SPATIO-TEMPORAL VARIATION OF HEAVY METAL CONCENTRATIONS IN WATER, SEDIMENT AND IN SELECTED FISH SPECIES IN SHIRORO LAKE, NIGER STATE, NIGERIA.

BY

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ABSTRACT

Anthropogenic activities contribute the most to heavy metals pollution of water bodies around the world. This study was conducted to determine the spatial and temporal variation of heavy metal concentrations in sediment, water and in selected fish muscle from Shiroro Lake Niger State, Nigeria. Sediments and water samples were collected from three different stations across the lake for a period of eight (8) months between February and September 2019. Heavy metals that were analyzed were chromium Cr, cadmium Cd, lead Pb, zinc Zn and copper Cu. Analysis of heavy metals was carried out on the muscles of three commercially important fish species in the lakes, which were *Alestes macrolepidotus*, *Bagrus bayad* and *Clarias gariepinus*. Water quality parameters showed that dissolved oxygen ranged from 2.20 - 4.10 mg/L, temperature, 26.60 - 30.20 ^{o}C, biological oxygen demand, 1.20 - 3.00 mg/L, conductivity 49 - 120 µS/cm, alkalinity 18 - 36 mg/L, phosphate 0.16 - 2.28 mg/L, sodium 7.56 - 14.00 mg/L, pH 6.56 - 7.96, total dissolved solids 75 - 99 mg/L, total hardness 30 - 48 mg/L and potassium 1.16 - 2.42 mg/L. Analysis of the concentration of heavy metals of sediment samples collected across the three stations showed that zinc ranged 0.095 - 0.25 mg/l, copper 0.015 - 0.905 mg/L, lead 0.00 - 0.15 mg/L, chromium 0-0.03 mg/L and cadmium 0 - 0.015 mg/L. Analysis of the concentration of heavy metals of water samples collected across the three stations showed that zinc ranged 0.01 - 0.18 mg/L, copper 0.01 - 0.165 mg/L, lead 0 - 0.2 mg/L, chromium 0.00 - 0.01 mg/L and cadmium 0 - 0.01 mg/L. Cadmium exceeded the toxicity threshold in the water sample in line with World Health Organization (WHO) standard in drinking water. The result also showed higher levels of Zn 1.47 ± 0.50 mg/g and Cu 0.73 ± 0.31 in fish in comparison to other heavy metals examined. All the heavy metals in fish samples were below WHO maximum stipulated limit. The results of the mean values of potential ecological risk index (PERI) across all stations showed that Zn 0.083, Cu 0.29, Pb 2.06, Cr 0.03 and Cd 0.48 while the comprehensive PERI value ranged between 0.617-6.902, therefore the PERI value obtained showed that the ecological risk level is slight. The results of the mean values of the Geo-accumulation index reported that Zn -2.42, Cu -2.06, Pb -1.56, Cr - 0.92, and Cr -0.75, therefore the geo-accumulation index values of the five heavy metals analyzed for across all three stations obtained from this study were negative i.e. (<0), this indicates an unpolluted state of the sampling stations. The results of the mean values of the enrichment factor (EF) reported that Zn 0.08, Cu 0.05, Pb 0.41, Cr 0.02, and Cr 0.02. Enrichment factor (EF) values of the five heavy metals analyzed for across all three stations obtained from this study were below one (<1), this indicates crustal enrichment origin of the sampling stations. The result of physicochemical parameters obtained from this research indicates a low level of pollution because all the water quality parameters recorded were either slightly below or within WHO permissible limit. The water in Shiroro Lake is not safe for human consumption as it can lead to Cd exposure.

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LIST OF ABBREVIATIONS

Abbreviations	**Meaning**
WHO	World Health Organization
DO	Dissolved Oxygen
BOD	Biochemical Oxygen demand
TDS	Total Dissolved Solids
EC	Electrical conductivity
PERI	Potential Ecological Risk Index
EF	Enrichment Factor
TSE	Turkish Standard
WPCL	Water Pollution Control Legislation
CIW	Criterions of the Irrigation water
EPA	Environmental Protection Agency
EC	European Community
THQ	Target Hazard Quotients
APHA	American Public Health Association
WAFT	Water Resources, Aquaculture and Fisheries Technology
SAAT	School of Agriculture and Agricultural Technology
AAS	Atomic Adsorption Spectrophotometer
ANOVA	Analysis of Variance
FEPA	Federal Environmental Protection Agency
NDSWQ	National Standard for Drinking Water Quality
FME	Federal Ministry of Education
NAFDAC	National Agency for Food and Drug Administration and Control

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Aquatic ecosystem is the ultimate recipient of almost everything including heavy metals. This has long been recognized as a serious pollution problem (Farombi *et al.*, 2007). The importance of freshwater ecosystems to human survival and sustenance can never be discounted. However, there is now persistent increase in pollution of water bodies that is directly or indirectly related to increasing urbanization and indiscriminate disposal of agrochemical and industrial effluents into aquatic systems (Dua and Gupta, 2005). Anthropogenic sources of heavy metal pollution in aquatic environments include industrial discharge, domestic sewage; non - point source runoff and atmospheric precipitation. However, metals also occur in small amounts naturally and enter aquatic systems through ore-bearing rocks, wind-blown dust, forest fires and vegetation (Fernandez-Leborans and Olalla-Herrero, 2000).

In developing countries, heavy metal analysis in freshwater is very important because these ecosystems provide drinking water and are habitats for flora and fauna (Asare *et al.*, 2018). Fish is considered as one of the most significant indicators of heavy metal pollution in aquatic environment (Rashed, 2001). Fish are well known for their major role in the aquatic food-web and they can take up and accumulate high metal concentrations from surrounding water and food (Mansour and Sidky, 2002). The concentrations of heavy metals in fish depend on body size and age of the individuals, ecological needs, their life cycle and life history, feeding habits, season of capture, some abiotic factors like temperature, dissolved oxygen, pH, conductivity of water (Shrivastava *et al.,* 2003) and other factors that influence the metabolic rate of fish

(Canpolat and Çalta, 2003). Abiotic factors change from season to season. And this affects the accumulation of heavy metals in tissues of fish (Canpolat and Çalta, 2003; Eastwood and Couture, 2002).

The results of many reported studies underlined that heavy metals in fish inhabiting polluted waters can be considerably accumulated by these organisms without causing mortality. Principally, fish assimilate the metals by three possible ways (body surface, gills or digestive tract) (Dallinger *et al*., 1987; Pourang, 1995). The body surface is generally assumed to play a minor role in heavy metal uptake of fish (Dallinger *et al*., 1987; Pourang, 1995). For these reasons, the estimation of risk potential for human consumption of fish accumulating high quantities of heavy metals in their tissues is very important (Oglu *et al*., 2015). Some edible species of fish have been widely investigated for those hazardous effects of heavy metals on human health (Begum *et al*., 2005).

Sediments are important sinks for heavy metals in aquatic ecosystem. These metals are non-biodegradable and once discharged into water bodies, they can either be adsorbed on sediment particles or accumulated in aquatic organisms. Heavy metal pollution may increase the susceptibility of aquatic animals to various diseases by interfering with the normal functioning of their immune, reproductive and developmental processes (US Environmental Protection Agency 2010).

Heavy metals could be found in water at the trace levels. Nonetheless, these constituents are very toxic and tend to accumulate in a long period of time. Heavy metals such as Pb, Cd and Cr are micro-pollutants and of special interest as they have both health and environmental significance due to their persistence, high toxic and bio-accumulation characteristics in water (World Health Organization 2008). Heavy metals in human body can cause serious health risks, hence the need to know the concentration of heavy metals in water, sediment and selected fishes in Shiroro lake because of its daily usage by man and proximity to urban pollution. In this study muscle was chosen as the target organ for accessing heavy metal accumulation because of its importance for human consumption and as a primary site of metal accumulation (Kotze *et al*., 2012).

1.2 Statement of Research Problem

Pollution by heavy metals has been of great concern in the last decades because of their health hazards to man and other organisms when accumulated within a biological system. In most Nigerian reports, heavy metals contamination results from absorption in contaminated water or via associated food (Aransiola *et al*., 2013). Over the last decades the freshwater environment has been polluted by different pollutants which originate from agricultural and industrial activities (Kalay and Canli, 2000). Heavy metals contamination in aquatic environment is of critical concern, due to toxicity of metals and their accumulation in aquatic habitats. Trace metals in contrast to most pollutants, are not bio-degradable, and they undergo a global ecological cycle in which natural water are the main pathways in which they are accumulated. Heavy metal being non-biodegradable, they can be concentrated along the food chain, producing their toxic effect at points after far removed from the source of pollution (Tilzer and Khondker, 1993).

All metals are virtually toxic if the exposure level is sufficiently high to exceed the tolerance limit. Specifically, some metals like (Cd, Pb, and Zn) have been reported to be extremely dangerous to human health even at low level of concentration (Ubalua *et al.*, 2007). Aquatic sediments can act both as a source and a sink for pollutants, whereby contaminants can lead to sediment concentrations that can exceed water concentrations (Barron, 1995). Sediment associated metals pose a direct risk to deposit feeding and detrital benthic organisms and may also represent long-term sources of contamination to higher trophic level (Eimers *et al*., 2001). Fish are at the higher levels of the food chain and may concentrate large amounts of some heavy metals from the water and also metals can accumulate in human tissues via food chain (Eimers *et al.*, 2001).

Shiroro Lake is a very important water body. It was majorly constructed for the purpose of hydro electrical power supply, which has now for so many years served as a good source of many fish species. With increase in human activities such as industrialization and urbanization around Shiroro Lake and its tributaries, activities such as washing of clothes and the use of detergents introduces pollutant into the water body daily in all the stations. Farming and application of fertilizers, herbicides and insecticides along the banks of the lake during rainy season frequently lead to pollution of the water body. All these human activities are quite rapidly increasing, and is threatening the sustainability and integrity of biodiversity and water quality. Thus there is need to assess the current status of the water quality and concentration of heavy metals in water, sediment, and some selected fish in the lake which will serve and provide baseline information on bio-monitoring guide of Shiroro Lake.

1.3 Justification for the Study

Shiroro Lake is an important source of drinking water for humans and animals. It serves as a means of irrigation of crops by both the rural and commercials rice farmers in the environ. The lake is a source of diverse species of fish for human consumption and commercial activities of the area generating income for young and old fish farmers in the area. Apart from being a source of fish, it provides a means of transportation for rural dwellers and serves as a lake for generating electricity.

Arimoro *et al*., (2018) carried out a study on mouthpart deformities in chironomid larvae as bioindicators of heavy metals pollution in Shiroro Lake. The study was carried out in relation to only sediment contamination. Auta *et al*. (2016) carried out a study on seasonal changes in environmental variables and how the changes affect the chironomid distribution and diversity in Shiroro Lake. Kolo and Oladimeji (2004) carried out a study on water quality and some nutrient levels in Shiroro Lake. So far, no research has been carried out on the lake to assess heavy metal pollution of the lake using fish as a bio-indicator. Assessment of the physicochemical parameters of the lake will provide a base line data and reference point for assessing periodic (short and long term) changes in the lake caused by anthropogenic activities of man over time. These data may be of high importance in environmental impact assessment for the water body and fisheries management. Monitoring water quality of Shiroro Lake would provide information and measures of improving and sustaining the aquatic ecosystem. This could also serve as bio-indication for monitoring changes in chemical condition and toxicity of the lake which could help to initiate policy for overall management of the ecosystem health and its productivity.

Information from the research would help in the improvement of sustainable fishing and other aquatic organisms without reducing their population density over a long period of time. This may help in the conservation, effective utilization, and sustainable exploitation of the vast aquatic resources that are available in the lake which is the mainstay of all the riparian communities around the lake.

1.4 Aim and Objectives of the Study

The aim of this study was to evaluate the spatio-temporal variation of heavy metal concentrations in sediment, water and in selected fish muscles in Shiroro Lake, Niger state.

The specific objectives of the study were to determine the:

i. Physicochemical parameters (pH, Alkalinity, Dissolved Oxygen (DO), Temperature, Total dissolved solid (TDS), Conductivity, and Biochemical Oxygen demand (BOD) of the lake

ii. Seasonal variations of heavy metal (Pb, Zn, Cr, Cu and Cd) concentrations in water, sediment and in the fish muscle

iii. Relationships between the metal levels in water, sediment and fish muscle

iv. Health status of the lake using ecological risk indices (Potential Ecological Risk Index (PERI), the Geo-accumulation index, and Enrichment Factor (EF)).

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Physicochemical Parameters

2.1.1 Water temperature

Temperature plays an important role for controlling the physicochemical and biological parameters of water and is considered as one of the most important factors in the aquatic environment particularly for freshwater (Umerfaruq and Solanki, 2015). Temperature is an important factor that affects the chemical and biological reactions in water. Temperature also regulates self-purification capacity of water (Pal and Chakraborty, 2014). A rise in water temperature accelerates chemical reactions which in turn reduces solubility of gases and also elevates metabolism of aquatic organisms, leading to decrease in dissolved oxygen and increase in free carbon dioxide (Pal and Chakraborty, 2014). Seasonal changes in precipitation and temperature have many indirect effects on the lakes, which result into changes in water temperature due to changing temperature conditions (Yurtseven *et al.,* 2016). Changes in water temperature also influence other water quality parameters and affect chemical reactions in water (Mustapha, 2009; Beylich and Laute, 2012).

2.1.2 Dissolved oxygen (DO)

Dissolved oxygen is essential for aquatic life (Mustapha, 2009). Its correlation with water body gives direct and indirect information like bacterial activity, photosynthesis, availability of nutrients and stratification (Premlata, 2009). A low DO (less than 2mg/l) indicates poor water quality and thus would have difficulty in sustaining many sensitive aquatic lives (Seema, 2015).

2.1.3 Biochemical oxygen demand (BOD_5)

Biochemical oxygen demand is a measure of organic material contamination in water, specified in mg/L. BOD_5 is the amount of dissolved oxygen required for the biochemical decomposition of organic compounds and the oxidation of certain inorganic materials (Patil *et al.*, 2012). Biochemical Oxygen Demand is the quantity of oxygen which is consumed in the course of aerobic processes of decomposition of organic materials, caused by microorganisms and therefore provides information on the biologically-convertible proportion of the organic content of a sample of water (Seema, 2015). Kuforiji and Ayadiran (2013) reported that high BOD values is an indication that organic matter is present and bacteria are decomposing this waste, and it is revealing that the water quality is poor.

2.1.4 Water pH (hydrogen ion concentration)

pH is the measure of the intensity of acidity or alkalinity and the concentration of hydrogen ions in water. pH of water affects the normal physiological functions of aquatic organisms, including the exchange of ions with the water and respiration (Ngodhe *et al.*, 2014). Such important physiological processes operate normally in most aquatic ecosystem under a relatively wide pH range for example 6-9 pH unit (Ngodhe *et al.*, 2014). Reduced rate of photosynthetic activity, the assimilation of carbon dioxide and bicarbonates are among the factors that bring about change in pH of water (Gupta *et al.*, 2014). The pH of a water body is also important in determining the suitability of different aquatic organisms that will survive in the habitat and exposure to extreme pH can be stressful or lethal to the organisms (Turker and Abrahamo, 2008).

2.1.5 Electrical conductivity

Conductivity is the capability of water to transmit electric current and it varies with concentration of ions present in the water. It also serves as a tool to assess the purity of water (Umerfaruq and Solanki, 2015). Abowei and Ekubo (2011) reported that electrical conductivity is often used as an indicator of primary production and can also be used to detect pollution discharge that have high ionic power. Pal and Chakraborty (2014) reported the acceptable water conductivity value for aquatic organisms to be between 250 and 500 μS/cm (maximum: 2000 μS/cm).

2.1.6 Total alkalinity

Alkalinity in aquatic environment is composed primarily of carbonate, bicarbonate, and hydroxide ions (Mustapha, 2009; Patil *et al.*, 2012). Alkalinity acts as a stabilizer or buffer for pH (Mustapha, 2009; Patil *et al.*, 2012). Alkalinity, pH and hardness affect the toxicity of many substances in the water due to the accumulation of organic matter produced by decay and decomposition of vegetation and in turn, add carbonate and bicarbonate concentrations in the water content (Patil *et al.*, 2012).

2.1.7 Nitrate and phosphate

Nitrates and phosphates are essential for the growth of aquatic organisms; however excess of this nutrient can lead to eutrophication which may lead to algal bloom and consequently deoxygenation (Mustapaha, 2008). Nitrates and phosphates aid the growth of macrophytes and phytoplankton which are the major primary producers in aquatic environment (Seema, 2015). The increasing concentration of available phosphorus allows plants to assimilate more nitrogen before the phosphorus is depleted. Thus, if sufficient phosphorus is available, high concentrations of nitrates will lead to plankton and macrophyte production. This is mostly due to the usage of fertilizer (Seema, 2015).

The increase in nutrients such as nitrates, sulphates and orthophosphate leading to low dissolved oxygen affects the life of aquatic organisms as shown from the BOD_5 result.

2.2 Heavy Metals

The term “heavy metals” refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). “Heavy metals” is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water (Hawkes, 1997). However, being a heavy metal has little to do with density but concerns chemical properties. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements.

2.2.1 Heavy metal in sediment, water and in fish

Monitoring the concentration of heavy metals in water, sediment and aquatic fauna is important since knowledge of heavy metal levels in these matrices especially sediment gives vital information regarding their sources, distribution and degree of pollution (Oyakhilome *et al.*, 2012). Aquatic sediments can act both as a source and a sink for pollutants, whereby contaminats can lead to sedimental concentrations that can exceed water concentrations (Barron, 1995). Sediment associated metals pose a direct risk to deposit feeding and detrital benthic organisms and may also represent long-term sources of contamination to higher trophic level (Eimers *et al*., 2001). Heavy metals that are introduced into the aquatic environment are ultimately incorporated into the aquatic sediments; organisms living in these sediments accumulate these heavy metals to varying degrees (Bryan and Hummerstone, 1977). The presence of metal pollutant in fresh water is known to disturb the delicate balance of the aquatic ecosystem. Fishes are notorious for their ability to concentrate heavy metals in their muscles and since they play important role in human nutrition, they need to be carefully screened to ensure that unnecessary high level of some toxic trace metals are not being transfer to man through fish consumption (Charis and Abbasi, 2005). The concentrations of heavy metals in fish depend on body size and age of the individuals, ecological needs, their life cycle and life history, feeding habits, season of capture, some abiotic factors like temperature, dissolved oxygen, pH, conductivity of water (Shrivastava *et al.,* 2003) and other factors that influence the metabolic rate of fish (Canpolat and Çalta, 2003). Abiotic factors change from season to season, and this affects the accumulation of heavy metals in tissues of fish (Eastwood and Couture, 2002).

Essentially, fish assimilate the metals by three possible ways (body surface, gills or digestive tract) (Pourang, 1995). The body surface is generally assumed to play a minor role in heavy metal uptake of fish (Pourang, 1995), whereas gills are regarded to be the important site for direct uptake from the water (Dallinger *et al*., 1987). Earlier reports showed that industrial and domestic effluent constitute largest sources of heavy metal which contribute to the steadily increasing metallic contaminant in aquatic and terrestrials environment in most part of the world (Jibiri and Adewuyi, 2008). The study of heavy metals and microbial contamination of Tilapia species in Lagos lagoon revealed a higher value in the whole body as well as different parts of the fish than the water samples. More studies in the distribution of heavy metals in water bodies reveal that the levels of heavy metals in the bottom sediment are usually higher than in the water columns which shows that sediments acts as sink for heavy metal (Adeniyi *et al*., 2008).

Adebayo (2017) reported that the concentration of heavy metals in water and sediments showed trace amount of heavy metals, mainly from anthropogenic input from the city of Ado Ekiti. The level of metal accumulation in fish, water and sediment in the study area does not constitute health hazards to aquatic life or man. But it is necessary to monitor the usage of the lake by appropriate agencies by adhering strictly to the rules guiding its safety. Government must ensure safe disposal of agricultural, domestic sewage and industrial effluents and recycled where possible to avoid these metals and other contaminants from going into the lake. It was recommended that, location of automobile workshops, dumping of domestic sewage and other activities that are inimical to the safe use of the lake should be discouraged, while regular assessment of the lake to see to its cleanness and proper maintenance should be encouraged.

Atobatele and Olutona (2017) reported that there was spatio-seasonal influence on reservoir water physicochemistry, sediment heavy metals; and observed a deterioration of Aiba reservoir water quality. The study also suggested that the reservoir water quality was affected by hydrology, catchment area as well as anthropogenic activities in and around the reservoir. Pollution migration strategies should focus on reversing encroachment into the reservoir catchment area and focusing on non-point source of run-off from the catchment areas. There is the need to determine the rate of degradation of Aiba reservoir through constant monitoring of its water quality even if anthropogenic impacts on the reservoir and not promptly abated.

Oyakhilome *et al.* (2013) reported that the distribution of the heavy metals in water, sediment and fish samples revealed that Fe recorded the highest concentrations while Cd was least. The elevated level of Fe is not surprising, since it has been established that iron occurs at high levels in Nigeria soil/sediment. Although, the concentration of these metals in the water body is considered not to cause trepidation to both the aquatic organisms and human consumers, the cumulative effect through bioaccumulation might be of concern in the future, thus calling for urgent attention on regular monitoring of the lake and control of anthropogenic input into the lake.

Asare *et al*. (2018) revealed that heavy metal concentrations in water samples were within recommended limit for drinking except Cd and Cr. The water in the Bontanga Reservoir is not safe for human consumption as it can lead to Cd and Cr exposure. The heavy metal concentrations in sediments were also within FAO/WHO set limits for the survival of aquatic organisms except Fe recorded in the upstream. Heavy metals in the various species were within the recommended limit for fish and fish products. Hence, these metals have no immediate threat on consumers' health. However, prolonged consumption of the fish species will have adverse effects since heavy metals accumulate. This study recommends regular monitoring of trace metal concentrations in reservoir as Bontanga Reservoir serves as a source of fish and water source for all-year-round irrigation farming as well as drinking water source for the inhabitants.

Öztürk *et al*. (2009) reported that the concentrations of heavy metals in water from Avsar Lake Lake are lower than the TSE-266 (Turkish Standard), WPCL (Water Pollution Control Legislation), CIW (Anonymous, Criterions of the Irrigation water), WHO (World Health Organization), EPA (Environmental Protection Agency) and EC (European Community) standards, with the exception of Fe. The average concentration of Fe in the lake water was higher than the TSE-266, WPCL, EPA and EC standards. The concentrations of Cr, Cu, Fe and Pb in sediments from Avsar Lake Lake were lower than the sediment samples obtained from Gediz River, which is known as a polluted site. There were high levels of heavy metals in fish. It was determined that the pollution has reached hazardous levels for the health of human. Also, a potential danger may exist in the future, depending on the agricultural development in this region. As the Avsar Lake Lake is also used for agricultural irrigation purposes, performance of pollution researches at certain periods is of significance for both environment and public health.

2.2.2 Potential ecological risk index

Genc and Yilmaz (2018) reported that the analysis of the potential ecological risk of sediment heavy metal concentrations showed that some area (Yuvarlakçay River and Sultaniye area on winter; Estuary area and Sultaniye on spring) presented considerable ecological risk. Conspicuously the potential ecological risk index for a single regulator (E) for Cd represented a considerable risk in all sites on winter. The estimated Target Hazard Quotients (*THQ)* value was higher than 1 further suggesting potential health risk for local people by consumption of fish. Although a *THQ* involving a single heavy metal could be considered not significant, it may experience a certain degree of adverse health effect because the total *THQ* was accounted for 60% by As. To conclude, this study suggested a potential health risk for the local inhabitants by consumption of contaminated fish especially in term of As.

Ntakirutimana *et al*. (2013) reported that the heavy metals under investigation in sediments reflected a low ecological risk to Lake Donghu, with an exception for cadmium, which posed a moderate ecological risk to the whole lake, and arsenic, which posed a moderate ecological risk to Guozheng Bay. The results of sediment samples taken from five locations showed that the lake has been slightly contaminated by heavy metals and its pollution can be attributed to human activities near and in the lake, as well as industrial pollution inputs. These observations suggest that the Pollution Board of Wuhan City should ensure that sewage disposal facility by residential complexes are efficient, adequate, and been satisfactorily operated. Potential reduction of industrial pollution input can be accomplished by meeting the wastewater discharge criteria. Elimination of potential future sources of pollution will help maintain good water quality in Lake Donghu.

2.2.3 Enrichment factor (EF)

Abrahim and Parker (2008) reported that normalized enrichment factor EF values for four heavy metals were calculated for Tamaki estuary using (1) the continental scale abundance of Fe and (2) the average concentration of Fe in the lower part of the studied cores. The results showed that using the Fe concentration in the continental scale as a normalizer produced higher average EF values for Cu, Pb, Zn and Cd as compared to average values determined using the actual Fe content in each core. The latter method is however the most relevant to Tamaki Estuary and the normalized EF results demonstrate a four-fold metal enrichment in the fine fraction sediment in the upper layers of Tamaki Estuary cores.

El-Amier *et al*. (2020) reported that the data concerning Ef of the heavy metals in the sediment samples from three main drains in the middle Nile Delta revealed that the contamination by heavy metals increased from downstream to upstream, heading toward the Burullus Lake, for Cu, Ni and Co, while the reverse holds for Cr, Zn, and Cd. Moreover, Mn, Cr, Co, Cu, Ni, and Zn were recorded within the normal limits, while Cd and Pb showed a high to very high ecological risk index, which could be attributed to unremitting industrial activities. This high concentration of pollutants could be ascribed to the unremitting industrial human activities, such as brick factories located on the sides of the drains, as well as paint and leather factories. Unfortunately, farmers unofficially use agricultural drainage water, and as such these two pollutants can bio-accumulate in plants and animals, or bio-concentrate in the food chains, and cause serious problems for human health.

2.2.4 The geo-accumulation index (Igeo)

Gupta *et al*. (2014) reported that the geo-accumulation index and principal component analysis were used for determining the environmental quality of soils/sludge from dumpsite in terms of heavy metal accumulation and other soil properties. The solid sludge was suffering from moderately to strongly contamination with the studied heavy metals according to Igeo values. The result revealed the following trend in their order of geo-accumulation in the sludge: Cr<Cu<As<Pb<Cd. The principal component analysis summarizes (reduces) the dataset into two major components representing possible different sources of the elements. The effectiveness of multivariate statistical analysis in evaluating heavy metal concentration in dumpsite soils has been demonstrated in the study. Due to the toxicity of heavy metals, the use of manure from the dumpsite for agricultural purposes should be discouraged as plants and vegetables can easily absorb them at elevated levels. In near future, the whole aquatic and terrestrial environment may be contaminated with the toxic elements. High concentrations of these trace metals may present potential health risk for the human populations residing in the vicinity of the whole area.

Jena *et al*. (2019) reported that most sediments samples exhibited low variation of metal distribution indicating similar and limited pollution sources. Heavy metal pollution is a nefarious issue with implications for life. Geo-accumulation index were used for determining the environmental quality of sediment in terms of heavy metal accumulation. The sediment samples were suffering from moderately contaminated with the studied heavy metals according to I_{geo} values. The result revealed the following trend in their order of geo-accumulation in the sludge: Cr<Cu<Pb<Cd<Zn. In near future, the whole aquatic and terrestrial environment may be contaminated with the toxic elements. High concentrations of these trace metals may present potential health risk for the human populations residing in the vicinity of the studied area.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of the Study Area

Shiroro lake is located in Shiroro Local Government Area, Niger State on latitude 9º.58'25.862''N and Longitude 6º.50'6.479''E and situated 550 meters downstream of the confluence of Kaduna River and its tributaries as shown in Figure 3.1. There are about 15 tributaries within the Shiroro watershed, the major among them being Rivers Dinya, Sarkin Pawa, Guni, Erina, and Munyi. The tributaries flow in the North South direction and few in the North-west to Southeast direction. The storage areas do not sustain the River during extended dry season. This explains the seasonality characteristics of these rivers, since they depend on rainfall. It is obvious therefore, that the volume of the rivers swells in volume with ranging torrent while in the dry season they dwindle to dry up (Kolo and Oladimeji, 2004).

The inhabitants of Shiroro community, residing along the river floodplains depend on the Kaduna River as a source of irrigation and for their household use and for drinking. Fishing activities is a daily affair in the lake. Another activity noticed at the lake is the weekly market that contributes to the pollution of the lake with a lot of waste materials and the grazing activity of Nomadic herdsmen around the shoreline of the lake was a prominent feature throughout the period of this study.

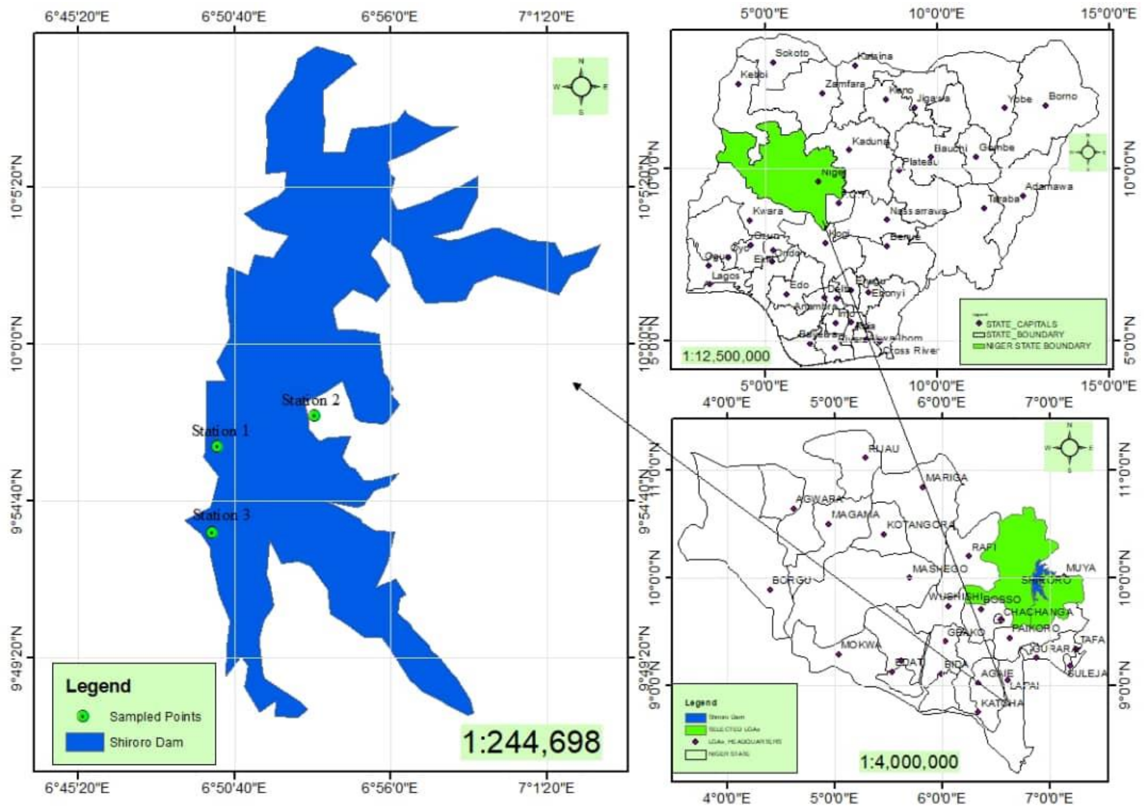

Figure 3.1 Map of the Study Area Showing Shiroro Lake in Shiroro, Niger State.

3.2 Description of Sampling Stations

3.2.1 Station 1

This is the reference point with latitude 9º56`29.862''N and longitude 6º50'6.474''E. The station is located at the power house close to the lake wall. Little human activities such as farming and cattle grazing takes place at this station

3.2.2 Station 2

This station is located close to Lokongoro village, latitude 9º57`33.054''N and longitude 6º53'26.958''E. There is a considerable amount of human activities around the station. Activities such as farming activities, cattle grazing, waste discharge from the human settlement, and a loading dock for canoes.

3.2.3 Station 3

This station is located in Kwata Zumba, a popular market area at Zumba located along the lake with latitude 9º53`34.029''N and longitude 6º49'57.234''E. This station was observed to have a lot of human activities majorly because of the market situated very close to the station. Waste materials from the market are discharged directly into the lake.

3.3 Water Sample Collection

Water samples for physico-chemical parameters were collected on a monthly basis for a period of eight months (February to September) from three (3) random stations (Power house, Lokongora, Kwata Zumba) based on the level of human activities around the stations. Water samples were placed in two plastic bottles at each sampling stations. Water samples collection was carried out by careful immersion of the sample containers at mid depth below the surface from the various sampling sites. The containers were sealed with tight fitting corks or stoppers after collection in order to avoid air bubbles. Before collection sampling bottles were pre-washed with 10% HCl acid and also pre-rinsed with deionized water to avoid any contamination from metal and non-metal ions and the water was preserved by adding 5ml of nitric acid (HNO_3) to it, thus preventing microbial growth in the water. One of the sampling bottles containing water sample collected at each site was immediately kept in black polythene bag to avoid further photosynthetic activities in the water sample, since it will be used to determine biochemical oxygen demand (BOD) after five days.

3.4 Sediment Sample Collection

The sediment samples were collected from three different sampling sites using a plastic shovel. Samples were transferred into clean polythene bags. The samples were kept in a container containing some ice-blocks and then taken to the laboratory. Sediment samples were air dried for three days at room temperature (25 °C) to remove moisture. The air dried samples were grounded in a mortar and pestle, sieved through 2 mm mesh screen to remove coarse materials. The homogenized samples were labeled and kept in clean containers pending analysis.

3.5 Fish Sample Collection

Fish samples of three (3) dominant species and commercially consumed fish species (*Alestes macrolepidotus*, *Bagrus bayad* and *Clarias gariepinus*) of the lake were collected at the fishing landing site. The fish samples were transferred in plastic bags and kept in an ice box at 4 ^{0}C and transported to the laboratory at F.U.T. Minna for heavy metal digestion and analysis.

3.6 Sample Preparation and the Determination of Physicochemical Variables

Water samples were processed according to the method prescribed by the American Public Health Association (APHA, 2008). The pH, Electrical conductivity (EC) and Total Dissolved Solids(TDS) of the water samples were tested using pre-calibrated pH, TDS and conductivity meter *in-situ* with (Hanna microprocessor pH/EC/TDS meter), while the determination of dissolved oxygen (DO), was determined *in-situ* using a portable dissolved Oxygen analyser, model JPB-607. Similarly, Air/water temperatures of the station were measured with a mercury-in-glass thermometer *in-situ* and the reading expressed in degrees Celsius (°C). Collected and preserved water sample was used to test for nitrate (NO_3), phosphate (PO_4), hardness, alkalinity, Biological Oxygen Demand (BOD), potassium and sodium using the methods of the APHA, (2008) in WAFT laboratory, (SAAT) Federal University of Technology, Minna for each sample station.

3.6.1 Biochemical oxygen demand (BOD)

This was determined according to APHA, (2008) method. At the field, the reagent bottles set aside for BOD was filled with water samples and tied in black polythene bags to avoid any form of photosynthesis. They were taken to the laboratory and kept in a dark cupboard. After five (5) days, they were untied and value of DO was determined by using dissolved Oxygen analyzer. The procedure for carrying out dissolved oxygen was repeated to check the amount of oxygen that has been used up by microorganisms.

CALCULATION:

BOD = $DO_1 - DO_5$(mg/L)

DO_1 = Initial dissolved oxygen at the first day

$DO_{5\,=}$ dissolved oxygen value after 5 days

Results were expressed in milligram per liter (mg/L)

3.6.2 Total hardness

Total hardness buffer (NH_4Cl-NH_4OH) 1 mL was added to 50 mL of the sample. A spatula of the total hardness indicator was added to the solution and titrated against 0.01N EDTA solution. The color change from pink to blue was an indication of the end point. The titre value was read, recorded and multiplied by 20 by the dilution factor (D.F).

Calculation:

Total Hardness = (Titre x 20 x D.F.) Calcium and magnesium hardness. The concentration of calcium carbonate (CaCO3) or magnesium carbonate (MgCO3) in the water was measured to get the Ca^{2+} and Mg^{2+} respectively. Total hardness was also determined.

3.6.3 Phosphate content

Phosphorus was also determined using APHA (2008) standard method. One hundred (100 mL) of the water samples was measured in 250 mL conical flask then 1mL of denigers reagent was added, 5 drops of Stannous Chloride ($SnCl_2$) was also added. A blue mixture was observed. The absorbance was determined at 690 nm using a spectrophotometer and distilled water as black. The PO_4-P was determined using the formular;

$$PO_4\text{-}P = \frac{\text{reading from curve x 1000 x D}}{\text{ml of sample}}$$

Where D is the dilution factor

3.6.4 Total alkalinity

Total alkalinity was determined using APHA (2008) standard method by measuring 100ml of water sample in a conical flask. A few drops of phenolphthalein indicator were added and there was no color change. Then a few drops (about 2-4 mL) of methyl orange indicator were added and yellow coloration develops. It was then titrated with 0.1NHCL until the yellow color changed to colorless (APHA 2008). The end point was noted and total alkalinity was calculated as:

$$\text{Total alkalinity} = \frac{\text{Volume of 0.1NHCL used x 100}}{\text{Volume of water used}}$$

3.6.5 Potassium (K) and sodium (Na)

Potassium and sodium ions were determined by flame photometric method. Trace amounts were determined in a direct reading of a frame spectrophotometer at wavelength of 766.5 nm for potassium and 589 nm for sodium ions. In case the sample was highly concentrated, which was indicated by high conductivity, it was diluted to a factor. The equipment was standardized and 1mL of sample analyzed.

3.7 Digestion of Samples

3.7.1 Digestion of water samples

Each 100 cm^3 of the sample was digested with 15 mL concentrated HNO^3 solution and 10 ml of 50 % concentrated HCl in ratio of 2**:** 1 (Wufem *et al.,* 2009). Samples were evaporated to almost dryness on a hot plate and then 7 mL of 50% concentrated hydrochloric acid is added and heated for 10 minutes. The digested samples were allowed to cool to room temperature. These were filtered through a Whatman 0.45 µm filter paper and the final volume is adjusted to 50 mL with double distilled water and stored for further Atomic Adsorption Spectrophotometer (AAS) analysis.

3.7.2 Digestion of sediment samples

After air drying the Sediment samples for 3 days and ground into smaller particles, it was sieved and digested. Two (2) gram of the sediment sample was weighed and poured into a beaker; 10 mL of hydrogen trioxonitrate (v) acid (HNO_3) was added together with 10 ml of hydrochloric acid (HCl) and heated for 1hour on a heater at 160 °C. After proper digestion, the sample was allowed to cool down and it was filtered. The filtrate was transferred into 100 mL volumetric flask and made up to mark with distilled water. The prepared sample solution was transferred into the pre-cleaned labeled sample bottles in readiness for Atomic Adsorption Spectrophotometer (AAS) analysis.

3.7.3 Digestion of fish samples

Fish samples were washed with distilled water and kept in clean plastic containers. Flesh close to the dorsal fin was taken with the use of a razor blade which were separated and labeled. The fish samples were oven dried at 105 ^{0}C. Dried sample was grounded into a fine powder using porcelain mortar and pestle; the powdered tissues were kept in desiccators prior for further analysis. Each of the dried powdered fish samples (2 g) was weighed and transferred into 250 mL round bottled flask, to each of this, a mixture of 10 mL of concentrated HNO^3 (65 %) and 10 mL of H_2O (30 %) was added. The flasks were covered with a watch glass and left to stand for 1 hour. Each of the flasks was then gently heated at 160 ºC in a sand bath on a hot plate till reduction of volume to about 5 mL. The digested samples were allowed to cool to room temperature. These were filtered through a Whatman 0.45 µm filter paper, the filtrate was then transferred to 25 mL volumetric flasks and made up to mark with de-ionized water. The digest were kept in Plastic bottles for heavy metal analysis using Atomic absorption spectrophotometer (Olaifa *et al*., 2004). Heavy metals analysis was done using a computerized Varian Atomic Absorption Spectrophotometer.

3.8 Metal Determination Procedure Using AAS

A black model 200A flame Atomic Absorption Spectrometer was used in the metal analysis of the sample (Perkin Elmer, 2000). The major underlining principle of AAS is that the ground state atoms are capable of absorbing radiant energy of their own specific resonance wavelength when passed through a solution containing the atoms in question, then part of the light will be absorbed. The extent of absorption is proportional to the number of ground state atoms present in the flame.

3.9 Ecological Risk Assessment

3.9.1 Potential ecology risk index (PERI)

The Potential Ecological Risk Index (PERI) was proposed by Hakanson, (1980) to evaluate the potential ecological risk of heavy metals. PERI is formed by three basic modules; degree of contamination (C_D), toxic-response factor (T_R) and potential ecological risk factor (E_R). According to this method, the potential ecological risk index of a single element (E^i_R) and comprehensive potential ecological risk index (RI) can be calculated via the following equations;

$C^i_f = C^i_D/C^i_R$

$E^i_R = T^i_R \times C^i_f$

$RI = \sum_{i=1}^{m} E^i_R$

Where C^i_D is the measured concentration of heavy metal in each sampling point; C^i_R is reference value, here the background value of each heavy metal in sediment was used ; $C^i_f = C^i_D/C^i_R$ is the pollution of a single element factor; E^i_R is the potential ecological risk index of a single element; RI is a comprehensive potential risk index; and T^i_R is the biological toxic factor of a single element, which was determined for Zn = 127 Cu = 32, Cr = 71, Cd =0.2, Pb =16, Ni =49 (Martin and Meybeck, 1979). The grading levels were summarized in the Table 3.1 below

Table 3.1: The Adjusted Grading Standard of Potential Ecological Risk of Heavy Metals in Sediment

E^i_R	Pollution degree	RI	Risk Level	Rick Degree
$E^i_R<30$	Slight	RI<40	A	Slight
$30\leq E^i_R<60$	Medium	40≤RI<80	B	Medium
$60\leq E^i_R<120$	Strong	80≤RI<160	C	Strong

$120 \leq E^i_R < 240$	Very strong	$160 \leq RI < 320$	D	Very strong
$E^i_R \geq 240$	Extremely	$RI \geq 320$	-	-

3.9.2 Enrichment factor (EF)

Enrichment factor (EF) method is an important indicator that quantitatively assesses the level and sources of heavy metal pollution.

EF is defined as:

$EF = (X/Fe)_{\text{sediment}} / (X/Fe)_{\text{background}}$

Where $(X/Fe)_{\text{sediment}}$ is the ratio of heavy (X) to Fe in the sediment samples from each sampled station and $(X/Fe)_{\text{background}}$ is the natural background value of the metal – Fe ratio. Normalizing element Fe, with natural background value of 232.7 mg/kg (Nweke and Ukpai, 2016). The EF values close to unity indicate crusted origin those less than 1.0 suggest a possible mobilization or depletion of metals, whereas $EF>1.0$ indicates that the element is of anthropogenic origin (Zsefer *et al.*, 1996). According to Sutherland, (2000), five contamination categories are generally recognized on the basis of the enrichment factor: $EF<2$, depletion to mineral enrichment; $2 \leq EF<5$, moderate enrichment; $5 \leq EF<20$, significant enrichment $20 \leq EF<40$, very high enrichment; and $EF>40$, extremely high enrichment.

3.9.3 The geo-accumulation index

The geo-accumulation index was determined by the following equation according to Muller, (1969) interpretation which was described (Boszk *et al.*, 2004).

$I\text{-}geo = \log_2 (Ci/1.5\ Cri)$

Where Ci is the measured concentration of the examined metals I in the sediment and Cri is the geochemical background concentration or the reference value of the metal i. factor 1.5 is used because of possible variation in background value for a given metal in the environment as well as very small anthropogenic influences (Nweke and Ukpai, 2016). The geo-accunulation index was distinguished into seven classes by Muller, (1969), and Chakravarty and Patgiri, (2009) Table 3.2

Table 3.2: The Degree of Metal Pollution in Terms of Seven Enrichment Classes

I_{geo} Value	I_{geo} Class	Designation of Sediment Quality
>5	6	extremely contaminated
4-5	5	strongly to extremely contaminated
3-4	4	strongly contaminated
2-3	3	moderately to strongly contaminated
1-2	2	moderately contaminated
0-1	1	uncontaminated to moderately contaminated
0<	0	Uncontaminated

3.10 Data Analysis

The physicochemical parameters data set was subjected to descriptive statistical test. Microsoft Excel 2010 was used to determine one way ANOVA and also heavy metal concentration. The mean values and standard deviation of each physicochemical characteristic and heavy metal concentration were calculated per station. Heavy metal concentration of Zinc, Copper, Lead, Chromium and Cadmium as well as physicochemical variables among all stations were compared using one way analysis of variance (ANOVA) at significant difference ANOVA ($p<0.05$) .

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Spatial and temporal variation of the physico-chemical parameters of Shiroro Lake, Niger State

The results of Spatial and Temporal variation in Physico-chemical parameters of Shiroro lake over a period of Eight (8) months (February to September 2019) are presented in Table 4.1 pH differed significantly ($p<0.05$) among all the three stations as indicated by ANOVA. There was no significant difference ($p>0.05$) in temperature, dissolved oxygen (DO), biological oxygen demand (BOD), electrical conductivity, alkalinity, phosphate, Total dissolved solid (TDS), Total hardness, potassium and Sodium among the three sampling stations of the lake.

Table 4.1 Mean and Standard Deviation, Minimum and Maximum Range of Physico-Chemical Parameters of Shiroro Lake, Niger State. Nigeria

Parameter	Power house (Station 1)	Lokongora (Station 2)	Kwata Zumba (Station 3)	p –value		Permissible limit
	mean±SD	mean±SD	mean±SD	Month	Station	
	(min-max)	(min-max)	(min-max)			
pH	7.27±0.50	7.16±0.49	7.44±0.44	4.60E-8.00	0.01	6.50-8.50[a]
	(6.58-7.87)	(6.66-7.82)	(6.77-7.96)			
E.Cond(μ/cm)	77.13±16.94	75.25±18.03	75.38±18.37	2.69E-11.00	0.36	1000[b]
	(53-120)	(49-98)	(50-104)			
TDS(mg/l)	86.13±9.42	86.62±8.45	85.88±7.94	1.16E-8.00	0.78	1000[b]
	(75-99)	(78-98)	(75-94)			
Tempt.(°C)	28.19±1.39	28.26±1.44	28.20±1.58	1.03E-11.00	0.77	<40[a]
	(26.7-30.1)	(26.70-29.90)	(26.60-30.20)			
DO(mg/l)	2.89±0.63	3.00±0.61	3.10±0.64	1.12E-7.00	0.10	>5[a]
	(2.3-4.0)	(2.20-3.90)	(2.30-4.10)			
BOD(mg/l)	1.81±0.63	1.93±0.54	2.00±0.60	7.17E-6.00	0.30	6[b]
	(1.30-3.00)	(1.20-2.70)	(1.30-3.00)			

Po4-P(mg/l)	0.22±0.03	0.21±0.04	0.21±0.05	0.00	0.82	2.2[b]
	(0.16-0.26)	(0.16-0.26)	(0.16-0.28)			
Alkalinity(mg/l)	26.75±6.23	25.75±5.20	27.13±5.00	6.43E-8.00	0.22	20[a]
	(18-36)	(18-34)	(20-34)			
T.Hardness(mg/l)	38.25±4.33	36.88±4.88	36.38±5.01	0.00	0.27	500[b]
	(32-44)	(32-48)	(30-46)			
potassium(mg/l)	1.66±0.49	1.62±0.42	1.62±0.50	1.98E-07	0.86	30[a]
	(1.24-2.42)	(1.16-2.22)	(1.16-2.28)			
Sodium(mg/l)	10.43±2.17	10.68±2.45	10.82±2.51	2.57E-09	0.36	200[b]
	(7.56-13.42)	(7.74-14.10)	(7.90-13.83)			

Permissible limit: FEPA (2003)[a] ; WHO (2011)[b]

4.1.2 Dissolved oxygen (DO)

The result of Spatial and Temporal variation of Dissolved oxygen values of the three stations are presented in Figure 4.1. Dissolved oxygen value ranged from 2.89 mg/l to 3.10 mg/l, with station 1 having the lowest value and station 3 with the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally, as recorded in the three stations the lowest value of Dissolved oxygen was recorded in February and there was a gradual increase from March, April, may and the highest value was recorded in June and July. There was a gradual decline from August to September.

4.1.3 Water temperature

The result of Spatial and Temporal variation of temperature of the three stations are presented in Figure 4.2. Temperature value ranged from 26.60 ºC to 30.20 ºC. Station 1 had the lowest value and station 2 had the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally, as recorded in the three stations the highest value of temperature was recorded in February, a slight decline was recorded in March, and the temperature value was relatively stable from April to May. There is a sharp decline in the value of water temperature between May and June; and then a relatively constant value of temperature was recorded from June to September.

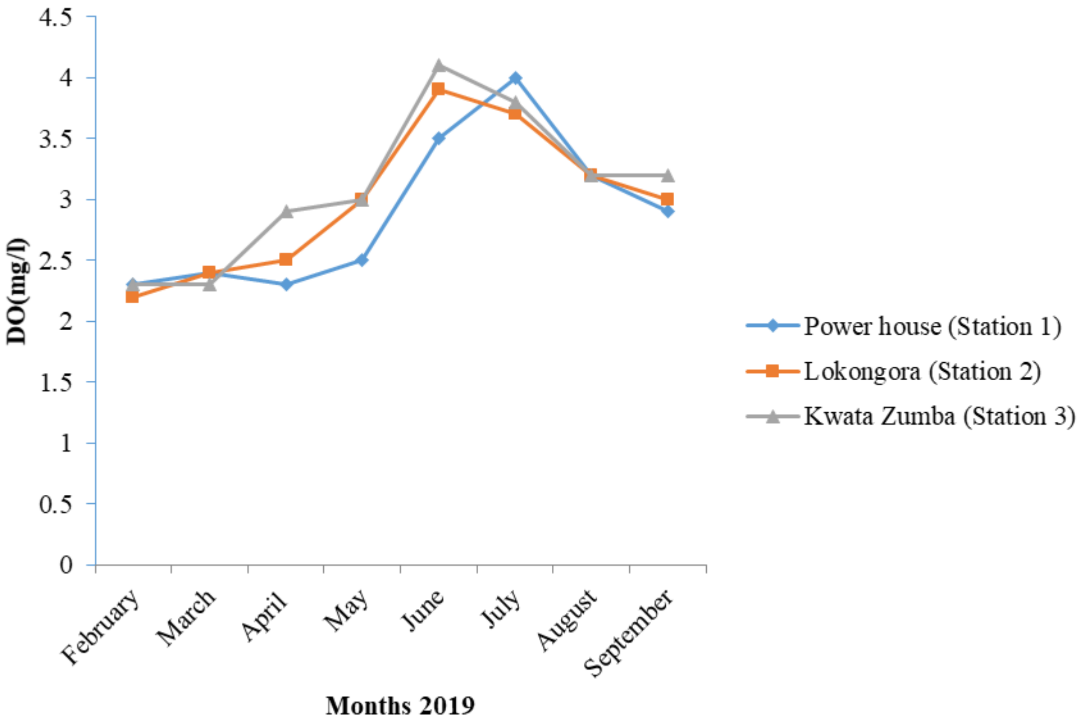

Figure 4.1: Spatial and Temporal Variation of Dissolved Oxygen across the Sampling Stations.

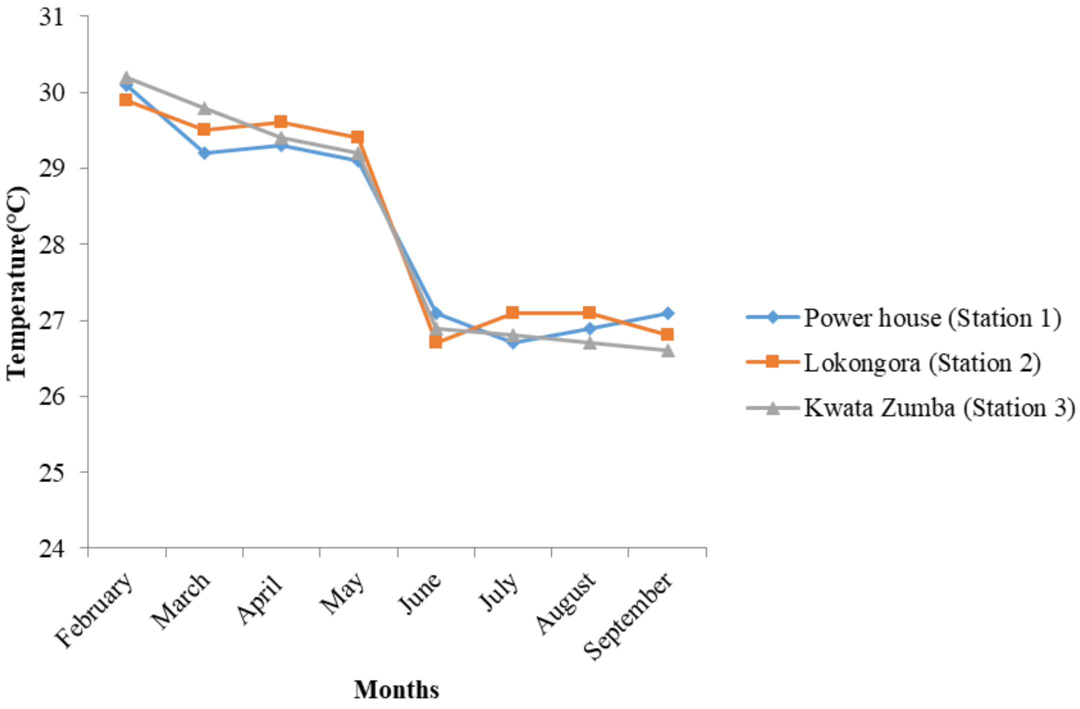

Figure 4.2: Spatial and Temporal variation of Water Temperature across the sampling stations.

4.1.4 Water pH

The result of Spatial and Temporal variation of pH valued obtained from the three stations are presented in Figure 4.3. pH values ranged from 7.16 to 7.44, with station 2 having the lowest value and station 3 with the highest value. There was significant difference ($p<0.05$) between sampling stations and seasons. Generally, as recorded in the three stations, the lowest value of pH was recorded between February and March, a slight increase was recorded in the month of April, the value of pH slightly declined in May to June (pH value also was lowest in June relative to the value recorded in February and March). A sharp increase was recorded from June to July; and remained steady from July to September.

4.1.5 Total dissolved solid (TDS)

The result of Spatial and Temporal variation of Total dissolved solids within the three stations are presented in Figure 4.4. Total dissolved solids values ranged from 85.88 mg/l to 86.62 mg/l. Station 3 had the lowest value, while station 2 had the highest value. There is no significance difference ($p>0.05$) between sampling stations and seasons. Generally, in the three stations there was a steady increase in the value of TDS recorded from February to May, the highest level of TDS was recorded in May, and then a gradual decline from May to July. A difference in the value of TDS was recorded from July to September. The lowest value of TDS was recorded in September.

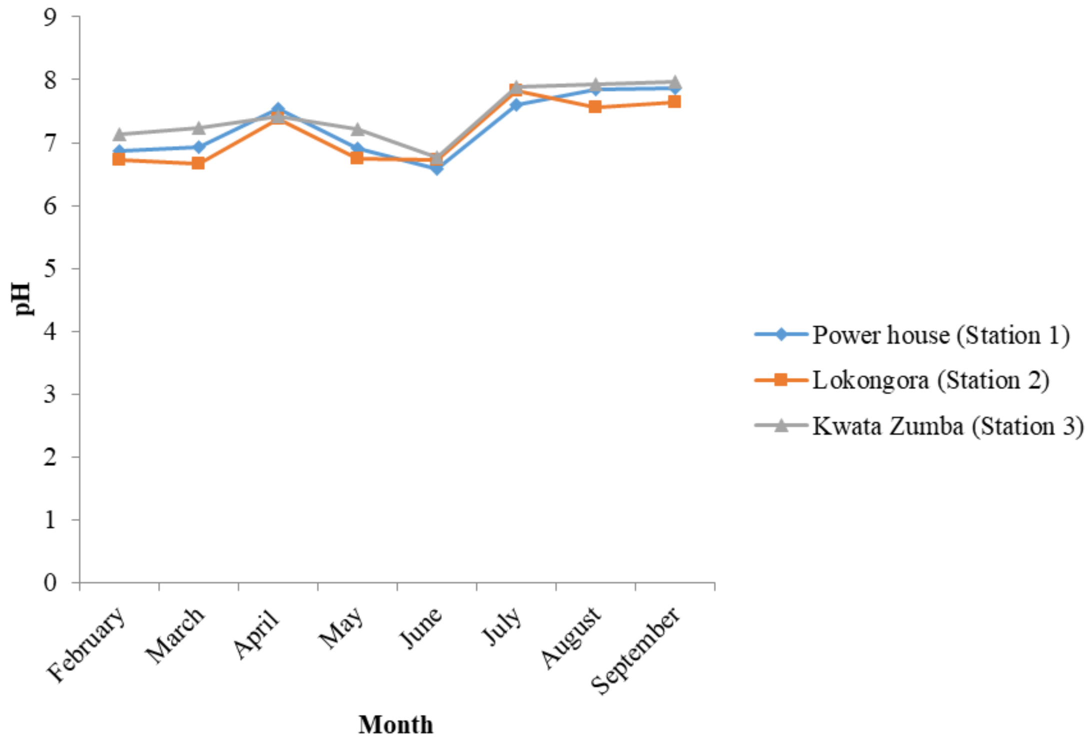

Figure 4.3: Spatial and Temporal Variation of Water pH across the Sampling Stations

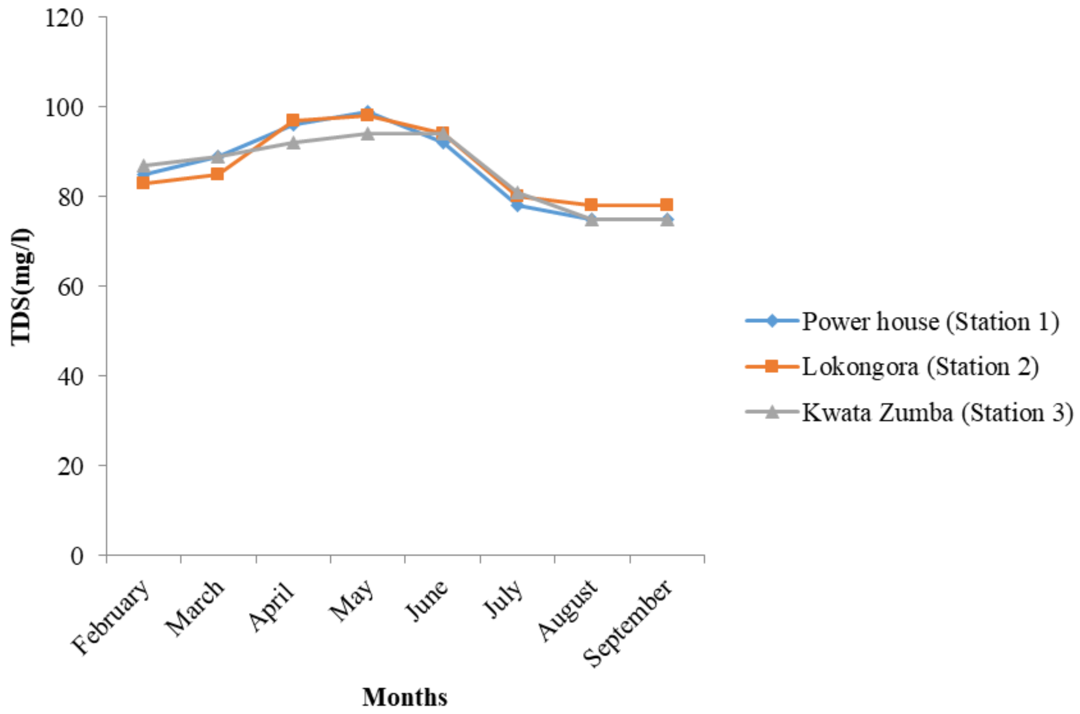

Figure 4.4: Spatial and Temporal Variations of Total Dissolved Solid (TDS) across the Sampling Stations

4.1.6 Biochemical oxygen demand (BOD)

The result of Spatial and Temporal variation of BOD within the three stations are presented in Figure 4.5. BOD values ranged from 1.813 mg/l to 2 mg/l, with station 1 having the lowest value and station 3 with the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally, as recorded in the three stations, the lowest value of Biological Oxygen Demand (BOD) was recorded in February and there was a gradual increase from March, April, May and the highest value was recorded in June and July. A gradual decline occurred from august to September.

4.1.7 Phosphate content

The result of Spatial and Temporal variation of Phosphate within the three stations are presented in Figure 4.6. Phosphate values ranged from 0.21 mg/l to 0.22 mg/l. Station 2 and 3 had the lowest value and station 1 had the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally as recorded in all stations the lowest value of Phosphate was recorded in February with station 3 having the lowest value. A relative increase in the value of phosphate was recorded from February to the July. Relative to the three stations, the highest value was recorded in July especially in station 3. The value slightly declined from July to September.

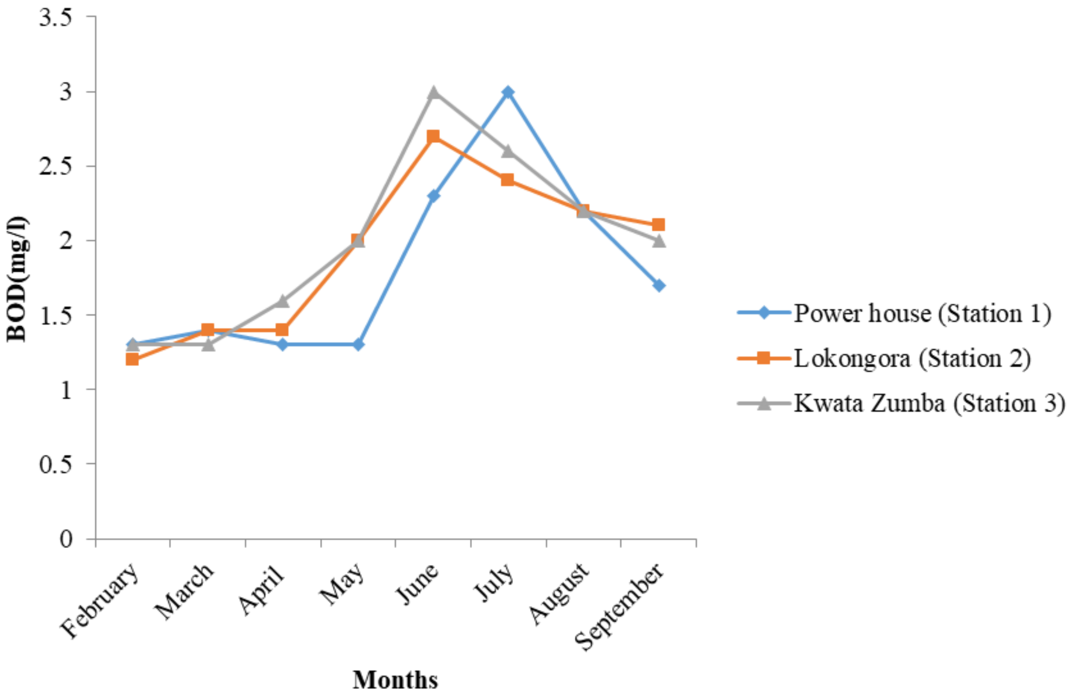

Figure 4.5: Spatial and Temporal Variations of Biochemical Oxygen Demand (BOD) across the Sampling Stations

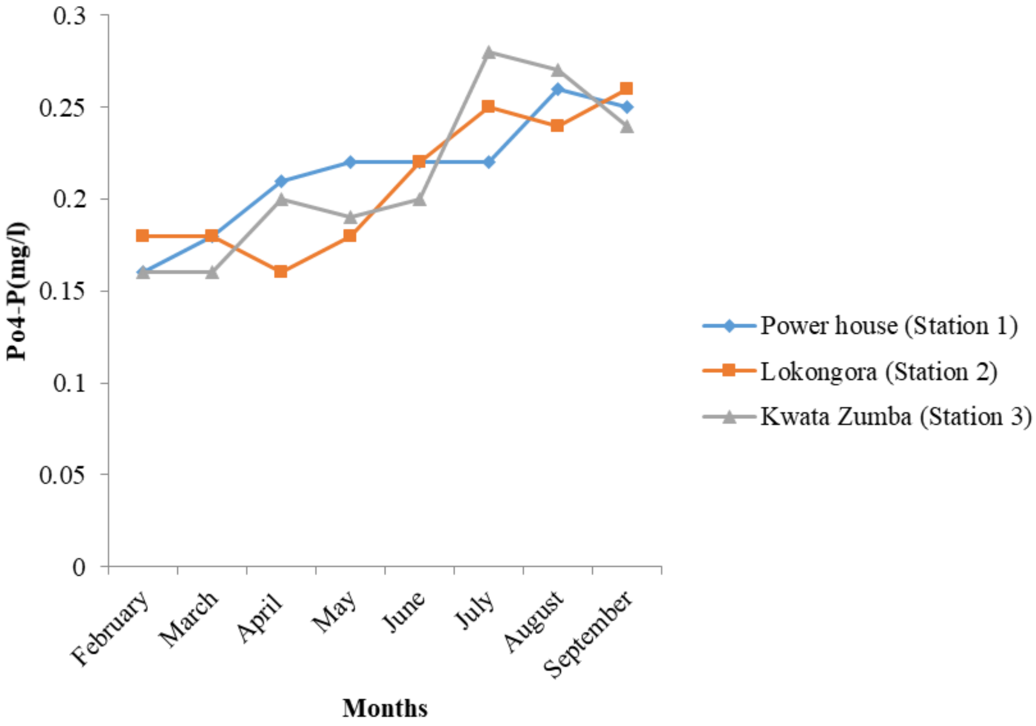

Figure 4.6: Spatial and Temporal Variations of Phosphate Content across the Sampling Stations

4.1.8 Total alkalinity

The result of Spatial and Temporal variation of Alkalinity within the three stations are presented in Figure 4.7. Alkalinity values ranged from 25.75 mg/l to 27.13 mg/l, with station 2 having the lowest value and station 3 had the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally as recorded in all station the Alkalinity value of station 1 gradually increased from February to April, but station 2 and 3 recorded a slight decline from February to March and later increased from March to April. The highest value was recorded in April in the three stations, and the value gradually declined from April to August. The lowest value of Alkalinity was recorded in August. A slight increase was then recorded between August and September.

4.1.9 Total hardness

The result of Spatial and Temporal variation of Total hardness within the three stations are presented in Figure 4.8. Total hardness values ranged from 36.38 mg/l to 38.25 mg/l, with station 3 having the lowest value and station 1 had the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally as recorded in all stations the value of total hardness gradually increases from February to April. The highest value of total hardness was recorded in April especially in station 2. There was a gradual decline in the value of total hardness from April to September.

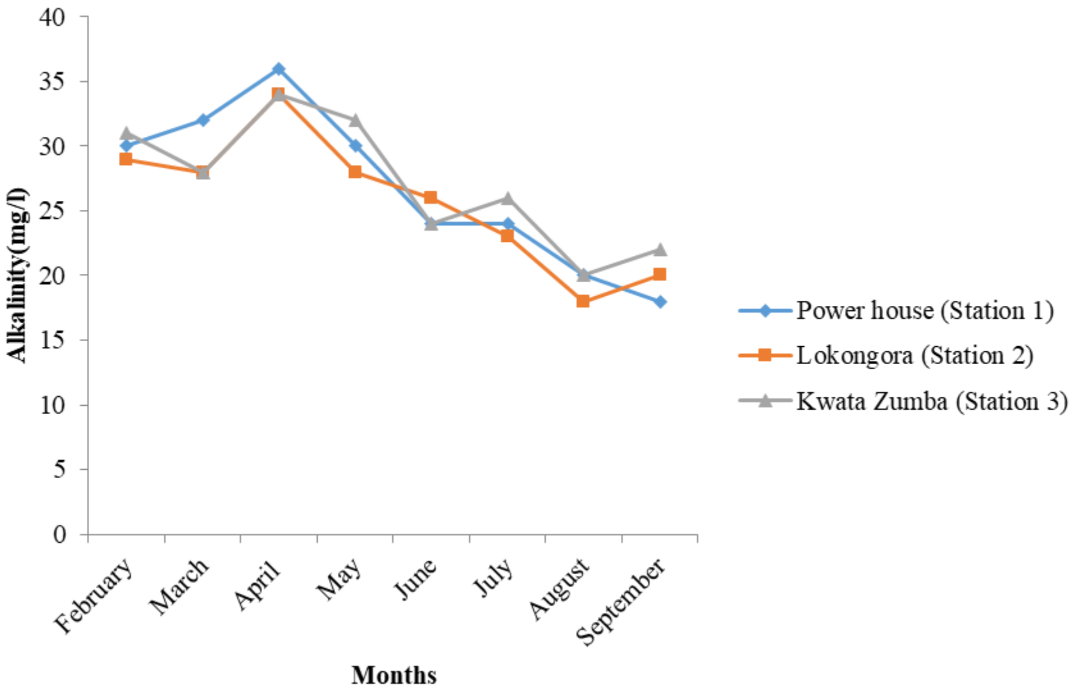

Figure 4.7: Spatial and Temporal Variations of Total Alkalinity across the Sampling Stations

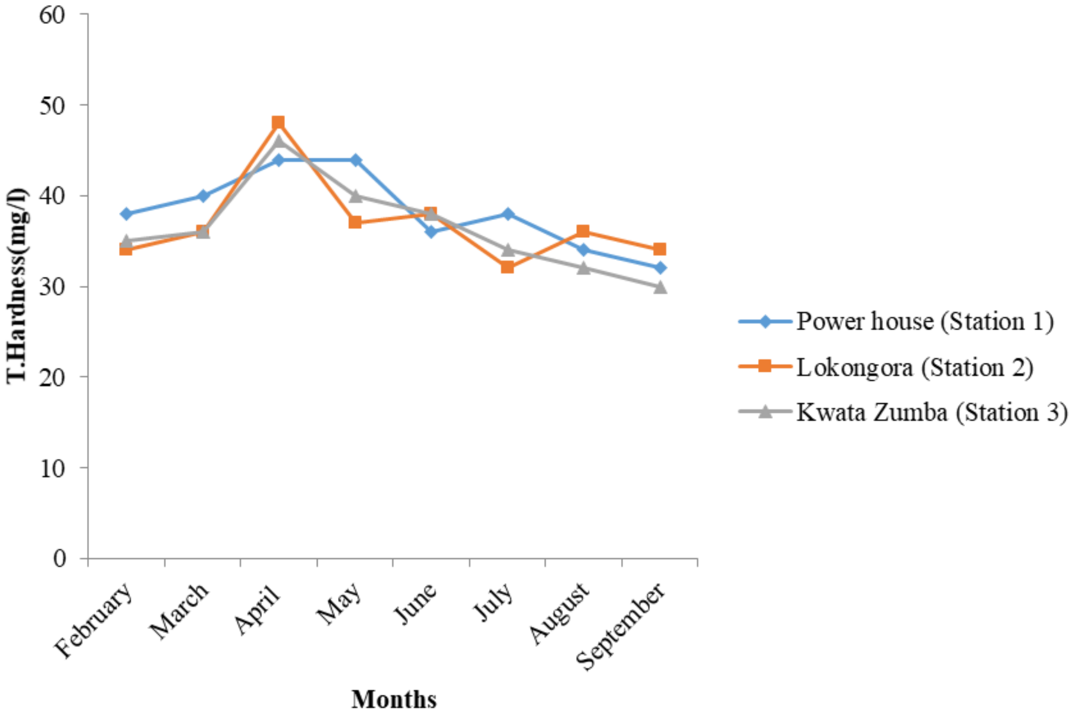

Figure 4.8: Spatial and Temporal Variations of Total Hardness across the Sampling Stations.

4.1.10 Potassium content

The result of Spatial and Temporal variation of Potassium within the three stations are presented in Figure 4.9. Potassium values ranged from 1.62 mg/l to 1.66 mg/l, with station 2 and 3 having the lowest value and station 1 had the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally as recorded in all stations the highest value of potassium was recorded in February especially in station 1. The value was relatively constant to March, and then gradually declined from March to July. A slight increase was recorded from July to August in Stations 1 and 3. The two stations then experienced a slight decline in September, while in station 2 there was a slight decline from July to August and a slight increase from August to September.

4.1.11 Sodium content

The result of Spatial and Temporal variation of Sodium within the three stations are presented in Figure 4.10. Sodium values ranged from 10.42 mg/l to 10.82 mg/l. Station 1 had the lowest value and station 3 had the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally as recorded in all stations the highest value of sodium was recorded in February relatively across the three stations. The value gradually declined from February to May, and then slightly increased from the May to June. The value gradually declined from June to September. The lowest value of Sodium was recorded in September.

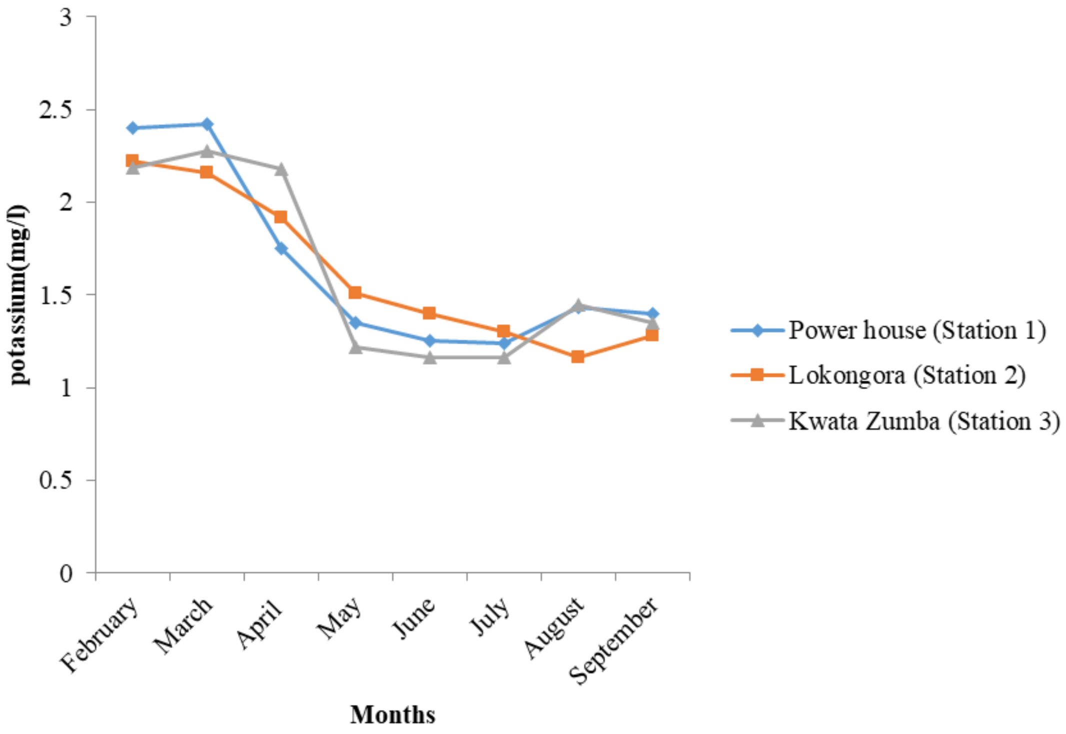

Figure 4.9: Spatial and Temporal Variations of Potassium Content across the Sampling Stations

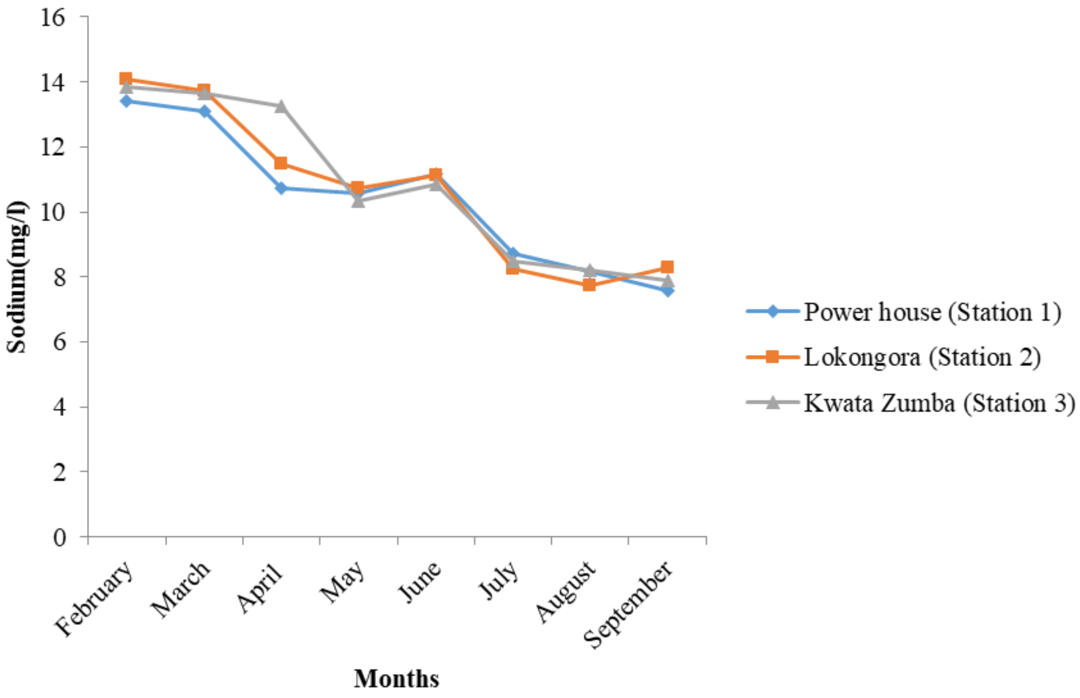

Figure 4.10: Spatial and Temporal Variations of Sodium Content across the Sampling Stations

4.1.12 Electrical conductivity (EC)

The result of Spatial and Temporal variation of Electrical Conductivity within the three stations are presented in Figure 4.11. Electrical conductivity values ranged from 75.25 µ/cm to 77.13 µ/cm, with station 2 having the lowest value and station 1 had the highest value. There was no significant difference ($p>0.05$) between sampling stations and seasons. Generally as recorded in all stations the value of Electrical conductivity was relatively stable from February to March. A sharp increase was recorded between March and April. The highest value of Electrical conductivity was recorded in April. The value gradually declined from April to September.

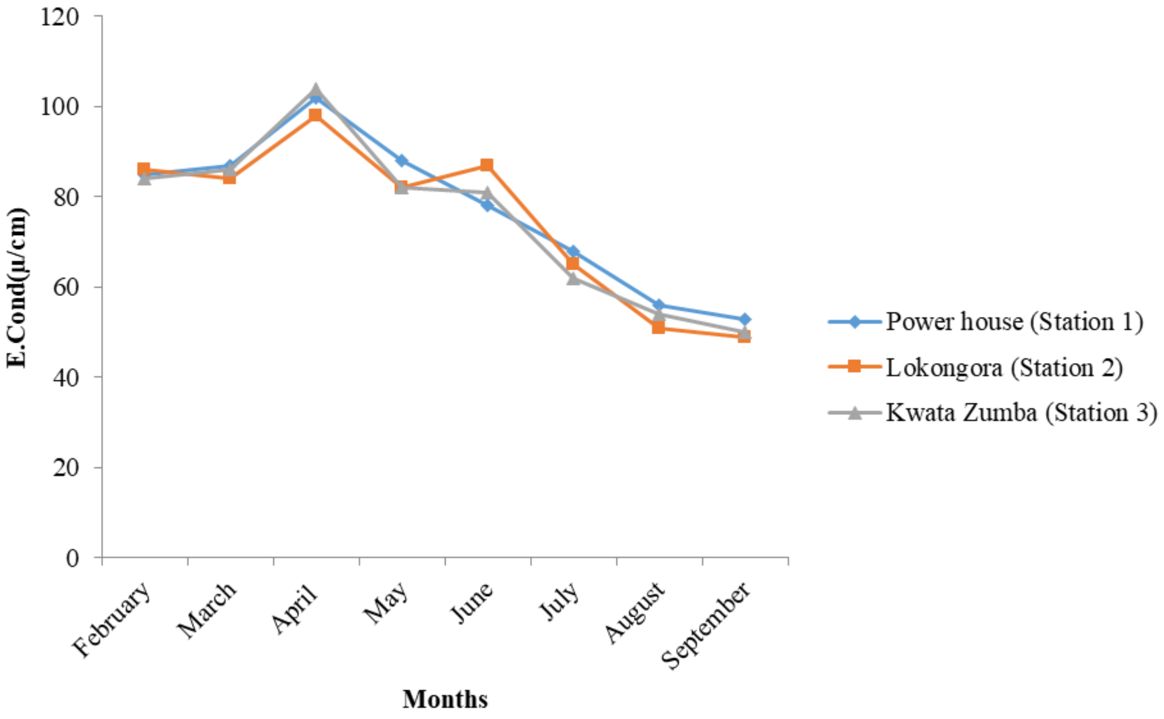

Figure 4.11: Spatial and Temporal Variations of Electrical Conductivity across the Sampling Stations

4.1.13 Spatial assessment of heavy metals concentration of water samples in shiroro lake

The results of the amount of heavy metals present in water samples collected over a period of eight months from Shiroro Lake are presented in Table 4.2. There was no significant difference (p>0.05) in Zinc, Copper, Lead, Chromium, and Cadmium across the three sampling stations of the lake as indicated by ANOVA.

4.1.14 Seasonal assessment of heavy metals concentration of water samples in Shiroro Lake

The seasonal variation of heavy metals concentration in water samples are presented in Table 4.3. Mean values of heavy metal concentration in Zn and Pb was higher in rainy season as compared to the mean values in dry season. Also, mean values of heavy metals concentration in Cu, Cr and Cd was higher in dry season.

4.1.15 Assessment of the level of heavy metals of sediment samples in Shiroro Lake

The results of the amount of heavy metals present in sediment samples collected over a period of eight (8) months from Shiroro Lake are presented in Table 4.4. There was no significant difference (p>0.05) in Zinc, Copper, Lead, Chromium and Cadmium across the three sampling stations of the lake as indicated by ANOVA.

Table 4.2 Spatial Assessment of Heavy Metals Concentration of Water Samples in Shiroro Lake

Metals	Power house (Station 1)	Lokongora (Station 2)	Kwata Zumba (Station 3)	p -value	
				Month	Station
Zinc	0.06±0.04 (0.01-0.11)	0.07±0.06 (0.02-0.18)	0.04±0.02 (0.02-0.07)	0.06	0.34
Copper	0.42±0.54 (0.02-1.13)	0.52±0.61 (0.01-1.34)	0.11±0.04 (0.05-0.20)	0.17	0.25
Lead	0.05±0.06 (0.00-0.11)	0.09±0.08 (0.00-0.2)	0.09±0.07 (0.00-0.15)	0.99	0.67
Chromium	0.01±0.01 (0.00-0.01)	0.01±0.01 (0.00-0.01)	0.01±0.01 (0.00-0.01)	0.36	0.31
Cadmium	0.00±0.00 (0.00-0.00)	0.00±0.01 (0.00-0.01)	0.00±0.01 (0.00-0.01)	0.50	0.27

Table 4.3 Seasonal Assessment of Heavy Metals Concentration of Water Samples in Shiroro Lake

Metals	Dry season Mean±SE (Range)	Wet season Mean±SE (Range)
Zinc	0.03±0.02 (0.01-0.08)	0.08±0.05 (0.02-0.18)
Copper	0.07±0.05 (0.01-0.17)	0.63±0.55 (0.05-1.34)
Lead	0.08±0.08 (0.00-0.20)	0.08±0.06 (0.00-0.15)
Chromium	0.01±0.01 (0.00-0.01)	0.01±0.01 (0.00-0.01)
Cadmium	0.01±0.01 (0.00-0.01)	0.00±0.00 (0.00-0.00)

Table 4.4 Spatial Assessment of the Level of Heavy Metals of Sediment Samples in Shiroro Lake

Metals	Power house (Station 1)	Lokongora (Station 2)	Kwata Zumba (Station 3)	p -value	
				Month	Station
Zinc	0.13±0.06 (0.10-0.25)	0.20±0.05 (0.11-0.25)	0.16±0.06 (0.10-0.24)	0.17	0.08
Copper	0.11±0.06 (0.07-0.23)	0.40±0.37 (0.09-0.91)	0.13±0.09 (0.02-0.27)	0.71	0.12
Lead	0.05±0.06 (0.00-0.10)	0.09±0.02 (0.05-0.11)	0.07±0.08 (0.00-0.15)	0.12	0.31
Chromium	0.01±0.01 (0.00-0.02)	0.01±0.01 (0.00-0.01)	0.01±0.01 (0.00-0.03)	0.57	0.53
Cadmium	0.01`±0.01 (0.00-0.01)	0.01±0.01 (0.00-0.01)	0.01±0.01 (0.00-0.015)	0.69	0.61

4.1.16 Seasonal assessment of heavy metals concentration of sediment samples in Shiroro Lake

The seasonal variation of heavy metal concentration in sediment samples are presented in Table 4.5. Mean values of heavy metal concentration in Cu and Pb was higher in rainy season as compared to the mean values in dry season. Also, mean values of heavy metals concentration in Zn, Cr and Cd was higher in dry season.

4.1.17 Assessment of the level of heavy metals of fish samples in Shiroro Lake

The results of the amount of heavy metals present in fish samples collected over a period of eight months from Shiroro Lake are presented in Table 4.6. Chromium differed significantly ($p<0.05$) among all the three species of fish as indicated by ANOVA There was no significant difference ($p>0.05$) in Zinc, Copper, Lead, and Cadmium among the three species of fish sampled from the lake as indicated by ANOVA.

4.1.18 The level of heavy metals presents in fish samples

Figure 4.12 shows the level of heavy metals present in the muscles of each fish species. The highest value of zinc was recorded in Claridae, and the lowest value of zinc was recorded in Bagridae. The highest value of Copper was recorded in Claridae, and lowest in Alestes. The highest value of Lead was recorded in Alestes, and then lowest in Bagridae. Chromium and Cadmium were relatively low, and was not detected in all the three fish species.

Table 4.5 Seasonal Assessment of Heavy Metals Concentration of Sediment Samples in Shiroro Lake

Metals	***Bagrus bayad***	***Alestes macrolepidotus***	***Clarias gariepinus***	**p –value**	
				Month	**Fish Sample**
Zinc	0.17±0.14 (0.08-0.44)	0.20±0.08 (0.09-0.3)	0.50±0.50 (0.12-1.47)	0.53	0.16
Copper	0.09±0.09 (0.02-0.21)	0.06±0.06 (0.02-0.17)	0.34±0.31 (0.05-0.73)	0.78	0.08
Lead	0.02±0.04 (0.00-0.10)	0.08±0.06 (0.00-0.15)	0.03±0.06 (0.00-0.15)	0.17	0.12
Chromium	0.00±0.00 (0.00-0.01)	0.01±0.00 (0.01-0.02)	0.00±0.00 (0.00-0.00)	0.96	0.00
Cadmium	0.00±0.00 (0.00-0.01)	0.00±0.00 (0.00-0.01)	0.01±0.01 (0.00-0.03)	0.14	0.27

Table 4.6 Assessment of the Level of Heavy Metals of Fish Muscle in Shiroro Lake

Metals	Dry season Mean±SE (Range)	Wet season Mean±SE (Range)
Zinc	0.17±0.067 (0.10-0.25)	0.16±0.06 (0.10-0.25)
Copper	0.13±0.05 (0.07-0.23)	0.30±0.33 (0.02-0.91)
Lead	0.11±0.03 (0.05-0.15)	0.03±0.05 (0.00-0.10)
Chromium	0.01±0.01 (0.00-0.03)	0.01±0.01 (0.00-0.02)
Cadmium	0.01±0.01 (0.00-0.02)	0.01±0.01 (0.00-0.01)

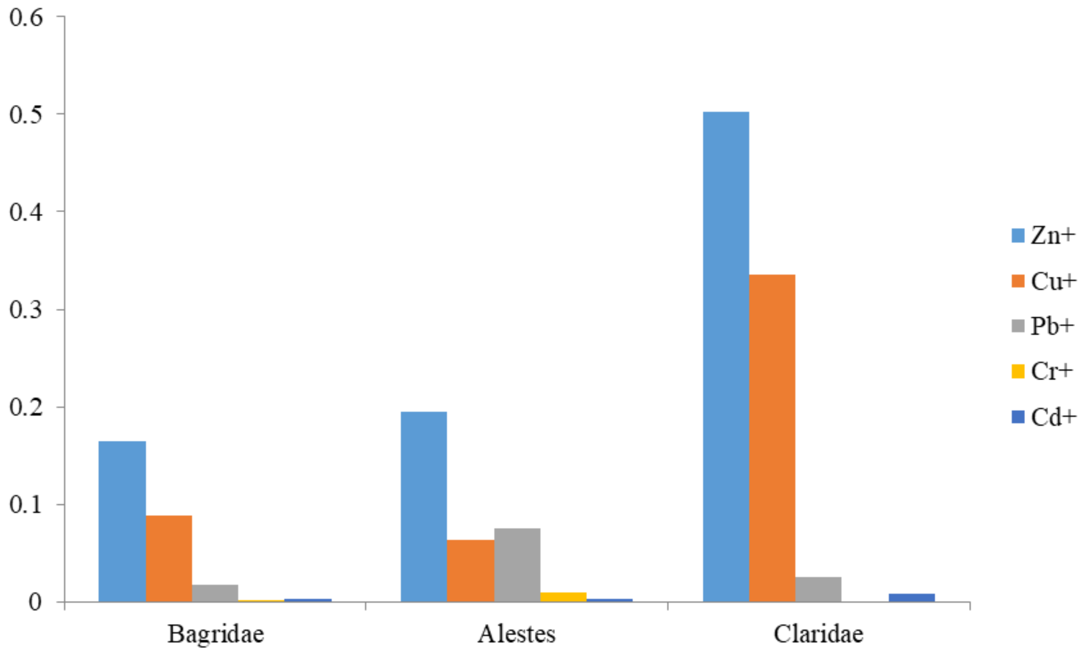

Figure 4.12 Levels of heavy metals presents in Fish muscles in Shiroro Lake.

4.1.19 The relationship between heavy metals in water, sediment and fish muscle samples in Shiroro Lake.

Correlation coefficient between heavy metals in water, sediment and fish muscle sample of Shiroro Lake is presented in Table 4.7. Correlation of the three variables is significant at p value of 0.05. The result shows that there is a positive correlation between the three variables.

4.1.20 Heavy metals in water, sediment and fish samples compared to WHO and FEPA maximum limit

The mean concentration of heavy metals in water, sediment and fish samples compared to WHO and Federal Environmental Protection Agency (FEPA) maximum limit is presented in Table 4.8. The result from this study shows that no heavy metals present in water, sediment or fish sample exceeded the maximum limit standard set by Food and Agriculture Organization (FAO), WHO and FEPA.

Table 4.7 Correlation Coefficient between Heavy Metals in Water, Sediment and Fish Muscle Sample in Shiroro Lake.

. Correlation is significant at the 0.05 level

	Water	**Sediment**	**Fish Muscle**
Water	1.00		
Sediment	0.82*	1.00	
Fish Muscle	0.38	0.84*	1.00

Table 4.8 Mean, Standard Deviation and Range Concentrations of Heavy Metals in Water, Sediment and Fish Samples Compared to WHO and FEPA Maximum Limit

Heavy Metals	Water Mean±SD (Range)	Maximum Limit WHO/FEPA (mg/L)	Sediment Mean±SD (Range)	Maximum Limit WHO/FEPA (mg/kg)	Fish Mean±SD (Range)	Maximum Limit WHO/FEPA (mg/kg)
Zinc	0.06±0.04 (0.01-0.18)	3.00[a]	0.16±0.06 (0.10-0.25)	40.00	0.29±0.32 (0.075-1.47)	40.00
Copper	0.35±0.48 (0.01-1.34)	1.00[a]	0.21±0.25 (0.02-0.91)	40.00	0.16±0.22 (0.02-0.73)	40.00
Lead	0.08±0.07 (0.00-0.20)	0.01[a,b]	0.07±0.06 (0.00-0.15)	0.30	0.04±0.06 (0.00-0.15)	0.30
Chromium	0.01±0.01 (0.00-0.01)	0.05[b]	0.01±0.01 (0.00-0.03)	5.00	0.00±0.01 (0-0.02)	5.00

Cadmium	0.00±0.00 (0.00-0.01)	0.03[a,b]	0.00±0.01 (0.00-0.02)	0.20	0.01±0.01 (0.00-0.03)	0.20

[a,b] WHO guideline value for drinking water quality: [a] = WHO (2011); [b] = FEPA (2003)

4.1.21 Potential ecological risk index (PERI)

The computed results and values of the potential ecological risk indices of Zn, Cu, Pb, Cr and Cd in the three sampling stations are shown in Table 4.9. The mean values ranged from 0.03-2.06 which revealed that the potential ecological risk of the metals across the three sampling stations, have very slight ecological risk level. The comprehensive potential ecological risk indices ranged 0.617-6.902, indicating that the ecological risk level was slight in all stations. The main donator of the potential ecological RIs came from Pb.

4.1.22 Index of geo-accumulation

The values of the I-geo of the study are presented in Table 4.10. The mean result of the I-geo for all the heavy metals ranged from -2.42 to -0.747, suggesting an unpolluted state of the 3 stations. The I-geo values were generally insignificant (<0) in all cases.

4.1.23 Enrichment factor (EF)

The values of the EF of this study are itemized in Table 4.11. The mean EF values ranged from 0.007 to 0.55. These mean values indicate that the sediment samples were from anthropogenic and of crustal enrichment origin. The crustal enrichment origin results of the enrichment factors showed that Pb contributed to the enrichment of the sediment and was considered high in stations 2 and 3.

Table 4.9 Potential Ecological Risk Index (PERI) of Sediment in Shiroro Lake.

		Potential Ecological Risk of Metals			**Comprehensive Ecological Risk Grade**	
Metals	**Min**	**Max**	**Mean**	**RI**	**Risk level**	**Risk degree interpretation**
Zinc	0.05	1.13	0.08		A	Slight
Copper	0.08	0.65	0.29	0.62	A	Slight
Lead	0.49	3.50	2.06	6.90	A	Slight
Chromium	0.00	0.09	0.03	2.94	A	Slight
Cadmium	0.00	1.53	0.48		A	Slight

Table 4.10 Index of Geo-accumulation (I-geo) of Sediment in Shiroro Lake.

	Index of Geo-accumulation					Class of Index of Geo Accumulation				
Stations	**Zinc**	**Copper**	**Lead**	**Chromium**	**Cadmium**	**Elements**	**Mean I-geo**	**Rank**	**Class**	**Results**
1	-2.51	-2.27	-1.69	-0.90	0.12	Zinc	-2.42	<0	0	Uncontaminated
2	-2.33	-1.71	-1.42	-1.15	-1.38	Copper	-2.06	<0	0	Uncontaminated
3	-2.42	-2.20	-1.57	-0.70	-0.98	Lead	-1.56	<0	0	Uncontaminated
Mean	-2.42	-2.06	-1.56	-0.92	-0.75	Chromium	-0.92	<0	0	Uncontaminated
						Cadmium	-0.75	<0	0	Uncontaminated

Table 4.11 Enrichment Factors (EFs) of Sediment in Shiroro Lake.

Enrichment Factors						**Class of Enrichment Factors (EFs)**			
Stations	**Zinc**	**Copper**	**Lead**	**Chromium**	**Cadmium**	**Elements**	**Enrichment factor (EF)**	**Risk**	**Interpretation**
1	0.07	0.01	0.29	0.02	0.02	Zinc	0.08	<1	Crustal origin
2	0.10	0.11	0.55	0.01	0.01	Copper	0.05	<1	Crustal origin
3	0.08	0.04	0.39	0.02	0.02	Lead	0.41	<1	Crustal origin
Mean	0.08	0.05	0.41	0.02	0.02	Chromium	0.02	<1	Crustal origin
						Cadmium	0.02	<1	Crustal origin

4.2 Discussion

4.2.1 Physicochemical parameters of Shiroro Lake, Niger State.

Temperature is one of the most important environmental variables because it regulates the physiological behavior and distribution of aquatic organism (Mustapha 2008). From this study, temperature of the lake ranged between 26.6-30.2 ºC. The mean temperature recorded from this study could be the time of sampling and the season. This finding is consistent with the work of Atobatele and Olutona (2017) from Aiba Reservoir, Iwo, and Osun State that reported a temperature range from 25.9-30.5 º C. Arimoro and Keke (2016) from Gbako River North Central Nigeria also reported a temperature of 23.10-30.0 ºC. Mohammed *et al.*, (2016) also reported a temperature range of 21-33 ºC from his study in Tungan Kawo (Wushishi Lake), north central, Nigeria. Anyanwu (2012) also reported a temperature range of 20-26.7 ºC from his study in Ogba River Benin City, Nigeria. Auta *et. al.*, (2016) reported a temperature range of 21-24 ºC from his study in Shiroro lake, Niger State. Dadi-mamud *et al.*, (2014) from River Ndakotsu Lapai, Niger State also reported similar findings. This work is in contrast with the findings of Edegbene *et al.*, (2015) who reported a mean temperature of 27.8-28.3 ºC in River Chanchaga Niger State. The result of this finding is contrary with the work of Ayoade *et. al.*, (2012) who reported a temperature range from 28.7-31.7 ºC from a southern Tropical River. Ndana (2017), reported a temperature range of 29.3-32.5 ºC from his study on Landzum River, Bida Niger State.

From this study the pH value ranged between 6.58 and 7.96 which fall within the recommended range of 6.5 to 8.5 set by WHO and National Standard for Drinking Water Quality in Nigeria (WHO 2005 and NDSWQ 2005). High pH values obtained in this study could be as a result of surface run off or decay of organic matters in the water (Mustapha, 2009). This finding is consistent with the work of Raji *et al.*, (2015) who recorded a similar pH value range of 6.24-8.50 from River Sokoto, Northwestern Nigeria. Similarly Dadi-mahmud *et al*., (2014) reported a pH range of 5.2-8.8 in River Ndakotsu, Niger State, Nigeria. Similar findings include Arimoro and Keke (2016) who reported pH range of 6.10-7.70 from Gbako River. Atobatele and Olutona (2017) from Aiba Reservoir, Iwo Osun state that reported a pH range of 6.4-9.2. Edegbene *et al*., (2015), reported pH range of 7.04-7.90 from Chanchaga River. Mohammed *et al*., (2016) also reported a pH range of 6.5-7.4 from his study in Tungan Kawo (Wushishi Lake), North Central, Nigeria. Ndana (2017) reported a pH range of 6.37-7.8 from Landzun River in Niger State. Auta *et. al*., (2016) reported a pH range of 6.4-8.11 from his study in Shiroro Lake, Niger State. Nehad and Reda (2016) reported similar observation of pH range value of 8.09-8.53 from their study in Egypt.

Dissolved oxygen values ranged from 2.2-4.1 mg/L, this is an indication of a moderately oxygenated lake throughout the study period. Higher DO value was recorded in raining season than in the dry season, this could be as a result of increase in the volume of water in raining season and high temperature coupled with high sunlight intensity in the dry season (Raji *et al*., 2015). Findings from this study is in conformity with Mohammed *et al*., (2016) that reported a DO range of 1.8-3.0 mg/L from his study in Tungan Kawo (Wushishi lake), north central, Nigeria. Auta *et. al*., (2016) reported a DO range of 2.0-5.6 mg/L from his study in Shiroro lake, Niger State. This findings was in contrast with the findings of Atobatele and Olutona (2019) from Aiba reservoir, Iwo Osun state Nigeria who reported a DO range from 5.9-8.2 mg/L.

Biochemical oxygen demand (BOD) recorded in this study ranged from 1.2-3 mg/L which falls within the maximum permissible limit (WHO 2005, NSDWQ 2005). The study recorded higher BOD values in rainy season than in dry season as a result of influx of organic matters into the lake through the tributaries around the lake, surface run off and erosion (Mustapha 2009; Abowei and Ekubo 2011). This finding is consistent with the findings of Atobatele and Olutona (2017) from Aiba Reservoir, Iwo Osun State Nigeria who reported a BOD range from 1.4-7.6 mg/L, Mohammed *et al*., (2016) also reported a BOD range of 1.0-11 mg/L from his study in Tungan Kawo (Wushishi lake), north central, Nigeria. Auta *et. al*., (2016) reported a BOD range of 1.0-9.6 mg/L from his study in Shiroro Lake, Niger State

Electrical Conductivity value of the lake ranged from 49 and 120 µS/cm. Lower conductivity value was recorded in the dry season than in rainy season indicating that the sampling station might contain more amount of suspended and dissolved solid materials, which increases the concentration of cation such as calcium, magnesium and sulphate (Mustapha 2008). Conductivity range obtained in this study was very similar to 32-110 µS/cm obtained from River Gbako, North Central Nigeria (Arimoro and Keke, 2016). Auta *et. al*. (2016) also reported a conductivity range of 27-135 µS/cm from his study in Shiroro Lake, Niger State. Mohammed *et al*. (2016) reported a much lower conductivity range of 22.4-23.4 µS/cm from his study in Tungan Kawo (Wushishi Lake), north central, Nigeria. Similarly Keke *et al*. (2015) reported a conductivity value range of 32-72 µS/cm from surface water of downstream Kaduna River, Zungeru. Atobatele and Olutona (2017) from Aiba reservoir, Iwo Osun state Nigeria reported a much higher value of conductivity which range from 90.0-140 µS/cm.

Alkalinity value ranged from 18-36 mg/L. High value of alkalinity was observed in the rainy season than in dry season. This could be as a result of surface run off from nearby farms and dissolution of calcium carbonate in the water column (Yalav 2013). This finding is consistent with the work of Atobatele and Olutona (2017) from Aiba reservoir, Iwo Osun state Nigeria, who reported a value of conductivity which ranged from 10-35 mg/L. In contrast, Keke *et al*. (2015) reported a relatively low alkalinity value range of 8.00-16.00 mg/L from surface water of downstream Kaduna River. Similarly Ibemenuga and Nzekwe (2017) reported alkalinity of 7.65-21.13 mg/L in Rainforest freshwater Ecosystem of southern Nigerian. Ibrahim *et al*., (2009) reported a higher value of alkalinity of 41.31-43.67 mg/L from Kontagora reservoir, Niger state.

Total dissolved solids which usually consist of organic and inorganic substances dissolved and washed into the lake by runoffs (Bala and Bolorunduro, 2011) are essential in the life of aquatic bio-community. Dissolved Solids values obtained during the study periods were relatively constant ranging between 75-99 mg/L and not above recommended values all through the months as values were not significantly different at ($P < 0.05$). Dissolved solids determination are important in water quality studies, though no serious health effect has been associated with dissolved solids ingestion in water but some regulatory agencies (Federal Ministry of Education (FME), National Agency for Food and Drug Administration and Control (NAFDAC), recommended a maximum dissolved solids value of 500 mg/L in drinking water supplies.

Phosphate and nitrate levels are a measure of level of eutrophication of a given lake (Kolo *et al*., 2010). Phosphate levels in the present study were significantly higher during the concluding months of the rainy season (August and September) than the other months. Phosphate recorded in this study ranged from 0.16-0.28 mg/L. This finding is in contrast with the work of Atobatele and Olutona (2017) from Aiba reservoir, Iwo Osun state Nigeria, who reported a higher value of phosphate which range from 0.2-1.2 mg/L.

4.2.2 Concentration of heavy metals in fish muscle

Clarias gariepinus is a dominant fish species in Shiroro Lake, and can live between 6-8 years. *C. gariepinus* have the ability to accumulate heavy metals in their body tissue considering their long life span, in addition to the fact that they are floor feeders, feeding on sediments at the bottom of the lake. In this study the heavy metal with the highest concentration present in *C. gariepinus* muscle was Zinc (0.502 µg/g) followed by Cu (0.34 µg/g) and other metals in this order: Zn>Cu>Pb>Cd> (Cr was not detected). The values of heavy metals concentration recorded in the muscle of *C. gariepinus* were below the maximum standard set by WHO. The finding is consistent with the work of Edward *et al*., (2013) who reported a similar amount of heavy metals in *C. gariepinus* muscle from Odo-Ayo River in Ado-Ekiti, Ekiti State, Nigeria. He reported that Zinc (0.75 µg/g) was the highest followed by Cu (0.38 µg/g) and other metals in this order: Zn>Cu>Pb>Cd>Cr. The work of El-Sayed *et al*., (2011) was in contrast to the findings of this study, he recorded a higher heavy metal concentration in *C. gariepinus* muscle. Chromium (6.68 µg/g) was also the highest, followed by Zinc (5.67 µg/g) then Copper was the lowest in this order: Cr>Zn>Pb>Cd>Cu. Asare *et al*. (2018) reported a lower heavy metal concentration value, Zinc (0.07 µg/g) was the highest followed by other metals in this order: Zn>Cr>Cu> (Pb and Cd not detected).

Bagrus bayad and *Alestes macrolepidotus* are also dominant fish species in Shiroro Lake. From the findings of this study Zinc (0.165) was higher than other metals in this order: Zn>Cu>Pb> (Cd & Cr having the same value) in *Bagrus bayad*. Zinc was also highest in Alestes in this order: Zn>Pb>Cu>Cr>Cd. Generally, in the three fish species Zinc was the highest especially in *C. gariepinus* followed by *Alestes macrolepidotus* and lowest in *Bagrus bayad*.

4.2.3 Concentration of heavy metals in water sample

A considerable low amount of heavy metal concentration of Zinc, Lead, and Chromium was recorded in the water samples from the three sampling stations. Values of metal in stations 2 and 3 was higher than that of station 1, suggesting direct anthropogenic influence on the water body probably through occupational and domestic activities. Values of metals recorded in the three stations were higher in the rainy season compared to values in dry season. This suggests a strong influence from municipal runoff from the catchment area of the stations and the impact of hydrogeological factors of the particular season. The value of metals obtained were below the minimum permissible limits for drinking water quality standard set by WHO, FAO and FEPA, but the value of Copper and Cadmium recorded in this study slightly exceeded the WHO maximum limit standard. Asare *et al*., (2018) on Bontanga Reservoir in Ghana who also reported that heavy metal concentration of Zn and Cu were both below the maximum limit standard in water samples from all his sampling stations. He reported that Pb was below detectable limit, but Cr and Cd were above WHO stipulated limit. Oyakhilome *et al*., (2013) in his work on Owena Multi-Purpose Lake, Ondo state, Southern Nigeria reported that the metal concentration values of Zn, Cu and Cd of water samples were below WHO stipulated limit, but he recorded a slightly high amount of heavy metal concentration above WHO stipulated limit in Pb and Cr.

4.2.4 Concentration of heavy metals in sediment sample

Heavy metals concentration below WHO permissible limit recorded in sediment samples collected from the three sampling stations was recorded in Zn, Cu, and Cr. Heavy metals concentration was slightly high in Pb and Cd. *Asare et al*. (2018) on Bontanga Reservoir in Ghana also reported that heavy metal concentration of Zn, Cu, Cr, and Cd were all below WHO stipulated limit, and Pb was below detectable limit.

Oyakhilome *et al*. (2013) in his work on Owena Multi-Purpose Lake, Ondo state, Southern Nigeria recorded a much higher level of heavy metal concentration of Cu, Pb, Cd, and Cr above WHO permissible limit, only Zn was below WHO permissible limit.

The correlation between heavy metals in water, sediment, fish muscle of *Alestes macrolepidotus*, *Bagrus bayad* and *Clarias gariepinus* was statistically tested with SPSS. The Pearson's correlation coefficient matrix for the heavy metals was performed, as there was a linear relationship among the metals. Copper, Zinc, Chromium, Cadmium and Lead were found to have relatively higher positive correlation coefficients (for Cu, $r = 0.30$ between sediments and muscle; for Zn, $r = 0.84$ between sediments and muscle)

For both the elements (Cu and Zn), the correlation coefficient between sediment and muscle was found to be higher than the correlation coefficient between sediment and Muscle. The present study shows that precautions are needed to be taken in order to obviate the metal pollution in future. Otherwise, these pollutions can be hazardous for fish and human health.

4.2.5 Ecological Risk Assessment

4.2.5.1 Potential ecological risk index (PERI)

In this study a detailed result of Potential ecological risk index was recorded. The single ecological risk indices of the sediment heavy metals in the study stations decreased in the order of Pb>Cd>Cu>Zn>Cr. However, single ecological risk of Pb in sediment was highest and ranged from 0.49 to 3.50, with a mean of 2.06, which indicated that Pb was in the low risk and the remaining heavy metals (Cu, Cr, Cd, and Zn) of E^i_r values with much lower levels, their maximum values were less than seven, which also specifies that all Cu, Pb, Cd, Cr, and Zn were in the low risk. The results of ERI ranged between 0.617 and 6.902, indicating that five heavy metals of sediment of the study area were in low risk category. Zhou *et al*. (2016) studied spatial variation of soil heavy metals in Eastern China and found that ERI was below 90, indicating that heavy metals in soils of Eastern China were in the light ecological risk. Diami *et al*. (2016) conducted a study on potential ecological and human health risk of heavy metals in surface soils in Malaysia and estimated the ERI ranged between 44 and 128, indicating low ecological risk.

4.2.5.2 The geo-accumulation index

The negative I_{geo} values of all the metals indicated that there was no contamination in the sediment, which fells in I_{geo} class (-1), and these are found in the soil mostly from the natural processes. The I_{geo} mean values of heavy metals in sediment across the stations are as follows: Zn (-2.42), Cu (-2.06), Pb (-1.56), Cr (-0.917), Cd (-0.747). The I_{geo} values therefore indicated uncontamination of the sampled stations. Adimalla and Wang (2018) studied the distribution, contamination, and health risk assessment of heavy metals in surface soils from northern Telangana, India and revealed that some sampling stations were uncontaminated (class -I), others were uncontaminated to moderately contaminated (class-II), while Cu with the highest mean value of 1.04 made some other stations fall into the third category of the index (class-III) indicating that the sediment are moderately contaminated.

4.2.5.3 Enrichment factor

The control sampling point was considered as the unpolluted or background point. Iron (Fe) was used as the normalizing element due to low occurrence variability. The enrichment factor (EF) of heavy metals around the three sampling stations showed that mean values of Zn (0.083), Cu (0.050), Pb (0.41), Cr (0.015), and Cd (0.016) had no enrichment i.e. enrichment values were less than one (<1), this indicates that the metals are entirely from crusted mineral or natural processes.

Zhang and Liu (2002), established the fact that EF values between 0.5-1.5 indicate that a metal is entirely from crustal material or natural processes, whereas EF greater than 1.5 suggest the source is more likely to be anthropogenic. The results of the EF in this study using Fe concentration as the background value that Pb, Zn, Cu, Cr and Cd enrichment factor were from crusted origin. Indicating no enrichment which suggested possible mobilization of metals (Zsefer *et al.*, 1996). While the enrichment factor of Pb was highly significant or significantly enriched (Sutherland, 2000).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Most of the physico-chemical parameters of the surface water in Shiroro Lake were within the stipulated standard limits. The analysis for both the surface water and sediment revealed strong relationship between the physical and chemical parameters and their source allotment where mainly from anthropogenic activity such as farming. This study revealed that heavy metal concentrations in water samples were within recommended limit for drinking except Cd. The water in Shiroro Lake is not safe for human consumption as it can lead to Cd exposure. The heavy metal concentrations in sediments were also within FAO/WHO set limits for the survival of aquatic organisms. Heavy metals in the various fish species were within the recommended limit for fish and fish products. Hence, these metals have no immediate threat on consumers' health. However, prolonged consumption of the fish species will have adverse effects since heavy metals accumulate. Results obtained from the three ecological indices revealed that the sampling stations are not contaminated.

5.2 Recommendations

1. This study recommends regular monitoring of trace metal concentrations in the lake, as Shiroro Lake serves as a source of fish and water sources for all-year-round irrigation farming as well as drinking water source for the inhabitants.
2. Management plan to restrict the dumping of wastes into surface water bodies is needed in order to reduce the impact on water quality and pollution related health problems. This can be achieved through effective waste management strategy and provision of reliable public water supply.

3. Regular monitoring exercises should be carried out by law enforcement agencies and the locals on the activities around the lake in order to ensure those effluents standards and other sanitary conditions are complied with.

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