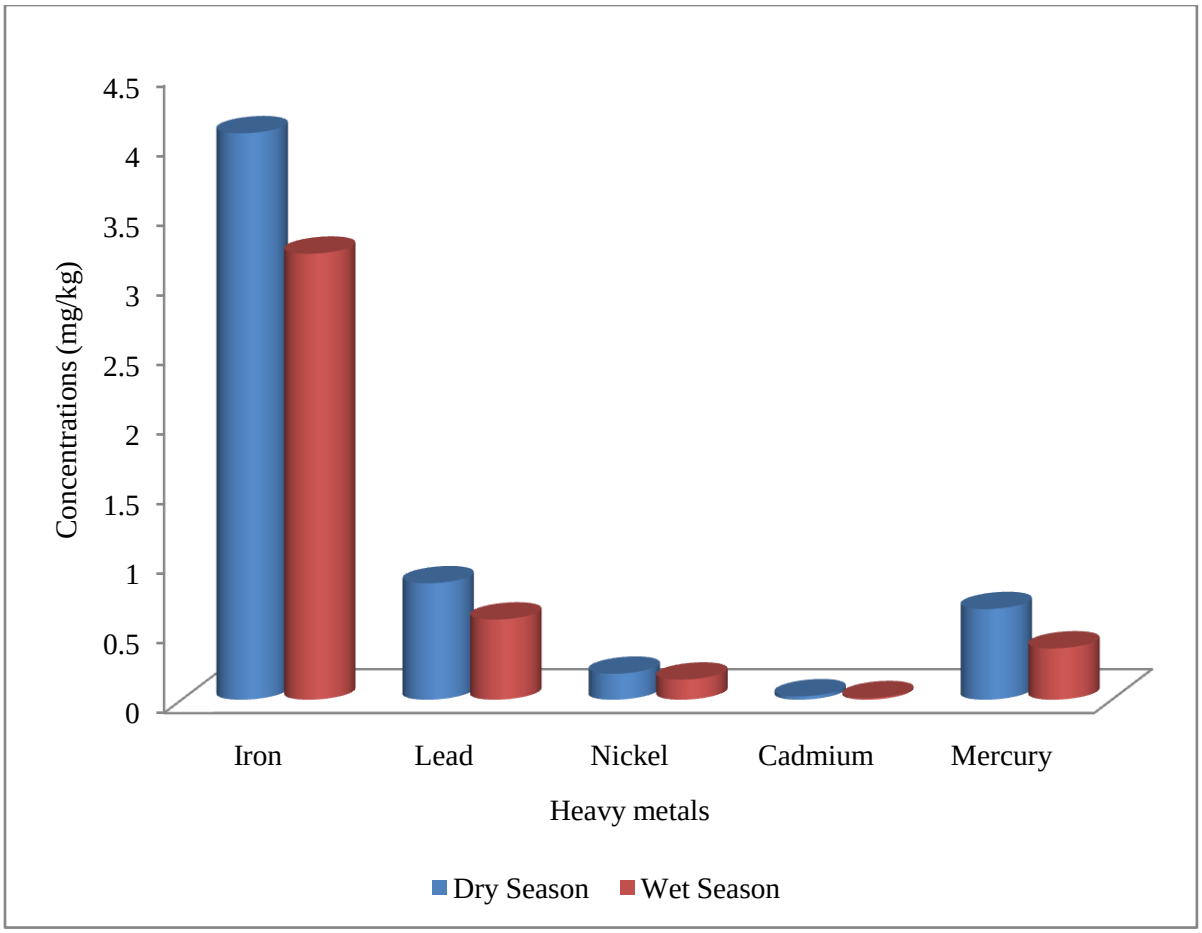


Fig.4.9 Heavy Metals Concentration in *C. gariepinus* – River Kaduna.

Nickel concentrations were low in fish muscle samples, with the wet season accounting for 0.14mg/kg and the dry season was 0.19mg/kg, while the average for both seasons stood at 0.17mg/kg. Cadmium (Cd) was 0.02mg/kg in the dry season, while the wet season value was 0.011 ± 0.005mg/kg.

The results of this study showed mean concentrations of Mercury with the dry season accounting for the highest value of 0.65mg/kg and the wet season – 0.37mg/kg and an average of the two seasons was 0.51mg/kg.

4.3.3 Analysis of Heavy Metals in Fish Samples from River Galma

Fish specimens obtained from the River Galma in the wet and dry seasons had different concentrations of heavy metals which ranged from as low as 0.03mg/kg (Cadmium) to over 3.87mg/kg for Iron as presented in Figure 4.10. The samples of fish muscle collected from five fish specimen of *C. gariepinus* showed a mean of very high Iron (Fe) concentrations. During the dry season mean Iron concentration was 3.87mg/kg, while in the wet season it dropped to 3.00mg/kg, with an average of 3.44mg/kg for both seasons.

Lead (Pb) was also high at 0.86mg/kg for the dry season and 0.33mg/kg for the wet, while the average for both seasons was 0.59mg/kg.

Nickel concentrations were low in fish muscle samples, with the wet season accounting for 0.14mg/kg and the dry season was 0.18mg/kg, while the average for both seasons stood at 0.16mg/kg.

Cadmium (Cd)was found to be 0.026mg/kg in the dry season, while the wet season value was 0.026mg/kg. The results for this study also showed that mean concentrations of

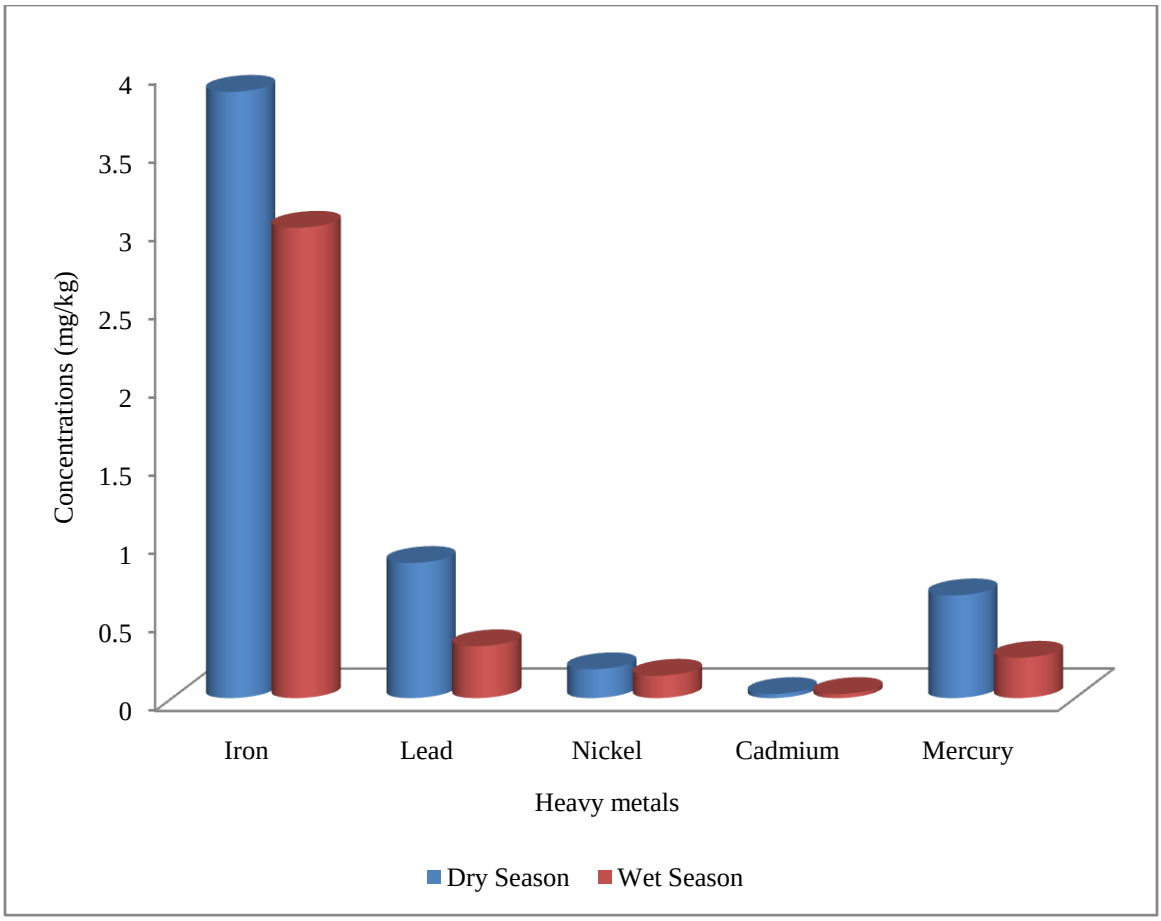


Fig.4.10 Heavy Metals Concentration in *C. gariepinus* – River Galma.

Mercury in the dry season recorded a high value of 0.66mg/kg, while the wet season stood at 0.26mg/kg and the average of the two seasons was 0.46mg/kg.

4.3.4 Analysis of Heavy Metals in Fish Samples from Farm 1

Heavy metals levels in fish samples differ with seasons with Iron (Fe) during the wet season reaching 1.43mg/kgand dry season was as high as 1.75mg/kgwith a mean of 1.59mg/kgfor both seasons (See Figure 4.11).

In addition, the Lead (Pb) levels inthe fish were low in the wet season (0.25mg/kg) and 0.28mg/kg in the dry season, with an average of 0.27mg/kg. While in the wet season Nickel concentrations was fairly low – 0.026mg/kg while the dry season was 0.037mg/kg, accounting for an average 0.032mg/kg.

Cadmium was fairly low in the wet season (0.001mg/kg) and 0.0013mg/kgin the dry season and 0.00139mg/kg on average for both seasons in Farm 1. Furthermore, Mercury (Hg) levels in both the wet and dry seasons were high with 0.15mg/kgand 0.14mg/kg, respectively with the average of both seasons at 0.15mg/kg. Figure 4.11 shows the various distributions.

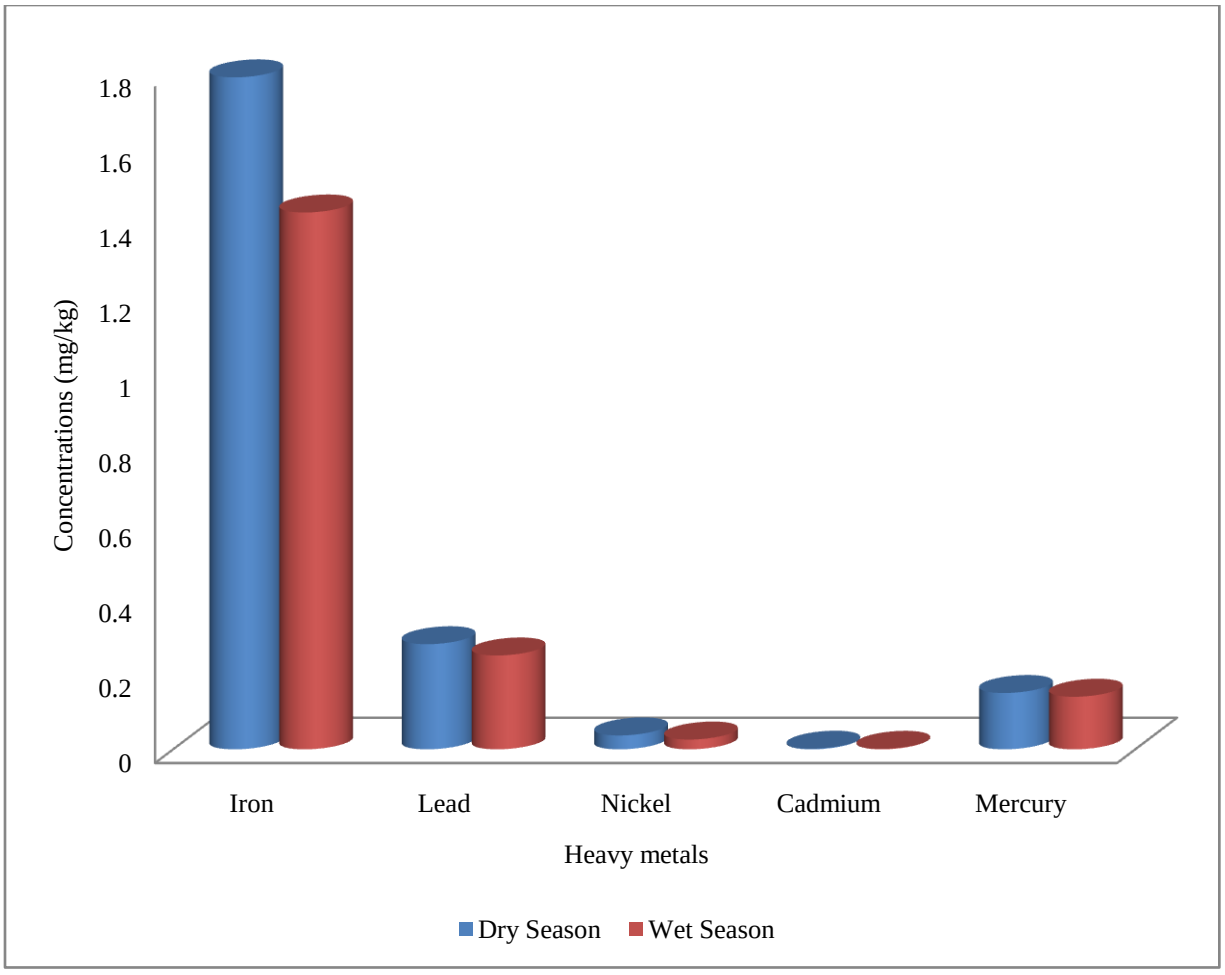


Fig.4.11 Heavy Metals Concentrationin *C. gariepinus* – Farm 1.

4.3.5 Analysis of Heavy Metals in Fish Samples from Farm 2

Fish samples (C. *gariepinus*) from Farm 2 had varying concentration levels of heavy metals. Heavy metals levels in fish samples differ with seasons and differ markedly from each other. For instance Iron (Fe) during the wet season reached levels of 1.14mg/kgand dry season was as high as 1.46mg/kgwith a mean of 1.30mg/kgfor both seasons (see Figure 4.12).

In the Farm 2 also, Lead (Pb) levels were low in the wet season (0.21mg/kg) and 0.25mg/kg in the dry season, with an average of 0.23mg/kg. In the wet season, Nickel concentrations was fairly low – 0.022mg/kg while the dry season was 0.035mg/kg, accounting for an average 0.029mg/kg. Cadmium which was a recurring low in *C. gariepinus* farmed in concrete fish pond located in Kaduna, in the fish pond in Dakace, Zaria in the wet season it was also fairly low at 0.0012mg/kg^{-1} and 0.0005mg/kgin the dry season and 0.0008mg/kg on average for both seasons.

Furthermore, Mercury (Hg) levels in both the dry and wet seasons were high with 0.14mg/kgand 0.08mg/kg, respectively; with the average of both seasons at 0.11mg/kg, when compared with permissible limit of 0.001mg/kg (WHO, 2012). Figure 4.12 shows the various distributions.

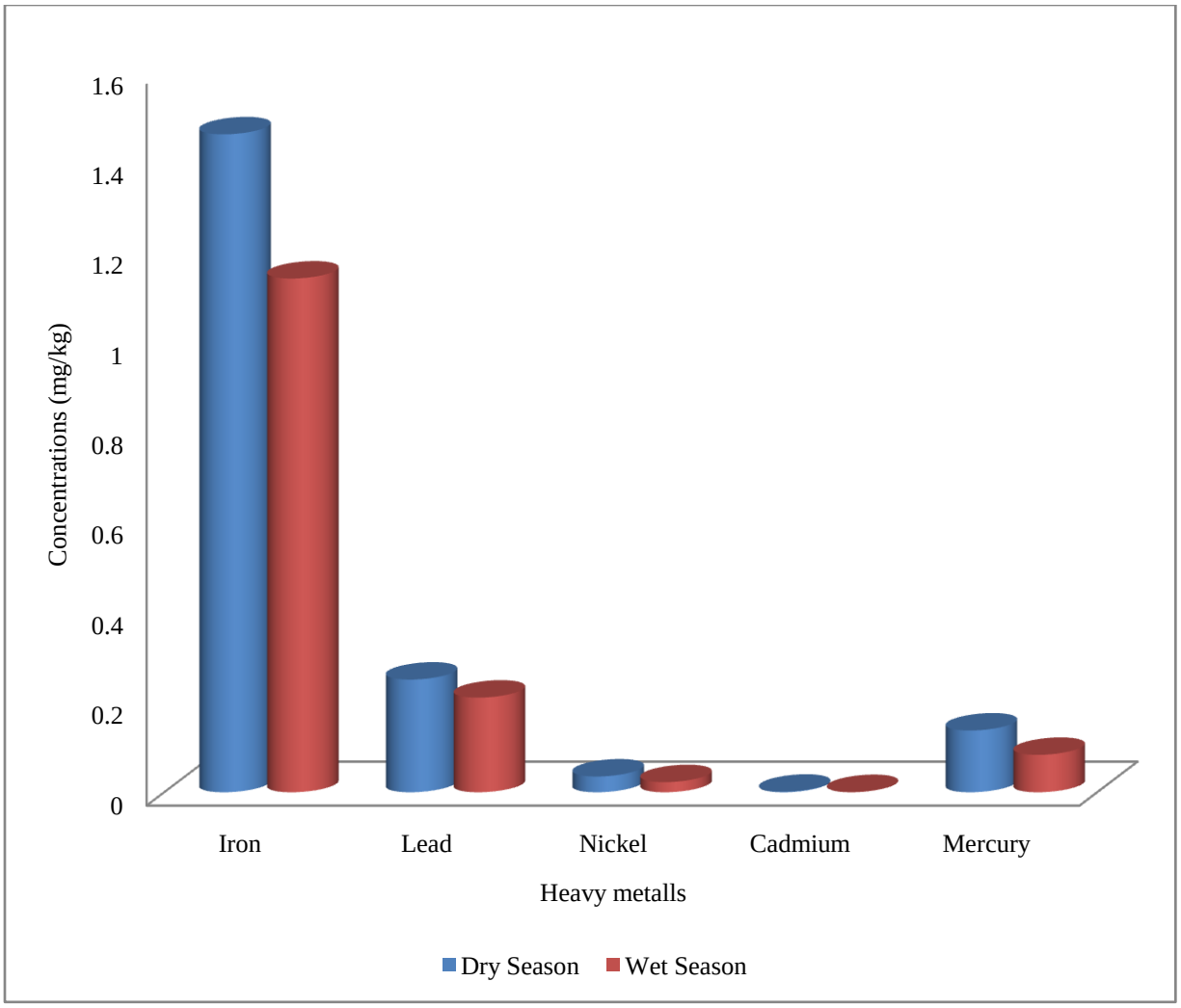


Figure 4.12 Heavy Metals Concentrationin *C. gariepinus* – Farm 2.

4.4 Comparative Analysis of Heavy Metals in Water Samples

There are varying concentrations of heavy metals distributed through both rivers in the wet season, while River Kaduna had high levels of Fe (3.33mg/l), Pb (0.72mg/l) and Hg (0.68mg/l); Fig.4.13 depicts the different levels of heavy metals. River Kaduna distribution in terms of crude measurement is quite similar to those of River Galma where Iron also ranked highest at 2.42 mg/l, followed closely by Lead (0.61 mg/l) and Mercury (0.56mg/l).

Figure 4.14 shows the results obtained for the dry season. Both rivers also showed parallel distributions, although at a slightly higher level than the wet season, where Fe, Lead, Mercury, Nickel and Cadmium in River Kaduna were in concentrations of 4.05mg/l, 0.96 mg/l, 0.81 mg/l, 0.35 mg/l, and 0.04mg/l, respectively. River Galma had Fe concentration of 3.14mg/l, Pb – 0.85mg/l, Hg – 0.77mg/l, Ni – 0.27mg/l, and Cd – 0.033mg/l.

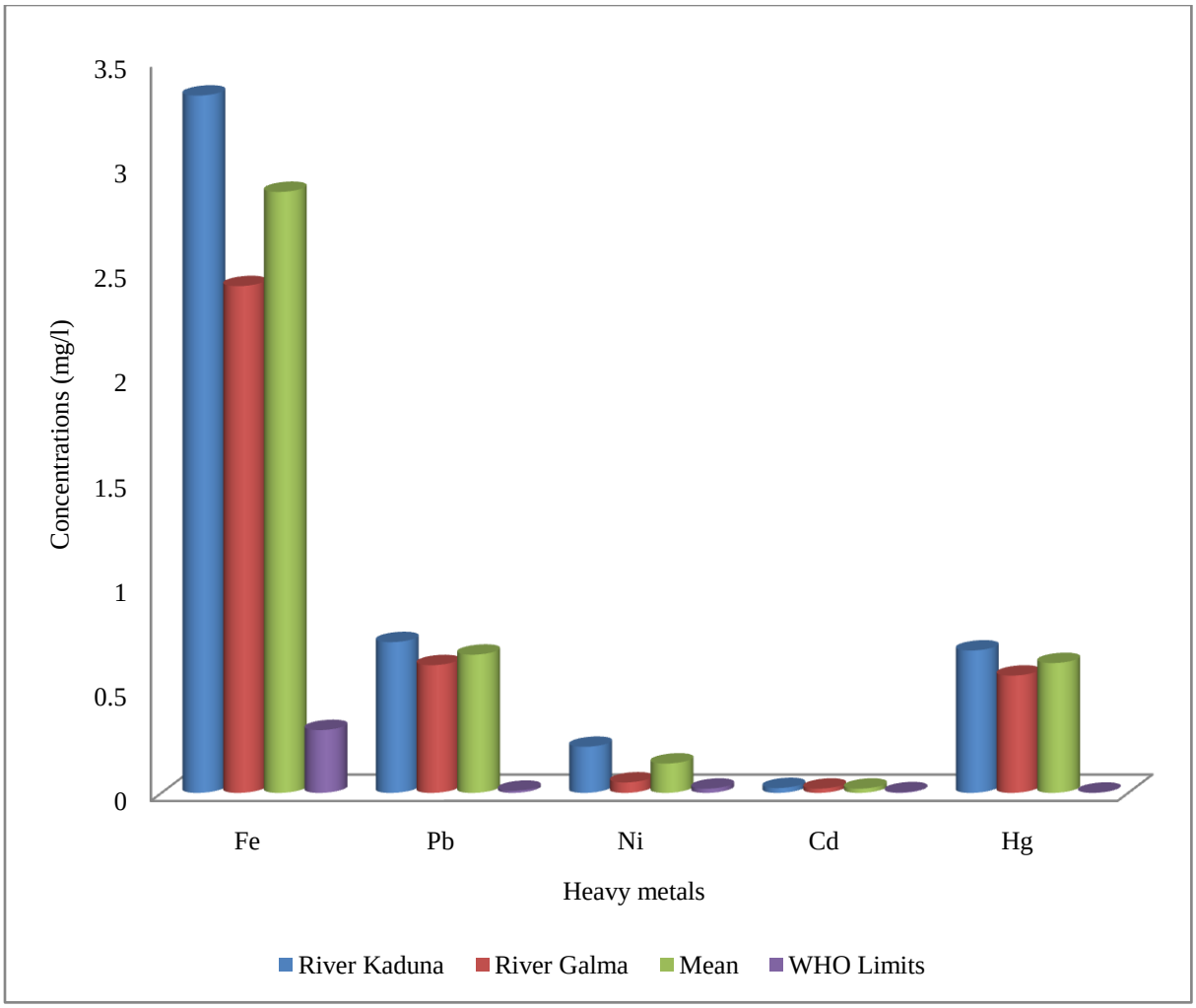


Fig. 4.13 Heavy Metals Concentration in River Kaduna and River Galma in Water Samples – Wet Season

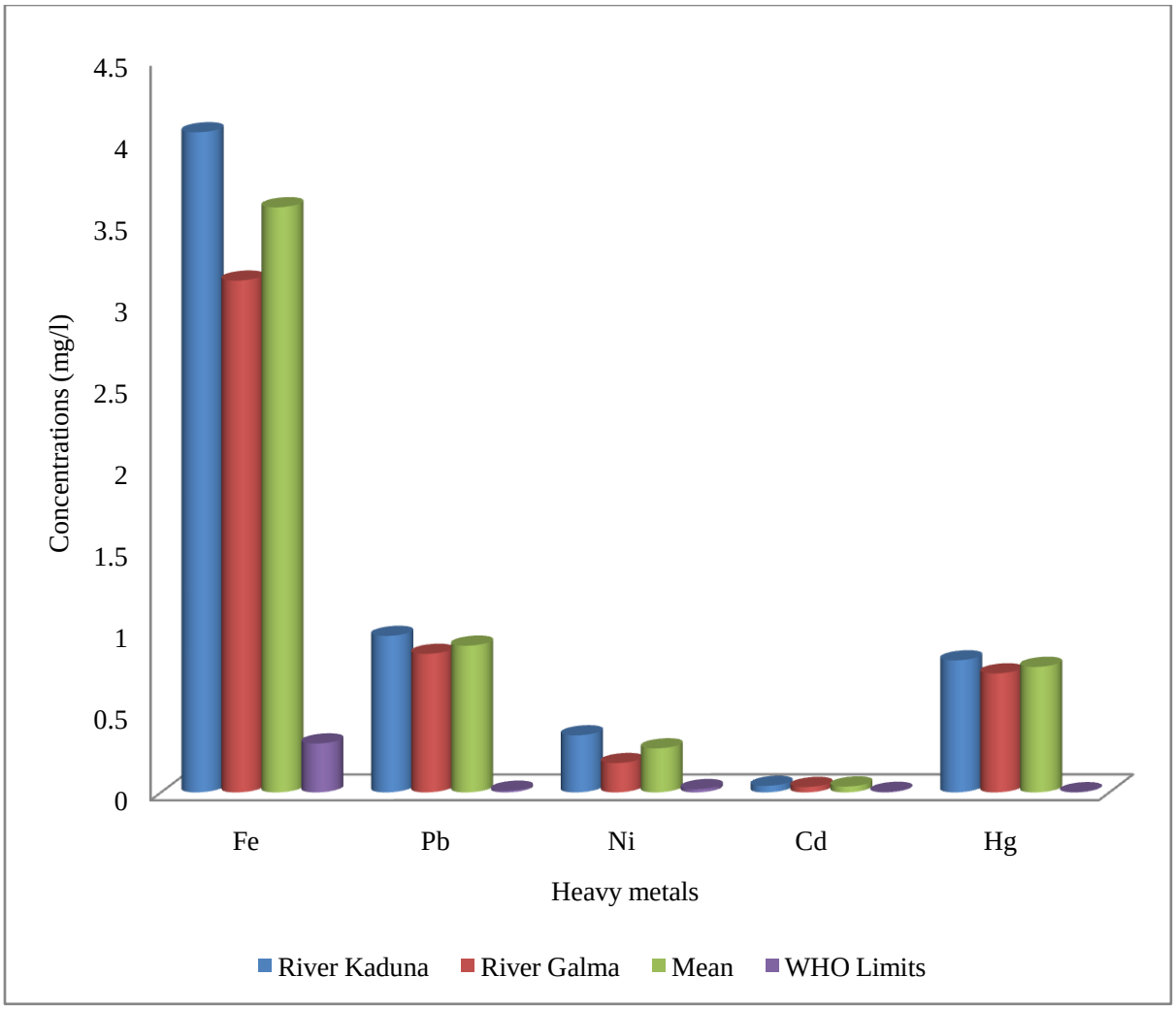


Fig.4.14 Heavy Metals Concentration in River Kaduna and River Galma Water Samples – Dry Season

Figure 4.15also shows the varying concentrations of heavy metals distributed through both farms located in Zaria and Kaduna in the wet season. Farm 1 had high levels of Fe (1.10mg/l), Pb (0.18mg/l) and Hg (0.034mg/l). Farm 2 had similar distribution, in terms of concentrations levels to those of Farm 1. Iron also ranked highest at 0.84 mg/l, followed closely by Lead (0.11 mg/l) and Mercury (0.026 mg/l).

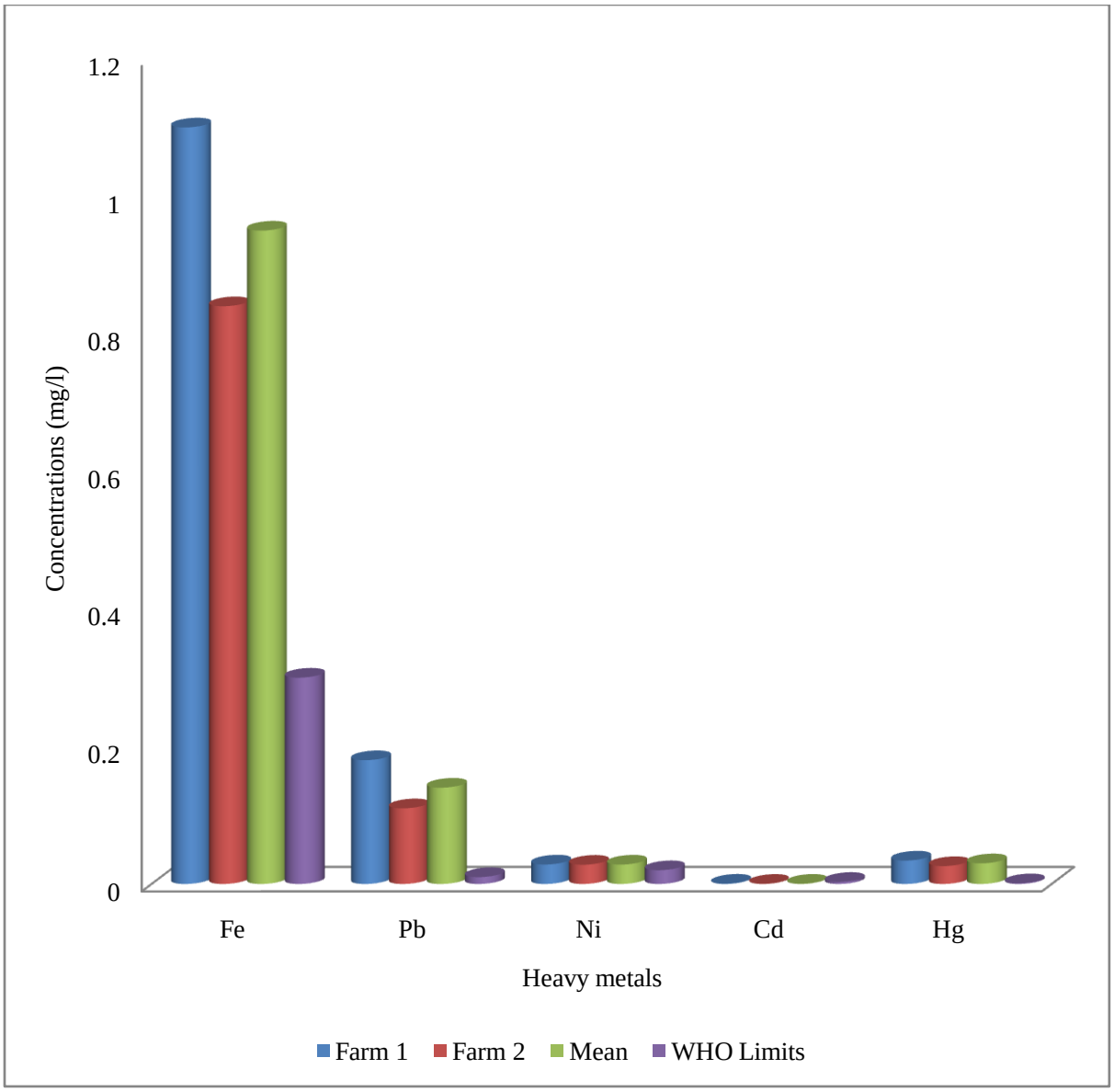


Fig.4.15 Heavy Metals Concentration in Water Samples from Farm 1 and 2 – Wet Season

During the dry season both farms also showed similar distributions, although at a slightly higher level than the wet season, Fe, Lead, Mercury, Nickel and Cadmium in Farm 1 were in concentrations of 1.78mg/l, 0.42mg/l, 0.154mg/l, 0.041mg/l, and 0.0016mg/l, respectively (Figure 4.16), while River Galma had Fe concentration of 1.56mg/l, Pb – 0.34mg/l, Hg – 0.146mg/l, Ni – 0.042mg/l, and Cd – 0.0014mg/l, respectively. All heavy metals analysed were higher than the WHO recommended limits.

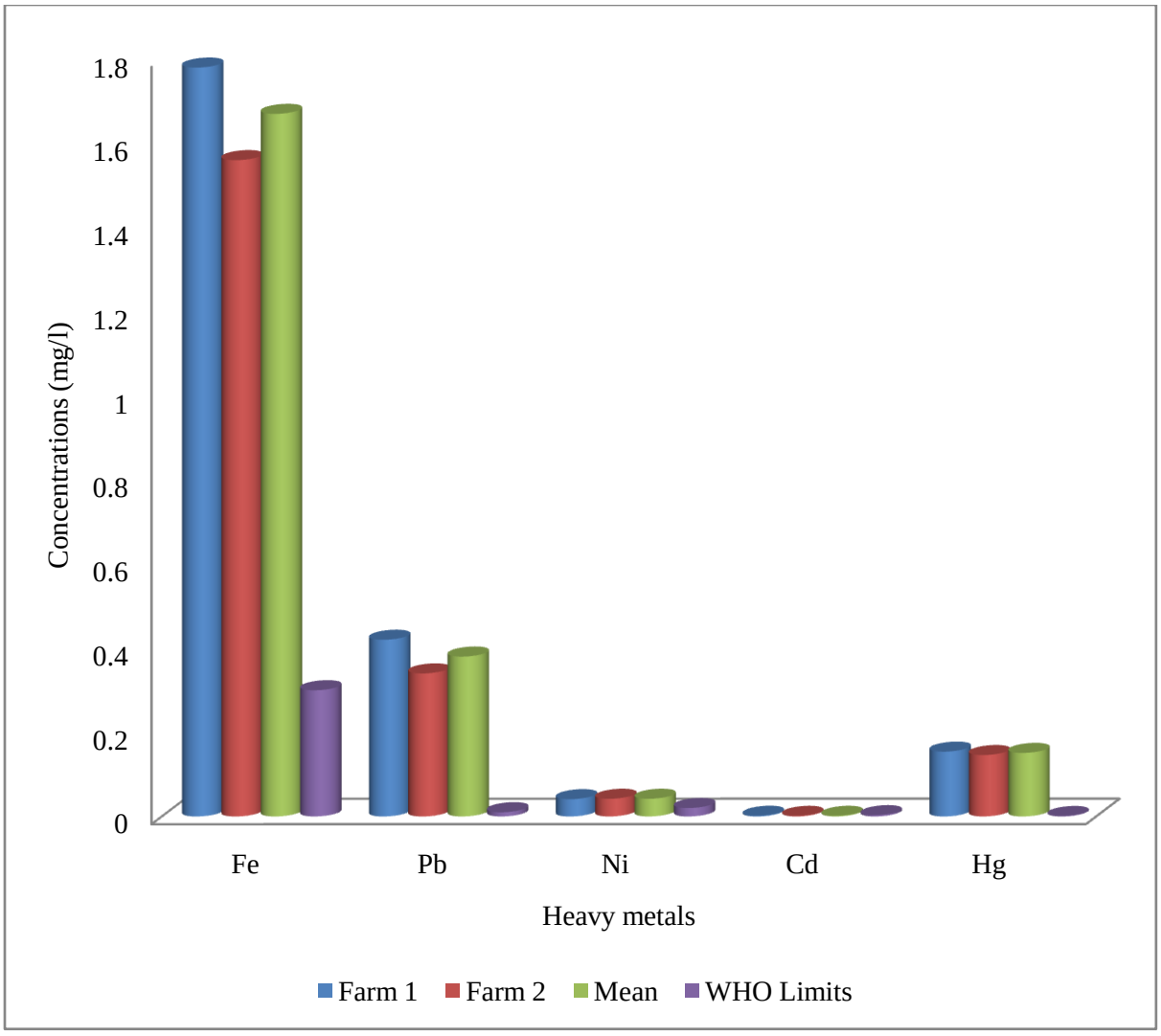


Fig.4.16 Heavy Metals Concentration in Water Samples from Farm1 and 2 – Dry Season

When means of both rivers and farms were compared together there was a glaring disparity between the concentration levels of heavy metals as shown in Figure 4.17, where the mean concentration for Fe in the rivers was 3.23mg/l, while that of the farms was 1.31mg/l. Pb in the rivers was 0.78mg/l, contrasting well with that of the farms at 0.26mg/l; Hg was also higher in concentration in the rivers than the farm at 0.69mg/l and 0.09mg/l, respectively.

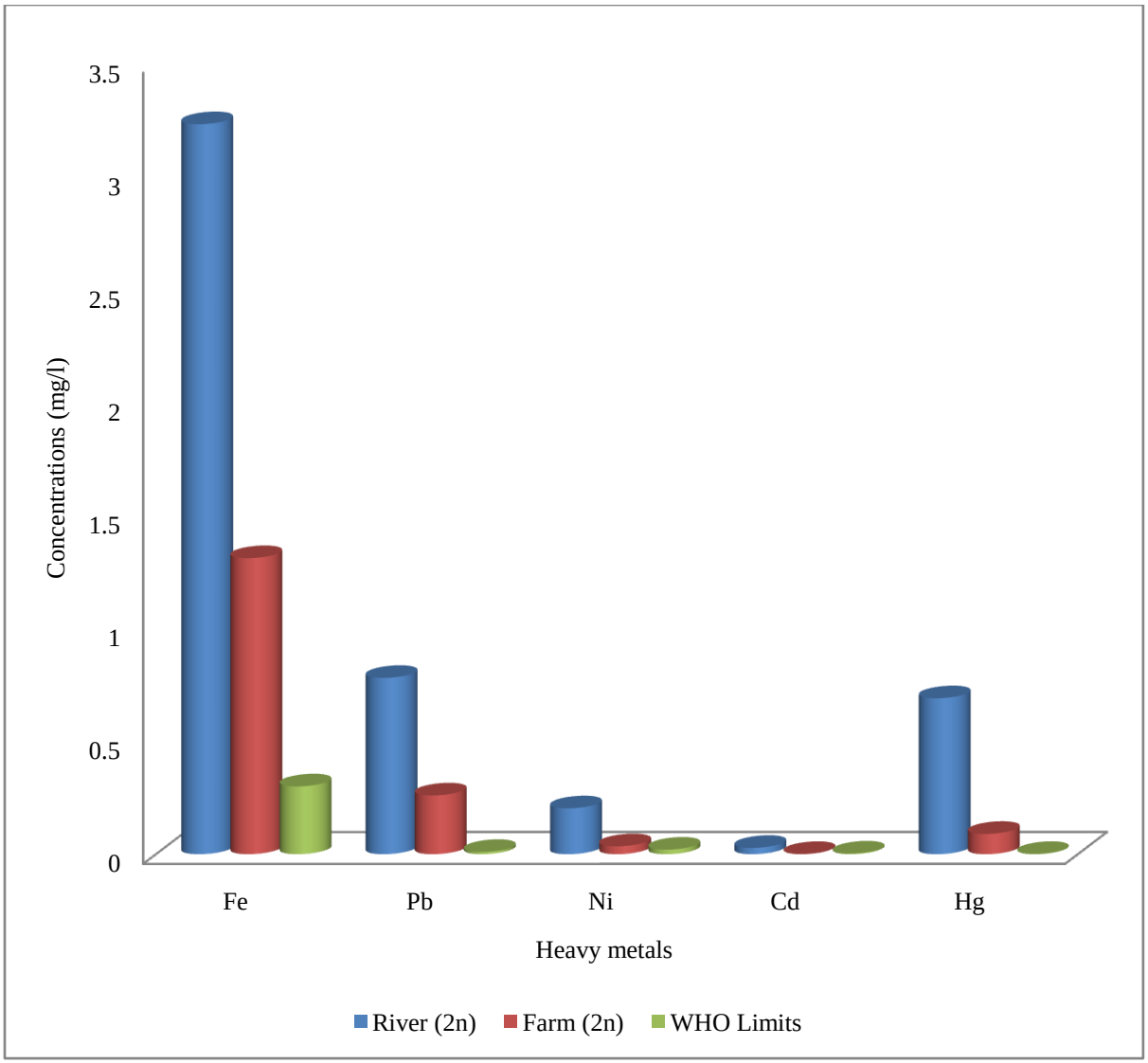


Fig.4.17 Heavy Metal Concentrations in Water Samples from Both Rivers and Farms

In addition, when subjected to t-test for all the heavy metals, River Kaduna showed significant difference ($p<0.05$) in the dry season for Fe (4.05mg/l), Pb (0.96mg/l), Ni (0.35mg/l) and Hg (0.81mg/l) compared to wet season values of Fe (3.33mg/l), Pb (0.72mg/l), Ni (0.22mg/l) and Hg (0.68mg/l) as presented in Table 4.9. However, only the concentration level of Cd showed no significant difference between the two seasons (Dry Season – 0.04mg/l and Wet Season – 0.02mg/l).

On the other hand there was no significant difference in the concentration of heavy metals in River Galma during the dry season (Fe – 2.67mg/l, Cd – 0.06mg/l and Hg – 0.61mg/l) compared to wet season values (Fe – 2.41mg/l, Cd – 0.02mg/l and Hg – 0.61mg/l) as shown in Table 4.9. However, heavy metals concentration level of 0.85mg/l and 0.30mg/l for Pb and Ni, respectively in the dry season revealed significant difference ($p<0.05$) when compared with the wet season values of 0.61mg/l and 0.05mg/l.

Furthermore, when water samples ofthe two rivers were compared for the dry season only, there existed significant differences ($p<0.05$) in Fe (4.05mg/l) and Hg (0.81mg/l) concentrations for River Kaduna, while for River Galma Fe and Hg concentrations level stood at 2.67mg/l and 0.61mg/l, respectively. However, concentrations of heavy metals in the dry season between the two river bodies showed no significant difference in Pb (River Kaduna - 0.96mg/l and River Galma – 0.85mg/l), Ni (River Kaduna - 0.35mg/l and River Galma – 0.30mg/l) and Cd (River Kaduna - 0.04mg/l and River Galma – 0.06mg/l) at $p>0.05$, which is represented in Table 4.9.

In the wet season only Pb (0.72mg/l) and Ni (0.22mg/l) for River Kaduna showed significant differences ($p>0.05$) when compared with River Galma's Pb (0.61mg/l) and

Ni concentrations (0.05mg/l). However, concentrations of heavy metals in the wet season between the two river bodies showed no significant difference in Fe (River Kaduna - 0.3.33mg/l and River Galma – 2.41mg/l), Cd (River Kaduna - 0.02mg/l and River Galma – 0.02mg/l) and Hg (River Kaduna - 0.68mg/l and River Galma – 0.56mg/l) at $p>0.05$, as represented in Table 4.9.

Table 4.9 Analysis of River Water Samples

Heavy Metals (mg/l)	Dry Season		Wet Season		Both Seasons	
	River Kaduna (Mean±SE)	River Galma (Mean±SE)	River Kaduna (Mean±SE)	River Galma (Mean±SE)	River Kaduna (Mean±SE)	River Galma (Mean±SE)
Fe	4.05 ±0.05[a]	2.67 ±0.48[b]	3.33 ±0.05[a]	2.41 ±0.06[a]	3.69 ±0.11[a]	2.54 ±0.12[b]
Pb	0.96 ±0.02[a]	0.85 ±0.01[a]	0.72 ±0.02[a]	0.61 ±0.01[b]	0.84 ±0.04[a]	0.73 ± 0.66[a]
Ni	0.35 ±0.04[a]	0.30 ±0.11[a]	0.22 ±0.04[a]	0.05 ±0.00[b]	0.29 ±0.03[a]	0.18 ±0.07[a]
Cd	0.04 ±0.00[a]	0.06 ±0.03[a]	0.02 ±0.00[a]	0.02 ±0.00[a]	0.03 ±0.00[a]	0.04 ±0.00[a]
Hg	0.81 ±0.10[a]	0.61 ±0.12[b]	0.68 ±0.09[a]	0.56 ±0.01[a]	0.74 ±0.05[a]	0.59 ±0.06[b]

Means with the same superscripts on same rows were not significantly different ($p<0.05$).

When the mean of both seasons for the two rivers were analysed Fe and Hg showed significant differences between the two water bodies, while Pb, Ni and Cd showed no significant difference. Put precisely, when the mean of the two seasons was obtained and subjected to t-test analysis to compare the means using a significant level of $p>0.05$, only Fe and Hg did show a significant difference, as Fe and Hg mean values for River Kaduna was 3.69mg/l and 0.74mg/l, respectively, while that of River Galma stood at 2.54mg/l and 0.59mg/l, for Fe and Hg, respectively. However, Pb (River Kaduna – 0.84mg/l and River Galma – 0.73mg/l), Ni (River Kaduna – 0.29mg/l and River Galma – 0.18mg/l), and Cd (River Kaduna – 0.03mg/l and River Galma – 0.04mg/l), all did not differ significantly between the both rivers (Table 4.9).

Table 4.10 show the analysis of heavy metals in farm water samples. When subjected to t-test, three of the heavy metals in Farm 1 showed significant differences ($p<0.05$) in the dry season, namely Fe (1.78mg/l), Pb (0.42mg/l), and Hg (0.15mg/l) compared to wet season values of Fe (1.06mg/l), Pb (0.18mg/l), and Hg (0.03mg/l) as presented in Table 4.10. However, the concentration level of Ni and Cd showed no significant difference ($p>0.05$) between the two seasons as Ni and Cd in the dry season had 0.04mg/l and 0.00mg/l, respectively, while for the wet season for Ni and Cd were 0.03mg/l and 0.00mg/l, respectively.

On the other hand Farm 2 showed significant difference in the concentration of heavy metals, in the dry season for Fe (1.56mg/l), Pb (0.34mg/l) and Hg (0.15mg/l) compared to wet season values of Fe (0.84mg/l), Pb (0.10mg/l) and Hg (0.03mg/l) as presented in Table 4.10. However, heavy metals concentration level of 0.04mg/l and 0.00mg/l for Ni and Cd, respectively in the dry season showed no significant difference ($p>0.05$) when compared with the wet season values of 0.03mg/l and 0.00mg/l for Ni and Cd, respectively. This is represented in Table 4.10.

Furthermore in Table 4.10, shows that there existed significant difference in only Fe (1.78mg/l) concentrations for Farm 1, while Farm 2 Fe concentration level stood at 1.56mg/l. However, concentrations of heavy metals in the dry season between the water samples from both farms showed no significant difference in Pb (Farm 1 - 0.42mg/l and Farm 2 – 0.34mg/l), Ni (Farm 1 - 0.04mg/l and Farm 2 – 0.04mg/l), Cd (Farm 1 - 0.00mg/l and Farm 2 – 0.00mg/l) and Hg (Farm 1 - 0.15mg/l and Farm 2 – 0.15mg/l) at $p>0.05$.

In the wet season (Ni – 0.03mg/l; Cd – 0.00mg/l and Hg – 0.03mg/l) for Farm 1 showed no significant differences ($p>0.05$) when compared with Farm 2(Ni – 0.03mg/l; Cd – 0.00mg/l and Hg – 0.03mg/l) concentrations. However, concentrations of heavy metals in the wet season between the water samples from the farms showed significant difference in Fe (Farm 1 - 1.06mg/l and Farm 2 – 0.84mg/l) and Pb (Farm 1 - 0.18mg/l and Farm 2 – 0.10mg/l) at $p<0.05$, as represented in Table 4.10.

Table 4.10 Analysis of Farm Water Samples

Heavy Metals (mg/l)	Dry Season		Wet Season		Both Seasons	
	Farm 1 (Mean±SE)	Farm 2 (Mean±SE)	Farm 1 (Mean±SE)	Farm 2 (Mean±SE)	Farm 1 (Mean±SE)	Farm 2 (Mean±SE)
Fe	1.78 ± 0.01[a]	1.56 ±0.00[b]	1.06 ± 0.00[a]	0.84 ±0.02[b]	1.42 ± 0.36[a]	1.20 ±0.36[b]
Pb	0.42 ± 0.00[a]	0.34 ± 0.00[a]	0.18 ± 0.00[a]	0.10 ±0.01[b]	0.30 ± 0.12[a]	0.22 ± 0.12[a]
Ni	0.04 ± 0.01[a]	0.04 ± 0.00[a]	0.03 ± 0.01[a]	0.03 ± 0.00[a]	0.04 ± 0.01[a]	0.04 ± 0.01[a]
Cd	0.00 ± 0.00[a]	0.00 ± 0.00[a]	0.00 ± 0.00[a]	0.00 ± 0.00[a]	0.00 ± 0.00[a]	0.00 ± 0.00[a]
Hg	0.15 ± 0.00[a]	0.15 ± 0.00[a]	0.03 ± 0.00[a]	0.03 ± 0.02[a]	0.09 ± 0.06[a]	0.09 ± 0.06[a]

Means with the same superscripts on same rows were not significantly different ($p \geq 0.05$).

When the mean for both seasons at the two farms were analysed, only Fe showed significant difference between water samples from the two farms,Fe mean value for Farm 1 was 1.42mg/l, while that of Farm 2 stood 1.20mg/l. However, Pb (Farm 1 - 0.30mg/l and Farm 2 – 0.22mg/l), Ni (Farm 1 - 0.04mg/l and Farm 2 – 0.04mg/l), Cd (Farm 1 - 0.00mg/l and Farm 2 – 0.00mg/l) and Hg (Farm 1 - 0.09mg/l and Farm 2 – 0.09mg/l), all did not differ significantly between the both farm waters (Table 4.10).

4.5 Comparative Analysis of Heavy Metals in Fish Samples

From the analysis of fish samples from the two selected sites in Zaria and Kaduna, respectively, reminiscent of the water samples, fish muscle samples in River Kaduna had the higher level of concentration of all five heavy metals identified namely Iron, Lead, Nickel, Cadmium and Mercury, both in the dry and wet seasons.

There are varying concentrations of heavy metals distributed in fishesof the two river bodies in the wet season, with River Kaduna having higher levels of Fe (3.20mg/kg), Pb (0.575mg/kg) and Hg (0.368mg/kg), Figure 4.18 depicts the different levels of heavy metals. Roughly, fish muscle samples from River Kaduna in terms of crude measurementare quite similar to those of River Galma where Iron also ranked highest at 3.003mg/kg, followed closely by Lead (0.331mg/kg) and Mercury (0.258mg/kg) as graphically represented on See Figure 4.18.

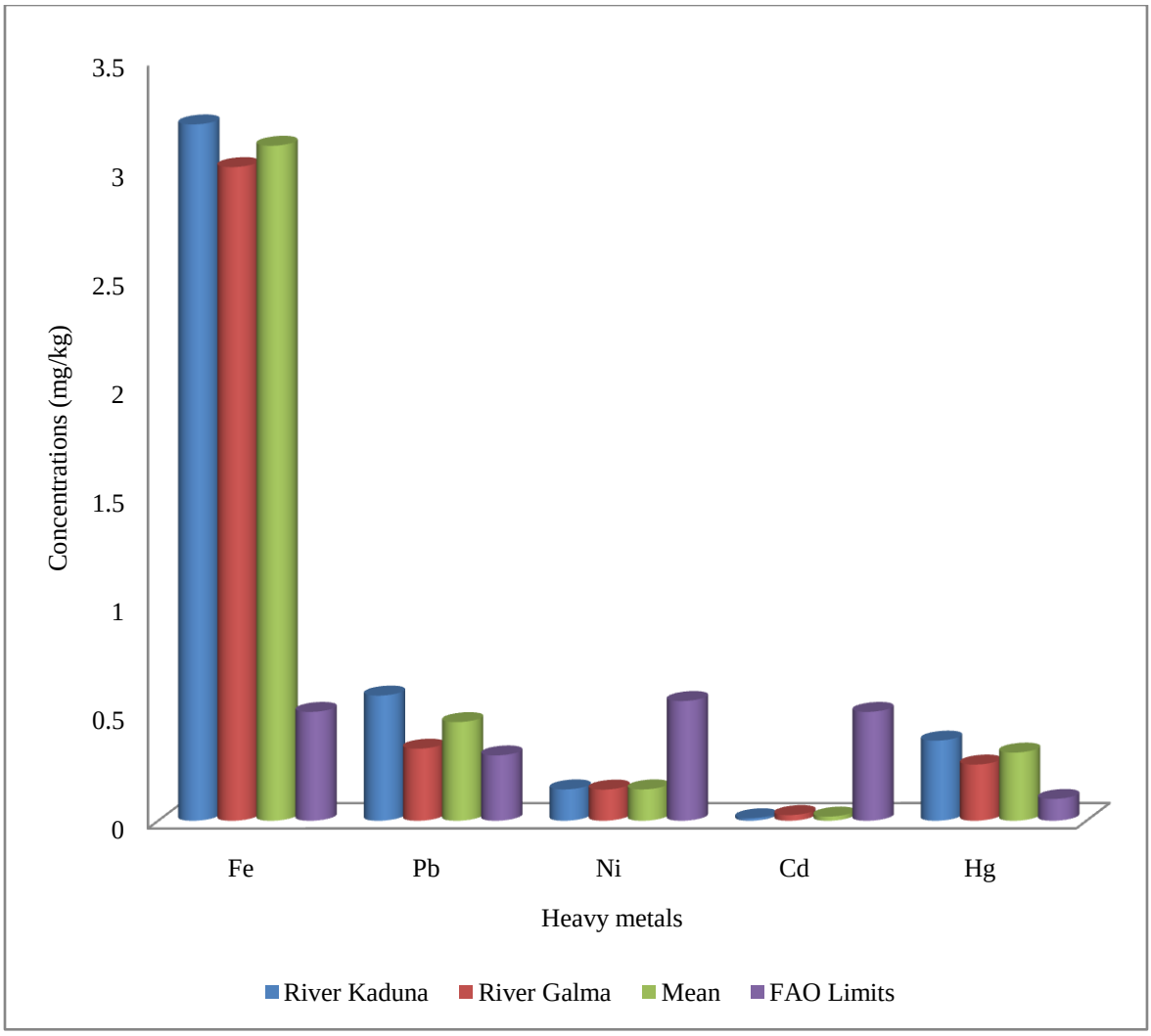


Figure.4.18 Heavy Metals Concentration in River Kaduna and River Galma Fish Samples – Wet Season

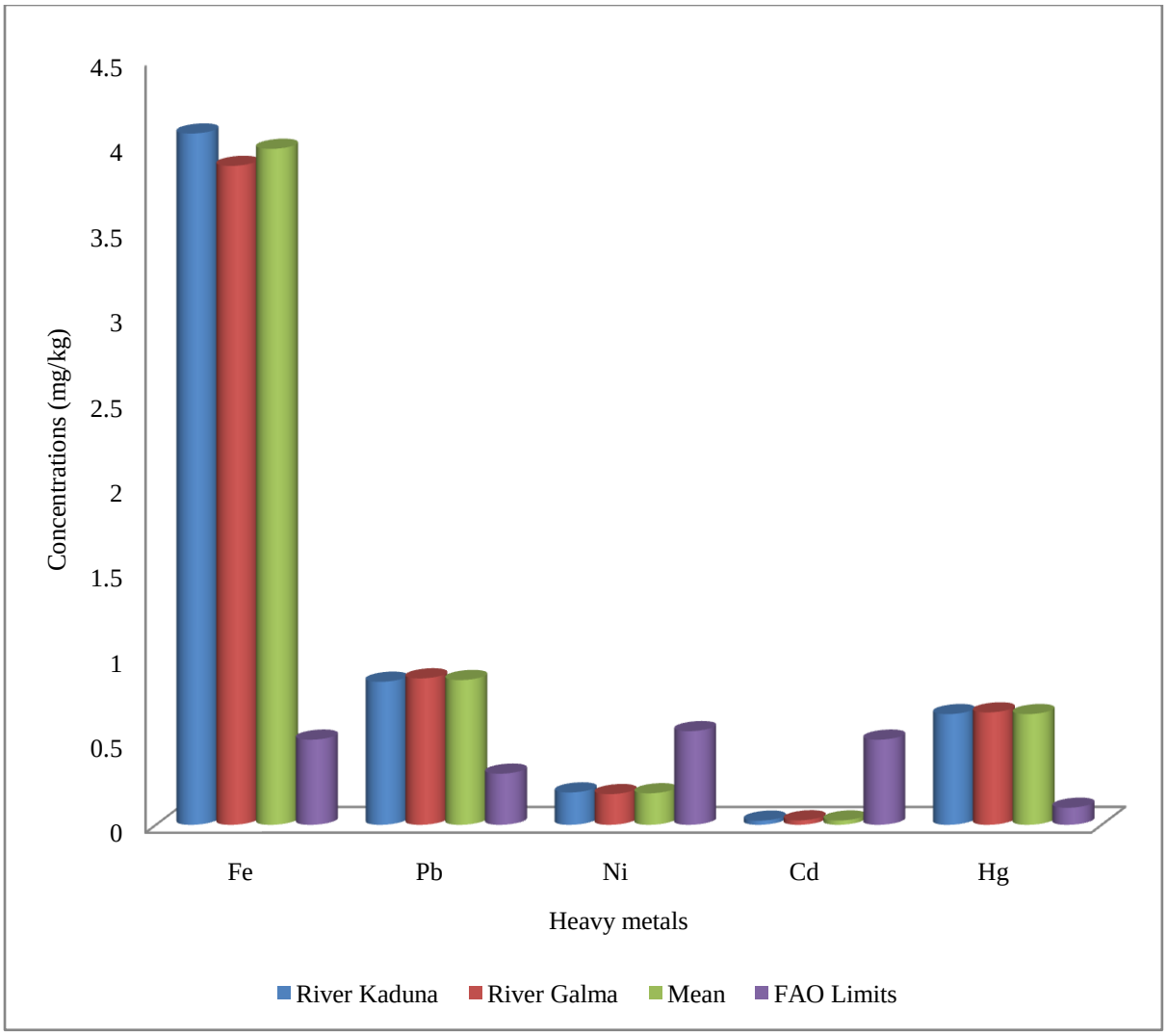


Fig.4.19 Heavy Metals Concentration in River Kaduna and River Galma Fish Samples – Dry Season

In the dry season both rivers also showed similar distributions, although at a slightly higher level than the wet season, where Fe, Lead, Mercury, Nickel and Cadmium in River Kaduna were in concentrations of 4.06mg/kg, 0.84mg/kg, 0.65mg/kg, 0.19mg/kg, and 0.024mg/kg, respectively. River Galma had Fe concentration of 3.87mg/kg, Pb – 0.86mg/kg, Hg – 0.66mg/kg, Ni – 0.18mg/kg, and Cd – 0.026mg/kg, as displayed in Figure 4.19.

Table 4.11 show the analysis of heavy metals in fish muscle samples from the two sampled rivers. When subjected to t-test, four of the heavy metals in fish muscles from River Kaduna showed significant differences ($p<0.05$) in the dry season, namely Fe (4.06mg/kg), Pb (0.84mg/kg), Ni (0.19mg/kg) and Hg (0.65mg/kg) compared to wet season values of Fe (3.20mg/kg), Pb (0.58mg/kg), Ni (0.14mg/kg) and Hg (0.37mg/kg) as presented in Table 4.11. However, the concentration level of only Cd showed no significant difference ($p>0.05$) between the two seasons as Cd levels in the dry season had 0.02mg/kg, while the wet season for Cd was 0.01.

On the other hand there was significant difference in the concentration of heavy metals at River Galma in the dry season for Fe (3.87mg/kg), Pb (0.86mg/kg) and Hg (0.66mg/kg) compared to wet season values of Fe (3.00mg/kg), Pb (0.33mg/kg) and Hg (0.26mg/kg) (Table 4.11). However, heavy metals concentration level of 0.18mg/kg and 0.03mg/kg for Ni and Cd, respectively in the dry season was not significantly different ($p>0.05$) when compared with the wet season values of 0.14mg/kg and 0.03mg/kg for Ni and Cd, respectively, which is represented in Table 4.11.

Table 4.11 Analysis of Fish Muscle Samples between Rivers

Heavy Metals (mg/kg)	Dry Season		Wet Season		Both Seasons	
	River Kaduna (Mean±SE)	River Galma (Mean±SE)	River Kaduna (Mean±SE)	River Galma (Mean±SE)	River Kaduna (Mean±SE)	River Galma (Mean±SE)
Fe	4.06 ± 0.14^{a}	3.87 ± 0.10^{a}	3.20 ± 0.13^{a}	3.00 ± 0.08^{a}	3.63 ± 0.17^{a}	3.44 ± 0.16^{a}
Pb	0.84 ± 0.05^{a}	0.86 ± 0.03^{a}	0.58 ± 0.03^{a}	0.33 ± 0.05^{b}	0.71 ± 0.05^{a}	0.60 ± 0.09^{a}
Ni	0.19 ± 0.00^{a}	0.18 ± 0.01^{a}	0.14 ± 0.00^{a}	0.14 ± 0.01^{a}	$0.17 \pm 0.0.1^{a}$	0.16 ± 0.01^{a}
Cd	0.02 ± 0.00^{a}	0.03 ± 0.01^{a}	0.01 ± 0.00^{a}	0.03 ± 0.01^{a}	0.02 ± 0.00^{a}	0.03 ± 0.00^{a}
Hg	0.65 ± 0.05^{a}	0.66 ± 0.06^{a}	0.37 ± 0.05^{a}	0.26 ± 0.05^{a}	0.51 ± 0.06^{a}	0.46 ± 0.08^{a}

Means with the same superscripts on same rows were not significantly different ($p \geq 0.05$).

Furthermore, when fish muscle samples of the two rivers were compared for the dry season only using t-test analysis, there was no significant difference in all heavy metal concentrations between River Kaduna and River Galma. Concentrations of Fe (River Kaduna – 4.06mg/kg and River Galma – 3.87mg/kg), Pb (River Kaduna – 0.84mg/kg and River Galma – 0.86mg/kg), Ni (River Kaduna – 0.19mg/kg and River Galma – 0.18mg/kg), Cd (River Kaduna – 0.02mg/kg and River Galma – 0.03mg/kg) and Hg (River Kaduna – 0.65mg/kg and River Galma – 0.66mg/kg) between the two rivers in the dry season, showed nosignificant difference at $p<0.05$. This is represented in Table 4.11.

A comparison of all heavy metals in fish muscles during the wet showed no significant differences $p<0.05$ for both rivers, with Fe (River Kaduna – 3.20mg/kg and River Galma – 3.00mg/kg), Ni (River Kaduna – 0.14mg/kg and River Galma – 0.14mg/kg), Cd (River Kaduna – 0.01mg/kg and River Galma – 0.03mg/kg) and Hg (River Kaduna – 0.37mg/kg and River Galma – 0.26mg/kg). However, concentrations of heavy metals in fish muscles during the wet season between the two rivers showed significant difference only in Pb where River Kaduna had 0.58mg/kg, and River Galma had a Pb level of 0.33mg/kg (Table 4.11).

The study also showed that there were varying concentrations of heavy metals in fish muscle samples from both farms located in Zaria and Kaduna in the wet season, Farm 1 had high levels of Fe (1.43mg/kg), Pb (0.25mg/kg) and Hg (0.15mg/kg). This is shown in Figure 4.20. The concentration levels for fish muscle from Farm 1is quite similar to Farm 2, with Iron ranking highest at 0.1.14 mg/kg, followed by Lead (0.21 mg/kg) and Mercury (0.08 mg/kg).

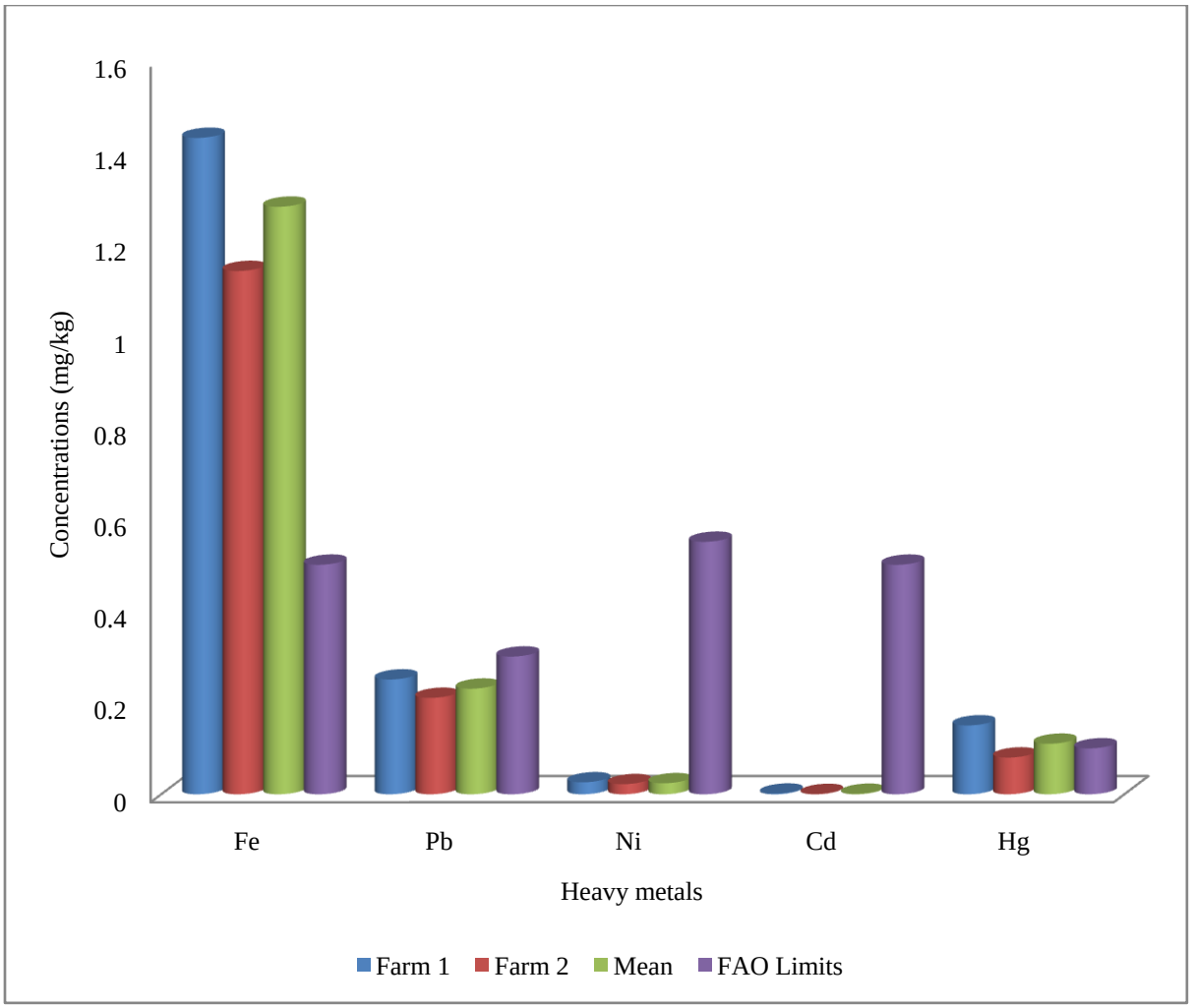


Fig.4.20 Heavy Metals Concentration in Farms 1 and 2 Fish Samples – Wet Season

During the dry season (Fig. 4.21) fish muscle samples in both farms also showed parallel distributions, although at a slightly higher level than the wet season, where Fe, Lead, Mercury, Nickel and Cadmium in Farm 1 were in concentrations of 1.75mg/kg, 0.28 mg/kg, 0.15mg/kg, 0.037mg/kg, and 0.0014mg/kg, respectively. Farm 2 had Fe concentration of 1.46mg/kg, Pb – 0.25mg/kg, Hg – 0.14mg/kg, Ni – 0.035mg/kg, and Cd – 0.0012mg/kg.

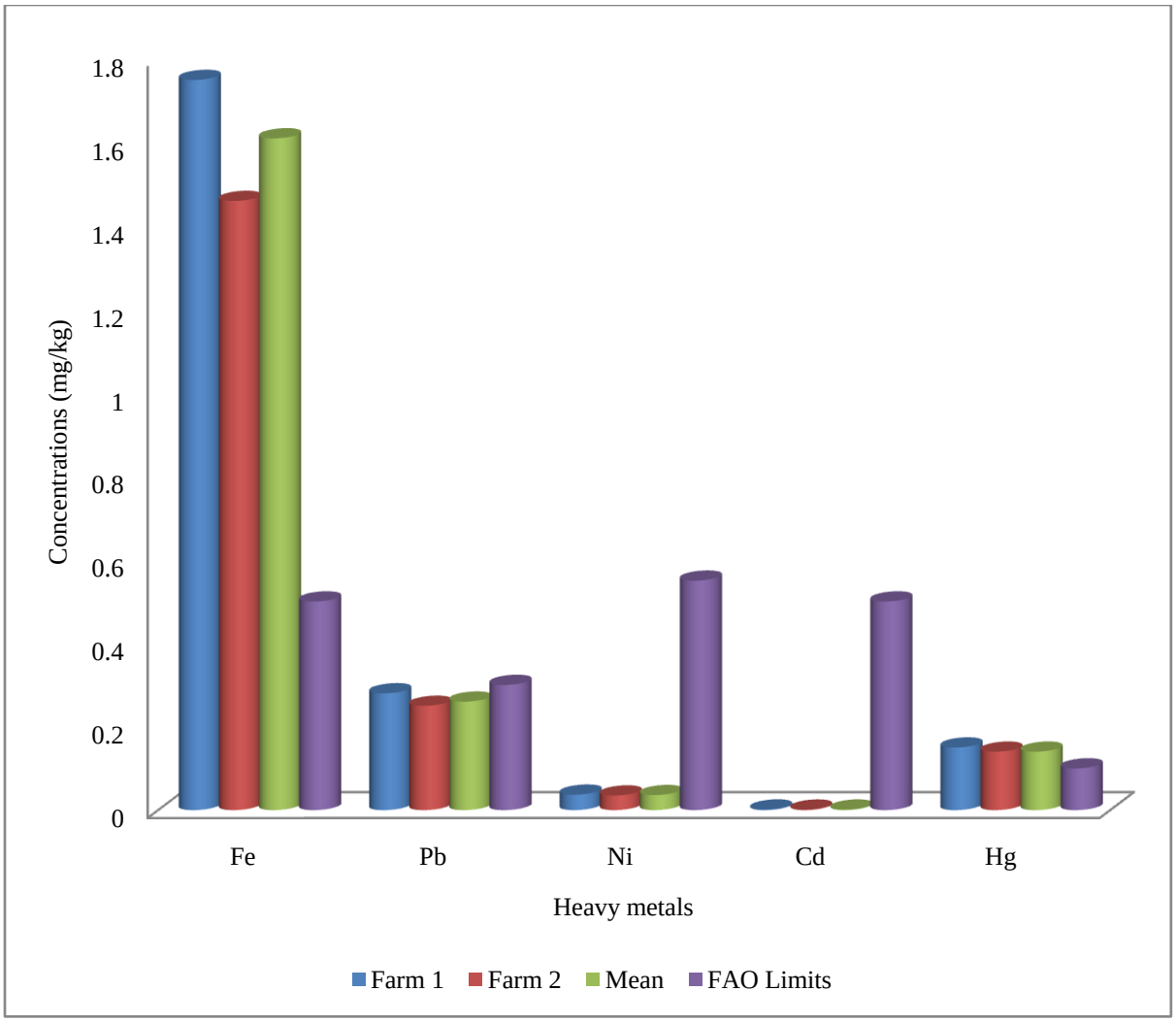


Fig.4.21 Heavy Metals Concentration in Farm 1 and 2 Fish Samples – Dry Season

Table 4.12showed that there was significant differences ($p<0.05$) in the dry season, for Fe (1.75mg/kg) and Ni (0.04mg/kg) compared to wet season values of Fe (1.43mg/kg) and Ni (0.03mg/kg). However, the concentration level of Pb, Cd and Hg showed no significant difference ($p>0.05$) between the two seasons. Pb concentration level for the dry season was 0.28mg/kg as against wet season concentration value of 0.25mg/kg. Cd levels in the dry season had 0.02mg/kg, whereas the wet season for Cd was 0.01mg/kg. Finally, Hg concentration level for the dry season was 0.15mg/kg as against a wet season concentration value of 0.15mg/kg, all in Farm 1.

On the other hand Farm 2 showed significant difference in the concentration of heavy metals, in the dry season for Ni and (0.04mg/kg)and Hg (0.14mg/kg) compared to wet season values of Ni (0.02mg/kg)and Hg (0.08mg/kg) as presented in Table 4.12. However, heavy metals concentration level of 1.46mg/kg, 0.25mg/kg and 0.00mg/kg for Fe, Pb and Cd, respectively in the dry season showed no significant difference ($p>0.05$) when compared with the wet season values of 1.14mg/kg, 0.21mg/kg and 0.00mg/kg for Fe, Pb and Cd, respectively, which is represented in Table 4.12.

Furthermore, there was no significant difference between values of four of the heavy metal concentrations forFarm 1 and Farm 2, as concentrations of Pb (Farm 1 – 0.28mg/kg and Farm 2 – 0.25mg/kg), Ni (Farm 1 – 0.04mg/kg and Farm 2 – 0.04mg/kg), Cd (Farm 1 – 0.00mg/kg and Farm 2 – 0.00mg/kg) and Hg (Farm 1 – 0.15mg/kg and Farm 2 – 0.14mg/kg)between the two farms in the dry season, showing that they all did not differ significantly ($p>0.05$), which is represented in Table 4.12. Only Iron (Fe) had its value for the dry season for Farm 1 as 1.75mg/kg, being significantly different from Farm 2 value of 1.46mg/kg.

Table 4.12 Analysis of Fish Muscle Samples between Farms

Heavy Metals (mg/kg)	Dry Season		Wet Season		Both Seasons	
	Farm 1 (Mean±SE)	Farm 2 (Mean±SE)	Farm 1 (Mean±SE)	Farm 2 (Mean±SE)	Farm 1 (Mean±SE)	Farm 2 (Mean±SE)
Fe	1.75 ± 0.07^{a}	1.46 ± 0.11^{b}	1.43 ± 0.05^{a}	0.94 ± 0.21^{b}	1.59 ± 0.07^{a}	1.20 ± 0.14^{b}
Pb	0.28 ± 0.02^{a}	0.25 ± 0.04^{a}	0.25 ± 0.02^{a}	0.21 ± 0.03^{b}	0.27 ± 0.01^{a}	0.23 ± 0.03^{b}
Ni	0.04 ± 0.03^{a}	0.04 ± 0.00^{a}	0.03 ± 0.02^{a}	0.02 ± 0.00^{a}	0.04 ± 0.00^{b}	0.03 ± 0.04^{a}
Cd	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.02^{a}
Hg	0.15 ± 0.02^{a}	0.14 ± 0.01^{a}	0.15 ± 0.02^{a}	0.08 ± 0.01^{b}	0.15 ± 0.01^{a}	0.11 ± 0.03^{a}

Means with the same superscripts along columns were not significantly different ($p \geq 0.05$).

When the results of heavy metals concentrations in the fish muscles from both farms were compared for the wet season [Fe (Farm 1 – 1.43mg/kg and Farm 2 – 1.14mg/kg), Pb (Farm 1 – 0.25mg/kg and Farm 2 – 0.21mg/kg)and Hg (Farm 1 – 0.15mg/kg and Farm 2 – 0.08mg/kg)] all showed significant differences ($p<0.05$). However, concentrations of heavy metals in fish muscles during the wet season between the two farms showed no significant difference only in Ni and Cd where Farm 1 had 0.03mg/kg and 0.00mg/kg for Ni and Cd, respectively, while Farm 2 had Ni and Cd levels of 0.02mg/kg and 0.00mg/kg, respectively, as shown in Table 4.12.

Fish muscle samples from the two farmsshowed that Fe and Pbhad significant differences between them. Fe mean value for Farm 1 was 1.59mg/kg, while that of Farm 2 stood 1.20mg/kg, Pb for Farm 1was 0.27mg/kg and that for Farm 2was 0.23mg/kg. However, Ni (Farm 1 - 0.04g/kg and Farm 2 – 0.03mg/kg), Cd (Farm 1 - 0.00mg/kg and Farm 2 – 0.00mg/kg) and Hg (Farm 1 - 0.15mg/kg and Farm 2 – 0.11mg/kg), did not differ significantly (Table 4.12).

When means of fish muscle samples from both rivers and farms were compared to each other, the mean concentration for Fe in the rivers was 3.53mg/kg, while that of the farms was 1.44mg/kg. Pb in the rivers was 0.65mg/kg, contrasting well with that of the farms at 0.25mg/kg; Hg was also higher in concentration in fish muscle samples of the rivers than the farm at 0.48mg/kg and 0.13mg/kg, respectively. All were metals analysed had significant differences ($p<0.05$).

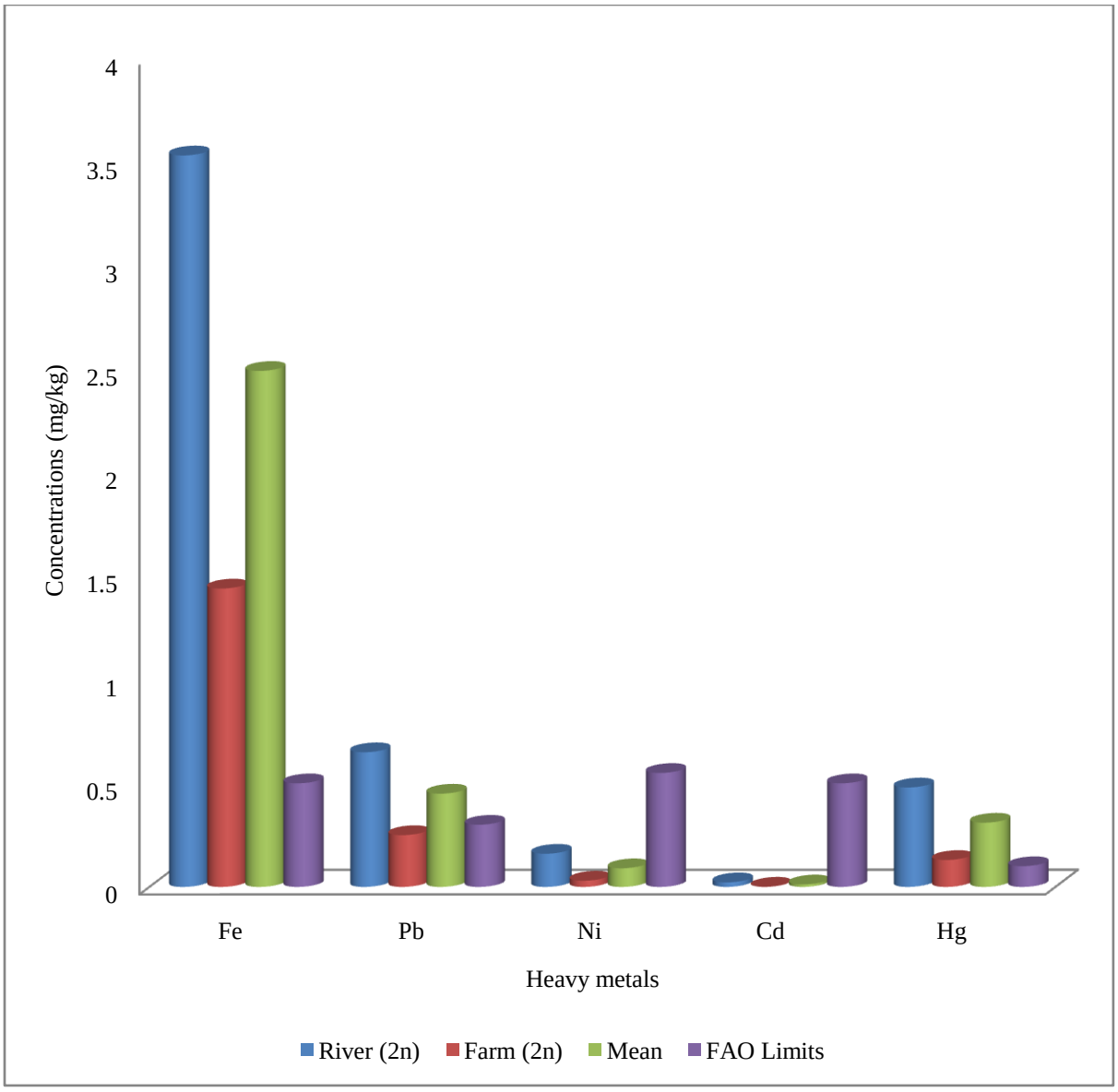


Fig.4.22 Heavy Metal Concentrations in Both Rivers and Farm Fish Samples

4.6 Correlation between Heavy Metal Concentrations and Physico-chemical Parameters

Correlational tables 4.13 through 4.17 shows the relationships between Physico-chemical parameters and heavy metal concentrations during the sampling period. Some Physico-chemical parameters correlated significantly ($p<0.05$) with one another, while there were weak negative correlation between other variables.

Correlation of Fe in fish muscle samples from rivers (RF_Fe) with Pb in Fish muscle samples from rivers (RF_Pb) – r = 0.96, Pb (RW_Pb) – r = 0.87, Ni (RW_Ni) – r = 0.86, Hg (RW_Hg) – r = 89, Turbidity – r = 0.84 and EC (r = 0.85) were significantly positive but negatively correlated with Cd in water RW_Cd (-0.55) and fish samples RF_Cd (r = -0.72) from river Kaduna. Other correlation variables are shown in Table 4.13. Furthermore, correlation of Pb in fish muscle samples from rivers (RF_Pb) with Hg in Fish muscle samples from rivers (RF_Hg) – r = 0.85, Pb (RW_Pb) – r = 0.89, Ni (RW_Ni) – r = 0.94, and EC (r = 0.97) were also significantly positive but was negatively correlated with Cd in water RW_Cd (-0.56) and fish samples RF_Cd (r = -0.66). Consequently, Nickel (Ni) in fish muscle samples from rivers (RF_Ni) revealed significant positive correlation with Hg in Fish muscle samples from rivers (RF_Hg) – r = 0.88. Nonetheless, it was negatively correlated with Cd in water RW_Cd (-0.72) and fish samples RF_Cd (r = -0.73).

Table 4.13 Correlation of Physico-chemical and Heavy Metal Parameters of River Kaduna

	RF_Fe	RF_Pb	RF_Ni	RF_Cd	RF_Hg	RW_Fe	RW_Pb	RW_Ni	RW_Cd	RW_Hg	PH	Temp	DO	Turb	BOD	TDS	EC
RF_Fe	1																
RF_Pb	0.96*	1															
RF_Ni	0.83	0.77	1														
RF_Cd	-0.72	-0.66	-0.73	1													
RF_Hg	0.66	0.85*	0.88*	-0.58	1												
RW_Fe	0.87*	0.58	0.41	-0.54	0.62	1											
RW_Pb	0.94*	0.89*	0.64	-0.61	0.66	0.92*	1										
RW_Ni	0.86*	0.94*	0.67	-0.77	0.58	0.63	0.84*	1									
RW_Cd	-0.55	-0.56	-0.72	0.85*	-0.44	-0.52	-0.61	-0.38	1								
RW_Hg	0.89*	0.68	0.51	-0.44	0.49	0.98*	0.89*	0.58	-0.34	1							
PH	0.69	0.53	0.58	-0.49	0.64	0.51	0.68	0.43	-0.95*	0.62	1						
Temp	0.52	0.47	0.54	-0.39	0.59	0.44	0.32	0.47	-0.88*	0.46	0.91*	1					
DO	0.63	0.56	0.59	-0.48	0.46	0.36	0.62	0.55	-0.48	0.37	0.95*	0.58	1				
Turb	0.84*	0.49	0.60	-0.35	0.67	0.58	0.43	0.42	-0.64	0.57	0.99*	0.58	0.84*	1			
BOD	0.52	0.41	0.20	-0.64	0.28	0.57	0.51	0.42	-0.61	0.57	0.52	0.60	0.45	0.56	1		
TDS	0.67	0.53	0.58	-0.62	0.45	0.38	0.59	0.62	-0.55	0.84	0.57	0.63	0.47	0.48	0.05	1	
EC	0.75*	0.97*	0.46	-0.52	0.33	0.77	0.82	0.48	-0.52	0.45	0.46	0.54	0.36	0.37	-0.06	0.86*	1

* = Significant ($p<0.05$)

RF – Fish Samples from River, RW – Water Samples from River, Temp – Temperature, Turb. – Turbidity, DO – Dissolve Oxygen, BOD – Biological Oxygen Demand, TDS – Total Dissolved Solids, EC – Electrical Conductivity

RF_Cd, i.e. fish muscle samples from River Kaduna, correlated with all other variables, as shown in Table 4.13, with the exception of Cd in water samples from River Kaduna (RW_Cd), where there was a significantly positive correlation of r = 0.85. In addition, Cd in water samples from River Kaduna showed a significantly negative correlation with pH (r = 0.79) and Temperature (r = 0.68).

Among the Physico-chemical parameters analysed there was significantly positive correlation between pH and Temperature (r = 91) and DO (r = 0.95) and Turbidity (r = 0.99), DO also showed a significant positive correlation with Turbidity (r = 0.84) and same goes for Turbidity with EC (r = 0.86). Only BOD showed a negativecorrelation with EC (r = 0.06).

Correlation of Fe in fish muscle samples from River Galma (RF_Fe) with Fe in water samples from the river (RW_Fe) – r = 0.98, RW_Pb(r = 0.92), RW_Hg (r = 0.97),and EC (r = 0.86) was significantly positive but negatively correlated with Cd in water RW_Cd (-0.41) and fish samples RF_Cd (r = -0.46) from river Galma (Table 4.14). In addition, correlation of Pb in fish muscle samples from rivers (RF_Pb) with Hg in Fish muscle samples from rivers (RF_Hg) – r = 0.75, RF_Ni (r = 0.97), Turbidity (r = 0.90) and EC (r = 0.88) was significantly positive but was negatively correlated with Cd in water RW_Cd (-0.44) and fish samples RF_Cd (r = -0.53). Consequently, Nickel (Ni) in fish muscle samples from rivers (RF_Ni) was significantly positive with Hg in Fish muscle samples from rivers (RF_Hg) – r = 0.71. There was also a significant positive correlation of RF_Ni with TDS (r = 0.86) and EC (r = 0.97), nonetheless, it was negatively correlated with Cd in water RW_Cd (-0.47) and fish samples RF_Cd (r = -0.65).

Table 4.14 Correlation of Physico-chemical and Heavy Metal Parameters of River Galma

	RF_Fe	RF_Pb	RF_Ni	RF_Cd	RF_Hg	RW_Fe	RW_Pb	RW_Ni	RW_Cd	RW_Hg	PH	Temp	DO	Turb	BOD	TDS	EC
RF_Fe	1																
RF_Pb	0.67	1															
RF_Ni	0.59	0.97*	1														
RF_Cd	-0.46	-0.53	-0.65	1													
RF_Hg	0.43	0.95*	0.91*	-0.67	1												
RW_Fe	0.98*	0.55	0.47	-0.58	0.40	1											
RW_Pb	0.92*	0.63	0.68	-0.52	0.49	0.55	1										
RW_Ni	0.54	0.38	0.26	-0.32	0.37	0.51	0.65	1									
RW_Cd	-0.41	-0.44	-0.47	0.53	-0.35	-0.33	-0.73	0.03	1								
RW_Hg	0.97*	0.51	0.62	-0.95*	0.65	0.91*	0.46	0.43	-0.38	1							
PH	0.55	0.69	0.63	-0.97*	0.62	0.66	0.50	0.27	-0.25	0.18	1						
Temp	0.69	0.40	0.43	-0.51	0.31	0.61	0.70	-0.07	-0.95*	0.66	0.53	1					
DO	0.45	0.56	0.59	-0.37	0.48	0.50	0.42	0.10	-0.28	0.34	0.25	0.38	1				
Turb	0.61	0.59	0.62	-0.68	0.52	0.46	0.54	0.15	-0.48	0.55	0.92*	0.32	0.96*	1			
BOD	0.70	0.27	0.30	-0.55	0.18	0.72	0.60	-0.21	-0.58	0.43	0.39	0.88*	0.64	0.53	1		
TDS	0.53	0.90*	0.86*	-0.61	0.57	0.59	0.37	0.68	-0.55	0.64	0.58	0.52	0.66	0.69	0.39	1	
EC	0.86*	0.88*	0.97*	-0.54	0.96*	0.53	0.41	0.59	-0.40	0.48	0.56	0.37	0.53	0.56	0.23	0.44	1

* = Significant ($p<0.05$)

RF – Fish Samples from River, RW – Water Samples from River, Temp – Temperature, Turb. – Turbidity, DO – Dissolve Oxygen, BOD – Biological Oxygen Demand, TDS – Total Dissolved Solids, EC – Electrical Conductivity

Comparable to River Kaduna, River Galma RF_Cd, i.e. fish muscle samples from River Galma, correlated negatively with all other variables, as shown in Table 4.14. RW_Hg (r = 0.95) and pH (r = 0.97) exhibits a significantly negative correlation. In addition, Hg in fish muscle samples (RF_Hg) showed a significantly positive correlation with pH (r = 0.96). Also there were significantly positive correlation between pH and Turbidity (r = 0.92). Temperature and BOD (r = 0.88), as well as DO and Turbidity (r = 0.69). Other correlation (r) results are shown in Table 4.14.

Correlation of Fe in fish muscle samples from Farm 1 (PF_Fe) with Pb (PF_Pb) in fish muscle samples gave – r = 0.96, PW_Pb(r = 0.97), andpH (r = 0.86) and EC (r = 0.87), were all significantly positive, but negatively correlated with Ni in water PW_Ni (-0.57) and fish samples PF_Ni (r = -0.56), as shown on the correlation table in Table 4.15. There was no correlation for Cd variables as values were not detectable.

Furthermore, there was a significantly positive correlation of Pb in fish muscle samples from rivers (PF_Pb) with pH (r = 0.87), but significantly negative correlation betweenNi in water PW_Ni (r = -0.61) and fish samples PF_Ni (r = -0.37) and PW_Hg (r = -0.13). A look at Nickel (Ni) in fish muscle samples from Farm 1(PF_Ni) showed significantly negative correlation with Hg in fish muscle samples from Farm 1(PF_Hg) – r = -0.91 and pH (r = 0.88). There was also a significant positive correlation of PF_Ni with PW_Ni (r = 0.96). Nonetheless, it was negatively correlated with Temperature (r = -0.55), DO (r = -0.66), Turbidity (r = -0.74), BOD (r = -0.36), TDS (r = -0.68) and EC (r = -0.37).

Table 4.15 Correlation of Physico-chemical and Heavy Metal Parameters of Farm 1

	PF_Fe	PF_Pb	PF_Ni	PF_Cd	PF_Hg	PW_Fe	PW_Pb	PW_Ni	PW_Cd	PW_Hg	PH	Temp	DO	Turb	BOD	TDS	EC
PF_Fe	1																
PF_Pb	0.96*	1															
PF_Ni	-0.56	-0.37	1														
PF_Cd	0.00	0.00	0.00	1													
PF_Hg	0.68	0.62	-0.91*	0.00	1												
PW_Fe	0.44	0.50	-0.54	0.00	0.58	1											
PW_Pb	0.97*	0.73	-0.62	0.00	0.65	0.49	1										
PW_Ni	-0.57	-0.61	0.96*	0.00	-0.98*	-0.55	-0.62	1									
PW_Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1								
PW_Hg	-0.08	-0.13	0.32	0.00	-0.28	0.62	0.54	0.32	0.00	1							
PH	0.86*	0.87*	-0.88*	0.00	0.97*	0.53	0.59	-0.96*	0.00	-0.35	1						
Temperature	0.65	0.56	-0.55	0.00	0.54	0.26	0.35	-0.63	0.00	-0.59	0.45	1					
DO	0.46	0.49	-0.66	0.00	0.63	-0.27	-0.18	-0.66	0.00	-0.62	0.68	0.56	1				
Turbidity	0.64	0.66	-0.74	0.00	0.63	0.24	0.33	-0.55	0.00	-0.61	0.59	0.94*	0.67	1			
BOD	0.66	0.55	-0.36	0.00	0.48	0.59	0.63	-0.46	0.00	0.20	0.54	0.66	0.19	0.65	1		
TDS	0.51	0.68	-0.63	0.00	0.67	0.92*	0.95*	-0.64	0.00	0.52	0.61	0.37	-0.16	0.35	0.48	1	
EC	0.87*	0.56	-0.37	0.00	0.40	0.88*	0.52	-0.25	0.00	0.17	0.67	0.69	0.23	0.68	0.93*	0.63	1

* = Significant ($p<0.05$)

RF – Fish Samples from River, RW – Water Samples from River, Temp – Temperature, Turb. – Turbidity, DO – Dissolve Oxygen, BOD – Biological Oxygen Demand, TDS – Total Dissolved Solids, EC – Electrical Conductivity

Cd in fish muscle samples from Farm 1(PF_Cd), did not show any correlation with all other variables (Table 4.15), as concentration values of Cd in samples were all below detectable limits. In addition, Hg in fish muscle samples from Farm 1 (PF_Hg) showed a significantly positive correlation with pH (r = 0.97), but a significantly negative correlation with PW_Ni (r = 0.98). Among the physico-chemical parameters analysed there was significantly positive correlation between Temperature and Turbidity (r = 0.94). EC also showed a significant positive correlation with BOD (r = 0.93), while DO showed a negative correlation with TDS – Total Dissolved Solid (r = -0.16), other correlation (r) results are also shown in Table 4.15.

Correlation of Fe in fish muscle samples from Farm 2 (PF_Fe) with Pb in fish muscle samples from Farm 2(PF_Pb) – r = 0.95, PW_Pb(r = 0.97), andBOD (r = 0.88), were all significantly positive; but significantly negatively correlated with Ni in water PW_Ni (-0.85) and fish samples PF_Ni (r = -0.89), as shown in Table 4.16. However, as observed earlier there was no correlation for Cd variables because values were not detectable.

Furthermore, correlation of Pb in fish muscle samples from rivers (PF_Pb) and Temperature (r = 0.80), DO (r = 0.79), BOD (r = 0.86), and EC (r = 0.87), was positive, but was significantly negatively correlated with Ni in water PW_Ni (r = -0.97) and fish samples PF_Ni (r = -0.95) and PW_Hg (r = -0.59). Consequently, Nickel (Ni) in fish muscle samples from Farm 2 (PF_Ni) was significantly positively correlated with Ni in water samples (PW_Ni) – r = -0.89, but significantly negative with pH (r = 0.95). Nonetheless, there existed a negative correlation with Temperature (r = -0.55), DO (r = -0.64), Turbidity (r = -0.63), BOD (r = -0.66), TDS (r = -0.65) and EC (r = -0.54).

Table 4.16 Correlation of Physico-chemical and Heavy Metal Parameters of Farm 2

	PF_Fe	PF_Pb	PF_Ni	PF_Cd	PF_Hg	PW_Fe	PW_Pb	PW_Ni	PW_Cd	PW_Hg	PH	Temp	DO	Turb	BOD	TDS	EC
PF_Fe	1																
PF_Pb	0.95*	1															
PF_Ni	-0.89*	-0.95*	1														
PF_Cd	0.00	0.00	0.00	1													
PF_Hg	0.51	0.23	0.10	0.00	1												
PW_Fe	0.61	0.75	-0.50	0.00	0.82	1											
PW_Pb	0.97*	0.71	-0.45	0.00	0.35	0.96*	1										
PW_Ni	-0.85*	-0.97*	0.89*	0.00	0.03	-0.55	-0.51	1									
PW_Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1								
PW_Hg	-0.32	-0.59	0.86*	0.00	0.66	0.10	0.15	0.77	0.00	1							
pH	0.47	0.53	-0.95*	0.00	-0.16	0.44	0.39	-0.98*	0.00	-0.85*	1						
Temperature	0.58	0.80	-0.55	0.00	-0.41	0.19	0.14	-0.63	0.00	-0.76	0.88*	1					
DO	0.57	0.79	-0.64	0.00	-0.42	0.18	0.13	-0.72	0.00	-0.76	0.86	0.85*	1				
Turbidity	0.53	0.76	-0.63	0.00	-0.47	0.13	0.08	-0.89*	0.00	-0.57	0.65	0.97*	0.93*	1			
BOD	0.88*	0.65	-0.66	0.00	0.69	0.98*	0.67	-0.71	0.00	-0.10	0.61	0.39	0.37	0.33	1		
TDS	0.47	0.56	-0.65	0.00	0.70	0.58	0.37	-0.69	0.00	-0.09	0.60	0.37	0.36	0.31	0.59	1	
EC	0.63	0.87*	-0.54	0.00	0.49	0.97*	0.96*	-0.59	0.00	0.05	0.48	0.24	0.22	0.18	0.97*	0.92*	1

* = Significant ($p<0.05$)

RF – Fish Samples from River, RW – Water Samples from River, Temp – Temperature, Turb. – Turbidity, DO – Dissolve Oxygen, BOD – Biological Oxygen Demand, TDS – Total Dissolved Solids, EC – Electrical Conductivity

Cd in fish muscle samples from Farm 2 (PF_Cd) did not show any correlation with all other variables, as shown in Table 4.16, as concentration values of Cd in samples were all below detectable limits. In addition, Fe in water samples from Farm 2 (PW_Fe) showed a significantly positive correlation with PW_Pb (r = 0.96), BOD (r = 0.98) and EC (r = 0.97), but a negative correlation with PW_Ni (r = 0.55).

Among the physico-chemical parameters analysed there were significantly positive correlations between pH and Temperature (r = 0.88). Temperature also showed a significant positive correlation with DO (r = 0.85) and Turbidity (r = 0.97). DO also showed a positive correlation with Turbidity (r = 0.93). EC showed significantly positive correlation with BOD (r = 0.97) and TDS (r = 0.92). Other results are shown in Table 4.16.

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physico-chemical Parameters of Water Samples

Seasonal variations in pH were evident in this study as pH values reported for both seasons were within the WHO standard of 6.50 – 8.50. The pH of a water body is very important as it determines water quality, since it affects other chemical reactions such as solubility and metal toxicity (Fakayode, 2005). Thus, pH values obtained in this study were all near the neutral point and are optimal for fish production (Cole *et al.,* 1999).The results of this study, in relation with pH, supports the report of Udiba *et al.* (2014) as they obtained a mean pH value of 6.78, while studying status of heavy metals in River Galma around Dakace Industrial Layout. However, it is hugely different from results obtained by Samuel *et al.*, (2015), who obtained a pH range of 7.94 – 8.76 from River Galma, albeit at different sampling points.

Furthermore, the pH results obtained from groundwater sampleswere also within WHO acceptable limits and were close to results obtained by Thilza and Muhammad (2010) who reported an average pH of 6.5 ± 0.76 and 6.80 ± 0.45 in concrete ponds.

Temperature ranges obtained in the rivers and the farms in this study were within aquaculture desirable limits (24.94°C – 30.68°C) as reported by Phelps and Popma (2000). Thus,it is logical to state that optimal fish production, as regards to the temperature, is "safe" in these waters.Temperature of the water is probably the most important environmental variable since it affects metabolic activities, growth, feeding, reproduction, distribution and migratory behaviours of aquatic organisms (Suski *et al*., 2006). Oniye *et al.,* (2002) also made similar observation for Zaria Dam.

Dissolved Oxygen (DO) in this study was slightly higher than 5mg/l, which if below this concentration could adversely affect aquatic life (Pearce *et al.*, 1999; Rao, 2005). Judging

from the results in comparison with WHO standards, River Kaduna (6.56mg/l), River Galma (5.51mg/l) and the two farms (Farm 1 – 10.17 and Farm 2 – 9.86mg/l) could be said to be within the limits ideal for aquaculture, as both rivers might not pose serious threat to the survival of the aquatic biota and might be used for other agricultural and domestic activities as advised by Rao (2005).Prolonged exposure to low dissolved oxygen levels(less than 5 to 6 mg/dm^{3}oxygen) might not directly kill an organism, but would increase its susceptibility to otherenvironmental stresses(Zeb *et al.*, 2011).

Results of DO levels obtained in the upstream of both rivers were higher than levels recorded in the midstream and downstream. For instance, Dissolved Oxygen (DO) level measuredin River Galma during the dry season varied widely as it was 6.62mg/l in the upstream, while there was a dip in the midstream and downstream to 4.25mg/l and 4.48mg/l, respectively. This probably could that the upper part of a freshwater body usually have higher amount of oxygen which diminishes downstream, as result of steep or shallow rapids, reduced aquatic activity, and low anthropogenic activity in such parts, which gradually increases downstream. This result is in agreement with the findings of Kumar (2004) and Rashimi *et al.* (2008), who both studied seasonal variations of physico-chemical parameters of River Yamuna in Uttar Pradesh, India.

Biological Oxygen Demand (BOD)values differed significantly in River Kaduna, River Galma and also in the farms, during both the dry and wet seasons. The high BOD values obtained in the sample sites suggested high variation in dissolved organic matter concentration from onelocation to another. This may likely be as a result of periodic discharge ofsewage containing varying amounts of substances with high BODinthe different locations. The values obtained in this study were in many cases lower than the average values reported by Bawa*etal*.(2007) for Lomé's water bodies (BOD >40mg/l).

Total dissolved solids gives an indication of the degree of dissolved substances (Amadi *et al.*, 2014), which can be attributed to the numerous anthropogenic activities taking place along the rivers.Turbidity,an important variable relative to transport and bioavailability of contaminantsdid not show much significant difference between the rivers, however, both farms did differ significantly in the dry and wet seasons.The lowest turbidity value in the rivers was obtained at the midstream (49.67 NTU) of River Kaduna in the dry season, while the highest (56.50 NTU) was at the upstream. The relatively highconsistent values for turbidity were obtained at all the locations during the wet sampling periods, andthis was as a result ofwaste discharge and other earth-disturbing activities that occur near the rivers, such as sand harvesting. Generally high turbidity value indicates a highconcentration of total dissolved and suspended solids (Ladipo *et al.*, 2011); this is why total dissolved solids (TDS)obtained in this study were all very high, with a mean of 79.72mg/l, which is lower than the WHO standardindicativeofportability (1000 – 1600mg/l).

TDS values in the rivers were highest in the dry season (River Galma – 82.09mg/l) and lowest in the wet season (River Galma - 54.91mg/l). However, TDS values inthe farms were quite very low and "permissible" (WHO, 2012), when contrasted to values reaching up to 24,896 mg/L obtained by Ladipo *et al.* (2011) and Imam and Balarabe (2012).

The mean values of electrical conductivity of the waters were high during the dry season in comparison with the wet season. The FEPA acceptable limit for conductivity in domestic water supply is 70µs/cm (DWAF, 1996), thus, values obtained in this research are higher and above this limit which ranged from 109.72µs/cm to 165.06µs/cm. The high values obtained might have been as a result of increased ionic concentration due to low water level, and conductivity value obtained during the dry season could be attributed to dilution factor as a result of increased water volume from the main tributary channels and the main water stream.

Ovie and Adeniji (1993) as well as Kolo and Oladimeji (2004) observed a similar trend for Shiroro lake.

Furthermore, electricalconductivityvalueswererelatively high in all the farm locations during dry season sampling period; this could be attributed to the drying of water bodies and salts, which accumulated through evaporation. Merz (2006) and Ladipo *et al.* (2011) also stated that during the drying phases EC concentrations could become high, which could have an impacton aquatic biota. However, in the wet season the farms' EC levels decreased to below 70µs/cm. It is thus logical to relate this scenario to the water table being refilled and salts had been diluted or reduced within the system.

There was a positive correlation between pH and Temperature, pH and DO, pH and Turbidity, while DO also showed a significant positive correlation with Turbidity, likewise TDS and EC in River Kaduna, which could be attributed to increase in anthropogenic influence (Oniye *et al*., 2002) could cause increaseinTDS. However, only BOD showed a negativecorrelation with EC. River Galma showed that there was significantly positive correlation between pH and Turbidity, Temperature and BOD, DO and Turbidity.

On the farms, Farm 1 showed that Temperature and Turbidity, EC and BOD had a significant positive correlation, while DO showed a negative correlation with TDS (Total Dissolved Solid), Farm 2 showed significantly positive correlation between pH and Temperature, Temperature and DO, Temperature and Turbidity, DO and Turbidity, EC and BOD. Onome *et al*. (2013) report similar relationships between pH and Temperature, DO and turbidity in concrete tanks.

Slightly similar report was observed by Adewumi *et al.*,(2015) when he observed that the correlation matrix for physico-chemical parameters revealed that there was a significant positive correlation between temperature, pH and conductivity, with a significant difference

between temperature, TDS, pH and conductivity in three sampling points in Ado, Ikere and Iyin Ekiti, all in Ekiti State, Nigeria. Similar results were also obtained by Farouk (1997) when he observed significantly positive correlation in some water factors such as pH, temperature, total hardness, total dissolved solid, total suspended solid, COD, BOD, dissolved oxygen, and turbidity in water bodies in Kano metropolitan area. They both concluded that results of physico-chemical parameters obtained and their interactions, which are similar to results obtained in this study, had minimal to no effects on water quality, and thus optimal for fish culture.

5.2 Heavy Metals in Water Samples

Result of Fe levels were very high in River Kaduna during the dry season, with Pb and Hg levels in the dry seasons also reaching alarming levels, the results were all significantly higher than concentrations obtained during the wet season, this is majorly due to the solvent nature of water which dissolves the concentration of elements and their compounds during the wet season, as opposed to the dry where they become more concentrated (Metz, 2006; Orisakwe, 2009; Ladipo *et al.,* 2011; Udiba, 2012). In addition, River Galma also had significant levels of heavy metals, where Fe, Pb and Hg had very high concentrations during the dry season, which differed from concentrations during the wet season, with the exception of Pb.

These observed levels are quite alarming, Pb for example (which has a WHO critical limit of 0.05mg/l), results in osteoporosis, lead poisoning, mottled teeth in children, kidney failure (Nephritis) and when in contact with other chemicals found in detergents could result in eutrophication of water tables (Ezeribe *et al*., 2012). Galadima and Garba(2012) also stated that highconcentrationsof Pb inthebodycould result to mentalretardation, coma and eventual death. Aina (2002) also reportedsymptoms of high level concentration of Pb to

includeconstant headache, loss of appetite,vomiting, nausea,irritability and/or behavioural problem.

Furthermore, Iron which is one of the most abundant metals in the Earth's crust is present inwater as a result of the deposition of iron coagulants or the corrosion of steel andcast iron materials dumped into water bodies (WHO, 2012). However, high iron levels causes discoloration and high turbidity of water, added to the fact thatiron interactions in biological tissues, due to excess amountof iron, causes rapid increasein pulse rate and coagulation ofblood in blood vessels, hypertension, and drowsiness (FAO, 2012). However, generally in Nigerian surface waters, there seem to be fairly high levels of Fe (Etim, 2012; Etim and Adie, 2012; Butu, 2013), for instance Butu (2013) found high concentrations of Fe (16.5 mg/l) in River Kubanni, Zaria, which was significantly higher than levels obtained in this study.

Mercury, whose concentration levels were very high downstream River Kaduna during the dry season, is largely emitted by both natural and anthropogenic activities in an inorganic form, predominantlymetallic vapour, which is carried off to great distances by winds and eventually falls unto waterbodies. This could pose very serious health risks to the populace living within the area (Ibeto and Okoye, 2010), with Clemente *et al.,* (2009) stating that in aquatic environments inorganic mercury is microbiologically transformed into lipophilic organic compounds, methyl mercury, this transformation makes mercury more prone to bio-magnifications in food chains and results in psychomotor retardation in children (Horsfall, 2001), autism (Lim *et al.,* 2008), and dysplasia of cerebral and cerebellar cortexes, neuronal ectopia and several other developmental disturbances (Zukowska and Biziuk, 2008).

Furthermore, access to safe water used as a culture media for fish farming is essential to health. It is a basic human right and a component of effective policy for health protection (FAO, 2012), thus, when Nickel (Ni) content in water samples in the dry season of River

Kaduna and River Galma showed over 16,000% above the WHO threshold limit of 0.0024 mg/lit becomes a crisis.

However, Ni concentrations dropped significantly in all sample sites when analysed in the wet season, but was still above threshold limits, thus demonstrating that individuals who constantly consume matter from these waters stand the risk of developing cancer. This inference is based on the Adelekan and Abegunde (2011) report which stated that metallic nickel is possibly carcinogenic, and possibly could result to abnormal growth and development of offspring due to post-implantation/peri-natal lethality, which was substantiated byWHO (2012). The latter, having examined heavy metals contamination levels in streams in 7 villages in Ibadan running from River Ogunpa as their source, stated that Nickel in the 7 sampled sites in the villages showed varying high levels of contamination ranging from 0.55 mg/l to 2.50 mg/l, thus surpassing levels in River Kaduna and River Galma.

Cadmium, which also varied in concentrations in the rivers during the wet and dry seasons, had the highest value of 0.06mg/l in River Galma in the dry season; with a least of 0.02mg/l, both in Rivers Kaduna and Galma, during the wet season. These values contrasted fairly when compared with readings from the Imo River Basin by Nwachukwu *et al.,* (2010), where a high concentrationof Cadmium was obtained at several surface waters in Okigwe (0.023mg/l), Orji(0.015mg/l) and Nekede (0.017mg/l) which marginally exceeded the WHO standard of 0.01 mg/l.

Similarly, water samples from the farms also showed varying levels of heavy metals, the least (and also negligible) being Cadmium, with levels below WHO threshold limits. These negligible values obtained from both Farms 1 and 2, are reasonably comforting; as high concentration of Cd in the liver, which is the principal organ responsible for detoxification,

transportation and storage of toxic substances, makes it an active site for pathological effects induced by Cd contamination. Uzairu *et al.* (2009) concurs that Cadmiumaccumulation in the kidney and liver would cause kidneydysfunction and liver failure, interferes with themetabolismofCalcium and Phosphorus, causing painfulbone diseases. This is in addition to being a teratogenic andcarcinogenicagent. Thus, Cd could be momentarily cleaned off the slate in ground water found in Zaria, as its levels is lower than the critical limit set by WHO at 0.01mg/l.Udiba *et al.* (2014) also noted that eating food or drinking water withhigh Cadmium concentration irritates the stomachcausingvomiting and diarrhoea. Chronic exposure canalsocauseirreversible damage to the lungs. The observation in this study is inagreementwithOwamah (2013) who reported a range of 0.001to 0.05 for groundwater in Ikpoba, Delta State. Also a mean value of 0.005 ± 0.02 mg/l was reported for groundwater in lower Niger basin, Niger State inNorth central Nigeria by Olatunji and Osibanjo (2012).

When compared to the WHO limit of 0.3mg/l (See Appendix II), Iron (Fe) levels were also high in both Farm 1 and 2, during the dry and wet seasons with an average of 1.42mg/land 1.20mg/lin Farm 1 and Farm 2, respectively. Such levels when compared to Fe concentrations in the rivers, is quite low, this is because high Fe levels promotes the growth of "iron bacteria," which contributes to its difficulty in percolating into ground water due to its (Fe) rapid utilization by the micro-arthropods. Ibeto and Okoye (2010) stated that this accounted for the huge variance between pond (which uses ground water) and river water samples. Additionally, figures obtained compares well with that of Udiba *et al.* (2014) who after analysing hand dug wells and boreholes in Zaria municipality revealed Fe concentrations levels of over 1.4mg/l and 1.7mg/l, respectively. Nnaji *et al.* (2011) also discovered high traces of Fe in groundwater wells around the Kubanni area in Zaria, with values exceeding 2.15mg/l on the average.

Another source of concern is Mercury levels obtained from the farms, whose levels ranged between 0.03mg/land 0.15mg/l, in both the wet and dry seasons. Although, lower than the WHO threshold limit of 0.5mg/l, Galadima and Garba(2012), Galadima *etal.*(2011)and Nubi *et al.*(2008) all stated that continuous exposure to mercury in minimal doses has resulted to many functionaldisturbances in humans,including Erethism (a state of abnormal mental excitement or irritation),excessiveshyness,and insomnia.With prolong exposure to mercury, affine tremor develops and may escalate to violent muscular spasms(Chen and Chen, 2001). Furthermore, Chen and Chen (2001) reported that tremor which develops as a result of mercury accumulation, initiallyinvolves the hands and later spreads to theeyelids, lips, and tongue, and severe exposure has been associatedwith more subtle symptoms of erythrism, including fatigue,irritability, vividdreams, depression and memory malfunction.

Additionally, Lead (Pb) levels were also significantly high registering over 0.1mg/l in the wet season to 0.42mg/l in the dry season of both farms. This low concentration of Lead in the wet season is due to its soluble nature in water, but becomes more concentrated as the solvent evaporates (Silbergeld, 1996). Such high Pb levels have also been registered by Galadima and Garba (2012) and Udiba (2015). The former discovered that Pb levels in groundwater within Zaria, especially in heavily commercialized areas, reached levels of over 0.6mg/l. Such levels are known to have serious health consequences in humans when ingested, primarily among which are impairments in intellectual functioning, kidney damage, miscarriage, increased bloodpressure and hypertension (Silbergeld, 1996).

Nickel was however low in the dry season of both Farm 1 and 2, however, it still surpassed the WHO limit of 0.024mg/l, while dry season concentrations of Niwas 0.03mg/lin water samples from both farms, accounting for an average of approximately 0.04mg/l for both seasons. This could be a result of high Nickel content in soils (Hussani, 1991). Also, it'suse in Ni/Cd batteries, welding, rods, pigments for paints, ceramics and glasscontainers,

computer components (Bradi, 2005), could leach into soils from the numerous wastes sites close to the farms locations.

Pearson Correlation Coefficient results revealed highly significant positive correlation between the concentrations of Fe and Pb, Pb and Hg, Ni and Hg in River Kaduna, which suggests that the association of these metals originates from a common source – untreated waste water, sludge and sewage – (Orisakwe, 2009), this is evident within the study area as mechanics, car painters and farms which make use of varied lubricants, oils, paints, pesticides and herbicides, which contains Fe, Ni, Hg and Pb compositions, are present and all have their wastes washing into the river as the only option. On the contrary, only Fe and Hg showed a significantly positive correlation in River Galma, which implies that, the source of contamination is primarily domestic, which is true as residential areas, inclusive of tertiary institutions such as Ahmadu Bello University, Kongo campus and the Federal College of Education, Zaria which accommodates large amounts of students who use cosmetics, detergents and bleaching agents, that contains varying concentrations of mercury, iron and nickel elements. All have their drainage systems emptying into river Galma, which was also reported by (Samuel *et al.*, 2015).

Farm 1 water samples did not show any significantly positive correlation between the heavy metals analysed, but had significant positive correlations with some physico-chemical properties, such as TDS, EC and pH, thus suggesting that the presence of these heavy metals amplifies the expression or inexpression of some Physico-chemical conditions (Sachchida *et al.*, 2011). However, Farm 2 showed a significantly positive correlation between Fe and Pb, suggesting that they are present in comparable quantities from the water source.

5.3 Heavy Metals in *C. gariepinus*

Fish specimens obtained from the sampled sites in the wet and dry seasons were of varying sizes and had different concentrations of heavy metals which were low, as in Cadmium, in fish muscles tissues from the farms to very high for Iron in fishes from the rivers.

In the dry season both rivers showed paralleled distributions, although at a slightly higher level than the wet season, where Fe in fish muscle samples in the dry season were higher than values obtained in the wet season. Fish muscle samples from River Galma had very high Fe values in the dry season which differed significantly from that of the wet season; these concentrations were above the recommended food limit as advised by the FAO (2012) whose fish food allowable limit is 0.5 mg/kg. Such high Fe variation in fish muscles during the wet and dry seasons could be attributed to the need of high oxygen during the dry seasons as water evaporates. Hence, fishes need more Fe for haemoglobin formation to take up scarce oxygen (Alinnnor and Obiji, 2010). The results obtained in this study (1.44 – 4.07mg/kg) were dissimilar to results obtained by Bashir *et al.* (2013) who reported Fe concentrations in *A. thalassinus* as high as 538.6mg/kg, while Abubakar *et al.* (2015) also reported Fe levels of 11.45 ± 0.02mg/kg and 21.87 ± 0.025mg/kg of *S. scombrus* sold in markets in Zaria metropolis.

Furthermore, Lead (Pb) in River Kaduna in the dry season (0.84mg/kg) was also significantly different than the wet season (0.58mg/kg), while fish muscle samples from River Galma in the dry season (0.86mg/kg) had Pb values which differed significantly from that of the wet season (0.33mg/kg), which were all below the WHO limit for fish food – 2.0mg/kg, it is still substantial to cause considerable damage to the human body which could result to inducing oxidative damage to brain, heart, kidneys, andreproductive organs (El-Ghasham *et al.*, 2008).

Nickel concentrations were low in fish muscle samples in the wet season for River Kaduna, while fish muscle samples from River Galma had similar values in the dry season with that of River Kaduna, but differed significantly from that of the wet season. This could be as a result of its property as an activator of enzymes (Bradi, 2005), especially when survival conditions (oxygen demand, low temperature, and rapid evaporation) becomes adverse. Hence, during the dry season when resources become scarce, Ni is stored in considerable quantities (Olaifa *et al.,* 2010). However, the values obtained (0.14 – 0.18mg/kg) were significantly below the WHO fish food limit of 0.5 – 0.6 mg/kg, but lethal enough to cause gastrointestinal upset(vomiting,cramps,diarrhoea)andneurological symptoms (giddiness, headache,weariness). The values obtained were also similar to those obtained by Obasohan and Eguavoen (2008) who analysed heavy metals concentrations in the muscle of *Erpetoichthys calabaricus* from the Ogba River in Benin City and found Nickel levels to range between 0.08 to 0.79mg/kg.

Cadmium (Cd) whose food intake limit is put at 2.0mg/kg by the WHO was low in fish muscle samples during the dry season, as well as that of the wet seasonin River Kaduna, while fish samples from River Galma in both the dry and wet seasons had equal values. The result obtained (0.024 – 0.026mg/kg) was relatively far lower than that obtained by Obasohan and Eguavoen (2008) – who analysed *Erpetoichthys calabaricus* and Abubakar *et al*. (2015) – who analysed *Scomber scombrus*, as their results of 0.07 – 0.17 mg/kg and 2.192 – 2.375 mg/kg, respectively far outstrips that of the allowable limits in food fish recommended by FAO (2003). However, Nnaji *et al.* (2007) reported Cd concentrations of 0.041 ± 0.0031mg/kg – 0.129 ± 0.0037mg/kg from 10 fish samples of *Oerochomis niloticus*, when they studied heavy metals in River Galma, while Gebremedhin and Berhanu (2015) reports of 1.21 ± 0.05mg/kg in *O. niloticus* and 1.28 ± 0.037 mg/kg in *C. gariepinus*.

Mercury concentrations from this study showed mean concentrations of Mercury ranging from 0.26 – 0.65mg/kg, most of which exceeded that of the permissible food limit of 0.5 mg/kg, with River Kaduna in the dry season accounting for the highest value and lower wet season value, while fish muscle samples from River Galma had equal values in the dry and wet season, and the average of the two seasons for River Kaduna exceeded that of River Galma. The values obtained in this study are basically within the threshold limits but still capable of inflicting harm to humans. This is because Hg which is generally and naturally found at verylow concentrations, becomes elevated when associated withpollutionfromhumanactivities, such elevated concentrations are usually found in fishes that ingest it and accumulate it from water bydiffusionvia skin and gills as well as oralconsumption/drinking ofwater (Nussey *et al*, 2000; Oguzie, 2003).

However, when compared with the results of Abubakar *et al.* (2015), who reported very high concentrations of Mercury within the range of 68.65 ± 0.02 to 80.35 ± 0.005 mg/kg, in imported *Scomber scombrus*, results obtained in this study are relatively safe. But it is pertinent to note that concentrations as low as 0.25mg/kghad been associated with a widespectrum of adverse health effects including damage to thecentral nervous system (neurotoxicity) and kidney failure.

Heavy metal concentrations of fish muscle samples from the farms, differed from one another, while Fe concentrations in Farm 1 during the dry season was higher when compared to value of the wet season. Farm 2 also had similar distinctive values between the dry and wet seasons. Literature suggests thatexcess amountofiron interactions in biological tissuescauses' rapid increasein pulse rate and coagulation ofblood in blood vessels, hypertension, and drowsiness as citedin FAO (2012). Thus, with the permissible limit of Fe in fish food tagged at 1 mg/kg(FAO, 2012), results obtained in this study is thus relatively low and within tolerable limits.

Furthermore, in the both farms Lead (Pb) levels were low during the wet season, while that for the dry season had slightly higher value in Farm 1 (0.28mg/kg) and Farm 2 (0.25mg/kg), which when compared to 2 mg/kg limit of the FAO (2012), is substantially low. This could be attributed to the reduced quantity of groundwater during the dry season, thus Pb becomes much more concentrated (Silbergeld, 1996). During the dry season, Nickel concentrations were fairly low for River Kaduna and River Galma, while the wet season was significantly lower for bothRiver Kaduna and River Galma, respectively. This demonstrates that individuals who constantly consume aquatic food emanating from these groundwater samples rarely stand at risk of developing cancer, as WHO (2012) reports that metallic nickel is possibly carcinogenic, which placed the permissible limit in fish food at 0.5 – 0.6 mg/kg.

Reassuringly, Cadmium levels was a recurring low in muscle samples of*C. gariepinus* farmed in concrete fish ponds of Farm 1 and Farm 2, as concentrations were all below WHO threshold limits, which is also significantly below the FAO (2012) permissible limit of 0.1mg/kg. When the results obtained here are compared with the values obtained in *O. niloticus* and *Synodontis schall*, reported by Nnaji *et al.* (2007). They reported levels of 0.006 ± 0.0014mg/kg in *S. schall* and 0.012 ± 0.0022mg/kg in *O. niloticus*.

Furthermore, Mercury (Hg) levels in Farm 1 during the dry and wet seasons were high, and similar to the high values in Farm 2 during the dry and wet seasons; with the average of both seasons at 0.15mg/kg for Farm 1 and 0.11mg/kg for Farm 2. When compared with permissible limit of 0.1mg/kg (FAO, 2012) it is relatively high, but markedly higher than the results obtained by Osman and Kloas (2010) who reported Hg levels of 0.0000 ± 0.0001 mg/kg and 0.001 ± 0.001 mg/kg in heavily industrialized towns of Aswan and Beni-Seuf in Egypt. These results are therefore a source of great concern, which suggests that there is some form of health risk(s) which consumers of *C.gariepinus* stand to suffer, such as damage to thecentral nervous system (neurotoxicity) and kidney failure.

When results were correlated they revealed severalsignificant relationships ($p<0.05$), amongst heavy metal species in the Riverwater and Fish samples. There existed a significant positivecorrelation between Fe in fish muscles and Fe in water samples, Fe and Pb (0.94), Fe and Ni (0.86), Fe and Hg (0.89). There also existed a significant positivecorrelation (0.89) between Pb in fish muscles and Pb in water samples, Pb and Ni, Cd in fish muscle samples and Cd in water samples (0.85), all in River Kaduna. Also, significant negativecorrelationwererecordedbetween Cd and Hg (-0.95) in River Galma, and between Hg and Ni (-0.98) in Farm 1, as well as Fe and Ni (-0.85) and Pb and Ni (-0.97) in Farm 2. Thepositive correlation between the heavy metals indicates thatthey are strongly associated.The negative correlationamongst the concentrations may be a result of precipitationof the elements as hydrous metal oxides (Greany, 2005).Pb can bio-accumulate in tissue of fish andhuman and cause severe health problems such as brain and kidney damage, diminishing learning ability in children,also Cd can bio-accumulate in tissuesof fish and human andcause several health impact such as weakenedimmunesystem and infertility(Akhionbare, 2011).

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

Pollution in water bodies is a serious problem the world over, in which millions of world inhabitants suffer health problem related to wastes (mostly heavy metals) generated from anthropogenic activities, (Abechi *et. al.*, 2010). Physico-chemical results in both the rivers and fish farms assessed revealed that pH, Temperature and TDS were all within WHO, NIS and FAO recommended limits for water quality and farming purposes, however, Electrical Conductivity and DO fall slightly short of the recommended limits, although the values obtained in this study do not affect fish production negatively.

In addition, results also revealed the presence of the selected heavy metals, viz.; Fe, Pb, Ni, Cd and Hg, in all the selected sites; i.e. River Kaduna, River Galma and one fish farm each from Kaduna and Zaria. Although some of these heavy metals are in negligible quantities when compared with WHO and FAO threshold limits, they could still pose health risks to humans. Fe, Pb and Hg all exceeded the WHO, NIS and FAO permissible limits in water and fish food, thus they could be a precursor to damages within the body, as they are capable of affecting every organ system causing and/or contributing to brain, nervous system, immune, cardiovascular and hormone problems.

6.2 Conclusions

The results obtained in this study showed that physico-chemical properties differed markedly between the selected rivers and farms. The parameters ranged as follows: pH, 6.67-7.04 and 6.44-6.89; Temperature, 27.03-29.03 and 28.16-30.68; DO, 5.62-7.69; Turbidity, 49.67-57.56

and 52.40-57.04; BOD, 2.19-3.88 and 2.68-4.62; TDS, 65.75 and 53.84; EC, 116.21 and 108.81 respectively in river Kaduna and River Galma.

Furthermore, the results of this investigation showed that heavy metal concentrations in River Kaduna had the least and highest in Ni (0.03) and Fe (4.06mg/l) respectively; Ni (0.03mg/l) and Fe (3.14mg/l) in River Galma. For farms, it ranged from Ni (0.03) to Fe (1.78) in Farm 1 and Farm 2 had 0.01mg/l and 1.56mg/l for Ni and Fe, respectively.

The concentrations of heavy metals in the wild and cultured catfish were as follows: Cadmium (0.02mg/l) in catfish from river Kaduna and 0.03 in river Galma. Fe was 3.63mg/l and 3.44mg/l in the catfish sampled from rivers Kaduna and Galma, respectively. Cadmium was also the least heavy element in cultured catfish with fish from Farm 1 recording 0.001mg/l while Farm 2 had 0.0009; Fe in Farm 1 was 1.59mg/l while Farm 2 had 1.30mg/l as the dominant assessed heavy metal in cultured catfish.

6.3 Recommendations

Based onthe findings in this study, the following are recommended.

1. The heavy metals in water samples of the two selected riverswhich all showed high concentrations than the WHO permissible limits should be monitored more closely and discharge points identified and regulated by relevant authorities. These are specifically Iron, Lead and Mercury, with mean concentration values of 2.87mg/l, 0.66mg/l, and 0.62mg/l, respectively.
2. A close monitoring of heavy metal pollution of Rivers Kaduna and Galma is strongly advocated, in view of the possible health implication to consumers of the fishes and other usersof these rivers.

3. Enlightenment on ways to collect and dispose of the mercurial based effluents to minimize contamination of river water should be advocated, as river water showed a mean high concentration value of 0.69mg/l, which is over six hundred times the recommended limit of 0.001mg/l.
4. Adequate monitoring of fishes, especially in the farms, which showed high mean concentration values of Fe (1.44mg/kg) and Mercury (0.13mg/kg) both above the FAO permissible limits of 1mg/kg and 0.1mg/kg, respectively, should beregularlycarried out by health officers.
5. With the comparatively lower concentrations of heavy metals, especially of Hg, Cd, and Ni, it is recommended that farm fish is relatively safe for human consumption, however, sources of Fe which measures between 0.94 mg/kg – 1.75 mg/kg should be closely monitored to avoid increase in iron contamination.
6. Detection of sources of heavy metals discharges in excess of WHO standards should be traced and such sources should be made to reduce their discharge to the barest minimal or be directed elsewhere where it will not influence the rivers.
7. Defaulters of the regulation should be made to pay heavy fines and/or penalties imposed.
8. Fish farms should deploy filters to reduce the infiltration of heavy metals on their farms.

REFERENCES

Abubakar, A., Uzairu, A., Ekwumemgbo, P.A. and Okunola, O.J. (2015). Risk Assessment of Heavy Metals in Imported Frozen Fish *Scomber scombrus* Species Sold in Nigeria: A Case Study in Zaria Metropolis,*Advances in Toxicology* Vol. 2(15):1 – 11.

Abubakar, A.J., Yusuf, S and Shehu, K. (2012). Heavy Metals Pollution on Surface Water Sources inKaduna Metropolis, Nigeria. *Science World Journal*, Vol. 10 (2): 1 – 5.

Abdul, K.M.D. and Singh, B. R. (1999). Heavy metal contamination of soil and vegetation in thevicinity of industries in Bangladesh. *Water, Air and Soil Pollution* 115: 347-361.

Adewumi, D.F., Daniyan, I.A., Adigun, K.A. and Adeodu, A.O (2015). Determination of Trace Metals in Fish, Water, and Sediments of Some Ponds in Ado, Ikere and Iyin Ekiti, Ekiti State, Nigeria, *Journal of Physical and Chemical Sciences,* 3 (2): 1 – 4.

Adewuyi, S. A., Phillip, B. B., Ayinde, I. A., and Akerele, D. (2010).Analysis of profitability of fish farming in Ogun State, Nigeria. *Journal of Human Ecology* 31(3):179-184.

Adelekan, B. A. and Abegunde K. D. (2011). Heavymetals contamination of surface, soil and groundwater atvillagestreams in Ibadan, Nigeria -*International Journal of the Physical Sciences* Vol.6(5): 1045-1058.

Agwu, M.O. (2012). Issues and Challenges of Solid Waste Management Practices inPortHarcourtCity, Nigeria- ABehavioural Perspective. *American Journal of Social and Management Sciences*, Vol. 3 (2): 83 – 92.

Aina, O. E. (2002). Solid water management in Zaria. Unpublished B.Sc. Project, Department of Geography, Ahmadu Bello University, Zaria.

Akhionbare, S.M.O. (2011). Factors in the migration ofHeavy metals in the OtamiriRiversystem.*International Journal of Science and Nature*, Vol.2(4): 856–860.

Akinbamijo O. B. (2000). Dynamics of Environmental Relationships: The Gender Route to Sustainable Living'. *Journal of Urban and Environmental Research*, Vol. 2 (1): 29 – 42.

Albretsen, J. (2006). The toxicity of iron, an essential element, *Veterinary Medicine* Vol. 10(2): 82 – 90.

Alinnor, J. and Obiji, I.A. (2010). Assessment of trace metal composition in fish samples from Nworie River. *Pakistan Journal of Nutrition*, Vol. 9 (1): 81 - 85.

Amadi, A.N., Okoye, N.O., Alabi, A.D., Tukur, A. and Angwa,E.M. (2014). Quality Assessment of Soil and Groundwater nearKaduna Refinery and Petrochemical, Northwest Nigeria. *Journal of Scientific Research & Reports* 3(6):885-893

Amin, A. M. (2006).Environmental Impact Assessment of Kaduna Refinery on the Rido Region of Kaduna Metropolis,Unpublished Ph.D. Thesis of the Department of Geography, Ahmadu Bello University, Zaria.

Amos, T.T and Bolorunduro, P.I (2000). Economics of Aquaculture Production. *Extension Bulletin* No 107Fisheries Series No. 5. National Agricultural Extension and Research Liaison Services, Ahmadu Bello University, Zaria, PP. 1 – 31.

Anetor, J.I., Adeniyi, F.A.A and Olaleye, S.B (2003). Molecular Epidemiology: ABetter Approachfor the Early Detection of Pathophysiologic Response to EnvironmentalToxicantsand Diseases.*African Journal of Biomedical Research*, Vol. 6: 113-118.

Annalee, Y., Kjellstrom, T., Dekok, T and Guidotti, T (1998).*Basic Environmental Health*. Office of Global and Integrated environmental Health. World Health Organization,Geneva, PP 24 – 78.

Annune, P.A. (1992). Effects of Cadmium and Zinc in Fresh WaterFish Species,*Clarias gariepinus* (Burch) and *Oreochromis niloticus* (Trewawas).Unpublished Ph.D. Thesis in the Department of Biological Sciences,Ahmadu Bello University, Zaria.

APHA (1998). *American Public Health Association: Standard methods for the examination of water and wastewater*. Washington, DC: American Public Health Association., 20, PP. 444-446, 466 – 471

ATSDR (2007). *Agency for Toxic Substances and Disease Registry*. 2007, from http://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=245&tid=44

Ayandiran,T.A., Fawole,O.O., Adewoye, S.O and Ogundiran, M.A. (2009).Bio-concentrationof Metals in the Body Muscle and Gut of Clarias gariepinus Exposedto Sublethal Concentrations of Soap and Detergent Effluent. *Journal of Cell and Animal Biology*, Vol. 3 (8): 113-118.

Ayres, D.C. andHellier,D.G. (1998). *Dictionary of environmentally important chemicals.*London, UK, PP. 98 – 117.

Bashir, F.H., Othman, M.S., Mazlan, A.G., Rahim, S.M. and Simon, K.D. (2013). Heavy metal concentration in fishes from the coastal waters of Kapar and Mersing, Malaysia. *Turkish Journal of Fisheries and Aquatic Sciences*, Vol.13 (2): 375–382.

Bashir, F.A., Shuhaimi-Othman, M and Mazlan, A.G (2012). Evaluation of trace metal levels in tissues of two commercialfish species in Kapar and Mersing coastal waters, Peninsular Malaysia, *Journal of Environmental and Public Health*, Vol.2: 10.

Bawa, L.M., Djaneye-Boundjou, G., Boyode, B.P. and Assih, B.T.(2007). Water qualityevaluationfrom Lomé's lagoon:Effects on heavy metals contamination on fishes. *Journal of Applied Science and Environmental Management*, 11(4): 33 – 36.

Billard, R. (2003). From polyculture to co-culture in fish-farming. In: Lee, C.S.(Ed.). *Aquaculture: retrospective and outlook – an aquaculture summit*, PP. 169-200

Botkin, D.B and Kelly, E.A (1998). *Environmental Science., Earth as a Living Planet*, 2nd Edition, John Wiley and Sons, USA, PP. 420-424.

Bradi, B.H. (2005). Heavy metalsintheenvironment.*Interface Science and Technology*, Vol. 6: 324 - 432.

Brown, F.M.J. and Walls, P.W. (1997). Trace metals in fish and shellfish from Scottish waters.*Scottish Fisheries Research Report* No. 60, Environment and Fisheries Department, The Scottish Office Agriculture.

Bury,N.R., Walker,P.A. and Glover,C.N. (2003). Nutritive metal uptake in teleost fish. *Journal of Experimental Biology*., 206: 11 – 23.

Butu, A.W. (2013). Concentration of Metal Pollutants in River Kubanni, Zaria, Nigeria.*Journal of Natural Sciences Research*, Vol.3 (2): 19 – 25.

Cangul, H., Broday, L., Salnikow, K., Sutherland, J., Peng, W., Zhang, Q., Poltaratsky, V., Yee, H., Zoeoddu, M.A and Costa, M. (2002). Molecular Mechanisms of Nickel Carcinogenesis. *Toxicology Letter*, 127: 67 – 76.

Chen,Y. and Chen, M. (2001).Heavy metal concentrations in Nine species of fishescaught incoastal waters off Ann-ping S.W.Taiwan. *Journal of Food and Drug Analysis*, 9(2): 219.

Christopher E., Vincent, O., Grace I., Rebecca, E. and Joseph, E. (2009). Distribution of Heavy Metals in Bones, Gills, Livers and Muscles of (Tilapia) *Oreochromis niloticus* from Henshaw Town Beach Market in Calabar, Nigeria. *Pakistan Journal of Nutrition*; 8:1209-1211.

Clemente, R., Dickinson, N.M and Lepp, N.W(2009).Mobility of metals andmetalloids in amulti-elementcontaminatedsoil20yearsaftercessationofthepollutionsourceactivity.*Environmental Pollution*, Vol. 155: 254 – 261.

Cole, S., Codling, I.D., Parr,W. and Zabel, T. (1999). Guidelines formanaging water quality impacts within UK European marine sites.Prepared by: WRC Swindon, Wiltshire SN5 8YF Prepared for the UK Marine SAC Project, PP. 422

Criselda R.A (2009). Total Mercury in Three Fish Species Sold in aMetro Manila Public Market: Monitoring and Health Risk Assessment. *Science Diliman*21(1):1-6.

Dan-AZumi, M. and Bichi, M.H. (2010).Industrialpollution and heavy metals profile of Challawa River in Kano, Nigeria. *Journal of Applied Sciences in Environmental Sanitation*, Volume 5 (1): 23-29.

Davies, B and Gasse, F. (1988). African wetlands and shallow waterbodies/Zones humides et lacspeu profonds d'Afrique.Bibliography/Bibliographie.Trav.Doc.Inst.Fr.*Research Science Development Cooperation*, (211): PP. 502

Denkhaus, E. and Salnikow, K. (2002). Nickel Essentiality, Toxicity and Carcinogenicity: Critical Review. *Oncology and Haematology Journal*, 42: 35 – 36.

DeZuane, J. (1997). *Handbook of Drinking Water Quality* (2nd Ed.). John Wiley and Sons, Ohio, USA, PP. 471-487.

Dimuna K.O.(2004). The Problem with the Managementof Environmental Pollution in Nigeria. *Journal of Applied and Basic Sciences*, 2(1&2): 5 – 9.

Dougherty, C.P., Hendricks, H.S., Reinert, I.C., Panyacosit, L., Axerald, D.A. and Woodruff, T.J. (2000). Dietary exposures to food contaminants acrossthe UnitedStates.*Environmental Research*, 84:170-185.

Duda-Chodak, A. and Blaszezyk, U. (2008). The Impact of Nickel on Human Health: Review Paper. *Journal of Elementology*, 13 (4): 685 – 696.

Dural, M., Goksu, L.M. andOzak, A.A. (2007). Investigation of heavy metal levels ineconomicallyimportantfish species captured from the Tuzla lagoon.*Food Chemistry*, 102: 415-421.

DWAF(1996). *South African Water Quality Guidelines: Domestic Uses*. 2nd.Ed. Department of Water Affairs and Forestry, Pretoria, Vol. 1. PP. 28-56.

Eletta, O.A., Adekola, F.A. and Omotosho, J.S. (2003). Determination of concentration of heavy metals in two common fish species from Asa River, Ilorin, Nigeria. *Journal of Toxicology and Environmental Chemistry*, 85 (1 – 3): 7 – 12.

El-Ghasham, A., Mehanna, E.E. and Abdel-Reheem, M. (2008). Evaluation of lead andcadmium levels in fresh water fish farms at Qassim region, *Journal of Agricultural and Veterinary Sciences*, Vol. 1, (2): 59–77.

Ellis, K.V., White, G. and Warn, A.E. (1989) *Surface water Pollution and its control*. London, The Macmillan Press Ltd, UK, PP. 100-101.

EPA (1993). Methods for Measuring the Acute Toxicity of Effluents and ReceivingWaters to Freshwater and Marine Organisms (4thEdition). Environmental Monitoring Systems Laboratory-CincinnatiOfficeOf Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. PP. 1 – 273.

Es'haghi, Z., Khooni, M.A.K. and Heidari, T. (2011). Determination of Brilliant Green from Fish Pond Water Using Carbon Nanotube Assisted Pseudo-Stir Bar Solid/Liquid Microextraction Combined with UV-Vis Spectroscopy-Diode Array Detection. *Spectrochimica Acta*, Part A, 79, 603-607.

Etim, E.U. (2012). PollutionAssessment of Ebute Meta Creek Impacted by Domestic Sewage, Lagos, Nigeria.*Research Journal of Environmental and Earth Sciences*, Vol. 4(8):769-775.

Etim, E.U. and Adie, G.U. (2012). Assessment of Qualities of Surface Water Sediment and Aquatic Fish from Selected Major Rivers in Southwest Nigeria. *Research Journal of Environmental and Earth Sciences,*Vol.4 (2012):1045-1051.

Ezeribe, A.I.,Oshieke, K.C.andJauro, A. (2012). Physico-chemical properties of well watersamples from some villages in Nigeria withcases of stained and mottle teeth. *Science World Journal* Vol. 7 (No 1): 67 – 75.

Fakayode, S.O. (2005). Impact of industrial effluents on water quality of the receiving Alaro River in Ibadan, Nigeria. *Ajeam-Ragee*, 10: 1-13.

FAO (2014). Cultured Aquatic Species Information Programme: *Clarias gariepinus* (Burchell, 1822). *FAO Technical Report*.

FAO (2012).Quality Control of Wastewater for Farming and Irrigated Crop production.*Water Reports*, Vol. 10: 1 – 56.

FAO (2007). The State of World Fisheries and Aquaculture 2006. *FAO Technical Report*.

FAO (2003).*Heavy Metals Regulations: Part 1*. Legal Notice no. 66, 2003, from http://www.faolex.fao.org/docs/pdf/eri42405.pdf.

Farouk, B.B.A. (1997).Water quality and uses of some surface water bodies in Kano metropolitan area.An unpublished B.Sc. Geography Dissertation, Bayero University Kano.

Fernandez, L.G. and Olalla, H.Y. (2000). Toxicity and bioaccumulation of lead and cadmium in marine protozoan communities", *Ecotoxicology and Environmental Safety*, Vol. 47: 266-276.

Fraga C.G. and Oteiza, P.I. (2002). Iron toxicity and antioxidant nutrients. *Toxicology*., 180: 23–32.

Franchini, M. (2006). Hereditary iron overload: update on pathophysiology, diagnosis, and treatment. *American Journal of Haematology*., 81: 202–9.

Froese, R. and Pauly, D. (2017). *FishBase,World Wide Web electronic publication*.www.fishbase.org

Galadima, A. and Garba, Z.N. (2012). Heavy metals pollution in Nigeria: causes and consequences. *Elixir Pollution* 45: 7917-7922.

Galadima, A., Garba, Z. N., Leke, L., Almustapha, M. N. andAdam, I. K. (2011). Domestic Water Pollution among LocalCommunities in Nigeria – Causes and

Consequences.*European Journal of Scientific Research* ISSN 1450-216X Vol.52 No.4: 592-603.

Galadima, A, and Garba, Z.N. (2011) *Recent Issues in Environemntal Science: Including incidences and reports from Nigeria*. Lap, Lambert Academic Publishers, Germany, ISBN: 978-3-8454-2915-1, PP. 1-100.

Galadima, A., Muhammad, N.U. and Garba, Z.N. (2010). Spectroscopic investigation of heavy metals in waste water fromUniversity students' halls of residence. *International Journal of Chemistry,* Vol. 20 (4): 239-244.

Gbem, T.T., Balogun, J.K., Lawal,F.A. and Annune, P.A. (2001). Trace metal accumulation in *Clarias gariepinus* (Tuegels) exposed to sublethal levels of tannery effluent. *Journal of Science and Total Environment.* 271: 1-9.

Gebremedhin, K. and Berhanu, T. (2015). Determination of some selected heavy metals in fishandwater samples from Hawassa and Ziway Lakes. *Science Journal of Analytical Chemistry*, Vol. 3(1): 10 – 16.

Goldstein, R.S. and Hewitt, R.W. (1990). *Toxic Interactions*, 1st Edition, New York, Academic Press, U.S.A: 211 – 234.

Grazuleviciene, R., Nadisauskiene, R., Buinauskiene, J. and Grazulevicius, T. (2009). Effects of elevated Levels of Manganese and Iron in Drinking Water on Birth Outcomes. *Polish Journal of Environmental Studies*, Vol. 18 (5): 819 – 825.

Güven, K., Ozbay, C., Unlu, E. and Satar, A. (1999). Abiotic and Biotic Factors Influencing In-situ Trace Metal Levels in Macroinvertebrates in Freshwater Ecosystems. *Japan Marine Fishery Resource Research Center*, Tokyo, Japan. PP. 519.

Hajeb, P., Jinap, S., Ismail, A., Fatimah, A.B., Jamilah, B. and Abdul Rahim, M.(2009). Assessment of mercury level in commonly consumed marine fishes in Malaysia. *Food Control*, Vol.20 (1): 79–84.

Horsfall, M. J. (2001).*Advanced Environmental Chemistry* 1stEd.La-Limesters PrinterPort Harcourt, Nigeria. PP. 130 – 159.

Huang,W.B. (2003).Heavymetalconcentrationsinthe common benthic fishes caught from the coastal waters of eastern Taiwan. *Journal of Food & Drug Analysis*,11(4):324 – 330.

Hussain, T. (1991) Study of environmental pollutants in and around the city ofLahore, *International Journal of Applied Chemistry,* Vol. 2 (1): 45-54.

Ibeto, C.N. and Okoye, C.O.B. (2010). High levels of Heavymetals in Blood of Urbanpopulationin Nigeria. *Research Journal of Environmental Sciences*, 4(4): 371-382.

Ibrahim, M. F. (2010). Quality of life of residents living near industrial estates in Kaduna, Kaduna State, Nigeria. *Social Indicators Research*, 61 (2): 203–225.

Ikema, A.andEgieborb, N. (2005). Assessment oftraceelementsincannedfishes (mackerel, tuna,salmon,sardinesandherrings)marketedinGeorgiaandAlabama(UnitedStatesofAmerica).*Journal of Food Composition and Analysis*, 2005, Vol. 18: 771-787.

Iguisi, E.O., Funtua,I.I and Obamuwe, O.D, (2001) A Preliminary Study of heavy metalconcentration in the surface water of the Kubanni Reservoir, Zaria. *Nigerian Journal of Earth Science* 1: 26-36.

Igwemmar, N. C., Kolawole, S. A and Odunoku, S. O. (2013) Heavy Metal Concentration in Fish Species Sold In Gwagwalada Market, Abuja.,*International Journal of Science and Research* (IJSR): 2319-7064.

Imam,T.S and Balarabe,M.L.(2012).Impactof Physico-chemical factorson zooplankton species richness and abundance in Bompai-Jakara catchment basin, Kano State,Northern Nigeria. *African Journals Online*, http://dx.doi.org/10.4314/bajopas.v5i2.6.

Isyagi, N.A., Veverica, K.L., Asiimwe, R. and Daniels, W.H. (2009). Manual for the commercial pond production of the African catfish in Uganda. *USAID-FISH Project*. PP. 251.

Jafari N.G. and Gunale, V.R (2006). The comparison of heavy metal concentrations (Cd, Cu, Mn, Pb, and Zn) in tissues of three economically important fish (*Anguilla anguilla, Mugil cephalus* and *Oreochromis niloticus*) inhabiting Koycegiz Lake-Mugla (Turkey), *Journal of Applied Sciences. Environmental Management* Vol 10: 153 – 158.

Jaffer, M., Ashraf, M and Rasoal, M.A. (1988). Heavy metals contents in some selected local freshwater fish and relevant water. *Pakistan Journal of Science and Industrial Research*, 31:189-193.

Jaishankar, M., Tseten, T., Anbalagan, N., Matthew, B.B. and Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals, *Interdisciplinary Toxicology*, Vol. 7 (2): 60 – 72.

Jobling, M. (1994). *Fish Bioenergetics*. Chapman and Hall, London, PP. 267-284.

KASUPDA - Kaduna State Urban Planning and Development Agency (2013) About Kaduna State from http://www.kasupda.org.ng/aboutkadunastate/watersupply.html

KEPA (1998). Effluent Limitation and Management. Regulation No. 2& 3 1998 – Control of Water Pollution Sources. Kaduna State Environmental Protection Agency.

Kolo, R.J. and Oladimeji, A.A. (2004). Water quality and some nutrient levels in Shiroro Lake Niger State. Nigeria. *Journals of Aquatic Sciences*, Vol. 19(2): 99.

Kudi, T. M., Bako,P. F., and Atala, T. K. (2008). Economics of fish production in Kaduna State Nigeria. *ARPN Journal of Agricultural and Biological Science* 3(5 & 6):17-21

Kumar, J.S.S. (2004).*Management of super-intensive farming of African catfish*. A publication by the Technical Services Division,Animal Care Konsult. Nigeria, PP. 5 – 17.

Kwaansa Ansah, E. E. (2012). Effect of pH, Sulphate concentration and total organic carbon on mercury accumulation in sediments in the Volta Lake at Yeji, Ghana. *Bulletin of Environmental Contamination and Toxicology*, 88:418.

Kyoung-Woong, K. (2010). Heavy Metals in Frozen and Canned Marine Fish of Korea. *Journal of Scientific Research*: Vol. 2 (3): 549 – 557.

Ladigbolu,I.A and Balogun,J.K. (2011). Distribution of HeavyMetalsinSedimentsofSelectedStreams in Ibadan Metropolis, Nigeria.*International Journal Of Environmental Sciences,*Vol. 1 (6): 11-20.

Ladipo, M.K., Ajibola, V.O and Oniye, S.J. (2011). Seasonal Variations in Physico-chemical Properties of Water in Selected Locations of the Lagos Lagoon, *Science World Journal*, Vol. 6 (No. 4): 5 – 12.

Lenntech (2014). Heavy Metal, from: http://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.html

Lim, H., Lee, J., Chon,H. and Sager,M. (2008). Heavy Metal Contamination and Health Risk Assessment in the Vicinity of the AbandonedSong-cheon Au-Ag Mine in Korea.*Journal of Environmental and Geochemical Exploration*, Vol. 96 (2): 223 – 230.

Linnik, P.M. and Zubenko, I.B. (2000). Role of bottom sediments in the secondary pollution of aquatic environments by heavy metal compounds" Lakes and Reservoir: *Research and Management*, Vol. 5: 11-21.

Little, D.C. and Edwards, P. (1999). Alternative strategies for livestock-fish integration with emphasis on Asia. *Ambio*, Vol. 28:118-124.

Manutsewee, N., Aeungmaitrepirom, W., Varanusupakul, P. and Inyim, A. (2007). Determination of Cd, Cu, and Zn in Fish and Massed by AAS after Ultrasound Assisted Acid Leaching Extraction. *Food Chemistry*, 2007 101: 817 - 824

Malik, B.N. (2004). Metal Bioremediation through Growing Cells, *Environment International*, 30 (2): 261-278.

Merz, S.K.(2006).*Hart Lagoon*. Available online: http:\WCMS\Wc02647\600-Reporting\REPORTS\FinalReports\Volume1\RMWBS_Vol1_Data8.doc, PP.309.

Mieiro, C.L., Coelho, J.P., Pacheco, M., Duarte, A.C. and Pereira, M.E. (2012). Trace elements in two marine fish species during estuarine residency: non-essential versus essential. *Marine Pollution Bulletin,* Vol.64 (12): 2844–2848.

Molina, V.B. (2011). Health Risk Assessment of Heavy MetalsBioaccumulation in Laguna De Bay Fish Products, Philippines. Being a paper presentation at the *14th World Lake Conference,* Austin Texas, 1 – 23.

Mumba, P., Phiri, O., Moyo, B.H.Z. and Kadewa, W. (2005). Assessment oftheimpact of industrial effluents onwater quality of receiving rivers in urban areas of Malawi. *International Journal of Environmental Science and Technology*,Vol. 2 (3): 237-244.

Murray, M. and Holmes,S.A. (2004).Assessmentof mercury emissions inventoriesfor the Great Lakes states, *Environmental Research*, 95 (3): 282–297.

National Research Council of Canada - NRCC (2011). Effect of Sodium and Potassium in the Canadian Environment. NO. 150154. Associate Committee on Scientific Criteria forEnvironmental Quality Ottawa.

Ngumbu, R.S. (2014).Exposure of the Population of Monrovia to Heavy Metals through Fish Consumption. Unpublished MSc Thesis submitted to the Department of Chemistry, Kwame Nkrumah University of Science and Technology.

Nnaji, C.J., Uzairu, A., Harrison, G.F.S. and Balarabe, M.L. (2011). Effect ofPollution on the Physico-Chemical Parameters of Water andSediments of River Galma, Zaria, Nigeria. *Research Journal of Environmental Earth Science,* Volume 3(4): 314-320

Nnaji, J.C., Uzairu, A., Harrison, G.F.S. and Balarabe, M.L. (2007). Evaluation ofCadmium, Chromium, Copper, Lead And Zinc Concentrations in the Fish Head/Viscera of *Oreochromis Niloticus* and*Synodontis Schall* of River Galma, Zaria, Nigeria, *Ejeafche,* 6 (10): 2420-2426.

NPC - National Population Commission (2006).*Nigerian Demographic and Health Survey 2006*, Calverton, Maryland.

Nubi, O.A., Oyediran, L.O. and Nubi, A.T. (2011). Inter-annual trends of heavy metals in marine resources from the Nigerian territorial waters. *African Journal of Environmental Science and Technology*, 5: 104-110.

Nubi, O.A., Osibanjo, O. and Nubi, A.T. (2008). Impact assessment of dumpsiteleachate on thequalities of surface water and sediment of river Eku,Ona-Ara local government, Oyo State, Nigeria. *Scientific World Journal*, Vol. 3(3): 17 – 20.

Nussey,G., VanVuren, J.H.J. and Du Preez, H.H. (2000). Bioaccumulation of Chromium, Manganese, Nickeland Lead in the tissues of the Moggel, *Labeoumbratus* (*Cyprinidae*), from Witbank Dam, Mpumalanga, South Africa. *WaterS.A.*Vol.26 (2): 269-284.

Nwachukwu, M.A., Feng, H. and Achilike, K. (2010). Integrated study for automobile wastes managementand environmentally friendly mechanic villages in theImo River basin, Nigeria. *African Journal of Environmental Science and Technology*, Vol. 4(4): 234-249.

Nwaedozie, J.M. (1998). The determination of heavy metal pollutants in fish samples from Kaduna river, *African Journal of Biotechnology*. Nigeria, Vol. 23: 21 - 23.

Obasohan, E. E. and Eguavoen, O.I. (2008). Seasonal variations of bioaccumulation of heavy metals ina freshwater fish (*Erpetoichthys calabaricus*) from Ogba River, Benin City, Nigeria. *African Journal of General Agriculture*., 4 (3): 153 – 164.

Obasohan, E. E. (2008). Bioaccumulation of chromium, copper, maganese, nickel and lead in a freshwater cichlid, *Hemichromis fasciatus* from Ogba River in Benin City, Nigeria. *African Journal of General Agriculture*., 4:141-152.

Obasohan, E.E.A., Oronsaye, A.O. and Obano, E.E. (2006). Heavy metal concentration in *Malapterurus electricus* and *Chrysichthys nigrodigitus* from Ogba in Benin City, Nigeria. *African Journal of Biotechnology*. Nigeria, 5: 974 – 982.

Offem, B.O., Yemi, A.S. and Omoniyi, I.T. (2010). Aspects of Ecology of Clarias in the Cross River, Nigeria. *Turkish Journal of Fisheries and Aquatic Sciences* 10: pp. 101-110.

Offem, B.O. and Ayotunde, E.O. (2008).Toxicity of leadto fresh waterinvertebrates (water fleas., *daphnia* and *cyclop sp*.)in fish ponds in atropical floodplain", *Water, Air Soil Pollution*, Vol. 192: 39 – 46.

Oforka, N.C., Osuiji, L.C. and Onwuachu, U.I. (2012). Estimation of Dietary intake of cadmium, lead, manganese, zinc and nickel due to consumption of chicken meat by inhabitants of Port-Harcourt Metropolis, Nigeria. *Archives of Applied Science Research*., 4:675-684.

Ogoyi, D.O., Mwita, C.J, Nguu, E.K. and Shiundu, P.M. (2011). Determination of Heavy Metal Content in Water, Sediment and Microalgae from Lake Victoria, East Africa. *The Open Environmental Engineering Journal*, Vol.4: 156-161.

Oguzie, F.A. (2003). Heavy metals in Fish, Water and Effluents of Lower Ikpoba River in Benin City, Nigeria.*Pakistan Journal of Science and Industrial Research*, Vol. 46(3): 156-160

Olaifa, F.E., Olaifa, A.K., Adelaja, A.A. and Owolabi, A.G. (2010). Heavy metal contamination of *Clarias gariepinus* from a lake and Fish farm in Ibadan, Nigeria. *African Journal of Biomedical Research*, Vol.7 (3):,145–148.

Olatunji, O.S. and Osibanjo, O. (2012). Determination of selected heavy metalsin inland fresh waterof lower River Niger drainagein North Central Nigeria, *African Journal of Environmental Science and Technology*,Vol. 6(10): 403-408

Olayinka, K.O. (2004). Studies on industrial pollutionin Nigeria: The effectof textileeffluentson the quality of groundwater in some parts of Lagos. *Nigeria Journal of Health and Biomedical Science*, Vol.3, pp. 44-50.

Oluyemi, E.A. and Olabanji, I.O. (2011). Heavy metals determination in some species of frozen Fish Sold at Ile-Ife main market. *Ife Journal of Science*, Vol.13 (2): 86–93.

Onianwa, P.C.(2001). Roadside topsoil concentrations of lead and other heavy metals in Ibadan, Nigeria. *Soil Sediment Contamination*, 10: 577-591.

Oniye, S.J., Ega, R.A., Ajanusi, O.J. and Agbede, R.I.S.(2002). Some aspects of the Physico-chemical parameters of Zaria Dam, Nigeria. *Journal of Agriculture and Environmental Sciences*, Vol. 11(2): 367 – 379.

Onome, A.D; Charles, C.T. and Keme-Iderikumo, K. (2013). Length-Weight Relationship, Condition Factor and Sex Ratio of *Clarias gariepinus* Juveniles Reared in Concrete Tanks. *International Journal of Scientific Research in Environmental Science (IJSRES).* Vol. 1(11): 324-329.

Orisakwe, O.E. (2009). Environmental Pollution and Blood Lead Levels in Nigeria: Who is Exposed? *International Journal of Occupational and Environmental Health*, 15 (3):315-317.

Ovie, S.I. and Adeniji, H.A. (1993). Zooplanktonenvironmental characteristics of Shiroro Lake at the extreme of its hydrological cycle. *Hydrobiologia*, Vol. 286: 175-182.

Owamah, H.I. (2013). Heavy Metals Determination and Assessment in a Petroleum Impacted River and Groundwater intheNigerDelta Region of Nigeria,*Journal of Petroleum and Environmental Biotechnology*, Vol. 4(1): 92 – 104.

Oze, O., Oze, R., Anunuso, C., Ogukwe, C., Nwanjo,H. and Korie, K. (2006).Heavy Metal Pollution of Fish of Qua-Iboe River Estuary: Possible Implications for Neurotoxicity. *The International Journal of Toxicology*, Vol. 3(1): 132 – 143.

Pearce, G.R., Chaudhry, M.R. and Ghulum, S. (1999). DFID: *A Simple Methodology for Water Quality Monitoring*, Department for International Development Report, Wallingford, pp. 100.

Phelps, R.P. and Popma, T.J. (2000).Sex reversal of tilapia. In: B.A Costa-Peirce and J. E. Rakocy (eds). *Tilapia Aquaculture in Americas*. The World Aquaculture Society, Bato Rouge, Louisiana, United States. 2:34-59

Phippen, B., Horvath, C., Nordin, R. and Nagpal, N. (2008). *Ambient water guidelines for iron: Overview*, Ministry of Environment, Province of British Columbia., 2008.

Rao, P.V. (2005). *Textbook of environmental engineering*.Eastern Economy Ed., Prentice-Hall of India Private Limited, New Delhi, PP. 280.

Rashimi, R.K., Tripathi, R.M. and Gupta, A.K. (2008). Seasonal Variation of heavy metal concentration in water of River Yamuna, Allahabad, Uttar Pradesh, India, *International Journal of Current Microbiology and Applied Sciences*, 3 (7): 945-949.

Rice, D. and Barone, Jr., S.(2000). Critical Periods of Vulnerability for the Developing Nervous System: Evidence from Humans and Animal Models. *Environmental Health Perspectives*, 108, 511-533.

Sachchida, N., Singhi,G.S. and Arunbhat, S. (2011). Physico-chemical Analysis of Different water Samples used for drinking Water Purpose in Delhi and Calcutta, India.*International Journal of Biotechnology*, Vol. 70 (5): 617-621.

Sakai, S., Isu, B.A. and Kofoworola, O. F. (1996). "World Trends in Municipal Solid Waste Management." *Waste Management* Vol. 16 (5/6): 341 – 350.

Samaila, K.I., Marcus, N.D. and Momale, S.B. (2011).**Efficient Management of Resources: Wastewater Application in Dry Season Farming in Kaduna Urban Area Nigeria**. *Agricultural Journal*, 2011, Volume: 6 (4): 188-193.

Samuel, P.O., Adakole, J.A. and Suleiman, B. (2015). Temporal and Spatial Physico-Chemical Parameters of River Galma, Zaria, Kaduna State, Nigeria. *Resources and Environment*, Vol. 5(4): 110 – 123.

Silbergeld, E.K. (1996). Getting Ahead of Lead, *Forum for Applied Research and Public Policy*, 11: 48-54.

Sivaperumal, P., Sankar,T. andViswanathan,P. (2007). Heavy metalconcentrations in fish, shellfish and fish product from internal markets of Indiavis-a-vis international standards. *Food Chemistry*, Vol. 102: 612-620.

Snyder, B.D. (1990). Methyl-mercury uptake and distribution kinetics in sheepshead minnows,*Cyprinodon variegatus*,afterexposuretoCh$_3$Hg-spiked food.*Environmental Toxicology and Chemistry*, 23(9), 2138–2146.

Sodoumou,Z.,Gnassia-Barelli,M.,Siau, Y.,Morton,V.andRomeo,M.(2005). Distribution and concentration of trace metals in tissues of different fish species from the Atlantic coast of western Africa. *Bulletin of Environmental Contaminants and Toxicology*; 74:988-995.

Spiegel, S.J. and Farmer, J.K. (1985). Heavymetalcontamination in Municipal wastetreatment plantsludge,*Bulletin of Environmental Contamination and Toxicology*, Vol. 35: 238-243.

Sunderman, F.W. (1993). Biological monitoring of Nickel in humans.*Scandinavian Journal of Work and Environmental Health*, 19: 34-38.

Suski, C.D., Killen, S.S., Keiffer, J.D. and Tufts, B.L.(2006). The influence of environmental temperature and oxygen concentration on the recovery of largemouth bass from

exercise. Implications for live-release angling tournaments. *Journal of Fish Biology*, Vol. 68: 120 – 136.

Tariq, J., Ashraf, M., Jaffar, M. and Afzal, M. (1996). Pollution Status of the Indus River,Pakistan, through HeavyMetal and Macronutrient contents of Fish, Sediment and Water. *Water Research*, Vol. 30(6): 1337-1344.

Tawari-Fufeyin, P. (1998). Heavy metal levels in some dominant fish of Ikpoba reservoir Benin City, Nigeria. *Journal of Environmental Health*. Vol. 2 (2): 61 – 69.

Thilza, I.B. and Muhammad, T. (2010). The Effects of Management Practices on the Physical and Chemical Water Qualities and Its Possible Implications on Fish Health in Maiduguri Metropolis.*Researcher*, Vol. 2(11): 15 – 23.

Udiba U. U., Gauje, B., Ashade N.O., Ade-Ajayi F.A., Okezie V. C., Aji B.M. and Agboun, T. D. T. (2014). An assessment of the heavy metal status of RiverGalma around Dakace industrial layout, Zaria, Nigeria. *Merit Research Journal of Environmental Science and Toxicology*, Vol. 2(8): 176-184.

USEPA (United States Environmental Protection Agency) (2009).*Supplemental guidance for assessing susceptibility from early-life exposure to carcinogens.*Washington DC, U.S.A.126 from http://www.epa.gov/cancerguidelines/guidelines-carcinogen-supplement.html

USEPA (United States Environmental Protection Agency) (2005). Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume 1, *Fish Sampling and Analysis 3rd Edition*, Office of Science and Technology of Water, Washington, DC EPA 823-B-00-007: 1-200.

USFDA (1993). United States Food and Drug Administration, *Guidance Document for Chromium in Shell Fish*. DHHS/PHS/FDA/CFSAN/Office of Seafood, Washington DC.

Uzairu, A., Harrison, G.F.S., Balarabe, M.L. andNnaji, J.C. (2009). Concentration levels of trace metalsin fish and sediment from Kubanni River, Northern Nigeria. *Bulletin of the Chemical Society of Ethiopia*, Vol.23 (1): 9–17.

Vesiland, P.A., Peirce, J.J. and Weiner, R.F. (1990). *Environmental Pollution and Control*, Burtonworth, Heinemann Publishers, USA, PP. 389

Voegborlo, R.B. and Adimado, A.A. (2010). A simple classical wet digestion technique for the determination of total mercury in fish tissue by cold-vapour atomic absorption spectrometry in a low technology environment. *Food Chemistry*., 123:936-940.

Voegborlo, R.B., Akagi, H., Matsuyama, A., Adimado, A.A. and Ephraim, J.H. (2006). Total Mercury and Methylmercury Accumulation in the Muscle Tissue of Frigate (*Auxis thazard thazard*) and Yellow Fin (Thunnus albacores) Tuna from the Gulf of Guinea, Ghana. *Bulletin of Environmental Contamination and Toxicology*, 76 (5): 840-847.

Vuori, K.M. (1995). Direct and Indirect effects of iron on river ecosystems. *Annal Zoo Fennici*, Vol. 32: 317 – 329.

Wade, T.L., Sweet, S.T. and Klein A.G. (2008). Accumulation of Toxic Trace Elements by Freshwater Fishes. *Environmental Pollution*, Vol. 152 (3): 505 – 521.

WHO (World Health Organization) (2012). Potential Pollutants, their Sources and their Impacts. Guideline for Drinking Water quality (electronicResource). Incorporating first Addendum 1, Recommendations-3 from http://www.whglibdoc.who.int/publications/2006/9241546964.eng.pdf

Yilmaz, A.B. (2003). Levels of heavy metals (Fe,Cu,Ni,Cr,Pb,andZn) in tissue of *Mugil cephalus* and *Trachurus mediterraneus* from Iskenderun Bay, Turkey. *Environmental Research*, Vol.92 (3): 277–281.

Zeb, B.S., Malik, A.H., Waseem, A. and Mahmood, Q.(2011).Water quality assessment of Siran river, Pakistan. *International Journal of Physical Sciences*, Vol. 6: 7789 –7798.

Zhuang, P., Li, Z.A., McBride, M.B., Zou, B. and Wang, G. (2013). Health risk assessment for consumption of fish originating from ponds near Dabaoshan mine, South China. *Environmental Science*., 118:422-429.

Zukowska, J. and Biziuk, M. (2008).Methodological evaluationofmethod fordietary heavy metalintake, *Journal of Food Science*, Vol. 10: 1 – 9.

Appendix I

WHO Recommended Limits of Physico-chemical Parameters for Water

Physico-Chemical Parameters	WHO Limits
pH	6.5 - 8.5
Temp (^{o}C)	30 - 36
DO (mg/l)	10
Turbidity (NTU)	5
BOD (mg/l)	20 - 40
TDS (mg/l)	500
EC (µs/cm)	1000
Colour (Units)	5
Taste	Unobjectionable
Odour	--
Hardness - CaCO3 (mg/l)	0.001
Ammonia (ppm)	0.3
COD (mg/l)	10
Total Suspended Solids	580

(WHO, 2012)

Appendix II

WHO Permissible Limits of Heavy Metals for Water

Heavy Metals	WHO Limits (mg/l)
Manganese (Mn)	0.1
Copper (Cu)	5
Zinc (Zn)	75
Calcium (Ca)	50
Magnesium (Mg)	200
Sulphate (SO4)	0.5
Chloride (Cl)	50
Fluoride (F)	1.5
Nitrate (NO3)	500
Magnesium + Sodium Sulphate	0.2
Hydrogen Sulphide (H2S)	0.05
Phenols	0.5
Iron (Fe)	0.3
Lead (Pb)	0.01
Nickel (Ni)	0.02
Cadmium (Cd)	0.003
Mercury (Hg)	0.001
Arsenic (As)	0.5
Selenium	0.01
Chromium (Cr)	0.05
Cyanide	0.01
Aluminium (Al)	0.2
Barium (Br)	0.1

(WHO, 2012)

Appendix III

FAO Threshold Limits of Heavy Metals for Fish

Heavy Metals (mg/l)	FAO Limits (mg/kg)
Cadmium (Cd)	0.5
Chromium	0.2
Copper	30
Iron (Fe)	0.5
Lead (Pb)	0.3
Mercury (Hg)	0.1
Nickel (Ni)	0.5 - 0.6
Arsenic	0.026
Tin (Sn)	156
Zinc	30

(FAO, 2012)