HEAVY METAL CONCENTRATIONS IN WATER , *Clarias gariepinus* and *Tilapia guineensis* FROM AGODI LAKE IN IBADAN.

BY

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Certification

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Dedication

This research work is dedicated to God almighty who has been my help in ages past and who is my hope in years to come.

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LINDA KELECHI UKACHUKWU

ABSTRACT

The presence of heavy metals in food remains an issue of public health concern. At low concentrations above threshold limit, they are poisonous and can lead to toxicity in humans. Several studies have assessed heavy metals concentration in water and fish from different lakes but there is paucity of information on Agodi lake in Ibadan, a recipient of treated effluent from the sewage treatment facility of the University College Hospital (UCH) and also a source of drinking water and fish for human consumption. The study was therefore designed to assess the concentration of heavy metals in water and two fish species (*Clarias gariepinus* and *Tilapia guineensis*) from the lake.

A laboratory based study was adopted. Fish and water samples were collected weekly at different locations from Agodi lake for four consecutive weeks between June and July, 2009 and analysed for physicochemical parameters using the American Public Health Association (APHA) standard method. The parameters included, pH, dissolved oxygen (DO), lead, cadmium, chromium, zinc and copper. At each sampling, six fish were randomly collected per specie. The body weight and length of each sample were measured, dissected and liver, gill, skin and muscle tissues were removed for analysis. The tissue samples were oven dried at 110 ^{0}C and homogenised. The homogenised tissue samples were acid digested and analysed for heavy metals using Atomic Absorption Spectrophotometer. Results obtained for heavy metal concentration were compared with National Guideline Limits (NGL), Standard Organisation of Nigeria (SON) and World Health Organisation (WHO) guideline limits. Descriptive statistics, t-test and ANOVA were used for the data analysis.

The mean pH and DO levels in water were 7.20 ± 0.31 and 4.39 ± 2.08 mg/L respectively. The mean concentrations (mg/L) of heavy metals in water were: 0.01±0.01 (cadmium) ; 0.01 ± 0.01 (chromium); 0.02 ± 0.01 (copper); 0.04±0.01 (zinc); 0.06±0.04 (lead). These were within SON and WHO permissible limit except Lead (Pb) which was above 0.01 mg/L and 0.05 mg/L limits respectively. The heavy metal with the highest concentration found in both fish species was Zinc and the one with the least concentration was Cadmium. The mean concentrations (mg/kg) of heavy metals in cat fish were, 0.73±0.25 (cadmium) ; 4.8 ± 0.34 (chromium) ; 7.51±1.8 (lead) ; 17.62±0.27 (copper) ; 119.22±0.51 (zinc) while those of tilapia fish were, 0.48 ±0.22 (cadmium); 3.57±1.13 (chromium); 7.91 ± 1.69 (lead); 17.37±0.34 (copper) ; 176.82±0.27 (zinc). All heavy metals assessed in fish were above WHO and National guideline limits. There was no significant difference in concentrations among heavy metals within each fish specie and no significant difference in heavy metals between species except zinc ($p<0.05$).

The release of heavy metals into Agodi lake has increased the risk of its use as source of water for human activities and the consumption of resident fin-fishes. The need for adoption and enforcement of appropriate monitoring and management strategies for the protection of the lake is therefore important.

Keywords: Heavy metals, Surface water pollution, Bio-accumulation, *Clarias gariepinus*, *Tilapia guineensis*

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CHAPTER ONE

1.0 INTRODUCTION

Metallic elements are environmentally ubiquitous, readily dissolved in and transported by water, and readily taken up by aquatic organisms (Alam *et al.,* 2002). Heavy or toxic metals are trace metals that are at least five times denser than water. They generally do not break down further into less harmful constituent; and accumulate where they are released (Kennicutt *et al.,* 1992). As such, they are stable (cannot be metabolized by the body) and bio-accumulative. They are sometimes passed up the food chain to humans (Fergosson, 1990). Some metals are essential to biota but could be very harmful when present in excessive concentration. Heavy metals are non-degradable and very harmful to plants, aquatic organisms and human health at certain level of exposure (Mustafa and Nilgun, 2006). At low levels, some heavy metals, such as copper or cobalt, are essential for enzymatic activity, but act as enzyme inhibitors at higher concentrations. Other metals, such as cadmium and lead, have no known essential role in living organisms, and are toxic even at low concentrations (Bryan, 1976). Heavy metals can be classified as potentially toxic; such as arsenic, cadmium, lead, mercury, etc., probably essential; such as nickel, vanadium, cobalt and essential; such as copper, zinc, iron, manganese (Kheradmand *et al.*, 2006).

In recent years, the need for a better understanding of heavy metal concentration and dispersion patterns in aquatic environments has been highlighted following the discovery of high levels of toxic heavy metals (particularly cadmium and lead) in fish and other living organisms (McConchie *et al.*, 2008). Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota, which generally exist in low levels in water and attain considerable concentration in sediments and biota (Camusso *et al.*, 1995). Heavy metals including essential and non-essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have the potential to be toxic to living organisms (Storelli *et al.*, 2005).

Fish, which is often at the top of the aquatic food chain concentrate large amount of these metals from the surrounding waters. Fishes are important and the largest groups of vertebrates in the aquatic system and heavy metals can be accumulated via both food chain and water (Gibson, 1994). Fishes have been considered good indicators for heavy metal contamination in aquatic systems because they occupy different trophic levels with different sizes and ages (Burger *et al*., 2002). Fish can be considered as one of the most significant indicators in freshwater systems for the estimation of metal pollution level (Rashed, 2001). In addition, fishes are widely consumed in many parts of the world by humans, and polluted fish may endanger human health.

Studies on heavy metals in rivers, lakes, fish and sediments (Özmen *et al.*, 2004; Begüm et al., 2005; Öztürk *et al.*, 2008; Praveena *et al.*, 2008) have been a major environmental focus especially during the last decade. The human body has need for approximately 70 friendly trace elements including heavy metals, but there are 12 poisonous heavy metals, such as lead, mercury, aluminium, arsenic, cadmium, nickel, chromium, etc., that act as poisonous interference to the enzyme systems and metabolism of the body. It is important to continuously monitor the levels of heavy metals in aquatic environments as the presence of metal pollutants in fresh water is known to disturb the delicate balance of the aquatic ecosystem. Furthermore, fishes are notorious for their ability to concentrate heavy metals in their muscles and since they play important role in human nutrition, they need to be carefully screened to ensure that unnecessary high level of some toxic trace metals are not being transferred to man through fish consumption (Adeniyi and Yusuf, 2007). *Clarias gariepinus* and *Tilapia guineensis* are among the most commonly harvested and consumed fresh water fish species in tropical waters. There is therefore a need for regular monitoring of the quality to prevent heavy metal contamination and bioaccumulation along the food chain.

In an aquatic environment, dissolved oxygen, hardness, pH, alkalinity and temperature have been reported to influence metal toxicity (Adhikari *et al*., 2006). Nsikak *et al*., (2007) also reported that accumulation of heavy metals is influenced by the length and weight of fish while Haffor and Al-Ayed (2003) identified time of exposure to heavy metals as another factor.

1.1 Statement of Problem

Among environmental pollutants, heavy metals are of particular concern; due to their potential toxic effect and ability to bio- accumulate in aquatic ecosystems (Censi *et al.*, 2006) thus, the pollution of the aquatic environment with heavy metals has become a public health problem worldwide during recent years. Heavy metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage as well as threat to human health (Van de Broek *et al.*, 2002; Gagnaire *et al.*, 2004). Studies have shown that fish accumulate these heavy metals from the surrounding water bodies thereby leaving a health risk if taken as food (Prusty, 1994; US.DPHHS, 2005). Heavy metal intake has also been reported to be essentially due to drinking contaminated water and ingestion of contaminated food (Idodo-Umeh, 2002; FEPA, 2003; Asonye *et al*, 2007).

Heavy metals such as copper, iron and nickel are essential metals since they play important roles in biological systems, whereas cadmium and lead are non-essential metals, as they are toxic, even in trace amounts (Fernandes *et al.*, 2008). However, these essential metals can also produce toxic effects when the metal intake is excessively elevated (Tüzen, 2003). Heavy metals are taken into biological systems via inhalation, ingestion and skin absorption. If they enter and accumulate in body tissue faster than the body's detoxification pathways can dispose of them, a gradual build-up of these toxins will occur and result in toxicity. High concentration exposure however, is not necessarily required to produce a state of toxicity in the body tissue as overtime low concentrations can also reach toxic levels (Prusty, 1994).

Humans, being the occupants of the apex of the food chain get the highest level of toxicity in their food intake. This was evident in the Serious human mass poisonings from seafood in Minamata in 1956 and 1965 in Niigata due to alkylmercury discharged from chemical manufacturing plants (Environment Agency, Japan, 1975). Similarly, the toxic threat from bio-accumulated cadmium was demonstrated by human "itai-itai" disease in Japan in 1947, where Industrial discharge of cadmium into Jintsu River area, resulted in the death of more than 100 people who consumed the contaminated water (Hutzinger , 1980; Ramade, 1987). In Nigeria, heavy metals have been implicated in the upsurge of liver and kidney diseases and believed to be responsible for a high proportion of mortality caused by kidney and liver morbidity (Ndiokwere, 2004).The acute neurological effects of cadmium toxicity manifests itself in the form of nausea, abdominal cramps, bloody diarrhoea, vomiting, dizziness and chest pain. Also Rheumatic arthritis, muscular pain and osteomalacia in the elderly are evidence of chronic cadmium exposure (Klaassen, 1995). Long term exposure of humans to chromium can cause kidney and liver damage as well as damage to the circulatory and nerve tissues (Jackson and Morris, 1989). Lead(Pb) exposure can result in a wide range of biological effects, with developing foetus more affected than adults. The fatality rate of Pb neurotoxicity is about 25% while about 40% of the survivors have to live with neurological sequel such as mental retardation, optic atrophy and cerebral palsy (Harvey, 1975).

Regular monitoring of water bodies is an effective method of protecting aquatic life as well as humans from the toxic effects of heavy metals. However, several lakes in Nigeria have not been adequately assessed for heavy metals concentration. Hence, this study assessed the concentration of heavy metals in water and fish species from Agodi lake; a recipient of sewage effluent as well as other anthropogenic inputs and a provider of water as well as fish consumed by humans.

1.2 Justification

Studies have shown the heavy metal burden of several lakes in different parts of the world but there remain paucity of information on the level of heavy metals in Agodi lake, Ibadan; a lake that serves as reservoir for drinking water and fishes for human consumption. Furthermore there is ongoing direct and indirect dumping of sewage effluents, hospital wastes and other anthropogenic wastes into the lake. Since these wastes may contain heavy metals as part of their constituents, it is therefore important that the concentration of some of these heavy metals in the fishes as well as the surrounding water be assessed. The five(5) heavy metals assessed in this lake were specifically chosen for the following reasons: Lead(Pb), Cadmium(Cd) and Chromium(Cr) are amongst the twelve(12) toxic heavy metals that act as poisonous interference to the enzyme systems metabolism of the body (Kakulu *et al.*,1987) while Zinc(Zn) and Copper(Cu) are essential metals needed by the body for normal metabolic activities but become toxic when accumulated in the body tissues faster than the body's detoxification pathways can dispose of them (Proti, 1989).The health risks associated with heavy metal poisoning in humans and aquatic animals systems cannot be overemphasised. It was therefore, against this backdrop that this research was conducted. Results obtained from this study would provide information on background levels of heavy metals in the water as well as the assessed fish species of Agodi lake, thus contributing to the effective monitoring of both the lake quality and the health of the organisms inhabiting the lake.

1.3 Public Health Significance

There is incumbent necessity to continuously assess the accumulation of heavy metals; particularly Cadmium, Lead, Mercury that pose serious health hazards to humans. Incidences of heavy metal poisoning in the past had resulted in several deaths; The itai itai cadmium poisoning in Japan 1947 (Hutzinger, 1980; Ramade, 1987) and the early 1950s mercury poisoning in Minamata bay (Environment Agency Japan, 1975) amongst others are citable examples. In Nigeria, a recent case of heavy metal poisoning occurred in Zamfara state in 2010, where Gold laced with lead was been mined by villagers. High doses of lead inhaled from the dust left over 500 children and many others dead while morbidities such as permanent brain damage was seen in affected individuals (Epimonitor, 2011). Such occurrences can be forestalled through constant environmental monitoring. This research provided information on the concentration of heavy metals in water and fish; two important media through which heavy metals get into the human system.

1.4 Broad Objective

The main objective of this study was to assess the levels of Lead, Cadmium, Chromium, Zinc and Copper in water, *Clarias gariepinus* and *Tilapia guineensis* from Agodi lake, Ibadan, Southwest Nigeria.

1.5 Specific Objectives

The broad objective of this study was achieved through the following specific objectives:

1) Determination of the physico-chemical quality of water samples from Agodi lake and its tributaries.

2) Determination of the level of lead, cadmium, chromium, zinc and copper in the water samples from the lake and its tributaries.

3) Determination of the level of lead, cadmium, chromium, zinc and copper in *Clarias gariepinus* and *Tilapia guineensis* from Agodi lake .

CHAPTER TWO

2.0 REVIEW OF LITERATURE

2.1 Description of Heavy Metals

Heavy metals belong to a subset of elements that exhibit metallic properties. Basically they include the transition metals, also known as the D-block elements and are found in groups three(3) through thirteen(13) and periods four(4) through seven(7) of the periodic table; some metalloids: these are known as the P-block elements found in group 13 or 3A of the periodic table; lanthanides and actinides which are the F-block elements occupying the two additional periods at the bottom of the periodic table (Scerri, 2007). Many different definitions have been proposed for heavy metals; some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity (Duffus, 2002).

Heavy metals occur naturally in the ecosystem with large variations in concentration. Some of them are dangerous to health or to the environment (e.g. mercury, cadmium, lead, chromium) (Hogan, 2010), some may cause corrosion (e.g. zinc, lead), while some are harmful in other ways (e.g. arsenic, which may pollute catalysts). Some heavy metals are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium) (Zevenhoven and Kilpinen, 2001). Some metals are highly absorbable while some are difficult to absorb and that is because the body has mechanisms that prevent their over-absorption.

However, once a saturation point is reached, the body's mechanisms that maintain balance no longer operates. None of the metals is biodegradable, although they can change forms from solid, to liquid, to dust and gas; they never completely disappear. The ones that are toxic even in the most minute amounts create instant cellular destruction in any of their forms. They all exist naturally on the earth's crust and the most toxic must be mined by man before they become a threat to plant and animal life (Livelongercleanse, not dated).

Heavy metals have been known to be responsible for historic diseases like; the Minamata disease resulting from mercury poisoning (Hightower, 2008), and the itai-itai disease from cadmium poisoning (ICETT, 1998). Heavy metals are chemical elements with specific gravity that is at least five (5) times the specific gravity of water. The specific gravity of water is one

(1) at 4°C (39°F). Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with specific gravity of five (5) or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Lide, 1992).They are non-biodegradable and persist in the environment.

2.1.1 Beneficial Heavy Metals

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as essential trace elements or micronutrients (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products (International Occupational Safety and Health Information Centre, 1999). Heavy metals that are useful in diagnostic medical applications also fall into this category; for instance, direct injection of gallium during radiological procedures, dosing with chromium in parenteral nutrition mixtures, and the use of lead as a radiation shield around x-ray equipment (Roberts 1999). Also, heavy metals are useful in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes and steel (International Occupational Safety and Health Information Centre, 1999). Many of these products are in our homes and actually add to our quality of life when properly used.

2.1.2 Toxic Heavy Metals

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or by absorption through the skin when they come in contact with humans in agriculture and manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults, while ingestion is the most common route of exposure in children (Roberts, 1999). Children may develop toxic levels from the normal hand-to-mouth activity of small children who come in contact with contaminated soil or by actually eating objects that are not food (dirt or paint chips) (Dupler, 2001). Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous (parenteral) nutrition, from a broken thermometer (Smith *et al.*, 1997), or from a suicide or homicide attempt (Lupton *et al.*, 1985).

As a rule, acute poisoning is more likely to result from inhalation or skin contact of dust, fumes or vapours, or materials in the workplace. However, lesser levels of contamination may occur in residential settings, particularly in older homes with lead paint or old plumbing (International Occupational Safety and Health Information Centre, 1999). The Agency for Toxic Substances and Disease Registry (ATSDR) in Atlanta, Georgia, (a part of the U.S. Department of Health and Human Services) was established by congressional mandate to perform specific functions concerning adverse human health effects and diminished quality of life associated with exposure to hazardous substances. The ATSDR is responsible for assessment of waste sites and providing health information concerning hazardous substances, response to emergency release situations, and education and training concerning hazardous substances (ATSDR Mission Statement, 2001). In cooperation with the U.S. Environmental Protection Agency, the ATSDR has compiled a Priority List for 2001 called the "Top 20 Hazardous Substances." The heavy metals arsenic (1), lead (2), mercury (3), and cadmium (7) appear on this list.

2.2 Characteristics/ Properties of Heavy Metals

2.2.1 Physical Properties of Heavy Metals

Metals in general have high electrical conductivity, thermal conductivity, lustre and density, and the ability to be deformed under stress without cleaving (Mortimer and Charles, 1975). While there are also several metals that have low density, hardness, and melting points, these (the alkali and alkaline earth metals) are extremely reactive, and are rarely encountered in their elemental, metallic form. Optically speaking, metals are opaque, shiny and lustrous. This is because visible light-waves are not readily transmitted through the bulk of their microstructure. The large number of free electrons in any typical metallic solid (element or alloy) is responsible for the fact that they can never be categorized as transparent materials.

The majority of metals have higher densities than the majority of non-metals. Nonetheless, there is wide variation in the densities of metals; lithium is the least dense solid element and osmium is the densest. The metals of groups one or IA and two or IIA are referred to as the light metals because they are exceptions to this generalization. The high density of most metals is due to the tightly packed crystal lattice of the metallic structure. The strength of metallic bonds for different metals reaches a maximum around the centre of the transition metal series, as those elements have large amounts of delocalized electrons in tight binding type metallic bonds. However, other factors (such as atomic radius, nuclear charge, number of bonding orbitals, overlap of orbital energies, and crystal form) are involved as well (Mortimer and Charles, 1975).

2.2.2 Chemical Properties of Heavy Metals

Chemically, the metals differ from the non-metals in that they form positive ions and basic oxides and hydroxides. Upon exposure to moist air, a great number of metals undergo corrosion, i.e., enter into a chemical reaction; e.g., iron rusts when exposed to moist air, the oxygen of the atmosphere uniting with the metal to form the oxide of the metal. Aluminium and zinc do not appear to be affected, but in fact a thin coating of the oxide is formed almost at once, stopping further action and appearing unnoticeable because of its close resemblance to the metal. Tin, lead, and copper react slowly under ordinary conditions. Silver is affected by compounds such as sulphur dioxide and becomes tarnished when exposed to air containing them (Columbia Encyclopaedia, 2007).

2.3 Sources of Heavy Metals in the Environment

Heavy metals are introduced into the environment by a wide spectrum of natural and anthropogenic sources. Natural sources include volcanic activities, erosion and atmospheric condensation as well as natural disasters such as earthquakes, landslides, tornadoes and cyclones have been implicated (Nemerow, 1986; Nathaniel *et al*., 2000)

The commonest forms of anthropogenic sources of heavy metals are industrial and mining activities, industrial waste, petroleum exploration and exploitation, processing and effluent management, domestic and industrial sewage, nuclear reactor accidents and solid weapons. Heavy metals obtained from all these sources constitute potential dangers to the environment.

Industrial discharges, domestic sewage, non-point source such as urban run-off and atmospheric precipitation are the main sources of toxic heavy metals that enter aquatic systems (Van den Broek *et al*., 2002; Joyeux *et al*., 2004).

2.4 Heavy Metal Toxicity on Life

There are 35 metals that concern humans because of occupational or residential exposure; 23 of these are heavy metals and include: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Glanze, 1996). Interestingly, small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning) in all forms of life.

Heavy metal toxicity in humans can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (International Occupational Safety and Health Information Centre, 1999). Some elements are required by our body in various quantities but if their quantity limit exceeds the danger level, they can be toxic (Jackson and Morris, 1989). For some heavy metals, toxic levels can just be above the background concentrations naturally found in nature.

The accidental accumulation of these metals in the body results in "heavy metal poisoning". The most important metals regarding accumulation factor, includes mainly four metals, these are lead, mercury, arsenic, and cadmium (Thivierge and Frey, 2006).

Several studies have shown different means by which these metals enter the human body and cause poisoning. These metals may enter the body through contaminated food and water, through contaminated air we inhale during breathing or by absorption through the skin. Once in the human system, they displace some essential minerals including copper, zinc, calcium, magnesium and disturb organs and functioning processes. Humans may be exposed to these metals during work in manufacturing industries, or during agricultural activities. Children are particularly exposed to the above dangerous elements, during play on soil containing high concentration of these metals. Other harmful elements like arsenic and thallium are used for suicide or murdering purposes. These toxic metals may cause defects like memory loss, high blood pressure, poor concentration, aggressive behavior, sleeplessness, and a number of other defects. Metallic mercury is used as medicine in various cultures (Thivierge and Frey, 2006).

Heavy metal poisoning symptoms actually varies and might include; vomiting, pain in stomach, sweating, diarrhea, nausea and bad metallic taste in mouth depending on the nature as well as quantity of heavy metals that enter the body. If unrecognized or inappropriately treated, heavy metal toxicity can result in significant illness and reduced quality of life (Ferner, 2001).

Metals are non-biodegradable and are considered as major environmental pollutants causing cytotoxic, mutagenic and carcinogenic effects in animals (More *et al*., 2003). Aquatic organisms have the ability to accumulate heavy metals from various sources including sediments, soil erosion and runoff, air depositions of dust and aerosol, and discharges of wastewater (Labonne *et al*., 2001; Goodwin *et al*., 2003). Therefore, accumulation of heavy metals in aquatic organisms can pose a long lasting effect on biogeochemical cycling in the ecosphere.

The aquatic habitat of fish is intimately associated with their body functions, including immune reactivity which is susceptible to adverse changes in water quality. Occurrence of aquatic pollutants such as heavy metals has been correlated to alterations in the fish immune system and the incidence of infectious diseases. Very low sub-lethal doses of certain heavy metals can have profound effects upon the structure and / or functions of the immune system; and this could be almost as harmful as direct toxic doses (Saxena *et al*., 2009). Adverse effects in the immune system of fish could lead to decreased production, increased susceptibility to diseases and mortality.

In water bodies, the obvious sign of high heavy metal pollution; dead fish, is readily apparent while sub-lethal heavy metal pollution might result only in the occurrence of unhealthy fish. However, very low-levels of pollution may have no apparent impact on the fish itself, which would show no obvious signs of illness but may decrease the fecundity of fish populations, leading to a long-term decline and eventual extinction of this important natural resource (Krishnani *et al*., 2003 and Burger and Gochfeld, 2005). Such low-level of heavy metal pollution could have an impact on reproduction, either indirectly via accumulation in the reproductive organs, or directly on the free gametes (sperm or ovum) which are released into the water (Ebrahimi and Taherianfard, 2011). Figure 2.1 below is an illustration of some of the toxic effects of heavy metals on the human system;

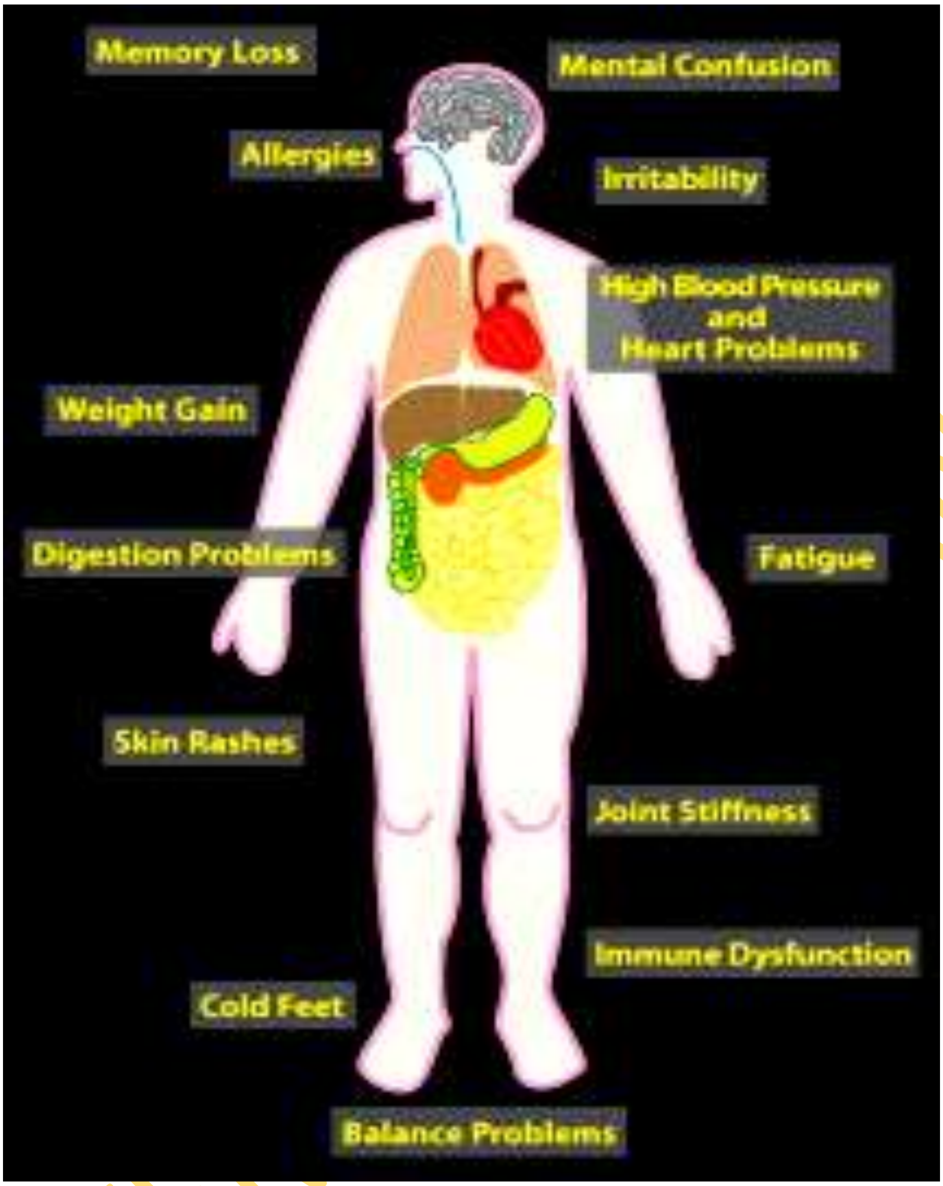

Fig 2.1: Effects of Heavy metals in the human system

Source: SadinAmerica, 2008.

2.5 Review of Some Heavy Metals

2.5.1 Lead

Lead, with the chemical symbol Pb is found in Group 14 (IVA); period six (6) of the periodic table (Stewart, 1996). It has an atomic number of 82 and an atomic mass of 207.2. Although a member of the carbon family, lead looks and behaves very differently from carbon. Four naturally occurring isotopes of lead occur. They are lead-204, lead-206, lead-207, and lead-208. About sixteen radioactive isotopes of lead are also known. One radioactive isotope of lead, lead-210; is sometimes used in medicine. This isotope gives off radiation that can kill cancer cells. It is also used to treat non-cancerous eye disorders (Earnshaw and Green, 1997).

The abundance of lead in the Earth's crust is estimated to be between 13 and 20 parts per million. It ranks in the upper third among the elements in terms of its abundance. Lead rarely occurs as a pure element in the earth. Its most common ore is galena, or lead sulfide (PbS). Other ores of Lead are anglesite, or lead sulfate ($PbSO_4$); cerussite, or lead carbonate ($PbCO_3$); and mimetite ($PbCL_2 . Pb_3(AsO_4)_2$) (Earnshaw and Green, 1997).

Lead is one of the few elements known to ancient people and throughout history; Lead has been used to make water and sewer pipes; roofing; cable coverings; alloys with other metals; paints; wrappings for food; tobacco and as an additive in gasoline. In spite of its vast application, Lead is number two on the ATSDR's (Agency for Toxic Substance and Disease Registry; Atlanta, USA.) 'Top 20 List'' (ATSDR, 2001ToxFAQs).

2.5.1.1 Discovery and Naming

It is impossible to say when humans first discovered the element. It does not occur as an element in the earth very often. But one of its ores, lead sulphide (PbS), is fairly common. It is not difficult to obtain pure lead metal from lead sulphide. Humans probably discovered methods for doing so thousands of years ago. In the Roman times, lead metal was widely used. The far-reaching system that brought water to Rome contained many lead pipes. Sheets of lead were used as writing tablets and some Roman coins were also made of lead. Perhaps of greatest interest was the use of lead in making pots and pans. Modern scientists believe many Romans may have become ill and died because of this practice. Cooking liquids in lead utensils tends to make the lead dissolve and entered into the food being cooked. People who ate those foods got more and more lead into their bodies. Eventually, the effects of lead poisoning must have begun to appear. The Romans had little understanding of the connection between lead and disease. They probably never realized that they were poisoning themselves by using lead pots and pans. No one is quite sure how lead got its name. Romans called the metal *plumbum*. It is from this name that the element's chemical symbol; Pb comes. Compounds of lead are sometimes called by this old name, such as plumbous chloride (Cotton *et al*., 1999).

2.5.1.2 Properties of Lead

Lead as a heavy metals has a number of physical and chemical properties that are associated with it. The following are some of the physical properties of lead:

- Lead is a heavy, soft, gray solid.
- Lead is both ductile and malleable. Ductile means capable of being drawn into thin wires. Malleable means capable of being hammered into thin sheets.
- It has a shiny surface when first cut, but it slowly tarnishes (rusts) and becomes dull.
- Lead is easily worked. That is it is easy to bend, cut, shape and pull.
- The melting point of lead is 327.4°C (621.3°F), and its boiling point is 1,750 to 1,755°C (3,180 to 3,190°F).
- Its density is 11.34 grams per cubic centimetre.
- Lead does not conduct electric current, sound, or vibrations very well. (Barbalace, 2011 and Greenwood and Earnshaw, 1997)

Chemically, lead has the following properties;

- Lead is a moderately active metal.
- It dissolves slowly in water and in most cold acids. It reacts more rapidly with hot acids. It does not react with oxygen in the air readily and does not burn.
- Lead exists in three oxidation states: Pb(0), the metal; Pb(II); and Pb(IV).
- In the environment, lead primarily exists as Pb(II). Pb(IV) is only formed under extremely oxidizing conditions and inorganic Pb(IV) compounds are not found under ordinary environmental conditions.
- While organo-lead (II) compounds are known, organo-lead chemistry is dominated by the tetravalent (+4) oxidation state. (Greenwood and Earnshaw, 1997)

2.5.1.3 Uses of Lead and Lead Compounds

Lead and its derivatives are being used extensively in all spheres of life. Several products are manufactured with lead, examples of such products include ammunition, such as shot and bullets; sheet lead used in building construction; solder; water and sewer pipes; ball bearings; radiation shielding; storage batteries (a device for converting chemical energy into electrical energy) and gasoline**.**

One way to prevent knocking in vehicle engines is to use high-grade gasoline. Another way is to add chemicals to the gasoline. The best gasoline additive discovered was a compound called Tetraethyl lead ($Pb(C_2H_5)_4$). Tetraethyl lead was usually called "lead" by the automotive industry, the consumer; and advertisers. When someone bought "leaded" gasoline, it contained not lead metal, but tetraethyl lead.

Only a small percentage of lead is used to make lead compounds. Although the amount of lead is small, the variety of uses for these compounds is large. Some examples of important lead compounds and their uses are:

- Tetraethyl lead ($Pb(C_2H_5)_4$): A gasoline additive used to prevent knocking in automobile engines (presently, use is prohibited by legislation).
- Lead acetate ($Pb(C_2H_3O_2)_2$): Used in manufacturing insecticides; waterproofing; varnishes; dyeing of cloth; production of gold; hair dye
- Lead antimonate ($Pb_3(SbO_4)_2$): Used for staining of glass, porcelain and other ceramics
- Lead azide ($Pb(N_3)_2$): used as a "primer" for high explosives
- Lead chromate ("chrome yellow"; $PbCrO_4$): Used for producing industrial paints (use restricted by law)
- Lead fluoride (PbF_2): used to make lasers; specialized optical glasses
- Lead iodide (PbI_2): photography; cloud seeding to produce rain
- Lead naphthenate ($Pb(C_7H_{12}O_2)$): wood preservative; insecticide; additive for lubricating oil; paint and varnish drier
- Lead phosphite ($2PbO.PbHPO_3$): used to screen out ultraviolet radiation in plastics and paints
- Lead stearate ($Pb(C_{18}H_{35}O_2)_2$): used to make soaps, greases, waxes, and paints; lubricant; drier for paints and varnishes

- Lead telluride (PbTe): used to make semiconductors, photoconductors, and other electronic equipment. (ATSDR, 2001)

2.5.1.4 Sources of Lead

Lead occurs naturally in all soils, generally at the rate of 15-40 parts per million depending on the location of the soil sample taken. Since it never disintegrates, it is much higher in older cities; where large quantities of dust from leaded paint have mixed with the soil. Lead is the most ubiquitous heavy metal on the planet and can be found in lead paint dust, car exhaust, and industrial waste. In addition, over four (4) million tons of lead are liberated from the earth's crust each year so that manufacturers can use it in their products (ATSDR, 2001). It is contained in such diverse things as insecticides, glass, heavy duty greases, certain plastics, cisterns, lead wires, metal alloys, roof coverings, solder, storage batteries, and varnishes. Another major source of lead is recycled car batteries. It can also found in sewerage systems.

2.5.1.5 Toxicity of Lead on life

Lead is a protoplasmic poison with affinity for the grey matter of our brains. It invades neurons, damages cells, nerve synapses and dendrites, and reduces the number of oxygen carrying red blood cells. It combines with phosphorous and enters the blood stream where it moves to the spleen, liver, and kidneys. After it has done its damage to the spleen, liver, and kidneys, it then goes to the bones, which become its permanent storage site. If the phosphorous intake is inadequate, the body will liberate lead from the bones and put it back into the blood stream so that it can do another round of damage to liver, spleen, kidneys and brain (Livelongercleanse, nd). Therefore, the poor and malnourished are at particular risk when it comes to lead poisoning.

Lead is known to cause both immediate and long-term health problems, especially with children. It is toxic when swallowed, eaten, or inhaled. Children are at the highest risk for lead poisoning, simply because their bodies absorb over 50% of all they come in contact with, as compared to an adult who only absorbs 10%. Children under the age of seven (7) are the most vulnerable as their nervous systems are undeveloped and easily damaged (Landrigan et al., 2002). Also, lead tastes sweet and so small children who have access to lead paint chips enjoy its taste and are eager to chew down. Furthermore, some children with the condition known as pica have an abnormal desire to eat materials like dirt, paper, and chalk. Children with "pica" sometimes eat paint that chips from walls. At one time, many interior house paints were made with lead compounds. Thus, crawling babies or children with pica ran the risk of eating large amounts of lead and being poisoned. Over a long period of time, these children often suffer brain damage. They lose the ability to carry out normal mental functions. Eventually, in later life, lead poisoning reduces intelligence, causes memory loss, promotes peripheral neuropathy and deteriorates thinking. It can also cause bone pain, gout, high blood pressure, iron deficiency anaemia, headaches, muscle tremors, hallucinations, and numbness and tingling in the extremities (Hazardous Substances Data Bank (HSDB), 2009).

Other forms of lead poisoning can also occur. For example, people who work in factories where lead is used can inhale lead fumes. The amount of fumes inhaled at any one time may be small. But over months or years, the lead in a person's body can build up. This kind of lead poisoning can lead to nerve damage and problems with the gastrointestinal system (stomach and intestines) which can be seen as nausea, vomiting, extreme tiredness, high blood pressure, and convulsions (spasms) (Sanders *et al*., 2009) .

Today, there is an effort to reduce the use of lead in consumer products. For instance, older homes are often tested for lead paint before they are resold. Lead paint has also been removed from older school buildings. In 1972, addition of lead to gasoline was banned. However, the 100 million Kilograms of lead that was discharged into our atmosphere by car exhaust still remain, for it will never break down, but will be blown about in the air we breathe for eternity. In addition, another 1.36 billion kilograms of lead have been released into the atmosphere by the smoking chimneys of manufacturing plants that use it to produce a variety of products. Lead poisoning presents no discernible symptoms in its early stages. Sometimes, one never has any symptoms until Alzheimer’s disease takes hold (Livelongercleanse, nd).

The symptoms initially present as fatigue, irritability, abdominal pain, constipation, and lack of appetite. Children frequently become hyperactive and aggressive, with a shortened attention span, sensorimotor deficits, and disordered behaviour, which are the same symptoms as emotional trauma (HSDB, 2009).

2.5.2 Cadmium

Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Most cadmium is obtained as a by-product from zinc refinement. Cadmium and zinc melt at different temperatures, providing one way of separating the two metals. As a liquid mixture of zinc and cadmium is cooled, zinc becomes a solid first. It can be removed from the mixture, leaving liquid cadmium behind (Cotton et al., 1999). Cadmium also exists in the industries as an inevitable by-product of zinc, lead and copper extraction. Naturally, a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing. Cadmium presents a threat to the environment because of its many applications (ATSDR, 2001).

Eight naturally occurring isotopes of cadmium exist. They are cadmium-106, cadmium-108, cadmium-110, cadmium-111, cadmium-112, cadmium-113, cadmium-114, and cadmium-116. About 20 radioactive isotopes of cadmium are known (Cotton et al., 1999).

2.5.2.1 Discovery and Naming of Cadmium

It was discovered by German chemist Friedrich Stromeyer (1776-1835) in 1817. The name Cadmium comes from the ancient term for zinc oxide, *cadmia*. Stromeyer, on one inspection trip, found that many pharmacies were stocking a compound of zinc called zinc carbonate ($ZnCO_3$) instead of the usual zinc oxide (ZnO). Stromeyer was told that the supplier had problems making zinc oxide from zinc carbonate and had offered the substitution. The normal process was to heat zinc carbonate to produce zinc oxide: $ZnCO_3 \text{ heat} \longrightarrow ZnO + CO_2$

The supplier explained that zinc carbonate turned yellow when heated. Normally, a yellow colour meant that iron was present as an impurity. The supplier found no iron in his zinc carbonate, but it was still yellow. Pharmacies would not buy yellow zinc oxide, so the supplier sold white zinc carbonate instead.

Stromeyer analyzed the odd yellow zinc carbonate. What he discovered was a new element cadmium. The cadmium caused the zinc carbonate to turn yellow when heated (Gschneidner and Eyring, 1999).

2.5.2.2 Properties of Cadmium

The physical properties of cadmium include the following;

- Cadmium is a lustrous, silver-white, ductile, very malleable metal.
- Its surface has a bluish tinge and the metal is soft enough to be cut with a knife
- Its melting point is 321°C (610°F) and its boiling point is 765°C (1,410°F).
- The density of cadmium is 8.65 grams per cubic centimetre.
- Cadmium tarnishes in air. (Lide, 2002).

Its chemical properties include the following;

- Cadmium does not react with water
- Cadmium is soluble in acids but not in alkalis
- In combination with certain metals, it lowers the melting point. Some common low-melting-point alloys are Lichtenberg's metal, Abel's metal, Lipowitz' metal, Newton's metal, and Wood's metal.
- Cadmium reacts slowly with oxygen in moist air at room temperatures, forming cadmium oxide: $2Cd + O_2 \longrightarrow 2CdO$ (Lide, 2002)

2.5.2.3 Uses of Cadmium and Cadmium Compounds

The earliest and most important usage of cadmium was in the electroplating of steel. Electroplating is a process by which a thin layer of one metal is deposited on the surface of a second metal. An electric current is passed through a solution containing the coating metal. The metal is electrically deposited on the second metal. A thin layer of cadmium protects steel from corrosion (rusting) (Lansche *et al.*, 1956).

In the last 30 years however, the use of cadmium for electroplating has dropped by about 70% due to environmental concerns. Discarded electroplated steel puts cadmium into the environment. Alternative coating methods are usually used now (Gschneidner and Eyring, 1999).

Today, about 70% of cadmium produced worldwide is used in the manufacturing of nickel-cadmium (nicad) batteries. Nicad batteries can be used over and over. When a nicad battery has lost some or all of its power, it is inserted into a unit that plugs into an electrical outlet. Electricity from the outlet recharges the battery. Nicad batteries are used in a large variety of appliances, including compact disc players, cellular telephones, pocket recorders, handheld power tools, cordless telephones, Laptop computers, camcorders, and scanner radios. Two French automobile manufacturers are exploring the possibility of using nicad batteries in electric cars (Cotton et al., 1999).

Most of the remaining 30% of cadmium produced is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission. Another popular use of cadmium compounds is as colouring agents. The two compounds most commonly used are cadmium sulphide (CdS) and cadmium selenide (CdSe). The sulphide is yellow, orange, or brown, while the selenide is red; these compounds are used to colour paints and plastics (Gschneidner and Eyring, 1999). There is concern about possible environmental effects of using cadmium for this purpose; however, no satisfactory substitutes have been found (ATSDR, 2001).

2.5.2.4 Sources of Cadmium

Cadmium due to its wide application is found in almost all environmental matrices. It is found in the air we breathe as an industrial contaminant. Acidic water leaches metal water from pipes. It is in black polyethylene, black rubber, burned motor oil, dental prosthetics, ceramics, evaporated milk, fungicides, rust proofing paint, organ meats such as kidney and liver, oysters and other sea foods, paint pigments, pesticides, plastic tape, polyvinyl plastics, processed foods, rubber carpet backing, rubber tyres, silver polish, solders, and super phosphate fertilizers (Cotton et al., 1999).

In terms of industry, it is prevalent in the jewellery making industry, marine hardware manufacturing, paint manufacturing, ceramics manufacturing, fungicide manufacturing, and electroplating metals. One cannot discuss the sources of cadmium without talking about cigarette smoking, for there is an immense amount of it in tobacco leaves, which are sprayed with cadmium fungicides. Each cigarette averages 1.4 micrograms of cadmium (Gschneidner and Eyring, 1999). Besides smoking, cadmium is found in food as it is a natural part of the earth’s crust. However, modern practices of processing often remove the zinc that could keep the cadmium from harming us. For example, there is one part cadmium to 120 parts zinc in wheat. Refining reduces this ration to 1 part cadmium to 12 parts zinc. The same is also true for rice (Earnshaw and Greenword, 1997).

2.5.2.5 Toxicity of Cadmium on Life

Cadmium is toxic to every body system and should never be mined in the first place. Almost all of the cadmium we are exposed to gets absorbed. Cadmium, like all heavy metals, accumulates over a lifetime. It is stored in fat, which keeps it from circulating in the blood. Therefore, it is one of the reasons why dieting can be hazardous to your health. When one diets or becomes ill with a wasting disease that causes weight loss, the cadmium is released from the fat to do its damage. For this reason, people who are losing weight are at the highest risk for cadmium poisoning. Therefore, everyone who diets should know how to chelate this metal while they are dieting.

2.5.2.6 Health Effects of Cadmium

Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. An exposure to significantly higher cadmium levels occurs when people smoke. Tobacco smoke transports cadmium into the lungs. Blood will transport it through the rest of the body where it can increase effects by potentiating cadmium that is already present from cadmium-rich food. Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry. When people breathe in cadmium it can severely damage the lungs. This may even cause death. Cadmium is first transported to the liver through the blood. There, it is bond to proteins to form complexes that are transported to the kidneys where it accumulates and damages the liver, causing anaemia. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It also impairs calcium metabolism and contributes to osteoporosis and osteo-malacia. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body. Other health effects that can be caused by cadmium are:

- Diarrhoea, stomach pains and severe vomiting
- Bone fracture
- Reproductive failure and possibly even infertility
- Damage to the central nervous system
- Damage to the immune system
- Psychological disorders

- Possibly DNA damage or cancer development. (Jarup, 1998; HSDB, 2009)

2.5.2.7 Environmental Effects

Cadmium strongly absorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants. Cows may have large amounts of cadmium in their kidneys due to this (Nogawa *et al.*, 2004). Earthworms and other essential soil organisms are extremely susceptive to cadmium poisoning. They can die at very low concentrations and this has consequences for the soil structure. When cadmium concentrations in soils are high they can influence micro-organisms that aid in soil processes, thereby threatening the whole soil ecosystem (Grant and Sheppard, 2008). In aquatic ecosystems cadmium can bio-accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms. Animals eating or drinking cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage (Nogawa *et al*., 2004).

2.5.3 Chromium

Chromium with the chemical symbol Cr and atomic number 24 is a transition metal found in the centre of the periodic table. It belongs to group 6 or VIB and has an atomic mass of 51.996. The abundance of chromium in the Earth's crust is about 100 to 300 parts per million. It ranks about number 20 among the chemical elements in terms of their abundance in the earth. Chromium does not occur as a free element. Today, nearly all chromium is produced from chromite, or chrome iron ore ($FeCr_2O_4$) (Cotton et al., 1999).

2.5.3.1 Discovery and Naming of Chromium

Chromium was discovered in a mineral known as Siberian red lead. The mineral was first described in 1766 by German mineralogist Johann Gottlob Lehmann (1719-67). Scientists were puzzled about what elements this new mineral contained. It had a form and a colour not seen in other minerals. Scientists had only small amounts of the mineral to study. They guessed that it contained lead as well as arsenic, molybdenum, or some other metal. In 1797, a French chemist Louis-Nicolas Vauquelin (1763-1829) began his own studies of Siberian red lead. He was convinced that the mineral contained a new element. None of the elements then known could account for his results. He reported "a new metal, possessing properties entirely unlike those of any other metal." A year later, Vauquelin was able to isolate a small sample of the metal itself. He heated charcoal (nearly pure carbon) with a compound of chromium, chromium trioxide (Cr_2O_3). When the reaction was complete, he found tiny metallic needles of chromium metal. The name chromium was suggested by two French chemists, Antoine Francois de Fourcroy (1755-1809) and René-Just Haüy (1743-1822), because chromium forms so many different coloured compounds. The colours range from purple and black to green, orange, and yellow (Gschneidner and Eyring, 1999)

2.5.3.2 Properties of Chromium

The physical properties of chromium include the following;

- Chromium is a hard, steel-gray, shiny, metal that breaks easily.
- It has a melting point of 1,900°C (3,450°F) and a boiling point of 2,642°C (4,788°F).
- The density of chromium is 7.1 grams per cubic centimetre.
- All chromium compounds are coloured. (Lide, 1999; 2002)

The chemical properties of chromium include the following;

- Chromium is a fairly reactive metal.
- It does not react with water, but reacts with most acids.
- Its ability to combines with oxygen at room temperature to form chromium oxide (Cr_2O_3). Chromium oxide forms a thin layer on the surface of the metal, protecting it from corrosion i.e. rusting (Lide, 1992 and 2002)

2.5.3.2 3 Uses of Chromium and Compounds of Chromium

- About 87% of chromium used in the United States goes into alloys. The addition of chromium makes the final product harder and more resistant to corrosion. About 70% of all chromium is used in the production of stainless steel. The applications of stainless steel are almost endless. They include automobile and truck bodies, plating for boats and ships, construction parts for buildings and bridges, parts for chemical and petroleum equipment, electric cables, machine parts, eating and cooking utensils, and reinforcing materials in tyres and other materials.

- Two other major uses of chromium are electroplating and the manufacture of refractory bricks. Electroplating is the process by which an electric current is passed through a water solution of a metallic compound. The current causes the material to break down into two parts, the free chromium produced in this reaction is laid down in a thin layer on the surface of another metal, such as steel. The chromium protects the steel from corrosion and gives it a bright, shiny surface. Many kitchen appliances are "chromeplated" this way. Some chromium is also used to make refractory bricks. A refractory material can withstand very high temperatures by reflecting heat. Refractory materials are used to line high-temperature ovens.

Chromium compounds also have many different uses. Some include:

- Chromic fluoride (CrF_3):used for printing, dyeing, and mothproofing woollen cloth
- Chromic oxide (Cr_2O_3): a green pigment (colouring agent) in paint, asphalt roofing, and ceramic materials; refractory bricks; abrasive
- Chromic sulphate ($Cr_2(SO_4)_3$): a green pigment in paint, ceramics, glazes, varnishes and inks; chrome plating
- Chromium boride (CrB): used to manufacture refractory; high-temperature electrical conductor
- Chromium dioxide (CrO_2): used as covering for magnetic tapes ("chromium" tapes)
- Chromium hexacarbonyl ($Cr(CO)_6$): catalyst; gasoline additive. (Cotton et al., 1999)

2.5.3.4 Sources of Chromium

About three-quarters of chromium produced today are used in alloys, including stainless steel. An alloy is made by melting and mixing two or more metals. The mixture has different properties than the individual metals. Chromium is also used to cover the surface of other metals. This technique protects the base metal and gives the surface a bright, shiny appearance at a low cost. Chromium can also be obtained by passing an electric current through its compounds. Sometimes chromite is converted directly to an alloy known as ferrochromium (or ferrochrome). Ferrochromium is an important chromium alloy. It is used to add chromium to steel. All chromium compounds are sources of chromium (Livelongercleanse, not dated).

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2.5.3.5 Toxicity of Chromium on Life

Chromium is an element with two faces, as far as health effects are concerned. Small amounts of chromium are essential for the health of plants and animals. In humans, a chromium deficiency leads to diabetes-like symptoms. Diabetes is a disease that develops when the body does not use sugar properly. Chromium seems to play a role in helping the body use sugar. In larger amounts, chromium is harmful. Some compounds are dangerous, causing a rash or sores if spilled on the skin (Gschneidner and Eyring, 1999). They can also cause sores in the mouth and throat if inhaled. If swallowed, some chromium compounds can seriously damage the throat, stomach, intestines, kidneys, and circulatory (blood) system. Scientists believe exposure to some chromium compounds on a long-term basis causes cancer (ATSDR, 1999; HSDB, 2009).

2.5.4 Zinc

Zinc is a bluish-white, lustrous metal. It is brittle at ordinary temperatures but malleable at 100 to 150°C. It is a fair conductor of electricity, and burns in air at high red heat with evolution of white clouds of the oxide. In addition, it is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen. Zinc can be obtained by roasting its ores to form the oxide and by reduction of the oxide with coal or carbon, with subsequent distillation of the metal. Other methods of extraction are possible. Naturally occurring zinc contains five stable isotopes. Twenty three other unstable isotopes and isomers are recognized. The metal is employed to form numerous alloys with other metals. Brass, nickel silver, typewriter metal, commercial bronze, spring brass, German silver, soft solder, and aluminium solder are some of the more important alloys (Cotton et al., 1999).

2.5.4.1 Discovery and Naming of Zinc

Metallic zinc was produced in the 13th century A.D. in India by reducing calamine with organic substances such as wool. The metal was rediscovered in Europe by Marggraf in 1746, who showed that it could be obtained by reducing calamine with charcoal. The principal ores of zinc are sphalerite or blende (sulphide), smithsonite (carbonate), calamine (silicate), and franklinite (zinc, manganese, iron oxide). Zinc can be obtained by roasting its ores to form the oxide and by reduction of the oxide with coal or carbon, with subsequent distillation of the metal. Other methods of extraction are possible (Earnshaw and Green, 1997).

2.5.4.2 Properties of Zinc

According to Lide (2002), the physical properties of Zinc are summarized below;

Atomic number	- 30
Atomic mass	- 65.37 g.mol -1
Electronegativity	- 1.6
Density	- 7.11 g.cm^{-3} at 20°C
Melting point	- 420 °C
Boiling point	- 907 °C
Vanderwaals radius	- 0.138 nm
Ionic radius	- 0.074 nm (+2)
Isotopes	- 10
Electronic shell	- [Ar] 3d10 4s2
Energy of first ionization	- 904.5 kJ.mol -1
Energy of second ionization	- 1723 kJ.mol -1
Standard potential	- - 0.763 V

The chemical properties of Zinc also include the following: (Lide, 1992; 2002).

Reaction of zinc withair:
Zinc metal tarnishes in moist air. Zinc metal burns in air to form the white zinc (II) oxide, a material that turns yellow on prolonged heating.

$2Zn(s)+O_2(g) \rightarrow 2ZnO(s)$

Reaction of zinc withwater:

Zinc does not react with water.

Reaction of zinc with the halogens:

The reactions of zinc and bromine(Br_2) or iodine(I_2) result in the formation of Zinc dibromide, zinc (II) dibromide, and zinc diiodide, zinc (II) diiodide. The reactions are illustrated below;

$Zn(s)+Br_2(g) \rightarrow ZnBr_2(s)$

$Zn(s)+I_2(g) \rightarrow ZnI_2(s)$

Reaction of zinc withacids:

Zinc metal dissolves slowly in dilute sulphuric acid to form solutions containing the aquated Zn(II) ion together with hydrogen gas, H_2. In practice, the Zn (II) is present as the complex ion:

$[Zn\ (OH_2)_6]^{2+}.Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4 + H + H_2(g)$

Reaction of zinc withbases:

Zinc metal dissolves in aqueous alkalis such as potassium hydroxide, KOH, to form zincates such as $[Zn(OH)_4]^{2-}$. The resulting solutions contain other species as well.

2.5.4.3 Uses of Zinc and Zinc Compounds

Large quantities of zinc are used to produce die castings, used extensively by the automotive, electrical, and hardware industries. An alloy called Prestal (R), consisting of 78% zinc and 22% aluminium is reported to be almost as strong as steel but as easy to mould as plastic. It is said to be so plastic that it can be moulded into form by relatively inexpensive die casts made of ceramics and cement. It exhibits super plasticity. Zinc is also extensively used to galvanize other metals such as iron to prevent corrosion. Neither zinc nor zirconium is ferromagnetic; but $ZrZn_2$ exhibits ferromagnetism at temperatures below 238^0C (Cotton et al., 1999).

Zinc oxide is a unique and very useful material to modern civilization. It is widely used in the manufacture of paints, rubber products, cosmetics, pharmaceuticals, floor coverings, plastics, printing inks, soap, storage batteries, textiles, electrical equipment, and other products. It has unusual electrical, thermal, optical, and solid-state properties that have not yet been fully investigated. Lithopone, a mixture of zinc sulphide and barium sulphate, is an important pigment. Zinc sulphide is used in making luminous dials, X-ray and TV screens, and fluorescent lights. The chloride and chromate are also important compounds (Gschneidner and Eyring, 1999).

Zinc is an essential element in the growth of human beings and animals. Tests show that zinc-deficient animals require 50% more food to gain the same weight as an animal supplied with sufficient zinc. Zinc is not considered to be toxic, but when freshly formed ZnO is inhaled a disorder known as the oxide shakes or zinc chills sometimes occurs. It is recommended that where zinc oxide is encountered good ventilation should be provided (HSDB, 2009).

2.5.5 Copper

In the periodic table, copper is found in group IB that includes transition metal elements such as silver and gold. The abundance of copper in the Earth's crust is estimated to be about 70 parts per million. It ranks in the upper quarter among elements present in the Earth's crust. Small amounts (about 1 part per billion) also occur in seawater. At one time, it was not unusual to find copper lying on the ground. However, this is no longer true. Today, copper is obtained from minerals such as azurite, or basic copper carbonate ($Cu_2(OH)_2CO_3$); chalcocite, or copper glance or copper sulphide (Cu_2S); chalcopyrite, or copper pyrites or copper iron sulphide ($CuFeS_2$); cuprite, or copper oxide (Cu_2O); and malachite, or basic copper carbonate ($Cu_2(OH)_2CO_3$). There are two naturally occurring isotopes of copper, copper-63 and copper-65. Nine radioactive isotopes of copper are known also (Cotton et al., 1999).

Copper is a component of more than 30 enzymes, some of which are involved in collagen synthesis. It is necessary for connective tissue, nerve coverings, and bone. It is also involved in iron and energy metabolism. Copper is a metal used by people who lived in prehistoric times. Jordan, Egypt and Israel have copper smelting locations that date back to 4500 B.C. The people who lived in that historical period combined copper with iron or tin to produce an alloy called bronze. Another alloy of copper is brass. Brass and bronze are stronger than copper; hence, it was used to make weapons such as spear tips, hammers, axes and so on. Copper occurs in nature mixed with other elements in a number of compounds. It is responsible for the green pigmentation in turquoise, malachite, and azurite. It is the third most widely used metal in the world after aluminium and steel, and has therefore been mined for centuries. Being a natural substance that is part of the earth's crust, like all metals it is found in air, soil, water, and other organisms (Gschneidner and Eyring, 1999).

As copper is needed for human health, the body has a natural mechanism for maintaining the proper amount of it, however; this balance is affected when overexposure occurs. In order to maintain its balance, all of copper's co-factors must also be ingested. Its co-factors are called copper antagonists. They are chromium, molybdenum, sulphur, nickel, vitamin C, hesperidins, and others. One can chelate high copper levels by taking either extra chromium, sulphur in the form of glucosamine sulphate (HSDB, 2009).

2.5.5.1 Discovery and Naming

The oldest objects made of copper are beads found in northern Iraq, which date to about 9000 B.C. Tools for working with copper, made in about 5000 B.C., have also been found. In the New World, Native Americans used copper objects as early as 2000 B.C. The symbol for copper, Cu, comes from the Latin word *cuprum*. Cuprum is the ancient name of the island of Cyprus. The Romans obtained much of their copper from Cyprus. Bronze was one of the first alloys produced. It is primarily copper and tin. The two metals can be melted together rather easily. Humans discovered methods for making the alloy as early as 4000 B.C. Over the next thousand years, bronze was used for a great variety of tools, weapons, jewellery, and other objects. It was such an important metal that the period from 4000 to 3000 B.C. is now known as the Bronze age. The Iron age followed the Bronze age when iron began to replace bronze in tools and weapons (Earnshaw and Greenword, 1997).

2.5.5.2 Properties of Copper

The physical properties of copper are summarized below (Lide, 1992 and 2002);

- Copper is a substance with a reddish-brown tint.
- Copper metal is fairly soft and ductile. Ductile means capable of being drawn into wires.
- Copper has high electrical conductivity. Both heat and electricity pass through copper very easily. The high electrical conductivity makes it ideal for many electrical purposes.
- Copper has a melting point of 1,083°C (1,982°F) and a boiling point of 2,595°C (4,703°F).
- Its density is 8.96 grams per cubic centimetre. When polished copper glows and looks bright.
- Copper absorbs moisture and a green layer is formed on top of it. This layer is called “patina"; this coating protects the metal from being eroded.

Chemical Properties of Copper: Table 2.1 below summarises the chemical properties of copper.

Table 2.1: Chemical properties of Copper

Chemical Property	Value
Atomic number	29
Atomic mass	63.546 g.mol^{-1}
Electronegativity according to Pauling	1.9
Vanderwaals radius	0.128 nm
Ionic radius	0.096 nm (+1); 0.069 nm (+3)
Isotopes	6
Electronic shell	[Ar] 3d^{10} 4s1
Energy of first ionization	743.5 kJ.mol^{-1}
Energy of second ionization	1946 kJ.mol^{-1}
Standard potential	+0.522 V

Source: http//www. Buzzle.com

2.5.5.3 Uses of Copper and Copper compounds

Copper and its compounds have many important uses in modern society. Copper is also used to make many alloys. An alloy is made by melting and mixing two or more metals. The mixture has properties different from those of the individual metals. The most familiar alloys of copper are brass and bronze. Many compounds of copper are commercially important, too. They are used as colouring agents in paints, ceramics, inks, varnishes, and enamels. The most important application of copper metal is electrical wiring. Nearly every electrical device relies on copper wiring because copper metal is highly conductive and inexpensive. These devices include electric clocks, stoves, portable CD players, and transmission wires that carry electricity. Computers also depend on circuit boards imprinted with minute copper pathways. Alloys of copper, such as bronze and brass, are also used in construction (Gschneidner and Eyring, 1999).

A number of copper alloys have been developed for special purposes. For example, gun metal is an alloy used to make guns. It contains about 90% copper and 10% tin. Money metal is an alloy of nickel and copper that is resistant to corrosion (rusting). Coinage metal is a copper alloy from which U.S. coins are made (Cotton et al., 1999).

A number of copper compounds are used as pesticides, chemicals that kill insects and rodents such as rats and mice. These include:

Basic copper acetate ($Cu_2O(C_2H_3O_2)_2$): insecticide (kills insects) and fungicide (kills fungi)

Copper chromate ($CuCrO_4.2CuO$): fungicide for the treatment of seeds

Copper fluorosilicate ($CuSiF_6$): grapevine fungicide

Copper methane arsenate ($CuCH_3AsO_3$): algicide (kills algae)

Copper-8-quinolinolate ($Cu(C_9H_6ON)_2$): protects fabric from mildew

Copper oxalate (CuC_2O_4): seed coating to repel rats

Copper oxychloride ($3CuO.CuCl_2$): grapevine fungicide

Tribasic copper sulphate ($CuSO_4.3Cu(OH)_2$): fungicide, used as a spray or dust on crops,

Other copper compounds are found in battery fluid; fabric dye; fire retardants; food additives for farm animals; fireworks (bright emerald colour); manufacture of ceramics and enamels; photographic film; pigments (colouring agents) in paints, metal preservatives, and marine paints; water purification; and wood preservatives (Gschneidner and Eyring, 1999).

2.5.5.4 Sources of Copper

Food sources of copper include dark chocolate and cocoa, colas, coffee, tea, beer, liver, organ meats, oysters, nuts, seeds, whole grains, potatoes, raisins, mushrooms, soy products, chickpeas, and other legumes. Foods cooked or stored in copper containers absorb a significant amount of copper. Besides plumbing and cookware, copper can also be found in sewage sludge, swimming pools, inorganic mineral supplements, and dental crowns. Blue green water stains below your water faucets indicate a high copper content in your water supply. It is also found in fungicide, pesticide, and in treatment chemicals used for killing aquatic vegetation. Copper is abundantly found in the earth's crust from where it can be introduced into the environment (Livelongercleanse, not dated).

2.5.5.5 Toxicity of Copper on Life

Copper is an essential micronutrient for both plants and animals. A micronutrient is an element needed in minute amounts to maintain good health in an organism. A healthy human has no more than about 2 milligrams of copper for every kilogram of body weight (Gschneidner and Eyring, 1999). Some people are born without the ability to eliminate copper from their bodies and as such the amount of copper they retain increases. The copper level can become so high it begins to affect the brain, liver, or kidneys resulting in mental illness and death. Fortunately, this problem can be treated. The person can be given a chemical that combines with the copper and the damaging effects on the body are reduced or eliminated (HSDB, 2009).

Copper deficiency or excess can be a problem. Deficiency causes anaemia, connective tissue, nerve and nervous system abnormalities. Although because of copper pipes, and the fact that many copper rich foods are somewhat addictive, deficiency is seldom a problem. The exception would be in the case of Menke’s disease, which is a rare genetic disease that causes copper mal-absorption in infant males. Wilson’s disease, on the other hand, is a genetic disease that causes copper overload. In addition, because infants have not yet developed the mechanism that prevents overload, they are highly susceptible to liver toxicity, especially if they are given formula made from hot tap water that comes out of copper pipes. Excess copper in the human system is generally caused by copper pipes, especially in newer houses, or houses that have brass faucets, which have copper in them. Hot water leaches more copper from the pipes than cold water, so it is always important to use cold water for cooking, as opposed to hot tap water. It is also important to let the first water of the day run through the pipes for a minute or two before using it, as excess copper accumulates in water that’s stored in the pipes over night (ATSDR, 1999). Inhaling copper dust and fumes can affect the respiratory tract and cause nausea and diarrhoea. It will also decrease the body’s haemoglobin and erythrocyte count. It can affect the liver and endocrine system. In addition, it can cause eye irritation, headaches and muscle aches (HSDB, 2009).

2.6 The Aquatic Ecosystem

Aquatic systems are those that contain plants and animals that predominantly depend on a significant amount of water to be present for at least part of the year. An aquatic ecosystem is an ecosystem located in a body of water. The term *body of water* most often refers to large accumulations of water, such as oceans, seas, and lakes, but it may also include smaller pools of water such as ponds, puddles or wetlands. Some bodies of water are man-made (artificial), such as reservoirs or harbours, but most are naturally occurring geographical features. Bodies of water that are navigable are known as waterways. Some bodies of water collect as well as move water, such as rivers and streams while others primarily hold water, such as lakes and oceans (Moustakas and Karakassis, 2005; Alexander, 1999).

The two main types of aquatic ecosystems are marine ecosystems and freshwater ecosystems (Barange *et al*., 2010). Aquatic ecosystems perform many important environmental functions. For example, they recycle nutrients, purify water, attenuate floods, recharge ground water and provide habitats for wildlife (Levner *et al*., 2005). Aquatic ecosystems are also used for human recreation, and are very important to the tourism industry especially in coastal regions (Christensen and Pauly, 1993).The health of an aquatic ecosystem is degraded when the ecosystem's ability to absorb a stress has been exceeded. A stress on an aquatic ecosystem can be a result of physical, chemical or biological alterations of the environment. Physical alterations include changes in water temperature, water flow and light availability. Chemical alterations include changes in the loading rates of bio-stimulatory nutrients, oxygen consuming materials, and toxins. Biological alterations include the introduction of exotic species. Human populations can impose excessive stresses on aquatic ecosystems (Levner *et al*., 2005).

2.6.1 Composition of an Aquatic Ecosystem

An aquatic ecosystem is composed of biotic and abiotic characteristics, which form a self-regulating and self-sustaining unit.

2.6.1.1 Biotic characteristics

The living organisms present in an aquatic ecosystem constitute the biotic characteristics. The organisms (also called biota) found are either autotrophic or heterotrophic. Autotrophic organisms are producers that generate organic compounds from inorganic material. Algae use solar energy to generate biomass from carbon dioxide and are the most important autotrophic organisms in aquatic environments (Mann and Lazier, 2006). Chemosynthetic bacteria are found in benthic marine ecosystems. These organisms are able to feed on hydrogen sulphide in water that comes from volcanic vents. Heterotrophic organisms consume autotrophic organisms and use the organic compounds in their bodies as energy sources and as raw materials to create their own biomass. These organisms include animals that feed on chemosynthetic bacteria like the Giant tube worms (*Riftia pachyptila)and clams (Calyptogena magnifica*); and also, all kinds of fishes and aquatic mammals incapable of producing their own food (Moustakes and Karakassis, 2006).

2.6.1.2 Abiotic characteristics

Some abiotic characteristics of an aquatic ecosystem include temperature, salinity, flow and dissolved oxygen (Levner *et al.*, 2005).

The amount of dissolved oxygen in a water body is frequently the key substance in determining the extent and kinds of organic life in the water body. Fish need dissolved oxygen to survive. Conversely, oxygen is fatal to many kinds of anaerobic bacteria.

The salinity of the water body is also a determining factor in the kinds of species found in the water body. Organisms in marine ecosystems tolerate salinity, while many freshwater organisms are intolerant of salt. Euryhaline organisms are salt tolerant and can survive in marine ecosystems, while stenohaline or salt intolerant species can only live in freshwater environments (Boyd *et al.*, 2006).

In terms of temperature, fish have upper and lower thermal tolerant limits and optimum temperature for growth, egg incubation, food conversion and resistance to specific diseases. Water temperature also affects other properties of the aquatic environment important for fish health. Surface waters are subject to temperature fluctuations of up to 40^0C caused by latitude, season, altitude, time of the day, depth and other factors. Dissolved gases generally decrease in solubility with increasing temperature whereas the solubility of toxic compounds which are only sparingly soluble in water, such as crude oil, heavy metals, pesticides, increases with temperature rise. The toxicity of some substances such as heavy metals increases with temperature (Roberts, 1978).

2.6.2 Some Parameters that affect the Aquatic Ecosystem

2.6.2.1 Physical Parameters

These are the abiotic factors in the aquatic environment and they determine the ability of organisms to live and reproduce in it. Some of them include such factors like flow velocity, volume of water, bottom contour, currents, depth, light penetration, and temperature and they govern to a large extent, the ability of a system to receive and assimilate pollution (Levner, 2005).

pH (Hydrogen ion concentration)

pH is an important factor in the chemical and biological systems of natural waters. The toxicity of many compounds is affected by pH. One example is hydrogen cyanide (HCN). Cyanide toxicity to fish increases as the pH is lowered. Similar results have been shown for hydrogen sulphide (H_2S). The solubility of metal compounds contained in bottom sediments or as suspended material is also affected by pH. As pH decreases, certain metals such as aluminium, copper, and lead are more easily dissolved and are leached from soil and sediments into runoff and groundwater entering surface water. These metals can accumulate on fish gills or cause deformities in fish fry, reducing their chances to survive. Since pH has a direct effect on organisms and an indirect effect on the toxicity of certain other pollutants in the water, the buffering capacity is important to water quality (EPA, 1994). The buffering capacity of natural water is also important because it determines the effect of acid precipitation (Mann and Lazier, 2006). Fish and many other organisms are unable to survive large drops in pH. Trout are especially sensitive to decreases in pH; sudden acid inputs to pH below 4.5 - 5.0 can kill fish. Fish eggs and fry are sensitive to changes in pH, and may not develop. Species diversity generally decreases with increased acidity (Moustakas and Karakassi, 2005).

At either very high or low pH, the water cannot support most organisms. Serious problems occur in lakes with pH below 5, and in streams that get a massive acid dose in spring when the acid snows melt (Levner, 2005).

2.6.2.2 Chemical Parameters

Alkalinity

The alkalinity of water expresses its capacity to neutralize acid; in other words, it’s buffering capacity. Alkalinity is commonly expressed as milligrams per liter (mg/L) of calcium carbonate. Examples of commonly occurring materials in natural waters that increase the alkalinity are carbonates, bicarbonates, phosphates and hydroxides (EPA, 1972). The lower the alkalinity, the greater the sensitivity of surface water to acid precipitation. Acid precipitation is suitable for heavy metals dissolution.

Dissolved Oxygen

Dissolved oxygen is essential for the survival of nearly all aquatic life. Its concentration in water is very low compared with that in air. Temperature, the types and concentrations of dissolved and suspended solids affect the amount of oxygen dissolved in a lake or stream, agitation of the water, and biotic activity (especially algae). Low dissolved oxygen concentration is damaging to aquatic life and only the hardiest organisms survive (Manahan, 2005). Oxygen super-saturation can also be harmful (Mann and Lazier, 2006). Critical conditions can occur during the dry season when temperatures are high for two reasons:

- The solubility of oxygen is lower at higher temperatures,
- Oxygen demand is higher when temperatures rise, because the metabolic rates of the organisms increase.

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand or BOD estimates the total organic matter in a water sample available for oxidation (Chapman and Reiss, 1998). The measurement of oxygen demand is an easy way to detect the degree of pollution by organic matter. BOD is the difference in oxygen concentration in a water sample before and after incubation for a length of time under specific conditions. During this time, micro organisms in the sample oxidize the organic matter, using the dissolved oxygen present in the water (Mann and Lazier, 2006). Organic material comes from natural sources and from pollution with sewage, animal wastes, or any kind of organic refuse.

2.6.2.3 Biological Parameters

Biological parameters detect water quality problems that other methods may miss or underestimate. Organisms in their environments are continual monitors of environmental quality, increasing the detection of events such as spills, dumping, treatment plant malfunctions, nutrient enrichment, non-point source pollution (such as agricultural pesticides), cumulative pollution (multiple events over time or continuous low level inputs) or other impacts that chemical sampling is unlikely to detect. Impacts on the physical habitat such as sedimentation from storm water runoff and the effects of physical or structural habitat changes such as dredging, filling, or channelization can also be detected (Loeb, 1994).

"Resident biota are continual monitors of environmental quality, increasing the detection of episodic events (spills, dumping, treatment plant malfunctions, nutrient enrichment), non-point source pollution (agricultural pesticides), cumulative pollution (multiple impacts over time or continuous low-level stress) or other impacts that chemical sampling is unlikely to detect. Impacts on the physical habitat such as sedimentation from storm water runoff and the effects of physical or structural habitat changes (dredging, filling, channelization) can also be detected" (EPA, 1994). Plankton (phytoplankton and zooplankton), benthic macro-invertebrates, aquatic plants, and fish are the most commonly used in assessing biological integrity. Algae are often used in lakes to examine eutrophication (Loeb, 1994).

2.6.3 Types of Water Bodies

2.6.3.1 Marine Ecosystem

The marine ecosystems cover approximately 71% of the Earth's surface and contain approximately 97% of the planet's water. They generate 32% of the world's net primary production (Barange *et al*., 2010). They are distinguished from freshwater ecosystems by the presence of dissolved compounds, especially salts, in the water. Approximately 85% of the dissolved materials in seawater are sodium and chlorine (Boyd *et al*., 2006).

Marine ecosystems can be divided into the following zones: oceanic (the open part of the ocean where animals such as whales, sharks, and tuna live); profundal (bottom or deep water); benthic (bottom substrates); intertidal (the area between high and low tides); estuaries; salt marshes; coral reefs; and hydrothermal vents (where chemosynthetic sulphur bacteria form the food base) (Barange *et al.*, 2010).

Classes of organisms found in marine ecosystems include brown algae, dinoflagellates, corals, cephalopods, echinoderms, and sharks. Fish caught in marine ecosystems are the biggest source of commercial foods obtained from marine populations (Barange *et al.*, 2010).

Environmental problems concerning marine ecosystems include unsustainable exploitation of marine resources (for example over fishing of certain species), marine pollution, climate change, and building on coastal areas (Barange *et al.*, 2010).

2.6.3.2 Freshwater Ecosystem

Freshwater ecosystems cover 0.80% of the Earth's surface and inhabit 0.009% of its total water. They generate nearly 3% of its net primary production. Freshwater ecosystems contain 41% of the world's known fish species (Christensen and Pauly, 1993). There are three basic types of freshwater ecosystems:

- Lentic: slow-moving water, including pools, ponds, and lakes.
- Lotic: rapidly-moving water, for example streams and rivers.
- Wetlands: areas where the soil is saturated or inundated for at least part of the time (Davenport, 2008).

Lake ecosystems can be divided into zones: pelagic (open offshore waters); profundal; littoral (near shore shallow waters); and riparian (the area of land bordering the body of water). Two important subclasses of lakes are ponds, which typically are small lakes that intergrades with wetlands, and water reservoirs. Many lakes, or bays within them, gradually become enriched by nutrients and fill in with organic sediments, a process called eutrophication. Eutrophication is accelerated by human activity within the water catchment area of the lake (Barange *et al.*, 2010).

2.6.4 The Lake as a Water Body

A lake is a body of relatively still fresh or salt water of considerable size, localized in a basin, not to be confused with a lagoon; that is surrounded by land. Lakes are inland and not part of the ocean, and are larger and deeper than ponds (Britannica online, 2008). Lakes can be contrasted with rivers or streams, which are usually flowing. However most lakes are fed and drained by rivers and streams which make them more susceptible to pollution. Natural lakes are generally found in mountainous areas, rift zones, and areas with on-going glaciations while some others are found in endorheic basins or along the courses of mature rivers. All lakes are temporary over geologic time scales, as they will slowly fill in with sediments or spill out of the basin containing them (Downing *et al.*, 2006).

Furthermore, many lakes are artificial and are constructed for industrial or agricultural use, for hydro-electric power generation or domestic water supply, or for aesthetic or recreational purposes (Veltrop, 1993). Changes in the level of a lake are controlled by the difference between the input and output compared to the total volume of the lake. Significant input sources are precipitation onto the lake, runoff carried by streams and channels from the lake's catchment area, groundwater channels and aquifers, and artificial sources from outside the catchment area. Output sources are evaporation from the lake, surface and groundwater flows, and any extraction of lake water by humans. As climate conditions and human water requirements vary, these will create fluctuations in the lake level (Downing *et al.*, 2006).

Lakes can also be categorized on the basis of their richness in nutrients, which typically affect plant growth. Nutrient-poor lakes are said to be *oligotrophic* and are generally clear, having a low concentration of plant life. *Mesotrophic lakes* have good clarity and an average level of nutrients. *Eutrophic* lakes are enriched with nutrients, resulting in good plant growth and possible algal blooms. *Hypertrophic* lakes are bodies of water that have been excessively enriched with nutrients. These lakes typically have poor clarity and are subject to devastating algal blooms. Lakes typically reach this condition due to human activities, such as heavy use of fertilizers in the lake catchment area. Such lakes are of little use to humans and have a poor ecosystem due to decreased dissolved oxygen (Moss *et al*., 1996; Petr, 1978).

Due to the unusual relationship between water's temperature and its density, lakes form layers called thermoclines, layers of drastically varying temperature relative to depth. Fresh water is most dense at about 4 degrees Celsius (39.2 °F) at sea level. When the temperature of the water at the surface of a lake reaches the same temperature as deeper water, as it does during the cooler months in temperate climates, the water in the lake can mix, bringing oxygen-starved water up from the depths and taking oxygen down to decomposing sediments. Deep temperate lakes can maintain a reservoir of cold water year-round, which allows some cities to tap that reservoir for deep lake water cooling (Moss *et al*., 1996). Since the surface water of deep tropical lakes never reaches the temperature of maximum density, there is no process that makes the water mix. The deeper layer becomes oxygen starved and can become saturated with carbon dioxide, or other gases such as sulphur dioxide if there is even a trace of volcanic activity. Exceptional events, such as earthquakes or landslides, can cause mixing which rapidly brings the deep layers up to the surface and release a vast cloud of gas which lay trapped in solution in the colder water at the bottom of the lake. This is called a limnic eruption (Petr, 1978). The amount of gas that can be dissolved in water is directly related to pressure. As deep water surfaces, the pressure drops and a vast amount of gas comes out of solution. Under these circumstances carbon dioxide is hazardous because it is heavier than air and displaces it, so it may flow down a river valley to human settlements and cause mass asphyxiation.

The material at the bottom of a lake, or *lake bed*, may be composed of a wide variety of in-organics, such as silt or sand, and organic material, such as decaying plant or animal matter. The composition of the lake bed has a significant impact on the flora and fauna found within the lake's environs by contributing to the amounts and the types of nutrients available (Petr, 1978).

Some Notable Lakes the World

- Lake Michigan-Huron is the largest lake by surface area: 117,350 km². It also has the longest lake coastline in the world: 8,790 km. If Huron and Michigan are considered two lakes, Lake Superior is the largest lake, with 82,414 km². However, Huron still has the longest coastline at 6,157 km (2980 km excluding the coastlines of its many inner islands). The world's smallest geological ocean, the Caspian Sea, at 394,299 km² has a surface area greater than the six largest freshwater lakes combined, and it's frequently cited as the world's largest lake.
- The deepest lake is Lake Baikal in Siberia which is the world’s deepest and oldest lake. Its mean depth is also the greatest in the world (749 m). It is also the world's largest lake by volume (23,600 km³, though smaller than the Caspian Sea at 78,200 km³), and the second longest (about 630 km from tip to tip).
- Lake Tanganyika is the world’s longest lake, with a length of about 660 km (measured along the lake's centre line).
- The highest large freshwater lake in the world is Lake Manasarovar in Tibet Autonomous Region of China.

- The world's lowest lake is the Dead Sea, bordering Israel and Jordan at 418 m (1,371 ft) below sea level. It is also one of the lakes with highest salt concentration.
- Oku Lake in Bamenda Plateau in the Northwest Region of Cameroon

Notable lakes in Nigeria include;

- Lake paida in Former Bendel state (Delta state)
- Lake peu in Lagos
- Lake Shisha in Former Bendel state (Delta state)
- Lake Ukwa in Abia state
- Lake Yimirdiva in Abuja
- Lake Zaru in Former Bendel state (Delta state)
- Langido Lake in Kebbi state
- Oguta Lake in Imo state
- Osiam Lake in Former Bendel state (Delta state)
- Tombo Lake in Former Bendel state (Delta state)

Sources: Downing *et al.*, 2006 and the US National Imagery and Mapping Agency, 2005.

2.7 Pollution in the Aquatic Ecosystem

Human activities mainly associated with urbanisation and Industrialization have resulted in increasing pollution of the aquatic environment. Hence, the survival of aquatic systems and their biodiversity are seriously under threat owing to various effluents that are released into them (Asonye *et al*., 2007). This condition is now becoming more noticeable in developing countries where urbanization and industrialization are proceeding rapidly. Pollution in the aquatic ecosystem is catalysed by several agents, notable amongst them are the following;

2.7.1 Sewage

In developing countries, where many people still lack clean water and basic sanitation (hygienic toilet facilities), the use of water bodies as sanitation facility is a common practice (WHO, 2008). Sewage disposal affects people's immediate environments and leads to water-related illnesses such as diarrhoea that kills 3-4 million children each year (Farmer, 1997). According to the World Health Organization (2008), water-related diseases could kill 135 million people by 2020. In developed countries, most people have flush toilets that take sewage quickly and hygienically away from their homes. Yet the problem of sewage disposal does not end there, because this sewage will ultimately end-up somewhere and most times in water bodies thereby polluting the aquatic ecosystem. In theory, sewage is a completely natural substance that should be broken down harmlessly in the environment since 90 per cent of sewage is water. However, in practice, sewage contains all kinds of other chemicals, from the pharmaceutical drugs people take to the paper, plastic, and other wastes they flush down their toilets. Sewage is also an efficient carrier of pathogenic organisms into the aquatic environment.

2.7.2 Waste Water

There is abounding evidence on the problems that waste water (chemicals washed down drains and discharged from factories) can cause. Around half of all ocean pollution is caused by sewage and waste water. Each year, the world generates 400 billion tons of industrial waste, much of which is pumped untreated into rivers, oceans, and other waterways (Harrison, 2001).

Factories are point sources of water pollution, but quite a lot of water is polluted by individuals domestically from non-point sources. Virtually everyone pours chemicals of one sort or another down their drains or toilets. Even detergents used in washing machines and dishwashers eventually end up in rivers and oceans. So also do the pesticides used on gardens. A lot of toxic pollutants also enter wastewater from highway runoff. Highways are typically covered with numerous toxic chemicals such as spilled fuel and brake fluids to bits of worn tyres (made from chemical additives) and exhaust emissions. When it rains, these chemicals are washed into drains and rivers. It is not unusual for heavy rainstorms to wash toxic chemicals into rivers in such concentrations that kill large numbers of fish overnight. Some highway runoff runs away into drains while others can pollute groundwater or accumulate in roadside land, making it increasingly toxic as the years go by (Harrison, 2001).

2.7.3 Oil Pollution

There are different sources of water pollution as evident in the literature. These include both within and externally induced pollution. For instance, Harrison (2006) showed that only 12% of the oil that enters the oceans comes from tanker accidents while over 70% of oil pollution at sea comes from routine shipping and from the oil people pour down drains on land.

However, what makes tanker spills so destructive is the sheer quantity of oil they release at once — in other words, the concentration of oil produced in one localized part of the marine environment. The biggest oil spill in recent years (and the biggest ever in US waters) occurred when the tanker Exxon Valdez broke up in Prince William Sound in Alaska in 1989. Around 12 million gallons (44 million litres) of oil were released into the pristine wilderness. Estimates of the marine animals killed in the spill vary from approximately 1000 sea otters and 34,000 birds to as many as 2800 sea otters and 250,000 sea birds. Several billion salmon and herring eggs were also destroyed (Woodford, 2006). In the Niger Delta Nigeria and most other oil producing countries off-shore oil spillage occur routinely and most of these incidents go unreported with endless effects on the aquatic life and the stability of the aquatic ecosystem in general.

2.7.4 Plastics

According to Woodford (2006), plastics are by and large, the most common substance that washes up with the waves. There are three reasons for this: plastic is one of the most common materials, used for making virtually every kind of manufactured object from clothing to automobile parts; plastic is light and floats easily so it can travel enormous distances across the oceans; most plastics are not biodegradable (they do not break down naturally in the environment), which means that things like plastic bottle tops can survive in the marine environment for a long time. Although plastics are not toxic in quite the same way as poisonous chemicals, they nevertheless present a major hazard to seabirds, fish, and other marine creatures. For example, plastic fishing lines and other debris can strangle or choke fish.

2.7.5 Alien Species

Most people's idea of water pollution involves things like sewage, toxic metals, or oil slicks, but pollution can be biological as well as chemical. In some parts of the world, alien species are a major problem. Alien species (sometimes known as invasive species) are animals or plants from one region that have been introduced into a different ecosystem where they do not belong. Outside their normal environment, they have no natural predators, so they rapidly run wild, crowding out the usual animals or plants that thrive there. Common examples of alien species include zebra mussels in the Great Lakes of the USA, which were carried there from Europe by ballast water (waste water flushed from ships). The Mediterranean Sea has been invaded by a kind of alien algae called Caulerpa taxifolia. In the Black Sea, an alien jellyfish called Mnemiopsis leidyi reduced fish stocks by 90% after arriving in ballast water. In San Francisco Bay, Asian clams called Potamocorbula amurensis, also introduced by ballast water, have dramatically altered the ecosystem (Woodford, 2006).

2.7.6 Chemical Waste

Chemical wastes include a large number of substances from detergents which are relatively mild substances to highly toxic chemicals such as polychlorinated biphenyls (PCBs). PCBs were once widely used to manufacture electronic circuit boards, but their harmful effects have now been recognized and their use is highly restricted in many countries. Nevertheless, an estimated half million tons of PCBs were discharged into the environment during the 20th century. In a classic example of trans-boundary pollution, traces of PCBs have been found in birds and fish in the Arctic. These were carried there through the oceans thousands of miles away from their environment. Although PCBs have widely been banned, their effects will be felt for many decades because they have a lasting effect on the environment without breaking down (Woodford, 2006).

Other kinds of toxic pollution come from heavy metals, such as lead, cadmium, and mercury. Lead was once commonly used in gasoline (petrol), though its use is now restricted in some countries. Mercury and cadmium are still used in batteries (though some brands now use other metals instead). Until recently, a highly toxic chemical called tributyltin (TBT) was used in paints to protect boats from the ravaging effects of the oceans. Ironically, however, TBT was gradually recognized as a pollutant: boats painted with it were doing as much damage to the oceans as the oceans were doing to the boats (Harrison, 2001).

Prominent heavy metal pollution on the ocean took place in 1938 when a Japanese factory discharged a significant amount of mercury metal into Minamata Bay, contaminating the fish stocks there. It took over a decade to remediate the problem. By that time, many local people had eaten the fish and around 2000 were poisoned. Hundreds of people were left dead or disabled (Environmental Agency Japan, 1975).

2.7.8 Other forms of Pollution

Heat or thermal pollution from factories and power plants also causes problems in rivers. By raising the temperature, it reduces the amount of oxygen dissolved in the water, thus reducing the level of aquatic life that the river can support (Woodford, 2006). Another type of pollution involves the disruption of sediments (fine-grained powders) that flow from rivers into the sea. Dams built for hydroelectric power or water reservoirs can reduce the sediment flow. This reduces the formation of beaches, increases coastal erosion (the natural destruction of cliffs by the sea), and reduces the flow of nutrients from rivers into seas (potentially reducing coastal fish stocks). Increased sediments can also present a problem. During construction work, soil, rock, and other fine powders sometimes enter nearby rivers in large quantities, causing it to become turbid (muddy or silted). The extra sediment can block the gills of fish, effectively suffocating them (Harrison, 2001).

2.8 Fish as a Biota

A fish is any gill-bearing aquatic vertebrate (or craniate) animal that lacks limbs with digits. Included in this definition are the living hagfish, lampreys, and cartilaginous and bony fish, as well as various extinct related groups. The term is negatively defined, and excludes the tetrapods (i.e., the amphibians, reptiles, birds and mammals) which descend from within the same ancestry, which is paraphyletic. The traditional term pisces (also ichthyes) is considered a typological, but not a phylogenetic classification. Most fish are "cold-blooded", or ectothermic, allowing their body temperatures to vary as ambient temperatures change. Fish are abundant in most bodies of water. They can be found in nearly all aquatic environments, from high mountain streams (e.g., char and gudgeon) to the abyssal and even hadal depths of the deepest oceans (e.g., gulpers and anglerfish). At 32,000 species, fish exhibit greater species diversity than any other class of vertebrates (Fish base, 2005). Fish, especially as food, are an important resource worldwide. Commercial and subsistence fishers hunt fish in wild fisheries or farm them in ponds or in cages in the ocean. They are also caught by recreational fishers, kept as pets, raised by fish keepers, and exhibited in public aquaria.

2.8.1 Fish Morphology

The diagram below presents the basic features of a typical fish.

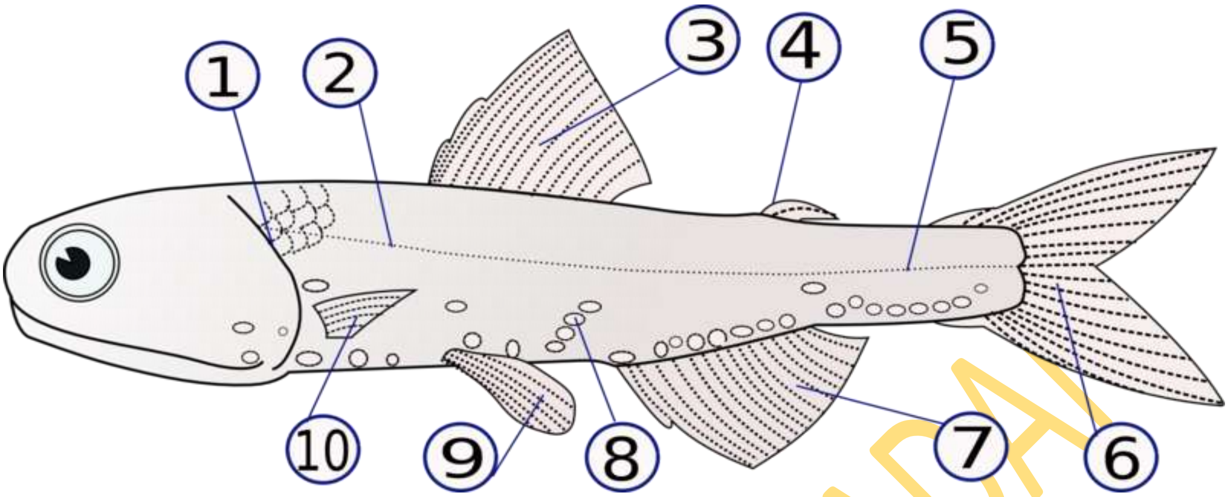

Fig 2.2: Fish morphology **Source:** Odums, 1971

Key:

(1) - operculum (gill cover), (2) - lateral line, (3) - dorsal fin, (4) - adipose fin, (5) - caudal peduncle, (6) - caudal fin, (7) - anal fin, (8) - photophores, (9) - pelvic fins (paired), (10) - pectoral fins (paired)

2.8.2 Fish Biology

2.8.2.1 Respiration

Most fish exchange gases using gills on either side of the pharynx. Gills consist of threadlike structures called filaments. Each filament contains a capillary network that provides a large surface area for exchanging oxygen and carbon dioxide. Fish exchange gases by pulling oxygen-rich water through their mouths and pumping it over their gills. In some fish, capillary blood flows in the opposite direction to the water, causing counter-current exchange. The gills push the oxygen-poor water out through openings in the sides of the pharynx. Some fish, like sharks and lampreys, possess multiple gill openings. However, most fish have a single gill opening on each side. This opening is hidden beneath a protective bony cover called an operculum. Juvenile bichirs have external gills, a very primitive feature that they share with larval amphibians (Fishbase, 2005).

Many fish can breathe air via a variety of mechanisms. The skin of anguillid eels may absorb oxygen. The buccal cavity of the electric eel may breathe air. Catfish of the families Loricariidae, Callichthyidae, and Scoloplacidae absorb air through their digestive tracts.

Lungfish, with the exception of the Australian lungfish, and bichirs have paired lungs similar to those of tetrapods and must surface to gulp fresh air through the mouth and pass spent air out through the gills. Gar and bowfin have a vascularized swim bladder that functions in the same way. Loaches, trahiras, and many catfish breathe by passing air through the gut. Mudskippers breathe by absorbing oxygen across the skin (similar to frogs). A number of fish have evolved so-called accessory breathing organs that extract oxygen from the air. Labyrinth fish (such as gouramis and bettas) have a labyrinth organ above the gills that performs this function. A few other fish have structures resembling labyrinth organs in form and function, most notably snakeheads, pikeheads, and the Clariidae catfish family (Odums, 1971).

Breathing air is primarily of use to fish that inhabit shallow, seasonally variable waters where the water's oxygen concentration may seasonally decline. Fish dependent solely on dissolved oxygen, such as perch and cichlids, quickly suffocate, while air-breathers survive for much longer, in some cases in water that is little more than wet mud. At the most extreme, some air-breathing fish are able to survive in damp burrows for weeks without water, entering a state of aestivation until water returns. Fish can be divided into obligate air breathers and facultative air breathers. Obligate air breathers, such as the African lungfish, must breathe air periodically or they suffocate. Facultative air breathers, such as the catfish *Hypostomus plecostomus*, only breathe air if they need to and will otherwise rely on their gills for oxygen. Most air breathing fish are facultative air breathers that avoid the energetic cost of rising to the surface and the fitness cost of exposure to surface predators (Odums, 1971).

2.8.2.2 Circulation

Fish have a closed-loop circulatory system. The heart pumps the blood in a single loop throughout the body. In most fish, the heart consists of four parts, including two chambers and an entrance and exit (Setaro and John, 1999). The first part is the sinus venosus, a thin-walled sac that collects blood from the fish's veins before allowing it to flow to the second part, the atrium, which is a large muscular chamber. The atrium serves as a one-way antechamber, sends blood to the third part, ventricle. The ventricle is another thick-walled, muscular chamber and it pumps the blood, first to the fourth part, bulbus arteriosus, a large tube, and then out of the heart. The bulbus arteriosus connects to the aorta, through which blood flows to the gills for oxygenation (Albert and Crampton, 2005).

2.8.2.3 Digestion

Jaws allow fish to eat a wide variety of food, including plants and other organisms. Fish ingest food through the mouth and break it down in the esophagus. In the stomach, food is further digested and, in many fish, processed in finger-shaped pouches called pyloric caeca, which secrete digestive enzymes and absorb nutrients. Organs such as the liver and pancreas add enzymes and various chemicals as the food moves through the digestive tract. The intestine completes the process of digestion and nutrient absorption (Albert and Crampton, 2005).

2.8.2.4 Excretion

As with many aquatic animals, most fish release their nitrogenous wastes as ammonia. Some of the wastes diffuse through the gills. Blood wastes are filtered by the kidneys. Saltwater fish tend to lose water because of osmosis. Their kidneys return water to the body. The reverse happens in freshwater fish; they tend to gain water osmotically. Their kidneys produce dilute urine for excretion. Some fish have specially adapted kidneys that vary in function, allowing them to move from freshwater to saltwater (Helfman et al., 2009).

2.8.2.5 Immune System

Immune organs vary by type of fish (Zapata *et al.*, 1996). In the jawless fish (lampreys and hagfish), true lymphoid organs are absent. These fish rely on regions of lymphoid tissue within other organs to produce immune cells. For example, erythrocytes, macrophages and plasma cells are produced in the anterior kidney (or pronephros) and some areas of the gut (where granulocytes mature). They resemble primitive bone marrow in hagfish. Cartilaginous fish (sharks and rays) have a more advanced immune system. They have three specialized organs that are unique to chondrichthyes; the epigonal organs (lymphoid tissue similar to mammalian bone) that surround the gonads, the Leydig's organ within the walls of their oesophagus, and a spiral valve in their intestine. These organs house typical immune cells (granulocytes, lymphocytes and plasma cells). They also possess an identifiable thymus and a well-developed spleen (their most important immune organ) where various lymphocytes, plasma cells and macrophages develop and are stored. Chondrostean fish (sturgeons, paddlefish and bichirs) possess a major site for the production of granulocytes within a mass that is associated with the meninges (membranes surrounding the central nervous system).

Their heart is frequently covered with tissue that contains lymphocytes, reticular cells and a small number of macrophages. The chondrostean kidney is an important hemopoietic organ; where erythrocytes, granulocytes, lymphocytes and macrophages develop (Fishbase, 2005).

The major immune tissues of bony fish (or teleostei) like chondrostean fish, include the kidney (especially the anterior kidney), which houses many different immune cells (Anderson, 1977). In addition, teleost fish possess a thymus, spleen and scattered immune areas within mucosal tissues (e.g. in the skin, gills, gut and gonads). Much like the mammalian immune system, teleost erythrocytes, neutrophils and granulocytes are believed to reside in the spleen whereas lymphocytes are the major cell type found in the thymus (Chilmonczyk, 1992; Hansen and Zapata, 1998). In 2006, a lymphatic system similar to that in mammals was described in one species of teleost fish, the zebrafish. Although not confirmed yet, this system presumably will be where naive (unstimulated) T cells accumulate while waiting to encounter an antigen (Kutcher *et al.*, 2006).

2.8.2.6 Diseases

Fish suffer from diseases and parasites like other animals. To prevent disease they have a variety of defences. Non-specific defences include the skin and scales, as well as the mucus layer secreted by the epidermis that traps and inhibits the growth of micro-organisms. If pathogens breach these defences, fish can develop an inflammatory response that increases blood flow to the infected region and delivers white blood cells that attempt to destroy pathogens. Specific defences respond to particular pathogens recognised by the fish's body, i.e., an immune response (Helfman *et al.*, 1997). In recent years, vaccines have become widely used in aquaculture and also with ornamental fish, for example furunculosis vaccines in farmed salmon and koi herpes virus in koi (Cipriano *et al.*, 2001 and Hartman *et al.*, 2004).

Moreover, some species use cleaner fish to remove external parasites. The best known of these are the Bluestreak cleaner wrasses of the genus *Labroides* found on coral reefs in the Indian and Pacific Oceans. These small fish maintain so-called "cleaning stations" where other fish congregate and perform specific movements to attract the attention of the cleaners (Helfman *et al.*, 1997). Cleaning behaviours have been observed in a number of fish groups, including an interesting case between two cichlids of the same genus, *Etroplus maculatus*, the cleaner, and the much larger *Etroplus suratensis* (Richard and Jack, 1972).

2.9 *Tilapia Guineensis*

Tilapia guineensis in Figure 2.3 is a euryhaline species found along the West Coast of Africa. There is an increasing interest in this fish for aquaculture purposes, particularly in areas of high or variable salinities, characteristic of the estuaries and extensive lagoon systems which constitute its natural range. In this habitat, other species more traditionally used in ‘tilapia’ culture are either not locally available (*Oreochromis mosambicus*) or do not tolerate the prevailing saline conditions *(O. niloticus*). *Tilapia guineensis* shares much the same range and habitat as *Sarotheromis melanotheron*, but neither species is well known for aquaculture purposes (Philippart and Ruwet, 1982).

Figure 2.3: *Tilapia guineensis*

2.9.1 Identification

The usual coloration of *T. guineensis* is shiny, dark greenish yellow on the back and flanks becoming lighter in shade near the abdomen. The lower lip is white. The ventral part is usually white although in some specimens black and red coloration appears. All scales on the flanks have a black spot at the base. The anal fin is grey and the ventral fins are grey or black and marked by a white line in the anterior edge. The dorsal fin is gray or transparent with the black "tilapia" mark very prominent. The tail is bluish grey and banded with lighter colored spots and a distinctly shaded upper and lower portion. *T. guineensis* is closely related to *T. zilli*. It is most easily differentiated from the latter by the mean number of spines in the dorsal fin (*T. zilli* = 15; *T. guineensis* = 16) and coloration (*T. zilli* has two horizontal dark bands, T. guineensis does not (Campbell, 1987)

Philippart and Ruwet (1982) noted that *T. guineensis* is geographically separated from other similar species (*T. zilli*, *T. rendalli*, *T. tholloni*, *T. congica*) and that they exclude each other. *T. guineensis* is found in the coastal waters of Africa from Senegal to Angola

Classification

Phylum	*Vertebrata*
Subphylum	*Craniata*
Superclass	*Gnathostomata*
Series	*Pisces*
Class	*Teleostomi*
Suborder	*Percoidei*
Family	*Cichlidae*
Genus	*Tilapia*
Specie	*guineensis*

2.9.2 Feeding Habits

2.9.2.1 Larvae and First Feeding

First feeding is defined as the transitional phase where the larvae shift from the yolk sac to external sources of nourishment. Feeding habits and preferences of larvae *T. guineensis* at this stage are poorly understood. Whereas other tilapia species at first feeding will accept and digest either zooplankton or plant material (Bodganova, 1970) and there is usually no problem at this stage using artificial compound feeds, this is not the case with *T. guineensis*. Poor success using compound feeds has discouraged several workers. Legendre (1983) noted a heavy mortality at first feeding using a mixture of egg yolk, powdered molk, and vitamins. In the Niger Delta, there was a poor survival with a variety of mixtures using crab meal, powdered molk, and powdered cereal. Although survival rates are not available, growth was very poor using other artificial diets. These same or very similar formulae are often used successfully with other species of tilapia, indeed other genera of fishes (Legendre, 1983).

2.9.2.2 Fry and Juveniles

In the estuaries of Sierra Leone, Payne (1978) reported that the fish of less than 6 cm in length fed on algae, and principally filamentous blue greens which they are able to digest. In brackish water ponds in the Niger Delta receiving only inorganic fertilizers, fish of 1.1 to 5.5 cm standard length are benthic feeders showing a strong preference for rotifers (Limnia, Pholidina, Branchionus sp.). They also fed on copepod nauplii, small (2 to 5 micron) benthic diatomes, and detritus (Mahatane, 1986).

2.9.2.3 Adults

There is preponderance of evidence regarding the feeding habit of fish in the literature. Fagade (1971) found the fish feeding on algae, detritus, sand, and invertebrates in the Lagos Lagoon. Moreover, Philippart and Ruwet (1982) considered the species to be macrophagous. Cisse (1985) considered the fish a benthic grazer. However, Payne (1978) found adults feeding on decaying leaves in the estuaries in Sierra Leone, and this author considered this species the only true estuarine leaf chewer. It can be concluded that *T. guineensis* is an opportunistic feeder, apparently able to consume and digest a variety of food items. The stomach pH values are extremely low; 1.0 to 3.7 with 75% of the observations being less than 2.0. A pH value of less than 2 will considerably help in the digestion of algae and bacteria (Payne, 1978).

2.10 *Clarias gariepinus*

2.10.1 Clarias gariepinus and it's Typical Characteristics

Figure. 2.4 is a picture of *Clarias gariepinus* or African sharp tooth catfish; a species of catfish of the family Clariidae, the air breathing catfishes. It got its binomial name in 1822 by a scientist named Burchell (Coetzee et al., 2002).

Figure 2.4: *Clarias gariepinus (* The African Catfish)

2.10.1.1 Natural Distribution

Clarias gariepinus are found throughout Africa and the Middle East and live in freshwater lakes, rivers, swamps, as well as human-made habitats, such as oxidation ponds or even urban sewage systems. The African sharp tooth catfish has been moved all over the world in the early 80s for rearing purposes and is therefore found in countries far outside its natural habitat like Brazil, Vietnam and India. The African sharp tooth catfish is a large, eel-like fish, usually of dark gray or black coloration on the back, fading to a white belly. In Africa, this catfish is second in size only to the Vundu of the Zambesian waters (De Graaf and Janssen, 1996). *Clarias gariepinus* has an average adult length of 1-1.5 meters. These fish have slender bodies, a flat bony head, notably flatter than in the genus *Siluris*, and a broad, terminal mouth with four pairs of barbels. They also have a large, accessory breathing organ composed of modified gill arches. Also, only the pectoral fins have spines. They can weigh up to 29 kg (UNDP/FAO, 1995).

2.10.1.2 Habit

It is a nocturnal fish like many catfish. It feeds on living as well as dead animal matter. Because of its wide mouth, it is able to swallow relatively large prey whole. It has been known to take large water birds such as the Common Moorhen. It is also able to crawl on dry ground to escape drying pools. Furthermore, it is able to survive in shallow mud for long periods of time, between rainy seasons (De Graaf and Janssen, 1996).

2.10.2 Biology of *Clarias gariepinus*

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. Prior to mating, males compete aggressively for females with which they mate in single pairs, the female swishing her tail vigorously to mix the eggs and sperm and distribute the fertilized eggs. The adhesive eggs stick to submerged vegetation and hatch in 20–60 hours, depending on temperature. The yolk sac is absorbed within 3–4 days and the stomach is fully functional within 5–6 days after onset of exogenous feeding. Sexual differentiation begins between 10 and 15 days after hatching. Larvae feed and grow rapidly in the warm (usually >24 °C) nutrient rich floodplains, reaching 3-7 g within 30 days. As flooded marginal areas dry up with the end of the rains, juveniles and adults make their way back to deeper water (UNDP/FAO, 1995).

In areas with two rainy seasons, there are usually two reproductive peaks during the year, corresponding with the intensity and magnitude of the rains. Stomach contents of *Clarias* species typically include insects (adults and larvae), worms, gastropods, crustaceans, small fish, aquatic plants and debris, but terrestrial seeds and berries, and even birds and small mammals, have also been observed. Larvae are almost exclusively dependent on zooplankton for the first week of exogenous feeding. Large *C. gariepinus*, because of their high number of gillrakers, also target zooplankton as a primary food source. Although generally omnivorous, *C. gariepinus* relatively better digests high-protein diets than carbohydrates. Most species of *Clarias* are slow foraging predators, with very small eyes, using their four pairs of barbels to feel their way around in the dark and find food detected by the array of sensitive taste buds covering the barbels and head. Approximately 70 percent of feeding activity takes place at night.

Research in South Africa showed that removal of the barbels reduced feeding efficiency in *C. gariepinus* by 23 percent. In general, *Clarias* catfishes capture their prey by gulping them with a rapid opening of the mouth and then retaining them either on the gillrakers or fine recurved teeth arranged on dentary, premaxillary, vomerine and pharyngeal bands. *C. gariepinus* exhibits a variety of feeding strategies including sucking the surface for terrestrial insects and plant fragments washed into the water by heavy rains and pack-hunting of small cichlids. Growth is relatively rapid, approaching maximum size within a couple of years (UNDP/FAO, 1995).

2.11 Heavy Metals in the Aquatic Environment

The contamination of freshwaters with a wide range of pollutants has become a matter of great concern over the last few decades, not only because of the threat to public water supplies, but also the hazards to human consumption of fishery resources (Terra *et al.*, 2008). Heavy metals are natural trace components of the aquatic environment (Al-Weher, 2008) and enter the aquatic environment through the earth crust which has led to steady state background level in aquatic environment. However their concentrations have increased due to human activities.

Municipal and industrial wastes, beside the atmospheric route have also introduced large quantities of heavy metals to localized areas in the aquatic environment. Furthermore, there is also the pollution of streams and rivers flowing through agricultural areas where pesticides, fungicides, etc. may have been applied, and industrial districts where there may have been metal waste deposits. These present varied and difficult problems due to drainage into the different water bodies. Discharge of heavy metals through effluents into rivers, lakes or any aquatic environment can change both aquatic species diversity and ecosystem due to their toxicity and accumulative behaviour (Allen-Gill and Martynovs, 1995). As heavy metals cannot be degraded, they are deposited, assimilated or incorporated in water, sediment and aquatic animals (Linnik and Zubenko, 2000), thus causing heavy metal pollution in water bodies.

The commonest causes of heavy metal poisoning in an aquatic environment are: copper, lead, mercury, zinc, chromium, cadmium, manganese and iron (Roberts, 1978). In the aquatic environment, heavy metal toxicity can be influenced by various abiotic environmental factors such as oxygen, hardness, pH, alkalinity and temperature (Adhikari *et al.*, 2006). Also the presence of other heavy metals is important, as heavy metals often act synergistically. However, some heavy metals counteract the effects of some other e.g. Cadmium in the presence of zinc or copper (La Roche, 1972). Heavy metal contamination may have devastating effects on the ecological balance of the recipient water body and a diversity of aquatic organisms (Farombi *et al.*, 2007; Vosyliene and Jankaite, 2006 and Ashraj, 2005) and among animal species, fishes are the inhabitants that cannot escape from the detrimental effects of heavy metals (Olaifa *et al.*, 2004; Dickson and Leung, 1998).

2.11.1 Heavy Metals in Fish

Contamination of freshwater fish with heavy metals is a recognised environmental problem. The world health organisation as well as the food and drug organisation of the United Nations stated that monitoring eight elements in fish; Hg, Cd, Pb, As, Cu, Zn, Fe and Sn is obligatory and monitoring of other heavy metals is suggested (Staniskiene, 2006). Heavy metals after contaminating water penetrate fish directly through skin and later gill (Sinha et al., 2002). Fishes develop a protective defence against the deleterious effects of essential and inessential heavy metals and other xenobiotics that produce degenerative changes like oxidative stress in the body (Abou El-Naga *et al*., 2005; Filipovic and Raspor, 2003). However, heavy metals are capable of causing the mutation of fish inner organs, disturb immune reactions, change blood parameters, and reduce fish adaptation qualities, vitality and resistance to diseases.

Fry loss and degeneration as well as diminution of valuable varieties of fish are observed as a result of heavy metal pollution (Blasco et al., 1999; Bird *et al.*, 1998; Alabaster and Lloyd, 1994). Heavy metal contamination not only directly affects fish health, but it can also disrupt the normal steroidogenesis pattern in fish, leading to impaired hormone production in both male and female fish, and decrease the quality and quantity of sperm and ova production (Ebrahimi and Taherianfard, 2011). Heavy metals may exert their deleterious effects on fish reproduction and gamete development via disruption of the endocrine system and the inhibition of hormone production, such as disruption of hypothalamic-pituitary system as well as depression of plasma androgens in females (Thomas *et al*., 1989).

The ingestion of these heavy metal contaminants, may affect not only the productivity and reproductive capabilities of fishes but ultimately affect the health of man that depends on fish as a major source of protein (Oyedepo *et al.*, 2007). Studies carried out on various fishes have shown that heavy metals may alter the physiological activities and biochemical parameters both in tissues and in blood (Basa and Rani, 2003; Canli, 1995). Heavy metals in the fish Gonads may be transferred to the next fish generations resulting in diseases or illnesses (Terra *et al.*, 2008). Fish accumulate metals to concentrations many times higher than present in water and sediment (Olaifa *et al.*, 2004). Fish can take up metals concentrated at different levels in their different body organs (Khaled, 2004). The rate at which heavy metals concentrate in fish are affected by several factors; apart from environmental factors such as salinity, pH, water hardness, it is also affected by the length and weight of fishes (Nsikak et al., 2007) and the time of exposure to metals (Haffor and Al-Ayed, 2003).

The major parts of the fish usually with the highest load in terms of concentration of metals are the liver, kidney and gills. However, among the different organs of fish subjected to heavy metals pollution, liver is the worst affected; liver being the principle site of detoxification, most of the toxic substances while passing through it may bring about biochemical changes (Evans *et al.*, 1993). Organs such as the gonads, bones, and brain may also show high metal levels, while the muscles, compared to the other tissues, usually show low concentrations of metals but are often examined for metal content due to their use for human consumption (Jezierska and Witeska, 2006).

At low levels, some heavy metals such as copper, cobalt, zinc, iron and manganese are essential for enzymatic activity and many biological processes while other heavy metals such as cadmium, mercury and lead have no known essential role in living organism and are toxic at even low concentrations. The essential metals may also become toxic at high concentrations (Bryan, 1976).

2.11.2 Uptake and Metabolism of Heavy Metals in Fish

Bioaccumulation of trace metals by fish, together with the underlying mechanisms, has been extensively studied in field and laboratory studies (Boudou and Ribeyre, 1989). Essentially, fish assimilate metals by: ingestion of particulate material suspended in water, ingestion of food, ion exchange of dissolved metals across lipophilic membranes e.g. the gills and adsorption on tissue and membrane surfaces. Excretion of heavy metals occurs via the faeces, urine and respiratory membranes while heavy metals distribution between the different tissues depends on the mode of exposure, i.e., dietary and/or aqueous exposure (Alam *et al.*, 2002).

According to Jezierska and Witeska (2006), heavy metals may be deposited in considerable amounts in fish tissues without causing mortality of fish. In addition, various heavy metals accumulate in fish body in different amounts; these differences result from different affinity of metals to fish tissues, different uptake, deposition and excretion rates. Heavy metal levels in live fish usually follow the ranking: Fe > Zn > Pb > Cu > Cd > Hg. The levels of Zn may be very high, up to over 300 µg/g dry weight (dw); the maximum concentrations of lead and copper are lower and usually do not exceed 10 µg/g (dw) while Cadmium and mercury are accumulated by fish in very low amounts, below 1 µg/g (dw).

Heavy metal accumulation in fish depends on pollution, and may differ among fish species living in the same water body (Jezierska and Witeska, 2001) since each fish specie has a particular rate of accumulating or eliminating heavy metals when exposed to such contaminants (Terra *et al.*, 2009). Generally, the higher the heavy metal concentration in the environment, the more the amount taken up and accumulated by fish. Relationship between heavy metal concentrations in fish and in the water was observed in both field and laboratory studies by many researchers (Moiseenko *et al.*, 1995; Linde *et al.*, 1996; Yamazaki *et al.*, 1996 and Zhou *et al.*, 1998).

Heavy metal level in the fish body is only related to its waterborne concentration if metal is taken up by the fish from water. If food is main source of metal, such a relationship does not necessarily occur. Some environmental factors affect the uptake and accumulation of metals in fish. Water temperature may cause the differences in metal deposition in various organs. Higher temperatures promote accumulation of cadmium especially in the most burdened organs: kidneys and liver (Yang and Chen, 1996). Studies have indicated that water acidification directly affects heavy metal accumulation rates by the fish. Comparison of the data concerning heavy metal levels in fish from various lakes indicates that the concentrations of cadmium and lead, but not zinc, are considerably higher in the fish from acidified lakes (Haines and Brumbaugh, 1994 and Horwitz *et al.*, 1995). Accumulation of copper is also higher at lower pH (Cogun and Kargin 2004). Water acidification, as stated by Rai *et al.*, (2011) affects bioaccumulation of heavy metals by the fish in an indirect way, by changing solubility of metal compounds or directly, due to damage of gill epithelia which become more permeable to heavy metals. On the other hand, competitive uptake of H^+ ions may inhibit heavy metal absorption. According to Playle *et al.*, (1992), water hardness (mainly calcium concentration) considerably affects uptake of heavy metals across the gill epithelium with reduced copper accumulation in the gills following enrichment of water with calcium.

Baldisserotto *et al.*, (2005) reported that elevated dietary Ca^{2+} protected against both, dietary and waterborne Cd uptake. The results obtained by Barron and Albeke (2000) indicated that calcium reduces zinc uptake by *Oncorhynchus mykiss.* Pagenkopf (1983) revealed that calcium might compete with other metals for binding sites on the gill surface. Similarly like hardness, salinity also reduces uptake and accumulation of heavy metals by fish. According to Stagg and Shuttleworth (1982), seawater adapted *Platichthys flessus* showed lower copper concentration than freshwater-adapted individuals. The rate of lead accumulation by *Gillichthys mirabilis* was inversely proportional to the salinity of the medium (Somero *et al.*, 1977). Natural waters are usually contaminated with mixtures of heavy metals and other toxic compounds. Accumulation of certain heavy metals in fish may be altered in the presence of the others (Allen, 1994, 1995 and Pelgrom *et al.*, 1995).

Inter-species differences in heavy metals accumulation may be related to living and feeding habits as observed by Kidwell *et al.*, (1995) that predatory fish species accumulated more mercury but the benthivores contained more cadmium and zinc. Higher concentrations of mercury in the predatory fishes compared to the non-predatory ones was also reported by Voigt (2004). Ney and Van Hassel (1983) found that lead and zinc concentrations were higher in benthic fish. The results obtained by Campbell (1994) indicated that predators accumulated more zinc and nickel than benthivores, while the latter contained more cadmium. The age of an organism can also increase or reduce the uptake of heavy metals; Cadmium and mercury accumulation increase with age, while Mn, Cr, Cu and Zn accumulation decrease with age. Thus, the different patterns reflect different metabolism for each metal (Khalid, 2008).

2.12 Fish as an Indicator of Heavy Metal Pollution in Water

The relationships between the physico-chemical properties of organic compounds and physiological responses in organisms have been studied since the late 19th century (as cited by Arnot and Gobas, 2006); however, it was not until the 1960s that the risk of anthropogenic chemicals on humans and environmental health drew public attention (Fox *et al.*, 1991 and Carson, 1962).

Fishes are a major component of most aquatic habitats and are often at the top of the aquatic food chain; as such, they may concentrate large amounts of certain heavy metals from water (Mansour and Sidky, 2002) and other organisms. In addition to adsorption on tissue and membrane surface, fish may assimilate metals by ingestion of particulate material or food in water, or ion-exchange of dissolved metals through lipophilic membranes such as the gills (Mendil *et al.*, 2005). Metal distribution between different tissues depends on the mode of exposure, which that is either dietary or aqueous exposure, and can serve as a pollution indicator (Alam *et al.*, 2002). Apart from the fact that fish occupies the highest trophic level in aquatic system (APHA, 1981); it has high economic value, is a suitable water quality symbol and easy to be interpreted by public.

Fish can also respond to environmental changes that can be used for pollution indication study. Monitoring heavy metal contamination in water bodies using fish tissues are considered as one of the most indicative factors for estimation of heavy metal pollution in fresh water systems (Rasheed, 2001) since heavy metals concentration in tissues reflects past and present exposure (Canli *et al.*, 1998 and Yilmaz, 2003). Furthermore, fish is a good bio-indicator because it can be obtained in large quantity, and have potential to accumulate heavy metals, long lifespan with optimum size for analysis and easy to sample (Batvari *et al.*, 2007). The use of fish as bio-indicator can determine the actual situation of pollution level before and during monitoring.

According to Teodorovic *et al.*, (2000) and Abdullah *et al.*, (2008), heavy metals studies in aquatic biota give an idea that heavy metals in aquatic organisms could be a more reliable water quality indicator than chemical analysis of water column and sediment. Furthermore, the study of organisms such as fish as pollutant monitors has several advantages over the chemical analysis of an ecosystem. Organisms only accumulate the biologically available forms of the pollutants and are also available in the environment, thus enabling the continuous monitoring of pollutants (Marcovecchio, 2004) as fishes are constantly exposed to pollutants in contaminated water, could serve as excellent biological markers of heavy metals in the aquatic ecosystem (Nsikak *et al.*, 2007).

Heavy metals content in aquatic organisms has also been successfully used in evaluation of heavy metals input into European and American rivers. Fish are often the top consumers in the aquatic ecosystem (Van *et al.*, 2002) and thus metal concentrations in fish can serve as an environmental indicator of the state of the environment (Widianarko *et al.*, 2000). Fishes are important source of food for humans and are a key unit in many natural webs as prominent component of aquatic ecosystems. Fishes equally impact on the physicochemical properties of the human system, plankton, macrophytes and other aquatic organisms. They also serve as environmental indicators. Changes in the composition of a fish assemblage often indicate a variation in pH, salinity, temperature regime, solutes, flow clarity, dissolved oxygen, substrate composition or pollution level. Fish are the primary indicators of the toxification of streams or lakes (APHA, 1989). Fish share many physiological properties with mammals and are used in both the laboratory and the field by environmental managers and health specialists as assay tools.

2.13 Bio-concentration, Bio-accumulation and Bio-magnification of Heavy Metals in Fish

Heavy metals are dangerous because they tend to bio-concentrate, bio-accumulate and bio-magnify. Bio-concentration is the intake of chemical contaminants through an organism's epithelial tissues or gills, and the subsequent concentration of that chemical contaminant within the organism's tissues to a level that exceeds ambient environmental concentrations (Konasewich *et al.*, 1982 and Gobas *et al.*, 1999).

Bio-accumulation was defined by Arnot and Gobas (2006) as a process in which a chemical substance is absorbed in organism by all routes of exposure as occurs in the natural environment i.e. dietary and ambient environmental sources. Bio-accumulation is the net result of competing processes of chemical uptake into the organism at the respiratory surface and from the diet and chemical elimination from the organism including respiratory exchange, fecal egestion, and metabolic biotransformation of the parent compound and growth dilution.
The Bio-accumulation factor (BAF) can be calculated as the ratio of the chemical concentration in the organism to the chemical concentration in the water at steady state.

$$BAF = C_B / C_{WD}$$

Where

C_B = Chemical Concentration in the organism

C_{WD} = Chemical Concentration in the water

A bioaccumulation factor of >5000 is regarded as high by Canadian criteria for standard.

Bio-magnification is the process by which chemical contaminants are concentrated at levels that exceed chemical equilibrium from dietary absorption of the chemical and increases with each step in the food chain (Gobas *et al.*, 1999) over time, compared to the chemical's concentration in the environment.

The bio-concentration, bio-accumulation, and bio-magnification of chemical contaminants in marine biota are dynamic processes that involve many interconnected variables. For example, the ability of a chemical to bio-concentrate, bio-accumulate, or bio-magnify in organisms and food webs is dependent upon the properties of the chemical (e.g. hydrophobicity, lipophilicity, and resistance to degradation), environmental factors (e.g. salinity, temperature, concentration of other organic chemicals, and redox potential), biotic factors (e.g. the organism's mode of feeding, trophic position, lipid concentration, and metabolism), and bioavailability (e.g. current chemical inputs, transport mechanisms, and degree of contamination) (Konasewich *et al.*, 1982; Shin and Lam 2001; Gobas *et al.*, 1999; Morrison *et al.*, 1996; and Lee *et al.*, 2000).

Biological magnification also refers to the process whereby certain substances such as pesticides or heavy metals move up the food chain, work their way into rivers or lakes, and are eaten by aquatic organisms such as fish, which in turn are eaten by large birds, animals or humans. The substances become concentrated in tissues or internal organs as they move up the chain. Bio-accumulants are substances that increase in concentration in living organisms as they take in contaminated air, water, or food because the substances are very slowly metabolized or excreted.

The aquatic organism take in heavy metals through three ways: -The body surface,-the gills,-the food. In an aquatic environment, micro-organisms accumulate metals and consequently small fish become enriched with the accumulated substances. Predatory fish, generally display higher levels of heavy metals than their prey (Khalid, 2008).

2.14 Heavy Metals Monitoring and Assessment

Excessive accumulation of heavy metals can have deleterious effects on aquatic biota, water quality, affect ecosystem functions and constitute a risk to animals and human health (Sun *et al*., 2001). To avoid undesirable toxic effects on animals, sensitive monitoring systems of bio-indices should be employed in advance, to predict hazardous effects through scientifically recognised mechanisms. In the light of this, it is necessary to know the level of pollution of the aquatic ecosystem so as to develop technologies for improving the level of water purification and the remediation of contaminated sites as well as techniques to reduce and manage the effluents discharged into them. The presence of a metal does not necessarily indicate an environmental problem, however, it is a matter of concern when the amount detected approaches or exceeds the concentration that can harm organisms, including humans (Sawyer *et al*., 1994).

The consequences of heavy metal pollution in the aquatic environment can be hazardous to man through the consumption of fish and water. Therefore, it is important to monitor the level of heavy metals in aquatic environment; water, sediment and biota. Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota, which generally exist in low levels in water and attain considerable concentration in sediments and biota (Camusso *et al.*, 1995).

Heavy metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage and threat to human health (Van *et al.*, 2002; Gagnaire et al., 2004). Potential damage is forestalled when fishes are constantly monitored. It is important to determine the concentrations of heavy metals in commercial fishes in order to evaluate the possible risk of consuming fish (Cid *et al.*, 2001).

2.15 Previous Studies on Assessment and Monitoring of Heavy Metals Levels in Some Aquatic Ecosystems

Several studies have been done globally to evaluate the extent of heavy metals distribution and pollution of the aquatic ecosystem. These studies have been carried out in rivers, dams, lakes and ponds. Cited below are some of these studies;

Farombi *et al*, (2007) carried out a study on the biomarkers of oxidative stress heavy metal levels as indicators of environmental pollution in African catfish (*Clarias gariepinus*) from Ogun River; a river located close to six major industries in the south western part of Nigeria. The result of the study showed that heavy metals ranged from 0.25-8.96 ppm in the heart, 0.69-19.05 ppm in the kidneys, 10-19.75 ppm in the liver and 1.95-20.35 in the gills. Overall, the result demonstrates that alteration in the antioxidant system, glutathione system and induction of lipid peroxidation reflects the presence of heavy metals which may cause oxidative stress in the *clarias gariepinus* from Ogun River.

Olowu *et al.*, (2009) evaluated heavy metals in fish tissues, water and sediment from Epe and Badagry Lagoons, Lagos, Nigeria. The result of the study showed that the concentration of Zn in the water was within the limits permitted by the Lagos State Environmental Protection Agency (LASEPA) of 1.0 mg/L Zn set for water. None of the trace metals investigated was above the maximum permissible level set by world health organization (WHO). Furthermore, higher concentration of Zinc was detected in the Catfish than in Tilapia fish.

Sadik (1990) studied heavy metal contaminants in some Nigerian marine fishes of commercial importance. Using WHO acceptable standards, it was concluded from the results that it is unlikely that any of the concentration found represent an acute risk to the biota of Nigerian waters or to man as a consumer.

Omitoyin and Ajani (2007) studied the feeding habits and bio-accumulation of heavy metals in three fish species of Lake Eleyele, Ibadan, Nigeria. The result of the study showed that *Hydrocynus forskalli* (a carnivore), had the highest mean concentration of heavy metals while the lowest mean concentration was recorded in *Tilapia zilli* (Herbivore). Although bioaccumulation of heavy metals in relation to feeding habits did not show any significant difference

Ekpo *et al.*, (2008) determined Lead, Cadmium and Mercury in surrounding water and organs of some species of fish from Ikpoba River in Benin City, Nigeria. From their results it was seen that the levels of these metals in the fishes were higher than that obtained from the surrounding waters from which the fishes were obtained.

Mazlin *et al.*, (2009) carried out a study to assess the level of heavy metals in Penaeus Monodon and Oreochromis spp in selected Aquaculture ponds of high density development area in Malaysia. They discovered that the concentration of the heavy metals studied were lower than the recommended maximum level allowed in food thus indicating that *Penaeus monodon* and *Oreochromis spp* from the investigated ponds were safe for human consumption.

Ozturk *et al.*, (2008) assessed heavy metals in fish, water and sediments of Avsar dam lake in Turkey. Amongst the heavy metals assessed, the concentration of iron (Fe) was highest in the water and sediment samples while in the fish samples, Cadmium, Chromium, Nickel and Lead concentrations exceeded the tolerable values provided by international standard regulatory institutions.

Amaal and Yasser (2009) evaluated the heavy metal status in Ecosystem of lake Manzalah, Egypt. The results of the heavy metal analyses indicated that the sediment and fishes were heavily contaminated with Cadmium and Lead. It was also seen that *Eichhornia crassipes* had a high affinity to accumulate Nickel and Cobalt especially in the roots.

Benjamin (2003) studied the levels of Cadmium and Lead in water, sediments and selected fish species in Mombasa, Kenya. Overall, Pb and Cd concentrations were low in the water column with a few incidents of elevated levels in sediments and some fish species especially during the rainy season. The levels of Pb and Cd in most of the fish species analysed were generally within acceptable limits by FAO standards.

Obasohan *et al.*, (2007) determined post-dredging concentrations of selected trace metals in water, sediment and freshwater mudfish (*Clarias gariepinus*) from Ikpoba River in Benin City, Edo state, Nigeria. The study showed that the levels of Mn, Ni and Pb in water; Cu, Mn, Cr and Pb in fish were higher than the recommended levels in drinking water and food fish and could pose health hazards. Furthermore, the post-dredging metal contamination levels in water and sediments of the river were lower than available pre-dredging levels, but in fish the difference was not significant.

2.16 Guideline/Standard of Heavy Metals in Water and Fish

Heavy metals are known to be mostly toxic even in minute concentrations. It is against this backdrop that several regulatory institutions both within the country and internationally have put forward various recommendations on the concentration of heavy metals allowed in edible fish and surface water. These guidelines are shown in Table 2.2 and 2.3.

Table 2.2 Guideline/Standard of Heavy Metals in Water

	WHO 1993 mg/L	FEPA 2003 mg/L	SON 2007 mg/L	WHO 2003 mg/L
Lead	0.01	<1.0	0.01	0.05
Cadmium	0.003	<1.0	0.03	0.01
Chromium	0.05	<1.0	0.05	0.05
Zinc	3.0	20	3.00	5.0
Copper	2.0	<1.0	1.00	1.00
Manganese	0.01	0.05	0.20	0.50
Nickel	0.05	<1.0	0.02	0.02

Sources: Obasohan *et al.*, 2007 and Obasohan, 2008

Table 2.3 Guidelines/Standard of Heavy Metals in Fish

	WHO 1972 mg/Kg	**FAO 1983 mg/Kg**	**WHO 1985 mg/Kg**	**FEPA 2003 mg/Kg**
Lead	2.00	0.50-6.00	2.00	2.00
Cadmium	1.00	0.05-5.50	2.00	
Chromium		1.00	0.15	0.15
Zinc	100	30-100	10-75	75
Copper	30	10-100	3.00	1-3
Manganese	1.00	-	0.5	0.5
Nickel	0.5-1.0	-	0.6	0.5

Source: Obasohan, 2008

CHAPTER THREE

3.0 METHODOLOGY

3.1 DESCRIPTION OF STUDY AREA

Agodi Lake, on which this study was conducted, is one of the natural lakes in Ibadan. It runs along the state secretariat, premier hotel/ cultural centre road in Ibadan north local government area of Oyo state. Agodi Lake is the property of Oyo state government of Nigeria and is managed by the Fisheries Department of the Ministry of Agriculture, Natural Resources and Rural Development. It was established as a result of Ibadan flooding of 1980 during which thousands of lives and properties were lost, a loss attributed to Ogunpa river overflowing its boundaries. The lake was hence built primarily as a flood control device and impounded within the vicinity of the headquarters of the fisheries department for easy monitoring and exploitation. The lake is an unrestricted one and may have waste from remote and immediate environs channelled into it. A pictorial description of the study area is shown in Plate 3.1.

3.1.1 Geographical and Topographical Features

Agodi Lake lies between longitude $07^{0}40$'N and latitude $03^{0}89$'E of the equator with an altitude of 200 meters. Basically, apart from municipal run-off it is fed by three major tributaries: Ashi/ Bodija River, Oremeji River and University College Hospital (UCH) sewage treatment plant. The lake is bounded by these water bodies as well as areas of land used for agricultural activities and motor-able highways on the eastern and western axis respectively. Water from the lake ultimately empties into Ogunpa river across the road. The Lake covers an area of approximately 4.05 hectares and a depth of 12 meters though mostly silted at the base (Verbal communication). The vegetation here is mainly of the rainforest type with crippling and standing plants. About 1/3 of the surface area of the lake is covered by a variety of the aquatic weed species but mostly of the specie *Eichhornia crassipes* commonly known as water hyacinth. The proliferation of this weed across the lake, makes navigation on the lake difficult. The lake is surrounded by a number of trees that serve in the capacity of watershed and ecological support.

Plate 3.1: Cross Section of Agodi Lake

3.1.2 Fish Species Abundance

Since impoundment, the lake has not been stocked with any fish seed. All the stocks in the lake are from the wild and the escaped fish species from the adjoining government fish farm (Inland fish breeding centre) during flooding or when fishes escape and pass through the channel way to the lake. Fish species of different morphology and feeding pattern are cultivated in the lake. In terms of abundance the most commonly harvested fish species are Clarias gariepinus, *Oreochromis niloticus, Heterotis niloticus* and *Tilapia guineensis* (Verbal Communication) .

3.2 Sampling Stations

Sampling for the study was performed in three different stations.

3.2.1 Station One

Station one (1) is the UCH sewage treatment plant effluent which is channelled into Agodi Lake. It lies between longitude $07^{0}40'$ N and latitude $03^{0}90'$ E of the equator with an altitude of 203 meters. It is one of the main tributaries that feeds the lake and served as one of the sampling stations from where water samples were collected.

3.2.2 Station Two

Station two (2) is the Oremeji river which runs through Iwo road axis of Ibadan. The specific area chosen is the point of the river that channels water into the lake at a distance of approximately 20 meters from the lake along cultivated agricultural lands. It lies between longitude $07^{0}40'$ N and latitude $03^{0}89'$ E of the equator with an altitude of 206 meters. It is also a major tributary that feeds the lake and served as one of the sampling stations from where water samples were collected.

3.2.3 Station Three

Station three (3) is the Ashi/Bodija River that runs across Bodija axis of Ibadan. The area of interest was the point where the river empties into Agodi Lake. This is approximately 20 meters away from the lake and is within the Agodi zoological gardens. It lies between longitude $07^{0}40'$ N and latitude $03^{0}90'$ E of the equator with an altitude of 205 meters. It is another major tributary that feeds the lake and served as one of the sampling stations from where water samples were collected.

3.3 Study Design

The study was analytical in design. It involved both field and laboratory work.

3.4 Entry Procedure and Approval for the Study

Approval for conducting the study on Agodi Lake was sought in writing from the Commissioner, Ministry of Agriculture, Natural Resources and Rural Development through the Director, Department of Fisheries of the same ministry. Approval was subsequently granted for the study to commence. Community entry and familiarisation with members of staff of the lake establishment, local fishermen as well as all other protocols that aided the study was well established. The process of obtaining approval lasted for a period of eight weeks.

3.5 Sample Collection

This study was carried out between June and July in the rainy season. Water samples for assessment of physico-chemical parameters were collected from the lake and its tributaries. Samples of *Clarias gariepinus* and *Tilapia guineensis* were collected from lake for assessment of Lead, cadmium, chromium, zinc and copper. Sampling was done once weekly between the hours of 9am-12noon for four consecutive weeks. Details of sampling procedure are found in subsequent sections.

3.5.1 Collection of Water Samples

Water samples were collected from the lake and the major tributaries that feed the lake. On the lake, samples were collected from three (3) points at 50 meters apart while from the lake tributaries, samples were collected from seven (7) stations. The three points chosen on the lake were an approximate representation of the navigable areas (areas not covered by weeds) of the lake while the seven stations chosen for the tributaries have the following description;

POINT I= UCH sewage effluent at point of discharge

POINT 2= Oremeji river about 20 meters from lake

POINT 3= UCH effluent as it mixes with municipal run-off in Agodi garden

POINT 4= Ashi/Bodija river about 20 meters from lake

POINT 5=Oremeji river as it mixes with lake water

POINT 6= UCH effluent as it mixes with lake water

POINT 7= Ashi/Bodija as it mixes with lake water

Water samples were collected in three different kinds of containers, which were dependent on the sort of analysis to be performed. For the determination of heavy metals, water sample was collected in 60ml polyethylene bottles; for dissolved oxygen (DO) determination, water sample was collected in 250ml DO bottles (dark bottles) while for the determination of the other physico-chemical parameters i.e. Temperature, pH, Conductivity and Total dissolved solids, water samples were collected in 0.5L polyethylene bottles. Polyethylene containers were used to collect water samples meant for heavy metals analysis because eroding of the inner surface can not contribute to the concentration of heavy metals in the water samples.

At each sampling site, the polyethylene sampling bottles were rinsed at least three times before sampling was done. Pre-cleaned polyethylene sampling bottles were immersed about 10 cm below the water surface and required volume of water samples were taken at each sampling site. Replicate water samples were collected at each sampling site to ensure quality assurance. Samples for heavy metals determination were acidified with two(2) drops of conc. HNO_3; Samples used for Dissolved oxygen determination were fixed with 2ml each of Manganese(II)sulphate solution (winkler A) and Alkali-iodide Azide reagent (Winkler B) per sample. These operations were carried out on the field. All samples were then placed in an ice chest and taken to the laboratory on the same day.

3.5.2 Collection of Fish Samples

Fish samples (Catfish; *Clarias gariepinus* and Tilapia; *Tilapia guineensis*) were harvested from lake with the assistance of local fishermen using standard fishing gears prescribed by UNEP (1984). Catfish was collected with baited fishing hook with line number 9 while tilapia fish was collected with fishing net of mesh size three (3) inches by local fishermen. The difference in fishing gear was due to the variation in size of the two fish species. Six (6) fishes per specie were collected at each sampling. Also, the same number of fishes per specie were collected from another natural lake (Eleyele Lake) which served as the control sampling location. A total of twenty-four (24) fish samples were collected at each sampling and sampling was done for four consecutive weeks. Fish Samples were washed with lake water at the point of collection, separated by species, placed on ice and taken to the laboratory on the same day. Fish samples were either prepared at once or kept at 0°C until analysis. The fish samples collected were identified and classified based on their characteristic features using standard texts (Odum, 1971). Only adult fishes were sampled. The samples of *Tilapia* *guineensis* used for study are shown Plate 3.2 while the samples of *Clarias gariepinus* are depicted in Plate 3.3.

Plate 3.2: ***Tilapia guineensis*** **Samples Used for Study**

Plate 3.3: *Clarias gariepinus* samples used for study

3.6 Sample Preparation Procedure

All collected water and fish samples were prepared for subsequent laboratory analysis using standard methods.

3.6.1 Preparation of Water Samples

Water samples collected for Temperature, pH, conductivity and total dissolved solids determination were not subjected to any kind of preparation or pre-treatment.

3.6.2 Preparation of Fish Samples

In the laboratory, the morphometric characteristics of the fish samples were taken. The fish samples were put onto a dissection tray and thawed at room temperature if already frozen before dissecting or dissected directly using stainless steel scalpels and Teflon forceps on a laminar flow bench. Dissection of the fish samples was done to separate liver, gill, skin and muscle tissues using the methods recommended by UNEP/FAO/IAEA/IOC (1984) and Bernhard (1976). Composite samples of liver, gill, skin and muscle tissues of each species were drawn. Each composite comprised of three (3) fishes of same species. They were then weighed separately in clean, labelled Petri-dishes and dried in the laboratory oven at 110°C to constant weight. Pulverization and homogenization were achieved by grinding the tissue samples in a Teflon mortar.

Plate 3.4: Harvested Fish Tissues

Key

a = Muscle

b = Skin

c = Gill

d = Liver

3.7 Laboratory Procedures

Apart from the Temperature and pH of the water samples that were measured in-situ, all other analyses were carried out in the laboratory using standard procedures.

3.7.1 Water Samples

Collected water samples on arrival at the laboratory were assessed for dissolved oxygen, conductivity, total dissolved solids and heavy metals.

3.7.1.1 Physico-Chemical Analysis of Water Samples

All physico-chemical analyses were done using APHA (1998) standard methods.

TEMPERATURE DETERMINATION (^oC)

Temperature is a measure of the degree of hotness or cold of a substance. A standardised mercury in glass centigrade thermometer was used for this determination. The thermometer was placed vertically with the bulb containing the mercury completely immersed in each water sample. It was then allowed to stand till the temperature reading was constant, thereafter the reading was taken. The thermometer probe was rinsed with distilled water between samples and readings taken to the nearest half degree.

HYDROGEN ION (pH) DETERMINATION

pH is the term used to express the intensity of the acid or alkaline condition of a solution. The pH value can be defined as the logarithm to base 10, of the reciprocal of the concentration; or, pH value is equal to the logarithm of the hydrogen-ion concentration. This is mathematically expressed as:

$$pH= -\log_{10} [H^+] = \log_{10} [1/H^+] \qquad (1)$$

Where $[H^+]$ is the hydrogen-ion concentration.

The pH of the water samples was measured by electrometric method using a laboratory pH meter. This device makes use of a combination of glass electrode with a reference potential provided by a standard calomel electrode. Before use, the pH meter was standardised with two buffer solutions of pH 4 and 9 which are acidic and alkaline in nature and serve as check for proper instrument response. The pH meter electrode was placed vertically into each water sample, allowed to stand until reading stabilised, then constant pH reading was recorded. The pH electrode was rinsed thoroughly with distilled water between samples. JENWAY pH meter 370 model was used for all pH measurements.

CONDUCTIVITY AND TOTAL DISSOLVED SOLIDS DETERMINATION

Electrical conductivity is a measure of the ability of a substance to conduct electricity. Electrical conductivity of potable water is mainly due to dissolved mineral matter, free carbon (IV) oxide and Ammonia. The electrical conductivity of wastewaters, Treatment plant effluents and polluted waters is due to the presence of ionic solutes. The magnitude of conductivity is a useful indication of the total concentration of the ionic solutes. It is given as μScm^{-1}.

The total dissolved solids present in a liquid substance is the total amount of matter left behind after a clear liquid has been evaporated to dryness at 103^0C. It is given as mg/L.

Conductivity and Total dissolved solids of the water samples was measured using JENWAY Conductivity meter model MC METTLER TOLEDO, manufactured in 2005. The conductivity meter probe was inserted vertically into individual water samples and the measurement recorded when reading became stable for conductivity and TDS respectively. Probe was rinsed thoroughly with distilled water between samples.

DISSOLVED OXYGEN DETERMINATION (TITRIMETRIC METHOD)

The amount of oxygen found by determination in a sample of water or wastewater at the time of collection is the dissolved oxygen (DO). The method used to determine the DO in the water samples was Winkler’s Titrimetric method. This method operates according to the principle shown below.

PRINCIPLE

In solution, Manganese (II) hydroxide ($Mn(OH)_2$) is formed from anhydrous manganese (II) sulphate. DO in water combines with the Manganese (II) hydroxide and oxidises the Mn^{2+} to higher valency state Mn^{4+} which is precipitated as brown hydrated oxide. On subsequent addition of acid in the presence of iodide, iodine is liberated in an amount equivalent to the original DO content of the water sample. The iodine is then determined by titration with standard 0.0125M Sodium Thiosulphate solution ($Na_2S_2O_3$). The amount of $Na_2S_2O_3$ used in the titration is equal to the amount of DO present in the sample**.**

STANDARDISATION

About 2g of potassium iodide KI was dissolved in an Erlenmeyer flask with 100 to 150ml distilled water. Added to this was a solution containing 1 volume H_2SO_4 + 9 volume distilled water followed by 20ml standard dichromate solution (0.0125M). The entire mixture was then placed in the dark for 5minutes, after which it was diluted to 400ml with distilled water. This was titrated with $Na_2S_2O_3.5H_2O$ solution and its exact molarity calculated.

Molarity(C_2) =$C_1V_1n_2/V_2n_1$

Where

C_1= molarity of standard dichromate solution

C2= molarity of sodium thiosulphate solution

n_1= number of moles of dichromate solution

n_2= number of moles of sodium thiosulphate

V_1= volume of dichromate solution

V_2=Volume of sodium thiosulphate solution

The value obtained as the molarity of the sodium thiosulphate used was approximately 0.0125M which is the standard molarity.

PROCEDURE

The water samples were collected in a 250ml bottle into which 2ml each of $MnSO_4$ solution and alkali-iodide azide reagent was added well below the surface of the liquid. The bottle was stoppered with care to exclude air bubbles and mixed by inverting a number of times until a clear supernatant was obtained. This mixture was allowed to settle for about two minutes and then 2ml of H_2SO_4 was added, re-stoppered and mixed gently until completely dissolved. About 203ml of this mixture was then titrated with 0.0125M $Na_2S_2O_3.5H_2O$ solution to a pale straw colour. Two drops of starch solution was added and the mixture changed to blue, titration continued by adding sodium thiosulphate solution dropwise until the blue colour disappeared. The volume of Sodium thiosulphate used for each sample was recorded and this was equivalent to the amount of DO present in the sample. Dissolved oxygen (DO) was expressed in **mg/L.**

3.7.1.2 Determination of Heavy Metals in Water Samples

Water samples were analysed directly without further digestion. A volume of 25ml of each water sample was measured using a Teflon measuring cylinder, aspirated into Buck scientific Atomic Absorption Spectrophotometer model 210 VGP shown in Plate 3.5 and analysed for the concentration of heavy metals; Lead(pb), Cadmium (Cd), Chromium (Cr), Zinc (Zn), Copper (Cu) that is present. Calibration of the machine was done using standard solution of known concentrations of the analysed heavy metals. Samples were analysed in replicates. Blanks were also run intermittently to confirm machine's performance. Heavy metal concentration was expressed in mg/L. Results obtained were compared with national and international standards/guidelines for heavy metals in water.

3.7.2 Determination of Heavy Metals in Fish Samples

Pulverised and homogenised fish samples were digested using a mixture of nitric/perchloric acid as suggested by the American Chemical Society (AMC) (Reilly, 1980). For each pulverised fish sample, 0.5g was weighed with Mettler H10 sensitive weighing balance and poured into Teflon digestion tubes. Into each digestion tube containing samples, 5ml of a mixture of Nitric/perchloric acid in the ratio of 2:1 was added. This addition was done for all samples. The digestion tubes were placed unto a rack and conveyed to the digestion chamber for digestion. The digestion system used was Tecator Digestion System model 40. Samples were digested for 2hours at a temperature of 150^0C. At the end of the digestion time, a colourless liquid was obtained in the tubes as the digest. Each digest was then transferred into a 25ml Erlenmeyer flask and made up to mark with distilled water. The diluted samples were then aspirated into Buck Scientific Atomic Absorption spectrophotometer model 210 VGP and analysed for Lead, Cadmium, Chromium, Zinc and Copper. Procedural blanks were run alongside samples to ensure quality of results obtained. commercial standards (Buck scientific) containing known concentration was further diluted to provide working standards of the following concentrations; 0,0.2, 0.4, 0.8, 1.6 for each heavy metal, their corresponding absorbance was recorded and was used to plot the standard curve. From the standard curve unknown concentrations of heavy metals in the samples were extrapolated. For each heavy metal, there is a specific hollow cathode lamp and an operational wavelength. The following; 283nm, 228.9nm, 357.9nm, 213.9nm and 325nm are the wavelengths for lead, cadmium, chromium, zinc and copper respectively. The concentrations were expressed in mg/Kg.

All chemicals used for analysis were of analytical grade. Results obtained were compared with national and international guidelines for heavy metal concentration in fish.

Plate 3.5: An Atomic Absorption Spectrophotometer

3.8 Quality Control and Assurance

Quality control was assured by the analysis of reagent blanks and procedural blanks and also samples were analysed in triplicates. The accuracy of analytical procedure was checked by analyzing the standard reference materials (water: SRM-143d, National Institute of Standards and Technology; fish: DORM-2, National Research Council). All reagents and chemicals used during analysis were of analytical grade and pre-tested for possible heavy metal contamination. Distilled water was used throughout the study. All the glassware and plastics were soaked overnight in 10% nitric acid and rinsed twice with distilled water before use. The instruments used were all calibrated and standardised with standard solutions prepared from commercially available chemicals. Distilled water was used for preparing working solutions and all analytical work.

3.9 Data Management and Statistical Analysis

All data obtained from this study were quantitative in nature. They were entered, cleaned and analysed with the Statistical Package for Social Science (SPSS) version 15.0. Coding guide was adopted to facilitate entry. The data was first summarised using descriptive statistics and later subjected to a series of inferential analyses such as independent and paired sample t-test at 5% level of significance as well as ANOVA. The results of the data analyses are presented in tables and figures in the results section.

CHAPTER FOUR

4.0 RESULTS

The results of physico-chemical analyses of water samples collected from Agodi Lake, University college hospital (UCH) sewage treatment plant effluent, Oremeji river as well as Ashi/Bodija river which are the major tributaries that feed Agodi lake are presented first, the latter part of this chapter includes the result on the investigation of heavy metals such as Lead, Cadmium, Chromium, Zinc and Copper in the Liver, Gill, Skin and Muscle tissues of *Clarias gariepinus* (Catfish) and *Tilapia guineensis* (Tilapia fish) Samples from Agodi lake (study lake) as well as from Eleyele (control lake).

4.1: Physico-chemical Quality of Water Samples From Lake's Main Tributaries.

Summary of physico-chemical parameters of water samples from the lake's tributaries are presented in Table 4.1. The physicochemical parameters determined in the samples were Temperature (^{0}C), conductivity (µs/cm), Total dissolved solids (TDS) in mg/L, Dissolved Oxygen (DO) in mg/L and pH. Their levels were compared with National guideline limit (NGL) formerly FEPA (1991) permissible limits for these parameters in effluent discharged into fresh water bodies and NESREA (2011) permissible limits for fresh water. Effluent discharge from UCH sewage treatment plant had the following in terms of physico-chemical quality; water temperature (28.00 ± 0.00), conductivity (914.00 ± 679.69 µS/cm), TDS (548.93±408.41 mg/L), pH (7.03±0.25), DO (0.00±0.00) mg/L. Water samples from Ashi/Bodija recorded the following mean values; Water temperature (27.50±0.58), conductivity (248.50±177.43µS/cm), TDS (148.93±106.43 mg/L), pH (7.15±0.33), DO (6.30±1.44) mg/L. Water samples from Oremeji recorded the following; Temperature (28.00±0.00), conductivity (282.23±203.23 µS/cm), TDS (169.40±122.10) mg/L, pH (7.27±0.40), DO (3.95±0.65) mg/L.

Water temperature and pH did not vary greatly among the various tributaries as they both revolved around 27.5^{o}C and 7.0 respectively. Conductivity level as well as Total dissolved solids (TDS) level were observed highest for effluent from UCH sewage treatment plant effluent; 914.0±679.68µscm^{-1} for conductivity and 548.93±408.41 mg/L for TDS. Dissolved oxygen (DO) was not detected in the water samples from UCH treatment plant effluent as depicted by the table but was found to be highest in samples from Ashi/Bodija River corresponding to 6.30±1.44 mg/L. The range for the different parameters are as follows: Temperature (^{0}C) ; 27.00-28.00, DO (mg/L) ; 0.00-6.30, TDS (mg/L) ; 144.20-548.93, pH; 6.80-7.67, Conductivity (µS/cm) ; 240.73-914.00. All assessed parameters were within FEPA (1991) and NESREA (2011) standards for effluent and fresh water except conductivity that was above 200µS/cm stipulated.

4.2 Heavy Metal Concentration in Water Samples From Lake's Main Tributaries.

Summary of the results of heavy metals (lead, cadmium, chromium, zinc and copper) in samples from tributaries are presented in Table 4.2. All the water samples had heavy metals at concentrations within national limits. Water samples from Oremeji River had the highest concentration of lead (0.15±0.23) mg/L while none (0.00±0.00) mg/L was detected in samples from Ashi/Bodija River, Effluent samples from UCH sewage treatment plant had the highest concentration of zinc and copper corresponding to 0.32±0.37 mg/L and 0.06±0.07 mg/L respectively while samples from Oremeji River had the lowest concentration of 0.11±0.07 mg/L and 0.04±0.02 mg/L for zinc and copper respectively. The concentrations of cadmium and chromium in all samples were similar, averaging 0.01±0.01 mg/L. From the table, it can be deducted that Effluents from UCH sewage treatment plant, on the average, contributes the highest concentration of heavy metals to Agodi Lake. The range for the various heavy metals are as follows: Lead (mg/L) ; (0.00-0.15), Cadmium (mg/L) ; (0.00-0.02), Chromium (mg/L); (0.00-0.02), Zinc (mg/L); (0.04-0.32), Copper (mg/L); (0.02-0.06).

Table 4.1: Summary Of Physico-chemical Quality of Water Samples From Lake's Main Tributaries.

Parameters	Range Mean±SD	UCH Sewage	Oremeji River	UCH in Agodi	Ashi Bodija	Oremeji in Lake	UCH in Lake	Ashi in Lake	FEPA (1991 Std limit	NESREA (2011) Std limit
Ambient Temp. (^{0}C)	Range	28.00-29.50	29.50-29.50	25.00-27.50	22.00-26.00	28.00-28.00	26.00-28.00	25.50-27.50		
	Mean±SD	28.80±0.60	29.50±0.00	26.25±1.44	24.00±2.31	28.00±0.00	27.00±1.15	26.50±1.15	Nil	Nil
Water temperature(^{0}C)	Range	28.00-28.00	28.00-28.00	27.00-27.50	27.00-28.00	26.50-27.50	27.0-27.50	27.00-28.00		
	Mean±SD	28.00±0.00	28.00±0.00	27.25±0.29	27.50±0.58	27.00±0.58	27.25±0.29	27.50±0.58	< 40	25
Conductivity (µScm^{-1})	Range	269.00- 569.00	94.50-462.00	79.0-576.0	94.6-412.0	93.5-439.0	78.50-504.00	92.90-393.00		
	Mean±SD	914.00±679.68	282.23±203.23	315.70±250.90	248.50±187.40	269.70±193.20	295.30±219.70	240.73±168.42	Nil	200
Total Dissolved solids(mg/L)	Range	161.70-942.00	56.60-277.00	47.5-339.00	56.5-247.00	56.10-263.00	46.90-303.00	55.60-236.00		
	Mean±SD	548.93±408.41	169.40±122.10	187.9±148.40	148.9±106.40	161.50±115.56	176.43±131.22	144.20±100.88	2000	2000
pH	Range	6.66-7.21	6.86-7.68	6.48-7.24	6.81-7.51	7.23-7.91	6.48-7.24	6.85-7.71		
	Mean±SD	7.03±0.25	7.27±0.40	6.80±0.34	7.15±0.33	7.67±0.30	7.03±0.37	7.24±0.36	6-9	6-8.5
Dissolved Oxygen (mg/L)	Range	0.00-0.00	3.30-4.60	0.00-0.00	4.20-7.30	5.30-6.30	0.00-0.00	5.50-7.10		
	Mean±SD	0.00±0.00	3.95±0.65	0.00±0.00	6.30±1.44	5.63±0.46	0.00±0.00	6.18±0.73	Nil	8-10

Table 4.2 : Summary of Heavy Metal Concentration in Water Samples From Lake's Main Tributaries.

Parameters	Values	UCH Sewage	Oremeji River	UCH in Agodi	Ashi Bodija	Oremeji in Lake	UCH in Lake	Ashi Bodija in Lake	FEPA (1991) Standard limit	NESREA (2011) Standard limit
Pb (mg/L)	Range	0.00-0.07	0.00-0.41	0.00-0.19	0.00-0.00	0.00-0.00	0.00-0.10	0.00-0.30		
	Mean±SD	**0.04±0.04**	**0.15±0.23**	**0.10±0.10**	**0.00±0.00**	**0.00±0.00**	**0.03±0.06**	**0.12±0.16**	<1.0	0.05
Cd (mg/L)	Range	0.00-0.03	0.00-0.01	0.00-0.03	0.00-0.03	0.00-0.02	0.00-0.03	0.00-0.05		
	Mean±SD	**0.01±0.02**	**0.00±0.00**	**0.01±0.01**	**0.01±0.01**	**0.01±0.01**	**0.01±0.02**	**0.02±0.02**	<1.0	1.0
Cr (mg/L)	Range	0.00-0.02	0.00-0.00	0.00-0.03	0.00-0.04	0.00-0.08	0.00-0.02	0.00-0.00		
	Mean±SD	**0.01±0.01**	**0.00±0.00**	**0.01±0.01**	**0.01±0.02**	**0.02±0.04**	**0.01±0.01**	**0.00±0.00**	<1.0	0.05
Zn (mg/L)	Range	0.00-0.71	0.04-0.20	0.02-0.28	0.05-0.38	0.03-0.12	0.03-0.09	0.04-0.06		
	Mean±SD	**0.32±0.37**	**0.11±0.07**	**0.10±0.12**	**0.15±0.15**	**0.07±0.04**	**0.05±0.03**	**0.04±0.01**	<1.0	1.5
Cu (mg/L)	Range	0.00-0.16	0.01-0.06	0.00-0.10	0.01-0.09	0.00-0.10	0.01-0.03	0.02-0.04		
	Mean±SD	**0.06±0.07**	**0.04±0.02**	**0.05±0.04**	**0.04±0.03**	**0.03±0.04**	**0.02±0.01**	**0.03±0.01**	<1.0	1.0

4.3 Spatio-Temporal Variations in Physico-chemical quality of Water Samples from tributaries and Agodi Lake.

Figures 4.1-4.6 present the variations that existed in temperature, pH, dissolved oxygen, conductivity and total dissolved solids determined in the effluent samples from UCH sewage treatment plant, water samples from Oremeji River and Ashi/Bodija River as well as water samples from the lake during the duration of the study. In addition to spatial differences, it also shows the changes that occurred across weeks i.e. the temporal variations. Figure 4.1 shows that there was no significant variation in the Ambienttemperature throughout the study except Ashi Bodija River which recorded the lowest temperature in week one and two corresponding to 22^0C and point one (1) on the lake which recorded the highest temperature of 32^0C in week three and four. Figure 4.2 shows that there was no remarkable difference in the temperature of samples collected from the three main tributaries all through the duration of sampling although this was not the case with water samples collected from the lake as water temperature rose from an average of 27.5^oC in the first and second week to an average of 30^0C in the third and fourth week.

The pH of effluent samples did not change across locations and among weeks and the same was noticed for water samples from the lake, details are shown in Figure 4.3. It is worthy to note that conductivity and total dissolved solids levels were remarkably higher in weeks one and two than in subsequent weeks for all samples. Conductivity and Total dissolved solids were coincidentally highest in effluent samples collected from UCH sewage treatment plant on the second week. Figure 4.6 shows that DO was not detected in effluent samples from UCH sewage treatment plant while samples from Ashi/Bodija River had the highest dissolved oxygen level. Furthermore, for water samples from the lake, the lowest level of dissolved oxygen was recorded in the third week.

Figures 4.7-4.11 highlight the concentrations of lead, cadmium, chromium, zinc and copper in the effluent samples as well as the water samples collected for the four weeks duration of sampling. Lead was not detected at all in any of the samples on the third and fourth week while the highest concentration was found in water samples from Oremeji (0.41 mg/L) on the second week. Cadmium just like lead, was not found in the samples on the third and fourth week. The lowest contributor of Cadmium to Agodi lake as is being depicted by Figure 4.8 is sample from Oremeji river (0.01 mg/L) while the highest concentration of cadmium was effluent from UCH sewage treatment plant (0.03 mg/L) on the second week. The highest level of cadmium was found in water samples collected from the lake (0.05 mg/L) on the second week. Chromium was detected in the effluent samples as well as the water samples only on the fourth week of the study (Figure 4.9). In addition, chromium was not detected in water samples from Oremeji river. From Figure 4.10 it can be seen that zinc was detected in varying concentrations for various weeks across the different points from which samples were collected except in effluents samples from UCH sewage treatment plant on weeks one and two where it was not detected at all (0.00 mg/L). Copper was also found in varying amounts across points for the four weeks but was highest in effluents samples from UCH sewage treatment plant on the third week (0.16 mg/L) as shown in Figure 4.11. The mean concentration of heavy metals across the four (4) weeks for the different points are as follows: UCH; Lead (0.04±0.04 mg/L), Cadmium (0.01±0.02 mg/L), Chromium (0.01±0.01 mg/L), Zinc (0.32±0.37 mg/L), Copper (0.06±0.07 mg/L), Oremeji; Lead (0.15±0.23 mg/L), Cadmium (0.00±0.00 mg/L), Chromium (0.00±0.00 mg/L), Zinc (0.11±0.07 mg/L), Copper (0.04±0.02 mg/L), Ashi/Bodija; Lead (0.00±0.00 mg/L), Cadmium (0.01±0.01 mg/L), Chromium (0.01±0.02 mg/L), Zinc (0.15±0.15 mg/L) and Copper (0.04±0.03 mg/L).

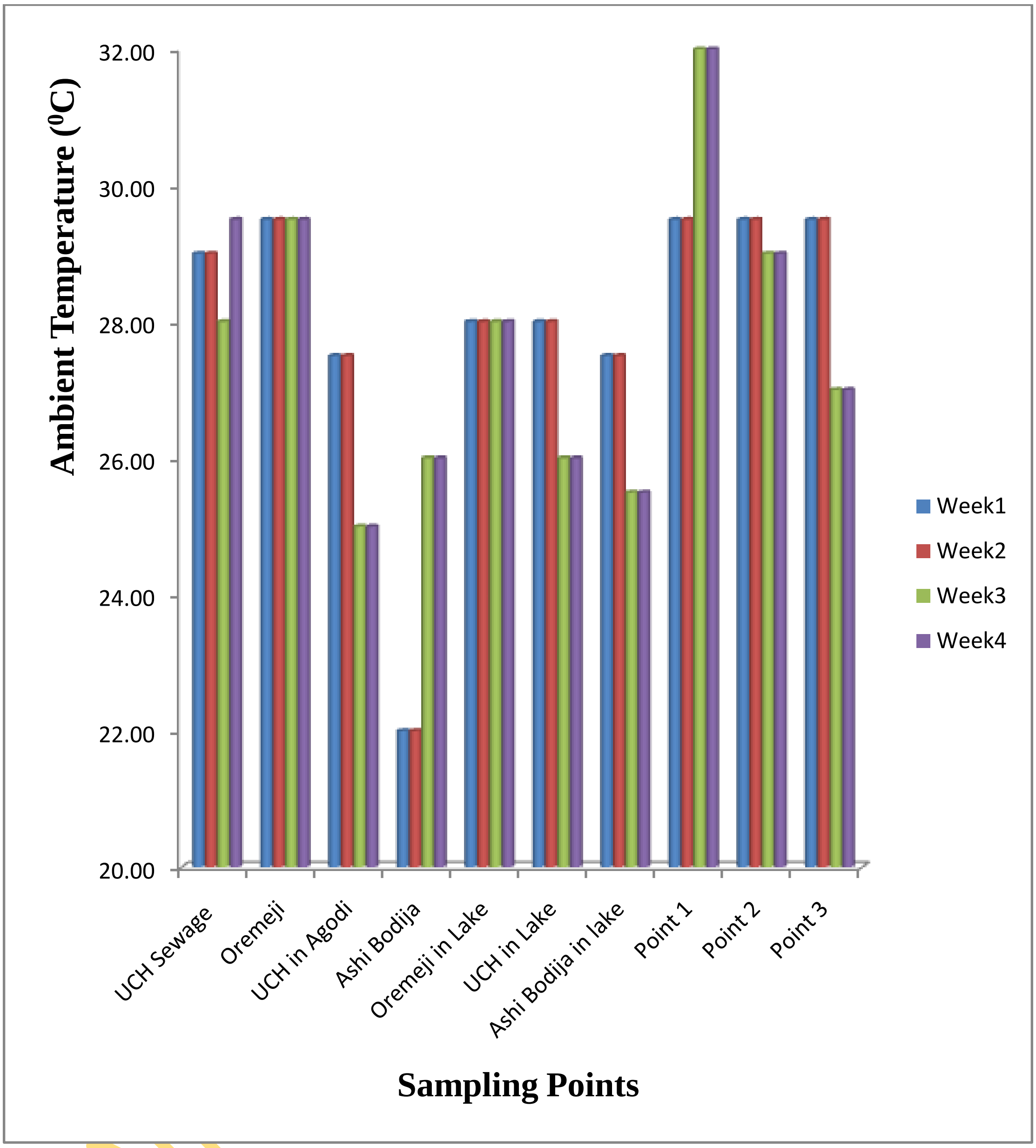

Figure 4.1: Spatio-Temporal Variations in Ambient Temperature for Duration of Study

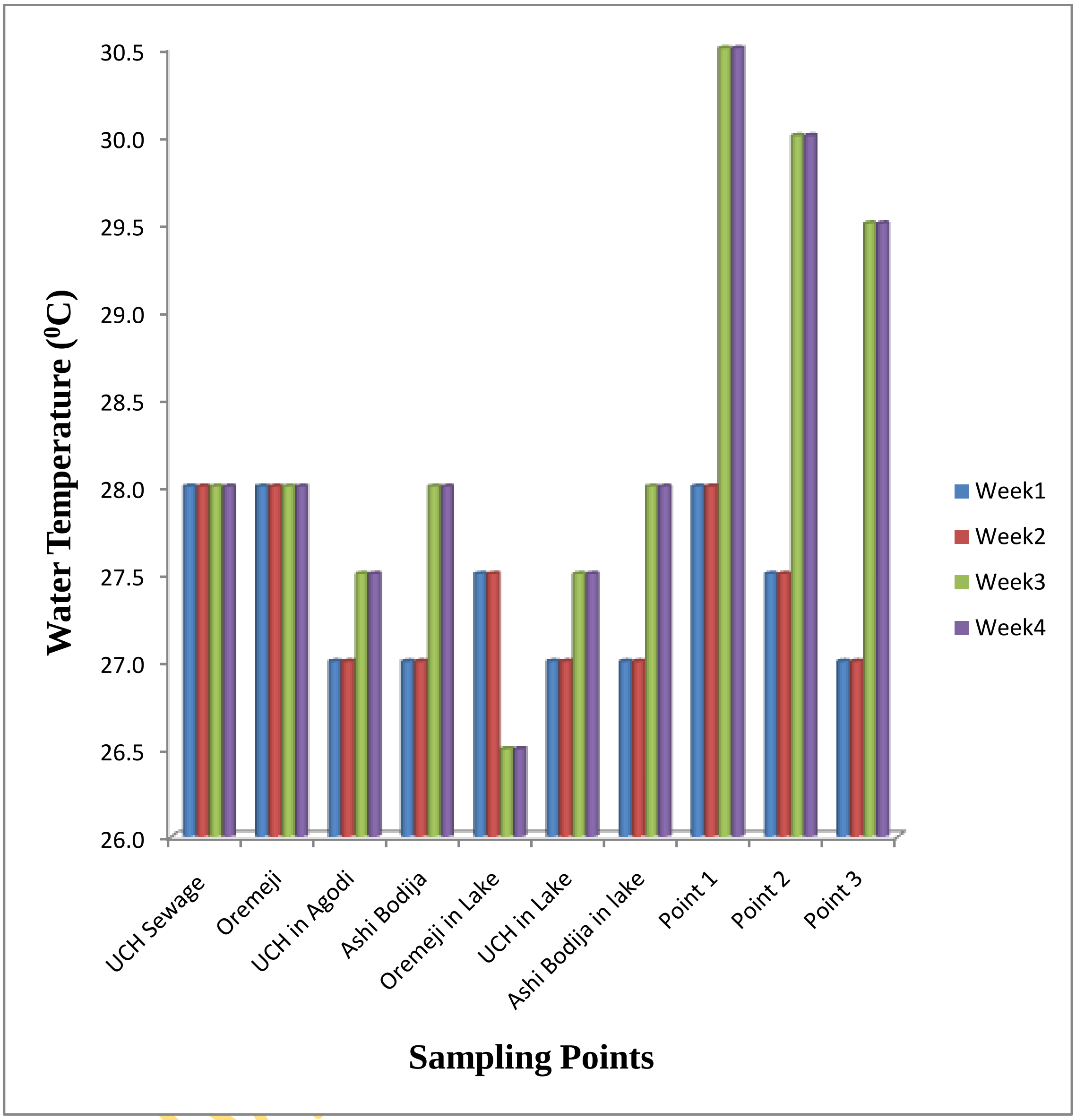

Figure 4.2: Spatio-Temporal Variations in Water Temperature for the Duration of the Study

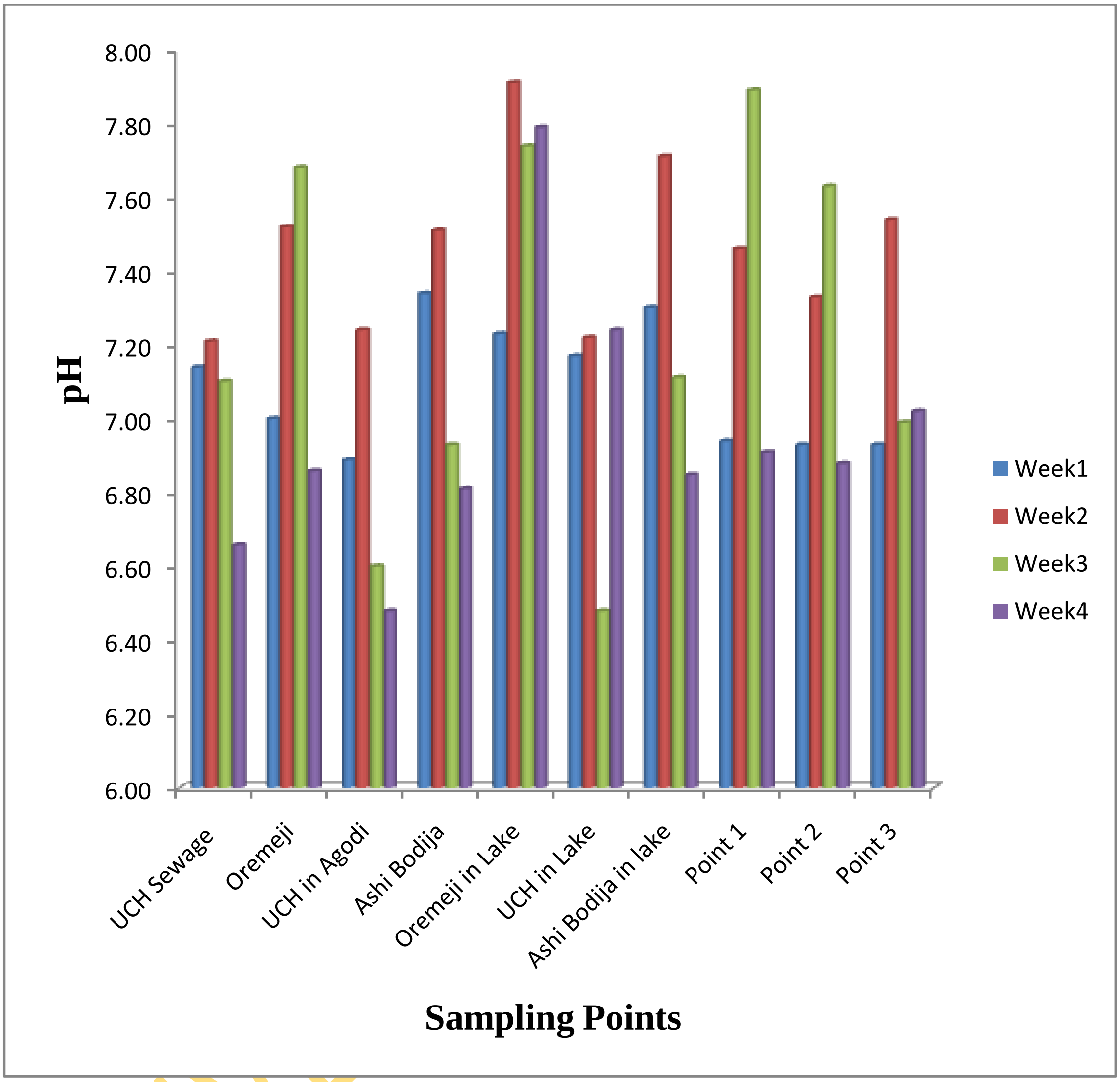

Figure 4.3: Spatio-Temporal Variations in pH for the Duration of the Study

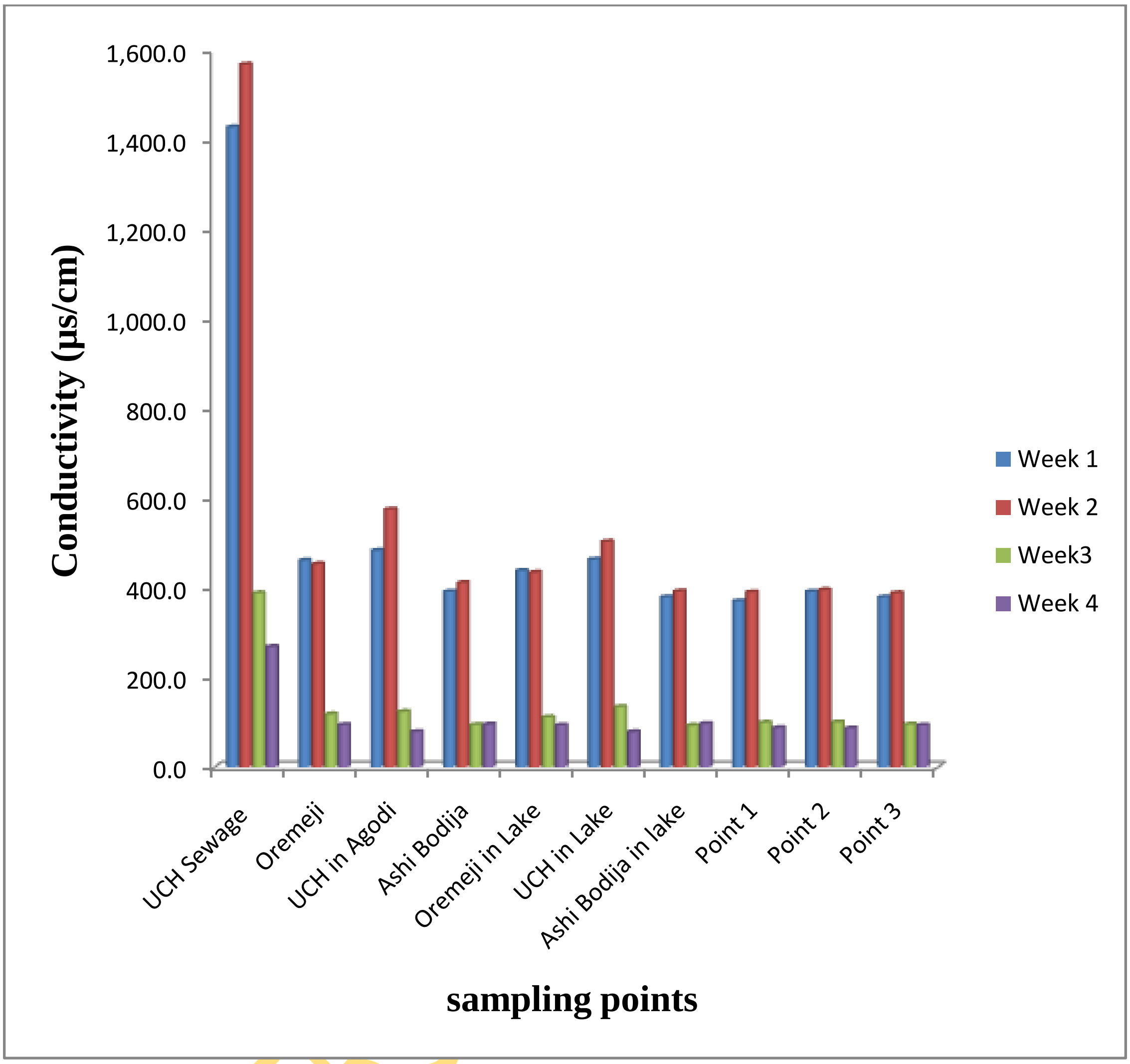

Figure 4.4: Spatio-Temporal Variations in conductivity for the Duration of the Study

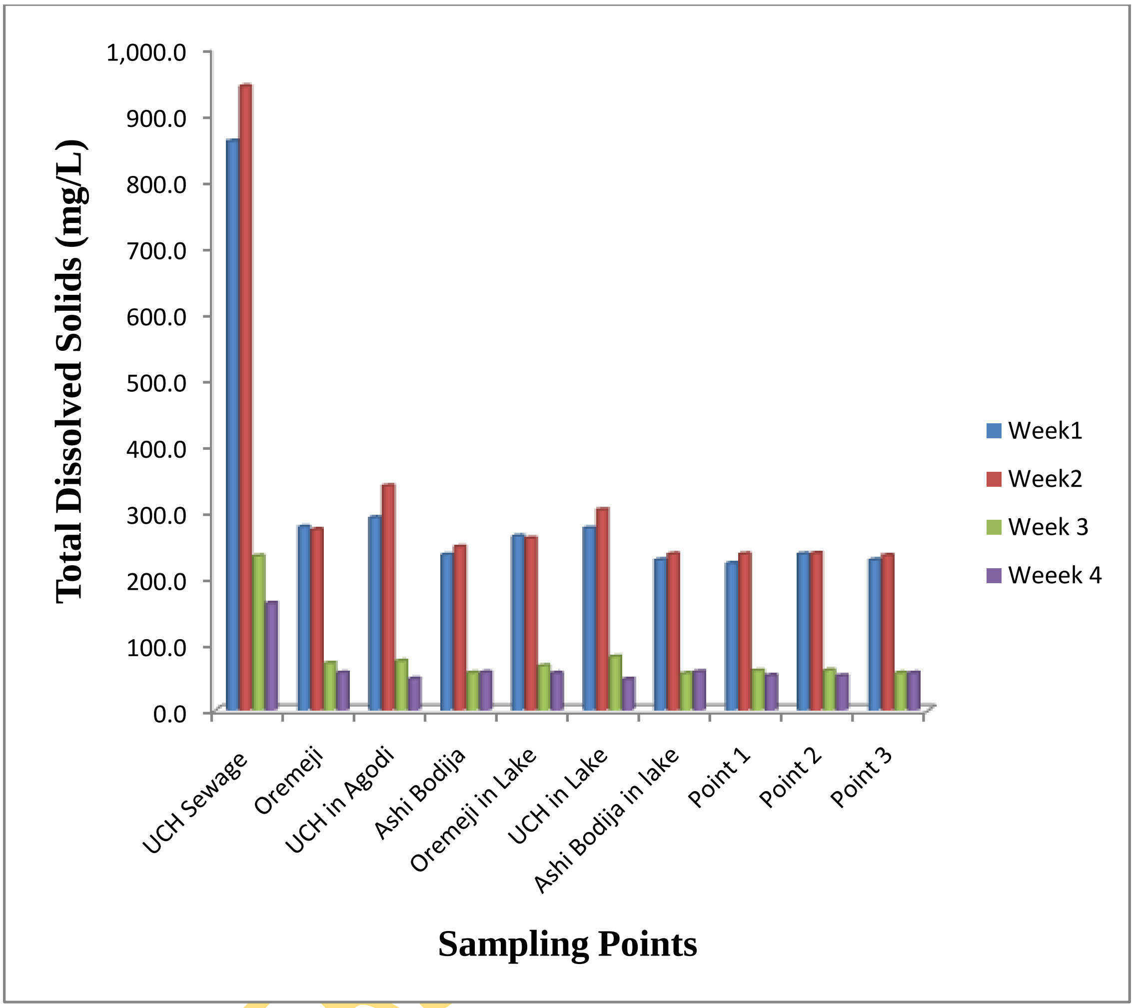

Figure 4.5: Spatio-Temporal Variations in Total Dissolved Solids for the Duration of the Study

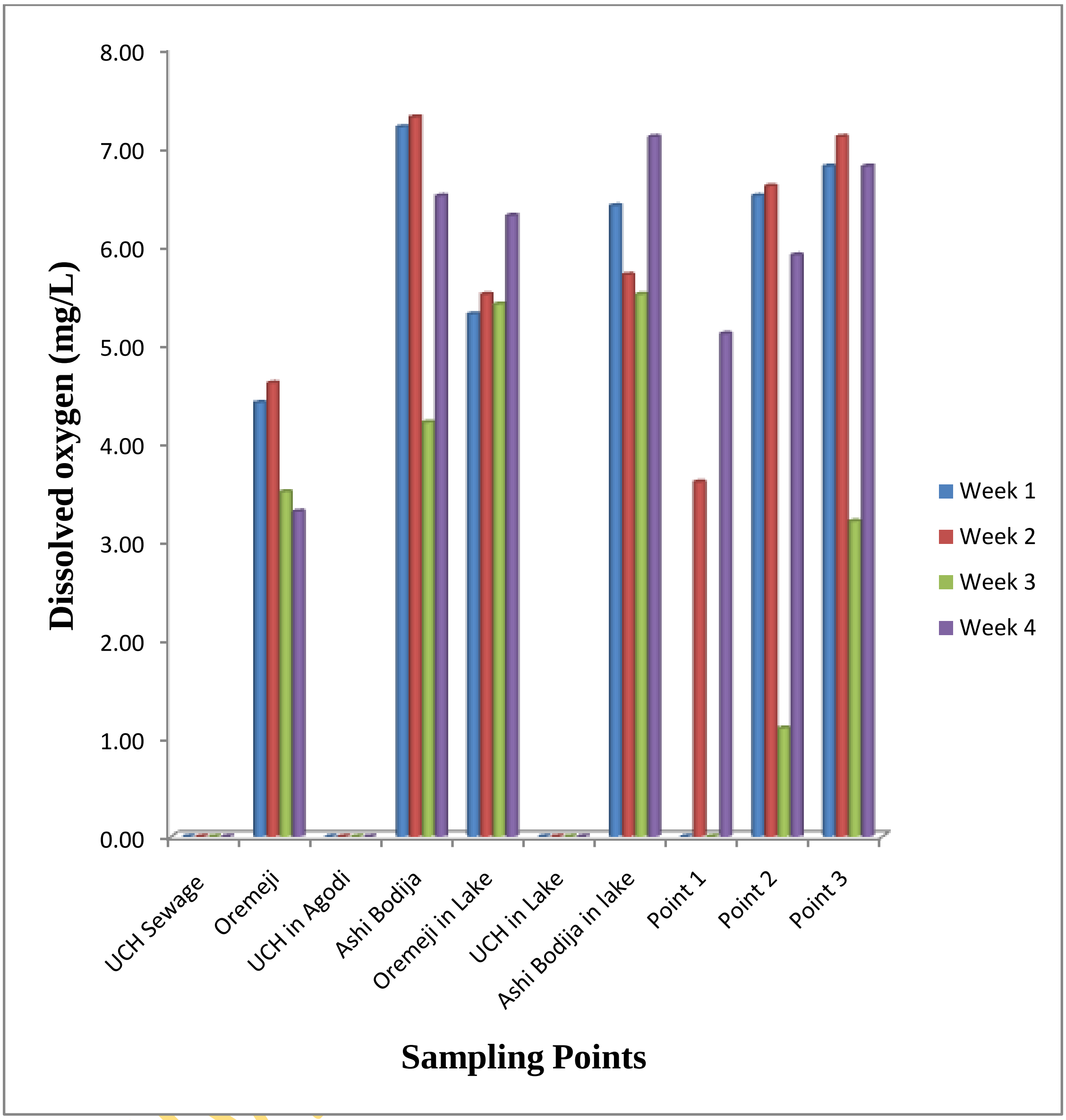

Figure 4.6: Spatio-Temporal Variations in Dissolved Oxygen for the Duration of the Study

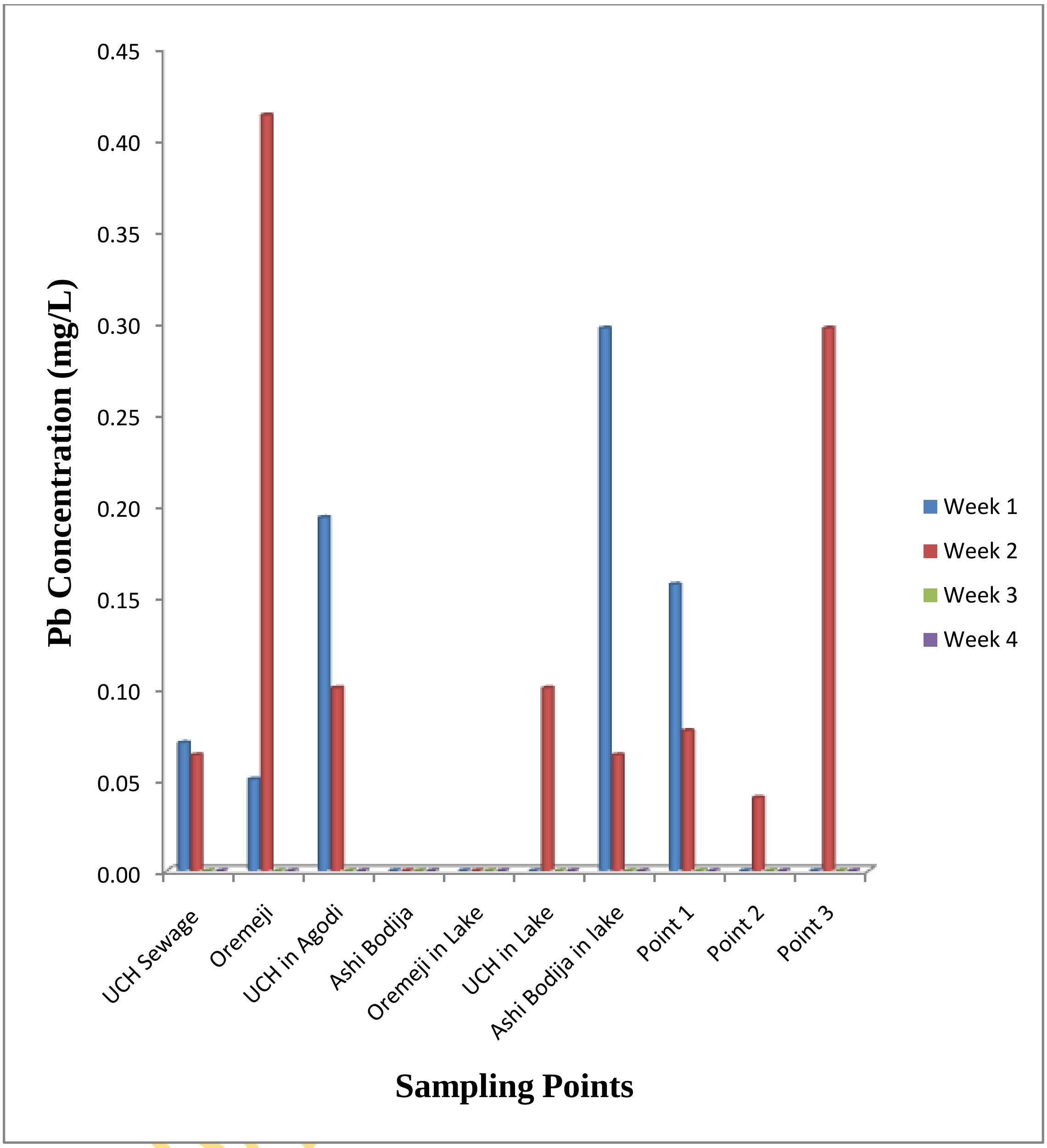

Figure 4.7: Spatio-Temporal Variations in Lead (Pb) for the Duration of the Study

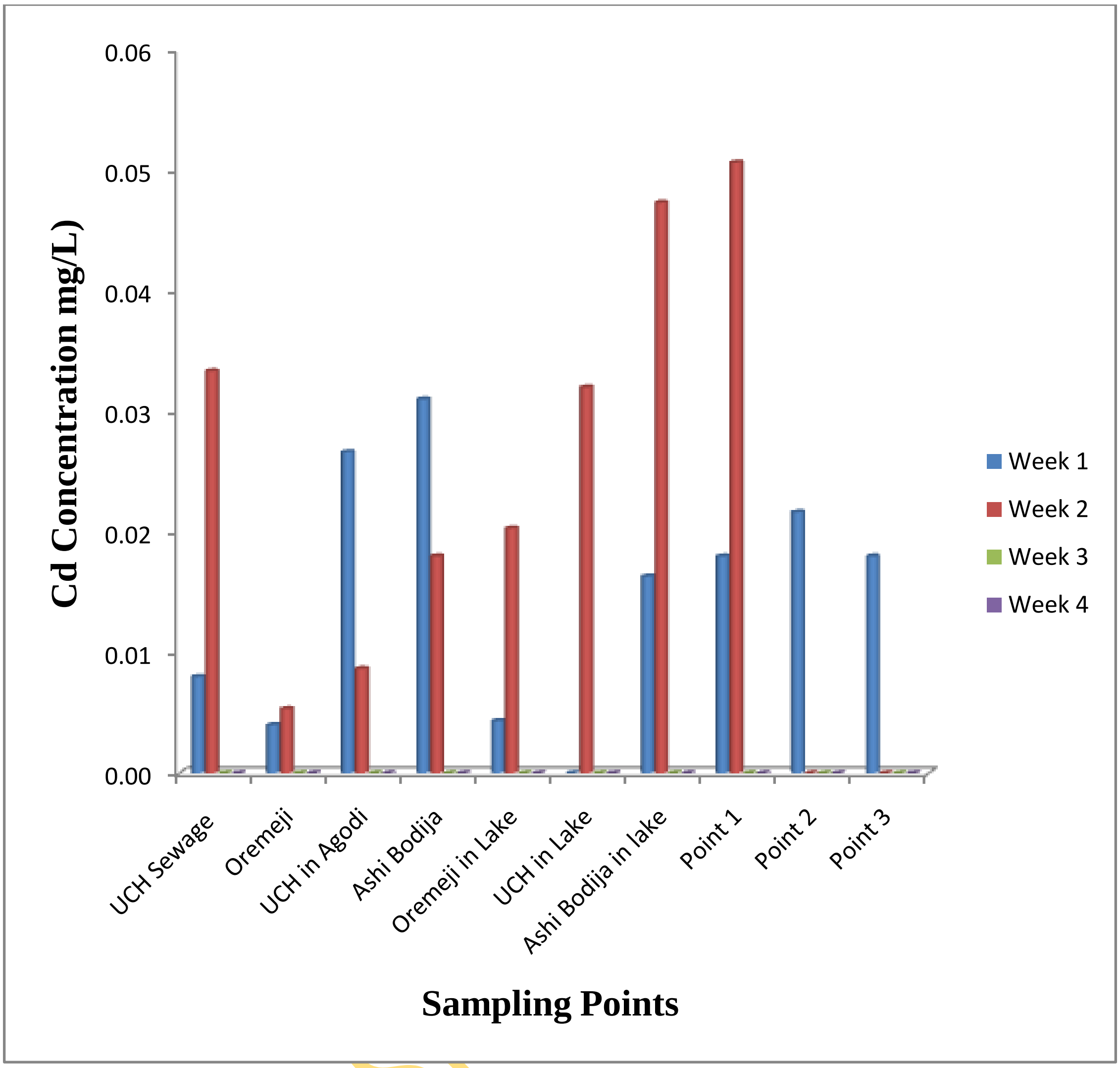

Figure 4.8: Spatio-Temporal Variations in Cadmium (Cd) for the Duration of the Study

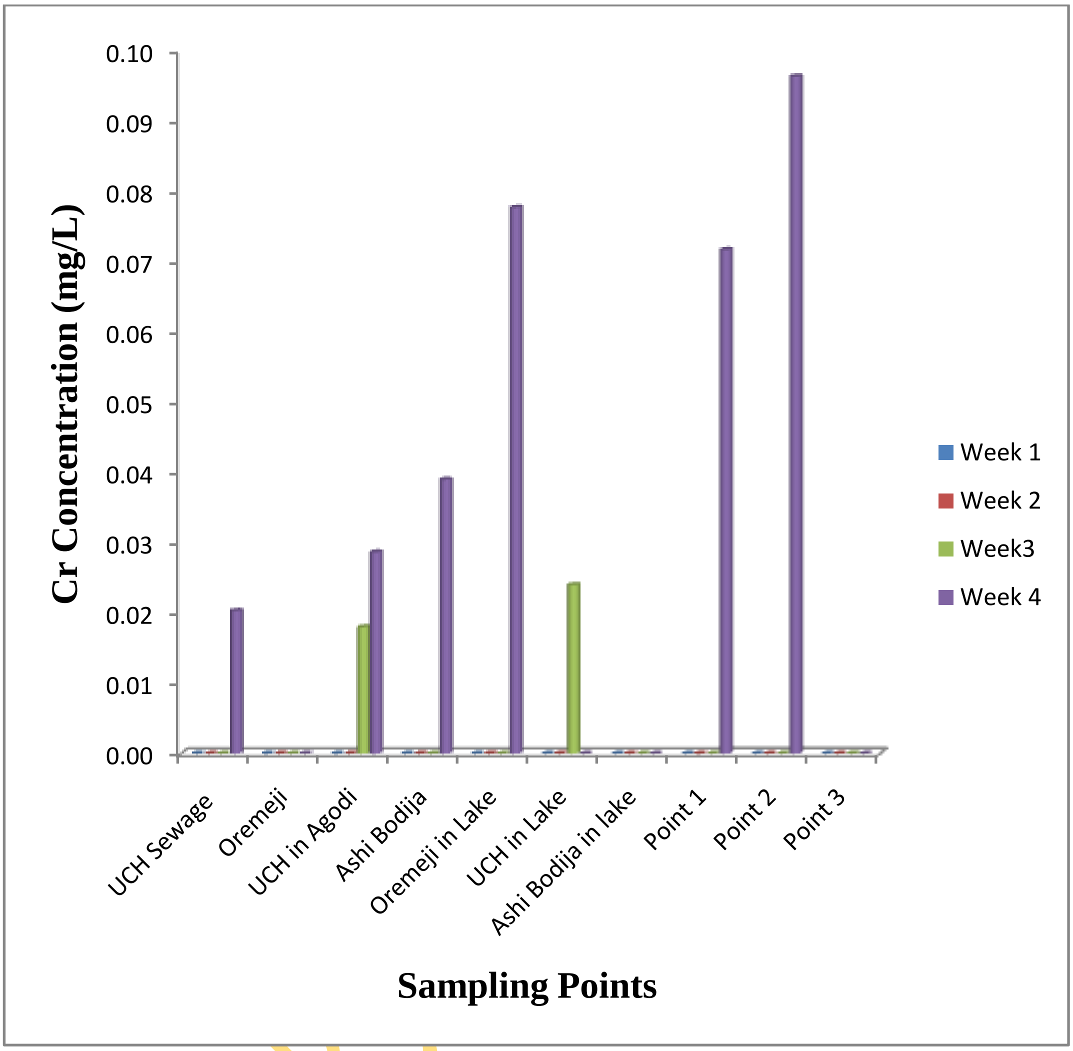

Figure 4.9: Spatio-Temporal Variations in Chromium (Cr) for the Duration of the Study

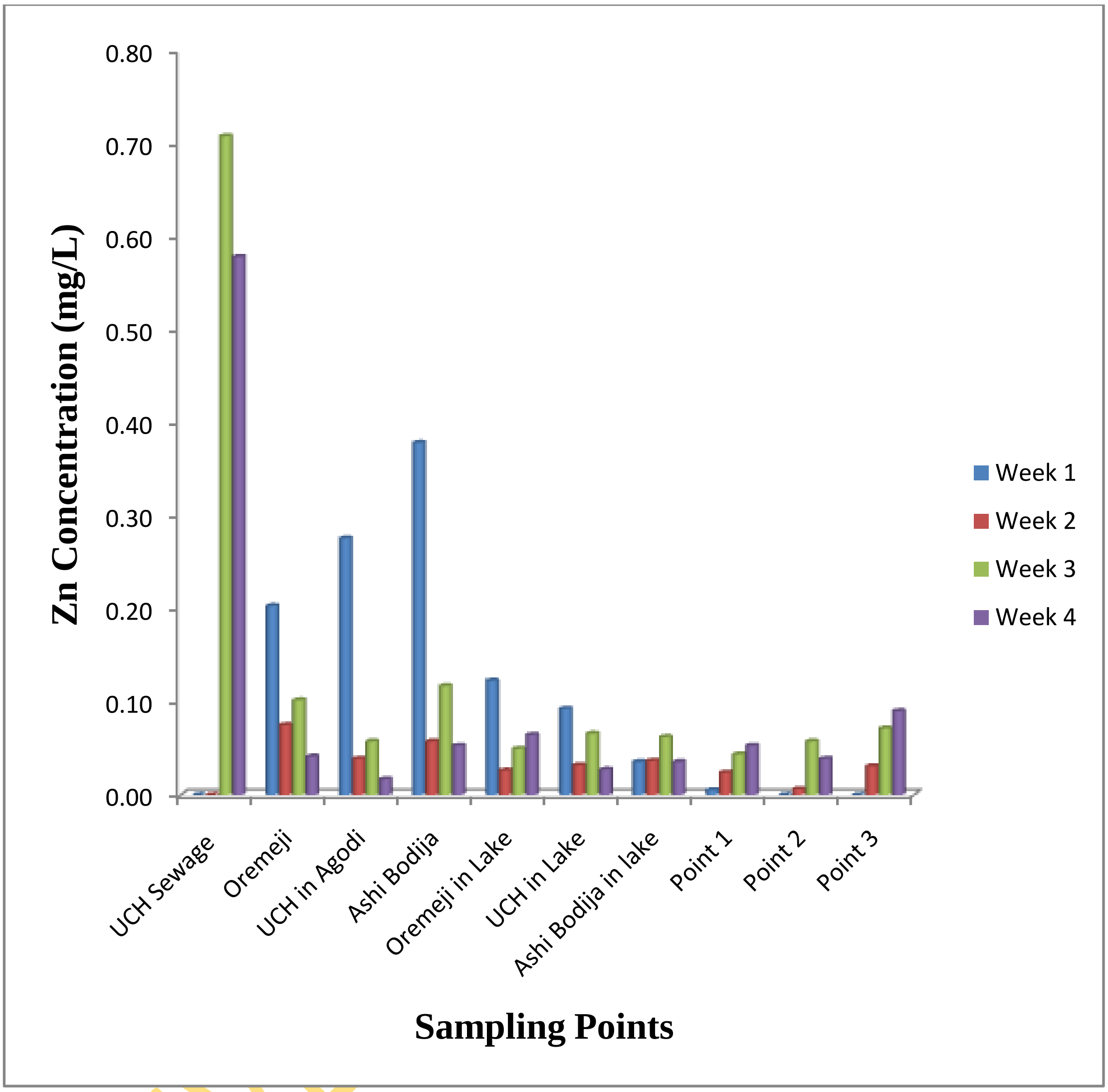

Figure 4.10: Spatio-Temporal Variations in Zinc (Zn) for the Duration of the Study

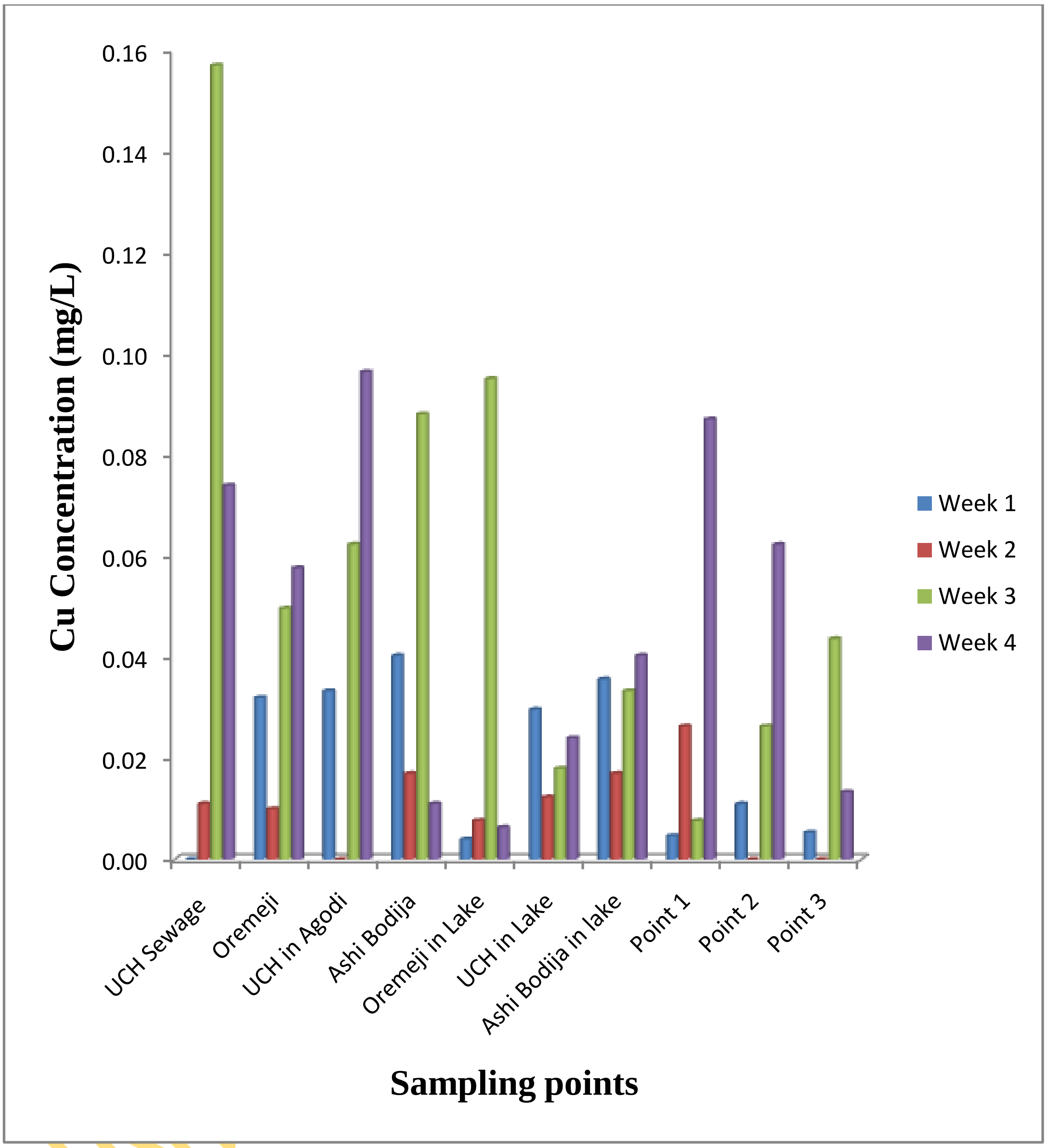

Figure 4.11: Spatio-Temporal Variations in Copper (Cu) for the Duration of the Study

4.4 Physico-chemical Characteristics of Agodi Lake.

The result of analyses for temperature, pH, Dissolved oxygen, Conductivity and Total dissolved solids and concentration of heavy metals (Lead, Cadmium, Chromium, Zinc and Copper) in water samples from Agodi lake are summarised in Table 4.3. The table shows that all the physico-chemical parameters assessed were within NESREA, 2011 permissible limits for the survival of aquatic life in freshwater except dissolved oxygen level (4.39±1.97 mg/L) which was found to be lower and conductivity (240.21±3.32µS/cm) which was found to be higher than the 8-10 mg/L and 200µs/cm stipulated limits for dissolved oxygen and conductivity respectively.

Table 4.3: Summary of Physico-chemical Characteristics of Agodi Lake.

PARAMETERS	MEAN±S.D	WHO (2003)	NGL (2011)
AMBIENT TEMP.(^{0}C)	29.41±1.25	Nil	Nil
WATER TEMP.(^{0}C)	28.75±0.50	Ambient	25
CONDUCTIVITY(µS/cm)	240.21±3.32	1000	200
TOTAL DISSOLVED SOLID(mg/L)	144.06±1.97	500	2000
pH	7.20±0.09	6.5-8.5	6 - 8.50
DO (mg/L)	4.39±1.97	Nil	8 -10
LEAD(mg/L)	0.06±0.04	0.01	0.05
CADMIUM (mg/L)	0.01±0.01	0.003	1.00
CHROMIUM (mg/L)	0.01±0.01	0.05	0.05
ZINC(mg/L)	0.04±0.01	3.00	1.50
COPPER(mg/L)	0.02±0.01	2.00	1.00

4.5 Summary of Heavy Metal Concentration in Catfish and Tilapia Fish Samples from Agodi Lake.

Summary of Lead, Cadmium, Chromium, Zinc and copper concentration in the liver, gill, skin and muscle tissue of catfish and tilapia fish samples from Agodi lake are presented in Table 4.4. The concentrations of heavy metals in the muscle tissues are; lead (5.17, 4.62) mg/Kg, cadmium (0.73, 0.44) mg/Kg, chromium (6.24, 3.78) mg/Kg, zinc (66.60, 94.49) mg/Kg, copper (6.58, 5.16) mg/Kg for catfish and tilapia fish respectively. Details on the concentration of heavy metals in the other tissues are also found in Table 4.4. All the heavy metals in fish tissues of both species exceeded the standard limits stipulated by FEPA (2003) and WHO (1985) for fish food except the concentration of zinc in the muscle of catfish which was 66.60 mg/Kg and lower than the stipulated 75 mg/Kg as shown in the table. The concentrations of Cadmium and Copper in the fish tissues fell within the standard stipulated by Food and Agriculture Organisation (FAO), 1987; those of Lead, Chromium and Zinc were above FAO standard except Zinc concentration in muscle for both catfish and tilapia fish as shown in the table.

Lead level was significantly different ($p<0.05$) between the gills of both fish species; The difference in Cadmium and Chromium levels between all the tissues of both fish species were found to be significantly different ($p<0.05$) while those of Zinc and Copper were not significant as shown in Table 4.5.

TABLE 4.4: Summary of Heavy Metal Content in Catfish and Tilapia Fish Samples From Agodi Lake.

HEAVY METAL	TISSUES	CATFISH mg/Kg MEAN±S.D	TILAPIA FISH mg/Kg MEAN±S.D	FAO (1987) Standard mg/Kg	WHO (1985) Standard mg/Kg	FEPA (2003) Standard mg/Kg
LEAD	LIVER	6.94±2.01	13.12±2.38	0.50-6.00	2.00	2.00
	GILL	12.80±2.20	10.22±1.81			
	SKIN	7.13±3.37	6.58±2.63			
	MUSCLE	5.17±4.49	4.62±2.01			
CADMIUM	LIVER	1.23±0.86	0.73±0.38	0.05-5.50	2.00	
	GILL	0.62±0.47	0.41±0.31			
	SKIN	0.47±0.25	0.31±0.14			
	MUSCLE	0.73±0.54	0.44±0.34			
CHROMIUM	LIVER	3.46±1.04	4.49±2.01	1.00	0.15	0.15
	GILL	4.88±0.62	2.31±1.34			
	SKIN	5.45±0.58	3.78±0.99			
	MUSCLE	6.24±0.77	3.78±0.94			
ZINC	LIVER	233.42±0.81	203.17±0.81	30-100	10-75	75
	GILL	137.03±0.65	164.95±0.38			
	SKIN	96.72±1.39	300.99±0.69			
	MUSCLE	66.60±0.20	94.49±0.90			
COPPER	LIVER	168.82±0.69	124.89±0.86	10-100	3.0	1-3
	GILL	11.30±0.54	10.74±0.54			
	SKIN	6.41±0.20	8.77±1.31			
	MUSCLE	6.58±0.28	5.16±0.58			

ignificant

TABLE 4.5: Comparison of Heavy Metal Content in Tissues of Cat fish and Tilapia Fish Samples From Agodi Lake.

Heavy metals	**Liver mg/Kg**			**Gill mg/Kg**			**Skin mg/Kg**			**Muscle mg/Kg**		
	Mean ±S.D	t-val	p-val	Mean ±S.D	t-val	p-val	Mean ±S.D.	t-val	p-val	Mean±S.D.	t-value	p-value
Lead												
Catfish	6.94±2.01	1.24	0.254	12.80±2.20	3.31	0.013	7.13±3.37	1.77	0.120	5.17±4.49	0.97	0.363
Tilapia	13.12±2.38			10.22±1.81			6.58±2.63			4.62±2.01		
Cadmium												
Catfish	1.23±0.86	4.80	0.002	0.62±0.47	2.61	0.035	0.47±0.25	2.91	0.022	0.73±0.54	3.50	0.010
Tilapia	0.73±0.38			0.41±0.31			0.31±0.14			0.44±0.34		
Chromium												
Catfish	3.46±1.04	17.58	0.000	4.88±0.62	3.79	0.007	5.45±0.58	2.55	0.038	6.24±0.77	3.02	0.019
Tilapia	4.49±2.01			2.31±1.34			3.78±0.99			3.78±0.94		
Zinc												
Catfish	233.42±0.81	2.28	0.056	137.03±0.65	2.21	0.063	96.72±1.39	0.78	0.456	66.60±0.20	2.32	0.053
Tilapia	203.17±0.81			164.95±0.38			300.99±0.69			94.49±0.90		
Copper												
Catfish	168.82±0.69	1.23	0.257	11.30±0.54	0.32	0.757	6.41±0.20	1.86	0.105	6.58±0.28	1.03	0.334
Tilapia	124.89±0.86			10.74±0.54			8.77±1.31			5.16±0.58		

- Significant at $p<0.05$

4.6 Rate of Bio-accumulation of Heavy Metals in Catfish and Tilapia Fish Tissues

The result for the rate of bioaccumulation of heavy metals in the tissues of catfish are presented on Table 4.6 while that of Tilapia fish is shown on Table 4.7. From Table 4.6, it can be seen that lead bio-accumulated most in the gill of catfish with a Bioaccumulation Factor (BAF) of 213.3 and least in the muscle with BAF corresponding to 86.16. Zinc was the most bio-accumulated heavy metal; with BAF as follows: Liver (5.835.5), Gill (3425.7), skin (2418), Muscle (1665). This is followed by Copper with the following BAFs; Liver (8441), Gill (565), Skin (320.5), Muscle (329). Cadmium bio-accumulated least in catfish, BAF was; 123 in Liver, 62 in Gill, 47 in Skin and 73 in Muscle. The corresponding bio-accumulation factors for chromium are found on the Table.

The BAFs for heavy metals in Tilapia fish are as follows: Lead; liver (218.7), gill (170.3), skin (109.7), muscle (77), Cadmium; liver (73), gill (41), skin (31), muscle (44), Chromium; liver (449), gill (23), skin (378), muscle (378), Zinc; liver (5079.2), gill (4123.7), skin (7524.7), muscle (2362.2) and Copper; liver (6244.5), gill (537), skin (438.5), muscle (258). From the results on Table 4.7, it can be deducted that zinc was the most bio-accumulated heavy metal while cadmium was the least. Furthermore, the liver was the tissue with the highest heavy metal bio-accumulation. These values were compared with the Canadian standard of > 5000 (Arnot and Gobas, 2006).

4.7 Distribution of Heavy Metals in Catfish and Tilapia Fish Tissues of Agodi Lake

Heavy metal concentration across the liver, gill, skin and muscle tissues of catfish and tilapia fish are shown in Figs. 4.12-4.16. Lead concentration was found to be highest in the gill (12.8 mg/Kg) of catfish and lowest in the muscle (5.17 mg/Kg) while for tilapia fish it was highest in the liver (13.12 mg/Kg) and lowest in the muscle (4.62 mg/Kg). Cadmium recorded its highest concentration in the liver and the lowest concentration in the skin for both fish species, details of these values are in Figure 4.13.

The pattern of distribution of chromium in tilapia fish in terms of concentration was Gill (2.31 mg/Kg) < Skin (3.78 mg/Kg) = Muscle (3.78 mg/Kg) < Liver (4.49 mg/Kg) while chromium concentration in catfish was in the following order Liver (3.46 mg/Kg) < Gill (4.88 mg/Kg) < Skin (5.45 mg/Kg) < Muscle (6.24 mg/Kg) as shown in Figure 4.14.

Zn in tilapia has its highest concentration in the skin (300.99 mg/Kg) and its lowest concentration (94.49 mg/Kg) was found in the muscle while zinc in catfish has its highest concentration (233.42 mg/Kg) in the liver and its lowest concentration (66.60 mg/Kg) in the muscle.

The concentration of copper was found to be remarkably higher in the liver than in all the other tissues of both catfish and tilapia fish. Generally, heavy metals affinity for the various tissues of both fish species was in the following order; Liver > Gill > Skin >Muscle. Furthermore, the heavy metals determined tend to have accumulated more in tissues of catfish than in tilapia fish however the reverse was observed for zinc as depicted by Figure. 4.15.

Table 4.6: Bioaccumulation of Heavy Metals in Catfish Tissues.

Heavy Metals	Concentration in Water (mg/L)	Concentration in Tissues (mg/Kg)	Bioaccumulation Factor (BAF)	Canadian Standard (BAF)
Lead	0.06	Liver (6.94)	115.6	>5000
		Gill (12.80)	213.3	
		Skin (7.13)	118.8	>5000
		Muscle (5.17)	86.16	
Cadmium	0.01	Liver (1.23)	123	>5000
		Gill (0.62)	62	
		Skin (0.47)	47	>5000
		Muscle (0.73)	73	
Chromium	0.01	Liver (3.46)	346	>5000
		Gill (4.88)	488	
		Skin (5.45)	545	>5000
		Muscle (6.24)	624	
Zinc	0.04	Liver (233.48)	5835.5	>5000
		Gill (137.03)	3425.7	
		Skin (96.72)	2418	>5000
		Muscle (66.60)	1665	
Copper	0.02	Liver (168.82)	8441	>5000
		Gill (11.30)	565	
		Skin (6.41)	320.5	>5000
		Muscle (6.58)	329	

Table 4.7: Bioaccumulation of Heavy Metals in Tilapia fish Tissues.

Heavy Metals	Concentration in Water (mg/L)	Concentration in Tissues (mg/Kg)	Bioaccumulation Factor (BAF)	Canadian Std (BAF)
Lead	0.06	Liver (13.12)	218.7	> 5000
		Gill (10.22)	170.3	
		Skin (6.58)	109.7	> 5000
		Muscle (4.62)	77	
Cadmium	0.01	Liver (0.73)	73	> 5000
		Gill (0.41)	41	
		Skin (0.31)	31	> 5000
		Muscle (0.44)	44	
Chromium	0.01	Liver (4.49)	449	> 5000
		Gill (2.31)	231	
		Skin (3.78)	378	> 5000
		Muscle (3.78)	378	
Zinc	0.04	Liver (203.17)	5079.2	> 5000
		Gill (164.95)	4123.7	
		Skin (300.99)	7524.7	> 5000
		Muscle (94.49)	2362.2	
Copper	0.02	Liver (124.89)	6244.5	> 5000
		Gill (10.74)	537	
		Skin (8.77)	438.5	> 5000
		Muscle (5.16)	258	

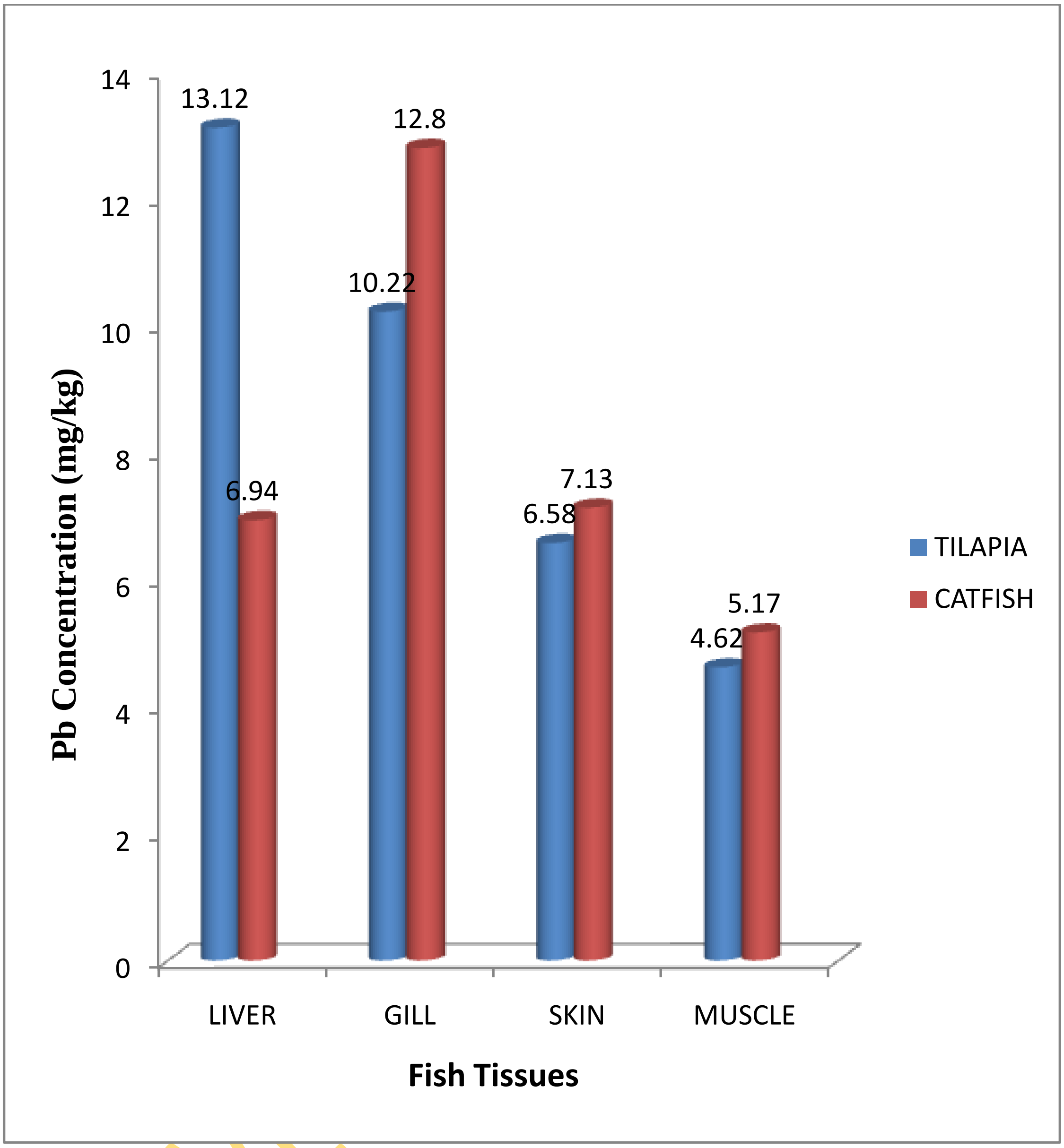

Figure 4.12: Lead Concentration in Tilapia and Catfish Tissues of Agodi Lake

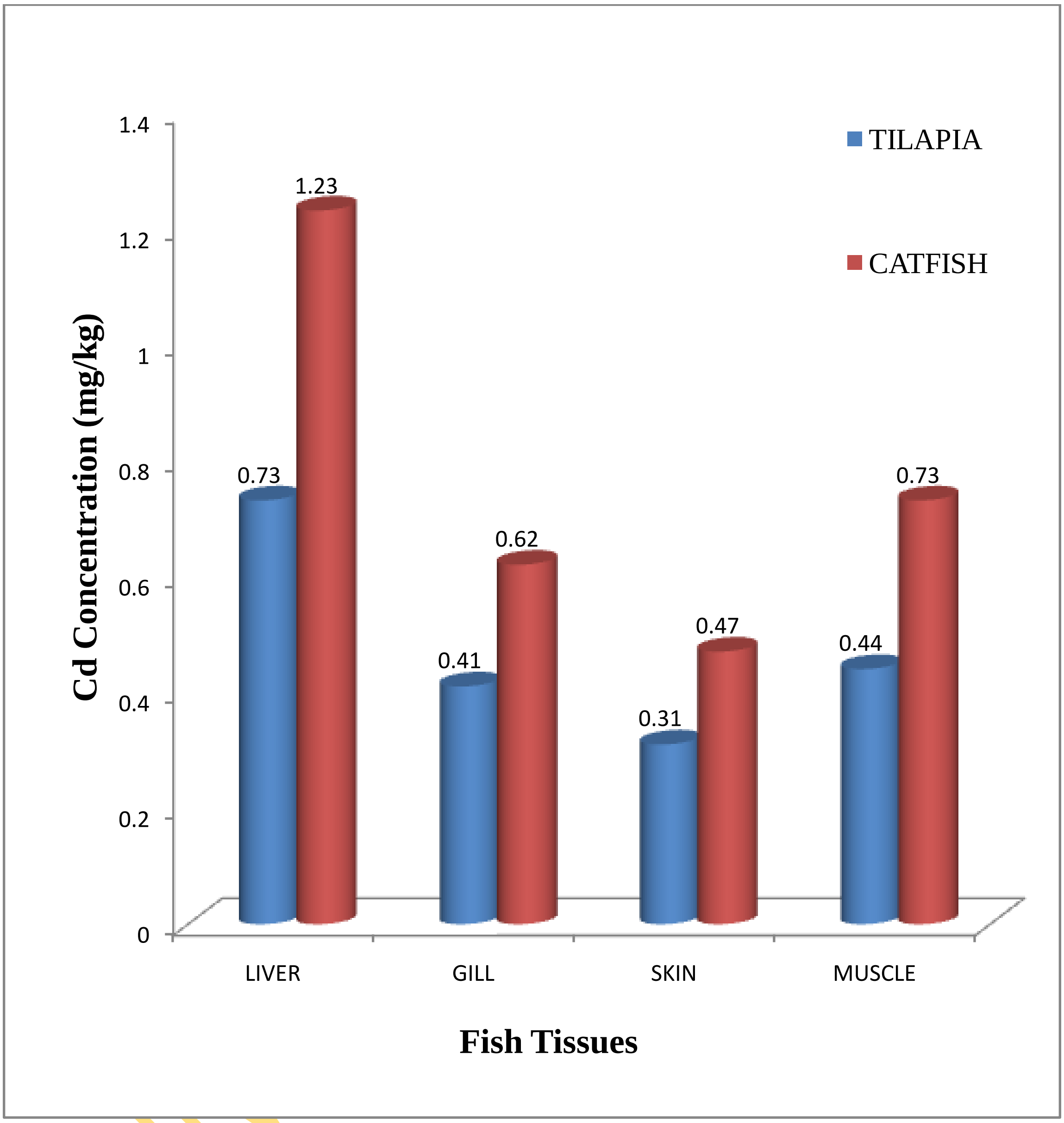

Figure 4.13: Cadmium Concentration in Tilapia and Catfish Tissues of Agodi Lake

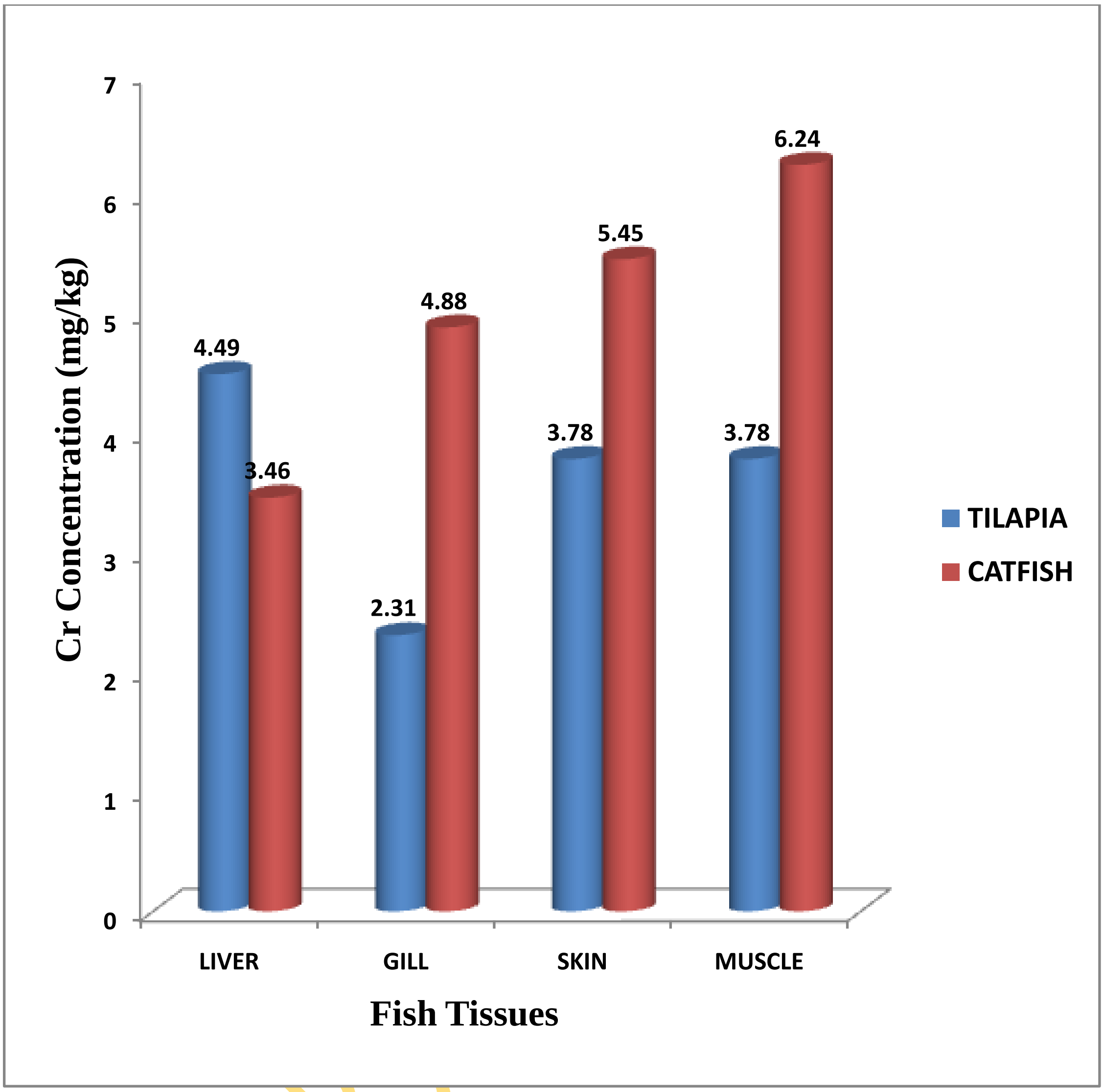

Figure 4.14: Chromium Concentration in Tilapia and catfish Tissues of Agodi Lake

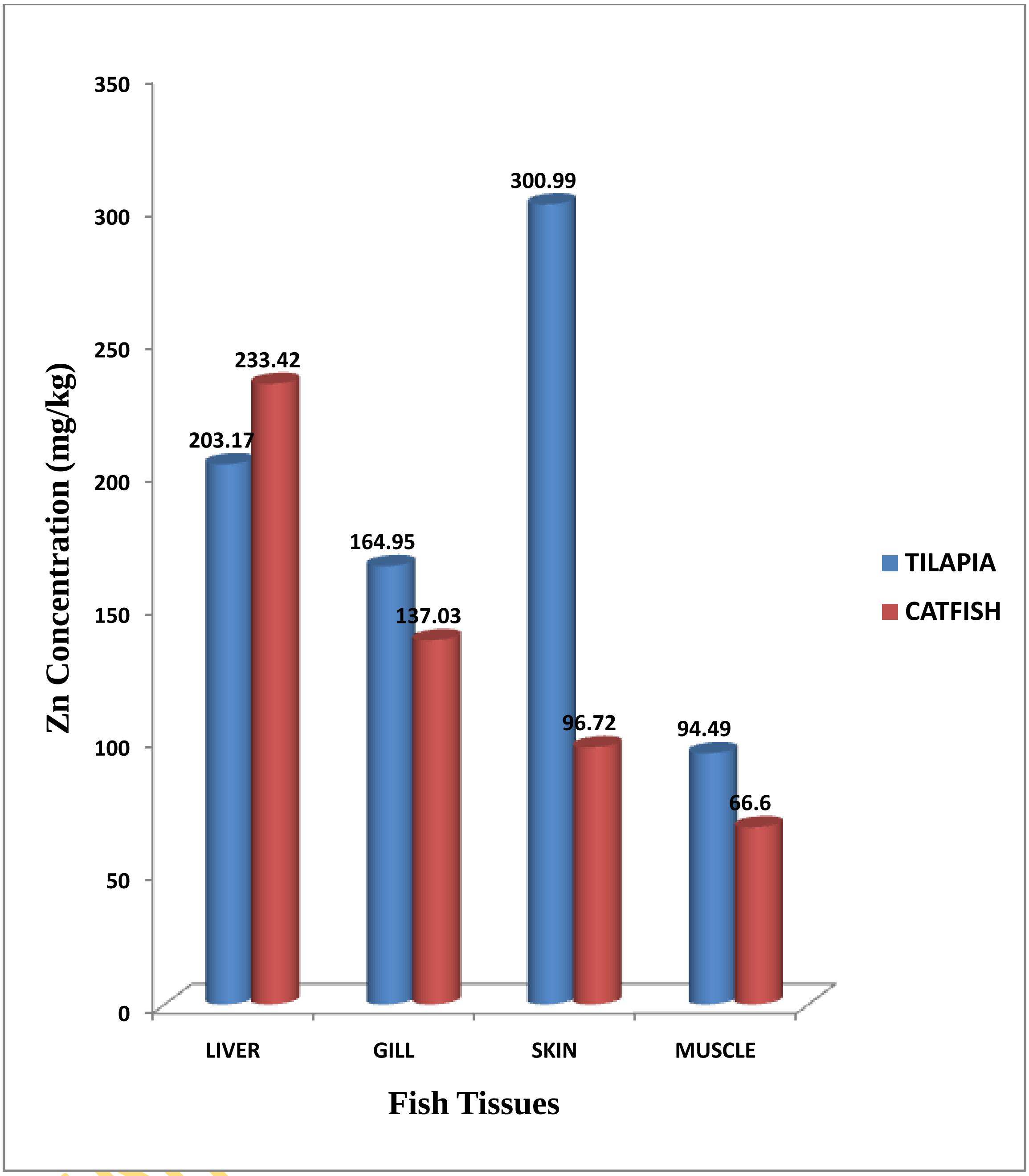

Figure 4.15: Zinc Concentration in Tilapia and Catfish Tissues of Agodi Lake

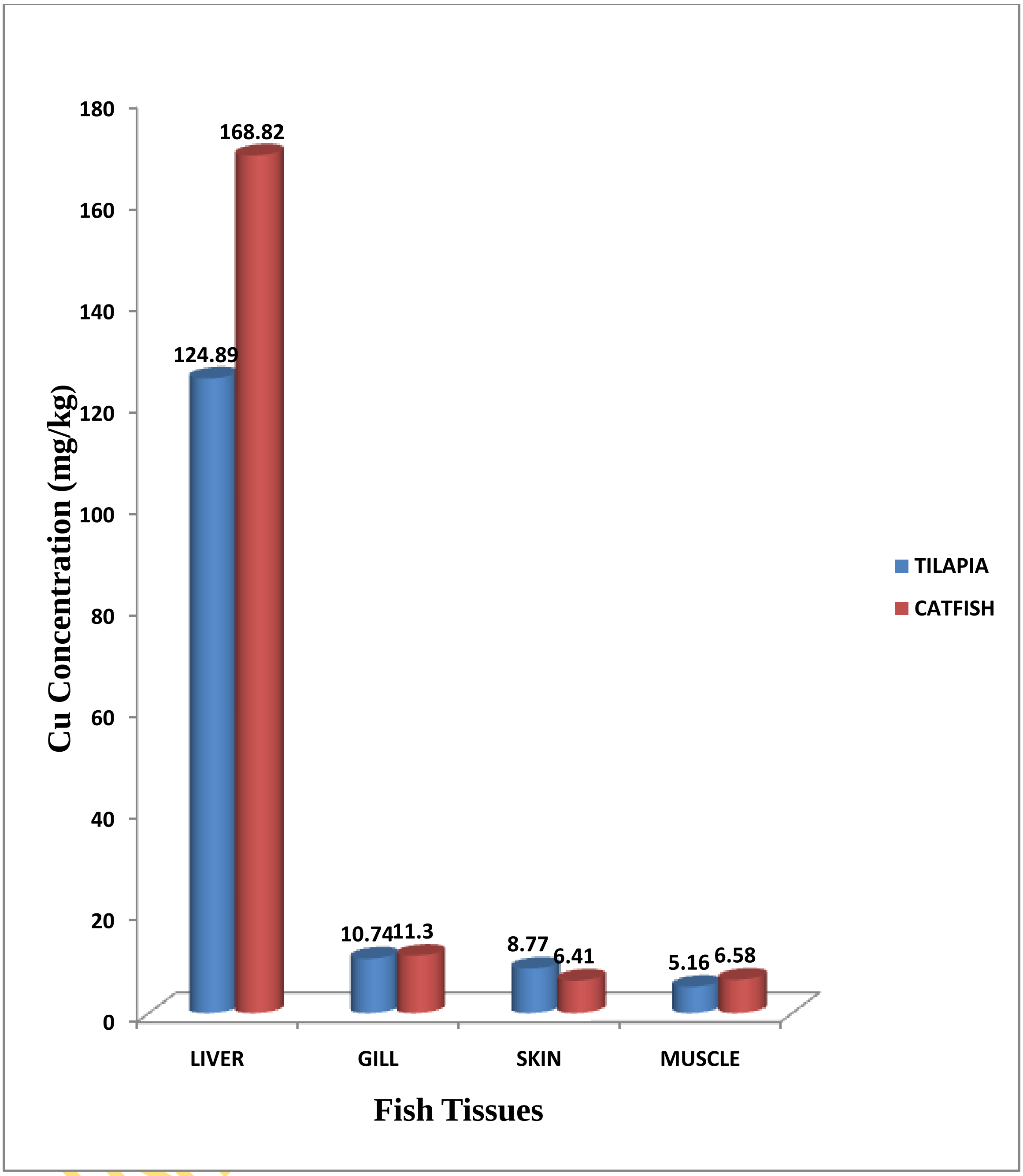

Figure 4.16: Copper Concentration in Tilapia and Catfish Tissues of Agodi Lake

4.8 Concentration of Heavy Metals in tissues of Catfish Samples from Study and Control Lakes.

Concentrations of heavy metals in the tissues of catfish samples from Agodi Lake as well as from Eleyele (Control Lake) are presented in Table 4.8. From the table, the concentration of heavy metals were higher in Catfish samples from Agodi Lake except zinc concentration which was higher in the fishes from Eleyele Lake. The concentrations of lead were the following: liver (6.94, 4.01) mg/Kg; gill (12.80, 3.16) mg/Kg; skin (7.13, 2.81) mg/Kg; muscle (5.17, 3.57) mg/Kg in Catfish tissues of Agodi and Eleyele Lakes respectively while the concentrations of zinc was as follows: liver (233.42, 244.47) mg/Kg; gill (137.03, 189.54) mg/Kg; skin (96.72, 150.35) mg/Kg; muscle (66.60, 88.12) mg/Kg in Catfish tissues of Agodi and Eleyele Lakes respectively.

Table 4.9 highlights the statistical differences in heavy metals concentrations in the tissues of fish samples from Agodi lake and those from Eleyele Lake. From the table, it can be seen that there is significant difference in the concentrations of chromium in the skin and muscle of Catfish from both Lakes; significant difference in zinc concentration in the muscle and significant difference in copper concentration in liver, with $p<0.05$.

4.9 Concentration of Heavy Metals in tissues of Tilapia fish from Study and Control Lakes.

Concentrations of heavy metals in the tissues of tilapia fish from Agodi lake as well as from Eleyele (Control Lake) used for this study are presented in Table 4.10. The concentrations of lead, chromium and copper were higher in the tissues of tilapia fish samples from Agodi Lake while the reverse was observed for cadmium and zinc since these heavy metals were found at higher concentrations in tilapia fish samples from Eleyele lake than in samples from Agodi Lake. The concentration of lead in Tilapia fish tissues from Agodi lake and Eleyele lakes are as follows: liver (13.12, 9.47) mg/Kg; gill (10.22, 5.16) mg/Kg; skin (6.58, 3.78) mg/Kg; muscle (4.62, 4.37) mg/Kg respectively while the following are the concentration of zinc in Tilapia fish tissues: liver (203.17, 217.77) mg/Kg; gill (164.95, 176.82) mg/Kg; skin (300.99, 262.02) mg/Kg; muscle (94.49, 106.15) from Agodi and Eleyele lakes respectively.

Their percentage differences are also presented with details of corresponding values are found in the table.

Table 4.11 highlights the statistical differences in heavy metals concentrations in the tissues of Tilapia fish samples from Agodi lake and those from Eleyele lake. From the table, it can be gathered that there was no significant difference in heavy metals concentration between Tilapia from Agodi Lake and Tilapia from Eleyele Lake except for chromium where the differences in concentration in the gill, skin and muscle were statistically significant with $p<0.05$.

Table 4.8: Summary of Concentration of Heavy Metals in tissues of Catfish Samples from Study and Control Lakes

HEAVY METAL	TISSUES	CAT FISH AGODI mg/Kg	CATFISH ELEYELE mg/Kg
LEAD	LIVER	6.94±2.01	4.01±1.82
	GILL	12.80±2.20	3.16±2.46
	SKIN	7.13±3.37	2.81±2.09
	MUSCLE	5.17±4.49	3.57±1.63
CADMIUM	LIVER	1.23±0.86	0.77±0.54
	GILL	0.62±0.47	0.77±0.44
	SKIN	0.47±0.25	0.31±0.34
	MUSCLE	0.73±0.54	0.90±1.04
CHROMIUM	LIVER	3.46±1.04	2.54±1.45
	GILL	4.88±0.62	2.23±1.18
	SKIN	5.45±0.58	1.23±0.62
	MUSCLE	6.24±0.77	1.04±0.65
ZINC	LIVER	233.42±0.81	244.47±0.69
	GILL	137.03±0.65	189.54±0.54
	SKIN	96.72±1.39	150.35±0.14
	MUSCLE	66.60±0.20	88.12±0.09
COPPER	LIVER	168.82±0.69	78.43±1.18
	GILL	11.30±0.54	6.94±0.58
	SKIN	6.41±0.20	4.88±0.54
	MUSCLE	6.58±0.28	4.12±0.77

TABLE 4.9: Comparison of Concentration of Heavy Metals in Tissues of Cat fish Samples From Study and Control Lake.

Heavy metals	**Liver mg/Kg**			**Gill mg/Kg**			**Skin mg/Kg**			**Muscle mg/Kg**		
	Mean ±S.D	t-value	p-value	Mean ±S.D	t-value	p-value	Mean ±S.D.	t-value	p-value	Mean ±S.D.	t-value	p-value
Lead												
Study	6.94±2.01	0.88	0.33	12.80±2.20	1.21	0.40	7.13±3.37	2.91	0.45	5.17±4.49	0.97	0.08
Control	4.01±1.82			3.16±2.46			2.81±2.09			3.57±1.63		
Cadmium												
Study	1.23±0.86	3.60	0.16	0.62±0.47	2.55	0.22	0.47±0.25	1.24	0.31	0.73±0.54	3.61	0.17
Control	0.77±0.54			0.77±0.44			0.31±0.34			0.90±1.04		
Chromium												
Study	3.46±1.04	2.50	0.08	4.88±0.62	1.10	0.30	5.45±0.58	2.05	0.03	6.24±0.77	1.95	0.02
Control	2.54±1.45			2.23±1.18			1.23±0.62			1.04±0.65		
Zinc												
Study	233.42±0.81	2.26	0.08	137.03±0.65	1.22	0.60	96.72±1.39	0.87	0.54	66.60±0.20	3.42	0.04
Control	244.47±0.69			189.54±0.54			150.35±0.14			88.12±0.09		
Copper												
Study	168.82±0.69	2.13	0.01	11.30±0.54	0.23	0.57	6.41±0.20	1.68	0.22	6.58±0.28	0.33	0.43
Control	78.43±1.18			6.94±0.58			4.88±0.54			4.12±0.77		

Table 4.10: Summary Of Concentration of Heavy Metals in Tissues of Tilapia Fish Samples from Study and Control Lakes.

HEAVY METAL	TISSUES	TILAPIA AGODI mg/Kg Mean±S.D	TILAPIA ELEYELE mg/Kg Mean±S.D
LEAD	LIVER	13.12±2.38	9.47±2.31
	GILL	10.22±1.81	5.16±2.38
	SKIN	6.58±2.63	3.78±1.81
	MUSCLE	4.62±2.01	4.37±1.88
CADMIUM	LIVER	0.73±0.38	1.04±1.08
	GILL	0.41±0.31	0.54±0.34
	SKIN	0.31±0.14	0.51±0.34
	MUSCLE	0.44±0.34	0.44±0.32
CHROMIUM	LIVER	4.49±2.01	5.91±2.71
	GILL	2.31±1.34	0.77±0.47
	SKIN	3.78±0.99	0.77±0.69
	MUSCLE	3.78±0.94	1.63±0.99
ZINC	LIVER	203.17±0.81	217.77±4.88
	GILL	164.95±0.38	176.82±2.16
	SKIN	300.99±0.69	262.02±2.09
	MUSCLE	94.49±0.90	106.15±0.62
COPPER	LIVER	124.89±0.86	101.32±1.08
	GILL	10.74±0.54	9.23±0.28
	SKIN	8.77±1.31	6.41±0.38
	MUSCLE	5.16±0.58	5.91±1.88

TABLE 4.11: Comparison of Concentration of Heavy Metals in Tissues of Tilapia Fish Samples From Study and Control Lakes.

Heavy metals	**Liver mg/Kg**			**Gill mg/Kg**			**Skin mg/Kg**			**Muscle mg/Kg**		
	Mean ±S.D	t-value	p-value	Mean ±S.D	t-value	p-value	Mean ±S.D.	t-value	p-value	Mean ±S.D.	t-value	p-value
Lead												
Study	13.12±2.38	2.33	0.09	10.22±1.81	4.80	0.13	6.58±2.63	1.86	0.07	4.62±2.01	1.23	0.16
Control	9.47±2.31			5.16±2.38			3.78±1.81			4.37±1.88		
Cadmium												
Study	0.73±0.38	3.20	0.33	0.41±0.31	1.03	0.25	0.31±0.14	3.22	0.10	0.44±0.34	0.78	0.46
Control	1.04±1.08			0.54±0.34			0.51±0.34			0.44±0.32		
Chromium												
Study	4.49±2.01	2.41	0.70	2.31±1.34	3.79	0.02	3.78±0.99	2.52	0.01	3.78±0.94	1.24	0.03
Control	5.91±2.71			0.77±0.47			0.77±0.69			1.63±0.99		
Zinc												
Study	203.17±0.81	4.21	0.32	164.95±0.38	2.01	0.14	300.99±0.69	1.77	0.08	94.49±0.90	3.77	0.31
Control	217.77±4.88			176.82±2.16			262.02±2.09			106.15±0.62		
Copper												
Study	124.89±0.86	1.86	0.56	10.74±0.54	3.50	0.52	8.77±1.31	0.97	0.13	5.16±0.58	1.42	0.09
Control	101.32±1.08			9.23±0.28			6.41±0.38			5.91±1.88		

4.10 Correlation Between levels of Heavy Metals in the Liver tissue of Catfish

Figs. 4.17- 4.19 showed the relationship between heavy metals in the liver of catfish. The correlation coefficient as well as the p-values are highlighted in these figures. Figure 4.17 shows that the concentrations of zinc and copper in the liver are positively correlated r=0.761 i.e. the increase and decrease of both heavy metals occur in the same direction and this correlation is statistically significant $p<0.05$. Figure 4.18 depicts that the concentration of zinc and lead in the liver are positively correlated as well r=0.656 but the correlation is not statistically significant since the p-value is greater than 0.05 while it can be deducted from Figure 4.19 that zinc and cadmium are weakly positively correlated r=0.171 and the correlation is also not statistically significant.

4.11 Correlation Between levels of Heavy Metals in the Liver tissue of Tilapia fish

The relationship that exist between heavy metals in the liver of tilapia fish are presented in Figs. 4.20-4.22. The correlation coefficient as well as the p-values are also presented in these figures. From Figure 4.20 it can be seen that the concentration of zinc and copper in the liver are positively correlated r=0.492 but the correlation is not statistically significant. Zinc and lead concentration in the liver of tilapia fish are negatively correlated r=-0.204 i.e. the increase or decrease of both heavy metals occur in opposite directions. However, this negative correlation is not statistically significant. On the other hand, zinc and cadmium are positively correlated r=0.190 but their correlation is weak and not statistically significant as shown in Figure 4.22.

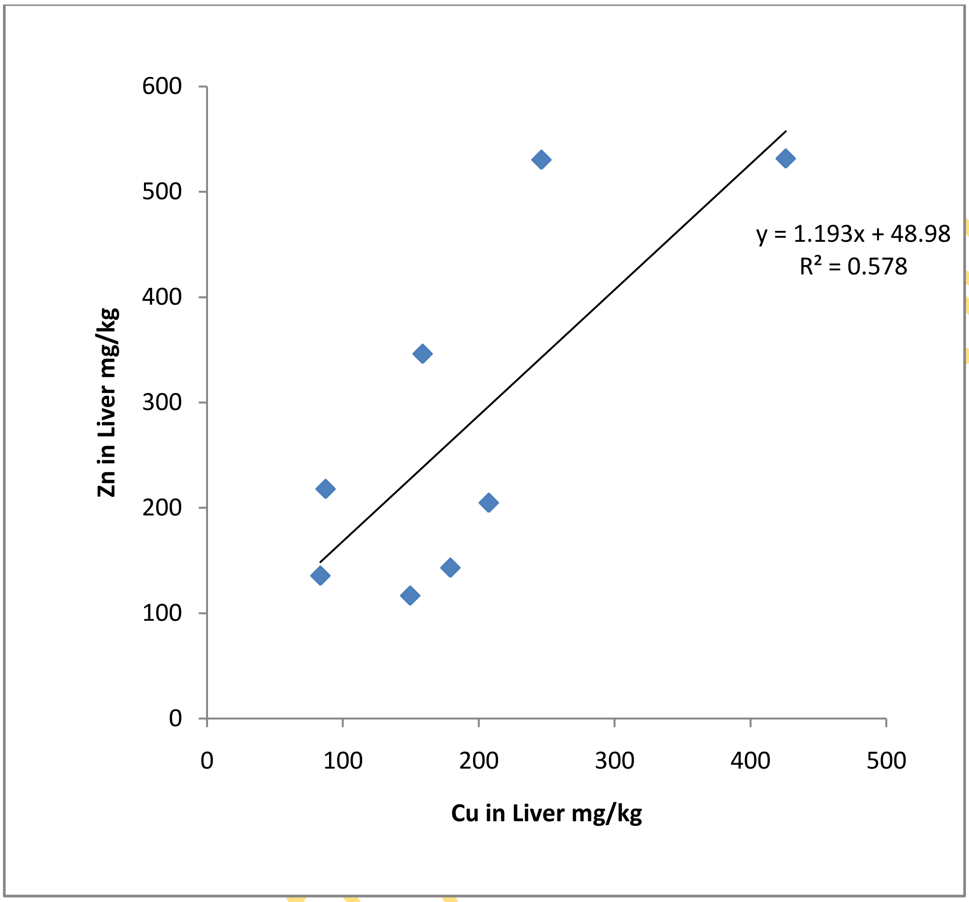

Fig. 4.17: Correlation between Zinc and Copper in the Liver of Catfish

r=0.761

p< 0.05

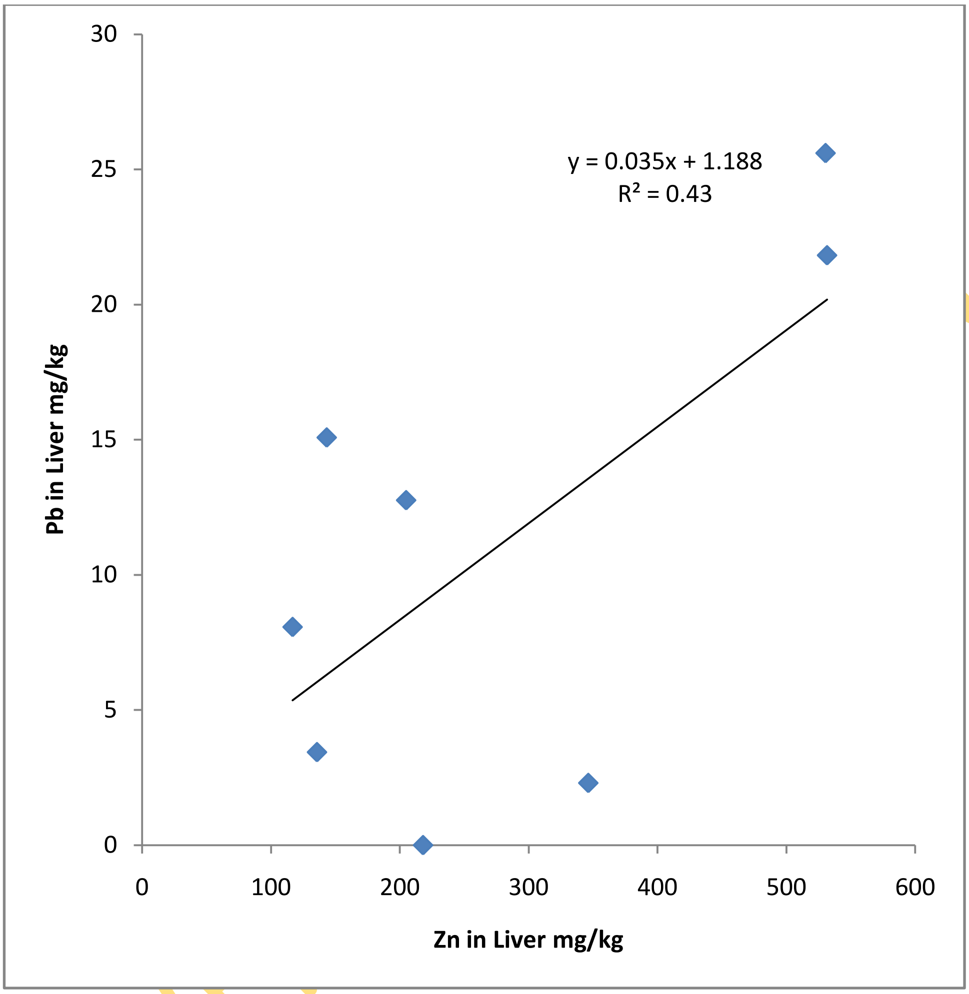

Fig. 4.18: Correlation between Zinc and Lead in Liver of Catfish

$r = 0.656$

$p > 0.05$

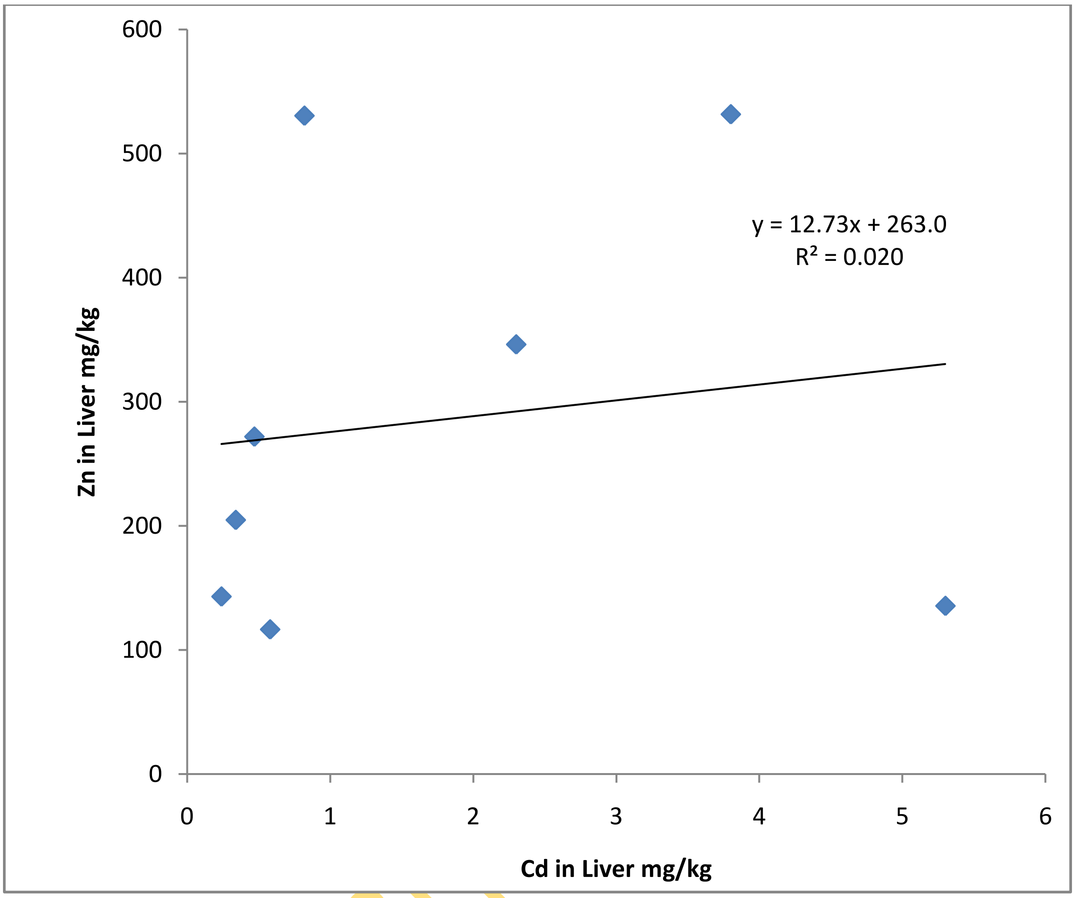

Fig. 4.19: Correlation between Zinc and Cadmium in the liver of Catfish

r= 0.171

P>0.05

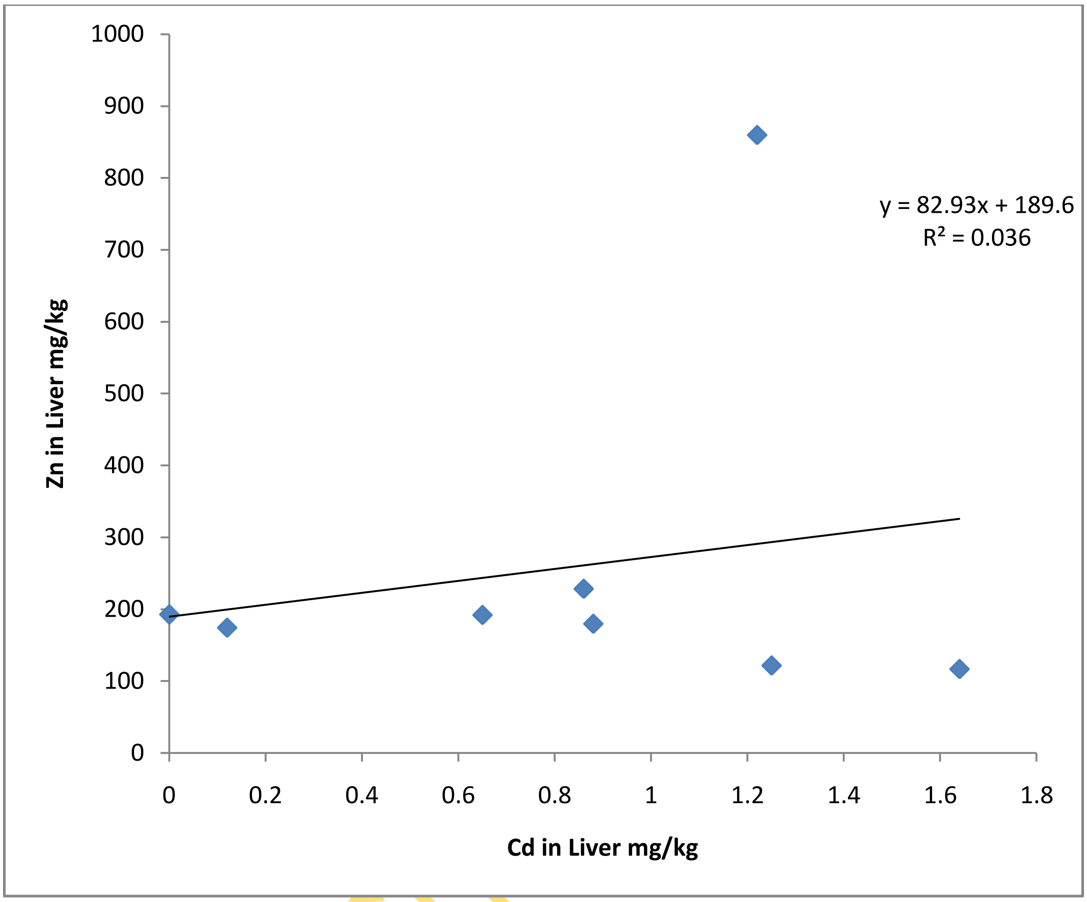

Fig. 4.20: Correlation between Zinc and Cadmium in Tilapia fish

r=0.190

P> 0.05

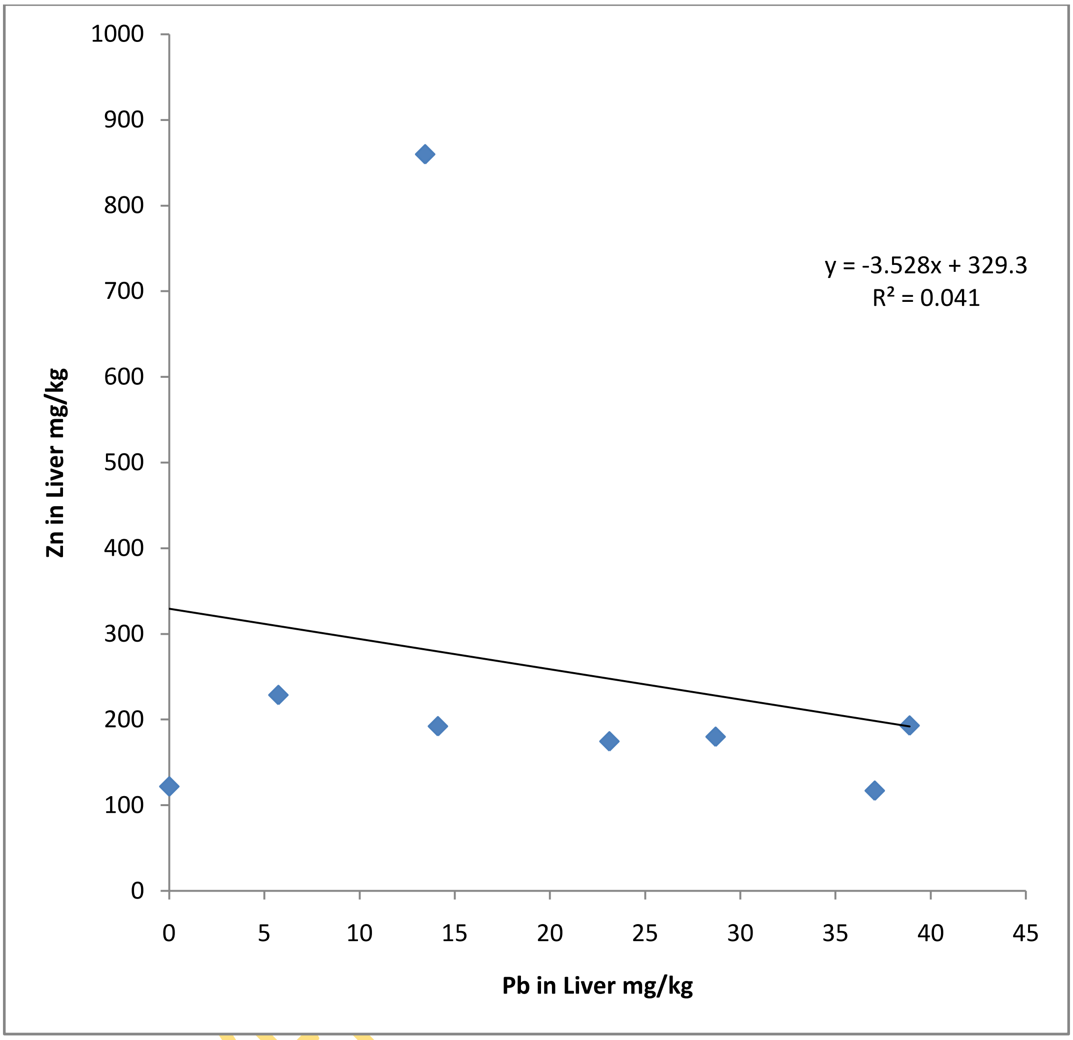

Fig. 4.21: Correlation between Zinc and Lead in Tilapia fish

r= -0.204

P>0.05

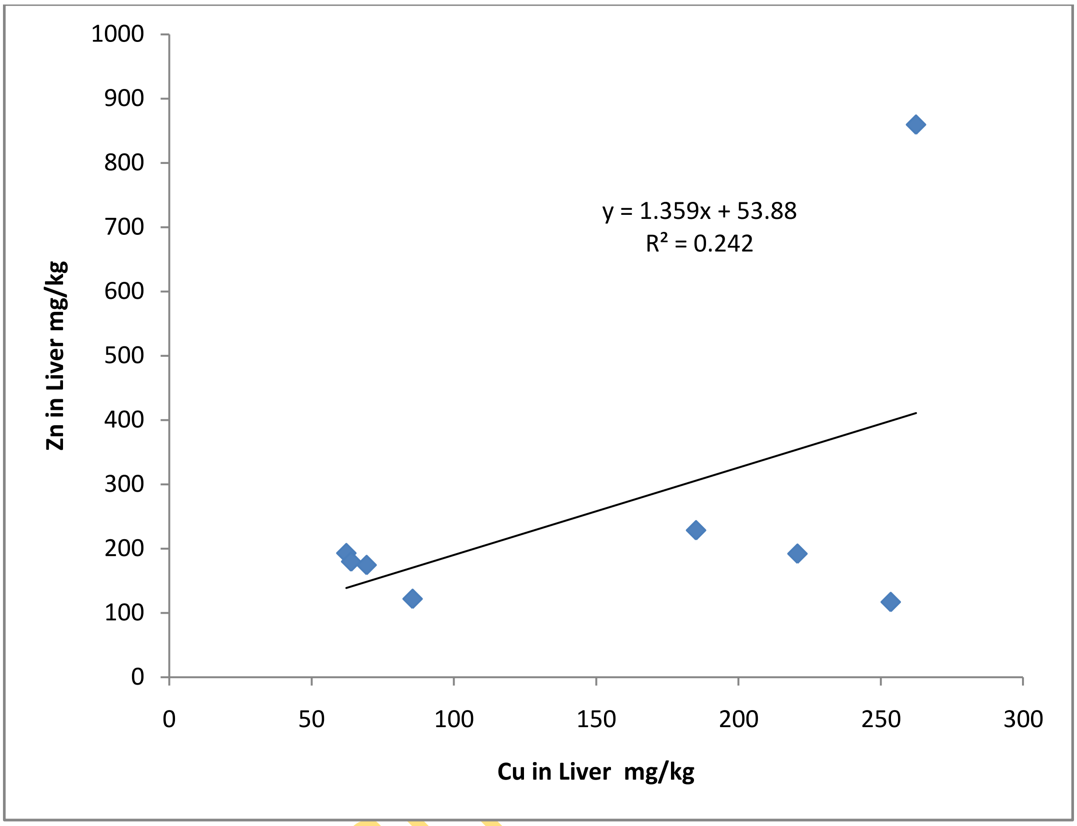

Fig. 4.22: Correlation between Zinc and Copper in liver of tilapia fish

r=0.492

P>0.05

4.12 Correlation between Concentration of Heavy Metals in Water and the Liver of Catfish from Agodi Lake.

Table 4.12 summarises the correlation between concentration of heavy metals in water and the liver of catfish from Agodi lake. Also presented on this table are the r-values (correlation value) as well as the p-values of the correlation relationship. Lead and cadmium concentrations in water were negatively correlated with their concentrations in the liver, meaning that increase or decrease in water and liver were in opposite direction though the correlation was not statistically significant. Chromium, zinc and copper concentration in water were positively correlated with their concentration in liver but the correlation was not statistically significant. Details of their corresponding values are found in Table 4.12.

4.13 Correlation between Concentration of Heavy Metals in Water and the Liver of Tilapia fish from Agodi Lake.

Table 4.13 highlights the relationship between the concentration of heavy metals in the water and liver of Tilapia fish samples from Agodi lake. The table also presents the correlation coefficient values as well as the p-values. Lead and cadmium in water negatively correlated with their concentration in the liver, r=-0.351 and r=-0.314 respectively. However, the correlation was not statistically significant. While chromium, zinc and copper concentration in water correlated positively with their concentration in liver r=0.629, r=0.290 and r=0.267. However, the correlation was weak and not statistically significant.

4.14 Correlation between pH level and Concentration of Heavy Metals in Water

Table 4.14 presents the relationship between the concentration of heavy metals and pH level in the water samples from Agodi lake. The table also presents the correlation coefficient values as well as the p-values. Lead and Zinc concentration positively correlated with pH, r= 0.308 and r= 0.117 respectively. The correlation was however, not statistically significant. While Cadmium, Chromium and Copper correlated negatively with pH, r= - 0.143, r= -0.572, r=-286. However, the correlation was weak and not statistically significant.

Table 4.12: Correlation Between Concentration of Heavy Metals in Water and Liver of Catfish Samples from Agodi Lake.

Heavy metals	Correlates	Mean±SD	r-value	p-value
Lead	Water Liver	0.06±0.04 6.94±2.01	-0.587	0.126
Cadmium	Water Liver	0.01±0.01 1.23±0.86	-0.339	0.411
Chromium	Water Liver	0.01±0.01 3.46±1.04	0.455	0.258
Zinc	Water Liver	0.04±0.01 233.42±0.81	0.234	0.578
Copper	Water Liver	0.02±0.01 168.82±0.69	0.431	0.287

Table 4.13: Correlation Between Concentration of Heavy Metals in Water and Liver of Tilapia fish from Agodi Lake.

Heavy metals	Correlates	Mean±SD	r-value	p-value
Lead	Water Liver	0.06±0.04 13.12±2.38	-0.351	0.394
Cadmium	Water Liver	0.01±0.01 0.73±0.38	-0.314	0.448
Chromium	Water Liver	0.01±0.01 4.49±2.01	0.629	0.095
Zinc	Water Liver	0.04±0.01 203.17±0.81	0.290	0.486
Copper	Water Liver	0.02±0.01 124.89±0.86	0.267	0.523

Table 4.14: Correlation Between Concentration of Heavy Metals pH Level in Water from Agodi Lake.

Correlates	Mean±SD	r-value	p-value
pH Lead	7.20±0.09 0.06±0.04	0.308	0.692
pH Cadmium	7.20±0.09 0.01±0.01	-0.143	0.857
pH Chromium	7.20±0.09 0.01±0.01	-0.572	0.428
pH Zinc	7.20±0.09 0.04±0.01	0.117	0.883
pH Copper	7.20±0.09 0.02±0.01	-0.286	0.714

4.15 Mean Differences in Concentration of Heavy Metals Among the Tissues of Catfish Samples from Agodi Lake

Table 4.15 highlights the results of the mean differences in each heavy metal among the tissues of Catfish. This was done using ANOVA. From the table, it can be seen that the mean differences in lead, cadmium and chromium concentration among liver, gill, skin and muscle were not statistically significant as the p-value for each was above 0.05. On the other hand, the mean differences in zinc and copper concentration among the tissues were statistically significant $p<0.05$. See table for details.

4.16 Mean Differences in Concentrations of Heavy Metals Among the Tissues of Tilapia Fish Samples from Agodi Lake

The result of analyses done to ascertain the statistical significance of the mean difference in each heavy metal among the tissues of Tilapia fish samples from Agodi lake are presented in Table 4.16 below. The mean difference in the concentrations of chromium and that of copper among the liver, gill, skin and muscle were found to be statistically significant $p<0.05$ while on the other hand, the mean differences in the concentrations of lead, cadmium and zinc among the tissues were not statistically significant. See table for details.

Table 4.15: F-statistics for Mean Difference in Concentration of Heavy Metals in Catfish Tissues from Agodi Lake.

Heavy metals	Tissues(mean) mg/Kg	F-value	p-value
Lead	Liver 6.94±2.01 Gill 12.80±2.20 skin 7.13±3.37 muscle 5.17±4.49	0.45	0.714
Cadmium	Liver 1.23±0.86 Gill 0.62±0.47 Skin 0.47±0.25 Muscle 0.73±0.54	1.21	0.321
Chromium	Liver 3.46±1.04 Gill 4.88±0.62 Skin 5.45±0.58 Muscle 6.24±0.77	1.04	0.388
Zinc	Liver 233.42±0.81 Gill 137.03±0.65 Skin 96.72±1.39 Muscle 66.60±0.20	6.27	0.002
Copper	Liver 168.82±0.69 Gill 11.30±0.54 Skin 6.41±0.20 Muscle 6.58±0.28	122.74	0.000

Table 4.16: F-statistics For Mean Difference in Concentration of Heavy Metals in Tilapia Fish Tissues From Agodi Lake.

Heavy metals	Tissues(mean) mg/Kg	F-value	p-value
Lead	Liver 13.12±2.38 Gill 10.22±1.81 Skin 6.58±2.63 Muscle 4.62±2.01	0.37	0.771
Cadmium	Liver 0.73±0.38 Gill 0.41±0.31 Skin 0.31±0.14 Muscle 0.44±0.34	0.30	0.819
Chromium	Liver 4.49±2.01 Gill 2.31±1.34 Skin 3.78±0.99 Muscle 3.78±0.94	4.18	0.014
Zinc	Liver 203.17±0.81 Gill 164.95±0.38 Skin 300.99±0.69 Muscle 94.49±0.90	1.96	0.143
Copper	Liver 124.89±0.86 Gill 10.74±0.54 Skin 8.77±1.31 Muscle 5.16±0.58	63.52	0.000

CHAPTER FIVE

5.0 DISCUSSION

This chapter presents the discussion of the results of the study and their implications for health. It also highlights the similarity as well as variation in the results with previous studies on this subject matter. The chapter is divided into sections; starting with the physico-chemical analyses of the water samples; then the concentration of heavy metals in the water samples. The last aspect, focuses on the concentration of heavy metals and distribution in the tissues of the fish samples.

5.1 Physico-chemical Characteristics of Effluent and Water Samples From Agodi Lake's Tributaries

The levels found in these samples were within NGL, 1991 stipulated limits of $<40^0$C for temperature, 6-9 for pH, 2000 mg/L for TDS and <1.00 mg/L for lead, cadmium, chromium, zinc and copper in effluents and also, within NESREA, 2011 standard for fresh water. These therefore, do not pose any immediate threat to the receiving water body; Agodi lake. It is important to note that, NESREA stipulated no guideline for dissolved oxygen and conductivity in effluents. However, effluent samples from UCH sewage treatment plant recorded zero level DO and very high conductivity which are detrimental to the health and quality of Agodi lake.

According to DFID (1999), dissolved oxygen is an important factor for water quality control and the effect of waste discharged into a river is largely determined by the oxygen balance of the system as its presence is essential to sustenance of aquatic life within the system. This supports the fact that the absence of dissolved oxygen in UCH sewage treatment plant effluent discharged into Agodi lake is detrimental to the survival and functioning of organisms in the lake. Furthermore, heavy metal levels in the effluent as well as water from the other tributaries might presently be within FEPA and NESREA stipulated limits but from a more conservative standpoint cannot be considered safe because heavy metals have the ability of persisting and accumulating in the aquatic ecosystem where they impair the potability of the water and also its ability to sustain aquatic life.

Roberts (1978), observed that sewage discharges may reduce water quality depending on the degree of dilution achieved, the degree of treatment of the original material, its composition and the response of the ecosystem. Oxygen depletion is the most common result of such discharges (sewage) and this is not healthy for aquatic life. According to WHO (1993); Adakole (2000) and Asonye *et al.*, (2007), municipal sewage sludge may contain high concentrations of heavy metals such as cadmium, lead and chromium and this is in accordance with the results obtained in this study where effluents from UCH sewage treatment plant contained the highest levels of heavy metals.

5.2 Physico-chemical characteristics of Agodi Lake

The physico-chemical parameters in a water body are influenced by natural and anthropogenic processes. They are also dependent on the depth of the aquatic system (Malik *et al.*, 2008). These parameters are very vital in determining the quality of water found in a water body. In this study, the water temperature, pH, Conductivity, Total dissolved solids and Dissolved oxygen levels of Agodi Lake were assessed.

The mean temperature of Agodi lake was 28.75^0C which is slightly above NESREA's set standard of 25^0C as being most suitable for the existence and development of aquatic life, this is in conformity with the result of Lawson (2011) on swamps in Lagos. Boyd (1999) suggest an optimum growth temperature range of $26\text{-}28^o$C for fishes in tropical and subtropical waters. Temperature, has a large impact on the biological activity of aquatic organisms. It affects metabolic activities, growth, feeding, reproduction, distribution and migratory behaviours of aquatic organisms (Suski *et al.*, 2006).

All aquatic organisms have a preferred temperature range. If the water temperature gets too far above or below this range, then the biological community becomes stressed and may have difficulty maintaining a stable population. Temperature is also important because of its influence on water chemistry. The rate of chemical reactions generally increases at higher temperature, which in turn affects biological activity. Another important example of the effects of temperature on water chemistry is its impact on oxygen. Warm water holds less oxygen than cool water, so it may be saturated with oxygen but still not contain enough for survival of aquatic invertebrates or certain types of fish. It is also a known fact that temperature influences the rate of chemical reactions.

Conductivity is a measure of water's ability to conduct electrical current. It is also an indicator of dissolved ions or solutes such as metals present in the water. The conductivity level of Agodi Lake was 240.21µS/cm. It is above 200µS/cm limit stipulated by NESREA, 2011 for the survival of aquatic organisms in fresh water. This higher level is not unconnected with effluent discharged into the lake from UCH sewage treatment plant.

The study by Ewa *et al.*, (2011) lends credence to this assumption, where higher mean conductivity level of 426.3µS/cm in Omoku creek was also recorded due to industrial effluent discharged into the creek. High conductivity levels may also be due to several of the following factors: untreated wastewater infiltration, mining, and agricultural runoff. Excessively high conductivity concentrations can be damaging to aquatic life because of increased salinity in the stream and possible smothering of the stream bottom. Conductivity of fresh water normally ranges from 10 – 1000 µS/cm but may exceed 1000 µS/cm (Asuquo, 1999). Adakole *et al.*, (2008) noted that the low conductivity of 69.20 µS/cm recorded in their study was indicative of infertile water. According to Umeham (1989), a high surface electrical conductivity of about 400.00µS/cm of a water body could be used to assign a high morphoedaphic index to it and therefore a high fish production potential.

Total dissolved solids (TDS) is a measure of the total ions present in water. TDS could either be high or low depending on the concentrations of these ions in the water. Most often, high levels of TDS are caused by the presence of potassium, chlorides and sodium, these ions have little or no short-term effects, but toxic ions such as lead ions, arsenic ions, cadmium ions, nitrate ions and others may also be dissolved in the water. These ions get introduced into surface water through several means, inclusive are: sedimentation, mining, or storm water runoff.

NESREA (2011) stipulates 450 mg/L as the standard limit in freshwaters for optimum growth and development of aquatic organisms. The mean TDS level of Agodi Lake was 144.06 mg/L and this falls within the standard level for the sustenance of aquatic organisms. When TDS levels exceed 1000 mg/L it is generally considered unfit for human consumption (Lawson, 2011). Lawson (2011) recorded a very high average TDS value of 836.78 mg/L for Lagos swamps which he attributed to organic sources such as leaves, silt, plankton and industrial waste and sewage. Increased TDS may impart a bad odour or taste; which could be salty, bitter, or metallic to drinking water. It could also indicate the presence of toxic minerals that can cause scaling of pipes and corrosion. Water can be classified according to Ela (2007) by the amount of TDS per litre of water: freshwater < 1500 mg/L TDS, brackish water 1500 to 5000 mg/L TDS and saline water > 5000 mg/L TDS. Going by this classification, Agodi Lake falls under the ambit of a freshwater body.

pH is the measurement of the potential activity of hydrogen ions in a liquid sample. pH is not static, it changes over time, in fact it changes over the course of a single day. pH of the water body is affected by several factors (Rai *et al.*, 2011) such as agricultural runoff, mining, or infiltration of untreated wastewater. Low pH is acidic and can cause corrosion of pipes, as well as increased dissolved metals concentrations in surface water. High pH is alkaline and can cause scale build-up in fixtures, bad taste, and reduce the effectiveness of chlorine disinfection, as well as increased metal concentrations in stream sediments. When the pH of water is high or slightly alkaline, the availability of heavy metals in the water is reduced and as such fishes uptake of heavy metals from the water which is their immediate environment is low. Most heavy metals are known to become more bio-available and have increased toxicity with decreasing pH (Shaw and Brown, 1973).

The pH of Agodi Lake was 7.20 which is neutral. The pH status of Agodi lake is within NESREA and EU (Chapman, 1996) permissible limit (6-9) for the protection, survival and development of aquatic life. It is also within the natural background level of 6.5-8.5 that exist in most natural waters (Mechenich and Andrews, 2006). pH value obtained in this study agrees with those documented by Swingle (1969); Boyd (1981); EEC (1976); Baijot *et al.*, (1997) and Unoha (2001) as values most suitable for maximum productivity of aquatic organisms. Furthermore, the value is within the range commonly found in oligotrophic and eutrophic lakes where typical reading lies between pH 6.0 and 9.8 (Rippey and Rippey, 1986). It is also in accordance with the result obtained by Schlotfeldt and Alderma (1995) that pH 5.5–8.0 is the most suitable range for freshwater. Lawson (2011) however recorded average pH value of 6.97 which is slightly lower than the average pH value recorded for Agodi lake. Considering these guidelines, the mean pH value of Agodi Lake shows suitability for sustenance of the aquatic ecosystem.

Dissolved oxygen (DO) is an important limnological parameter considered by Boyd (1989) as the most critical water quality variable in aquaculture. Survival of aquatic organisms especially fishes depend upon the level of DO in water. DO in liquid provides a source of oxygen needed for the oxidation of organic matter; when the concentration is high, very low or lacking, it causes the water body to become dead or devoid of aquatic life (Chukwu, 2008). Anoxia occurs when dissolved oxygen levels in the environment decrease to the point where aquatic life can no longer be supported. Low DO level is an indication of high organic matter content and consequently high rate of decomposition. The most common cause of low DO in an aquatic ecosystem is high concentration of biodegradable organic matter including sewage in the water, resulting in a high BOD. This problem is further exacerbated at high temperatures (Zweig *et al.*, 1999).

WHO and NESREA stipulate at least 5.0 mg/L and a limit of 8-10 mg/L respectively in surface waters. The DO level of Agodi lake is 4.39 ± 1.97 mg/L which is below standard level showing that Agodi is burdened with a lot of Organic matter. It also falls below the range of 5.0- 9.0 mg/L documented by Swingle (1969) and Boyd, (1981) for good water quality suitable for aquatic organisms. Similarly, Dissolved oxygen level recorded in this study is lower compared to 4.94-5.9 mg/L for Ogun River and 3.4-7.0 mg/L for Calabar River both in Nigeria recorded by Golterman (1969) in his study. However, low values of DO have been observed by Nwankwo *et al.*, (2003) in lakes or creeks in Western Nigeria which they said may be a reflection of the high amount of decomposing materials within the water arising from the surrounding derived vegetation. High organic enrichment of lakes is the possible reason for low oxygen values.

Dissolved oxygen (DO) level recorded in this study is also similar to those reported for many other polluted Nigerian waters including , 4.00-7.50 mg/L for Luubara creek in Niger Delta (Deekay *et al.*, 2010a; 2010b) and 1.20 - 9.40 mg/L documented by Edokpayi and Osimen (2001).

Studies on Nigerian aquatic ecosystem impairment have been reported and most of the researchers established that a knowledge of hydrological conditions of any body of water is not only useful in assessing its potability but will also permit a better understanding of the population and life cycle of the fish community (Antia and Holzlohner, 1996).

5.3 Concentration of Heavy Metals in Agodi Lake

Domestic sewage, combustion emission, mining operations, metallurgical activities and industrial effluents are among the sources of anthropogenic heavy metal inputs into water bodies and heavy metals such as Pb, Cd, Cu and Zn are released as a result of these processes

(Chinni and Yallapragda, 2000). Many water bodies in Nigeria are known to be polluted by heavy metals due to increasing industrial and agricultural activities and the heavy metals of greatest concern to the health of humans and aquatic organisms include aluminium, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel and zinc (Svobodova *et al.*, 1993). As a result, several attempts have been made in the last few decades regarding the evaluation of heavy metals in various water bodies in some parts of Nigeria and beyond.

This present study assessed the concentration of heavy metals in water samples from Agodi Lake. The mean concentrations (mg/L) of the heavy metals determined were: Pb; 0.06±0.04, Zn; 0.04±0.01, Cu; 0.02±0.01, Cr; 0.01±0.01 and Cd; 0.01±0.01 mg/L in the order of Pb > Zn > Cu > Cr = Cd. The concentration of heavy metals are usually higher in the dry season and lowest in the rainy season due to the " dilution effect" as reported by Malik *et al.*, (2008) and Jain and Sharma (2001). In addition, review of the study by Camusso *et al.*, (1995) showed that heavy metals generally exist in low levels in water and attain considerable concentration in sediments and biota. These statements explain and support the low levels of heavy metals reported in this study.

Adakole, *et al.*, (2008) assessed heavy metals levels in Kubanni and observed that the mean zinc level was 0.44 mg/L, average lead concentration was 1.22 mg/L, copper was 0.88 mg/L. Their result is in conformity with the result obtained in this present study where the concentration of lead was the highest. The sources of the heavy metals encountered were attributed to sewage and landfill. In similar fashion, Obasohan *et al.*, (2008) assessed the concentration of heavy metals in Ikpoba river in Benin City and their result showed that Lead concentration was higher than WHO recommended level in drinking water. However, Ozturk *et al.*, (2008) assessed the concentration of Cadmium, Chromium, Copper, Iron, Nickel and Lead in Avsar Dam Lake in Turkey and the following concentrations were found; 0.001, 0.006, 0.01, 0.9, 0.006 and 0.005 mg/L respectively and these are lower than the values obtained in this study.

The concentrations of heavy metals in Agodi Lake were also within NESREA (2011) stipulated limits for heavy metals in freshwater. DWAF (1996) stated that background levels of heavy metals in natural freshwaters are usually very low, generally ranging from 0.0 to 0.13 ppb (0.00013 mg/L). For the protection of aquatic life especially fish, different maximum admissible concentrations have been recommended by different authors depending on the species of fish and physico-chemical state of the water (Svobodova,1993). DWAF

(1996) suggested < 0.0002–0.0018 mg/L for cadmium; <0.005 mg/L for copper; <0.02 mg/L for chromium; <0.001 mg/L for lead and <0.005 mg/L for zinc in freshwater.

The values of Lead and indeed the other heavy metals detected in Agodi Lake might not pose acute or immediate threat to fishes and human consumers but could be sufficient hazard in the long-run due to the cumulative effect of heavy metals. The relatively high concentration of Lead in the lake may be as a result of the direct release of public waste including sewage into the lake, anthropogenic activities around the lake and vehicular emissions.

5.4 Concentration of Heavy Metals and Distribution in Tissues of the Fish Samples

This present study constitutes a case of passive monitoring within the Agodi Lake ecosystem where organisms (fish species) already present naturally in the ecosystem were examined to study the levels of heavy metals in them. The absorption of heavy metals is to a large extent a function of their chemical forms and properties. Pulmonary intake causes the most rapid absorption and distribution through the body of fish via the circulatory system. Absorption through the intestinal tract is influenced by pH, rate of movement through the tract and presence of other materials among others. Combination of these factors can decrease or increase metal absorption (Manahan, 1992). It has also been documented by Campbell *et al*., (1997) that bottom sediment composition including the metal speciation, nature of complexes, metal-metal interactions and other factors such as temperature, pH, dissolved oxygen and organic ligands play an important role in respect to bioavailability of elements and concentration in the tissues of consumer organisms.

Results from this study showed that the concentration of heavy metals in the fish was by far higher than the concentrations in the surrounding waters from which the fishes were sampled. This may either be due to the fact that these fishes have bio-accumulated heavy metals over time from their diet; or because the heavy metals are lipophilic and as such reside and accumulate in fatty tissues (Ekpo *et al*., 2008). Furthermore, it was seen that heavy metals accumulated in the fish tissues at concentrations far above WHO, FEPA and FAO stipulated limits for heavy metals in fish. According to Arnot and Gobas (2006) and Barron (2003), bioaccumulation is the result of competing rates of chemical uptakes and elimination. It can be assumed therefore, that for fishes of Agodi Lake, the rate of uptake of elements is higher than the rate of elimination.

The mean concentration in mg/Kg of heavy metals in the various tissues of Catfish and tilapia fish were above FEPA (2003) and WHO (1985) standard limits of 2.0, 0.05, 0.15, 75 and 3.0 mg/Kg for lead, cadmium, chromium, zinc and copper respectively in fish except the concentrations of copper and zinc in the skin and muscle tissues that are within FAO permissible limits of 10-100 mg/Kg and 30-100 mg/Kg for copper and zinc respectively. Accumulation of these heavy metals in the fish tissues is dependent on bio-availability in water and sediments (Obasohan *et al.,* 2007) as well as dietary intake.

Bio-Accumulation Factor (BAF) is an indication of previous and on-going pollution and highlights the extent to which fish accumulates chemicals from their ambient environment. It is used to assess chemical accumulation when fishes are found in an unregulated environment. The BAF for heavy metals in Catfish and Tilapia fish in Agodi lake was calculated based on the concentration of heavy metals in the lake and the corresponding concentrations in the fish tissues. The fishes in Agodi lake are bio-accumulating heavy metals as evident in the high concentration of heavy metals in the fish compared with the concentration in the water. However, the Canadian regulatory criteria stipulates ≥ 5000 BAF for critically accumulating chemicals (Arnot and Gobas, 2006). Based on this, zinc and copper are critically accumulating especially in the liver tissues. This is expected as the liver tissue is crucial for storage and detoxification of chemical substances in fish.

5.4.1 Trend of Heavy metals Accumulation in the Tissues

Heavy metals bio-accumulated at varying levels and were clearly distinguishable in the different tissues. The trend of heavy metals accumulation in the tissues of both fish species was in the following order; Liver > Gill > Skin > Muscle. The differences in the levels of accumulation in the different tissues of a fish, according to Kotze *et al*., (1999) can primarily be attributed to the differences in the physiological role of each organ.

Furthermore, regulatory ability, behaviour and feeding habits are other factors that could influence the differences in the rate of accumulation of metals in the organs. In this present study, the highest concentrations of heavy metals were found in the liver and the lowest were detected in the muscle tissues. This finding is in agreement with those of other studies regarding the differences in heavy metal accumulation in fish tissues (Carpene and Vasak, 1989; Allen-Gil and Martynov, 1995). The Liver and Gills were the prime sites for bioaccumulation of heavy metals in all the fishes assessed in this study. The high concentration of heavy metals in the liver and gills observed in this study is in support of the work of Sehgal and Sexana (1986) on heavy metal toxicity in *Clarias gariepinus*. The liver and gill in fish are more often recommended as environmental indicator organs of water pollution than any other fish organs (Carpene and Vasak, 1989; Karadede *et al.*, 2004).

Though the liver may not be in direct contact with heavy metals in the water, high concentration of heavy metals in the liver may possibly reflect its major role in detoxification as well as storage (Kotze, 1999) and may also be due to the fact that the liver being a target and centre for metabolism may accumulate heavy metals. Furthermore the liver has the ability to concentrate heavy metals presumably due to the presence of metal binding proteins like metallothionein in the liver (Kargin and Cogun, 1999). Metallothionein is a binding protein which is believed to influence the uptake, distribution and toxicity of heavy metals by binding to them and reducing their toxicity (Wimmer *et al.*, 2005). The high concentrations and accumulation of heavy metals in liver may alter the levels of various biochemical parameters in liver. This may also cause severe liver damage in fish (Ferguson, 1989; Mayers and Hendricks, 1984). The concentration of heavy metals in the liver represents storage of heavy metals (Rao and Padmaja, 2000).

High concentration of heavy metals in the gills could be attributed to the fact that the gills serve as respiratory organs in fishes and are in direct contact with the contaminated medium (water) through which metal ions are absorbed. Also gills have the thinnest epithelium of all the tissues and metals can penetrate through the thin epithelia (Bebianno *et al.*, 2004). In addition, the concentration of heavy metals in the gills could be due to the element complexing with the mucus, which is impossible to remove completely from between the lamellae before tissue is prepared for analysis (Yilmaz, 2007). However it was observed in this study that there was a remarkably lower concentration of copper in the gill when compared to the liver of both fish species, this difference can be attributed to the lower binding affinity of copper on the gill surface (Chatterjee *et al.*, 2006) and is in conformity with the speculation of Reid and McDonald (1991) who proposed that copper had a greater likelihood of entering the fish tissues rather than binding on the gills as it was a lower binding affinity metal. The concentration of heavy metals in the gill reflects the concentration of heavy metals in the waters where the fishes live (Yilmaz, 2007).

The muscles, compared to the other tissues, usually show low concentrations of metals but are often examined for metal content due to their use for human consumption. The low level of heavy metals in the muscles reflects the low level of binding proteins in the muscles

(Allen-Gil and Martynov, 1995). The muscle is not an organ in which metals accumulate as results have been reported from a number of fish species showing that muscle is not an active tissue in accumulating heavy metals (Karadede and Unlo, 2000). These results are in agreement with the findings of the present study.

The skin is not a much studied tissue in previous works, although it is a consumed part of fish (Al-Weher, 2008). This study indicated that gills and liver accumulated more heavy metals than skin and muscle but the reverse was observed in the case of zinc concentration in *Tilapia guineensis,* where higher concentration was observed in the skin. This is in agreement with the work of Yielmaz (2003). This high concentration is not unconnected with the presence of scales on the skin of tilapia fish. Al-Weher (2008) recorded higher concentration of heavy metals in the bones and scales of *Oreochromis aureus,* a species of tilapia fish. The skin also plays a role in the excretion of heavy metals and adherence of heavy metals to the scales on the skin may have occurred.

5.4.2 Pattern of Heavy Metals Accumulation

From this study, concentration of heavy metals in the various tissues are in the order of Zinc >Copper >Lead >Chromium >Cadmium. The affinity of various metals for fish tissues may differ and be organ-specific, particularly accumulation of essential or bioactive metals such as iron, zinc, copper, manganese or cobalt which play important roles in metabolism, physiology and pathology of fish. Heavy metals like zinc, copper and manganese function as a cofactor in several enzyme systems while iron is involved with haemoglobin formation in fish blood (Bury *et al.*, 2003).

Accumulation of bioactive metals are actively controlled by the fish through different metabolic processes and the level of accumulation usually independent of ambient concentrations for example, even at low environmental concentrations, copper shows distinct affinity to the liver (Jezierska and Witeska, 2006)**,** this statement supports the result from this present study on the high accumulation of copper in the liver of both catfish and tilapia fish even when water concentration was low. According to Bordajandi *et al.*, (2003) the diet of the fish has a remarkable role in the bio-concentration process for some heavy metals (e.g. copper and zinc) which may have low concentration in the water but high concentration in the fish. However when in excessively high concentration these metals may pose serious threats to normal metabolic processes (Chatterjee *et al.*, 2006). On the other hand, environmental concentrations affect the accumulation of non-essential toxic elements like lead (Pattee and Pain, 2003).

In addition to zinc being a bioactive metal, the high concentrations of zinc in the fish parts as reported in this study could be associated with the fact that this metal is naturally abundant in Nigeria soils; soil being a major source of metal depositories in the aquatic system (Adefemi *et al.*, 2008; Kakulu and Osibanjo, 1988; Nwajei and Oruvwuje, 2001). This is in agreement with the result of Sadik (1990) which found zinc to be higher than other heavy metals in their fish samples. Coetzee *et al.*, (2002) reported that both the liver and gills of *Clarias gariepinus* had high affinity to accumulate zinc. This is in agreement with results from this study which showed values of 233.42 and 137.03 mg/L as the mean zinc concentrations in the liver and gills of *Clarias gariepinus* as compared to 99.72 and 66.60 mg/L mean concentrations in the skin and muscle. Zinc toxicity is rare but at high concentrations could induce toxicity characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite and nausea (NAS-NRC, 1974). Incidentally zinc happens to have a protective effect against the toxicities of both lead and cadmium (Calabrese *et al.*, 1985; Sanstead, 1976).

Copper, though essential in human diet can be harmful when large intake occurs. At excessive levels, copper can cause anaemia, disorders of bone and connective tissues and liver damage (Al-weher, 2008). The harmful toxicity is largely attributed to its cupric (Cu^{2+}) form, which is the most commonly found specie in the environment (Olaifa *et al.*, 2004). Although there is no clear evidence about Copper dietary transfer (Eisler, 1988), many studies have demonstrated that diet is the most important route of copper accumulation in aquatic animals and this explains the high concentrations of copper in the liver than other tissues in both fish species in this study. Ingested food must pass through the liver where it is being metabolized and detoxified leaving behind copper residues.

Worthy of note is the fact that Copper and Zinc as essential heavy metals are usually found in sewage; therefore their high concentration in fishes from Agodi Lake may be due to influx of effluent discharged from UCH sewage treatment plant into the lake. It should be noted that Lead (Pb) accumulated in the fish tissues at levels above standard limits and since most human exposure to Pb is from food, these fishes pose a threat to consumers. As it is known, Lead is toxic and may damage the brain, the central nervous system, kidney, liver and the reproductive system when it exceeds the tolerable limit in humans (Ademoroti, 1996a).

The low level of Cadmium reported in this study is within the range reported in other studies that evaluated metal contamination of fishes. In another similar study, Kalay *et al.,* (1999) reported Cadmium level of 1.98 mg/Kg in the liver of *Mullus barbatus* from the coastal region of Mediterranean sea. Lower concentration of Cadmium compared to other heavy metals has been reported in previous studies (Olaifa *et al.*, 2004) and maybe due to low tendency of cadmium species towards the available active sites (N and/or O donor atoms) in the tissues to form tetrahedral Cd (11) complex species (Kappus, 1987).

The difference in mean concentrations of Zinc and Copper amongst the tissues of catfish was statistically significant ($p<0.05$). It was also observed that there was significant difference in the mean concentrations of Chromium and Copper amongst the tissues of Tilapia fish ($p<0.05$).

5.4.3 Difference in Heavy Metals Accumulation Between Fish Species

Dietary habits may have an impact on heavy metals concentrations in different species (Papagiannis *et al.*, 2004). Differences in heavy metals bioaccumulation between the two fish species could be ascribed to differences in feeding habits and ecological behaviour. *Tilapia guineensis* feeds primarily on plant materials and detritus (Fagade, 1971). Juveniles take many small crustaceans but mainly feed on algae especially unicellular diatoms while adults feed on filamentous green algae; ingest aquatic insects, crusteceans, earth worms, small fish as well as bottom sludge rich in organic matter. *Clarias gariepinus* on the other hand, is an omnivorous scavenger and predator of other fish and is mainly associated with the bottom especially when muddy. Large amounts of silt are also taken in with the food (Kotze, 1999). Silt particles play an important role in the transport and availability of metals as they are adsorbed onto the silt particles (Ward *et al.*, 1986).

Apart from diet, pollution exposure and behaviour can influence accumulation of metals (Henry *et al.*, 2004). Also, the age, size and length of the fish (Linde *et al.*, 1998) and their habitats (Canli and Atli, 2003) influence heavy metals levels among different fish species. Heavy metals tend to be biomagnified with increase in trophic level in a variety of aquatic food webs and lake types (Chen *et al.*, 2000). This bio-magnification that occurs between trophic levels might be the explanation for the difference in mean heavy metal concentrations in tilapia and catfish. According to Philips (1990) carnivorous species are prone to have higher metal concentrations than herbivorous, omnivorous or planktivorous species. This general pattern can change as that seems to be the case in this present study for Zinc concentration in both fish species where Zinc concentrated more in the tissues of *Tilapia guineensis* a herbivore than in the tissues of *Clarias gariepinus* an omnivore. Similarly, in a study conducted on lake Pamvotis by Papagiannis *et al.*, (2004), fish feeding mostly on invertebrates such as *R. ylikiensis*, display higher concentrations of zinc than omnivores like *C. carpio* and piscivores like *S. aristotelis*.

From these findings, it seems that Zinc concentration is inversely related to fish status or trophic level and this is in agreement with the findings of Amundsen *et al.*, (1997) regarding trophic status and heavy metal contamination in different freshwater fish species. However, according to Eisler (1988) little or no biomagnifications of Copper is evident in freshwater food chains.

It remains very difficult to compare heavy metal concentrations even between the same tissues of different species because of the different feeding habits and other differences in the aquatic environments concerning the type and the level of water pollution (Papagiannis *et al.*, 2004). Result from comparisons of heavy metals concentrations in catfish and tilapia fish using t-test shows that; there was no statistically significant difference in the concentrations of Copper and Zinc between catfish and tilapia fish using tissues. Although, there was not much difference in mean concentrations of Cadmium and Chromium in tissues of catfish and tilapia fish, these difference were statistically significant ($p<0.05$). The difference in the mean concentration of Lead in catfish and tilapia fish was not statistically significant in all the tissues except in the gills ($p<0.05$).

5.5 Correlation Relationships.

Correlation between concentration of heavy metals and pH level in Agodi was weak and not statistically significant. The possible reason for this is likely the near neutral nature of Agodi lake corresponding to a value of 7.20. According to DWAF (1996), heavy metal dissolution and availability is high in acidic medium and low in alkaline medium. It can therefore be deducted, that neutral pH has little or no effect on the concentration of heavy metals.

Correlation between heavy metals concentration in water and heavy metals concentration in the fish liver was weak and equally not statistically significant. The fish liver was chosen because of its strategic function as a storage organ and as such reflects storage or accumulation of heavy metals in the fish. This insignificant correlation between concentration in water and in fish supports the fact that bio-accumulation of heavy metals was more from other sources like fish diets than from surrounding water.

Correlation between the concentration of Zinc and the concentration of Copper in the liver of catfish was positive and statistically significant ($p<0.05$) while in tilapia it was not statistically significant. Zinc toxicity is synergistic with copper explaining the positive correlation between zinc and copper. Additive (synergistic) effects have also been found with copper and cadmium (DWAF, 1996). There was a negative correlation between zinc and lead concentration in the liver of tilapia fish although this was not statistically significant. The sort of correlation observed in this study is in conformity with the results obtained by Marcovecchio, 2004 where it was found that hepatic cadmium concentration increased simultaneously with that of hepatic zinc and it was proposed also that increase in zinc concentration is a compensation for the increase in cadmium compensation due to pollution processes. According to Svobodova (1993) Cadmium is usually associated with zinc in surface waters, but at much lower concentrations.

Worthy of note here is the fact that at the time of this study only very limited information concerning correlation relationship among heavy metals in fish tissues was available in the literature.

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