

**CONCENTRATION OF HEAVY METALS IN WATER AND SEDIMENT OF
IKPOBA RIVER BENIN CITY, EDO STATE**

BY

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**A PROJECT WORK SUBMITTED TO THE DEPARTMENT OF PHYSICAL
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CERTIFICATION

We the undersign, satisfy that this project work titled “**Concentration Of Heavy Metals In Sediment Of Ikpoba River**” was carried out by **OZENIH ESTHER AMUNUOME** with Matriculation Number **AST/2372070425** of the department of **Physical Science Laboratory Technology (Chemistry Option)**, Federal Polytechnic, Auchi in partial fulfillment of the requirement of the award of **HIGHER NATIONAL DIPLOMA (HND)** in **CHEMISTRY**.

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DEDICATION

This project work is dedicated to God Almighty for giving me the strength and wisdom to make this work a success

ACKNOWLEDGEMENT

I give thanks to God Almighty the maker of the universe for my life and also for making me to accomplish my goal in life, also for giving me the strength and determination to put this project work together.

Special regard to my parent **MR. AND MRS. OZENIH** for their love support throughout my stay in school. And to my friends, siblings who have made this project a great success.

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Abstract

Concentrations of five heavy metals (Cu), Zinc (Zn), iron (Fe), Lead (Pb), Chromium (Cr) in sediments and Ikpoba river was analyzed in the work. The mean concentration of the metals present in the sediment was 1.00, 14.00, 1280.0, 2.00 and 4.00 mg/kg Cu < Zn < Fe < Pb < Cr respectively, the concentration of heavy metal Cu < Zn < Fe < Pb < Cr present in water are 0.01,0.37.8.50,0.01, 0.01 mg/l respectively. The concentration levels of all the heavy metals in sediment studied were lower than world health organization standard. From the results obtained, the Ikpoba River sediments and water have low contamination level and are said to be unpolluted by the study heavy metals.

CHAPTER ONE

1.0 Introduction

1.1 Background of the Study

Water is essential for life. It is utilized for domestic purposes, agricultural production, industrial activities, and among many other uses. Water is a basic amenity to humanity on the planet earth. Water is managed poorly in many parts of the world despite it being important for life (Bakan, 2012). Water is a good solvent; and due to this characteristic, water will always dissolve and contain mineral constituents and other substances that it leaches out on contact. Naturally, pure water is hard to find. The contamination of water in a particular area is always directly related to the degree of contamination of its environment (Durali *et al.*, 2010). While trickling down rainwater collects impurities from the atmosphere. Consequently, impurities from surface run-off, sewage discharges and industrial effluents are collected by rivers and streams in their course of flow (Egborge, 2014). Rivers and streams are important sources and channels for the movement and transportation of anthropogenic metals to the ocean. Water pollution from anthropogenic activities has been documented in many parts of the world (Ogbeibu & Anagboso, 2014). Many rivers, lakes, wetlands, ground waters and oceans suffer a great loss of degradation from various human activities. These activities have effects on water quality, changing both its physiochemical and biological parameters making it unsuitable not only for domestic use, but also for other purposes. Water pollution also has effects on habitats, causing species migration for species that cannot adopt, while exterminating

others due to impacts that affect their reproductive abilities. There are many sources of water pollution but the main ones are pollution from industrial and municipal waste-water discharges, inputs from agricultural activities that include the use of fertilizers and chemicals, seepage from waste sites, decaying plant life, road, railway and sea accidents involving large oil tankers etc., all leading to environmental degradation, and the necessity for environmental protection. New challenges in environmental protection and conservation that have resulted due to global changes bring the need for baseline data to evaluate the potential impact of pollutants to ecosystems (Tandyrak *et al.*, 2012).

Heavy metals in the environment lack natural elimination processes. As such, heavy metals occur naturally in the earth's crust at varying concentrations in all ecosystems. Unfortunately, human activities have drastically interfered with the biogeochemical cycle and balance of heavy metals in the various ecosystems (Jimoh, 2016). Environmental pollution became extensive as mining, industrial activities and mechanized agriculture activities increased in the 19th century and have intensified since then. Pollution of ecosystems such as river, oceans, lakes and wetlands by heavy metals resulting from anthropogenic impact is causing serious ecological problems in many parts of the world. This is exacerbated by the lack of natural elimination processes for heavy metals in the environment (Iwuoha *et al.*, 2012)

In the past microbial quality of water for potable uses was of concern and was often given the first priority due to the immediate and potential devastating consequences of waterborne infectious diseases (Idodo-Umeh *et al.*, 2014). Currently however, increased

concern has shifted over to that the concentration of heavy metals in water because the public has now become aware of the toxic effects of heavy metals on human health. In that case, globally heavy metal pollution has been marked as a serious environmental problem owing to their persistent and accumulative properties (Kpee & Nwadinigwe, 2014).

Heavy metals are persistent in the environment and they tend to shift from one compartment of the ecosystem to another. In the aquatic environment these metals shift from water to the sediments and then the biota. Some of the heavy metals like iron, copper, cobalt, zinc, manganese and chromium(III) are essential metals since they are required by the body to perform physiological functions of living tissue and regulate many biochemical processes (Ana *et al.*, 2014).

Non-essential metals are those metals that are not required by living systems and can be toxic even in trace amounts, these include: cadmium, mercury, lead, titanium, arsenic, bismuth and antimony. Whether essential or non-essential, all metals are toxic at higher concentrations with their toxicity linked to chronic diseases such as renal failure, liver cirrhosis, brain syndrome, and many others (Calmano *et al.*, 2013). These metals continue to pile in concentration to higher levels when they are discharged into natural waters at increased concentrations from agricultural, industrial and domestic wastes, pesticides or mining operations. As a result, they end up having severe toxicological effects on humans and the aquatic ecosystem. Heavy metals are also common in industrial applications such as their use in manufacture of pesticides, fungicides,

batteries, alloys, electroplated metal parts, textiles, pigments, dyes, and steel industries (Anden *et al.*, 2015). Other uses of heavy metals include; industrial use in pharmaceuticals, cosmetic, dental amalgam and paints manufacturing

1.2 Objectives of the Study

The project research is designed:

- i. To assess the current level of heavy metal concentration in sediment of River Ikpoba in Benin with respect to water quality standard by the Federal Ministry of Environment
- ii. Determine the level of the heavy metals Cu, Zn, Fe, Pb and Cr in the water of River Ikpoba during short rains, heavy rains and dry seasons.

1.2 Statement of the problem

There is a high possibility for the heavy metals present in the ores to enter and accumulate in the soil and waters of the region through runoffs, seepages and leaching operations, rendering the water unfit for human use, in an otherwise, water scarce area – an occurrence that calls for water conservation. This study undertakes to elaborate on the land based activities undertaken along the course of River in Benin to determine the potential levels of heavy metal contamination that could occur as a result of the land based activities along the river. This focus of the study is therefore the determination of the levels of some selected heavy metals in water and sediments of this river.

1.4 Justification

Water pollution and quality degradation is a growing problem, exacerbated by the growing anthropogenic activities in developing countries. It is becoming a threat to the existing natural water resources functions and uses. This is attributed to the increasing quest of industrialization and exploration of resources and diversification of national development goals, experienced globally, with Nigeria not being an exception (Kithiia et al., 2011). The justification for this study is that the pollution of water resources is one of the major causes of the scarcity of freshwater in the Nigeira coast necessitating the need for conservation of freshwater sources and supplies. Heavy metal pollution poses danger to the life of humans and organisms. Heavy metal pollution affects the availability of freshwater sources for domestic use (Okoth and Otieno, 2017).

1.5 Scope of Study

The study focused only on five metals (Cu, Zn, Fe, Pb and Cr). These heavy metals were considered prevalent in the area, as informed from literature survey. The study also focused itself on River Ikpoba in Benin since a lot of studies haven't been done in this river, proof of its importance in the area.

1.6 Limitation to the Study

The limitations of the study are as follows:

- Difficulty in combining lectures and project work.
- Lack of funds to carry out the project work effectively.

- Bad road while collecting the samples.

1.7 Definition of Terms

Concentration: is the abundant of a constituent divided by the total volume of a mixture.

Heavy metals: Heavy metals are defined as metallic elements that have a relatively high density compared to water. Eg. Iron, copper, lead etc.

Rivers: is a large natural stream of fresh water flowing along a definite course, usually into the sea, being fed by tributary streams.

Sediment: Sediment is solid material that is moved and deposited in a new location. Sediment can consist of rocks and minerals, as well as the remains of plants and animals.

Environment: the surroundings or conditions in which a person, animal, or plant lives or operates.

Anthropogenic Activities: Are all the phenomena which can be consequent of the presence or the action of the human being. The anthropogenic activities include mining, release of industrial waste, smelting of As ore, incineration of fossil fuel, particularly coal, utilization of As-loaded water for irrigation, and As-based pesticides, herbicides, and fertilizers (Karimi et al., 2015).

CHAPTER TWO

2.0 Literature Review

2.2 Rivers and Pollution from Land Based Activities.

Aquatic ecosystems such as river, dams and lakes are sources of livelihood to many rural communities in Africa. However, in the recent past, they have been subjected to various forms of degradation due to pollution arising from domestic wastes, industrial effluent, agricultural run offs and bad fishing practices (Bentu *et al.*, 2014).

Many studies have indicated that surface waters are majorly polluted by land based activities as compared to ground water. River is conduits and channels for the transportation and movement of water to the ocean. River tend to collect impurities and other materials as they move as a result of activities that occur and are conducted along their course of flow, this may reduce the capacity of the river and also the availability of its waters for various uses as it travels downstream. The bulk of the pollutants come from activities related to man though natural sources also play part. It has been studied that the intensity of land uses and activities that are carried alongside a river's channel is directly related to the pollution status of that river, this is explained that the amount of waste discharged tends to increase with increasing water demand (Chen *et al.*, 2012).

2.3 Heavy Metal and Pollution

The contamination of ground, stream and river water ecosystem by heavy metals is a worldwide environmental problem. The public has become more concern over the

potential accumulation of heavy metals in various ecosystems. Global chemical pollution has been a great concern with the increase awareness of the public towards environmental issues (AOAC, 2016).

Pollution of ground water and surface water systems is a major environmental issue throughout the globe. Land based activities have a major impact on natural resources including water, soil and plants. Heavy metals in river are contributed by both natural and anthropogenic sources. Heavy metals have been accumulating for years in sediments, water and biota of lakes and streams, (Uzu, 2012) stated that heavy metals may heavy effects on the ecosystem as greater than those of more common pollutants. Heavy metals and their salts are also found in industrial wastes and agricultural runoffs.

Heavy metals always gain access into the river systems from both natural and anthropogenic sources and these get distributed in water and sediments in the course of their transportation. The spatial distribution and the temporal behavior of metals is essential information for environmental research (Obasohan *et al.*, 2016).

Copper concentrations as low as 1-2 µg/L have been shown to have adverse effects on aquatic organisms. Copper can affect the reproduction, physiology and behavior on a variety of aquatic organisms. Moreover, high intakes of copper have been associated with liver failure and gastrointestinal problems in humans (FAO, 2012).

Iron is one of the most abundant elements in the world. It is found in a number of minerals, rocks, sediment and soil. It is an essential mineral to all organisms. However,

iron has been associated with acute poisoning in young children (30lb) who took 5-9 iron supplement tablets of 30 mg each. Iron is absorbed rapidly once ingested and becomes corrosive. Iron poisoning targets organs like liver, kidneys and cardiovascular system (FAO, 2012).

2.4 Sources of Heavy metal pollution

Heavy metals always gain access into river systems from both natural and anthropogenic sources, these get distributed to sediments and biota as they move from one level to another. An area that naturally contains mineralized rocks usually contains an elevated level of metals, the trace metal level of river water is always controlled by the abundance of metals in rocks of the river's catchment area and their mobility (Oguzi, 2015).

Natural sources are, soil erosion, primarily rock weathering and dissolution of water soluble salts. Naturally occurring metals always move through aquatic environments usually without detrimental effects. They move independently of human activities (Garbarino et al., 2017). Degrading environmental conditions and growing reliance on agrochemicals have led to an increasing public concern over the potential accumulation of heavy metals and other contaminants in agricultural soils (Oguzi, 2015).

Heavy metals are released to a river from various sources, they enter the ecological systems through anthropogenic activities such as sewage sludge disposal, organic fertilizer and pesticide application and also through atmospheric deposition (Oguzi & Ogubere, 2012). Anthropogenic activities like mining, ultimate disposal of treated and

untreated waste effluents containing toxic metals as well as metal chelates from different industries (Oguzi & Ogubere, 2012) and also the use of heavy metal containing fertilizers and pesticides in agriculture indiscriminately resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings and sustaining aquatic biodiversity. Some fertilizers and pesticides are known to contain various levels of heavy metals including Cd and Cu. There is therefore a possibility that the continuous and heavy application of agrochemicals and other soil amendments can potentially exacerbate the accumulation of heavy metals in agricultural soils over time (Oguzi & Izevbigie, 2014).

Copper is the active ingredient in some pesticides applied to agricultural crops to inhibit fungal growth. Copper is generally present in only trace levels in natural surface waters up to a concentration of 0.005 mg/l and higher levels are usually associated with anthropogenic sources. Ground and surface water is threatened by the excessive use of fertilizer and pesticides in agricultural activities (Igwe, 2015). Agricultural runoff containing heavy metals reaches natural water bodies affecting aquatic species and in turn ecosystems. Heavy metal contamination of soil in agricultural areas is linked to the use of fertilizers, pesticides and herbicides by farmers. The use of agrochemicals such as pesticides and fertilizers may have resulted in undesirable accumulation of trace elements such as arsenic, cadmium, copper, lead and zinc in soil (Duffs, 2019).

Metal mining activities release huge amounts of tailing and waste containing heavy metals which pose a serious threat to water sources and the environment. Heavy metals

can also be introduced into soils from various sources, including atmospheric deposition of metal/ metalloids bearing particles (Abolagba *et al.*, 2017).

2.5 Heavy Metals and Water Pollution

Water pollution is a major threat to human population and dumping of pollutants into water body resulted in rapid deterioration of water quality and affects the ecological balance in the long run. Pollution refers to any direct or indirect alteration of physical, thermal, biological or chemical property of water or water source so as to make it less fit for any beneficial purpose for which it is expected to be used or make it harmful or potentially harmful to the welfare, health or safety of human beings, any aquatic or non-aquatic life and property or the environment (Wangboje & Oronsaye, 2011).

Water pollution has been suggested to be the leading worldwide cause of deaths and diseases and it accounts for the deaths of more than 140,000 people daily. Current concerns in environmental protection are majorly focused on water due to its importance in maintaining human health and ecosystem health. Water will always contain minerals and organisms that it collects from materials it comes into contact with due to its chemical properties. Depending on the type and the concentration, these constituents may be toxic and therefore harmful to human beings (Wangboje & Oronsaye, 2011).

Recently however, increased concern over the concentration of heavy metals in water has developed as the public becomes more aware of their toxicity and impact on human health. Many metals occurring in nature are not harmful at trace concentrations and some

such as iron, copper, cobalt, Manganese, Zinc and Chromium are even essential for proper functioning of the human body. All metals however are toxic at higher concentrations, with their toxicity being linked to chronic diseases such as renal failure, liver cirrhosis, hair loss and chronic anemia (Salem *et al.*, 2017). Heavy metal pollution has received huge worldwide concern owing to its persistence, toxicity, accumulation in the ecological system and risk to human health (Sreedevi *et al.*, 2012).

Heavy metals find their way to the waters through underground seepage of effluents arising from human activities, runoff from farms and industries, leaching and dissolution of metals occurring naturally in rock and soil. However, water pollution has been focusing on other aspects of water with a minimal interest in heavy metals. Heavy metal pollution has usually been relegated. It has only been brought to the fore if contamination due to anthropogenic sources such as poor waste disposal is suspected. In this respect, heavy metal content in water is given little attention in many rural areas due to fewer sources of pollution. This notwithstanding, heavy metal contamination of water in rural areas is still possible arising from obscure sources, fertilizers and the existence of mineral resources (Sreedevi *et al.*, 2019). Among the inorganic contaminants of the river water, heavy metals are getting importance for their persistent nature and often accumulate through trophic levels causing a deleterious biological effect (Jain, 2012). Heavy metals exposure to human beings has been associated with development retardation, kidney damage, various forms of cancer and in some instances death.

2.6 Heavy Metals 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 (Miroslav, 2014).

Sediments are indicators of environmental contamination of water bodies by heavy metals and toxic compounds. Sediments act as sink for pollutants hence their monitoring is important for tracing the spreading and impact of pollution related changes; sediments accumulate heavy metals from the surrounding geogenic and anthropogenic sources. In a river, bed sands perform a container and carrier for settlement and conveying of heavy metals and heavy metal is a persistent. Sediments are sinks of heavy metals in aquatic environments (Murugan *et al.*, 2012). When favorable conditions occur, the heavy metals settled in the sediments could gradually be released in the water and this phenomenon is one of the critical problems facing aquatic environments. Given their toxicity and bio-accumulation, many studies have shown that high heavy metal content in sediments could impact significantly the health of aquatic ecosystems.

Heavy metals in sediments are not permanently fixed, and can be released back to the water in case of changes in environmental conditions like pH, redox potential, and among others. This is because sediment act as carriers of the heavy metals in aquatic ecosystems. Many studies have found that sediments in aquatic ecosystems harbour persistent and toxic chemicals more than the water column. Monitoring of sediments is therefore very

important in tracing the spreading and impact of pollution related changes (Albergoni *et al.*, 2012).

2.7 Heavy Metal Treatment Technologies

Heavy metals are well-known toxic agents and heavy metal contamination has caused global deterioration of human health and environmental quality. The needs to comply with the stringent regulatory standards, various treatment technologies have been invented to resolve these issues. In general, heavy metal treatment technologies can be divided into two groups, namely, in-practice and progressing treatment technologies. Elaboration of heavy metal treatment technologies are discussed in subsequent sections (Albergoni & Paccini, 2016).

2.8 Research Regarding Sediment Heavy Metal Content in Inland Aquatic Ecosystems

The concentrations of heavy metals in receiving environments have both natural causes, such as sea-bed volcanic activity, atmospheric convection, rivers or erosion, and man-made causes, such as mining, the rapid increase of treatment and refining systems, the excessive use of fossil fuels, and the use of metallic products in agriculture (like arsenic pesticides). Of the heavy metals that are transported into the water, one portion is diffused in the water and the other portion forms solid compounds with carbonate, sulfate and sulfur, sinks to the bottom, and is accumulated in the sediment (Karadede, 2014). Accordingly, the sediment forms a trap for heavy metals, and thus, concentrations of

heavy metals in the sediment can be several orders of magnitude greater than in the overlying water. Metals found in the sediment directly threaten detrital and deposit-feeding benthic organisms, and could possibly be a long-term source of contamination higher up the food chain. Fish can take in heavy metals through respiration (through the gills or the skin), adsorption to body surfaces or feeding (Boyd & Tucker, 2012).

The intake of heavy metals and their accumulation in the organisms in aquatic ecosystems are affected by several factors, such as differences in the amount of metals entering the environment, the condition of the organism and the physical and chemical properties (temperature, salinity, pH and dissolved oxygen) of the aquatic environment in which the organisms are found. Quantitative sediment quality guidelines (SQG) exist for freshwater ecosystems, and these provide a reliable benchmark for assessing sediment quality in freshwater ecosystems. The threshold effect level (TEL) and the probable effect concentrations (PEC) for different sediment contaminants in freshwater ecosystems were determined by (Boyd & Tucker, 2012). TEL corresponds to the concentration of a contaminant below which harmful effects on benthic organisms are expected to occur only rarely, and PEC represents the concentration above which harmful effects on aquatic biota are expected to occur frequently. For this review, studies on the interaction between water, sediment and aquatic organisms conducted over the past 15 years in five different types of aquatic ecosystem in Turkey (lakes, reservoirs, wetlands, river and streams) were compiled, and the surface sediment concentrations of arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc reported by these studies were compared with

threshold effect level (TEL) and probable effect concentration (PEC) values for these metals. Additionally, studies performed under field and laboratory conditions regarding the release of nutrients from the sediment in Turkey's inland aquatic ecosystems were evaluated in the light of lake management practices (MacDonald *et al.*, 2010).

2.9 Sediment Physico-chemistry and Metal Pollution

Sediments form a natural buffer in river and are important habitat as well as a main nutrient source of aquatic organisms. A much interesting work on the physicochemical properties of sediment is that of benthic sediments of Qua Iboe estuary. For this estuary Essien and Benson, (2012) reported monthly concentrations for NH_3^- , Cl^- , CO_3^{2-} , SO_4^{3-} and NO_3^- in its benthic sediment during the wet season (June 2015 – Sept. 2015). Similarly, the mean monthly values for the dry season (Nov, 2015 – February 2016) also were reported (MacDonald *et al.*, 2017).

2.10 Techniques for Heavy Metals Determination

Different analytical methods can be used for determination of heavy metals, each with its advantages and disadvantages. Before the actual analysis, some common steps are required for a successful determination. Among them, sampling, sample handling and sample preparation play a significant role. Given that the amounts of heavy metals in inputs can be divided into 'total' and 'available' (which is the fraction that can be absorbed by plants), the sample may suffer some extraction procedures. Although the total concentrations of heavy metals offer incomplete information about potentially plant-

available fractions, they provide a helpful indicator that shows if a sample has high or low concentrations. This provide information if the analyzed sample is contaminated and had a possible risk of toxicity (Alloway, 2013). Techniques available are listed below:

1. **Atomic Absorption Spectroscopy (AAS):** It relies on the atomization of the determination by flame sources to form free atoms which can absorb radiation at discrete wavelengths. Each wavelength corresponds to only one element and the width of an absorption line is only of the order of a few picometers (pm) which gives the technique its elemental selectivity. The amount of energy absorbed is proportional to the concentration of the determinant present in the sample as the Beer Lambert Law applies.
2. **Flame Emission Spectroscopy (FES):** It involves the excitation of the sample in a spark or flame to produce line spectra of the elements present. It is a more sensitive technique than flame AAS for some elements & is suitable for multi element analysis.
3. **UV / VIS Spectroscopy:** It is a relatively fast and simple method for the determination of heavy metals. For the application of this method metals, however, be converted to coloured complexes prior to the analysis using different chemical reagents. This analytical technique is mainly used to obtain quantitative information about a substance. The sample solutions are placed into cuvettes & exposed to UV and/or visible light. The unabsorbed light is then focused onto a photomultiplier tube detection system using a double beam design. The measured

absorbance is proportional to the metal concentration as the Beer Lambert Law applies.

Preferred Analytical Technique

Adesoye et al., (2014), Atomic Absorption Spectroscopy (AAS) is the preferred analytical technique due to the following reasons:

- i. AAS is most widely used technique which uses simple, inexpensive instrumentation and is rapid.
- ii. AAS can be used to analyze the concentration of over 62 different metals in a solution.
- iii. AAS is very sensitive and can measure down to parts per billion of a gram ($\mu\text{g}/\text{dm}^3$) in a sample.
- iv. AAS can also be used for the analysis of metals like arsenic, antimony, tin, selenium, bismuth and mercury if hydride (generation) AAS is used.
- v. FES is not the preferred analytical technique as it has a relatively low precision and suffers from matrix effects & high instrumentation costs.
- vi. UV / Vis spectroscopy is not the preferred analytical technique as although it has a broad area of applicability, high sensitivity and rapid automatic method, BUT the sample preparation is time intensive as well as the measuring procedure (binding to complexes, adjusting pH value, special extraction procedures to obtain coloured metal complexes to be determined by UV / Vis. ALSO it is affected by interferences by other coloured substances in the sample.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

All chemicals used for this study was of analytical grade and was purchased and used without further purification. They include;

- Nitric acid (HNO₃)

3.2 Equipment/apparatus

The equipment/apparatus and software used in this work include;

- Atomic absorption spectrophotometer (AAS)
- Thermometer
- Beakers
- Volumetric flask
- Measuring cylinder
- Whatman no. 42 filter paper
- Hot plate
- Oven (Town+Mercer, England)
- Separating funnel (BS2021, England)
- Electrical balance (Mark 8055, Adam Equipment Co. LTD)

3.4 Study area

The Ikpoba River, flows through Benin city, Edo State, Nigeria and lies within lat. 6.5°N and Long. 5.8°E. The river is dendritic in the upper reaches and its head waters originate from the Ishan Plateau (Oguzie, 2012). The river receives domestic, industrial and agricultural wastes through flood run-off water.

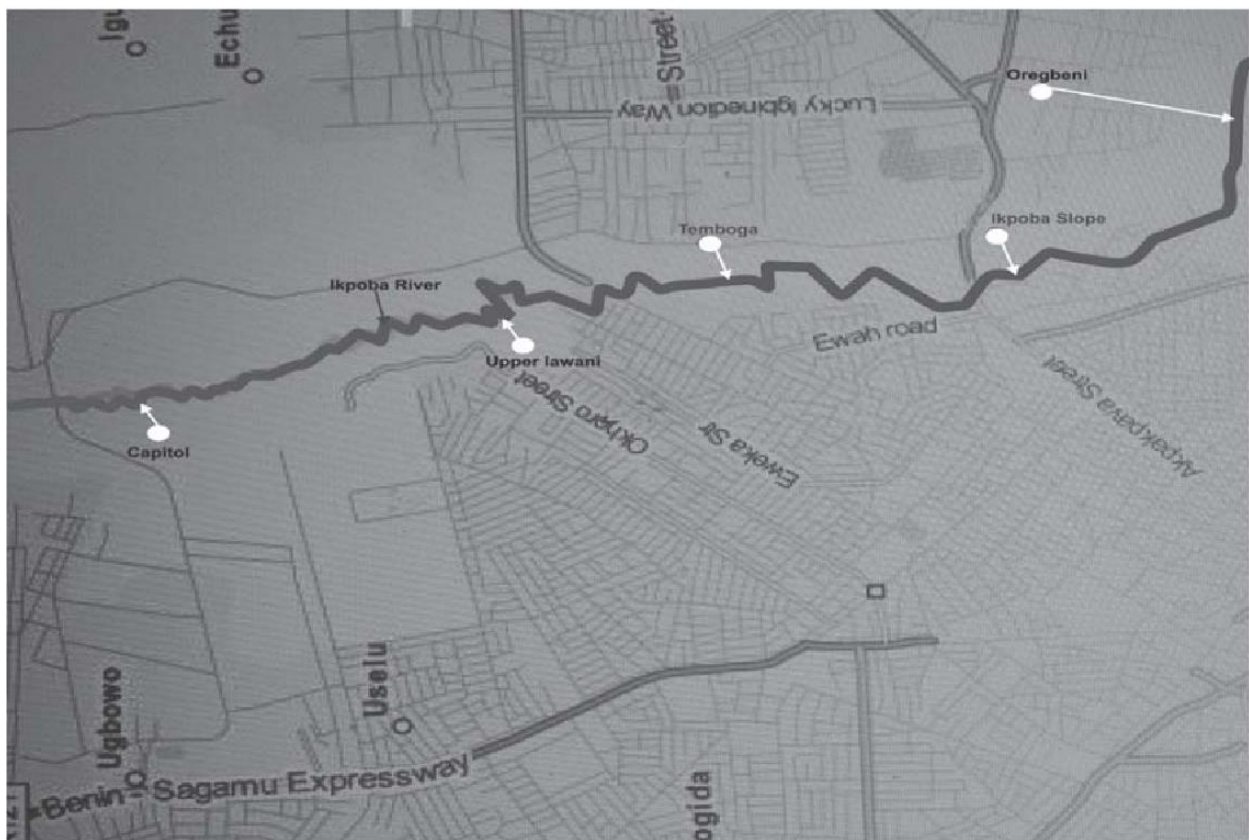


Figure 1: Map showing Ikpoba River

3.5 Sampling

Water and sediment samples were taken from two different points each from the Ikpoba River in order to get a fairly representative specimen. A clean High density polyethylene

sampling bottles (plastic bottle or container) were used in collecting the river water. At each sampling point, sampling bottles were firstly rinsed with the river water, filled with the river water at a depth of 20 cm to 30 cm and later filtered through a Whatman no. 42 filter paper. The filtrate was then acidified with concentrated HNO_3 to make a pH of <2 and preserved at 4°C in a refrigerator. Also, a sterile 2 cm diameter polyvinylchloride (PVC) tube was used to collect sediment samples from two points into pretreated sample bags and. All samples were labeled after collection and transported to the chemistry laboratory for further analysis.



Fig. 2: Water sample and sediment of Ikpoba river

3.6 Sample preparation

The water and sediment samples was digested according to the method described by (Ali *et al.*, 2016). 50 ml of the water sample was poured into a 100-ml beaker. About 5 ml of concentrated HNO_3 was added and boiled at 130°C on hot plate till the volume came to about 25–30 ml and light color. Addition of HNO_3 and boiling were repeated till solution

becomes light colored or clear. After digestion, the solution was allowed to cool to room temperature and filtered through a Whatman no. 42 filter paper into a 100 ml volumetric flask. It was then made up to the 100 ml mark with distilled water for the analysis of heavy metals (Cu, Pb, Fe, Zn and Cr) using the Atomic Absorption Spectrophotometer. The sediment samples were air-dried for twenty-one days, ground in porcelain mortar and sieved using a 2 mm sieve to reduce its size. About 2.0 g portion of dried sediment was taken in a 100 ml beaker and 15 ml of concentrated HNO₃ was added. The content was heated at 130 °C for 5 h until 2–3 ml remaining in the beaker, after which similar steps were followed as the water samples.



Figure 3: Atomic absorption spectroscopy

CHAPTER FOUR
RESULTS AND DISCUSSIONS

4.1 Results

Table 1: Heavy metal concentration in water and sediment of Ikpoba River

Parameters		
Metals	Water (mg/l)	Sediments (mg/kg)
Cu	0.01	1.00
Zn	0.37	14.00
Fe	8.50	1280.0
Pb	0.01	2.00
Cr	0.01	4.00

Table 2: The permissible limits of heavy metal ions in drinking water and sediment

Metals	WHO Standard Water MAC (mg/l)	WHO Standard sediment MAC (mg/kg)
Cu	0.05	32.00
Zn	5.00	127.00
Fe	NGL***	35900.0
Pb	0.05	16.00
Cr	0.05	71.00

No Guideline, because it is not of health concern at concentrations normally observed in drinking water, but may affect the acceptability of water at concentration above 0.3mg/l (Gebrekidan and Samuel, 2011; Mahmud *et al.*, 2016 and Ameh, 2016).

4.2 Discussion

The metal concentrations of water and sediments are presented in Table 1. The average concentration of studied metals in water followed the decreasing order of: Fe > Zn > Cr, Cu and Pb. while the corresponding profile for the sediment is: Fe > Zn > Cr > Pb and >Cu. The Fe concentration in the water and sediment of the Ikpoba river was higher than all the other elements investigated with a concentration of 9.8mg/l and 130mg/kg respectively. Similar findings were reported on the Lagos lagoon, Warri River and Ogba River (Igwegbe, 2012). The phenomenon was generally attributed to the low water pH and discharge of iron-laden waste and effluent replete into the river. This may be further explained by the fact that Fe being the most abundant in the environment could conceivably be bio accumulated more than the other trace metals. Furthermore, Metal enrichment of sediment compared to water is reflected by the sedimentation of metals ions when they compete with H⁺ ions for sorption sites in the aquatic environment. The physical process of degrading in the zone could help to release of pore solutions rich in heavy metals into the sediment. These metals have high content of detrital mineral bonds and form complexes that precipitate at river bottom (Oguzie and Ogubere, 2017). Although the investigated metals of Fe, Cu, Zn, Cr and Pb in water and sediment of Ikpoba-river were lower than the World Health Organization (WHO) maximum permissible limit as presented in table 2 (Gebrekidan and Samuel, 2011; Mahmud *et al.*, 2016 and Ameh, 2016).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The results of this study supply valuable information about metal heavy contents and permissible limits of heavy metal concentrate in drinking water of Ikpoba River. Sample were collected from Ikpoba river measured using AAS. The mean concentration values of all the heavy metals were below world Health Organization standard. The order of the mean concentrations of tested heavy metals: $Fe > Zn > Cr > Pb > Cu$ and it is found in this study that, the parameter of heavy metal present in the river are Cu (0.01mg/l), Zn(0.37 mg/l), Fe(8.50 mg/l), Pb (0.01 mg/l) Cr(0.01 mg/l) while heavy metal present in sediment: Cu (1.00mg/kg), Zn (14.00 mg/kg), Fe (1280.0 mg/kg) Pb (2.00 mg/kg) Cr (4.00mg/kg). World health organization (WHO) has permissible standard of heavy metal concentrate of water and sediment, the permissible concentrate of water: cu (0.05 mg/l), Zn (5.00 mac/l), Fe (nil), Pb (0.005 mg/l), Cr (0.05 mg/l). Cu (32.00 mg/kg), Zn (127.00 32.00 mg/kg), Fe (35900.00 32.00 mg/kg), Pb (16.0032.00 mg/kg), Cr (71.0032.00 mg/kg) are permissible heavy metal concentrate in sediment. Considering all assessment criteria, Fe, and Zn are considerable higher than other metals present in the sample.

5.1 Recommendation

The investigated metals in water and sediment of ikpoba river were lower than the world health organization (WHO) maximum permissible limit, based on the result it is recommended that the water is good for both domestic and industrial purpose.

It is also recommended that the anthropogenic activities that lead to the concentration of the heavy metal should be controled by National Environmental Standards and Regulations Enforcement Agency (also known as NESREA).

Reference

- Abolagba, O.J., Igene, J.O. and Oronsaye, J.A.O, Investigations on the fishing practices in Ekenwan area of Ovia North East Local Government Area of Edo State, Nigeria. *J. Agr. For. Fis.* 6(1) 35-40. Nov. 2017.
- Albergoni, V. and Paccini, E, (2012). Biological response to trace metal and their effects In: Trace element speciation in surface water, (ed) G.G. Lepard, Plenum Press, New York *Biochem* 159-175.
- Ali, M.M., Ali, M.L., Islam, M.-S.I., Rahman, M.-Z. Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh. (2016). *Environmental Nanotechnology, Monitoring & Management* 5: 27–35.
- Ameh, O.S. (2016). Heavy Metal Seasonal Distribution in Shore Sediment Samples along the Coastline of Erongo Region, Western Namibia. *European Journal of Scientific Research ISSN 1450-216X / 1450-202X Vol. 139 No 1 April, 2016, pp.49-63*
- Ana, G.R., Sridhar, M.K.C. and Bamgboy, E.A. (2014). Environmental risk factors and health outcomes in selected communities of the Niger Delta Area, Nigeria *Perspectives in Public Health* 129:183-191.
- Anden, A. B., Okorafor, K. A., Oku, E. S., Ugwumba, A. A. (2015). Evaluation and characterization of trace metals contamination in the surface sediment using pollution load index (PLI) and Geo-accumulation index (Igeo) of Ona River, Nigeria. *International Journal of Scientific and Technical, Research* 4(1):29-34.
- AOAC (Association of Official Analytical Chemist) (2012). Official methods of Analysis of the AOAC Association of Official Analytical Chemist, Washington DC, USA.
- Bakan, G. and Böke-Özkoç, H. (2012). An ecological risk assessment of the impact of heavy metals in surface sediments on biota from mid-Black sea coast of Turkey. *International Journal of Environmental Studies*, 64: 45-57.
- Bentu, J.K., Amang, M., Boadu, K.O., Koranteng-Allo, E.J. and Owusu, A.E. (2011). Assessment of heavy metals pollution of sediments from Fosu Lagoon in Ghana, *Bull. Chem. SOC. Ethiop.*, 25(2): 191-196.
- Boyd, C.E. and Tucker, C.S. (2012) *Pond Aquaculture Water Quality Management*. Kluwer Academic Publishers, 698 p. <http://dx.doi.org/10.1007/978-1-4615-5407-3>
- Calmano, W. Hong, J.U. and Forstner, U. (2013). Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Water, Science and Technology*, 1:28:223-35.
- Chen, G., Zeng, G., Tang, I., Du, C., Jiang, X. Huang, G., Liu, H. And Shen, G. (2012). Cadmium removal from simulated wastewater to Biomass by product of *lentinus edodes*. *Bioresource Technol*, 99, 7034-7040.

- Durali, M., Demirci, Z., Tüzen, M. and Soylak, M. (2010). Seasonal investigation of trace element contents in commercially valuable fish species From the Black Sea, Turkey, *Food and Chemical Toxicology*, 48: 865-870.
- Egborge, A.M. (2014). Industrialization and heavy metal pollution in Warri. 32nd Inaugural lecture. University of Benin. Benin City. Environment. Springer-berlag, Berlin. Heidelberg, New York. 486PP.
- Enujuigha, V.N. and Nwanna, L.C. (2014). Aquatic Oil Pollution Impact indicators. *J. App. Sci. Environ. Mgt.*, 8(2), 71-75.
- Food and Agricultural Organization (FAO). Committee for Inland Fisheries for Africa: Working party on Pollution and Fisheries FAO fish, 2: 105-119
- Gebrekidan, M., and Samuel, Z. (2011). Concentration of Heavy Metals in Drinking Water from Urban Areas of the Tigray Region, Northern Ethiopia. *Volume 3 (1):105-121, 2011*
- Idodo-Umeh, G. and Oronsaye, J.A.O. (2014). Heavy metals in sediments from Eriora River in Olomero town, Niger Delta, Nigeria. *Journal of sustain prop. Agric. Res.* 21:74-81.[15]
- Igwe, J.C. and Abia, A.A, (2013). Maize Cob and Husk as Adsorbents orremoval of Cd, Pb, and Zn ions from waste water. *The physicalSci .*, 2: 83-94. Aug. 2015.
- Iwuoha, G.N., Osuji, L.C. and Horsfall, M. Jnr. (2012). Index model analysis approach to heavy metal pollution assessment in sediments of Nworie and Otamiri Rivers in Imo State of Nigeria, *Research Journal of Chemical Sciences*, 2(8):1-8.
- Jimoh, H.E. (2016). Surface water physico-chemical and bottom sediment quality of the Ikpoba River, Benin City and stated Recovery after five (5) years of Dredging. B.Sc. Thesis, University of Benin, Benin City. 82pp.
- Karadede-Akın, H. (2014). Seasonal Variations of Heavy Metals in Water, Sediments, Pondweed (*P. Pectinatus L.*) and Freshwaterfish (*C. c. umbla*) of Lake Hazar. Elazığ-Turkey. *Fresenius Environmental Bulletin*, 18, 511-518.
- Kpee, F. and Edori, O.S. (2014). Trace metal content in shore crabs (*Cardisoma guanhumi*) from coastal area of Port Harcourt City. Rivers State Nigeria, *Archives of Applied Science Research* 6(6):16-21.
- MacDonald, D.D., Ingersoll, C.G. and Berger, T.A. (2010) Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. *Archives of Environmental Contamination and Toxicology*, 39, 20-31.
- Miroslav, R. and Bashkin, V.N (2014). Practical Environmental analysis. Royal Society of Chemistry, Madison. 466pp.
- Miroslav, R. and Bashkin, V.N, Practical Environmental analysis. Royal Society of Chemistry, Madison. 1999, 466pp.

- Murugan, S.S., Karuppasamy, R., Podngodi, K. and Rivaneswari S., (2012). Bioaccumulation pattern of Zinc in freshwater fish *ChannaPunctatus* (Bioch.) after chronic exposure Turk. *J. Fish. Aquat Sci* .8: 55-59.
- Murugan, S.S., Karuppasamy, R., Podngodi, K. and Rivaneswari,S, (2012). Bioaccumulation pattern of Zinc in freshwater fish *ChannaPunctatus* (Bioch.) after chronic exposure Turk. *J. Fish. Aquat Sci* .8: 55-59.
- Obasohan, E.E., Oronsaye, J.A.O. & Obano, E.E, (2016). Heavy metal concentrations in *Malapterirus electricus* and *chrysichthysnigrodigitatus* from Ogba river Benin City, Nigeria. *Afr. J. BioTechnol* 5(10), 914-982. Sept.
- Ogbeibu, A.E. and Anagboso, M.U. (2014). Baseline limnological investigation of the Utor river in Esan Southeast, Edo State, Southern Nigeria. 1: Physical and chemical hydrology. *Tropical Freshwater Biology*. 12/13:45-62.
- Oguzie, F.A. and Ogubere, C.A, (2017). Bioaccumulation of Heavy metals in the African Catfish, (*Clarias gariepinus* from Aze River and Idonior Fish in Isoko, Delta State, Nigeria Nig. J. Appl. Sci. 25:185-196.
- Oguzie, F.A. (2012). Heavy Metals in Sediments of the Lower Ikpoba River, Benin City, Nigeria. *Sri, Lanka J. Aquat. Sci*. 7:35-44.
- Sreedevi, P.A., Suresh, A., Siraramakrishna, B., Prebhavathi, B and Radhadrishanaib, K. (2012). Bio accumulation of nickel in the organs of the freshwater fish, *Cyprinus carpio* and the water mussel *Lamethodens marginals* under lethal and sublethal nickel stress. *Chemosphere* 24(1), 29-36.
- Uzu A.P, (2012). Heavy metals of surface waters in Ovia River, Nigeria B.Sc. Project, University of Benin, Benin City. 46pp.
- Wangboje, O.M. and Oronsaye J.A (2011). Bioaccumulation of iron, lead, mercury, copper, zinc and chromium by fish species from Ogba River, Benin City, Nigeria. *Afr. J. Appl Zool. Environ. Biol* 3 45-49.