

**Human Health Risk Assessment of Potentially Toxic Elements (PTEs) in Water,  
Sediments and Tilapia Fish (*Oreochromis niloticus*) of Ogun River**

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**Being a MSc Thesis Presented to the Department of Chemical Sciences, Faculty  
of Natural and Applied Sciences, Lead City University, Ibadan, Oyo State,  
Nigeria**

**In Partial Fulfillment of the Requirements for the Award of Master's of Science  
Degree (MSc) in Environmental and Analytical Chemistry**

**2023**

## Certification

This is to certify that Oluwayemisi Idayat, AKINDELE with matriculation number LCU/PG/001348 carried out this research work titled “Health Risk Assessment of Potentially Toxic Elements (PTEs) in Water, Sediments and Tilapia Fish (*Oreochromis niloticus*) of Ogun River” in the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Oyo State, for the award of Master Degree in Environmental and Analytical Chemistry and that this has not been previously submitted.

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## **Dedication**

This research is dedicated to Almighty God for his grace and mercy that see me through this programme.

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## Acknowledgement

I would like to acknowledge following institutions; Lead City University, Ibadan, Oyo State, Moshood Abiola Polytechnic, Abeokuta, Ogun State and Institute of Agriculture and Research Moore plantation, Ibadan, Oyo State, for opportunity to make use of their laboratories and libraries.

I appreciate my amiable Supervisor, Dr. O.O John-Dewole, H.O.D Professor O.M Ighodaro, and my lecturers Professor A.K. Akinlabi, Dr. O.O Ogunlaja, Dr. A.O. Bamisaye, Dr. O. Oderinde, Mrs. S.O. Oni, Mr. O. Bamidele, Mrs. M. Akinleye and Miss O. Akintobi.

My colleagues, Mr. O. Olalekan and Mr. A. Olatise, I am very grateful.

I appreciate my lovely husband, Mr. S.A Akindele and my children: Samuel, Mary and Lydia for their understanding, love and support throughout this programme.

Though, the above institutions and persons have assisted in the process of this research work, I alone stand responsible for any error(s) that may be found in the research work.

## Abstract

Potentially Toxic Elements (PTEs) are ubiquitous especially in water bodies and they have tendencies to bio-accumulate and hamper human body metabolic and endocrinal processes. This study aimed to assess the levels of PTEs in water, sediments and tissues of Tilapia Fish (*Oreochromis niloticus*) samples of Ogun River and its human health risk assessment. Water, sediments and fish samples were collected seasonally to assess 8 selected PTEs (Cu, Zn, Ni, Pb, Mn, Fe, Cr and Cd) using Atomic Absorption Spectrophotometer, while the physic-chemical parameters were determined using standard methods. Highest water pH value of 7.86 was recorded during dry season while the lowest of 6.10 was for the wet season. Temperature ranged from  $26.59 \pm 0.17$  °C to  $27.27 \pm 0.72$  °C and  $26.47 \pm 1.05$  °C to  $26.77 \pm 1.10$  °C for dry and wet seasons respectively. The Electrical Conductivity (EC) ranged from  $13.84 \pm 4.38$   $\mu$ S/cm to  $36.67 \pm 29.51$   $\mu$ S/cm and  $13.84 \pm 4.67$   $\mu$ S/cm to  $47.21 \pm 32.86$   $\mu$ S/cm for dry and wet seasons respectively. Total dissolved solids (TDS) showed slight positive relationship with the electrical conductivity. The mean TDS ranged from  $53.50 \pm 10.21$  mg/L to  $57.25 \pm 9.74$  mg/L and  $23.00 \pm 4.62$  mg/L to  $40.00 \pm 2.58$  mg/L for wet and dry seasons respectively. Water, sediment and fish tissues samples were analyzed for Cd, Cr, Pb, Zn, Ni, Mn, Fe and Cu contaminations. Concentrations were compared with NIS, FEPA and WHO. However, Fe levels were highest in both surface water, sediment, and fish samples while Cu level was least in both sample locations. Cd, Cr, Ni, Fe, Mn and Pb exceeded the NIS, FEPA and WHO. Pb was the largest contributor to non-carcinogenic risks. Risk from the other PTEs followed the order Cd > Mn > Fe > Ni > Cu > Cr > Zn for children and Fe > Cd > Mn > Ni > Cr > Cu > Zn for adults. Hence, Ogun River is found to have an appreciable level of metal toxicity especially at lafenwa and alagada points.

**Keywords:** Metal Bioaccumulation, PTEs, Ogun River, Tilapia, Toxicity.

**Word Count:** 340

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## List of Acronyms

<b>Abbreviation</b>	<b>Meaning</b>
<b>AAS</b>	Atomic Absorption Spectrophotometry
<b>ADI</b>	Average Daily Intake
<b>BOD</b>	Biological Oxygen Demand
<b>COD</b>	Chemical Oxygen Demand
<b>CR</b>	Carcinogenic Rate
<b>DO</b>	Dissolved Oxygen
<b>EC</b>	Electrical Conductivity
<b>FEPA</b>	Federal Environmental Protection Agency
<b>GPS</b>	Global Positioning System
<b>HI</b>	Hazard index
<b>HQ</b>	Hazard quotient
<b>MDL</b>	Medical Diagnostic Laboratory
<b>NIS</b>	Nigerian Industrial Standard
<b>Ppm</b>	Part per million
<b>PTEs</b>	Potentially Toxic Elements
<b>SD</b>	Standard Definition
<b>SE</b>	Standard Error
<b>TDS</b>	Total Dissolved Solids
<b>TOC</b>	Total Organic Carbon
<b>USEPA</b>	United State Environmental Protection Agency
<b>WHO</b>	World Health Organization

## Chapter One

### Introduction

#### 1.1 Background to the Study

Water is vital to the existence of all living organisms, but this valued resource is increasingly being threatened as human population grows and developmental activities increase. Yet, the demand for water of good quality for various domestic and economic activities keeps increasing. Water constitutes 70 % of the total earth surface, 97.5 % of this is saltwater and the remaining 2.5 % is the freshwater. 70 % is frozen in the polar ice caps while other 30 % is mostly present as soil moisture or trapped in underground aquifers<sup>1</sup>. Consequently, less than 1 % of the world's freshwater (about 0.007 % of all water on earth) is readily accessible for direct human general use<sup>2</sup>. In developing countries, where potable water supply is not adequate, most of the inhabitants rely solely on surface water from rivers and streams. About 48 % Nigerians depend on surface water for most domestic uses and only 14 % population have access to pipe-borne water. Unfortunately, most of the water users are not aware of the enormity of the risk attached to unhygienic water use<sup>3</sup>.

Although, water plays an essential role in supporting human life and biodiversity, it also has a great potential for transmitting diseases when contaminated<sup>4</sup>. Population growth in conjunction with other factors such as urbanization, agricultural activities, industrial and commercial processes have resulted in the accumulation of wastes and pollutants which ultimately end up in water bodies, thereby altering the water quality<sup>5</sup>. Many rivers or streams particularly in developing countries are heavily polluted due to industrial and municipal wastewater discharges, as well as agricultural runoffs<sup>6</sup>. Adversely, anthropogenic activities are major factors determining the quality of surface and ground

water through atmospheric pollution, effluent discharges, use of agricultural chemicals, eroded soils and land use<sup>7</sup>.

Surface water is the water mass that fails to penetrate into the soil, subsoil or flows along surface of the ground and eventually enters the lakes, rivers or oceans. The quality of surface water within a region is dictated by some natural processes (such as precipitation rate, weathering processes and soil erosion, hydrological processes; physical, chemical and biological processes)<sup>8</sup>. Anthropogenic acts such as urban, industrial, agricultural activities and the human exploitations of water resources are another set of factors that determines surface water quality<sup>9</sup>. Rivers, pools and springs are the most common source of surface water resource for man use, both industrially and domestically. Unfortunately, river waters are being polluted by indiscriminate disposal of sewage, industrial wastes and other plethora of human activities, which affects water's physicochemical characteristics and microbiological qualities<sup>10</sup>.

Naturally, water is not pure as it acquires contaminants from its surrounding and those arising from humans, animals as well as other biological entreats<sup>11</sup>. Water pollution is defined to be the presence of excessive amounts of hazardous foreign deposits (pollutants) in water in such a way that it is no long suitable for drinking, bathing, cooking or other uses<sup>12</sup>. The pollution can either be of point source or non-point source. Point source pollution occurs when pollutants are discharged directly into the water body from industrial sewage or municipal wastewater pipes. A non-point source delivers pollutants indirectly to the water body through environmental changes such as pollution from urban run-offs<sup>13</sup>.

In Nigeria, many rivers and streams are heavily polluted with high concentrations of some PTEs of variable and unsuitable physicochemical characteristics<sup>14</sup>. These PTEs have particular significance in eco-toxicology, since they are highly persistent and all have the

potential to be toxic to living organisms<sup>15</sup>. PTEs are non-biodegradable metallic chemical elements which have relatively high densities, have toxic tendencies at low concentrations, and tend to accumulate in the sediments of water bodies in association with organic and inorganic matters found in the sediments<sup>16</sup>. PTEs of significant importance include; mercury (Hg), arsenic (As), lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), chromium (Cr), antimony (Sb), nickel (Ni) and iron (Fe). The presence of these metals, especially lead and cadmium, in the environment have been a source of worry to environmentalists, government agencies and health practitioners as a result of their hazardous health implications to man<sup>17</sup>. The presence of these metals has far reaching consequences on man and their effects include; dermal, lung and nasal cancers<sup>18</sup>. PTEs are commonly found in natural waters and some are essential to living organisms, yet they may become highly toxic when present in high concentrations. Among environmental pollutants, metals are of particular concern; due to their potential toxic effects and ability to bio-accumulate in aquatic ecosystems<sup>19</sup>. As PTEs cannot be biodegraded, they are deposited, assimilated or incorporated in water, sediment and aquatic animals<sup>20</sup>. Thus, causing PTEs pollution in water bodies. As a result of that, PTEs can be bio-accumulated and biomagnified via the food chain and finally assimilated by human consumers resulting in health risks<sup>21</sup>.

Fish is an important food resource for humans, especially as source of animal protein, commercial or subsistence farming<sup>22</sup>. In Nigeria, fish are well eaten in most homes as fresh, cooked, fried or smoked and form a much cherished delicacy that cut across socio-economic classes<sup>23</sup>. Unfortunately, the ability of aquatic environment to sustain this important resource has come under threat, as a result of increasing pollution of surface water and sediment contamination. In this regards, the accumulation of PTEs in water and bioaccumulation in aquatic organisms have become a global concern<sup>24</sup>. In most

developing countries, it is a common practice to dispose PTEs laden effluents into the aquatic environment<sup>23</sup>. PTEs are regarded as serious pollutants of the aquatic ecosystems because of their toxicity even at low concentrations<sup>25</sup>. These metals are ploughed back into the food chains through bioaccumulation in plankton and invertebrates to fishes and finally biomagnified in man<sup>26</sup>.

Thus, fish not only indicates the pollution status of aquatic ecosystem but have significant impact on the food web<sup>27</sup>. Accumulation of metals in various organs and tissues of fish depends on the manner of exposure such as through diet or their elevated level in surrounding environment<sup>28</sup>. Also, PTEs exhibit different accumulation pattern in fish organs<sup>29</sup>. Gills, liver and kidneys accumulate PTEs in higher concentrations in comparison to muscles, which exhibit lowest levels of metals accumulation<sup>30</sup>. Among different organs, liver accumulates higher concentrations of metals and has been used widely to investigate the process of bioaccumulation<sup>31</sup>.

Concentration of metals becomes toxic to the fish when its level exceeds the permissible one<sup>32</sup>. This threshold limit not only varies from metal to metal but also from one fish species to another<sup>33</sup>. The toxic effects become more pronounced when various metabolic activities inside the organism fail to detoxify metals bioaccumulated<sup>34</sup>. Exposure to PTEs could ultimately lead to health risks associated with the consumption of contaminated fish by man. Adverse effects of PTEs may include serious threats like renal failure, liver damage, cardiovascular diseases and even death<sup>35</sup>.

Nile Tilapia is one of the most important fish species that is widely cultured in Nigeria to meet the increased protein demand and for its profitability. This fish species are native to Africa but also have become one of the most widely farmed fish across the world with an increasing production output<sup>36</sup>. Nile tilapia inhabits fresh and brackish water of Africa, Middle East, Coastal India, Central and South America. The Nile tilapia prefers shallow,

still waters on the edge of lakes and wide rivers with sufficient vegetation<sup>37</sup>. Given their importance in the world aquaculture markets, they are being extensively studied among the researchers. In Nigeria, considerable number of studies have focused on the toxicity and bioaccumulation of PTEs in tilapia and other fish species<sup>38</sup>.

As an important component in riverine ecosystems, sediment serves as both a sink and a source of PTEs<sup>39</sup>. Most PTEs quickly deposit into the sediment after entering rivers, and are much more concentrated in the sediment than in the water body of riverine systems<sup>40</sup>. Conversely, when the physicochemical or hydrological conditions change, PTEs in the sediment may desorb to cause secondary pollution in the water body<sup>41</sup>. The accumulation of PTEs in the sediment directly affects benthic organisms and also influences many other organisms through the food web and endangers the wellbeing of the aquatic ecosystem<sup>42</sup>.

## **1.2 Statement of the Problem**

In South western part of Nigeria, River Ogun and most other rivers are used for municipal water supply, domestic uses, agriculture, hydropower and transportation purposes. Thus, the river is usually prone to environmental pollution. This is due to the ignorance of control measures to be installed to guide against indiscriminate waste disposals<sup>43</sup>. Fish from the river, being used as food product, is prone to accumulation of PTEs and could in turn cause serious health issues. One of the challenge is that the stakeholders of the river basin lacks adequate knowledge of what sorts of wastes are being discharged; its quality and the control measures to guide against further pollution of the river. Thus, its implication poses threat to the health of the river users and the environment.

### 1.3 Justification of the Study

Rivers have become the main point of much activities and primary candidate as a sink for waste from all kinds of human activities<sup>44</sup>. A wide range of contaminants are continuously introduced into the aquatic environment mainly due to increased industrialization, technological development, growing human population and exploitation of natural resources, agricultural and domestic wastes run-off<sup>41</sup>.

Among these contaminants, PTEs constitute one of the most dangerous groups because of their persistent nature, tendency to accumulate in organisms and undergo food chain amplification and more still, they are non-degradable<sup>41</sup>. Acute PTEs intoxications may damage central nervous function, the cardiovascular and gastro intestinal (GI) systems, lungs, kidneys, liver, endocrine glands and bones<sup>42</sup>.

The scarcity of clean water and pollution of fresh water has led to a situation in which one-fifth of urban dwellers in developing countries and three quarters of their rural dwelling population do not have access to reasonably safe water supplies<sup>45</sup>. Fishery products constitute an important aspect of human food due to the high level of protein and essential amino acids for the proper growth and development of the body<sup>46</sup>.

Production of wholesome aquatic foods demands adequate management of the aquatic environment through effective screening for toxicants for corrective actions. Thus, there is a need for control measures to be put in place. This control measures cannot be put in place without having a scientific assessment of the water quality itself, the advantages of the activities carried out on the river and future usefulness of the river water. Therefore, this study was designed to determine the toxicity of the pollutants discharged at the sampling areas and their bioaccumulation in tissue of tilapia fish.

#### **1.4 Aim and Objectives of the Study**

The aim of the study is to assess human health Risk of PTEs in water, sediments, and tissues of tilapia fish (*Oreochromis niloticus*) samples of Ogun River

The specific objectives of the study include to:

- i. assess the physiochemical properties of the water samples
- ii. assess the concentrations of Cr, Cu, Pb, Mn, Fe, Zn, Cd and Ni of Ogun River water and sediments in the selected sampling areas.
- iii. evaluate the bioaccumulation potential of Cr, Cu, Pb, Mn, Fe, Zn, Cd and Ni in selected tissue of fishes from the river to determine the human health risk.
- iv. to assess human health risk of PTEs to children and adult

#### **1.5 Significance of the Study**

The increasing rate of urbanization and human activities in Ogun State has led to continuous pollution of the Ogun River. The aquatic habitat being the ultimate receiver and reservoirs of these pollutants, also serve as the hub for aquatic animals which are rich protein sources for human nutrition. There is relative heavy fishing activities at Alagada and Lafenwa points of the Ogun River and are also being suspected as potential contamination and (or) pollution sources due to various anthropogenic activities at those two locations. This study is therefore to evaluate the potential contamination contribution of the two points to the Ogun River.

#### **1.6 Scope of the Study**

The study on River Ogun consisted of field survey, sampling exercise for (water, sediments and fish) laboratory analysis, interpretation of data gotten using statistical approach. Samples collected were analyzed for PTEs (Lead, Zinc, Iron, Copper, Cadmium, Chromium, Nickel, Manganese) and physicochemical parameters

(Temperature, pH, Total dissolved solids, Electrical conductivity). Eight samples were taken at the shallowest point along the course of the river (dry season and wet season) to reflect the present condition of the river after pollution and a total sixteen fishes were collected. Also, human health risk assessment was evaluated to know its impact.

### **1.7 Limitation of the Study**

The research was limited to Lanfenwa and Alagada sections of Ogun River in Abeokuta, Ogun State. Alagada and Lanfenwa sections of Ogun River is a difficult terrain to source for fish especially during the raining season. Fishermen and fishing tools were outsourced in order to get sizeable amount of desired fish sample for the analysis.

### **1.8 Definition of Operational Terms**

**Aquatic Ecosystem**- is an ecosystem formed by surrounding a body of water, in contrast to land-based terrestrial ecosystems. Aquatic ecosystems contain communities of aquatic lives that are dependent on one another and on their environment.

**Bioaccumulation** – refers to how pollutants (metals) enter a food chain and relates to the accumulation of contaminants, in biological tissues by aquatic organism.

**Ecotoxicity** - refers to the biological, chemical or physical stressors that affect ecosystems.

**Environmental Management**- deals with the regulation process and protection of the health of our planet, by promoting human behaviours that make a positive impact on the natural environment.

**Environmental Pollution** – the contamination of the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected.

**Health Risk**- the chance or likelihood that something will harm or otherwise affect your

health.

**Physicochemical Parameter**- refers to things that involve the principles of both physics and chemistry, meaning that they are dependent on, or produced by, the combined actions of physical and chemical attributes

**PTEs**- elements which can be present in substance (food, water, air) in amounts that can be potentially hazardous to human health such as cadmium, arsenic, nickel, chromium, lead, and mercury.

**Toxicity** - the quality of being very harmful or unpleasant in a pervasive or insidious way

**Toxic Metals** - A toxic metal is any metallic element that can potentially pose a risk to either the environment or human health.

**Risk Assessment**- a systematic process of evaluating the potential risks that may be involved in a projected activity or undertaking.

**Sediment**- matter that settles to the bottom of a liquid; dregs.

**WHO Limits**- Target values are specified to indicate desirable maximum levels of elements in unpolluted substance such water, soils, air etc.

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## Chapter Two

### Literature Review

#### 2.1 Aquatic Ecosystems

Aquatic ecosystems such as rivers, dams and lakes provide livelihood for rural populations in many developing countries in Africa. However, in the recent past, they have been subjected to various forms of degradation due to pollution arising from domestic wastes, industrial effluents, agricultural run offs and bad fishing practices. Industrialization and human activities have partially or totally turned the environment into dumping sites for waste materials. As a result, many water resources have been rendered polluted and hazardous to man and other living systems<sup>1,2</sup>.

Stable metals or metalloids whose densities are greater than  $4.5 \text{ gcm}^{-3}$  are termed as heavy metals and these include; lead, cadmium, mercury, iron, copper, zinc, nickel and manganese. Metals are an integral component of the environment and living matter. Some of them are essential elements without which the biochemical processes in living organisms would collapse but when they exceed the normal concentrations, they could become detrimental to the organisms<sup>1</sup>. Heavy metal contamination particularly the non-essential elements may have distressing effects on the ecological balance of the recipient aquatic environment with a diversity of organisms. This has particular significance in ecotoxicology, since the heavy metals are highly persistent and have the potential to bio-accumulate and bio-magnify in food chain, and become toxic to living organisms at higher trophic levels in nature<sup>2</sup>.

Heavy metal contaminations in inland waters can be monitored by using the metal levels in water; sediments and resident biota especially fish. Heavy metals tend to accumulate in soils and sediments after weathering processes and can be deposited in water bodies due to surface run-offs. Once the heavy metals get discharged into the aquatic environment,

they scatter in various components such as water, suspended solids, sediments and biota. Contamination by these heavy metals can be expressed by their high concentrations in water, as well as in sediments and aquatic organisms<sup>2</sup>. Cadmium, copper, lead and zinc salts are usually found in agricultural and industrial liquid wastes which are discharged into water resources. The metals, most times, accumulate from diluted concentrations in water to higher levels in fish tissues. The concentration of metals in water correlates positively with concentrations in fish tissues<sup>2,3</sup>.

Water is one of the vital and most precious resources that exist on our planet earth without which life cannot flourish<sup>1</sup>. Its nature and properties have interested the philosophers, naturalists and scientists since ancient times<sup>2</sup>. Water continues to engage the attention of scientists today as it remains incompletely understandable, in spite of intense study over many years. This is primarily because water behaves abnormally in many of its physical and chemical properties. Some of water's unique properties are literally essential for life<sup>3</sup>, while others have profound effect on the size and shape of living organisms, how they work, and the physical limits or constraints within which they must operate<sup>3,4</sup>.

## **2.2 Water as a Unique Natural Resource**

Water is the only naturally occurring substance on earth that can be found in three physical states; solid, liquid, and gas. In its solid form (ice), it is less dense than when it is in its liquid form. Water is almost the only substance in the universe for which the solid floats in the liquid. Water is unusual in several other ways as well<sup>2</sup>. The heat capacity of water is higher than just about any other substance. The heat capacity of a substance is the amount of heat you need to add to a mass of material to raise its temperature by a given amount<sup>4</sup>. The heat capacity of water is more than twice the heat capacity of natural

mineral and rock material. This tends to even out temperature differences in earth, from day to night and from summer to winter. Water is also the best all-around solvent. More solid substances dissolve in water than in any other liquid.

### **2.2.1 Basic Physical Properties of Water**

Water is an inorganic polar substance with unique physiochemical properties that makes it discrete from other molecules of comparable molecular mass. Water is highly cohesive because of the strong intermolecular interactions (hydrogen bonds, or H-bonds) between the oxygen and hydrogen atoms<sup>12</sup>. Water also has the remarkable properties of expanding when it is cooled from 4 °C to its freezing point<sup>14</sup>.

Water with the valence angle of 104.5° is characterized by the tetrahedral structure of water molecules. The polar nature of water accounts for its high solvating ability, high surface tension, viscosity, heat of vaporization and for a number of other properties, all of which can be attributed to the extensive intermolecular hydrogen bonding network<sup>12</sup>.

### **2.3 Surface Water**

At least 27 % Nigerians depended absolutely on streams, pond, river and rainwater for their drinking water source<sup>16</sup>. Surface water is defined as one that fails to penetrate into the soil, subsoil or flows along surface of the ground and eventually enters the lakes, rivers or oceans<sup>17</sup>. The natural quality of rivers and streams at any point reflects the quality of upstream contributions of surface run-off and groundwater discharge. The various water bodies in the country are used for various purposes such as fishing, transportation, sand mining, irrigation, recreation, abstraction for industrial and domestic purposes as well as electric generation.

Research has shown high prevalence of waterborne diseases such as cholera, diarrhoea, dysentery, hepatitis and so on among Nigerians<sup>18</sup>. The necessity for water quality monitoring is vital to safeguard the public health and also to protect the water resource in Nigeria.

### **2.3.1 Distinction and Similarities between Surface Water and Groundwater Bodies**

All water body interactions are interrelated. Water in lakes, wetlands, and streams recharges groundwater reservoirs while groundwater discharges back into lakes, wetlands, and streams, providing base-flow maintenance. Groundwater contributes to most streams, thereby maintaining stream flow during periods of low flow or drought. Development of surface water resources can affect ground water resources and vice versa. Large withdrawals of groundwater can reduce the amount of groundwater inflow to surface water and significantly reduce the supplies of surface water available to downstream users<sup>19</sup>.

Although groundwater and surface water are closely related and in many areas comprise a single resource, two principal features of groundwater bodies distinguish them from surface water bodies. Firstly, the relatively slow movement of water through the ground means that residence times in groundwaters are generally longer than in surface waters. Hence once polluted, a groundwater body could remain so for decades, or even for hundreds of years, because the natural processes of through-flushing are so slow<sup>10</sup>. There is also a considerable degree of physical and chemical interdependence between the water and the containing material.

The word groundwater is generally understood to mean all the water underground, occupying the voids within geological formations. It follows, therefore, that in dealing with groundwater, the properties of both the ground and the water are important, and

there is considerable scope for water quality to be modified by interaction between the two<sup>20</sup>.

#### **2.4 Surface Water Pollution**

Water pollution, which is mostly by effluent, has become a question of considerable public and scientific concern in the light of evidence of their extreme toxicity to human health and to biological ecosystems<sup>21</sup>. Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and does not support human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish<sup>11</sup>. Water pollution occurs when energy and other materials are released; degrading the quality of the water for other users and these include all of the waste materials that cannot be naturally broken down by water<sup>22</sup>. In other words, anything that is added to the water, above and beyond its capacity to break it down is pollution. Pollution, in certain circumstances, can be caused by nature itself, such as when water flows through soils with high acidities<sup>23</sup>.

Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water. Most water pollutants are eventually carried by rivers into the oceans. The water we drink contains essential ingredients for our well-being and a healthy life<sup>14</sup>.

The WHO stated that one sixth of the world's population; approximately 1.1 billion people do not have access to safe water and 2.4 billion lack basic sanitation<sup>15</sup>. Polluted water consists of industrial discharged effluents, sewage water, and rainwater pollution and polluted by agriculture or households wastes, which causes damage to human health or the environment<sup>16</sup>. This water pollution affects the health and quality of soils and vegetation<sup>17</sup>. Some water pollution effects are ascertained immediately, whereas others

are observed up for months or years<sup>18</sup>. Estimation from several studies indicates that more than fifty countries of the world with an area of twenty million hectares are treated with polluted or partially treated polluted water including parts of all continents<sup>19</sup>. Poor water quality causes health hazard and death of human being, aquatic life and distorts the production of different agricultural crops<sup>22</sup>. In fact, the effects of water pollution are said to be the leading cause of death for humans across the globe, moreover, pollutants affects our oceans, lakes, rivers, and drinking water, making it a widespread and global concern<sup>21</sup>. These facts have over the years called for a red alert on the degrading state of many water bodies that mainly meets the needs of humans by many organizations globally.

But more often than not, human activities are responsible for the pollutants that enter the water. The pollution can either be of point source or non-point source. Point sources of pollution occur when pollutants are emitted directly into the water body e.g. from industrial sewage or municipal waste water-pipes. A non-point source delivers pollutants indirectly through environmental changes such as pollution from urban run-offs<sup>24</sup>.

In most urban-rural communities in the developing countries especially the Sub-Saharan Africa, surface waters (rivers, streams, and lakes among others) have been the most available sources of water used for domestic purposes. The water from these sources is contaminated with domestic, agricultural, and industrial wastes and likely to cause water related diseases<sup>25</sup>. A philosophical saying that “the solution of pollution is dilution”, but unfortunately, the growth of cities has given rise to such large volume of wastes that dilution alone no longer assures the natural processes of self-purification.

## **2.5 Sources of PTEs in Surface Water**

### **2.5.1 Electronic Waste**

Electronic goods manufacturing companies must be legally ensured to mention the disposal methods of their products in their user manuals. As electrical electronics

equipment-wastes are the known major source of PTEs, hazardous chemicals and carcinogens, certainly diseases related to skin, respiratory, intestinal, immune, and endocrine and nervous systems including cancers can be prevented by proper management and disposal of electrical electronics equipment wastes. With a view to bridge the digital divide, there is exponential growth in the use of electrical and electronic equipment (EEE) and so there is alarming effect on environment and human health when the ICT wastes are not disposed of scientifically and hygienically<sup>23</sup>.

It produces large volumes of metal-rich effluents, will naturally be a more likely polluter than the food processing industry, for example, this is not to say that players in this industry will necessarily pollute, and it is in fact in the electroplating industry's best economic interests to minimize metal discharges, since these are inversely proportional to resource efficiency. Reducing losses by minimizing drag-out from plating baths leads to reduced metal discharges. The lead-acid battery manufacturing industry is another example of an industry which can generate metal-rich effluents as well as airborne lead pollution which can subsequently be deposited in surface water resources (and of course on land). So clearly, where an industry uses PTEs as key input materials, pollution risks is always at an increase<sup>24</sup>.

### **2.5.2 Power Generation Plants**

A large non-point source of PTEs pollution is coal-fired power generation, which can contaminate water resources through aerial deposition of mercury emitted from boiler flues. The industry also generates large amounts of ash which itself contains PTEs, including uranium<sup>27</sup>. Pollutants such as Hg, Pb, As, Se, Cd and Cr leach into ground water from unlined coal ash storage ponds or landfills pollute water, possibly for decades or centuries. Mercury emissions from coal-fired power plants can fall back on to land and water in rain, and then be converted into methylmercury by bacteria. Through

biomagnification, this mercury can then reach dangerously high levels in fish. More than half atmospheric mercury comes from coal-fired power plants<sup>27</sup>.

### **2.5.3 Cadmium-Generating Industries**

Cadmium is produced as an inevitable by-product of zinc (or occasionally lead) refining, since these metals occur naturally within the raw ore. However, once collected the cadmium is relatively easy to recycle. The most significant use of cadmium is in nickel/cadmium batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance, particularly in high stress environments such as marine and aerospace applications where high safety or reliability is required; the coating is preferentially corroded if damaged. Other uses of cadmium are as pigments, stabilizers for PVC, in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products<sup>28</sup>.

### **2.5.4 Biological Practices**

The degassing of the earth's crust, emissions from volcanoes and evaporation from natural bodies of water is the major natural source of mercury. World-wide mining of the metal leads to indirect discharges into the atmosphere. The usage of mercury is widespread in industrial processes and in various products (e.g. batteries, lamps and thermometers). It is also widely used in dentistry as an amalgam for fillings and by the pharmaceutical industry<sup>29</sup>.

### **2.5.5 Industrial Sources**

Studies carried out in most cities in Nigeria had shown that industrial effluent is one of the main sources of surface water pollution in Nigeria<sup>30</sup>. Industrial effluents when

discharged directly into the rivers without prior treatment have capacity of impeding water quality parameters.

These discharges usually contain specific pollutants, which are related to the nature of products handled in the industry and the production processes being employed<sup>31</sup>. Such pollutants may originate from metallurgical, paper and pulp, cloth and cellulose fibres, food, tannery wastes, detergents, petrochemicals, discharge from hospitals, power generation plants. Researches also indicated that less than 10 % of industries in Nigeria treat their effluents before being discharged into the rivers<sup>31</sup>. The impacts these could pose include water quality deterioration, reduction in fish abundance and effect on water-usage for recreation, industrial and domestic purposes.

#### **2.5.6 Municipal Wastes**

Waste management is a major problem in most developing nations of the world including Nigeria<sup>32</sup>. Indiscriminate disposal of municipal wastes remains a major threat to surface water pollution in Nigeria. Municipal wastes include used waters from houses, offices and other buildings in the area. It is also called sanitary wastes. The nature of these impurities and the large volume of wastes in which they are carried make disposal of domestic or municipal wastes a significant technical problem. In most cases, sewage and waste water from homes are routed into the rivers and streams.

#### **2.5.7 Urban Runoff**

Urbanization in most Nigeria cities has resulted in the concentration of large population in some areas living under poor sanitation conditions<sup>33</sup>. This invariably has led to increased waste generations with heaps of waste almost everywhere. During rainfall, some of these wastes are washed into the poor drainage systems and subsequently, into nearby rivers<sup>34</sup>. Lack of town planning architecture and strategies in Nigerian cities and towns had aggravated the risks of urban run-offs with resultant effect on surface water.

The poorly managed drainage system in the country had caused the surface water impairment due to erosions during rainfall. Rainfall runoff carries all sorts of pollutants from houses, industries, farmland and dumping sites.

### **2.5.8 Agricultural Wastes**

Due to increased population, there is an obligation in the increase of food production, which involve the use of fertilizers, pesticides and other production enhancers. Thus, agricultural wastes are generated, which consist of organic products, pesticides, fertilizers, and other chemicals. These materials, animals and crop enter into water bodies mainly in run-off from watershed lands and causes pollution<sup>35</sup>. The inflow of wastes from livestock feed, pesticides, fungicides, herbicides and other industrial chemicals are highly toxic to the aquatic environment.

### **2.5.9 Mining Wastes**

Mining, milling, dressing and processing of ores give rise to dust, ore and metal discards and large quantities of effluents, which are often discharged into aquatic bodies. They not only increase sediments contamination but also release toxic metals into the water sources. Some common metals found in mine effluents are Cd, Cu, Fe, Pb, Cr, Mn, Ni and Zn<sup>40</sup>. Unfortunately, these wastes are highly poisonous, which has effect on both the human health and the environment<sup>33</sup>. Mineral processing operations can also generate significant PTEs pollution, both from direct extraction processes (which typically entails size reduction - greatly increasing the surface area for mass transfer and generate effluents) as well as through leaching from ore and tailings stockpiles<sup>35</sup>.

### **2.5.10 Oil Spillage**

Oil spillage is one of the common pollution events of global water-soil ecosystems. An oil spill represents an immediate negative effects on human health, including respiratory

and reproductive problems as well as liver, and immune system damage. Oil spills causing future oil supply to decline also effects the everyday life of humans such as the potential closure of beaches, parks, fisheries and fire hazards. Contamination can also have impact on tourism and marine resource extraction industries.

## **2.6 Effects of Surface Water Pollution**

Water pollution has a dual effect on the nature. This is true because it has negative effects on the living and also on the environment. The effects of pollution on human beings and aquatic communities are many and varied. Water pollution causes approximately 14,000 deaths per day, mostly due to contamination of drinking water by untreated sewage in developing countries<sup>36</sup>. Water pollution has wider ecological impact than just being unsuitable for consumption or posing health hazards. Most of the water withdrawn from the resources is used for consumption which is a carriage of industrial wastes.

Thus, water is the major conduit in direct transmission of toxic agents, metal elements like Pb, Cu, Cd, Cr, Zn, Ni, Fe, and Mg are infectious agents and vectors for diseases, such as cholera, gastrointestinal diseases, and malaria and so on. Also, increase in human settlement, urbanization poses a greater demand for water's domestic use, bathing, recreational activities, construction, agricultural and industrial operations. However, available water is limited, so adverse effect of water pollution on ecological systems becomes more serious. Definitely with all these, we can expect that there is going to be a reduction in productivity. Biomass and diversity of communities' wholesomeness are disrupted when large amount of toxic materials are released into the waterways as water pollution leads to damage to human health<sup>37</sup>.

## **2.7 Water Quality Parameters**

Water is a compound with unique physiochemical properties that make it distinct from other molecules of comparable molecular mass due to its tetrahedral configuration<sup>38</sup>. The following properties of water are of concern to this study:

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**Table 2.1:** Physico-Chemical Parameters of Water Quality

Physical Parameter	Chemical Parameter	Biological Parameters
Temperature	Ph	Algae
Colour	Alkalinity	Bacteria
Taste and Odor	Chloride	Protozoa
Solids	Chlorine Residual	Viruses
Turbidity	Acidity	
Electrical Conductivity	Nitrogen	
	Fluoride	
	Sulfate	
	Copper and Zinc	
	Dissolved Oxygen (DO)	
	Biochemical Oxygen	
	Demand (BOD)	
	Chemical Oxygen Demand	
	(COD)	
	Toxic Inorganic Substances	
	Toxic Organic Substances	

Source<sup>6</sup>

### 2.7.1 pH

pH which is a measure of the concentration of free H<sup>+</sup> ions, is affected by acid rain, surrounding rock formations, and certain wastewater discharges. Most fresh water aquatic

species prefer a pH range of 6.5 to 8.0<sup>41</sup>. Certain types of organisms prefer different ranges of pH, if the pH is high or low it will change the types of organisms found in surface water. A low pH can also allow toxic elements and compounds to become mobile and available for uptake by organisms<sup>38</sup>.

### **2.7.2 Temperature**

The temperature of the water may affect both chemical and biological water characteristics. Rates of many biological and chemical processes vary with temperature. Biological water quality may vary with temperature due to varying species survival rates in different temperatures. A chemical characteristic that varies with the temperature of the water is dissolved oxygen content. The saturation value of dissolved oxygen in water is inversely related to the temperature of the water. Therefore, in temperate climates, dissolved oxygen levels are typically higher in the winter and lower in the summer<sup>39</sup>.

### **2.7.3 Electrical Conductance**

Specific conductance or conductivity of water is a measure of the ease with which an electrical current can pass through water. A high conductivity is a result of the presence of inorganic dissolved solids that carry a charge. The specific conductance of surface water can be affected by both natural and anthropogenic factors in the watershed. The natural conductivity of a surface water body that has not been affected by human activities depends mainly on the geography of the area. The conductivity of surface water can vary depending upon the type of rock or soil that the water has come in contact with. Other natural variations in surface water conductivity can be caused by the type or amount of biological activity in a surface water<sup>40</sup>. The specific conductance of surface water is also influenced by human activities within a watershed.

### **2.7.4 Total Dissolved Solids**

Total dissolved solid (TDS) are the total amount of mobile charged ions, including minerals, salts or metals dissolved in a given volume of water, expressed in units of mg per unit volume of water<sup>27</sup> (mg/ L), or as parts per million (ppm). TDS is directly related to the purity of water and the quality of water purification systems and affects everything that consumes, lives in, or uses water.

The TDS usually correlates and affect pH reading. The presence of dissolved solids in the water will affect the taste of the water. The TDS cannot have a significant deviation of its levels from standard value in water. Not only is it not acceptable to consumers due to off taste, but also due to other effects. This condition may indicate that a possible bacterial contamination of the lower TDS water levels and which is also very harmful to human health<sup>41</sup>.

### **2.8. Total Alkalinity**

It is composed primarily of carbonate and bicarbonate. Alkalinity, pH and hardness affect the toxicity of many substances in the drinking water could be determined by dil. HCl titration in presence of phenolphthalein and methyl orange indicators. Alkalinity in hot water essentially results from the presence of hydroxyl and carbonate ions. Hydroxyl alkalinity in boiler water is necessary to protect the boiler against corrosion and lag. Too high a caustic solutions cause other operational problems, such as foaming. Excessively high causticity levels can result in a type of caustic attack of the boiler called "embrittlement".

#### **2.8.1 Dissolved Oxygen (DO)**

The DO is one of the most important parameter. Its correlation with water body gives direct and indirect information e.g. bacterial activity, photosynthesis, availability of

nutrients and stratification. In the progress of summer, DO decreased due to increase in temperature and also due to increased microbial activity. The high DO in summer is due to increase in temperature and duration of bright sunlight has influence on the percentage of soluble gases ( $O_2$  &  $CO_2$ ). During summer the long days and intense sunlight seem to accelerate photosynthesis by phytoplankton, utilizing  $CO_2$  and giving off oxygen. This possibly accounts for the greater qualities of  $O_2$  recorded during summer. Fresh water pond and DO amount recorded during monsoon season was 5.86 mg/L due to the turbulence of water facilitating the diffusion of atmospheric oxygen and the increased solubility of oxygen at lower temperature.

### **2.8.2 Carbonate**

Whenever the pH reaches 8.3, the presence of carbonates is indicated. It is measured by titration with standardized hydrochloric acid (HCl) using phenolphthalein as indicator. Below pH 8.3, the carbonates are converted into equivalent amount of bicarbonates. The pH titration can also be done metrically or potentiometrically<sup>30</sup>. Carbonates in water is present in the form of hardness and it needs to be removed as it can prove to be dangerous to human healths as well as affect the conveyance system.

### **2.8.3 Bicarbonate**

Bicarbonate is also measured by titration with standardized hydrochloric acid using methyl orange as indicator. Methyl orange turns yellow below pH 4.0. At this pH, the carbonic acid decomposes to give carbon dioxide and water<sup>30</sup>.

### **2.8.4 Biochemical Oxygen Demand (BOD)**

BOD is a measure of organic material contamination in water, specified in mg/L. BOD is the amount of dissolved oxygen required for the biochemical decomposition of organic

compounds and the oxidation of certain inorganic materials (e.g., iron, sulfites). Typically the test for BOD is conducted over a five-day period<sup>30</sup>. The demand of oxygen in the water was recorded during monsoon season was 3.20 mg/L due to the possible addition of high amount of waste along with rain water from the surrounding and addition of organic waste in Taal lake by certain human activities which also be responsible for the increase in BOD<sup>41</sup>.

### **2.8.5 Chemical Oxygen Demand (COD)**

COD is another measure of organic material contamination in water specified in mg/L. COD is the amount of dissolved oxygen required to cause chemical oxidation of the organic material in water. Both BOD and COD are key indicators of the environmental health of a surface water supply. They are commonly used in waste water treatment but rarely in general water treatment<sup>31</sup>.

### **2.8.6 Sulfate**

It is measured by nephelometric method in which the concentration of turbidity is measured against the known concentration of synthetically prepared sulfate solution. Barium chloride is used for producing turbidity due to barium sulfate and a mixture of organic substance (Glycerol or Gum acetia) and sodium chloride is used to prevent the settling of turbidity. As per IS; 10500-2012 desirable limit for sulphate is 200 and 400 mg/l in permissible limit<sup>31</sup>.

### **2.8.7 Ammonia (Nitrogen)**

It is measured spectroscopically at 425 nm radiation by making a color complex with Nessler's reagent. The conditions of reaction are alkaline and cause severe interference from hardness in water<sup>31</sup>. Total nitrogen exhibited higher value in monsoon season and very low in summer season the surface run of agricultural wastes, fertilizers, domestic wastes, house hold sewage and surface run-offs can also increases the concentration of total nitrogen and carbon in the study area. The total nitrogen level in water observed during raining season, phosphate value might be due to the regeneration and release of total phosphorus from bottom mud into the water column by turbulence and mixing<sup>31</sup>.

#### **2.8.8 Calcium**

It is measured by complexometric titration with standard solution of Ethylene diammineacetic acid (EDTA) using Patton's and Reeder's indicator under the pH conditions of more than 12.0. These conditions are achieved by adding a fixed volume of 4N Sodium Hydroxide. The volume of titre (EDTA solution) against the known volume of sample gives the concentration of calcium in the sample. The amount of calcium in water was recorded during monsoon season due to calcium absorbed by the large number of organisms for shell construction, bone building and plant precipitation of lime<sup>31</sup>.

#### **2.8.9 Magnesium**

It is also measured by complexometric titration with standard solution of EDTA using Eriochrome black T as indicator under the buffer conditions of pH 10.0. The buffer solution is made from ammonium chloride and ammonium hydroxide. The solution resists the pH variations during titration<sup>31</sup>.

#### **2.8.10 Sodium**

It is measured with the help of flame photometer. The instrument is standardized with the known concentration of sodium ion (1 to 100 mg/litre). The samples having higher concentration are suitably diluted with distilled water and the dilution factor is applied to the observed values<sup>30</sup>.

#### **2.8.11 Potassium**

It is also measured with the help of flame photometer. The instrument is standardized with known concentration of potassium solution, in the range of 1 mg to 5 mg/litre. The sample having higher concentration is suitably diluted with distilled water and the dilution factor is applied to the observed values.

#### **2.8.12 Chloride**

It is measured by titrating a known volume of sample with standardized silver nitrate solution using potassium chromate solution in water or eosin/fluorescein solution in alcohol as indicator. The latter indicator is an adsorption indicator while the former makes a red colored compound with silver as soon as the chlorides are precipitated from solution. The chloride amount in monsoon was 102 mg/L due to frequent run-off loaded with contaminated water from the surrounding slum area and evaporation of water<sup>43</sup>.

#### **2.8.18 Turbidity**

The turbidity is the cloudiness of the effects caused by various individual particles. These particles are generally invisible to the naked eye, just like what happens to smoke in the air. Turbidity results in a decrease in the intensity of light that passes through cloudiness or turbidity water due to light, absorption, and reflection of light. Technically, turbidity can be defined as a disorder or fluid disturbance caused by suspended solids that are

usually not visible to the naked eye. The turbidity can affect the growth rate of algae and other microaquatic plants in the water. Increased turbidity can lead to a decrease in aquatic plant growth due to a decrease in the amount of light for plants to perform photosynthesis.

Turbidity is also able to increase the water temperature because the particles in the water to the surface absorb more heat. These factors lead to the reduction of dissolved oxygen. Turbidity measurement is an important test when trying to determine water quality. In drinking water, the higher the turbidity level, then it is easier for a person to get water-related illnesses<sup>44</sup>.

#### **2.8.14 Secchi Disk Transparency**

Secchi disk transparency refers to the depth to which the white and black Secchi disk can be seen in the lake water. Water clarity, as determined by a secchi disk is affected by two primary factors: algae and suspended particulate matter. Particulates (soil or dead leaves) may be introduced into the water by either runoffs or sediments already on the bottom of the lake. Erosion from construction sites, agricultural lands, and riverbanks all lead to increased sediment runoffs. Bottom sediments may be resuspended by bottom-feeding fish such as carp, or by motorboats or strong winds in shallow lakes. The higher transparency occurred in lake water, during winter and summer due to absence of rain, runoff and flood water as well as gradual settling of suspended particles.

#### **2.8.15 Total Hardness**

Total hardness is a measurement of calcium and magnesium, and is expressed as calcium carbonate; our body needs both Ca and Mg to remain healthy. As per WHO standard desirable limit and permissible limit for hardness lies between 200 mg/l respectively. The

effect of hardness is scale in utensils and hot water system in boilers. Soap scum's sources are dissolved calcium and magnesium from soil and aquifer minerals containing limestone or dolomite. The Treatment of hard water is softener ion exchanger and reverse osmosis process. The amount of total hardness in the Suraila Taal lake water was recorded during monsoon was 346 mg/L due to presence of high content of calcium and magnesium in addition to sulphate and nitrate in the sewage waste added during monsoon<sup>45</sup>.

### 2.8.16 Fluoride

Fluoride occurs as fluorspar (fluorite), rock phosphate, phosphorite crystals and triphite in nature. These factors which control the concentration of fluoride in the water area and the presence of accessory minerals in the rock minerals assemblage through which the ground water is circulating<sup>43</sup>. Fluoride is most important in human body for the normal development of bones. As per BIS standard desirable limit for fluoride is 1 mg/l in permissible limit. The higher concentration of fluoride in drinking water may develop molting of teeth, skeleton fluorosis, and deformation in knee joints<sup>46</sup>.

**Table 2.2:** Different Analytical Water Quality Parameter with their Analytical Technique and Guideline Values as per WHO and Indian Standard.

Sr. No.	Parameter	Technique used	WHO Standard	Indian Standard	USEPA Standard
1	Temperature	Thermometer	-	-	-
2	Color	Visual / color kit	-	5 Hazen units	-
3	Odour	Physiological sense	Acceptable	acceptable	-
4	Electrical Conductivity	Conductivity meter / water analysis kit	-	-	2500 us/cm
5	pH	pH meter	6.5-9.5	6.5-9.5	-
6	Dissolved Oxygen	Redox titration	-	-	-
7	Total Hardness	Complexometric titration	200ppm	300ppm	<200ppm
8	Alkalinity	Acid-Base titration	-	200 ppm	-
9	Acidity	Acid-Base titration	-	-	-
10	Ammonia	UV Visible Spectrophotometer	0.3 ppm	0.5 ppm	0.5 ppm
11	Bi carbonate	Titration	-	-	-
12	Biochemical Oxygen Demand (BOD)	Incubation followed by titration	6	30	5
13	Carbonate	Titration	-	-	-
14	Chemical Oxygen Demand (COD)	C.O.D. digester	10	-	40
15	Chloride	Argentometric titration	250 ppm	250 ppm	250 ppm
16	Magnesium	Complexometric titration	150 ppm	30 ppm	-
17	Nitrate	UV Visible Spectrophotometer	45 ppm	45 ppm	50 mg/l
18	Nitrite	UV Visible Spectrophotometer	3 ppm	45 ppm	0.5 mg/l
19	Potassium	Flame Photometer	-	-	-
20	Sodium	Flame Photometer	200 ppm	180 ppm	200 ppm
21	Sulphate	Nephelometer Turbidimeter	250 ppm	200 ppm	250 ppm

Source<sup>46</sup>

**Table 2.3:** Different Analytical Water Quality Parameter used for Testing of Quality of Water and their Source of Occurance and Potential Health Effects with USEPA Guideline

Sr. No.	Parameter	Source of Occurrence	Potential Health Effect
1	Turbidity	Soil runoff	Higher level of turbidity is associated with disease causing bacteria's.
2	Color	Due to presence of dissolved salts	-
3	Odor	Due to biological degradation	Bad odour unpleasant
4	Electrical conductivity	Due to different dissolved solids	Conductivity due to ionizable ions. High conductivity increases corrosive nature of water.
5	pH	pH is changed due to different dissolved gases and solids.	Affects mucous membrane; bitter taste; corrosion
6	Dissolved oxygen	Presence due to dissolved oxygen	D.O. corrode water lines, boiler and heat exchangers, at low level marine animals cannot survive.
7	Total hardness	Presence of calcium and magnesium ions in a water supply. It is expressed. Hardness minerals exist to same degree in every water supply.	Poor lathering with soap; deterioration of the quality of clothes; scale forming.
8	Total alkalinity	Due to dissolved gases	Embrittlement of boiler steel. Boiled rice turns yellowish
9	TDS	Presence all dissolved salts	Undesirable taste; gastro-intestinal irritation; corrosion or incrustation
10	Calcium	Precipitate	Interference in dyeing, textile.
11	Magnesium	Surfactants, anionic emulsifiers	Paper industry etc.
12	Ammonia	Due to dissolved gases and degradation of organics	Corrosion of Cu and Zn alloys by formation of complex ions.
13	Barium	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits	Increase in blood pressure
14	Biochemical Oxygen Demand (B.O.D.)	Organic material contamination in water	High BOD decreases level of dissolved oxygen.
15	Carbonate	Due to dissolution	Product imbalance Unsatisfactory production short product life
16	Chloride	Water additive used to control microbes, disinfect	Eye/nose irritation; stomach discomfort. Increase corrosive character of water.
17	Nitrate	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits	Effect on infants below the age of six months symptoms include shortness of breath

<b>Sr. No.</b>	<b>Parameter</b>	<b>Source of Occurrence</b>	<b>Potential Health Effect</b>
18	Phosphate	-	and blue-baby syndrome. Stimulate microbial growth, Rancidity mold growth
19	Sodium	Natural component of water	
20	Sulphate	Due to dissolved Ca/Mg/Fe sulphate	Taste affected; gastro-intestinal irritation. Calcium Sulphate scale.

Source<sup>46</sup>

Do Not Copy, Lead City University, Nigeria

## **2.9 PTEs and its Associated Human Health Effects**

Potentially toxic elements are non-biodegradable and are considered as major environmental pollutants causing cytotoxic, mutagenic and carcinogenic effects in animals<sup>47</sup>.

PTEs are natural constituents of the earth's crust. They are stable and cannot be degraded or destroyed, and therefore they tend to accumulate in soils and sediments. However, human activities have drastically altered the biochemical and geochemical cycles and balance of some PTEs. The principal man-made sources of PTEs are industrial point sources, such as mines, foundries and smelters, and diffuse sources such as combustion by-products, traffic and so on.

Heavy metals such as zinc, iron, chromium and nickel are essential metals since they play an important role in biological systems, whereas cadmium and lead are non-essential metals, as they are toxic, even in trace amounts<sup>48</sup>. However, these essential metals can also produce toxic effects when the metal intake is excessively elevated.

There are about thirty chemical elements that play a pivotal role in various biochemical and physiological mechanisms in living organisms, and recognized as essential elements for life<sup>49</sup>. In fact, for many food components, the intake of metal ions can be a double edged sword because of bioaccumulation and bio-magnifications of PTEs in living organisms which describes the processes and path-ways of pollutants from one trophic level to another<sup>50</sup>.

Majority of the known metals and metalloids are very toxic to living organisms and even those considered as essential can be toxic if present in excess amounts<sup>48</sup>. Concentrations of several toxic metals and metalloids have been largely increased as a result of human activities. They can disturb important biochemical processes, constituting an important threat to the growth of plant and health of animals<sup>48</sup>.

Lately, contamination of foods by PTEs has become an inevitable challenge; this is because of air, soil, and water pollution contributing to the presence of harmful elements, such as cadmium, lead, and mercury are found in foodstuffs. The occurrences of PTEs

enriched ecosystem components arise from rapid industrial growth, advances in the use of chemicals in agriculture, or the urban activities of human beings. These agents have led to metal dispersion in the environment and, consequently impaired the health of the population by the ingestion of victuals contaminated by harmful elements<sup>51</sup>.

Percolation of runoff water often lead to horizontal leaching from dumpsites causing metal uptake by root of crops; the rest may find their way into open water bodies and the entire aquatic ecosystem. The entry into food chain of these metals leads to increased susceptibility and exposure to metal poisoning of the local population<sup>51</sup>. A number of serious health problems can develop because of excessive uptake of dietary PTEs. Furthermore, the consumption of PTEs-contaminated food can seriously deplete some essential nutrients in the body causing a decrease in immunological defenses, intrauterine growth retardation, impaired psycho-social behaviors, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer<sup>52</sup>.

In Nigeria, there is lack of food intake record to monitor the intake of PTEs and their levels in blood and urine. It is advocated that legislation is necessary to check Pb exposure to humans should be based on genuine scientific evaluation of the available data<sup>52</sup>.

### **2.9.1 Lead**

Lead with atomic number 82 is a bluish-white and very soft metal. Lead is a metal that occurs as Galena naturally in the earth. It has many industrial uses and is found in trace amounts everywhere in the human environment. Lead is used in many engineering and chemical industries such as lead batteries, sulphuric acid plants, soldering, automobile industry, pigments and paints.

Lead is resistant to corrosion and discoloration; its early uses included pipes for the collection, transport, and distribution of water and containers for the storage of food and

beverages<sup>53</sup>. Nevertheless, lead has adverse behavioural, physiological, and biochemical effects on humans. A major physiological and biochemical impact of lead is inhibition of two key enzymes needed for the synthesis of haemoglobin, the iron-containing protein in red blood cells that binds and transports oxygen to all cells in the human body<sup>54</sup>. When these enzymes are inhibited and haemoglobin synthesis is disrupted, there is insufficient transport of oxygen and anaemia as the result.

### **2.9.2 Zinc**

Zinc with atomic number of 30 is a white metal with a bluish-grey lustre. Zinc is a metal that occurs as sphalerite, calamine, and zinc blend naturally in the earth. It has a great variety of application as it is useful in the negative plates in some electric batteries, roofing in buildings and construction, as a white pigment in paints, pigment in plastics, cosmetics, photocopier papers, and printing inks<sup>54</sup>.

Zinc is used in drugs as it is believed to possess anti-oxidant properties. This protects against premature ageing of the skin and muscle of the body. However, zinc ingestion at extreme concentration can damage the pancreas, disturb protein metabolism, cause hypogonadism with impaired reproductive capacity and result in arteriosclerosis<sup>55</sup>.

### **2.9.3 Cadmium**

Cadmium with atomic number of 48 is a bluish-white rare metal. It occurs in association with zinc, lead, copper minerals and resembles zinc in many of its properties. Cadmium has many industrial uses such as in electroplating, Ni-Cd batteries and manufacture of fertilizers, paints and coloured glass.

The effects of cadmium on aquatic organisms can be directly or indirectly lethal and can impact populations and ecosystems as well as individuals, Vitamin D is necessary for deposition of calcium in bones and by blocking vitamin D synthesis, cadmium prevents the bones from having a normal amount of calcium<sup>55</sup>. Thus, the bones become soft or

brittle. Chronic cadmium exposure causes kidney damage by inhibiting enzymes responsible for re-sorption processes<sup>55</sup>.

#### **2.9.4 Chromium**

Chromium with atomic number of 24 is a hard steely-grey metal, occurring in nature as chromite. Chromium is used in plating and in the manufacture of stainless, acid resistant steels, tanning of hides in leather industry, and mordant in dyeing. Chromium is an essential trace nutrient that is required in small amounts for carbohydrate metabolism, but becomes toxic at higher concentrations). The most bioavailable and toxic form of chromium is the hexavalent ion  $\text{Cr}^{+6}$ . Therefore, water quality standards for protection of aquatic life are stricter for hexavalent chromium than for trivalent chromium ( $\text{Cr}^{+3}$ )<sup>56</sup>. Chromium and cadmium works together and the combined toxicity of these two metals is greater than the sum of their individual toxicity<sup>57</sup>.

#### **2.9.5 Iron**

Iron with atomic number of 26 is a silvery plastic metal and the next abundant metal in the globe after aluminum. It occurs naturally as magnetite and haematite. Iron is used mainly in the production of ferrous alloys, coagulants in water purification and pesticides. Although, iron is an essential mineral, disease of aging such as alzheimer's diseases, diabetes mellitus have been linked to excess iron intake<sup>58</sup>. Excess iron in drinking water can produce an unpleasant taste and stain home fixtures<sup>59</sup>. Iron at low concentration may cause nuisance algae species to replace inoffensive species. Likewise, iron may cause algae blooms, which create biological oxygen demand, smother aquatic plants and produce potent neurotoxins.

### **2.9.6 Nickel**

Nickel with atomic number 28 is a hard and silvery yellowish metal. It occurs in nature chiefly as compounds with arsenic or sulphur and resistant to corrosion. Nickel alloy is employed in turbines, jet engines and electrical heating elements<sup>57</sup>.

Nickel is one of many trace metals widely distributed in the environment. Nickel is being released into the environment from both natural sources from wind-blown dust, weathering of rocks and soils, volcanic emissions, forest fires, vegetation and anthropogenic sources from emissions from fossil fuel consumption<sup>60</sup>. Nickel is a nutritionally essential trace metal for at least several animal species, micro-organisms and plants, and therefore either deficiency or toxicity symptoms can occur when, respectively, too little or too much nickel is taken up. Inhalation exposure in occupational settings is a primary route for nickel-induced toxicity, and may cause toxic effects in the respiratory tract and immune system<sup>61</sup>.

### **2.9.7 Copper**

Copper with atomic number of 29 is a reddish metal, widely distributed in nature in form of free metal as ore such as malachite, copper glance and copper pyrite. Owing to its high thermal and electrical conductivity, high tensile strength; copper is in great demand in electrical and industrial equipment manufacture.

Copper occurs in drinking water from copper pipes, as well as additives in controlling algal growth. The major sources of its deposition into the environment are mining, smelting and fossil fuel combustion<sup>62</sup>. Although, copper is an essential substance to human life. But in high doses, may cause anemia, liver and kidney damage, and intestinal irritation.

### **2.9.8 Manganese**

Manganese is a chemical element with the symbol Mn and atomic number 25. It is a hard brittle silvery metal, often found in minerals in combination with iron. Manganese is also an essential human dietary element, important in macronutrient metabolism, bone formation, and free radical defense systems. Manganese toxicity can result in a permanent neurological disorder known as managasm. Symptoms of this include; tremors, irritability, difficulty walking and facial muscle spasms.

### **2.9.9 Mercury and Arsenic**

Mercury is toxic and has no known function in human biochemistry and physiology. Inorganic forms of mercury cause spontaneous abortion, congenital malformation and gastrointestinal disorders (like corrosive esophagitis and haematochezia)<sup>63</sup>. Poisoning by its organic forms, which include monomethyl and dimethyl mercury presents with erethism (an abnormal irritation or sensitivity of an organ or body part to stimulation), acrodynia (pink disease, which is characterized by rash and desquamation of the hands and feet), gingivitis, stomatitis, neurological disorders, total damage to the brain and CNS and are also associated with congenital malformation. As with lead and mercury, arsenic toxicity symptoms depend on the chemical form ingested.

Arsenic acts to coagulate protein, forms complexes with coenzymes and inhibits the production of adenosine triphosphate (ATP) during respiration. It is possibly carcinogenic in compounds of all its oxidation states and high-level exposure can cause death. Arsenic toxicity also presents a disorder, which is similar to, and often confused with Guillain-Barre syndrome, an anti-immune disorder that occurs when the body's immune system mistakenly attacks part of the PNS, resulting in nerve inflammation that causes muscle weakness.

Arsenic is one of the most important PTEs causing disquiet from both ecological and individual health stand points. It has a semi metallic property, is prominently toxic and carcinogenic, and is extensively available in the form of oxides or sulfides or as a salt of iron, sodium, calcium and copper. Arsenic is the twentieth most abundant element on earth and its inorganic forms such as arsenite and arsenate compounds are lethal to the environment and living creatures. Humans may encounter arsenic by natural means, industrial source, or from unintended sources. Deliberate consumption of arsenic in case of suicidal attempts or accidental consumption by children may also result in cases of acute poisoning. Arsenic is a protoplasmic poison since it affects primarily the sulphhydryl group of cells causing malfunctioning of cell respiration, cell enzymes and mitosis<sup>64</sup>.

## **2.10 Water Quality Assessment**

An assessment on the effect of anthropogenic activities on the surface water quality of river Ogun reported high concentration of total dissolved solids of 98 – 200 mg/L, which is within the WHO standards of < 500 mg/L<sup>64</sup>. This could be true because of salt intrusion as a result of short distances to ocean. High values of hydrogen ion concentration and total dissolved solids in river Ogun was reported, which is above the maximum permissible limit by WHO<sup>65</sup>. This is corroborated by similar findings obtained in Omi water of Ewekoro Local Government area of Ogun State<sup>66</sup>. Water quality assessment on river Ogun using multivariate statistical technique and discovered a slightly acidic condition<sup>67</sup>. Similar acidic condition in Asa River, which exceeded the recommended level for surface water quality<sup>68</sup>. The state of pollution of Ogun River at Kara Abattoir and revealed that cadmium, chromium, iron and lead exceeds the WHO limit standard<sup>66</sup>. Similar results were obtained revealing high concentration of lead and copper<sup>69</sup>. The scarcity of clean water and pollution of fresh water has therefore led to a situation in

which one-fifth of the urban dwellers in developing countries and three quarters of their rural dwelling population do not have access to reasonably safe water supplies<sup>70</sup>.

Available literature on environmental monitoring of surface water indicated that streams and rivers in the country are showing increasing trend of water pollution due to increase population, industrialization and urbanization<sup>21</sup>. Waste generations by the industries and households have continued to increase. These wastes are indiscriminately disposed-off into the water bodies. Urgent attention is therefore necessary to mitigate water pollution problems in Nigeria through monitoring as well as enforcement of emission standards by industries<sup>71</sup>.

The study of toxic PTEs in Ogun River is more important in comparison with other pollutants due to their non-biodegradable nature, accumulative properties and long biological half-lives. It is difficult to remove them completely from the environment once they enter into it. In light of the increased use of a wide variety of metals and petrochemicals in industries coupled with Nigerian style of dumping refuse indiscriminately around the basin, there is now a greater awareness of toxic metal pollution in the aquatic environment<sup>72,73</sup>.

### **2.11 Hazard Quotient (HQ)**

A hazard quotient is the ratio of the potential exposure to a substance and the level at which no adverse effects are expected. It is primarily used by USEPA to assess the health risks of air toxics. Another very important concept related to HQ is Hazard Index (HI). It is the sum of hazard quotients for substances that affect the same target organ or organ system. As with the hazard quotient, aggregate exposures below an HI of 1.0 derived using target organ specific hazard quotients likely will not result in adverse non-cancer health effects over a lifetime of exposure<sup>71</sup>.

Both hazard quotient (HQ) and risk quotient (RQ) are very important concepts in chemical risk assessment. They are used by regulatory authorities such as USEPA to describe the risk category of a chemical substance.

A hazard quotient less than or equal to 1 indicates that adverse effects are not likely to occur, and thus can be considered to have negligible hazard. HQs greater than 1 is not statistical probabilities of harm occurring. Instead, they are a simple statement of whether (and by how much) an exposure concentration exceeds the reference concentration (RfC).

## **2.12 Heavy Metal Contamination in Sediments**

Contamination of sediments by heavy metals and other pollutants is considered by many regulatory agencies to be one of the major threats to aquatic ecosystems. The importance of sediments as a sink for a range of substances including nutrients, hydrocarbons, pesticides and heavy metals has been highlighted in many past studies<sup>4</sup>. Sediments' qualities are one of the possible media in monitoring the health of aquatic ecosystems. They are ecologically important components of the aquatic habitat and play a significant role in maintaining the trophic status of any water body. It was observed that sediments play a significant role in remobilization of contaminants in aquatic systems under favorable conditions and interactions between water and sediments. Like soils in the terrestrial system, sediments are the primary sink for metals and precipitates in the aquatic environment. It was reported that sediments in rivers do not only play important roles at influencing the pollution, they also record the history of their pollution<sup>4,5</sup>.

Heavy metals once adsorbed on the sediments are not freely available for aquatic organisms. Under changing environmental conditions (temperature, pH, redox potential, salinity) of the overlying water, these toxic metals are released back to the aqueous phase. The occurrences of enhanced concentrations of heavy metals especially in sediments may

also be an indication of human-induced perturbations rather than natural enrichment through geological weathering<sup>4</sup>. Heavy metal distribution and bioavailability in both sediments and the overlying water column have to be considered to obtain a better understanding of interactions between the organisms and their environment. Hence, the assessment of sediment is significant to study the risk of aquatic ecosystem contamination and pollution. Apart from water, sediments are also responsible for nutrients and pollutant transportation in aquatic environments<sup>4,5</sup>.

Sediments capture hydrophobic chemical pollutants that enter water bodies and slowly release the contaminants back into the water column. Therefore, ensuring a good sediment quality is crucial to maintain a healthy aquatic ecosystem, which ensures good protection of human health and aquatic life. In addition to the physical and chemical relationships between sediments and contaminants, sediments are of fundamental importance to benthic communities in terms of providing suitable habitats for essential biological processes. Therefore, sediments' quality assessments provide an essential link between chemical and biological processes going on in the aquatic biodiversity<sup>6</sup>.

Sediments near urban areas commonly contain high levels of contaminants. This constitutes a major environmental problem faced by many anthropogenically impacted aquatic environments. Sediments act as both carrier and sources of contaminants in aquatic environments. The contamination of sediments with heavy metals leads to serious environmental problems. Heavy metals may adsorb onto sediments or be accumulated by the benthic organisms; their bioavailability and toxicity level depends upon the various metal forms (inorganic or organometallic) and amounts bound to the sediment matrices. Additionally, pollutants released to surface water from industrial and municipal discharges, atmospheric deposition and run-offs from agricultural, urban and mining areas accumulate to harmful levels in sediments<sup>6,7</sup>.

### 2.13 Heavy Metals in Fish

Fish enjoys a good reputation as a nutritious and healthy food. They are essential food items that provide high quality protein, vitamins, minerals and omega-3 fatty acids which have been associated with health benefits due to their cardio-protective effects. Despite the many health benefits associated with fish in a diet, there are also some health risks related to fish consumption, mainly due to potential adverse effects of heavy metal contamination<sup>8</sup>. It was noted that heavy metals are well known environmental pollutants that cause serious health hazards to human beings; their effects are not immediate and show up after many years. These environmental pollutants represent a major problem in both developed and undeveloped countries of the world.

Aquatic biota has been used to monitor heavy metal pollution in aquatic ecosystems for decades. The choice of biota depends on several factors like heavy metal accumulating potential of the organism, motility, economic value among others<sup>3,4</sup>. However, fish are the often preferred biota because of their big size which makes them easily identifiable and their ability to accumulate heavy metals. Also, fish is a bio-indicator because it is easy to be obtained in large quantity, potential to accumulate metals, long lifespan, easy to sample and optimum size for analysis<sup>4</sup>.

Therefore, fish are useful as sentinel species and biomonitors of metal pollution because they can help understand the risk to the aquatic ecosystem and to humans. The use of wild and cultured food fishes as biomonitors of metal pollution in aquatic ecosystems is becoming popular throughout the world<sup>7</sup>.

Heavy metals are non-biodegradable and they persist in the environment and may become concentrated up the food chain. This may lead to enhanced levels in tissues of fish and other aquatic biota. The region of accumulation of heavy metals within fish varies with

route of uptake, type of heavy metals and species of fish concerned. The accumulation of contaminant residues may ultimately reach concentrations hundreds or thousands of times above those measured in the water, sediment and food. For this reason, monitoring fish tissue contamination serves an important function as an early warning indicator of sediment contamination or related water quality problems. Monitoring fish tissue contamination also enables detection of toxic chemicals in fish that may be harmful to consumers, and take appropriate action to protect public health and the environment. Multiple factors including seasonal, physical and chemical properties of water can play a significant role in metal accumulation in different fish tissues. It is therefore of great significance to evaluate pollution effects on fish for both environmental protection and socio-economic reasons. A combination of biological monitoring (bioaccumulation) and measurements of water and sediment quality can provide a good indication of conditions and potential risks to a water body<sup>8,9</sup>.

Accumulation of metals in different fish species depends on their feeding habits, ecological needs, metabolism, age and size of fish. Heavy metals accumulate in many important organs. Evidently heavy metals accumulate frequently in fish flesh (muscle) and in internal organs. Supporting structures and gills mostly accumulate waterborne heavy metals, while stomach and intestines accumulate food-associated elements. The highest concentrations of heavy metals are found in fish liver, kidney and gills<sup>10,11,12</sup>. Diet is the main route of exposure to heavy metals in the case of population not exposed to them. Thus, heavy metals acquired through the food chain as a result of pollution are potential chemical hazards, threatening consumers. The consequence of heavy metal pollution can be hazardous to man through his food. Therefore, it is important to assess and monitor heavy metal in aquatic environments (water, sediment and biota)<sup>11,12</sup>.

## 2.14 Effects of Heavy Metals in Aquatic Organisms and Man

Despite progress made in environmental waste management, heavy metals still pose immense health hazards to human and aquatic biota. Unlike other classes of pollutants which can be biodegraded and totally destroyed, heavy metals are non-biodegradable, and can neither be created nor destroyed. However, heavy metals might be altered from more toxic form or complexes to more stable and less toxic compounds<sup>5</sup>.

Discharge of heavy metals into a river or any aquatic environment can change both aquatic species diversity and ecosystems, due to their toxicity and accumulative behavior. Aquatic organisms such as fish and shell fish accumulate metals to concentrations many times higher than present in water or sediment. They can take up metals concentrated at different levels in their different body organs<sup>5</sup>.

In an aquatic environment, toxicity can be influenced by various abiotic environmental factors such as; dissolved oxygen, calcium/water hardness, pH, and temperature. Temperature especially is an important factor affecting metal toxicity, since most aquatic organisms are poikilothermic. Studies have shown that as water temperature rises, toxicants in water become more lethal to fish at lower concentrations. Other factors that can play a role are; organic matter, carbon dioxide, metabolic activities, biological half-life of the metal, suspended solids, total organic carbon, interactions between pollutants and the developmental stages of the organisms, and intraspecific variations in susceptibility to metals. Studies carried out on fish have shown that heavy metals have toxic effects<sup>7</sup>. They alter physiological activities and biochemical parameters both in tissue and in blood of fish. Elements such as mercury, cadmium, copper and zinc are considered most dangerous in the ecotoxicological aspect<sup>13,14,15</sup>.

Consumption of biota from contaminated aquatic bodies is an important route of exposure to pollutant compounds. However, water quality criteria for fish have

not received the attention that they deserve. All too often, water has been considered quite adequate for fish as long as there is no obvious mortality ascribed to known pollutants<sup>8</sup>.

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## Chapter Three

### Methodology

#### 3.1 Description of the Study Area

The river Ogun is a permanent river with a total area of 22.4 km and a fairly large flow of about 393 m/s during the wet season<sup>1</sup>. The river originates from Oyo State [3° 28"E and 8°41"N] near Shaki, which flows through Ogun State and discharges into the Lagos Lagoon, which is the final sink. The river Ogun water is used for agriculture, transportation, human consumption, various industrial activities and domestic purposes<sup>2</sup>. The river serves as raw water for Ogun State and Lagos State water works, which treats it before dispensing it to the public. Along the river basin, effluents from breweries, abattoir, dyeing industry, domestic wastewater are discharged<sup>3</sup>.

The major climatic seasons are wet season, which begins in June, and ends in July and the dry season, which begins in January and ends in March. The people are mainly farmers and traders. As at the time of this research work, the study area is predominantly an urban area at Lafenwa areas and a rural area with an industrial activity (mining of sand) at Alagada area. The coordinates of each area were recorded using the Garmin-12 Global Positioning System (GPS) and are presented in Table 3.1.

#### 3.2 Sample Collection

The sampling exercise was carried out twice each month for two months of the two seasons in Nigeria (January to February and June-July) for dry and wet season respectively, with a total of thirty-two (32) water samples collected to assess four (4) physicochemical parameters and eight (8) PTEs.

**Table 3.1 Sampling Locations and their Activities**

S/N	Location	Coordinates	Activities
1	Alagada	7°4'23.888''N 3°20'0.6''E	Sand mining, rearing of animals and Agriculture
2	Lafenwa	7° 8''44.246''N 3°21'12.1896'' E	Wood Processing, Agriculture, Waste disposal, selling and buying of fishes, Bathing, laundry activities and Religious rites.

Source: Field Work, 2021

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The physiochemical parameters and metals (Pb, Zn, Cd, Cr, Ni, Cu, Fe and Mn) were assessed on each water sample collected. Four of the water samples were collected along the stretch of the river at the two sampling locations (Lafenwa and Alagada), at the shallowest part to reflect the present condition of the river after pollution. Water samples were collected according to standard methods<sup>4</sup>. All samples were collected using pre-cleaned 2.5 L plastic bottles. All plastics utilized were pre-washed with detergent water solution, rinsed with tap water and soaked for 48 hours in 50% HNO<sub>3</sub>, then rinsed thoroughly with distilled-deionized water. They were then air-dried in a dust free environment. Precautions were taken to avoid the trapping of atmospheric oxygen in the containers. Water samples for PTEs were collected separately in 2.5L capacity plastic bottles. Three replicates of surface water samples were collected from each location by lowering a pre-cleaned plastic bottles into the water at a depth of 30cm below the water surface and allowed to over flow before withdrawing<sup>4</sup>. To ensure that no foreign substance was introduced into the samples, the plastic bottles were washed with water from the river before collection. They were preserved with 2 drops of concentrated nitric acid to prevent sorption of metals to the container walls. Samples were preserved in the field by keeping them in cooler packs containing ice cubes.

They were transported to the Department of Science Laboratory Technology, Laboratory, Moshood Abiola Polytechnic, Ojere, Abeokuta for subsequent analysis within 24 hours of collection and kept in the refrigerator at 4°C.

Two fishermen from each location were employed throughout the period of the sampling. Four tilapia fishes were collected randomly from each established location (as shown in Plate 6 and 7) using fishing gears (mostly nets) available at the disposal of the fishermen. A total of thirty-two (32) tilapia fish samples were collected throughout the study period. The fish samples were transported to the laboratory in a thermos flask with ice on the

same day. Ice was used to minimize the tissue decay and to maintain moist conditions during transportation<sup>5</sup>. All fish samples were kept at -30 °C until they were analyzed.

### **3.3 Chemicals and Reagents Used**

Concentrated Hydrochloric acid, concentrated Nitric acid , concentrated Hydrogen peroxide, distilled water

### **3.4 Analyses of Physical Parameters of Water Samples**

Physical parameters of the river water samples were determined according to the standard method<sup>4</sup>. This include temperature (°C), pH, Electrical Conductivity ( $\mu\text{S}/\text{cm}$ ) and TDS (mg/L). They were carried out in-situ using pocket size HANNA COMBO pH/TDS/Conductivity meter. The probe was rinsed with distilled water before use in each case and allowed to stay in the sample till the timer was stabilized for reading. The meter displays the value of pH and temperature first, then when the mode button is pressed its value for electrical conductivity and total dissolved solids shows on the screen.

#### **3.4.1 Digestion of Water Samples**

The three replicated samples for each sampling site were composited for the procedures conducted in the laboratory. One hundred millimeter (100ml) of the raw unfiltered water samples were transferred into *pyrex* beakers containing ten millimeter (10ml) of concentrated nitric acid ( $\text{HNO}_3$ ) and were boiled slowly till evaporated to 20 ml on hot plate. The beakers were allowed to cool, while another 5 ml of concentrated nitric acid ( $\text{HNO}_3$ ) was added and heated until digestion was completed. The samples were then evaporated again to dryness and the beakers were cooled, followed by the addition of 5 ml of hydrochloric acid (HCl) solution (1:1 v/v) concentration. The solution was warmed; 5 ml of sodium hydroxide (NaOH) was added and then filtered. The filtrates were

transferred to one hundred 100 ml volumetric flasks and diluted with distilled water to be used for the elemental analysis.

All the measurements were carried out in triplicate as a standard procedure<sup>6,7</sup>. The PTEs were read using Atomic Absorption Spectrophotometer (Buck Scientific, Model 211).

### **3.4.2 Digestion of Fish Samples**

For the purpose of this study, only the fish edible tissue (skin and flesh) was used for the analysis as it is these parts of the fish that is mostly consumed by people<sup>8</sup>. In order to obtain a representative sample, composites were prepared by taking the edible tissues (flesh and skin) of the two fish samples collected at each sampling location. The fish samples were carefully cut using a plastic knife and the edible tissue of the fish was removed and dried in an oven of about 105 °C for 24 hours. After drying, it was ground and milled using a blender. The powdered form was sieved and put in a plastic container and stored in desiccators until digestion. 1g from the ground muscle was placed in a 25 ml beaker. Afterwards, about 10 ml of concentrated HNO<sub>3</sub> (analytical grade, 69 % w/w) was poured into the beaker. A watch glass was placed at the mouth of the beaker and the beaker was placed on a hot plate with magnetic stirrer. Initially, the temperature was kept at about 40 °C for one hour to prevent vigorous reactions. Then the temperature was maintained at 140 °C for another 3 hours. Once the digestion was completed, all tissue samples were completely dissolved in the acid. Then the mixture was cooled to room temperature. Double distilled water was added into the vessel to dilute the mixture for AAS detection of PTEs. The sample was filtered by filter paper (Whatman No.1 grade). The filtrates were stored at 4 °C until the metal determination by AAS<sup>9</sup>.

### **3.5 Preparation of Standard Metal Concentrations**

Aqueous stock solutions were prepared for Pb, Cr, Cd, Cu, Ni, Fe, Mn and Zn using appropriate salts. Four working standards were prepared in triplicates for each metal by serial dilution of the stock solutions. The blank solutions were aspirated into the Atomic Absorption Spectrophotometer (Bulk Scientific model 211) as described by the manufacturers to obtain the absorbance of each of the samples and standard solutions for each of the metals. A calibration curve for absorbance versus concentration of the standard metal concentrations was prepared for each metal from which calibration graph for each of the metals in the sample was determined<sup>10</sup>.

### **3.6 PTEs Determination**

The filterates obtained from digestion of the water and fish samples were analysed for Pb, Zn, Cd, Cr, Ni, Cu, Fe and Mn using AAS. All measurements were carried out in triplicates as standard procedures<sup>6,7</sup>.

#### **3.6.1 Preparation of Standard Curve**

The standard curves for the PTEs were prepared bearing in mind that these elements occur in trace concentrations. Standard solutions were prepared from 1000 parts per million (ppm) stock solutions. 1 ml of the 1000 ppm stock solution was pipetted into a 100 ml volumetric flask and made up with distilled water. This solution was 10 ppm of the solution. From this solution, standard solutions of 0.2, 0.4, 0.6, 0.8 and 1 ppm were prepared by taking 0.2, 0.4, 0.6, 0.8 and 1 ml portions into 10 ml volumetric flasks and put to mark. These were then run in the air acetylene flame and standard curves for the various elements were obtained.

### 3.7 Method of Detection Limit

Three replicate blank samples were digested following the same procedures utilized for digesting the fish and water samples. Each blank was assayed for its PTEs contents (Cr, Cd, Zn, Fe, Mn, Cu, Ni and Pb) by AAS. The standard deviation, SD of the three replicate blanks was calculated to determine the method detection limit (MDL). MDL was then calculated as shown in equation (3.1)<sup>11</sup>.

$$MDL = yB + 3SD \quad \text{Equation 3.1}$$

Where;  $yB$  = mean of the replicate blank

SD = Standard deviation of the blank

### 3.8 Recovery Test

Recovery is one of the most commonly used techniques for validation of the analytical results and evaluating how far the method is acceptable for its intended purpose. In the study, the validity of the digestion procedure, precision and accuracy of AAS was determined by spiking fish and water samples with standard of known concentration in accordance with procedure<sup>11</sup>. The spiked and non-spiked fish and water samples were digested following the same procedure employed in the digestion of the respective samples and analyzed in similar procedure. Then the percentage recoveries of the analytes were calculated as shown in equation 3.2<sup>11</sup>.

$$\text{Recovery} = \frac{\text{CM in spike samples} - \text{CM in non-spike samples}}{\text{Amount added}} \times 100\% \quad \text{Equation 3.2}$$

Where, CM = concentration of metal of interest.

According to Harvey (2000) the acceptable ranges of percentage recovery for PTEs analysis were within 80 – 120 %.

### **3.9 Questionnaire Administration**

#### **3.9.1 Research Design**

The questionnaire objective for this project is the survey type. It is based on the use of questionnaire for collecting the needed information and does not involve the manipulation of any variable as they have already occurred.

#### **3.9.2 Target Population**

The target population is the people living within Lafenwa and Alagada metropolis of Ogun State, Nigeria.

#### **3.9.3 Sample and Sampling Technique**

The sampling technique used in the study was stratified random sampling and was done on the basis of sampling areas, local government and residential area. Samples of 100 questionnaires were used with a proportion of 100 % at Lafenwa and Alagada area respectively.

#### **3.9.4 Variables of the Study**

The variable for this research are dependent and independent variables. It is of great importance to specify these variables. The independent variables include characteristics of respondent such as; age, gender, sex, and occupation while dependent variables are the public perception of the river water usage and pollution control<sup>12,13</sup>.

#### **3.9.5 Potential Health Risk of PTEs**

Potential non-carcinogenic and carcinogenic health risks were determined using USEPA methods and exposure parameters recommended for management of contaminated land in South Africa<sup>14,15</sup>. Exposure assessment was carried out by calculating the average daily intake (*ADI*) of each PTE through ingestion, and dermal contact for adults and children (Equations 3.3 & 3.4). Adults and children are considered separately because of their behavioral and physiological differences<sup>16,17</sup>.

$$ADI_{ing} = \frac{C \times IR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \text{Equation 3.3}$$

$$ADI_{dermal} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \text{Equation 3.4}$$

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where;

$ADI_{ing}$  is the average daily intake of a PTE from fish and water via ingestion in mg per kg per day (mg/kg/day)

$C$  is the concentration of PTE in the fish and water in mg/kg,  $IR$  is the ingestion rate

$EF$  is the exposure frequency,

$ED$  is the exposure duration

$BW$  is the body weight of the exposed individual

$AT$  is the time period over which the dose is averaged.

$ADI_{dermal}$  is the average daily intake of PTE from water via dermal contact in mg/kg/day

$SA$  is the skin surface area

$AF$  is the soil-to-skin adherence factor and  $ABS$  is the fraction of the applied dose absorbed across the skin.

Hazard quotient (HQ) and hazard index (HI) were used to estimate the non-carcinogenic risk of PTEs in soil. HQ characterizes the health risk of non-carcinogenic adverse effects due to exposure to toxicants and is defined as the quotient of ADI or dose divided by the toxicity threshold value, which is referred to as the chronic reference dose (RfD) in mg/kg/day for a specific PTE, as shown in Equation 3.5

$$HQ = ADI/RfD \quad \text{Equation 3.5}$$

To assess the overall potential of non-carcinogenic effects posed by a PTE, the calculated values of HQ are summed to give HI (Equation 3.6).

$$HI = HQ_{ing} + HQ_{dermal}$$

$$CR = ADI \times CSF$$

Equation 3.6

Where;

CSF (mg/kg/day) is the cancer slope factor, which converts the estimated daily in-take of a PTE to an incremental risk of an individual developing cancer. The total excess life time cancer risk for an individual is ultimately calculated from the average contribution of the individual PTE across all exposure pathways using

Equation 3.7

$$CR_{total} = CR_{ing} + CR_{dermal}$$

Equation 3.7

Where;

$CR_{ing}$  and  $CR_{dermal}$  are risk contributions through ingestion and dermal pathways, respectively.

Values for all of the parameters used in the risk calculations are presented in Table 3.2

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**Table 3.2: Parameters Used in Risk Calculations**

Parameter	Unit	Child	Adult
Ingestion rate ( <i>IR</i> )	mg/day	200	100
Exposure frequency ( <i>EF</i> )	days/year	350	350
Exposure duration ( <i>ED</i> )	Years	6	24
Body weight ( <i>BW</i> )	Kg	15	70
Average time ( <i>AT</i> )	Days		
Inhalation rate ( <i>Inr</i> )	m <sup>3</sup> /day	10	20
Particulate emission factor ( <i>PEF</i> )	m <sup>3</sup> /kg	1.3 × 10 <sup>7</sup>	1.3 × 10 <sup>7</sup>
Skin surface area ( <i>SA</i> )	cm <sup>2</sup>	2100	5800
Soil-skin adherence factor ( <i>AF</i> )	mg/cm <sup>2</sup>	0.2	0.07
Dermal absorption factor ( <i>ABS</i> )	None	1	1
For carcinogens		365 × 70	365 × 70
For non-carcinogens		365 × <i>ED</i>	365 × <i>ED</i>

Source<sup>18</sup>

### **3.10 Data Analysis**

#### **3.10.1 Statistical Analysis**

Data collected were analyzed for descriptive statistics. Analysis of variance (one-way) and correlation analysis using the SPSS for Windows version 19.0 were also employed to interpret the similarities and differences among the means of data.

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## Chapter Four

### Results and Discussion of Findings

#### 4.1 Physical and Chemical Parameters of River Ogun water

The results of the physical and chemical parameters of the water samples across sampling point at Lafenwa and Alagada, Ogun State for both dry and wet season are shown in Appendix 1 and 2. The mean values of the physical and chemical properties of water in Lafenwa and Alagada areas of River Ogun, Ogun State for dry and wet seasons are reported in this study and presented in Tables 1 and 2. The pH values of the river varied at each sampling points. In all the water samples, the highest pH value recorded was 7.86 for the dry season while the lowest pH was 6.10 for the wet season. The mean pH values across the sampling points ranged from  $6.57 \pm 0.33 - 7.43 \pm 0.43$  and  $6.77 \pm 0.41 - 6.79 \pm 0.33$  for dry and wet season respectively. However, mean value of pH across the sampling points were not significantly different from each other.

The water samples showed slight changes in temperature seasonally. The mean temperature ranged from  $26.59 \pm 0.17 \text{ }^\circ\text{C} - 27.27 \pm 0.72 \text{ }^\circ\text{C}$  and  $26.47 \pm 1.05 \text{ }^\circ\text{C} - 26.77 \pm 1.10 \text{ }^\circ\text{C}$  for dry and wet seasons respectively. The highest temperature value of  $28.64 \text{ }^\circ\text{C}$  at Lafenwa and Alagada  $28.42 \text{ }^\circ\text{C}$  was recorded for dry and wet season respectively. While the lowest temperature value of  $26.10 \text{ }^\circ\text{C}$  and  $16.0 \text{ }^\circ\text{C}$  at Lafenwa for wet and dry season respectively. In case of Alagada the highest temperature was  $28.10 \text{ }^\circ\text{C}$  and  $27.31 \text{ }^\circ\text{C}$  was recorded for dry and wet season respectively. While the lowest temperature value of  $26.12 \text{ }^\circ\text{C}$  and  $24.50 \text{ }^\circ\text{C}$  was recorded for dry and wet season respectively.

The mean electrical conductivity (EC) ranged from  $13.84 \pm 4.38 \text{ } \mu\text{S/cm} - 36.67 \pm 29.51 \text{ } \mu\text{S/cm}$  and  $13.84 \pm 4.67 \text{ } \mu\text{S/cm} - 47.21 \pm 32.86 \text{ } \mu\text{S/cm}$  for dry and wet season respectively.

The highest electrical conductivity (EC) value recorded was 37.45  $\mu\text{S}/\text{cm}$  and 43.70  $\mu\text{S}/\text{cm}$  for Lafenwa dry and wet season respectively while the lowest value of 10.18  $\mu\text{S}/\text{cm}$  and 10.48  $\mu\text{S}/\text{cm}$  for dry and wet season respectively. In case of Alagada the highest value obtained was 110.4  $\mu\text{S}/\text{cm}$  and 87.24  $\mu\text{S}/\text{cm}$  for wet and dry season respectively. While the lowest value was 10.10  $\mu\text{S}/\text{cm}$  and 10.72  $\mu\text{S}/\text{cm}$  for wet and dry season respectively.

The TDS showed slight relationship with the electrical conductivity. The mean total dissolved solids ranged from  $53.50 \pm 10.21 \text{ mg/L}$  –  $57.25 \pm 9.74 \text{ mg/L}$  and  $23.00 \pm 4.62 \text{ mg/L}$  –  $40.00 \pm 2.58 \text{ mg/L}$  for wet and dry season respectively.

In Tables 4.1.3 to 4.1.8, PTEs were detected in both surface water and fish tissues samples obtained from Lafenwa and Alagada. The presence of these PTEs may be attributable to discharges from agricultural wastes, municipal wastes, geology of dam bed and catchment area. These have been reported in other studies<sup>1</sup>. In similar studies, detected the presence of PTEs in fish tissue from rivers and lakes in different water bodies in Nigeria and they also attribute their presence in fish tissue to accumulation from water bodies<sup>2,3,4</sup>. Thus, the presences of PTEs contaminants in fresh water bodies and in fish tissue are common<sup>9</sup>.

In Table 4.1.9, with the exception of Ni, Mn, Fe and Cr, mean concentration of Cu, Cd, Pb and Zn in fish tissues were generally higher than levels found in water samples in Lafenwa and Alagada. This is similar to the pattern observed for the surface water resource, suggesting that high levels of Cr in the muscle of tilapia fish could have resulted through the ingestion of food and water from the river or through the gills or other biological membrane<sup>6</sup>. Similarly, for all the stations, Fe level were observed to be highest in fish and water samples.

**Table 4.1: Physical and Chemical Parameters (PTEs) of Ogun River Water for Dry Season**

Parameters	Lafenwa	Alagada	WHO (2011) Limit	
<b>pH</b>	7.43 ± 0.43	6.57 ± 0.33	6.5-8.5	
<b>Temp. (°C)</b>	26.59 ± 0.17	27.27 ± 0.72	30	
<b>EC (µS/cm)</b>	13.84 ± 4.39	36.67 ± 29.51	1,500	
<b>TDS (mg/ L)</b>	39.7 ± 1.80	38.87 ± 1.65	250	
<b>PTEs</b>	<b>Lafenwa Up</b>	<b>Lafenwa Down</b>	<b>Alagada Up</b>	<b>Alagada Down</b>

Source: Field Work, 2021.

**Table 4.2: Physical and Chemical Parameters of Ogun River Water for Wet Season**

Parameters	Lafenwa	Alagada	WHO (2011) Limits
pH	6.79±0.33	6.77±0.41	6.5-8-5
Temp. (°C)	26.78±1.10	26.47±1.05	30
EC (µS/cm)	13.84±4.67	47.21±32.86	1500
TDS (mg/ L)	72.09±2.70	72.81±5.27	250

Source : Field Work,. 2021.

Key SL1 = SAMPLING LOCATION 1 (Lafenwa)  
SL2 = SAMPLING LOCATION 2 (Alagada)

	Stream	Stream	Stream	Stream
Cu	0.787 ± 0.625	2.13 ± 2.378	0.907 ± 0.483	1.557 ± 2.161
Zn	0.950 ± 0.287	0.850 ± 0.195	0.46 ± 0.462	0.477 ± 0.330
Ni	0.580 ± 0.443	1.167 ± 0.819	0.627 ± 0.360	0.607 ± 0.203
Pb	1.040 ± 0.144	0.773 ± 0.841	0.787 ± 0.068	1.837 ± 0.115
Mn	0.590 ± 0.060	1.187 ± 0.398	1.163 ± 0.465	0.530 ± 0.254
Fe	3.050 ± 3.248	18.917 ± 22.589	5.20 ± 0.356	17.013 ± 3.213
Cr	1.250 ± 0.951	1.343 ± 0.847	0.233 ± 0.025	0.460 ± 0.044
Cd	0.270 ± 0.052	0.100 ± 0.046	0.263 ± 0.074	0.347 ± 0.081

**Table 4.3 Mean ± SD Concentration of PTEs in Water Ogun River Dry Season**

Source: Field Work, 2021

**Table 4.3.1 Mean ± SD Concentration of PTEs in Sediment Ogun River Dry Season**

Source: Field Work, 2021.

<b>PTEs</b>	<b>Lafenwa Up Stream</b>	<b>Lafenwa Down Stream</b>	<b>Alagada Up Stream</b>	<b>Alagada Down Stream</b>
Cu	8.677 ± 0.569	2.163 ± 2.435	1.557 ± 2.161	3.267 ± 0.393
Zn	0.880 ± 0.026	0.550 ± 0.426	0.477 ± 0.330	2.440 ± 0.495
Ni	0.870 ± 0.085	1.233 ± 0.791	0.607 ± 0.203	0.373 ± 0.047
Pb	0.720 ± 0.100	1.210 ± 0.680	1.837 ± 0.115	3.847 ± 0.112
Mn	2.523 ± 0.420	1.593 ± 0.716	0.530 ± 0.254	1.647 ± 0.130
Fe	2.270 ± 1.123	4.903 ± 1.683	17.013 ± 3.213	6.543 ± 1.500
Cr	0.010 ± 0.006	1.150 ± 1.099	0.460 ± 0.044	0.015 ± 0.007
Cd	0.307 ± 0.015	0.170 ± 0.165	0.347 ± 0.081	0.243 ± 0.025

**Table 4.3.2 Mean ± SD Concentration of PTEs in Fish Ogun River Dry Season**

PTEs	Lafenwa Up	Alagada Down	Alagada Up	Alagada Down
Cu	4.930 ± 0.096	0.380 ± 0.020		
Zn	1.263 ± 0.049	0.907 ± 0.021		
Ni	0.087 ± 0.015	0.743 ± 0.015		
Pb	2.300 ± 0.044	0.943 ± 0.575		
Mn	0.547 ± 0.047	0.647 ± 0.045		
Fe	5.673 ± 0.304	28.110 ± 2.025		
Cr	0.747 ± 0.057	0.487 ± 0.015		
Cd	0.447 ± 0.047	0.120 ± 0.010		

Source : Field Work, 2021

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	Stream	Stream	Stream	Stream
Cu	2.113 ± 0.993	3.00 ± 1.322	1.490 ± 0.483	3.673 ± 2.031
Zn	0.370 ± 0.454	0.523 ± 0.267	0.577 ± 0.206	0.713 ± 0.449
Ni	0.337 ± 0.307	0.463 ± 0.091	0.497 ± 0.333	0.990 ± 0.864
Pb	1.267 ± 0.744	2.430 ± 0.490	3.40 ± 0.291	1.453 ± 0.872
Mn	1.970 ± 1.446	0.720 ± 0.056	1.100 ± 0.460	0.770 ± 0.236
Fe	2.750 ± 1.997	8.197 ± 3.406	2.923 ± 2.301	6.180 ± 5.667
Cr	0.507 ± 0.757	1.597 ± 0.328	1.383 ± 0.210	0.527 ± 0.446
Cd	0.363 ± 0.126	0.617 ± 0.327	0.570 ± 0.157	0.370 ± 0.056

**Table 4.4 Mean ± SD Concentration of PTEs in Water Ogun River Wet Season**

Source: Field Work, 2021.

**Table 4.4.1: Descriptive Statistics of PTEs Concentration in Sediment Wet Season**

Source: Field Work, 2021.

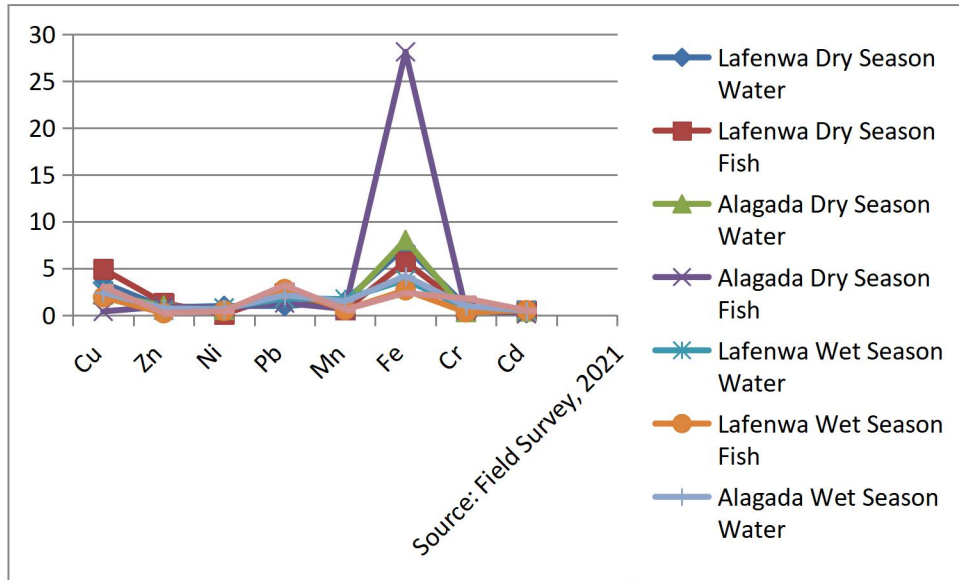
<b>PTEs</b>	<b>Lafenwa Up Stream</b>	<b>Lafenwa Down Stream</b>	<b>Alagada Up Stream</b>	<b>Alagada Down Stream</b>
Cu	3.423 ± 0.516	1.920 ± 2.669	1.687 ± 0.301	2.730 ± 0.255
Zn	0.633 ± 0.078	0.480 ± 0.257	0.170 ± 0.010	1.350 ± 0.246
Ni	1.043 ± 0.015	1.043 ± 0.635	0.317 ± 0.093	0.693 ± 0.177
Pb	1.83 ± 0.121	1.590 ± 1.254	1.457 ± 0.346	2.187 ± 0.505
Mn	2.183 ± 0.142	1.927 ± 0.707	3.497 ± 0.312	0.530 ± 0.123
Fe	2.84 ± 0.161	1.230 ± 0.528	4.697 ± 0.543	2.877 ± 0.957
Cr	0.21 ± 0.01	0.753 ± 0.192	0.090 ± 0.010	1.827 ± 0.116
Cd	0.597 ± 0.015	0.640 ± 0.036	0.061 ± 0.035	0.550 ± 0.038

**Table 4.4.2 Mean ± SD Concentration of PTEs in Fish Ogun River Wet Season**

<b>PTEs</b>	<b>Lafenwa</b>	<b>Alagada</b>
Cu	1.900± 0.030	3.023 ± 0.040
Zn	0.137± 0.119	0.207 ± 0.031
Ni	0.463 ± 0.025	0.427 ± 0.083
Pb	2.757 ± 0.021	1.173 ± 0.169
Mn	0.553 ± 0.042	0.577 ± 0.032
Fe	2.650 ± 0.026	2.360 ± 0.040
Cr	0.267± 0.015	1.767± 0.042
Cd	0.497 ± 0.015	0.503 ± 0.025

Source : Field Work, 2021

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**Figure 4.1:** Showing the Mean Concentration of PTEs in Water and Fish Tissue in the selected locations

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These metals could eventually reach the human biological system through consumption of the fish or drinking of the water from Lafenwa and Alagada. Long term exposure to Cr in humans can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation<sup>7</sup>. The mean concentrations of the Cr, Cd, Cu, Pb, Ni and Zn in the surface water samples and in Tilapia fish from the sample stations are illustrated in Table 4.1.9.

Generally, observed levels of metals concentrations in the fish tissue were higher when compared to patterns observed for surface water across all locations, with a few exceptions like Cu and Ni concentration. In Table 4.1.9, mean concentration of Fe, Cu, Pb and Zn in fish tissues were generally higher than levels found in water samples. Similarly, for both locations, Fe level was observed to be highest, while Cd was lowest for both fish and water samples.

Similarly, observed levels of metal concentrations in the fish tissue were higher when compared to patterns observed for surface water across all stations, with a few exceptions like Cu and Fe concentration at Lafenwa dry season, Fe and Pb concentrations in Alagada dry season, in Lafenwa wet season and Alagada wet season respectively<sup>9,11</sup>. Also, agreed with this trend of higher concentrations of PTEs found in fish compared to water<sup>11</sup>. Similar trend was concluded that PTEs are being transferred to fishes and to predators of fishes from water where the concentration of PTEs will increase until it finally ends up in human beings in a process referred to as biomagnification<sup>12</sup>. The presence of PTEs in the surface water of Lafenwa and Alagada as seen in this study could be attributed to the intense agricultural and industrial activities that occur around the dam. For example the presence of chromium in water has been linked to agricultural land use, emissions of chromium-based automotive catalytic converters as well as chromium compound which is leached by rain water<sup>13</sup>. This may account for the presence of chromium in the surface water of Lafenwa and Alagada as the reservoir is characterized by heavy presence of

agricultural land use, industries and residential activities. Again, the presence of Pb and Ni as seen from this study could be attributed to the discharge of hazardous wastes such as old battery wastes, components of automobiles and other items containing stainless steel including nickel alloys into Lafenwa and Alagada.

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**Table 4.5: t-Test Paired Sample for Means of PTEs levels in Water Sample and Fish Tissue**

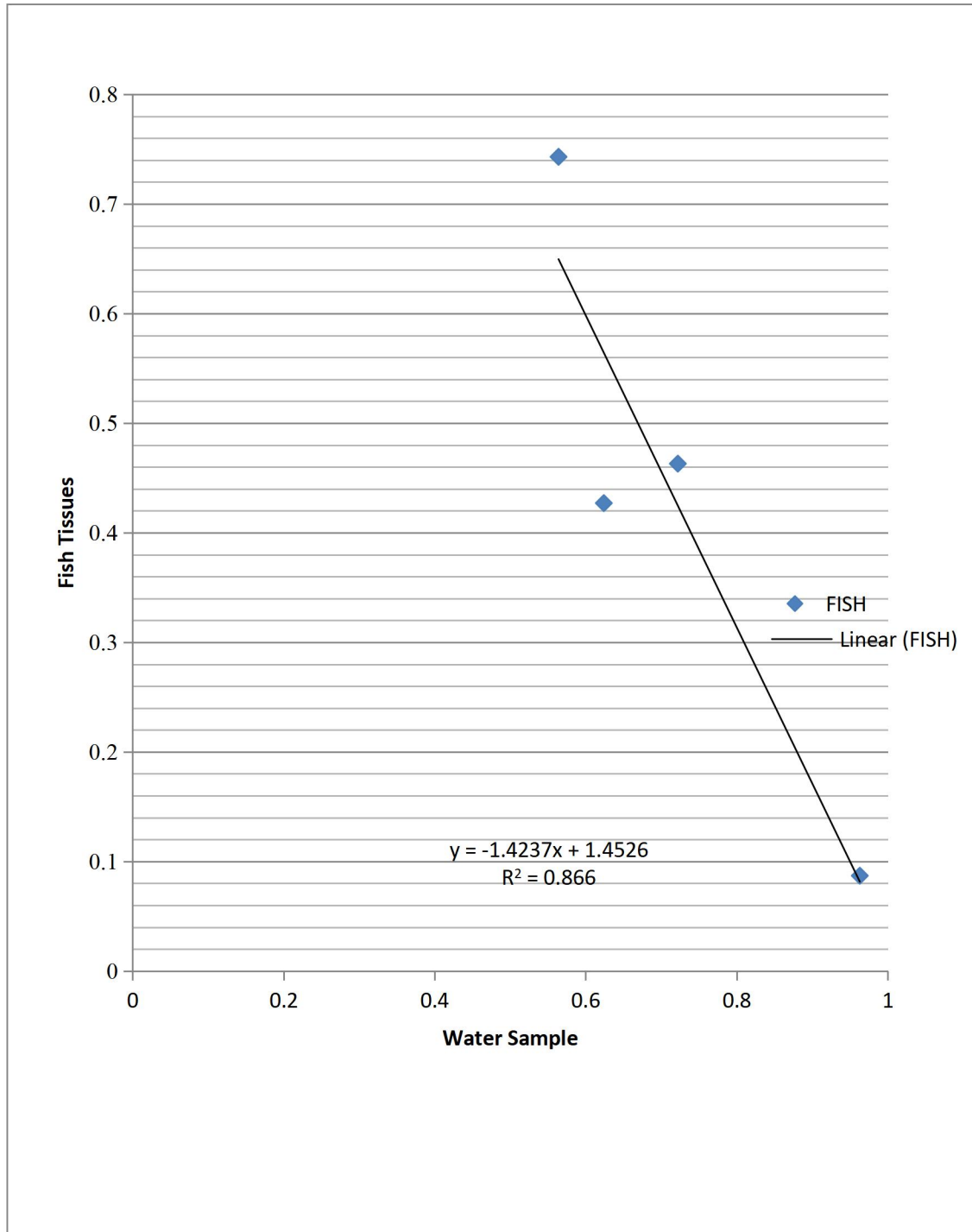
Station	Sample	Mean	Variance	Obs	Df	t Stat	P(T<=t) One-tail	t Critical one-tail	P(T<=t) two-tail	t Critical two-tail
SL1 (D)	Water Fish Tissue	2.008 2.001	5.459 4.635	8	7	0.01974	0.4924	1.89458	0.98480	2.36462
SL2 (D)	Water Fish Tissue	1.9707 4.0839	6.4709 94.3667	8	7	-0.8191	0.2199	1.8946	0.4397	2.3646
SL1 (W)	Water Fish Tissue	1.5490 1.3505	1.1654 1.1810	8	7	1.6045	0.0763	1.8946	0.1526	2.3646
SL2 (W)	Water Fish Tissue	1.6101 1.5712	1.5046 1.5140	8	7	0.3125	0.3819	1.8946	0.7637	2.3646

Source: Field work, 2021.

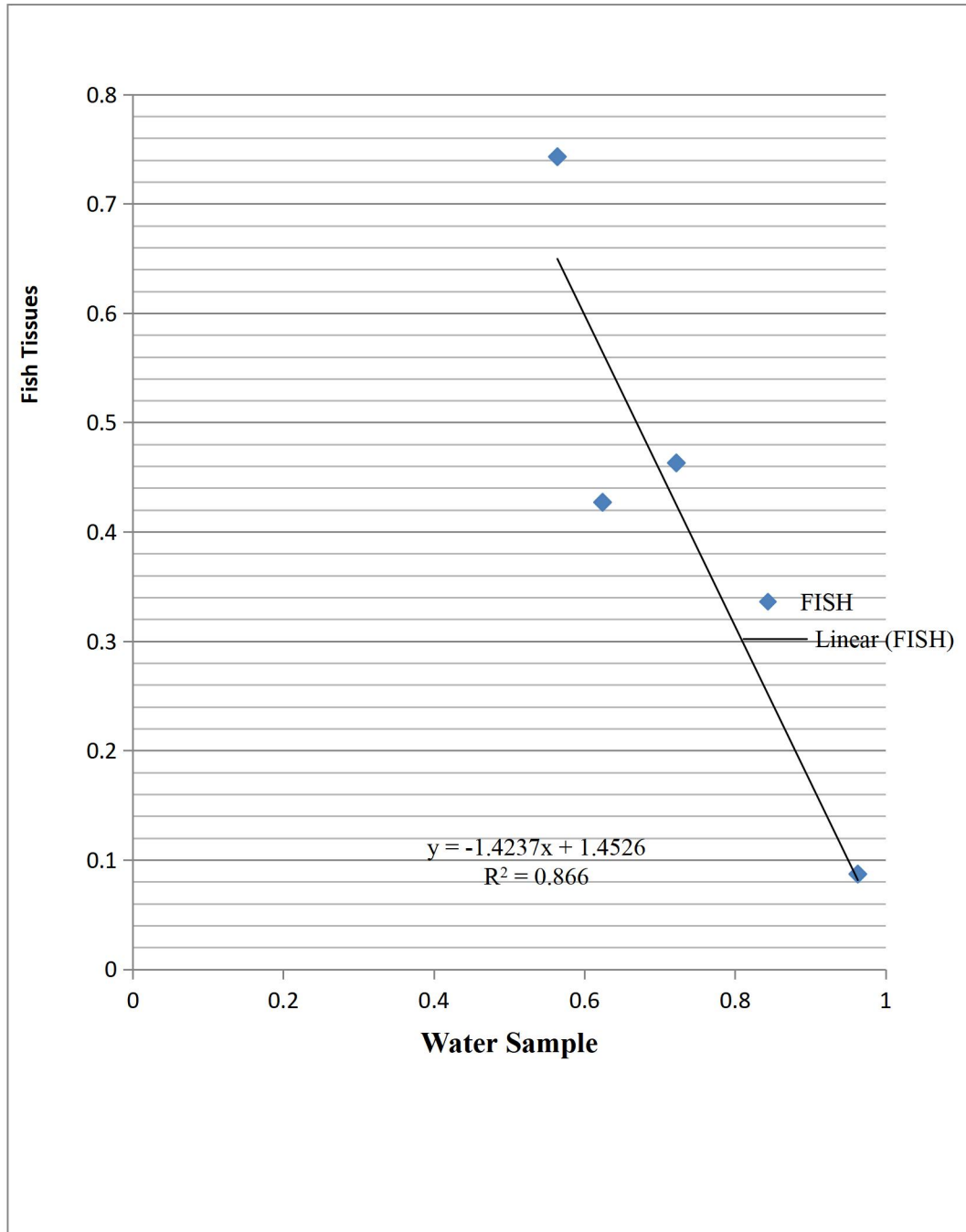
The results of student's t-test to determine the level of significant differences in levels of concentrations between water samples and fish tissues revealed a moderate to very strong relationship, implying that a unit increase in concentration level in water will lead to an increase in concentration levels in fish tissues.

In Lafenwa during dry season, there was a significant difference in the levels of metals concentrations between water sample and fish tissues at  $p < 0.05$ ,  $d = 0.0197$ . Similarly, in Alagada dry season, Lafenwa during wet season and Alagada wet season, the relationship between metals concentrations in water samples and accumulation in fish did not show any significant difference at  $p > 0.05$ ,  $d = -0.8191$ ,  $p > 0.05$ ,  $d = 1.6045$  and  $p > 0.05$ ,  $d = 0.3125$  respectively. The results of student's t-test to determine the level of significant differences in levels of concentrations between water samples and fish tissues revealed a moderate to very strong relationship, implying that a unit increase in concentration level in water will lead to an increase in concentration levels in fish tissues. Results of the multiple correlation between concentration levels of Cr, Cu, Zn, Ni, Pb, Mn, Fe and Cd in water and fish tissue are presented in Table 4.11 with fish tissue sample as dependent variable, while water sample as independent variable. Cr, Cu, Zn, Ni, Pb, Mn, Fe and Cd in water and fish recorded positive coefficient value (0.28927) with intercept values of 1.1514. This indicates that, for every increase in Cr, Cu, Zn, Ni, Pb, Mn, Fe and Cd in water will lead to increase in one unit of Cr, Cu, Zn, Ni, Pb, Mn, Fe and Cd in the fish tissue living in the water of the areas.

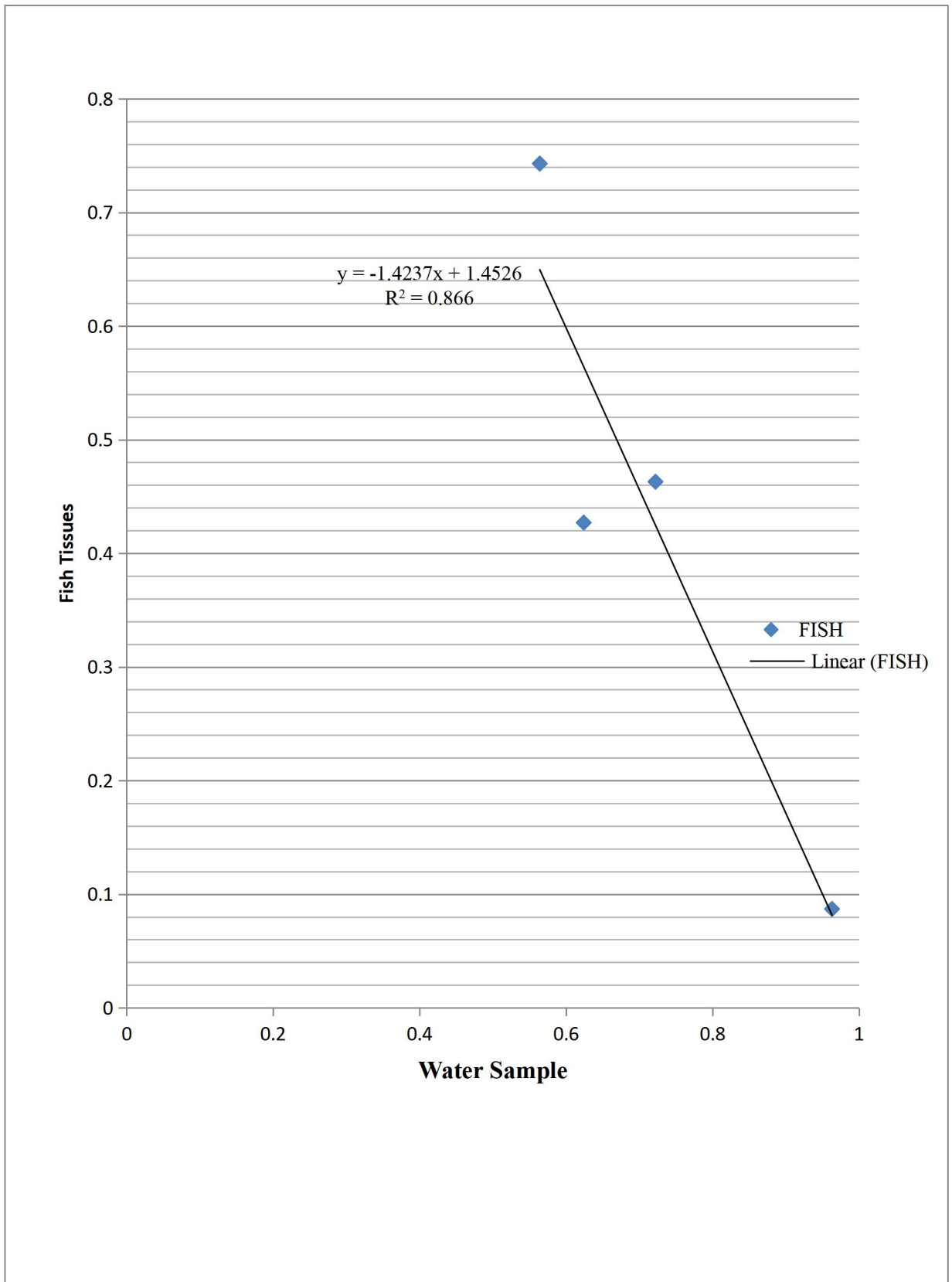
The mean values of the concentrations of each of the selected PTEs contaminants in the Tilapia fish and water samples were compared with the WHO guidelines, Federal Environmental Protection Agency (FEPA) and Nigerian Industrial Standard (NIS) in order to ascertain the pollution status of the chemical contaminants (Table 4.12).



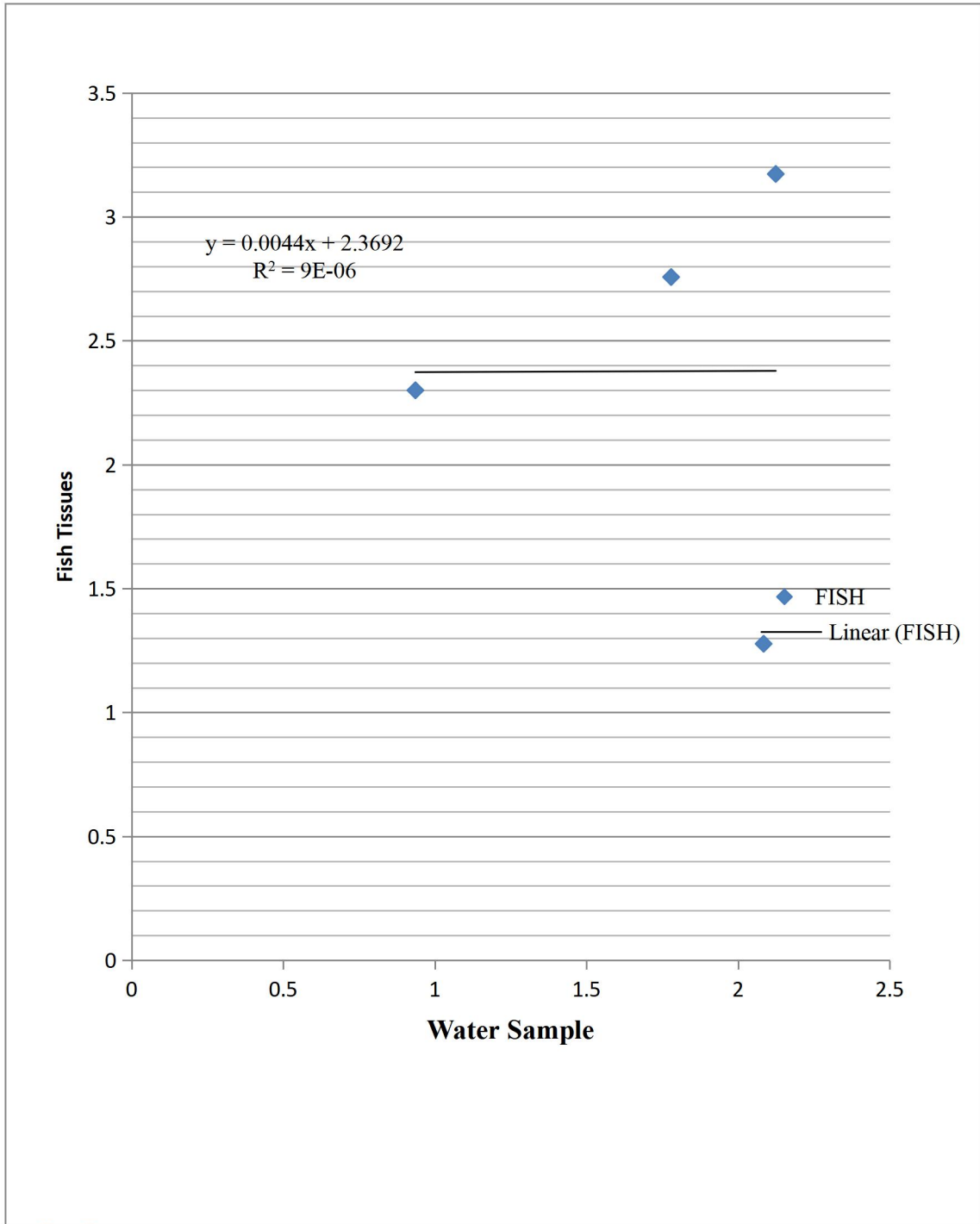
**Figure 4.2:** Relationship in the concentration of Cu in Surface Water and Fish Muscle  
 Source: Field Work, 2021.



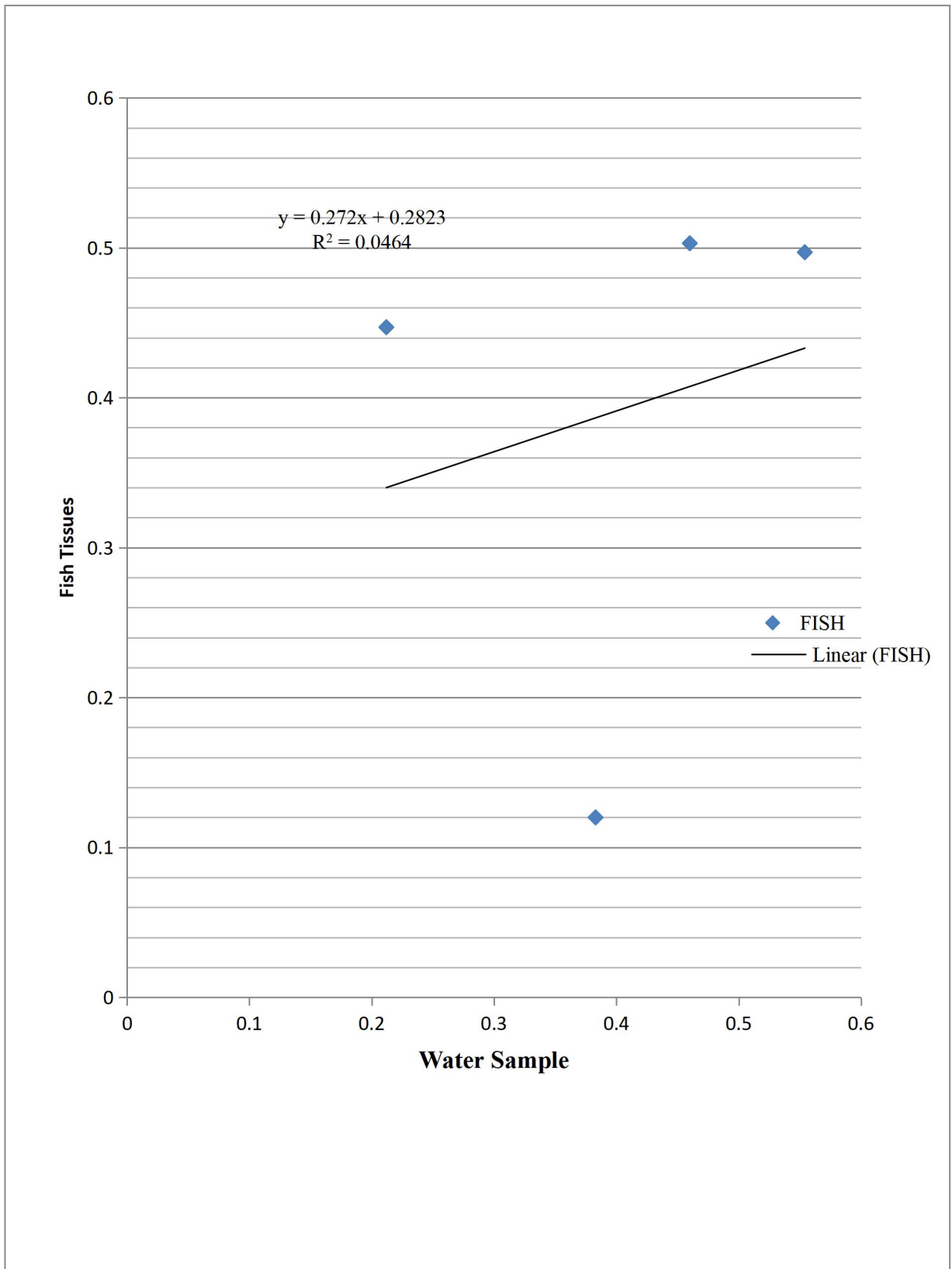
**Figure 4.3:** Relationship in the Concentration of Zn in Surface Water and Fish Muscle  
Source: Field Work, 2021.



**Figure 4.4:** Relationship in the concentration of Ni in surface water and fish muscle  
Source: Field Work, 2021.

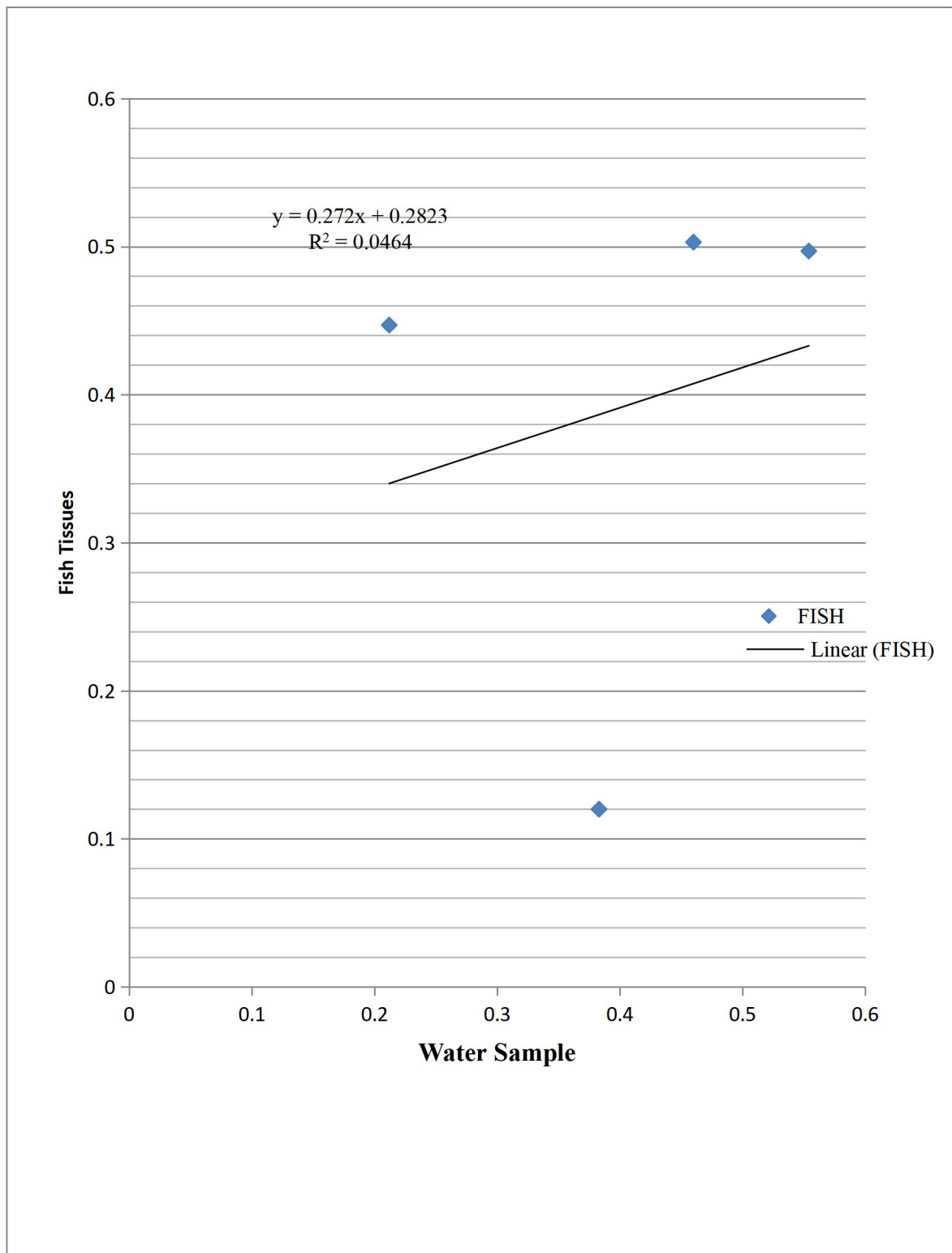


**Figure 4.5:** Relationship in the Concentration of Pb in Surface Water and Fish Muscle  
 Source: Field Work, 2021.



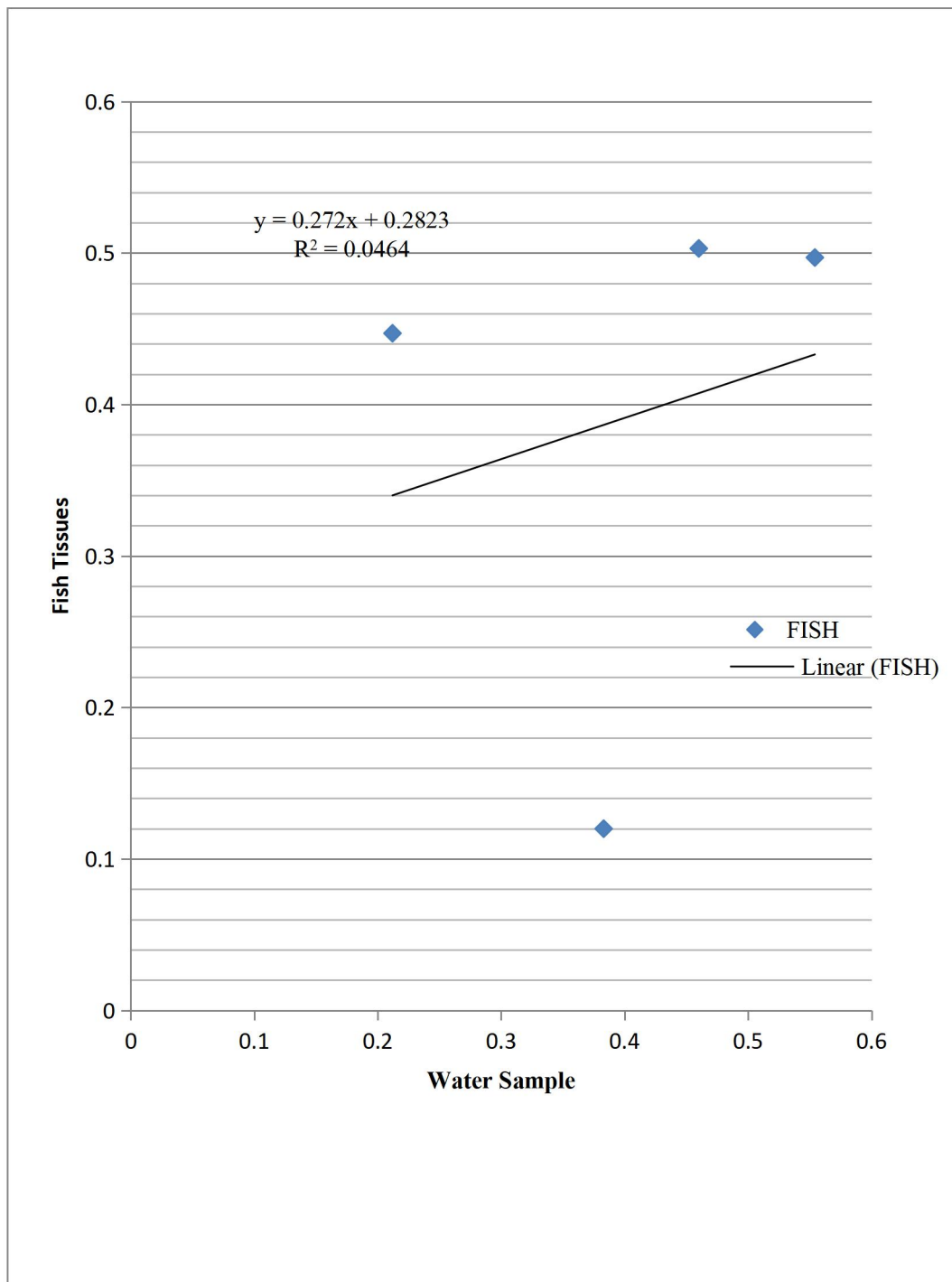
**Figure 4.6:** Relationship in the Concentration of Mn in Surface Water and Fish Muscle

Source: Field Work, 2021.



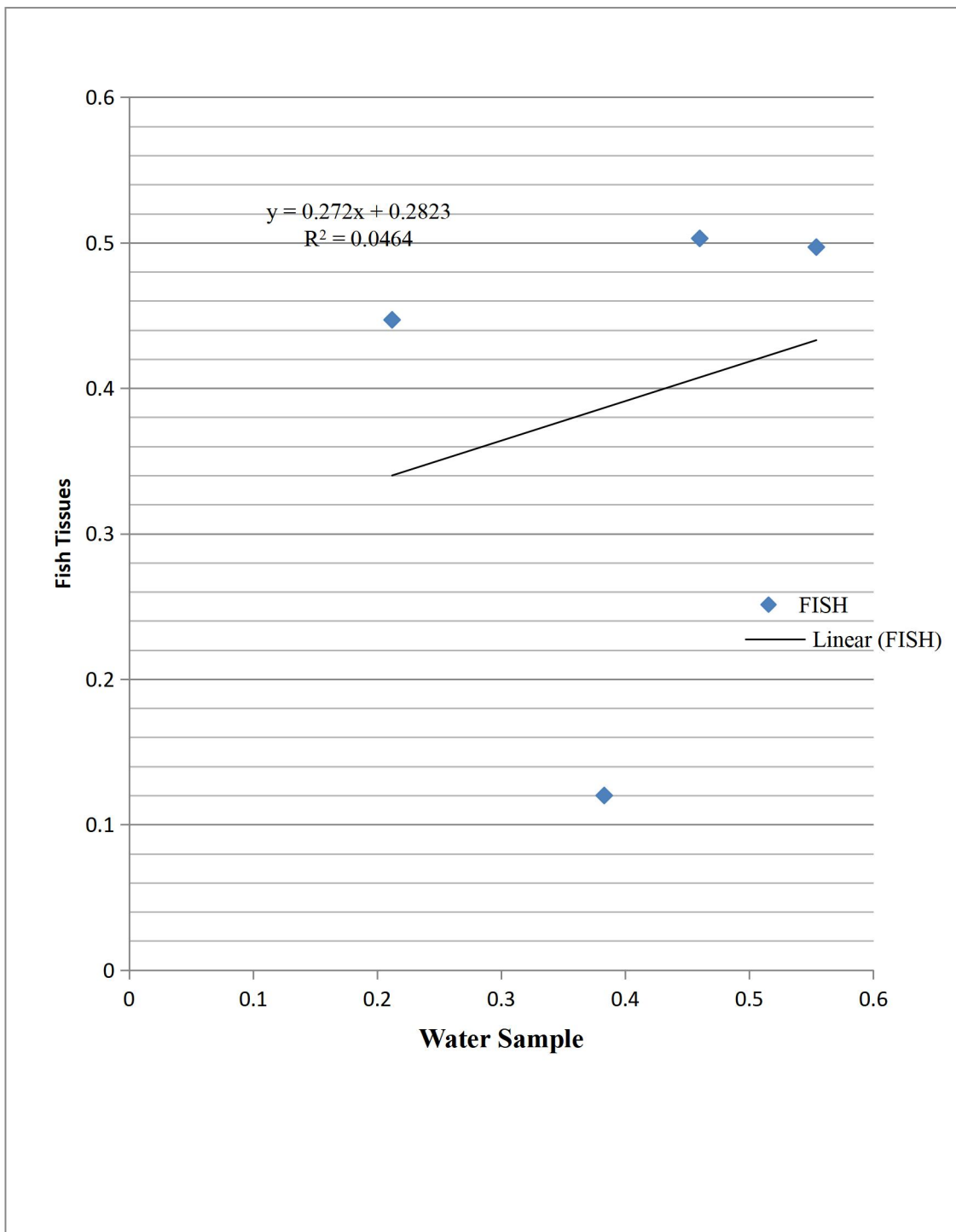
**Figure 4.7:** Relationship in the Concentration of Fe in Surface Water and Fish Muscle

Source: Field Work. 2021.



**Figure 4.8:** Relationship in the Concentration of Cr in Surface Water and Fish Muscle

Source: Field Work, 2021.



**Figure 4.9:** Relationship in the concentration of Cd in surface water and fish muscle

Source: Field Work, 2021.

In Fig. 4.1 to 4.3 the relationship between Cu, Zn and Ni level water sample and fish tissue was identified that, for every decrease in Cu in water will lead to decrease in one unit of Cu, Zn and Ni in the fish tissue living in the water of the area. This implies that, Cu, Zn and Ni content in the water is directly associated with Cu, Zn and Ni concentration with numerical coefficient values of 1.423. The coefficient of determination ( $r^2 = 0.866$ ) in shows that, variation Cu, Zn and Ni level in the fish tissue could be explained by 86 % variation in Cu, Zn and Ni level in water of the river, and fish recorded negative coefficient value (1.423) with intercept values of 1.452.

In Fig. 4.4 the relationship between Pb level water sample and fish tissue was identified that, for every increase Pb in water will lead to increase in one unit of Pb in the fish tissue living in the water of the area. This implies that, Pb content in the water is directly associated with Pb concentration with numerical coefficient values of 0.004. The coefficient of determination ( $r^2 = 9E-06$ ) in shows that, variation Pb level in the fish tissue could be explained by 0 % variation in Pb level in water of the dam, and fish recorded positive coefficient value (0.004) with intercept values of 2.369.

In Fig.4.5 to 4.8 the relationship between Mn, Fe, Cr and Cd level water sample and fish tissue was identified that, for every increase in Mn, Fe, Cr and Cd in water will lead to increase in one unit of Mn, Fe, Cr and Cd in the fish tissue living in the water of the area. This implies that, Mn, Fe, Cr and Cd content in the water is directly associated with Mn, Fe, Cr and Cd concentration with numerical coefficient values of 0.272. The coefficient of determination ( $r^2 = 0.046$ ) shows that, variation Cu, Zn and Ni level in the fish tissue could be explained by 4.6 % variation in Mn, Fe, Cr and Cd level in water of the dam, and fish recorded positive coefficient value (0.272) with intercept values of 0.282.

**Table 4.6: Relationship between PTEs in Water and Fish Tissue of the Entire Samples**

	Coefficients	Standard Error	t Stat	P value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	1.15144	0.23034	4.99889	2.33696E-05	0.68102	1.62185	0.68102	1.62185
Fish	0.28927	0.04328	6.68340	2.10105E-07	0.20088	0.37766	0.20088	0.37766

Source: Field work, 2021.

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**Table 4.7: Comparison of Mean Concentration of Selected PTEs in Tilapia fish and Water Sample of Ogun River with FEPA, WHO and NIS**

Mean Concentration of Selected PTEs in Tilapia Fish				Mean Concentration of Selected PTEs in Surface Water		
PTEs	Mean Values in mg/kg (Tilapia fish)	FEPA (2003) Standard	WHO (2008) Standard	Mean Values in ppm (Surface water)	NIS (2007) Standard	WHO (2011) Standard
Cadmium	0.120	NG	0.05	0.383	0.003	0.003
Chromium	0.487	0.15	10.0	0.333	0.05	0.05
Copper (Cu)	0.380	1-30	20.0	2.213	1.0	2.0
Lead (Pb)	1.277	2.0	0.05	2.084	0.01	0.01
Nickel (Ni)	0.743	0.5	2.0	0.564	0.02	0.02
Manganese	0.647	0.4	04	1.181	0.4	0.4
Zinc	0.007	75.0	40.0	0.998	NG	3.0
Iron	28.11	0.3	0.32	8.01	0.3	0.3

FEPA (2003); WHO (2008) NG = No guideline *WHO (2011)*; *NIS (2007)* NG = No guideline

Source: Field Survey, 2021.

Table 4.12 Comparison of Mean Concentration of Selected PTEs in Tilapia fish and Water Sample of Ogun River with Federal Environmental Protection Agency, World Health Organization and Nigerian Industrial Standard guideline/Recommendation.

From Table 4.12, it was found that with an exception of zinc, quality of water samples from Ogun River did not meet the NIS and WHO permissible limits for drinking water and thus unsafe for human and animal consumption due to contamination by Cr, Cd, Fe, Mn, Cu, Pb and Ni all of which are detrimental to human health. There are no guidelines for permissible concentrations of Cd in fish according to FEPA, but according to WHO (2011), the permissible level of Cd in fish is 0.05 mg/kg and the mean value of Cd in the fish muscle of this study is 0.120 mg/kg. This shows that the concentration of Cd in this study is higher than WHO limits; suggesting that the fish from river is contaminated with cadmium poisoning.

In view of the fact that river Ogun is used for drinking, fishing and tilapia fish is widely consumed by communities around the river, it is of great concern that Cd level in fish is higher above set permissible limit, more especially since Cr is extremely toxic and carcinogenic<sup>14</sup>. The observed finding is similar to other studies conducted on Nigerian Rivers<sup>15</sup>. A higher concentration of Cd (0.56 mg/kg) in the flesh of Tilapia fish from Elemi River, Ado-Ekiti<sup>15</sup>. Also, Cd average levels of 2.16 mg/kg in fish from Forcados River<sup>16</sup>. The Cd levels in both studies exceeded the WHO maximum permissible limit of 0.05 mg/kg for fish and fish products.

The concentration of Cr in the fish samples from Ogun River is seen to be lower than the WHO set standard for fish, but higher than the FEPA standards of 0.15 mg/kg, indicating contaminated with Chromium according to FEPA standards. Cr is actively poisonous, carcinogenic to humans and on contact with the skin, it triggers cancer, dermatitis, allergies and irritation of the eyes and respiratory passage, damage to the liver and kidney,

rickets in children, alteration, hypertension and possibly death<sup>17</sup>. 1.10 mg/kg Cr mean concentration in the fish tissue from Ikpoba River, Nigeria during the wet season constituting immediate hazards<sup>18</sup>. This concentration also exceeded the recommended levels for fish and fisheries products by the FEPA (2003). Hexavalent Cr is very toxic and mutagenic when inhaled and is a known human carcinogen, and exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation<sup>19</sup>. Mean concentration of Cu in fish samples (0.38 mg/kg), was below the WHO and FEPA standards of 20 mg/kg and 1 - 30 mg/kg respectively for human consumption.

This means that the fish from Ogun River is not polluted with copper, thus the consumption of tilapia fish from the river does not indicate an immediate health hazard as far as Cu concentration is concerned. Although copper is a trace element that is essential to humans, excess copper can cause health problems such as diarrhea, dizziness, gastrointestinal disorder, renal disease and vomiting<sup>20</sup>. Similar pattern was recorded for Tilapia fish from Lake Edku, likewise, fish of Northern Delta Lakes of Egypt and fish from Lake Köyceğiz of Turkey<sup>21,22,23</sup>.

Lead concentration is seen to be higher than the WHO standards of 0.05 mg/kg but lower than the FEPA standards of 2.0 ppm. This implies that the concentration of Pb in the fish sample from Ogun River is above the WHO limit indicating fish contamination with Pb. Pb is toxic even at a low concentration and has no known functions in biochemical processes<sup>24</sup>. Pb in fish could be detrimental to the health of residents who use the river water for irrigation and consume the fish therein<sup>25</sup>. Pb can also result in possible kidney damage, nervous system damage, nausea, severe vomiting, and damage to central nervous system and immune system, cancer, interference with vitamin D metabolism and constant headache<sup>26</sup>. Ni concentration in the fish was higher than level of FEPA permissible limits and below the WHO permissible limit of 2.0 mg/kg. This implies that the fish sample

from Ogun River is contaminated with Nickel according to FEPA but not contaminated according to WHO. Nickel is often used in electroplating of materials and readily released into the environment which is drained into the river. Excessive exposure to nickel can cause health effects on the blood, lungs, nose, kidney and reproductive system<sup>27</sup>. Other studies on bioaccumulation on fish from Nigerian rivers have recorded Ni levels that are higher than the present study<sup>28,29</sup>. Zinc (Zn) level in fish samples from in Ogun river was far below the WHO and FEPA standards of 40mg/kg and 75mg/kg. This shows that fish caught from the Dam is not polluted with zinc. This may not pose immediate problem, however once it accumulates, it becomes an issue of concern because excessive intake of zinc may lead to vomiting, dehydration, abdominal pain and lethargy<sup>30</sup>.

Results obtained for human health risk assessment are presented in Table 4.2. For non-carcinogenic risk, comparison of HQ values indicates that ingestion was the most significant exposure route for both children and adults, followed by dermal contact. The HI (summation of HQ across the two exposure pathways) values were less than 1 for Cr, Ni, Fe, Cu, Cd, Mn, Pb and Zn indicating that there is no significant on-carcinogenic risk associated with exposure to the average concentrations of the above PTEs in Ogun River. Among the PTEs studied, Pb was the largest contributor to non-carcinogenic risks. This is of particular concern, given the impact that this element can have on children's development, even at low concentrations. Risk from the other metals followed the order Cd > Mn > Fe > Ni > Cu > Cr > Zn for children and Fe > Cd > Mn > Ni > Cr > Cu > Zn for adults.

**Table 4.8: Health Risk Assessments for Children and Adult**

Element	HQ <sub>ing</sub>	HQ <sub>Dermal</sub>	HI <sub>Children</sub>	HQ <sub>ing</sub>	HQ <sub>Dermal</sub>	HI <sub>Adult</sub>	CR total children	CR total Adult
<b>Cu</b>	2.3x10 <sup>-4</sup>	1.3x10 <sup>-4</sup>	3.6x10 <sup>-4</sup>	6.0x10 <sup>-6</sup>	8.5x10 <sup>-5</sup>	9.1x10 <sup>-5</sup>		
<b>Zn</b>	2.8x10 <sup>-6</sup>	1.3x10 <sup>-5</sup>	1.6x10 <sup>-5</sup>	6.5x10 <sup>-6</sup>	1.1x10 <sup>-5</sup>	1.8x10 <sup>-5</sup>		
<b>Ni</b>	3.7x10 <sup>-4</sup>	1.8x10 <sup>-4</sup>	4.5x10 <sup>-4</sup>	8.5x10 <sup>-5</sup>	8.0x10 <sup>-5</sup>	1.7x10 <sup>-4</sup>	<b>4.5x10<sup>-4</sup></b>	<b>3.4x10<sup>-4</sup></b>
<b>Pb</b>	7.8x10 <sup>-3</sup>	4.0x10 <sup>-2</sup>	4.8x10 <sup>-2</sup>	1.9x10 <sup>-2</sup>	3.2x10 <sup>-3</sup>	2.2x10 <sup>-2</sup>	<b>4.8x10<sup>-2</sup></b>	<b>1.1x10<sup>-3</sup></b>
<b>Mn</b>	2.5x10 <sup>-3</sup>	1.2x10 <sup>-3</sup>	3.7x10 <sup>-3</sup>	5.5x10 <sup>-4</sup>	1.0x10 <sup>-3</sup>	1.6x10 <sup>-3</sup>		
<b>Fe</b>	5.0x10 <sup>-4</sup>	2.5x10 <sup>-3</sup>	3.0x10 <sup>-3</sup>	1.2x10 <sup>-4</sup>	2.6x10 <sup>-2</sup>	2.6x10 <sup>-2</sup>		
<b>Cr</b>	1.4x10 <sup>-5</sup>	7.0x10 <sup>-5</sup>	8.4x10 <sup>-5</sup>	3.3x10 <sup>-5</sup>	5.7x10 <sup>-5</sup>	9.2x10 <sup>-5</sup>	<b>8.4x10<sup>-4</sup></b>	<b>9.2x10<sup>-4</sup></b>
<b>Cd</b>	1.3x10 <sup>-2</sup>	4.6x10 <sup>-3</sup>	1.8x10 <sup>-2</sup>	3.0x10 <sup>-3</sup>	5.4x10 <sup>-3</sup>	8.4x10 <sup>-3</sup>		

Source: Field work, 2021

Value in bold indicate CR > 1x10<sup>-4</sup>

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Although similar trends were observed in both groups, non-carcinogenic risk was greater in children than in adults. This is expected, given their lower body mass and immatured physiology, has been reported in many previous studies<sup>31,32</sup>.

Carcinogenic risk was calculated for Cr, Ni and Pb based on their respective cancer slope factors (the other analytes are not considered a cancer risk, so slope factor data are not available). For Cr, a slope factor of 0.5 (the lower of the values commonly cited in literature<sup>33</sup> was used because results of the sequential extraction suggested that the element was not readily available. Risks greater than  $1 \times 10^{-4}$  are considered unacceptable, those between  $10^{-4}$  and  $10^{-6}$  acceptable and those less than  $1 \times 10^{-6}$  unlikely to lead to any detrimental health outcomes<sup>34,35</sup>. In the current study, total carcinogenic risk levels for children were greater than those for adults, and values for Pb and Ni exceeded the threshold for unacceptable risk in both age groups. In contrast, values for Cr were greater in adult than in children<sup>36,37</sup>.

However, it is important to emphasize that these risk calculations are based on average PTE concentrations. Given the remarkably wide range of analyte concentrations found and the fact that a few values markedly exceeded the mean for each element, it is probable that results overestimate risk on the Ogun River water.

## 4.2 Questionnaire Administration

**Table 4.9: Location of Respondent**

<b>Location</b>	<b>Frequency</b>	<b>Percentage</b>
Lafenwa	51	51
Alagada	49	49
Total	100	100

Source: Field Survey, 2021

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**Table 4.10: Gender Distribution of Respondent**

	<b>Frequency</b>	<b>Percent</b>
Valid Male	48	48.0
Female	51	52
Total	100	100.0

Source: Field Survey, 2021

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**Table 4.11: Age Distribution of Respondents**

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	<b>Frequency</b>	<b>Percent</b>
Valid less than 15	8	8.0
15-25	38	38.0
26-35	23	23.0
36-45	15	15.0
46-55	8	8.0
Above 55	8	8.0
Total	100	100.0

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Source: Field Survey, 2021

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**Table 4.12: Occupational Status of Respondent**

	<b>Frequency</b>	<b>Percent</b>
Civil Servant	12	12.0
Self Employed	52	52.0
Professional	4	4.0
Student	25	25.0
Unemployed	4	4.0
Informal Sector	3	3
Total	100	100

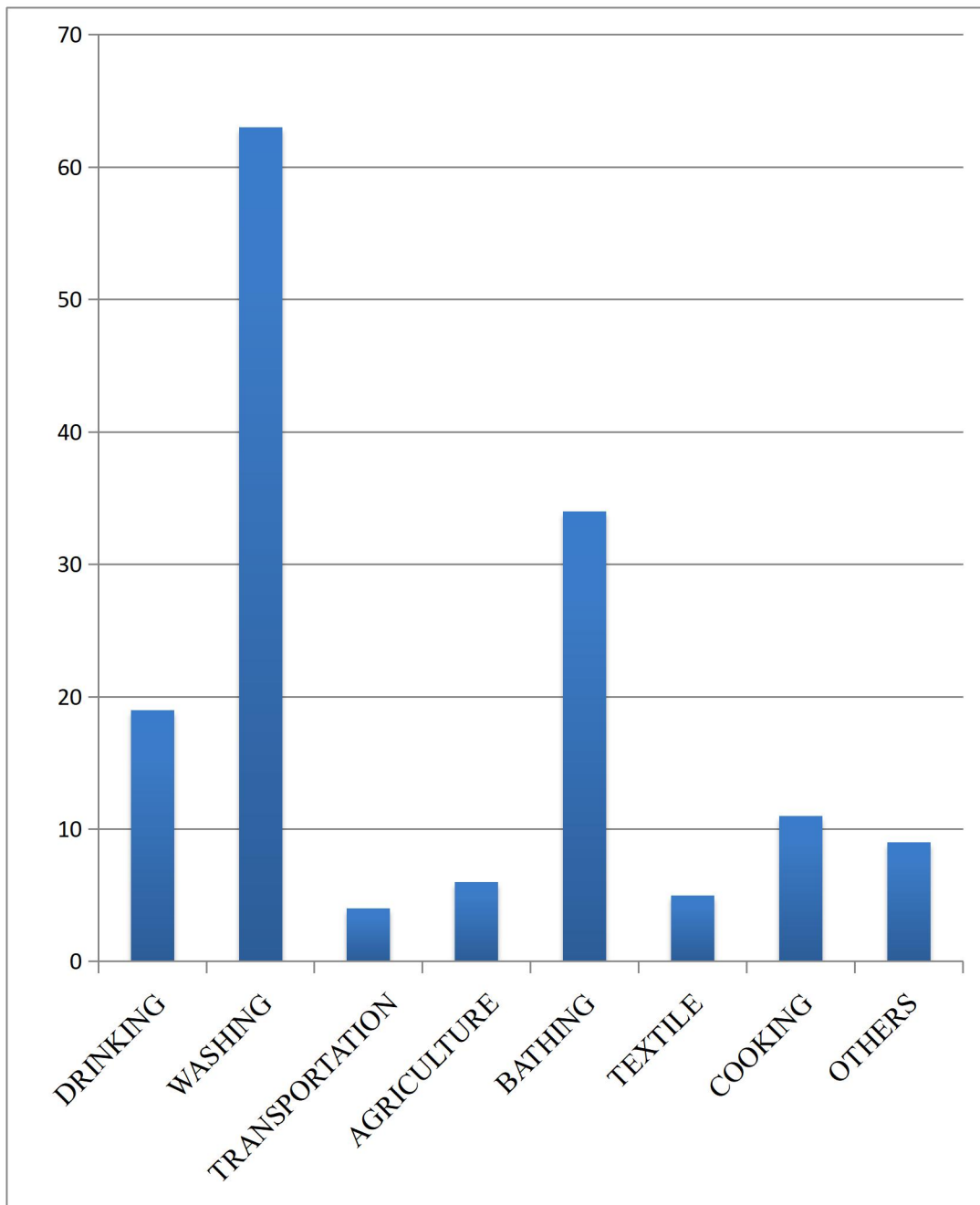
Source: Field work, 2021

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**Table 4.13: Educational Status of Respondent**

	Frequency	Percent
Valid SSCE	34	34.0
NCE/OND/HND	52	52.0
BA/BSc/B.Ed	12	12.0
M.A/M.Sc	1	1.0
PhD	1	1.0
Total	100	100.0

Source: Field Survey, 2021



**Figure 4.10** A Bar Chart Showing Water Usage Distribution of Respondents

Source: Field survey, 2021.

**Table 4.14: Alternative Source of Water Usage by Respondents**

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**Alternative Source of Water Usage by Respondents**

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Supply	82
Public	11
Communal	1

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Source: Field Survey, 2021

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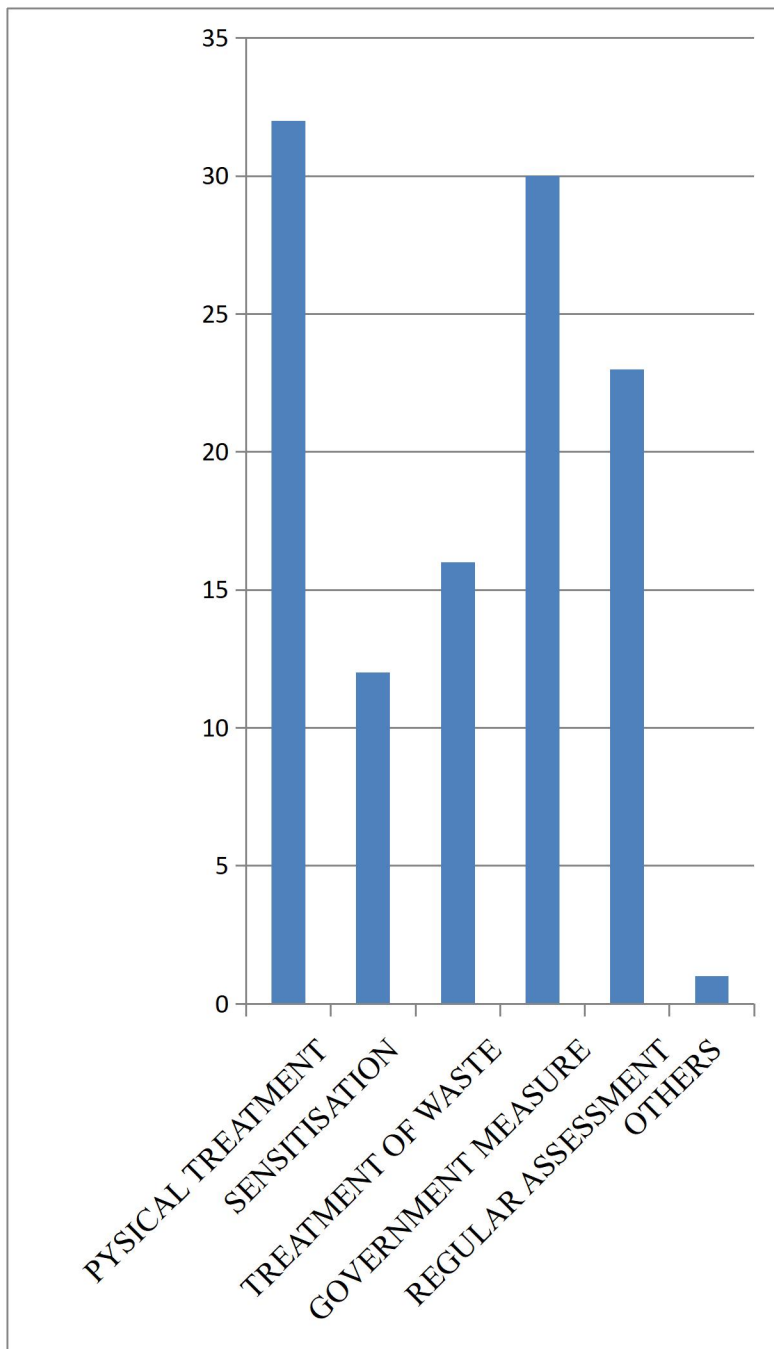
A total of 100 respondents were used in this study, 51% of the respondent of the respondent lives at Lafenwa while 49% of the respondents were from Alagada.

Table 4.10 show 48% of respondents used were male while 52% of respondent used were Female.

Their age distribution shown in Table 4.11 38% were between the age of 15-25, 23% were 26-35, 15% were 36-45, 8% were 46-55, 8% were above 55

Their occupation include civil servant 12%, self employed 52%, professionals 4%, student 25% , unemployed 4% and informal sector 3% , also their educational background were BSc 12%, PhD 1%, MSc 1% NCE/OND/HND 52%, and SSCE 34%.

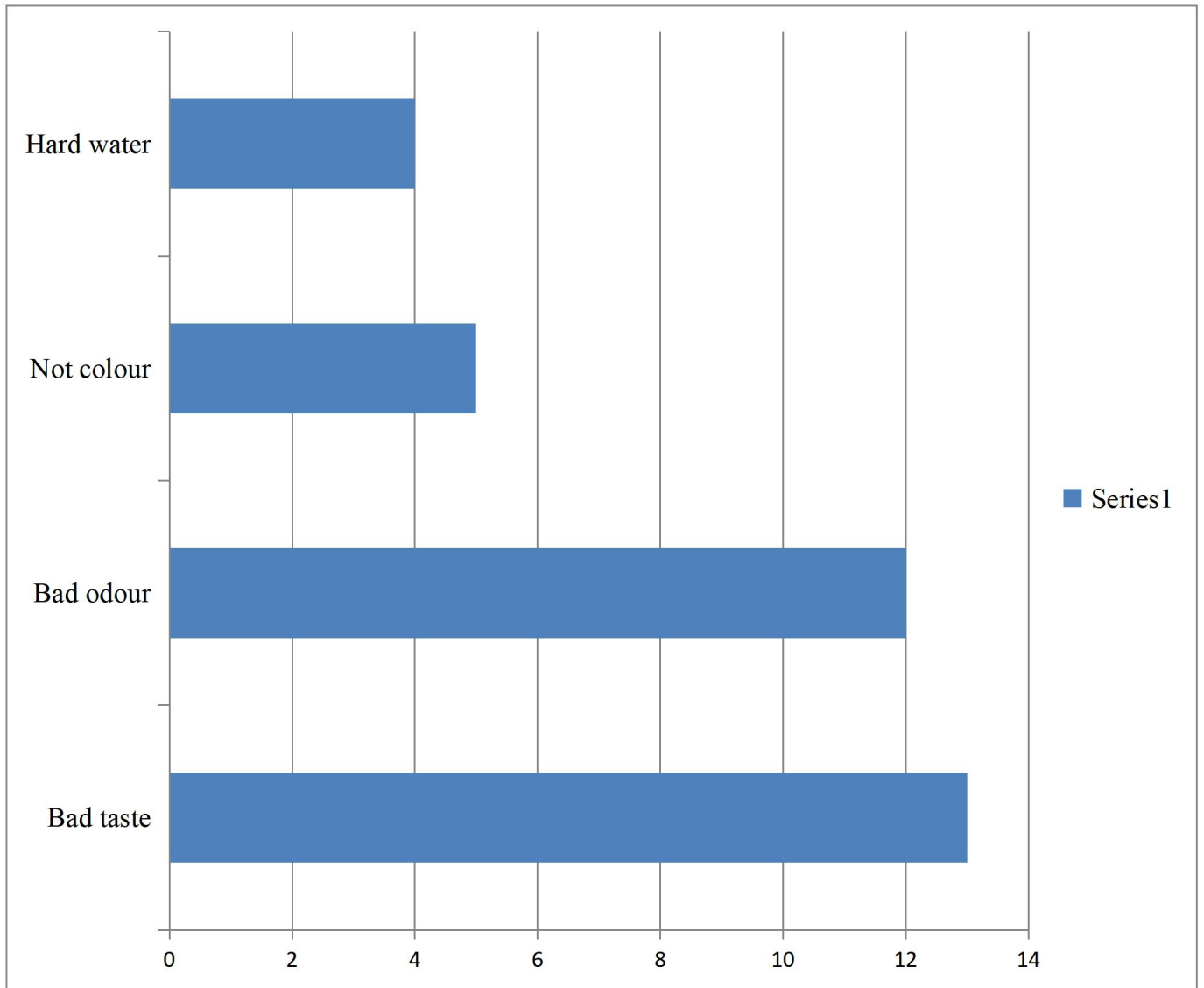
It was observe from the questionnaire that Ogun river is usually use for washing, transportation, agriculture, bathing, textile, cooking and others.



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**Figure 4.11:** A Bar Chart Showing Measure to Improve the Water Distribution of Respondents

Source: Field Survey, 2021



**Figure 4.12:** A Bar Chart Showing Rating of Bad Water Distribution of Respondents

Source: Field survey, 2021.

## Endnotes

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## Chapter Five

### Conclusion

#### 5.1 Summary of Findings

The study analyzed the concentration of Cd, Cr, Cu, Pb, Ni, Zn, Fe and Mn in the surface water, sediment and bioaccumulation in Tilapia fish obtained from Ogun River at Lafenwa and Alagada points at Abeokuta North and Obafemi Owode Local Government Areas of Ogun State using the Atomic Absorption Spectroscopy (AAS) technique.

The samples of tilapia fish muscles, sediment and surface water obtained from Ogun River were found to contain all the analyzed PTEs (Cd, Cr, Cu, Pb, Ni, Fe, Mn and Zn) at different levels. Concentrations of Cd, Cr, Ni, Cu, Fe, Mn and Pb in Tilapia fish muscle and water samples from Ogun river were found to have exceeded the WHO recommended limits in fish and fisheries products and drinking water.

The implication of this finding is that tilapia fish from Ogun River was contaminated to such levels that could pose potential hazards when consumed. This has serious implications in view of the large population which depend on the river as a source of their fish supply.

The presence of these contaminants in Ogun River are possibly caused by anthropogenic activities including the use of chemicals such as fertilizers and herbicides by farmers, dumping of solid wastes by residents within the reservoir and also weathering activities of the rock and soil. Although zinc was below permissible limits for drinking water and safety levels for fish and fishery, efforts should be made to ensure that these elements and other PTEs are regularly monitored as well as activities leading to this presence. This can be done through

regular studies in order to detect changes in water quality of the river and regulating of land use activities within the reservoir which influence the introduction of contaminants into the river.

## **5.2 Conclusions**

This study showed that PTEs were present in all the samples and human health risk assessment indicated it hazard effects on both adults and children

## **5.3 Recommendations**

It is recommended that:

1. A regular assessment of the river water quality is essential to ensure the water quality is safe for public health always.
2. Fishes from the areas of study possess health risk to their consumers therefore should not be consumed.
3. Public sensitization of the risk associated with indiscriminate waste disposal and as well as evolving measures to control pollution is encouraged.
4. Ogun River should be protected through conscious planning and re-organization activities along the river.

## **5.4 Contribution to Knowledge**

The concentrations of PTEs obtained from this study were higher compared to previous work on the same Ogun River, which means there were increase in the activities that led to pollution of the river. This is similar to the pattern observed for the surface water resource, suggesting that high levels of PTEs in the muscle of tilapia fish could have resulted through

the ingestion of food and water from the river or through the gills or their biological membrane<sup>6</sup>.

### **5.5 Suggested Areas for Further Study**

Microorganisms' pollution and its effects on the users of the Ogun river is also a good research area. Other bio-indicators (e.g. snails, crabs and waterlily) could be used to also evaluate the rate of metal uptakes by the aquatic animals and plants.

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### **Thesis**

Alene, A. *Assessment of heavy metals in edible muscle of Nile tilapia (*Oreochromis niloticus*) and Crucian carp (*Carassius carassius*) from Lake Ziway* (Doctoral dissertation, Haramaya University), 2022.

## Appendix 1

**Table 4.3: Descriptive Statistics of PTEs Concentration in Dry Season Water Sample**

	Sample Replicate	Cu	Zn	Ni	Pb	Mn	Fe	Cr	Cd
Lafenwa Up-Stream	1	0.97	1.14	0.07	0.88	0.59	0.67	0.54	0.24
	2	1.31	1.09	0.87	1.16	0.65	1.73	0.88	0.33
	3	0.08	0.62	0.80	1.08	0.53	6.75	2.33	0.24
Mean		0.787	0.950	0.580	1.040	0.590	3.050	1.250	0.270
±SD		0.635	0.287	0.443	0.144	0.060	3.248	0.951	0.052
SE		0.367	0.166	0.256	0.083	0.035	1.875	0.549	0.030
Lafenwa Down-Stream	1	4.86	1.00	0.88	0.15	1.07	45.00	0.69	0.15
	2	0.51	0.63	2.09	1.73	1.63	5.90	1.04	0.09
	3	1.02	0.92	0.53	0.44	0.86	5.85	2.30	0.06
Mean		2.13	0.850	1.167	0.773	1.187	18.917	1.343	0.100
±SD		2.378	0.195	0.819	0.841	0.398	22.589	0.847	0.046
SE		1.373	0.112	0.473	0.486	0.230	13.042	0.489	0.026
Alagada Up-Stream	1	0.69	0.97	0.26	0.71	1.70	5.61	0.21	0.18
	2	1.46	0.07	0.98	0.84	0.87	4.97	0.26	0.32
	3	0.57	0.34	0.64	0.81	0.92	5.02	0.23	0.29
Mean		0.907	0.46	0.627	0.787	1.163	5.20	0.233	0.263

$\pm$ SD	0.483	0.462	0.360	0.068	0.465	0.356	0.025	0.074
SE	0.279	0.267	0.208	0.039	0.269	0.206	0.015	0.043

Alagada Down- Stream	1	0.23	0.15	0.77	1.95	0.71	14.40	0.41	0.26
	2	4.05	0.47	0.38	1.84	0.24	20.60	0.49	0.42
	3	0.39	0.81	0.67	1.72	0.64	16.04	0.48	0.36
Mean		1.557	0.477	0.607	1.837	0.530	17.013	0.460	0.347
$\pm$ SD		2.161	0.330	0.203	0.115	0.254	3.213	0.044	0.081
SE		1.248	0.191	0.117	0.066	0.146	1.855	0.025	0.047

**Table 4.4: Descriptive Statistics of PTEs Concentration in Dry Season Sediment Sample**

	Sample Replicate	Cu	Zn	Ni	Pb	Mn	Fe	Cr	Cd
Lafenwa Up- Stream	1	9.00	0.90	0.96	0.82	2.85	2.41	0.01	0.32
	2	8.02	0.85	0.79	0.62	2.15	2.22	0.02	0.31
	3	9.01	0.89	0.86	0.72	2.67	2.18	0.03	0.29
Mean		8.677	0.880	0.870	0.720	2.523	2.270	0.020	0.307
$\pm$ SD		0.569	0.026	0.085	0.100	0.420	0.123	0.010	0.015
SE		0.328	0.015	0.049	0.058	0.242	0.071	0.006	0.009

Lafenwa Down- Stream	1	0.51	0.63	2.09	1.73	1.63	5.90	1.04	0.09
	2	1.02	0.93	0.53	0.44	0.86	5.85	2.30	0.06
	3	4.96	0.09	1.08	1.46	2.29	2.96	0.11	0.36
Mean		2.163	0.550	1.233	1.210	1.593	4.903	1.150	0.170
±SD		2.435	0.426	0.791	0.680	0.716	1.683	1.099	0.165
SE		1.406	0.246	0.457	0.393	0.413	0.972	0.635	0.095
Alagada Up- Stream	1	3.12	0.66	0.63	1.77	1.21	3.42	0.26	0.49
	2	3.51	0.81	0.58	1.82	1.32	3.54	0.28	0.87
	3	2.74	0.38	0.74	2.01	1.62	2.89	1.01	0.68
Mean		1.557	0.477	0.607	1.837	0.530	17.013	0.460	0.347
±SD		2.161	0.330	0.203	0.115	0.254	3.213	0.044	0.081
SE		1.248	0.191	0.117	0.066	0.146	1.855	0.025	0.047
Alagada Down- Stream	1	3.42	2.19	0.39	3.89	1.64	6.58	ND	0.24
	2	2.82	3.01	0.41	3.72	1.52	8.02	0.02	0.27
	3	3.56	2.12	0.32	3.93	1.78	5.03	0.01	0.22
Mean		3.267	2.440	0.373	3.847	1.647	6.543	0.015	0.243
±SD		0.393	0.495	0.047	0.112	0.130	1.500	0.007	0.025
SE		0.227	0.286	0.027	0.064	0.075	0.863	0.005	0.015

**Table 4.5: Descriptive Statistics of PTEs Concentration in Wet Season Water Sample**

	Sample Replicate	Cu	Zn	Ni	Pb	Mn	Fe	Cr	Cd
Lafenwa Up- Stream	1	1.52	0.05	0.09	0.60	0.98	2.06	1.38	0.23
	2	1.56	0.17	0.24	1.13	3.63	5.00	0.09	0.38
	3	3.26	0.89	0.68	2.07	1.30	1.19	0.05	0.48
Mean		2.113	0.370	0.337	1.267	1.970	2.750	0.507	0.363
±SD		0.993	0.454	0.307	0.744	1.446	1.997	0.757	0.126
SE		0.573	0.262	0.177	0.430	0.835	1.153	0.437	0.073
Lafenwa Down- Stream	1	1.56	0.22	0.38	2.78	0.71	12.13	1.22	0.27
	2	4.16	0.63	0.56	1.87	0.67	6.24	1.75	0.66
	3	3.28	0.72	0.45	2.64	0.78	6.22	1.82	0.92
Mean		3.00	0.523	0.463	2.430	0.72	8.197	1.597	0.617
±SD		1.322	0.267	0.091	0.49	0.056	3.406	0.328	0.327
SE		0.764	0.154	0.052	0.283	0.032	1.967	0.189	0.189
Alagada Up- Stream	1	2.01	0.34	0.75	3.70	0.47	0.27	1.31	0.39
	2	0.38	0.68	0.12	3.38	1.24	4.37	1.22	0.64
	3	2.08	0.71	0.62	3.12	1.29	4.13	1.62	0.68

Mean		1.49	0.577	0.497	3.40	1.00	2.923	1.383	0.570
±SD		0.932	0.206	0.333	0.291	0.460	2.301	0.210	0.157
SE		0.555	0.119	0.192	0.168	0.265	1.328	0.121	0.091
<hr/>									
Alagada Down- Stream	1	5.94	1.03	0.01	0.83	0.71	7.29	0.44	0.42
	2	3.06	0.20	1.64	2.45	0.57	11.21	0.13	0.31
	3	2.02	0.91	1.32	1.08	1.03	0.04	1.01	0.38
Mean		3.673	0.713	0.990	1.453	0.770	6.180	0.527	0.370
±SD		2.031	0.449	0.864	0.872	0.236	5.667	0.446	0.056
SE		1.172	0.259	0.499	0.504	0.136	3.272	0.258	0.032

**Table 4.6: Descriptive Statistics of PTEs Concentration Wet Season in Sediment Sample**

	Sample Replicate	Cu	Zn	Ni	Pb	Mn	Fe	Cr	Cd
Lafenwa Up- Stream	1	3.61	0.57	1.04	1.81	2.25	2.69	0.20	0.60
	2	2.84	0.61	1.03	1.72	2.28	3.01	0.21	0.61
	3	3.82	0.72	1.06	1.96	2.02	2.82	0.22	0.58
Mean		3.423	0.633	1.043	1.83	2.183	2.84	0.21	0.597
±SD		0.516	0.078	0.015	0.121	0.142	0.161	0.01	0.015
SE		0.298	0.045	0.009	0.07	0.082	0.093	0.006	0.009
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Lafenwa Down- Stream	1	0.30	0.28	0.31	2.97	1.25	0.62	0.96	0.63

	2	5.00	0.77	1.42	0.52	2.66	1.55	0.58	0.68
	3	0.46	0.39	1.40	1.28	1.87	1.52	0.72	0.61
Mean		1.920	0.480	1.043	1.590	1.927	1.230	0.753	0.640
±SD		2.669	0.257	0.635	1.254	0.707	0.528	0.192	0.036
SE		1.541	0.148	0.367	0.724	0.408	0.305	0.111	0.021
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Alagada Up- Sstream	1	1.56	0.17	0.24	1.13	3.63	5.00	0.09	0.38
	2	2.03	0.18	0.29	1.42	3.72	4.07	0.08	0.39
	3	1.47	0.16	0.42	1.82	3.14	5.02	0.10	0.28
Mean		1.687	0.170	0.317	1.457	3.497	4.697	0.090	0.350
±SD		0.301	0.010	0.093	0.346	0.312	0.543	0.010	0.061
SE		0.174	0.006	0.054	0.200	0.180	0.313	0.006	0.035
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Alagada Down- Stream	1	2.67	1.12	0.81	2.77	0.62	2.37	1.81	0.56
	2	2.51	1.32	0.49	1.89	0.39	2.28	1.72	0.61
	3	3.01	1.61	0.78	1.90	0.58	3.98	1.95	0.48
Mean		2.730	1.350	0.693	2.187	0.530	2.877	1.827	0.550
±SD		0.255	0.246	0.177	0.505	0.123	0.957	0.116	0.066
SE		0.147	0.142	0.102	0.292	0.071	0.552	0.067	0.038

**Table 4.7: Descriptive Statistics of PTEs Concentration in Fish Dry Season Sample**

	Sample Replicate	Cu	Zn	Ni	Pb	Mn	Fe	Cr	Cd
Lafenwa	1	4.97	1.26	0.09	2.28	0.51	5.59	0.73	0.41
	2	4.82	1.32	0.07	2.35	0.53	6.01	0.81	0.43
	3	5.00	1.24	0.10	2.27	0.60	5.42	0.70	0.50
Mean		4.93	1.263	0.087	2.300	0.547	5.673	0.747	0.447
$\pm$ SD		0.096	0.049	0.015	0.044	0.047	0.304	0.057	0.047
SE		0.056	0.028	0.009	0.025	0.027	0.175	0.033	0.027
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Alagada	1	0.36	0.90	0.73	1.25	0.65	28.10	0.47	snipp0.12
	2	0.38	0.93	0.74	1.28	0.60	28.14	0.49	0.13
	3	0.40	0.89	0.76	1.30	0.69	28.09	0.50	0.11
Mean		0.380	0.907	0.743	0.943	0.647	28.110	0.487	0.120
$\pm$ SD		0.020	0.021	0.015	0.575	0.045	0.026	0.015	0.010
SE		0.012	0.012	0.009	0.332	0.026	0.015	0.009	0.006

**Table 4.8: Descriptive Statistics of PTEs Concentration in Fish Wet Season Sample**

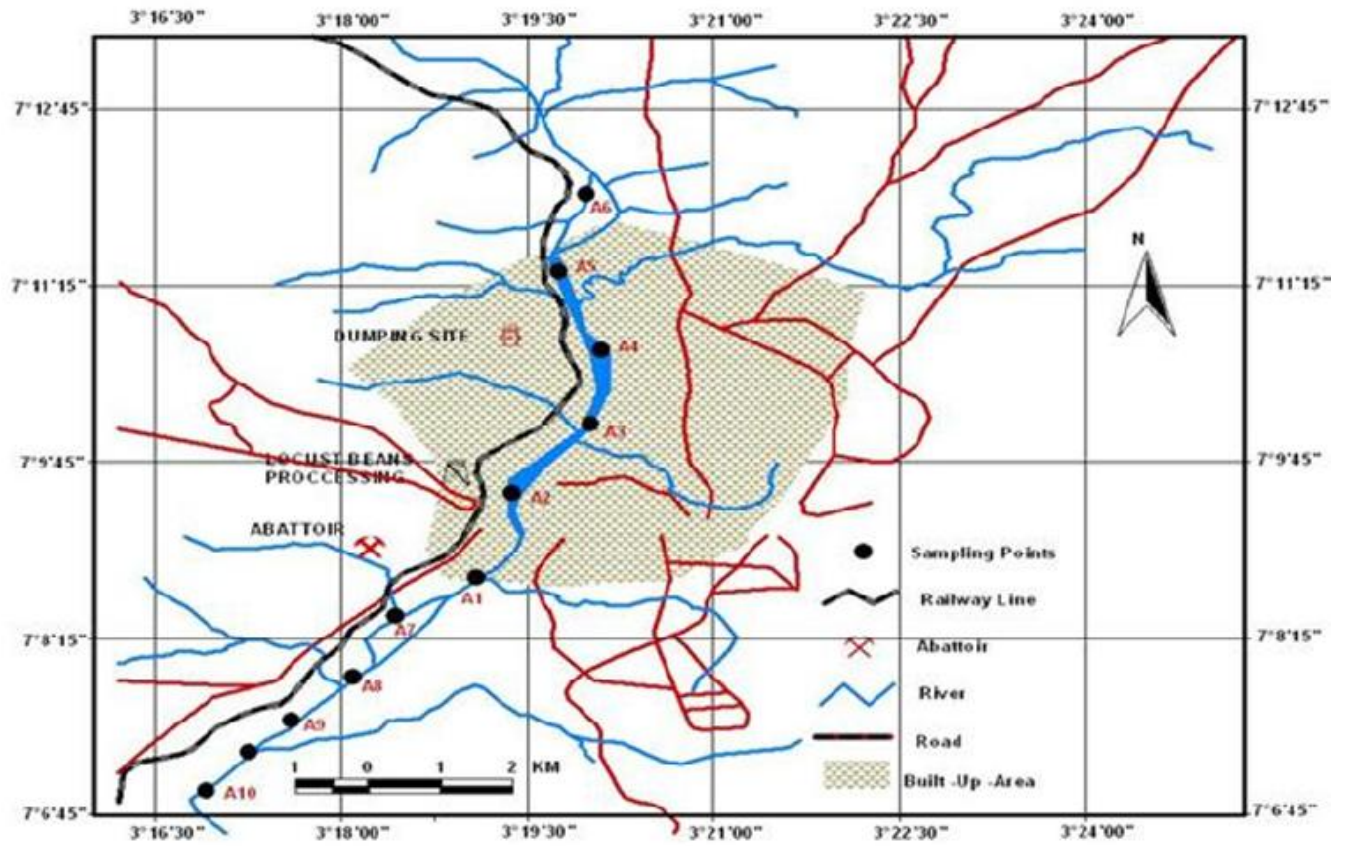
	Sample Replicate	Cu	Zn	Ni	Pb	Mn	Fe	Cr	Cd
Lafenwa	1	1.90	0.20	0.46	2.75	0.54	2.64	0.37	0.50
	2	1.87	0.22	0.49	2.78	0.60	2.63	0.25	0.51
	3	1.93	0.19	0.44	2.74	0.52	2.68	0.28	0.48

Mean		1.900	0.137	0.463	2.757	0.553	2.650	0.267	0.497
±SD		0.030	0.119	0.025	0.021	0.042	0.026	0.015	0.015
SE		0.017	0.069	0.015	0.012	0.024	0.015	0.009	0.009
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Alagada	1	3.03	0.20	0.40	3.25	0.59	2.32	1.78	0.50
	2	2.98	0.24	0.36	3.29	0.54	2.40	1.72	0.53
	3	3.06	0.18	0.52	2.98	0.60	2.36	1.80	0.48
Mean		3.023	0.207	0.427	3.173	0.577	2.360	1.767	0.503
±SD		0.040	0.031	0.083	0.169	0.032	0.040	0.042	0.025
SE		0.023	0.018	0.048	0.097	0.019	0.023	0.024	0.015

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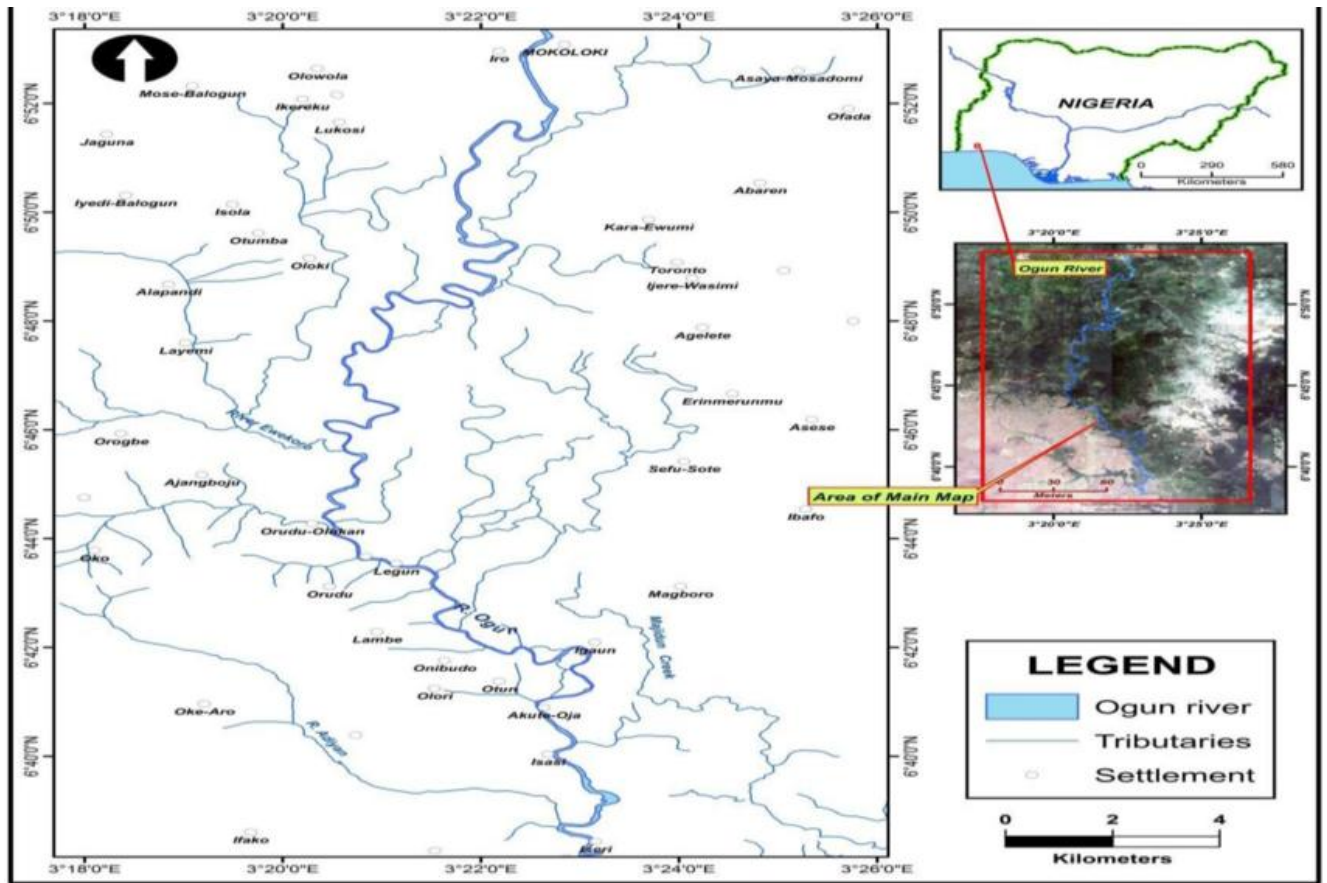
## Appendix 2



Appendix 2: Showing the Map of Study Area

Source: 3

### Appendix 3



Appendix 3 : Showing the Map of the Study Area

Source: 3

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**Plate 3. 1:** Lafenwa Site 1 x5

Source Field Work, 2021



**Plate 3.2: Lafenwa Site 2 X5**

**Source: Field Work, 2021.**



**Plate 3.3: Lafenwa site 3 X5**

**Source: Field Work, 2021**



**Plate 3.4: Alagada site 1X5**

**Source : Field Work, 2021**



**Plate 3.5: Alagada site 2X5**

**Source: Field Work, 2021.**



**Plate 3.6: Fishes (*Oreochromis niloticus*) from Lafenwa Mg x 5**

**Source: Field Work, 2021**

## Bio-data

### A. Personal Data

Name: Oluwayemisi Idayat Akindele

Address: Mile 7, Alagada Oba Road, Abeokuta Ogun State

Email: akindeleoluwayemisi399@gmail.com ,  
07032614705

Date and place of birth: 18 October, 1975, Lagos State

Nationality: Nigerian

Marital Status: Married

Number of Children: 3, 12years, 10years and 6years

Name and Address of Spouse: Mr. Samson Abiodun Akindele  
Mile 7, Alagada Oba Road Abeokuta, Ogun State  
akindelesamsaon@gmail.com,  
07060930177

Name and Address Next of Kin: Mr. Samson Abiodun, Akindele  
Mile 7, Alagada Oba Road, Abeokuta, Ogun State

Date of Assumption of Duty in Current Establishment: September 1<sup>st</sup>, 2009

Status on First Appointment in Current Establishment: Technologist II

Present Position: Principal Technologist

Date of Last Promotion: September, 2019

Date of Confirmation of Appointment: September, 2011

Present Salary: ₦185, 467, 09/Month

Faculty: School of Science and  
Technology

Department: Science Laboratory  
Technology

**B. Educational Institution Attended with Date and Qualification**

Bagada East Primary School, Bariga Lagos	First Leaving Certificate	1988
Shoyindo Community High School, Sagamu	Senior Secondary School Certificate	1994
Federal Polytechnic Ilaro, Ogun State.	National Diploma in SLT	1997
Moshood Abiola Polytechnic, Abeokuta Ogun State.	HND in SLT	2001
Bells University of Technology, Ota.	B.Sc. Industrial Chemistry	2019
Lead City University, Ibadan.	MSc Environmental & Analytical Chemistry	2020

**C. Awards and Fellowships**

**D. Work Experience**

Class Teacher: Awak Community Secondary Awak, Gombe State	NYSC	2005
OGUGRADE: Moshood Abiola Polytechnic, Abeokuta Ogun State		2007
Technologist: Moshood Abiola Polytechnic Teaching Chemistry Practical		2009
Course Taught: STC 112P, STC415P, GLT 111, GLT121, GLT 303		
Current National Diploma Project Supervision	five students	

**C. Membership of Academic Professional Bodies:**

NISLT, CSN, WITED

**D. Publications:**

**Projects**

Heavy metals in Canned Soft Drinks (HND Project)	2003
Determination of Heavy metals in Grounded Pepper from Two Market Selected at Sango Ota, Ogun State (BSc Project)	2019
Human Health Risk Assessment of Potentially Toxic Element (PTEs) in water, Sediments and Tissue of Tilapia Fish ( <i>Oreochromis niloticus</i> ) Samples of Ogun River. (MSc Thesis)	In view

**Paper Published:**

Environmental Impact of Heavy Metal Contaminations and Micronutrients in Soil Samples of Metal Dumpsite in Abeokuta, Ogun State, Nigeria IOSR Journal of Applied Chemistry	2014
Antidiabetic Effect of Ethanolic Extract <i>Clerodendrum volubile</i> Leaf on alloxan Induced Diabetes Male Wistar Rat. Akindele et al.	2022
International Journal of Novel Research in Healthcare and Nursing	2021

**E. Noticeable Scholarly or Professional Accomplishment**

F. Major Conference/Workshop Attended

**Conferences**

37 <sup>th</sup> Annual International Conference CSN Akwa Ibom,	2014
1 <sup>st</sup> National Conference of the School of Science and Technology Conference	2014

1<sup>st</sup> WITED Mapoly Chapter Conference 2022

FASCON 2022 Conference LCU 2022

### **Workshops**

2012 National Training Workshop on Sport Nutrition 2012

Laboratory Quality Management System at NISLT Ibadan 2014

Proposal Writing Accessing Grants and Development for Lecturer

Moshood Abiola Polytechnic, Abeokuta, Ogun State 2014

Instrumental, Application, Use and maintenance of Atomic Absorption

Spectrophotometer and Ultra-Violet/Visible Spectrophotometer 2015

MAPCED Workshop, Moshood Abiola Polytechnic, Abeokuta 2022

### **G. Service in Lead City University**

#### **H. Extra Curriculum Activities**

Reading and Singing

#### **I. Other**

### **Referees**

**Dr. (Mrs.) Khadijat Tolulope Duada**

Bells University of Technology, Ota, Ogun State

Senior Lecturer,

Department of Chemical Sciences

**Rev. S.A Adedina**

Zonal Superintendent,

Foursquare Gospel Church, Onikolobo, Abeokuta, Ogun State

*Do Not Copy, Lead City University, Nigeria*

.....  
**Signature**

.....  
**Date**

### **The University Compliance Certification**

This is to certify that this thesis written by Oluwayemisi Idayat, AKINDELE with matriculation number LCU/PG/001348 in the Department of Chemical Sciences, Faculty of Applied Sciences, Lead City University, Ibadan, Oyo State is in full compliance with the approved university format and style.

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**Signature**

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**Date**

*Do Not Copy, Lead City University, Nigeria*