ACCUMULATION OF HEAVY METALS IN FISH, WATER, AND SEDIMENT SAMPLES FROM OGUTA LAKE

BY

SHITTU, USMAN AKOREDE

20194198498

(B.Sc. LASU)

A DISSERTATION SUBMITTED TO THE SCHOOL OF BIOLOGICAL SCIENCES,
FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF
MASTER OF SCIENCE (M.Sc.) DEFENSE IN ENVIRONMENTAL CONSERVATION
AND MANAGEMENT

AUGUST, 2024

CERTIFICATION

We hereby certify that this dissertation, "**Accumulation of Heavy Metals in Fish, Water, and Sediment Samples from Oguta Lake,** was carried out by **SHITTU, USMAN AKOREDE,** with Reg. No. **20194198498** in partial fulfillment of the requirements for the award of the Degree of Master of Science in Environmental Conservation and Management in the Department of Biology, Federal University of Technology, Owerri.

.... **Dr. C. M. Duru** **(Principal Supervisor)**	12) 11) 2024 **Date**
.... **Dr. M.O. Nwachukwu** **(Co-Supervisor)**	12/11/2024 **Date**
.... **Dr. D. H. Ogbuagu** **(Head of Department)**	12.11.2024 **Date**
.... Prof. C. S. Alisi (Dean, School of Biological Sciences)	12.11.24 **Date**
.... Prof. Mrs. J. N. Nwosu (Dean, Postgraduate School)	.... **Date**
.... Prof. Gordian Chibuzor Obute (External Examiner)	14-11-2024 **Date**

DEDICATION

I dedicate this project to Almighty God, the Lord of incomparable Majesty.

ACKNOWLEDGEMENTS

First and foremost, praise and thanks to God the Almighty for his showers of blessings and guidance throughout my research work and for seeing the research to successful completion.

I would like to express my deep and sincere gratitude to my research supervisor and PG coordinator, Department of Biology, Dr. M. O. Nwachukwu. It’s been a great privilege working under your supervision, May God reward all your efforts towards making my studies here hitch free and worthwhile. And my co-supervisor, Dr. Mrs. P. N. Ofoegbu, for giving me the opportunity to work under her and providing all necessary guidance throughout this research.

To my wonderful and highly knowledgeable lecturers, your great tutelage has produced a young, knowledgeable student personified in my very self, and I owe you all an ultimate and everlasting thanks.

My gratitude goes also to my ever-supportive parents, Alhaji and Mrs. Shittu. I am extremely thankful for your love, prayers, care, support, and sacrifices in seeing me through this research, and to my very understanding wife, Mrs. Halimah Omolara Shittu, my children Mazeedah Oluwadarasimi and Moshood Adedayo, You people are just the very best part of my existence, and I can’t trade you for anything in the world.

Many thanks to my coursemates, especially my very good friend, Ikechukwu Osinomumu, Your excellent support, contributions, and assistance can never be forgotten, and I am forever grateful for everything.

To my colleague and good friend, Chisom Racheal Asoegwu, I can’t thank you enough for all your encouragement and assistance. You are that one friend everyone would love to have.

And to all the members of the School of Biological Sciences (SOBS) and the entirety of the Federal University of Technology, Owerri, I wish to express my heartfelt gratitude to you all, without whom this project wouldn't have been a success. To everyone out there who, in one way or another, contributed to the success of this great course, may God bless and reward you all immensely.

Shittu Usman Akorede

2023

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICE

ABSTRACT

This work was carried out to ascertain the accumulation of heavy metals in fish, water, and sediment samples from Oguta Lake. Triplicate batches of the samples were taken from three sampling points along the river coast, and the physicochemical parameters were analyzed in the laboratory using gravimetric, titrimetric, and spectrophotometric methods. The concentrations of heavy metals (Pb, Cd, As, Ni, Mn, Cu, and Hg) in water, sediment, and fish, insect, snail, and algal species from the lake were analyzed using Atomic Absorption Spectrophotometer. Carcinogenic risk models were used to estimate the potential risks through the ingestion of fish, insects, snails, and algal in Oguta Lake. Pearson correlation multivariate analyses of variance (MANOVA) were used to analyze the inter-relationship among heavy metals in water and sediments. Seasonal variation and the correlation matrix (ANOVA) of heavy metals were analyzed. The results obtained showed that the mean concentrations of physicochemical parameters ranged as follows: Temperature (26.04-29.35); pH (7.17-7.77); Free CO_2 (9.78-10.34); BOD (10.14-10.42); TDS (22.23-28.04); EC (0.30-0.49); DO (5.69-5.86); Total Hardness (18.49-21.00); Turbidity (15.03-17.76); Alkalinity (15.64-16.66); Sulfate (2.19-2.55); Ammonium (0.26-0.40). Comparison with WHO guidelines indicated that most parameters assayed were within permissible limits. The mean concentrations of heavy metals in water were: Pb (0.19±0.05); Cd (0.41±0.07); As (0.01±0.001); Ni (0.59 ±0.1); Mn (0.02±0.006); and Cu (2.24 ± 0.31). while the mean concentrations of heavy metals in sediment were: Pb (0.26±0.04); Cd (1.04±0.15); As (1.02±0.16); Ni (1.22± 0.24); Mn (1.98±1.68); and Cu (1.87 ± 0.58). Positive correlations were observed for the following pairs of metals in water and sediments: Pbw and Nis ($r = 0.356$), Cdw and Nis ($r = 0.237$), Cuw and Mns ($r = 0.325$), Cdw and Pbs ($r = 0.969^*$), and Asw and Ass ($r = 0.967$) at $p< 0.05$. Bioaccumulations of heavy metals were in the following order: fish > algal > snail > insect. The estimated daily intake of heavy metals from consuming fish, algae, and snails indicated that none of the heavy metals currently pose a health risk to consumers of these organisms in the study area, based on the dose. The results obtained from this study showed that heavy metal pollution is not yet a significant problem in Oguta Lake as of the time of this investigation.

Keywords: *Oguta Lake, heavy metals, bioaccumulation, fish, insects, snails, algal.*

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND INFORMATION

In Nigeria and throughout the globe, industries are crucial to economic development and play an important role in raising living standards. Pollution of the aquatic environment with heavy metals has become a worldwide problem because the metals are indestructible and most have toxic effects on organisms (Adekola & Eletta, 2007; Okareh & Adeolu, 2007; Adeolu *et al*., 2016). These pollutants enter rivers and lakes from a variety of sources, such as rock and soil directly exposed to surface water, in addition to the discharge of treated and untreated liquid wastes into water bodies. These harmful wastes and other dangerous industrial by-products constitute major sources of environmental pollutants (Okareh & Adeolu, 2007).

Most industrial pollutants discharged into the environment contain organic and inorganic pollutants in dissolved, suspended, and insoluble forms (Adeolu *et al*., 2016; Sawyer *et al*., 2017). Effluents discharged into water bodies may affect fish and other aquatic organisms, either directly or indirectly. Most rivers and freshwater streams are seriously polluted by industrial wastewater discharged from factories, as these pollutants are not treated before discharging into available water bodies. A large amount of water used in industry turns into wastewater that pollutes surface and groundwater, posing health hazards as these ions from heavy metal do not easily degrade into harmless end products; thus, they are toxic to humans and the surrounding environment (Ajayi *et al*., 2011; Maiti & Banerjee, 2012).

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least five times greater than that of water. They are persistent, bio-accumulative, and toxic micropollutants (Omoregie *et al.,* 2016). Their multiple industrial, domestic, agricultural, medical, and technological applications have led to their wide distribution in the environment raising global public health concerns over their potential effects on human health and the environment (Scientific India, 2017). The concentration of heavy metals in an organism is the product of equilibrium between the concentration of the metal in an organism's environment and its rate of ingestion and excretion (Idodo-Umeh, 2002). Toxic effects occur when excretory, metabolic, storage, and detoxification mechanisms are no longer able to counter uptake (Kalay & Canli, 2000). Unlike organic contaminants that lose toxicity with time by biodegradation, heavy metals cannot be degraded, and their concentration can be increased by bioaccumulation and biomagnification (Aksoy, 2008).

Bioaccumulation is an increase in the concentration of a chemical in a biological organism over a period compared to the chemical's concentration in the environment (Neff, 2002). These compounds which are certain non-essential chemicals that are persistent in the environment, therefore accumulate in living tissues any time they are taken up and stored faster than they are metabolized or excreted and occur when certain toxic chemicals and pollutants such as trace elements, pesticides, or polychlorinated biphenyls (PCBs) are absorbed by terrestrial and aquatic animals. They are highly soluble and can be stored in fats, and when the fatty tissues are used up for energy, the compounds are released and could cause acute poisoning which leads to eco-toxicological problems. The longer the biological half-life of the toxic substance the greater the risk of chronic poisoning, even if the environmental levels of the toxin are not very high (Ogbuagu *et al*., 2019). Majority of these persistent pollutants such as trace elements, pesticides or polychlorinated biphenyls (PCBs), and hydrocarbons are introduced into the environment basically by various anthropogenic activities, ranging from oil exploration, bunkering activities, pipe line vandalization, mining activities in the deep sea (which processes involve the extraction of minerals and metal ores like zinc, cobalt, silver, aluminum and gold), as well as other industrial and domestic activities in catchment areas.

Agricultural activities like the application of synthetic fertilizers and pesticides for the purpose of boosting food production and arresting food insecurity, also contribute to the pollution of the aquatic environment through runoffs water that leaches these chemicals into nearby water bodies. Once in the environment, these toxic substances can endanger public health by being incorporated in the food chain (Di Leo *et al*., 2010; Ogbuagu *et al*., 2011). In addition, some natural processes like volcanic eruption can as well discharge these compounds into the environment. These compounds thus released into terrestrial or aquatic environments directly are not easily destroy through any biological processes, thus they are Persistent Environmental Pollutants (PEPs), and they are easily assimilated at a very faster rate than they can be degraded, thus bioaccumulate in the tissues of aquatic organisms, which will gain access to the final consumers like man at the apex of food chain (Ogbuagu & Iwuchukwu, 2014; Ogbuagu *et al*., 2019). Aquatic organisms are thus, exposed to a myriad of chemicals in their environment.

Though some of these chemicals occur in trace concentrations in the environment, yet they may be selectively accumulated by organisms to much larger concentrations that can cause toxicity. It is rather of great concern that over 80% of the industries in Nigeria discharge their solid wastes, liquid and gaseous effluents containing toxic concentration of heavy metals and other pollutants into the environment without any prior treatment, while just only 18% undertake rudimentary recycling prior to disposal (Ayejuyo *et al*., 2001).

1.2 STATEMENT OF THE PROBLEM

Many heavy metals are environmentally stable and non-biodegradable, toxic to the living beings and tend to accumulate in plants and animals, causing chronic adverse effects on human health (Vijaya *et al*., 2010). They gain access into aquatic ecosystem through anthropogenic sources ranging from domestic waste, sewages, industrial effluents, fertilizer applications, pesticides, oil spillage, mine effluents and obnoxious fishing method and get distributed in the water (Njoku & Acho 2010). They are priority toxic pollutants that severely limit the beneficial use of water for domestic and industrial application (Vijaya *et al*., 2010).

In Nigeria, especially in rural and fishing communities, fish constitute approximately 75% of animal protein consumed (Edun *et al*., 2010). Hence, protecting sediment quality becomes an important part of restoring and monitoring the biological integrity of water as well as protecting aquatic life, wildlife, and general health. It is on this premise that the researcher is motivated to propose a study on the topic under review with a view of finding out the situation in Oguta Lake, being an industrial area with a lot of effluent.

1.3 AIM OF THE STUDY

The study aims to analyze the heavy metals accumulation in fish, water, and sediment from Oguta Lake, Imo State Nigeria.

1.4 OBJECTIVES OF THE STUDY

Specifically, the study will seek

1. To determine the physicochemical parameters of the water sample collected from Oguta Lake
2. To determine the level of heavy metals like Pb, Cd, As, Ni, Mn, Cu and Hg concentration in the fish, water and sediment samples collected from Oguta Lake
3. To determine the level of heavy metals like Pb, Cd, As, Ni, Mn, Cu and Hg concentration in some food chain components of the Fish.

4 To determine health risk associated with the consumption of the fish harvested from Oguta Lake

1.5 RESEARCH HYPOTHESIS

H_{01}: The concentrations of heavy metals in these locations will not have significant impact on the physico-chemical properties of the study area

H_{A1}: The concentrations of heavy metals in these locations will have significant impact on the physico-chemical properties of the study area

H_{02}: The concentration of the heavy metals in the fish does not have significant effects on human health

H_{A2}: The concentration of the heavy metals in the fish will have significant effects on human health

1.6 JUSTIFICATION OF STUDY

The impact of human activities in the urban, municipal, and populated area makes surface water bodies like streams, river, lagoons etc., and ground water bodies to be susceptible to contamination from pollutants. Pollution of soil and water by heavy metal occurs due to industrial wastes, application of fertilizer, corrosion of sheeting, wires, pipes, and burning of coal and wood (Nwankwoala & Ekpewerechi, 2007). Oguta Lake is a recipient of effluent/wastewater from Njaba River and a part of the River Niger. Hence, there is need to routinely carry out a study to determine the bioaccumulation, toxicity, and the associated health risk of heavy metals in the fish, water, and sediment of Oguta Lake to ascertain their heavy metal content if it is within the limit of FAO/WHO for human consumption

1.7 SCOPE OF THE STUDY

The study was carried out in Oguta Lake, Imo State Nigeria. The study was carried out in the following stages: Fish, water, and sediment samples were collected from different strategic locations, Analysis of physicochemical parameters was carried out on the water samples, Heavy metals content was determined on the samples collected from the study location, The physicochemical parameters and heavy metals content determined will help as baseline data for the study areas and the result were used to compute the extent of contamination by the heavy metals.

1.8 SIGNIFICANCE OF THE STUDY

Results from this study could bring to light the impacts of the industrial water effluent in the Oguta Lake. It will help residents from this study locations to know the health implications associated with consuming fish harvested from Oguta Lake.

CHAPTER TWO

LITERATURE REVIEW

2.1 HEAVY METALS

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration (Jaishankar *et al*., 2013). Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are natural components of the earth's crust. They cannot be degraded or destroyed. Heavy metals are dangerous because they tend to bioaccumulate (Begun *et al*, 2016). Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted (Trueby, 2013). Heavy metals can enter a water supply from industrial and consumer waste, or even from acidic rain, breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues (Duruibe *et al*., 2017). Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of contamination for adults. Ingestion is the most common route of exposure in children (Begun *et al,* 2016). Children may develop toxic levels from the normal hand-to-mouth activity of small children who come in contact with contaminated soil or by eating objects that are not food (dirt or paint chips) (Athar & Vohora, 2018). Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous (parenteral) nutrition, from a broken thermometer, or from a suicide or homicide attempt (Titilayo & Olufemi, 2012). Commonly encountered toxic heavy metals

- Arsenic (As)
- Lead (Pb)
- Mercury (Hg)
- Cadmium (Cd)
- Iron (Fe)
- Aluminum (Al)

Arsenic: Arsenic is the most common cause of acute heavy metal poisoning in adults and is number 1 on the ATSDR's "Top 20 List." Arsenic is released into the environment by the smelting process of copper, zinc, and lead, as well as by the manufacturing of chemicals and glasses. Arsine gas is a common biproduct produced by the manufacturing of pesticides that contain arsenic. Arsenic may also be found in water supplies worldwide, leading to exposure of shellfish, cod, and haddock. Other sources are paints, rat poisoning, fungicides, and wood preservatives. Target organs are the blood, kidneys, central nervous, digestive, and skin systems (Achieche *et al*., 2020).

Lead: Lead is number 2 on the ATSDR's "Top 20 List." Lead accounts for most of the cases of pediatric heavy metal poisoning (Cogun & Sahin, 2012). It is a very soft metal and was used in pipes, drains, and soldering materials for many years. Millions of homes built before 1940 still contain lead (e.g., in painted surfaces), leading to chronic exposure from weathering, flaking, chalking, and dust (Cogun & Sahin, 2012). Every year, industries produce about 2.5 million tons of lead throughout the world. Most of this lead is used for batteries (Cogun & Sahin, 2012). The remainder is used for cable coverings, plumbing, and fuel additives. Other uses are as paint pigments and in PVC plastics, x-ray shielding, crystal glass production, and pesticides. Target organs are the bones, brain, blood, kidneys, and thyroid gland.

Mercury: Mercury Number 3 on ATSDR's "Top 20 List" is mercury. Mercury is generated naturally in the environment from the degassing of the earth's crust, from volcanic emissions. It exists in three forms: elemental mercury, organic and inorganic mercury. Mining operations, chloralkali plants, and paper industries are significant producers of mercury (Trueby, 2013). Atmospheric mercury is dispersed across the globe by winds and returns to the earth in rainfall, accumulating in aquatic food chains and fish in lakes (Clarkson, 2017). Mercury compounds were added to paint as a fungicide until 1990. These compounds are now banned; however, old paint supplies and surfaces painted with these old supplies still exist. Mercury continues to be used in thermometers, thermostats, and dental amalgam. Many researchers suspect dental amalgam as being a possible source of mercury toxicity (Trueby, 2013). Medicines, such as mercurochrome and merthiolate, are still available. Algaecides and childhood vaccines are also potential sources. Inhalation is the most frequent cause of exposure to mercury. The organic form is readily absorbed in the gastrointestinal tract (90-100%); lesser but still significant amounts of inorganic mercury are absorbed in the gastrointestinal tract (7-15%). Target organs are the brain and kidney (Begun *et al*, 2016).

Cadmium: Cadmium, a by-product of lead and zinc mining and smelting, ranks as number 7 on ATSDR's 'Top 20 List.' It is commonly used in nickel-cadmium batteries, PVC plastics, and paint pigments. Cadmium can also be found in soil due to its use in insecticides, fungicides, sludge, and commercial fertilizers in agriculture. Reservoirs containing shellfish are another potential source of cadmium. Additionally, cigarettes contain cadmium, and lesser-known sources of exposure include dental alloys, electroplating, motor oil, and exhaust fumes. Inhalation leads to 15-50% absorption of cadmium through the respiratory system, while 2-7% of ingested cadmium is absorbed in the gastrointestinal system. The primary target organs affected by cadmium exposure are the liver, placenta, kidneys, lungs, brain, and bones (Daei et al., 2019).

Iron: Iron is not included on ATSDR's 'Top 20 List,' but it remains a heavy metal of concern, particularly due to the risk of acute poisoning in young children who ingest dietary iron supplements. Even a small quantity, such as five to nine 30-mg iron tablets, can be toxic for a 30-pound child (Daei et al., 2019). The primary route of toxicity is ingestion, as iron is rapidly absorbed in the gastrointestinal tract. Its corrosive nature may enhance this absorption. Many overdoses occur when children mistakenly consume red-coated ferrous sulfate tablets or adult multivitamin preparations, mistaking them for candy. The implementation of child-proof packaging, including blister packs and child-resistant caps for containers holding 250 mg or more of iron, has significantly reduced the incidence of accidental ingestion and fatal overdoses. Other common sources of iron exposure include drinking water, iron pipes, and cookware. The liver, cardiovascular system, and kidneys are the primary target organs affected by iron toxicity (Daei et al., 2019).

Aluminum: Although aluminum is not a heavy metal (specific gravity of 2.55-2.80), it makes up about 8% of the surface of the earth and is the third most abundant element. It is readily available for human ingestion through the use of food additives, antacids, buffered aspirin, astringents, nasal sprays, and antiperspirants; from drinking water; from automobile exhaust and tobacco smoke; and from using aluminum foil, aluminum cookware, cans, ceramics, and fireworks. Target organs for aluminum are the central nervous system, kidney, and digestive system (Begun *et al,* 2016).

2.2 EMISSION OF HEAVY METALS

Heavy metals are either released into the environment through natural or anthropogenic activities, with anthropogenic activities being the major sources of heavy metals as humans try to modify their environment via the use of different available technologies to meet the needs of its population (Rajeev, 2015). Their natural sources in the environment include weathering of metal-containing rocks and volcanic eruptions, while principal anthropogenic sources include industrial emissions, mining, smelting, foundries, agricultural activities like the application of pesticides and phosphate fertilizers, combustion by-products, and traffic (Rajeev, 2015). Cd is released as a by-product of Zn and occasionally Pb refining; Pb is emitted during its mining and smelting activities; from automobile exhausts by combustion of petroleum fuels treated with tetraethyl lead antiknock; and from old Pb paints, Hg is emitted by the degassing of the earth's crust. Heavy metals are emitted both in elemental and compound (organic and inorganic) forms (Trueby, 2013). Generally, heavy metals are emitted during their mining and processing activities. Environmental pollution by these metals is very prominent in areas of mining and old mine sites, and pollution reduces with increasing distance from mining sites. These metals are leached out and, in sloppy areas, are carried by acid water downstream or run-off to the sea. Through mining activities, water bodies are most emphatically polluted (Bagul *et al*., 2015). Their potential for contamination of aquatic environments is increased when some or most of these anthropogenic activities are carried out near coastal areas or are discharged as effluents directly into rivers from industries. Through rivers and streams, the metals are transported as either dissolved species in water or as an integral part of suspended sediments, (dissolve species in water have the greatest potential of causing the most deleterious effects). They may then be stored in riverbed sediment or seep into the underground water, thereby contaminating the water from underground sources, particularly wells, and the extent of contamination will depend on the nearness of the well to the mining site (Trueby, 2013).

2.3 SOURCES OF HEAVY METALS IN THE ENVIRONMENT

Heavy metals differ widely in their chemical properties and are used extensively in electronics, machines, and the artifacts of everyday life, as well as in high-tech applications (Duruibe *et al*., 2017). As a result, they can enter the aquatic and food chains of humans and animals from a variety of anthropogenic sources, as well as from the natural geochemical weathering of soil and rocks. The main sources of contamination include mining wastes, landfill leaches, municipal wastewater, urban runoff, and industrial wastewaters, particularly from the electroplating, electronic, and metal-finishing industries. With the increasing generation of metals from technological activities, the problem of waste disposal has become one of paramount importance. Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals, and humans (Ikpe *et al*., 2020). The problems are exacerbated because metals tend to be transported with sediments, are persistent in the environment, and can bioaccumulate in the food chain. Some of the oldest cases of environmental pollution in the world are due to heavy metal use, for example, Cu, Hg, and Pb mining, smelting, and utilization by ancient civilizations, such as the Romans and the Phoenicians (Habashi, 1992).

Heavy metals released to the atmosphere during mining, smelting, and other industrial processes return to the land through dry and wet deposition. Discharge of wastewater, such as industrial effluents and domestic sewage, adds heavy metals to the environment. Application of chemical fertilizers and combustion of fossil fuels also contribute to the anthropogenic input of heavy metals in the environment. Regarding the contents of heavy metals in commercial chemicals fertilizers, phosphate fertilizers are particularly important. In general, phosphate fertilizers are produced from phosphate rock (PR) by acidification. In the acidulation of single superphosphate (SSP), sulfuric acid is used, while in the acidulation of triple superphosphate (TSP), phosphoric acid is used (Dissanayake & Chandrajith, 2019). The final product contains all the heavy metals present as constituents in the phosphate rock. Commercial inorganic fertilizers, particularly phosphate fertilizers, can potentially contribute to the global transport of heavy metals. Heavy metals are added to agricultural soils through inorganic fertilizers, which may be leached into groundwater and contaminate it (Dissanayake & Chandrajith, 2019). Phosphate fertilizers are particularly rich in toxic heavy metals. The two main pathways for the transfer of toxic heavy metals from phosphate fertilizers to the human body are shown below:

(i) Phosphate rock⟶ fertilizer⊡ soil⟶ plant⟶ food ⟶ human body

(ii) Phosphate rock⟶ ferfertilizer⊡water⊡ ⟶ human body

The combustion of fossil fuels in industries, homes, and transportation is an anthropogenic source of heavy metals. Vehicle traffic is among the major anthropogenic sources of heavy metals such as Cr, Zn, Cd, and Pb (Ikpe *et al*., 2020). Higher concentrations of environmentally important heavy metals have been reported in soils and plants along roads in urban and metropolitan areas. Regarding anthropogenic sources of heavy metals, emissions from coal combustion and other combustion processes are very important. During coal combustion, Cd, Pb, and As are partially volatile, while Hg is fully volatile. The anthropogenic sources of Cr include electroplating industries, leather tanneries, textile industries, and steel industries (Palaniappan & Karthikeyan, 2019). The natural sources of Cd in the environment are volcanic action and weathering of rocks, whereas an anthropogenic source is nonferrous metal mining, especially the processing of Pb-Zn ores. Anthropogenic increases in Cd concentrations are also caused by excessive application of chemical fertilizers (Wang *et al*., 2015). P-containing fertilizers contain Cd as a contaminant at concentrations ranging from trace quantities to 300ppm on dry weight basis and hence may be a main source of input of this metal to agricultural systems (Grant & Shappard, 2008). Pb is released to the environment from different sources including acid batteries, old plumbing systems, and lead shots used for hunting of game birds. Combustion of leaded gasoline is also a source of Pb in the environment. Although use of the tetraethyl lead as an antiknock agent in gasoline has been banned, it is still used in some developing regions of the world.

Sources of heavy metals

Anthropogenic sources

- Mining and smelting
- Industries
- Combustion of fossil fuels
- Phosphate fertilizers
- Metallo-pesticides etc.

Geological/natural sources

- Volcanic eruptions
- Weathering of metal-containing rocks

Heavy metals enter into natural waters through dry and wet deposition, industrial effluents, domestic sewage and agricultural run-off.

Heavy metals are accumulated in sediments and biota. Retention of heavy metals in sediments depend on different physicochemical processes like adsorption/desorption, complexation and precipitation which in turn depend on different physical-chemical parameters e.g., temperature, pH, particulate organic matter (POM), redox state, ion exchange capacity (CEC) and hydrodynamics etc.

Fig 2.1: Sources of heavy metals (Sanyal *et al.,* 2015).

These heavy metals are among the most common pollutants found in wastewater and shows significant danger to humans and their animals even at low concentration. For instance, lead is extremely toxic and shows toxicity to the nervous system, kidneys, and reproductive system (Healey, 2019). Exposure to lead causes irreversible brain damage and encephalopathic symptoms. Cadmium is used widely in electroplating industries, solders, batteries, television sets, ceramics, photography, insecticides, electronics, metal-finishing industries, and metallurgical activities (Lindholmer, 2016). It can be introduced into the environment by metal-ore refining, cadmium containing pigments, alloys and electronic compounds, cadmium containing phosphate fertilizers, detergents, and refined petroleum products. Rechargeable batteries with nickel–cadmium compounds are also sources of cadmium (Clarkson, 2017). Cadmium exposure causes renal dysfunction, bone degeneration, liver, and blood damage. It has been reported that there is sufficient evidence for the carcinogenicity of cadmium. Copper, as an essential trace element, is required by biological systems for the activation of some enzymes during photosynthesis but at higher concentrations it shows harmful effects on the human body. High-level exposure of copper dust causes nose, eyes and mouth irritation and may cause nausea and diarrhea. Continuous exposure may lead to kidney damage and even death. Copper is also toxic to a variety of aquatic organisms even at very low concentrations. Mining, metallurgy, and industrial applications are the major sources of copper exposure in the environment.

Zinc is also an essential element in our diet. Too much zinc, however, can also be damaging to health. Zinc toxicity in large amounts causes nausea and vomiting in children (Lindholmer, 2016). A higher concentration of zinc may cause anemia and cholesterol problems in human beings. Mining and metallurgical processing of zinc ores and its industrial application are the major sources of zinc in the air, soil, and water. It also comes from the burning of coal. Nickel occurs naturally in soils and volcanic rocks. Nickel and its salts are used in several industrial applications such as in electroplating, automobile and aircraft parts, batteries, coins, spark plugs, cosmetics, and stainless steel, and is used extensively in the production of nickel–cadmium batteries on an industrial scale (Dickman & Leung, 2018). It enters the water bodies naturally by weathering of rocks and soils and through the leaching of the minerals. The water-soluble salts of nickel are the major problems of contamination in aquatic systems. Paint formulation and enameling industries discharges nickel containing effluents to the nearby bodies of water. Nickel is also found in cigarettes, as a volatile compound commonly known as nickel carbonyl. Arsenic is found naturally in the deposits of earth's crust worldwide and exists in powdery amorphous and crystalline forms in the ores. In certain areas the concentration of arsenic may be higher than its normal dose and creates severe health hazards to human beings and animals. It enters the environment through the natural weathering of rocks and anthropogenic activities, mining and smelting processes, pesticide use and coal combustion. The toxicity of arsenic because of the contamination of groundwater bodies and surface waters is of great concern. Arsenic exists as arsenate As (V), and arsenite As (III), in most of the groundwater (Kieber & Willey, 2017). Adsorption and solution pH commonly controls the mobility of arsenic in the aqueous environment. Metal oxides of Fe, Al and Mn play a role in the adsorption of arsenic in aquatic bodies. Arsenic has been found naturally at high concentration in groundwater in countries such as India, Bangladesh, Taiwan, Brazil, and Chile. Its high concentration in drinking water causes toxic effects on humans and animals.

The toxicity of mercury has been recognized worldwide, such as in Minamata Bay of Japan (Dickman & Leung, 2018). Mentally disturbed and physically deformed babies were born to mothers who were exposed to toxic mercury due to consumption of contaminated fish. The natural sources of mercury are volcanic eruption, weathering of rocks and soils, whereas anthropogenic mercury comes from the extensive use of the metal in industrial applications, its mining and processing, applications in batteries and mercury vapor lamps. Methyl mercury is more toxic than any other species of mercury (Clarkson, 2017).

Extensive use of chromium compounds in industrial applications has discharged huge amounts of wastewater containing toxic chromium species into water bodies. Chromium enters the environment by natural inputs and anthropogenic sources. Volcanic eruptions, geological weathering of rocks, soils and sediments are the natural sources of chromium, whereas anthropogenic contributions of chromium come from the burning of fossil fuels, production of chromates, plastic manufacturing, electroplating of metals and extensive use in the leather and tannery industries. Hexavalent chromium is more toxic than trivalent chromium (Kieber & Willey, 2017).

2.4 CONTAMINATION OF NATURAL WATERS, SEDIMENTS, AND SOILS BY HEAVY METALS

Heavy metals beyond an acceptable threshold pose an important threat to both aquatic and terrestrial ecosystems (Slaveykova & Cheloni, 2018). After being released from both natural and anthropogenic sources, heavy metals contaminate natural water bodies, sediments, and soils. Heavy metals released into the atmosphere via volcanic eruptions and other forms, like industrial emissions, also ultimately return to the land and cause contamination of waters and soils. Since heavy metals are persistent in the environment, they either accumulate in biota or leach down into groundwater. Contamination of biota and groundwater with potentially toxic heavy metals has important implications for human health. It is important to assess the degree of heavy metal pollution in riverine ecosystems by investigating the concentrations of these elements and their distribution (Islam *et al*., 2018). Different physicochemical and climatic factors affect the overall dynamics and biogeochemical cycling of heavy metals in the environment.

2.4.1 WATER

It is said that water is the "lifeblood of the biosphere." Since water is a universal solvent, it dissolves different organic and inorganic chemicals and environmental pollutants. Aquatic ecosystems, both freshwater and marine, are vulnerable to pollution. Contamination of water resources by heavy metals is a critical environmental issue that adversely affects plants, animals, and human health (Rezania *et al*., 2016). Heavy metals are extremely toxic to aquatic organisms, even at very low concentrations. These elements can cause significant histopathological alterations in the tissues of aquatic organisms such as fish (Ahmed *et al*., 2014). Aquatic ecosystems are contaminated by heavy metals from different sources. One source of heavy metals in aquatic ecosystems is effluent from mining operations (Zhuang *et al*., 2013). Other sources of water contamination with heavy metals include different industrial effluents, domestic sewage, and agricultural run-off. The release of industrial effluents without treatment into the aquatic bodies is a major source of pollution of surface and ground water (Afzal *et al*., 2018). Pollution of water bodies with heavy metals is a worldwide problem because of the environmental persistence, bioaccumulation, and biomagnification in food chains and toxicity of these elements (Rajaei *et al*., 2012).

2.4.2 SEDIMENTS

Contamination of sediments with heavy metals is an environmentally important issue with consequences for aquatic organisms and human health. Sediments act as the main pool of metals in the aquatic environment. Their quality can indicate the status of water pollution (Zahra *et al*., 2014). Sediments serve as both sink and source of heavy metals, releasing them into the water column (Fenandes & Nayak, 2012). Continuing deposition of heavy metals in sediments can also lead to contamination of groundwater with these pollutants (Sanyal *et al*., 2015). The adsorption, desorption, and subsequent concentrations of heavy metals in sediments are affected by many physicochemical factors such as temperature, hydrodynamic conditions, redox state, content of organic matter and microbes, salinity, and particle size (Zhao *et al*., 2014). Distribution of heavy metals in sediments is affected by chemical composition of the sediments, grain size, and content of total organic matter (TOM) (Azadi *et al*., 2018). An important determinant of metal bioavailability in sediments is pH. A lowering in pH increases the competition between metal ions and H^+ for binding sites in sediments and may result in dissolution of metal complexes, thereby releasing free metal ions into the water column (Nowrouzi *et al*., 2014). Higher concentrations of toxic heavy metals in riverine sediments may pose ecological risk to benthos (bottom-dwelling organisms) (Decena *et al*., 2018).

2.5 METALS AND THEIR ESSENTIALITY FOR LIFE

Chemically, metals are defined as "elements, which conduct electricity, have a metallic luster, are malleable and ductile, form cations, and have basic oxides". Terms usually used in relation to metals in biological and environmental studies are metal, metalloid, semimetal, light metal, heavy metal, essential metal, beneficial metal, toxic metal, abundant metal, and available metal, trace metal, and micronutrient (Duffus, 2002). Metals have very diverse applications and play an important role in the industry-dominated human society. Some metals have critically important physiological and biochemical functions in biological systems, and either their deficiency or excess can lead to disturbance of metabolism and therefore to various diseases. Some metals and metalloids are essential for (biological) life. They play important physiological and biochemical roles in the body as they may be part of bio- molecules such as enzymes, which catalyze biochemical reactions in the body.

2.6 ESSENTIAL AND NONESSENTIAL HEAVY METALS (HMS).

Regarding their roles in biological systems, heavy metals are classified as essential and nonessential. Essential heavy metals are important for living organisms and may be required in the body in quite low concentrations. Nonessential heavy metals have no known biological role in living organisms. Examples of essential heavy metals are Mn, Fe, Cu, and Zn, while the heavy metals like Cd, Pb, and Hg are toxic and are regarded as biologically nonessential (Tu¨rkmen *et* al., 2009; Ram´ırez1, 2013; Rahim *et* al., 2016). The heavy metals Mn, Fe, Co, Ni, Cu, Zn, and Mo are micronutrients or trace elements for plants. They are essential for growth and stress resistance as well as for biosynthesis and function of different biomolecules such as carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites (Appenroth, 2010). Either deficiency or excess of an essential heavy metal leads to diseases or abnormal conditions.

2.7 UPTAKE OF HEAVY METALS BY FISH

Heavy metals are mostly toxic, can cause severe damage and become lethal for most organisms since they are able to bioaccumulate and biomagnified. Bioaccumulation means an increase in the concentration of a xenobiotic in an organism over time compared with xenobiotic concentration in the environment (Govind & Madhuri, 2014). Biomagnification means transfer of a xenobiotic from food sources to an organism, resulting a higher concentration in the organism than the sources (Achieche *et al*., 2020). Uptake of heavy metals by fish from the environment primarily occurs through gills, food, and skin and in freshwater fish through water taken with food and taken heavy metals are carried to organs by carrier proteins via blood path and can reach high concentrations by bonding to metal binding proteins in these tissues (Sönmez *et al.,* 2016). The toxic element concentration in fish depends on sex and age of fish, season, and place. Pollution of water sources by anthropogenic activities leads to aquatic loss and therefore disrupts the balance of food chain (Afshan *et al*., 2014).

2.8 EFFECTS OF HEAVY METALS ON FISH

Some of the aquatic organisms can store heavy metals up to certain amount. Even though these heavy metals are not harmful or toxic, they can reach to humans via food chain and affect human health (Merlini, 1971) As a general rule toxicity occurs when heavy metal concentrations reach above certain threshold. Also, heavy metals piled in water join to the food chain from many stages and threaten ecosystem safety, fish, and human health. (Jain *et al*., 2008; Sönmez *et al*., 2013a). Fish are at the top of the aquatic food chain, and they can accumulate preexisting metals in various tissues and organs (Mansour & Sidky 2002; Sönmez *et al*., 2012). Aquatic organisms such as fish and shellfish accumulate metals to concentrations many times higher than present in water or sediment (Olaifa *et al*, 2004, Gumgum *et al*., 1994; Al-Weher, 2008). Accumulated metals in fish tissues up to toxic concentrations are based on certain environmental conditions such as food chain, predation competition, water chemistry (salinity, pH, water hardness,) and hydrodynamics in the water (Förstner & Wittmann, 1981; Guven *et al.,* 1999; Akgün *et al.*, 2007; Al-Weher, 2008). Furthermore, interaction between metals may also influence accumulation (Pagenkopf, 1983; Cicik, 2003).

Studies carried out on fish revealed that all heavy metals, even though some of them are essential for life, have adverse effects on living organisms through metabolic interference and mutagenesis. These adverse effects are decrease in fitness, interference in reproduction that leads to carcinoma and eventually death (Govind & Madhuri, 2014). In addition to reproduction, hypoxic conditions, excessive stocking and starvation, heavy metal effects also cause stress in fish (Levesque *et al*., 2002; Arslan *et al*., 2006). Stress factors including pollution affect growth, development, and reproduction adversely by changing metabolic, physiological, and biochemical functions (Heath, 1995; Çiftçi *et al*., 2017). Adverse impacts on physiological functions and biochemical parameters both in blood and tissue of the fish living in metal contaminated waters have been observed.

It has been reported that fish exposed to metals showed immune system malfunction and thus became vulnerable to contagious diseases and had a greater mortality risk (Larsson and Haux, 1985; Abel and Papoutsouglou, 1986; Sehgal and Saxena, 1986; Nemesok and Huphes, 1988;

Çelik, 2006; Akgün *et al.,* 2007; Al-Weher, 2008). Heavy metals enhance genotoxicity either directly or indirectly by inducing toxicity of other chemical agents (Bolognesi *et al*., 1999). Heavy metal exposure reduces estrogenic and androgenic secretion and causes pathological changes in fish (Ebrahimi & taherianfard, 2011).

Effects of Cadmium (Cd): Cadmium exhibits high toxicity at even very low concentrations and has acute and chronic effects on fish and environment. Long exposure of cadmium poses various acute and chronic effects on aquatic living beings (Thomas *et al.,* 1983; Kuroshima, 1992). Such effects are enhancement of humoral immune response (Descotes, 1992; Krumschnabel *et al*., 2010), inducement of structural and functional changes in gill, intestine, liver, and kidney (Kumar and Sing, 2010), pathological alterations in liver such as congestion, necrosis of pancreatic cells and fatty changes in the peripancreatic hepatocytes, congestion, and engorgement of blood vessels (Rani & Ramamurthi, 1989; Dangre *et al.,* 2010; Kumar & Sing, 2010). It also causes disruption of calcium metabolism, hypercalciuria and leads kidney stones to form. Short term effect of high concentrations of Cd caused hyperglycemia, whereas long term effect of low concentrations of Cd caused hypoglycemia and liver glycogen concentrations were enhanced in both situations (Çelik *et al.,* 2008). Cd caused decrease in hemoglobin levels and red blood cell count (Ruparella et al., 1990; Çelik, 2006). It also effects glucose levels of fish.

Effects of Copper (Cu): Copper reduces resistance of fish to diseases by disrupting migration; altering swimming; causing oxidative damage; impairing respiration; disrupting osmoregulation structure and pathology of vital organs such as gills, kidney, liver, and other stem cells (Hodson *et al.* 1979, Knittel, 1981, Rougier *et al*. 1994, Eisler 2000, Craig *et al*. 2010, Tierney *et al*. 2010; Woody & O'Neal, 2012). Cu exposed to different fish species posed behavioural changes such as decrease in swimming ability and food intake and increase in operculum movements (Ansari, 1984; Venkataramana & Radhakrishnaiah, 2001; Ali *et al.,* 2003; Arslan *et al*., 2006). Fish rely on their sense of smell to migrate, avoid predators, and find food. Cu affects sense of smell (olfaction) in fish thus causing alterations in appetite, navigation, and awareness of surroundings. It also reduces sperm and egg production, survival rates and increases abnormality incidences (Solomon, 2009).

Effects of Iron (Fe): Although iron is essential for physiological processes in animals, it may be detrimental to living organisms at higher concentrations than optimum conditions. (Davies, 1991; Misra and Mani, 1992). Smith et al. (1973) observed that more than 1.0 mg/l iron concentrations affected feeding of fry and juveniles, caused prolonged stress and reduced growth. Debnath *et al.* (2012) also showed that behavioural changes, decrease in feeding rate and reduced growth occurred in mrigal (*Chirrhinus mrigala*), catla (*Catla catla*) and roho labeo (*Labeo rohita*) larvae after iron exposure and suggested that such alterations might have taken place because of accumulation of iron in gills, therefore disrupting osmoregulation and respiration. Gill damage causes a disruption of carbon dioxide and oxygen exchange, hypercapnia, plasmatic acidosis, and hypoxia (Playle & Wood, 1989; Exley *et al.*, 1991).

Effects of Nickel (Ni): Ghosh *et al.* (2018) studied Ni toxicity on common carp (*Cyprinus carpio*) and suggested that Ni does not precipitate in water as fast as other heavy metals and therefore making it more bioavailable to pelagic organisms. Ni primarily accumulates in the gills of fish and are transported to liver, kidney, and muscle tissues is too little to detect within 96 hours of exposure (Ghosh *et al.*, 2018). High levels of Ni cause oxidative stress in fish, changes behavioral patterns and affects respiratory system in fish by causing gill lamellae to swell as well as increasing oxygen consumption, ventilatory stroke volume and respiration frequency.

Effects of Lead (Pb): Increase of lead levels in water may cause adverse effects in some aquatic organisms and may lead alterations of blood parameters and nervous system in fish and other animals. Pb is a dangerous environmental pollutant, and it has become much thought of due to its considerable danger risks for human health (Afshan *et al*., 2014). It has been detected that Pb inhibits Na+/K+-ATPase enzyme and d-aminolaevulinic acid dehydratase enzyme that participates in growth and hem synthesis in erythrocytes and affects lipid peroxidation enzyme. It has been shown that Pb also has influence on intercellular communication by changing alanine aminotransferase (ALT) and aspartate aminotransferase (AST) concentrations in tissues and organs (Çoğun & Şahin, 2012).

Effects of Zinc (Zn): Zinc is an essential element but at greater concentrations it may be toxic to fish as indicated previously. Zn accumulates in the gills of fish and creates adverse effects on fish by causing structural damages that affects growth, development, and survival. It also alters fish behaviour, hatchability, hematological parameters, balance, swimming ability (Afshan *et al*., 2014).

2.9 TROPHIC TRANSFER OF HEAVY METALS

Since heavy metals are persistent in the environment, they accumulate in living organisms and are transferred from one trophic level to another in the food chains. The extent of accumulation of heavy metals in biota depends on their rate of accumulation and their rate of elimination from the body (Sanyal *et al*., 2015). Thus, different heavy metals have different half lives in different species. Heavy metals may gain access to the body of an organism directly from the abiotic environment, i.e., water, sediments, and soil or may enter the organism body from its food/prey (Fenandes & Nayak, 2012). For example, heavy metals may enter the fish body directly from water or sediments through the fish gills/skin or from the fish food/prey through its alimentary canal. The concentration of a heavy metal may increase or decrease along successive trophic levels in a food chain. The retention of heavy metals in the body of an organism depends on many factors such as the speciation of the metal concerned, and the physiological mechanisms developed by the organism for the regulation, homeostasis, and detoxification of the heavy metal. Methylated forms of heavy metals such as Hg are accumulated in biota to a greater extent and therefore biomagnified in food chains due to their lipophilicity. Certain plants can thrive on metal-rich habitats and are called metallophytes. These special plants have developed special mechanisms for coping with higher heavy metal concentrations in soil and are divided into three categories, i.e., excluders, indicators, and hyper- accumulators (Fenandes & Nayak, 2012).

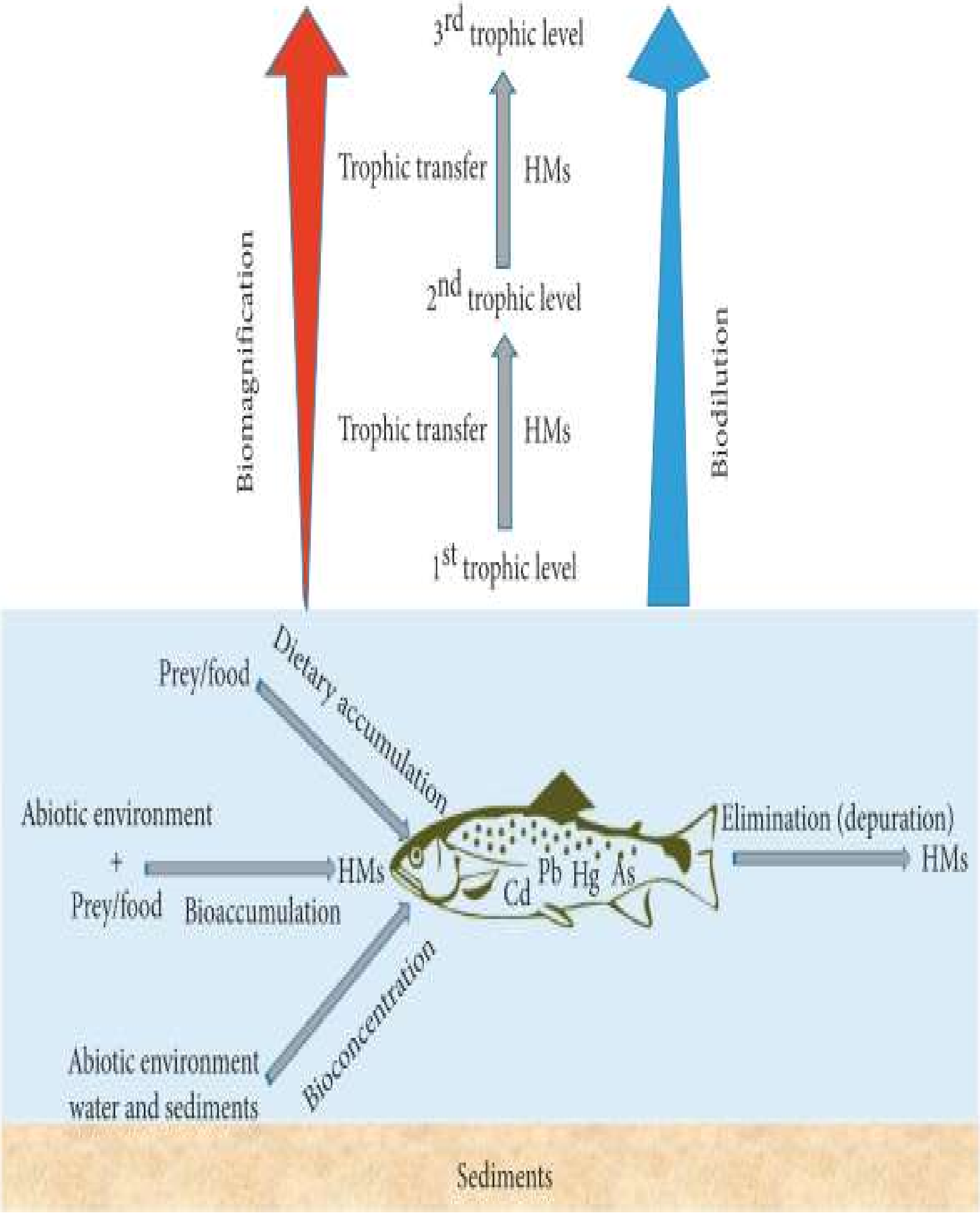

Fig. 2.2: Transfer of heavy metals across trophic levels (Fernandes & Nayak, 2012).

2.10 HUMAN EXPOSURE TO HEAVY METALS

Humans are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption. People are more exposed to toxic metals in developing countries (Eqani *et al*., 2016). Generally, people have no awareness and knowledge about exposure to heavy metals and its consequences for human health, especially in the developing countries (Afrin *et al*., 2015). People may be exposed to heavy metals in the workplace and in the environment. Human exposure to toxic chemicals in the workplace is called occupational exposure, while exposure to such chemicals in the general environment is called non-occupational or environmental exposure. Workers are exposed to heavy metals in mining and industrial operations, where they may inhale dust and particulate matter-containing metal particles. People extracting gold through the amalgamation process are exposed to Hg vapors. It has been reported that welders with prolonged occupational exposure to welding fumes had significantly higher levels of the heavy metals Cr, Ni, Cd, and Pb in their blood than the control group and showed increased oxidative stress (Mahmood *et al*., 2015). Cigarette smoking is also a principal source of human exposure to Cd and other toxic heavy metals present in tobacco leaves. Ingestion of heavy metals through food and drinking water is a major exposure source for the general human population. Industrialization, urbanization, and rapid economic development around the globe have led to intensification in industrial and agricultural activities. Such activities may cause contamination of water, air, and soils with toxic heavy metals. Growing human foods in heavy metal-contaminated media leads to bioaccumulation of these elements in the human food chains, from where these elements ultimately reach the human body.

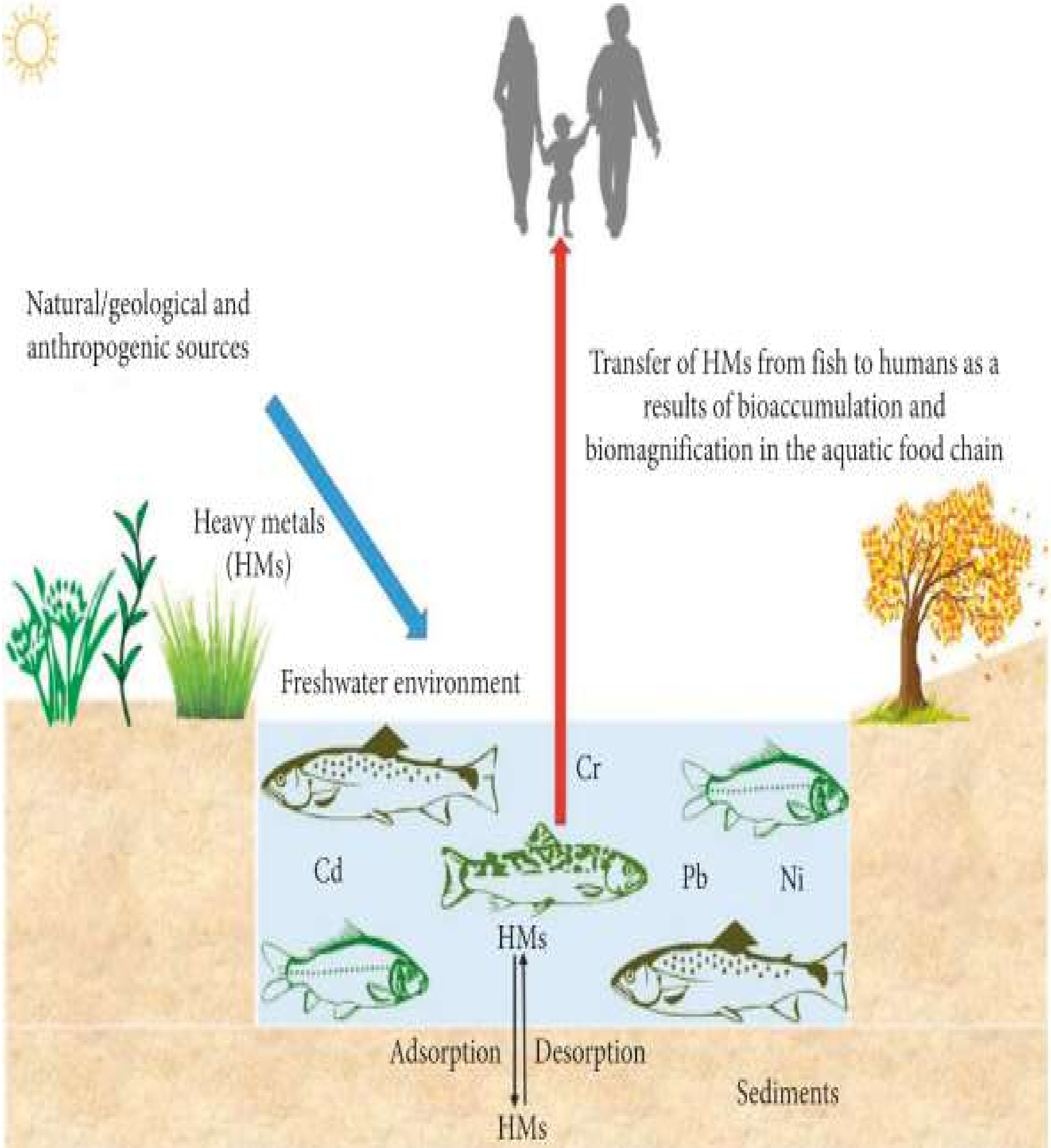

Fig. 2.3: Exposure of humans to heavy metals (Mahmood *et al.*, 2015).

2.11 HEAVY METAL TOXICITY

Although some heavy metals, called essential heavy metals, play important roles in biological systems, they are generally toxic to living organisms, depending on the dose and duration of exposure (Sanyal *et al*., 2015). It is a well-known fact in toxicology that “excess of everything is bad.” Nonessential heavy metals (Cd, Pb, and Hg) and metalloids (As, etc.) may be toxic even at quite low concentrations. Essential heavy metals are required in trace quantities in the body but become toxic beyond certain limits or threshold concentrations. For some elements, the window of essentiality and toxicity is narrow. Heavy metals have been reported to be carcinogenic, mutagenic, and teratogenic (Sanyal *et al*., 2015). They cause the generation of reactive oxygen species (ROS) and thus induce oxidative stress. Oxidative stress in organisms leads to the development of various diseases and abnormal conditions. Heavy metals also act as metabolic poisons. Heavy metal toxicity is primarily due to their reaction with sulfhydryl (SH) enzyme systems and their subsequent inhibition, e.g., those enzymes involved in cellular energy production.

2.12 TYPES OF HEAVY METALS AND THEIR TOXICITY MECHANISMS

Arsenic: Arsenic is the twentieth most abundant element on earth, and its inorganic forms, such as arsenite and arsenate compounds, are lethal to the environment and living creatures. It is one of the most important heavy metals, causing concern from both ecological and individual health standpoints (Hughes *et al*., 1988). It has a semi-metallic property, is prominently toxic and carcinogenic, and is extensively available in the form of oxides or sulfides or as a salt of iron, sodium, calcium, copper, etc. (Singh *et al*., 2017). Humans may encounter arsenic by natural means, from industrial sources, or from unintended sources. Drinking water may get contaminated by the use of arsenical pesticides, natural mineral deposits, or inappropriate disposal of arsenical chemicals. Deliberate consumption of arsenic in case of suicidal attempts or accidental consumption by children may also result in cases of acute poisoning (Mazumder, 2018). Arsenic is a protoplasmic poison since it affects primarily the sulphydryl group of cells causing malfunctioning of cell respiration, cell enzymes and mitosis (Mazumder, 2018).

Mechanism of arsenic toxicity

In arsenic biotransformation, harmful inorganic arsenic compounds get methylated by bacteria, algae, fungi, and humans to give Monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). In this biotransformation process, these inorganic arsenic species (As) are converted enzymetically to methylated arsenicals which are the end metabolites and the biomarker of chronic arsenic exposure. Biomethylation is a detoxification process and end products are methylated inorganic arsenic such as MMA (V) and DMA (V), which excreted through urine are bioindication of chronic arsenic exposure. However, MMA (III) is not excreted and remains inside the cell as an intermediate product. Monomethylarsonic acid (MMA III), an intermediate product, is found to be highly toxic compared to other arsenicals, potentially accountable for arsenic-induced carcinogenesis (Singh *et al*., 2017).

Lead: Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. Lead is a bright silvery metal, slightly bluish in a dry atmosphere. It begins to tarnish on contact with air, thereby forming a complex mixture of compounds, depending on the given conditions (Sharma & Dubey, 2015). The sources of lead exposure include mainly industrial processes, food, and smoking, drinking water and domestic sources. The sources of lead were gasoline and house paint, which has been extended to lead bullets, plumbing pipes, pewter pitchers, storage batteries, toys, and faucets (Thürmer *et al.,* 2017). Lead is an extremely toxic heavy metal that disturbs various plant physiological processes and unlike other metals, such as zinc, copper, and manganese, it does not play any biological functions. A plant with high lead concentration fastens the production of reactive oxygen species (ROS), causing lipid membrane damage that ultimately leads to damage of chlorophyll and photosynthetic processes and suppresses the overall growth of the plant (Najeeb *et al.,* 2014). Some research revealed that lead can inhibit the growth of tea plant by reducing biomass and debases the tea quality by changing the quality of its components (Yongsheng *et al*., 2016). Even at low concentrations, lead treatment was found to cause huge instability in ion uptake by plants, which in turn leads to significant metabolic changes in photosynthetic capacity and ultimately in a strong inhibition of plant growth (Mostafa *et al*., 2012).

Mechanisms of lead toxicity

Lead metal causes toxicity in living cells by following ionic mechanism and that of oxidative stress. Many researchers have shown that oxidative stress in living cells is caused by the imbalance between the production of free radicals and the generation of antioxidants to detoxify the reactive intermediates or to repair the resulting damage. Antioxidants, as e.g., glutathione, present in the cell protect it from free radicals such as H_2O_2. Under the influence of lead, however, the level of the ROS increases and the level of antioxidants decreases. Since glutathione exists both in reduced (GSH) and oxidized (GSSG) state, the reduced form of glutathione gives its reducing equivalents from its thiol groups of cysteine to ROS to make them stable. In the presence of the enzyme glutathione peroxidase, reduced glutathione readily binds with another molecule of glutathione after donating the electron and forms glutathione disulfide (GSSG). The reduced form (GSH) of glutathione accounts for 90% of the total glutathione content and the oxidized form (GSSG) accounts for 10% under normal conditions. Yet under the condition of oxidative stress, the concentration of GSSG exceeds the concentration of GSH. Another biomarker for oxidative stress is lipid peroxidation, since the free radical collects electron from lipid molecules present inside the cell membrane, which eventually causes lipid peroxidation (Wadhwa *et al*., 2012; Flora *et al*., 2012). At very high concentrations, ROS may cause structural damage to cells, proteins, nucleic acid, membranes, and lipids, resulting in a stressed situation at cellular level (Mathew *et al.,* 2011). The ionic mechanism of lead toxicity occurs mainly due to the ability of lead metal ions to replace other bivalent cations like Ca2+, Mg2+, Fe2+ and monovalent cations like Na+, which ultimately disturbs the biological metabolism of the cell. The ionic mechanism of lead toxicity causes significant changes in various biological processes such as cell adhesion, intra- and inter-cellular signaling, protein folding, maturation, apoptosis, ionic transportation, enzyme regulation, and release of neurotransmitters. Lead can substitute calcium even in picomolar concentration affecting protein kinase C, which regulates neural excitation and memory storage (Flora *et al.,* 2012).

Mercury: The metallic mercury is a naturally occurring metal which is a shiny silver-white, odourless liquid and becomes colourless and odourless gas when heated. Mercury is very toxic and exceedingly bioaccumulative. Its presence adversely affects the marine environment and hence many studies are directed towards the distribution of mercury in water environment. Major sources of mercury pollution include anthropogenic activities such as agriculture, municipal wastewater discharges, mining, incineration, and discharges of industrial wastewater (Chen *et al*., 2012). Mercury exists mainly in three forms: metallic elements, inorganic salts, and organic compounds, each of which possesses different toxicity and bioavailability. These forms of mercury are present widely in water resources such as lakes, rivers, and oceans where they are taken up by the microorganisms and get transformed into methyl mercury within the microorganism, eventually undergoing biomagnification, causing significant disturbance to aquatic life. Consumption of this contaminated aquatic animal is the major route of human exposure to methyl mercury (Trasande et *al*., 2015). Mercury is extensively used in thermometers, barometers, pyrometers, hydrometers, mercury arc lamps, fluorescent lamps and as a catalyst. It is also being used in the pulp and paper industries, as a component of batteries and in dental preparations such as amalgams. It is a very toxic element in its organic form and has been the cause of Minamata disease in Japan. It shows toxicity to the physiology of animals and human beings. Mercury toxicity has been found to be associated with physiological stress, abortion, and tremors.

Methyl mercury is highly toxic and causes toxic effects on the central nervous system in the human population.

Mechanism of mercury toxicity

Mercury is well known as a hazardous metal and its toxicity is a common cause of acute heavy metal poisoning with cases of 3,596 in 1997 by the American Association of Poison Control Centers. Methylmercury is a neurotoxic compound which is responsible for microtubule destruction, mitochondrial damage, lipid peroxidation and accumulation of neurotoxic molecules such as serotonin, aspartate, and glutamate (Patrick, 2014). The total amount of mercury emission into the environment has been assessed at 2,200 metric tons annually (Ferrara *et al*., 2016). Animals which are exposed to toxic mercury have shown adverse neurological and behavioural changes.

The brain remains the target organ for mercury, yet it can impair any organ and lead to malfunctioning of nerves, kidneys, and muscles. It can cause disruption to the membrane potential and interrupt with intracellular calcium homeostasis. Mercury binds to freely available thiols as the stability constants are high (Patrick, 2014). Mercury vapors can cause bronchitis, asthma, and temporary respiratory problems. Mercury plays a key role in damaging the tertiary and quaternary protein structure and alters the cellular function by attaching to the selenohydryl and sulfhydryl groups which undergo reaction with methyl mercury and hamper the cellular structure. It also intervenes with the process of transcription and translation resulting in the disappearance of ribosomes and eradication of endoplasmic reticulum and the activity of natural killer cells. The cellular integrity is also affected causing free radical formation. The basis for heavy metal chelation is that even though the mercury sulfhydryl bond is stable and divided to surrounding sulfhydryl consisting of ligands, it also contributes free sulfhydryl groups to pro-mote metal mobility within the ligands (Bernhoft, 2011).

Cadmium: Cadmium is one of the most toxic elements, even at its low concentration in the food chain and has been found to cause of *itai-itai* disease in Japan. Unlike other heavy metals, cadmium is not essential for biological systems. Hence it has no benefit to the ecosystem and only harmful effects have been reported. It is used in the manufacturing of nickel–cadmium batteries, plastics, and pigments. Phosphate fertilizers and waste dumping are both routes for cadmium transference into the environment. Concern regarding the role and toxicity of cadmium in the environment is on the increase because it can be highly toxic to human beings and animals at very low concentrations. Once this metal gets absorbed by humans, it will accumulate inside the body through-out life. Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer from acute and chronic intoxications. Cadmium distributed in the environment will remain in soils and sediments for several decades. Plants gradually take up these metals which get accumulated in them and concentrate along the food chain, reaching ultimately the human body (Bernard, 2018; Mutlu *et al*., 2012). Cadmium is predominantly found in fruits and vegetables due to its high rate of soil-to-plant transfer (Satarug *et al.*, 2011). Cadmium is a highly toxic nonessential heavy metal that is well recognized for its adverse influence on the enzymatic systems of cells, oxidative stress and for inducing nutritional deficiency in plants (Irfan *et al*., 2013). Cadmium toxicity causes renal dysfunction and lung cancer, and osteomalacia in the human population and animals, in addition to increasing blood pressure. Smoking of cigarettes is one of the sources of cadmium poisoning in humans.

Mechanism of cadmium toxicity

The mechanism of cadmium toxicity is not understood clearly but its effects on cells are known (Patrick, 2003). Cadmium concentration increases 3,000-fold when it binds to cysteine-rich protein such as metallothionein. In the liver, the cysteine-metallothionein complex causes hepatotoxicity and then it circulates to the kidney and gets accumulated in the renal tissue causing nephrotoxicity.

Cadmium has the capability to bind with cysteine, glutamate, histidine, and aspartate ligands and can lead to the deficiency of iron (Castagnetto *et al.,* 2002). Cadmium and zinc have the same oxidation states and hence cadmium can replace zinc present in metallothionein, thereby inhibiting it from acting as a free radical scavenger within the cell.

Chromium: Chromium is the seventh most abundant element on earth (Mohanty & Kumar, 2013). Chromium occurs in several oxidation states in the environment ranging from Cr2+ to Cr6+ (Rodríguez *et al*., 2009). The most commonly occurring forms of Cr are trivalent- Cr+3 and hexavalent- Cr+6, with both states being toxic to animals, humans, and plants (Mohanty & Kumar, 2013). Chromium is commonly used in the leather and tanning industries, paper and pulp and rubber manufacturing applications and occurs naturally by the burning of oil and coal, petroleum from ferrocromate refractory material, pigment oxidants, catalyst, chromium steel, fertilizers, oil well drilling and metal plating tanneries. Anthropogenically, chromium is released into the environment through sewage and fertilizers (Ghani, 2011). Cr (III) is immobile in its reduced form and is insoluble in water whereas Cr (VI) in its oxidized state is highly soluble in water and thus mobile (Wolińska *et al*., 2013). Chromium is extensively used in industries such as metallurgy, electroplating, production of paints and pigments, tanning, wood preservation, chemical production and pulp and paper production. These industries play a major role in chromium pollution with an adverse effect on biological and ecological species (Ghani, 2011). A wide range of industrial and agricultural practices increase the toxic level in the environment causing concern about the pollution caused by chromium. Pollution of the environment by chromium, particularly hexavalent chromium, has been the greatest concern in recent years (Zayed & Terry, 2017). During manufacturing of chromate, the deposit of the Cr residues and wastewater irrigation posed a serious Cr pollution to farmland. With the implementation of modern agriculture there is continuous release of Cr into the environment by means of Cr residues, Cr dust and Cr wastewater irrigation, resulting in soil pollution affecting the soil-vegetable system and disturbing the vegetable yield and its quality to humans (Duan *et al*., 2010). The presence of excess of chromium beyond the permissible limit is destructive to plants since it severely affects the biological factors of the plant and enters the food chain on consumption of these plant materials. Common features due to Cr phytotoxicity are reduction in root growth, leaf chlorosis, inhibition of seed germination and depressed biomass. Chromium toxicity greatly affects the biological processes in various plants such as maize, wheat, barley, cauliflower, Citrullus and in vegetables (Ghani, 2011).

Mechanism of chromium toxicity

In the environment, trivalent chromium Cr (III) is generally harmless due to its weak membrane permeability. Hexavalent chromium Cr (VI), on the other hand, is more active in penetrating the cell membrane through passages for isoelectric and isostructural anions such as SO_4^{2-} and HPO_4^{2-} channels and these chromates are taken up through phagocytosis. Cr (VI) is a strong oxidizing agent and can be reduced to give ephemeral species of pentavalent and tetravalent chromium that are different from that of Cr (III). Stabilization of the pentavalent form is carried out by glutathione and hence intracellular reduction of Cr [VI] is considered a detoxification mechanism when reduction occurs away from the target region. However, if intracellular reduction of Cr [VI] occurs near the target site, it may serve to activate Cr. The reactions between Cr (VI) and biological reductants like thiols and ascorbate result in the production of reactive oxygen species such as superoxide ion, hydrogen peroxide, and hydroxyl radical, ultimately leading to oxidative stress in the cell causing damage to DNA and proteins (Stohs & Bagchi, 1995).

Aluminum: Aluminum is the third most abundant element found in the earth's crust (Gupta *et al*., 2013). Aluminum occurs naturally in the air, water, and soil. Mining and processing of aluminum elevates its level in the environment (ATSDR, 2010). Recent investigations on environmental toxicology revealed that aluminum may present a major threat for humans, animals, and plants in causing many diseases (Barabasz *et al.,* 2015). Many factors, including pH of water and organic matter content, greatly influence the toxicity of aluminum. With decreasing pH its toxicity increases. The mobilization of toxic aluminum ions, resulting from changes in the pH of soil and water caused by acid rains and increasing acidification of the surrounding atmosphere, has an adverse effect on the environment. This is manifested by the drying of forests, plant poisoning, crop decline or failure, death of aquatic animals, and by various imbalances in the function of human and animal systems (Barabasz *et al.,* 2015). Aluminum in high concentrations is very toxic for aquatic animals, especially for gill breathing organisms such as fish, causing osmoregulatory failure by destructing the plasma and hemolymph ions. The activity of gill enzyme, essential for the uptake of ions, is inhibited by the monomeric form of aluminum in fish (Rosseland *et al*., 1990). Living organisms in water, such as seaweeds and crawfish, is also affected by Al toxicity (Bezak-Mazur, 2001). Aluminum has no biological role and is a toxic nonessential metal to microorganisms (Olaniran et al., 2013). Enzymes such as hexokinase, phosphodiesterase, alkalic phosphatase and phosphokinase are inhibited by aluminum since it has a greater affinity to DNA and RNA. Metabolic pathways in the living organism involving calcium, phosphorous, fluorine and iron metabolism are affected by aluminum. Aluminum has been found to be very harmful to nervous, osseous and hemopoietic cells (Barabasz1 *et al*., 2015).

Mechanism of aluminum toxicity

Aluminum interferes with most physical and cellular processes. The exact mechanism of absorption of aluminum by the gastrointestinal tract is not understood completely. Based on literature surveys, it is difficult to give a proper time for aluminum toxicity since some symptoms of aluminum toxicity can be detected in seconds and others in minutes after exposure to aluminum (WHO, 1997). Aluminum toxicity probably results from the interaction between aluminum and plasma membrane, apoplastic and symplastic targets (Kochian *et al.,* 2005). In humans Mg2+ and

Fe3+ are replaced by Al3+, which causes many disturbances associated with intercellular communication, cellular growth, and secretory functions. The changes that are evoked in neurons by aluminum are like the degenerative lesions observed in Alzheimer patients. The greatest complications of aluminum toxicity are neurotoxicity effects such as neuronal atrophy in the locus ceruleus, substantia nigra and striatum (Filiz & Meral, 2007).

Iron: Iron is the second most abundant metal on the earth's crust (EPA, 1993). Iron occupies the 26th elemental position in the periodic table. Iron is a most crucial element for growth and survival of almost all living organisms (Valko *et al*., 2015). It is one of the vital components of organisms like algae and of enzymes such as cytochromes and catalase, as well as of oxygen transporting proteins, such as hemoglobin and myoglobin (Vuori, 2017). Iron is an attractive transition metal for various biological redox processes due to its inter-conversion between ferrous (Fe2+) and ferric (Fe3+) ions (Phippen *et al*., 2018). The source of iron in surface water is anthropogenic and is related to mining activities. The production of sulphuric acid and the discharge of ferrous (Fe2+) takes place due oxidation of iron pyrites (FeS2) that are common in coal seams (Valko *et al*., 2015).

Mechanism of iron toxicity

A wide range of harmful free radicals are formed when the absorbed iron fails to bind to the protein, which in turn severely affects the concentration of iron in mammalian cells and biological fluids. This circulating unbound iron results in corrosive effect of the gastrointestinal tract and biological fluids. An extremely higher level of iron enters the body crossing the rate-limiting absorption step and becomes saturated. These free irons penetrate cells of the heart, liver, and brain. Due to the disruption of oxidative phosphorylation by free iron, the ferrous iron is converted to ferric iron that releases hydrogen ions, thus increasing metabolic acidity. The free iron can also lead to lipid peroxidation, which results in severe damage to mitochondria, microsomes and other cellular organelles (Albretsen, 2016). The toxicity of iron on cells has led to iron mediated tissue damage involving cellular oxidizing and reducing mechanisms and their toxicity towards intracellular organelles such as mitochondria and lysosomes. A wide range of free radicals that are believed to cause potential cellular damage are produced by excess intake of iron. The iron produced hydrogen free radicals attack DNA, resulting in cellular damage, mutation, and malignant transformations which in turn cause an array of diseases (Grazuleviciene *et al*., 2019).

2.13 BIOACCUMULATION

Bioaccumulation means an increase in the concentration of a chemical in the system of a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted (Neff, 2002). Understanding the dynamic process of bioaccumulation is very important in protecting human beings and other organisms from the adverse effects of chemical exposure, and it has become a critical consideration in the regulation of chemicals. The specific bioaccumulation process by which the concentration of a chemical in an organism becomes higher than its concentration in the air or water around the organism is called bioconcentration (Neff, 2002).

Biomagnification describes a process that results in the accumulation of a chemical in an organism at higher levels than are found in its food. It occurs when a chemical becomes more and more concentrated as it moves up through a food chain -- the dietary linkages between single-celled plants and increasingly larger animal species.

A typical food chain includes algae eaten by the water flea eaten by a minnow eaten by a trout and finally consumed by an osprey (or human being). If each step results in increased bioaccumulation, that is, biomagnification, then an animal at the top of the food chain, through its regular diet, may accumulate a much greater concentration of chemical than was present in organisms lower in the food chain (Ogbuagu *et al.,* 2019).

2.13.1 THE BIOACCUMULATION PROCESS

Bioaccumulation is a normal and essential process for the growth and nurturing of organisms. All animals, including humans, daily bioaccumulate many vital nutrients, such as vitamins A, D and K, trace minerals, and essential fats and amino acids. What concerns toxicologists is the bioaccumulation of substances to levels in the body that can cause harm (Ogbuagu *et al*., 2019). Because bioaccumulation is the net result of the interaction of uptake, storage and elimination of a chemical, these parts of the process was examined further.

Uptake: Bioaccumulation begins when a chemical passes from the environment into an organism's cells. Uptake is a complex process which is still not fully understood. Scientists have learned that chemicals tend to move, or diffuse, passively from a place of high concentration to one of low concentration. The force or pressure for diffusion is called the chemical potential, and it works to move a chemical from outside to inside an organism. Several factors may increase the chemical potential of certain substances. For example, some chemicals do not mix well with water. They are called lipophilic, meaning "fat loving," or hydrophobic, meaning "water hating." In either case, they tend to move out of water and enter the cells of an organism, where there are lipophilic microenvironments.

Storage: The same factors affecting the uptake of a chemical continue to operate inside an organism, hindering a chemical's return to the outer environment. Some chemicals are attracted to certain sites, and by binding to proteins or dissolving in fats, they are temporarily stored. If uptake is slowed or is not continued, or if the chemical is not very tightly bound in the cell, the body can eventually eliminate the chemical. One factor important in uptake and storage is water solubility; the ability of a chemical to dissolve in water. Usually, compounds that are highly water soluble have a low potential to bioaccumulate and do not leave water readily to enter the cells of an organism (Ogbuagu *et al*., 2019). Once inside, they are easily removed unless the cells have a specific mechanism for retaining them. Heavy metals like mercury and certain other water-soluble chemicals are such an exception because they bind tightly to specific sites within the body. When binding occurs, even highly water-soluble chemicals can accumulate. Many fat-loving (lipophilic) chemicals pass into organism's cells through the fatty layer of cell membranes more easily than water-soluble chemicals. Once inside the organism, these chemicals may move through numerous membranes until they are stored in fatty tissues and begin to accumulate.

Elimination: Another factor affecting bioaccumulation is whether an organism can break down and/or excrete a chemical. The biological breakdown of chemicals is termed metabolism. This ability varies among individual organisms and species and depends on characteristics of the chemical itself. Chemicals that dissolve readily in fat but not in water tend to be more slowly eliminated by the body and thus have a greater potential to accumulate. Many metabolic reactions change a chemical into more water-soluble forms called metabolites that are readily excreted (Abdallah, 2017).

2.13.2 BIOACCUMULATION: A STATE OF DYNAMIC EQUILIBRIUM

When a chemical enters the cells of an organism, it is distributed and then excreted, stored, or metabolized. Excretion, storage, and metabolism decrease the concentration of the chemical inside the organism, increasing the potential of the chemical in the outer environment to move into the organism (Neff, 2002). During constant environmental exposure to a chemical, the amount of a chemical accumulated inside the organism, and the amount leaving, reach a state of dynamic equilibrium. In an environmental chemical will at first move into an organism more rapidly than it is stored, degraded, and excreted. With constant exposure, its concentration inside the organism gradually increases. Eventually, the concentration of the chemical inside the organism will reach an equilibrium with the concentration of the chemical outside the organism, and the amount of chemical entering the organism was the same as the amount leaving (Neff, 2002). Although the amount inside the organism remains constant, the chemical continues to be taken up, stored, degraded, and excreted. If the environmental concentration of the chemical increases, the amount inside the organism will increase until it reaches a new equilibrium. Exposure to large amounts of a chemical for a long period of time, however, may overwhelm the equilibrium potentially causing harmful effects. Likewise, if the concentration in the environment decreases, the amount inside the organism will also decline (Duru & Akuugwo, 2019).

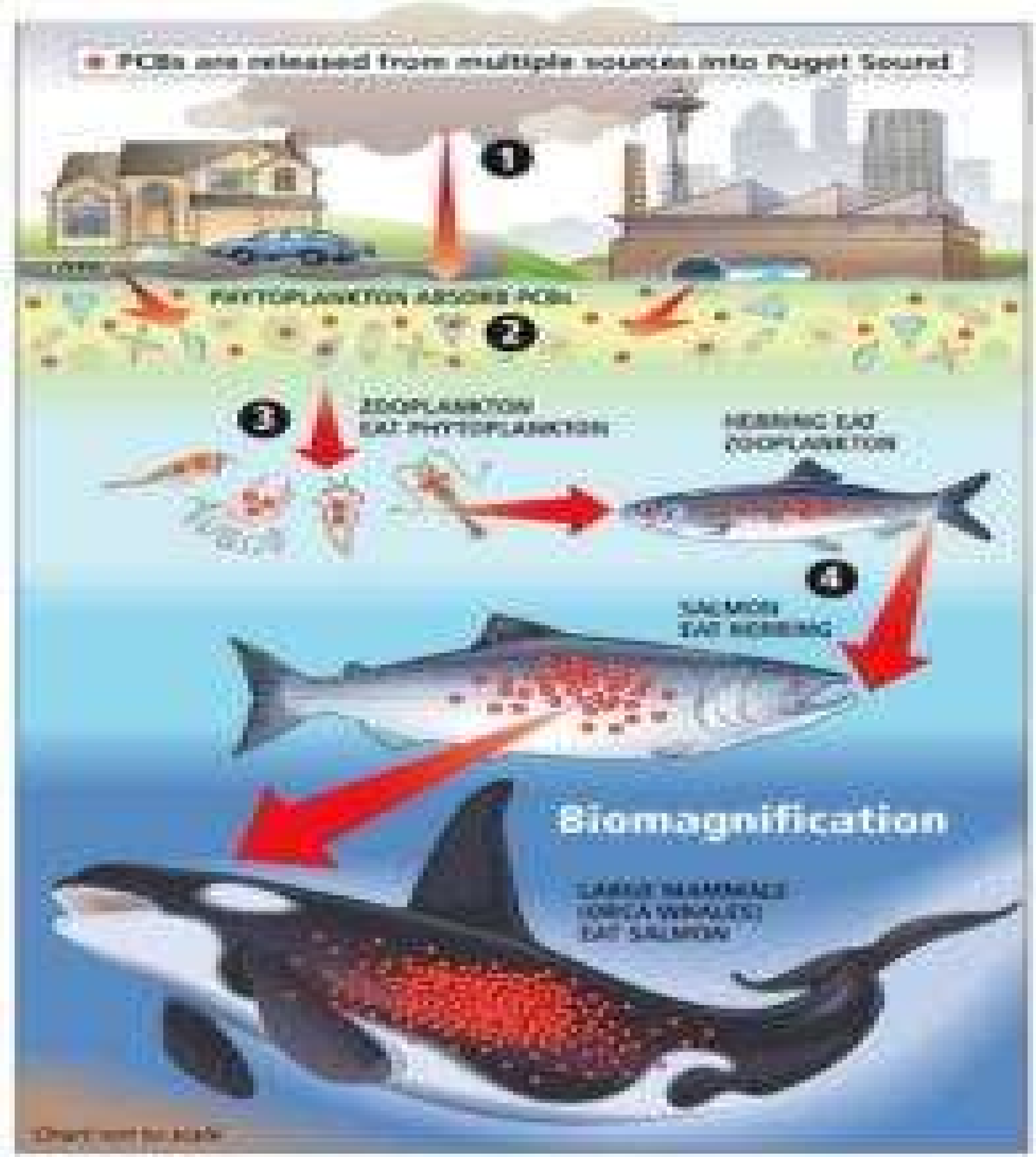

Fig.2.4: Biomagnification in Aquatic environment (Neff, 2002).

CHAPTER THREE

MATERIALS AND METHODS

3.1 STUDY AREA

The study area was carried out in Oguta lake Imo state Nigeria. It is a lean 'finger lake' formed by the damming of the lower Njaba River with alluvium (Neff, 2002). It is the largest natural lake in Imo State, Southeastern Nigeria; within the equatorial rainforest region of Niger Delta. Oguta Lake's catchment area comprises the drainage area of the Njaba River and a part of the River Niger floodplain in the region south of Onitsha (Neff, 2002). The lake is situated in Oguta about 50 kilometres (30 mi) from the junction of the Ndoni and Orashi River. It is about eight kilometres (5 mi) long from east to west and 2.5 kilometres (1+½ mi) wide. The stream from Njaba River is the major inflow to Oguta Lake (Neff, 2002). The other three tributaries are Awbana, Utu and Orashi. The Orashi River flows past Oguta Lake in its southwestern portion. The lake is important to the people of oil-rich Njaba-River basin including Oguta, Orsu, Mgbidi, Nkwesi, Osemotor, Nnebukwu, Mgbele, Awa Awo-Omamma Akabo as a source of water, fish, tourism, and an outlet for sewerage.

The river route Njaba and Orashi via Oguta Lake to the coast, passing through Awo-omamma, Mgbidi, Oguta, Ndoni, Abonnema, Degema made Oguta, Osemotor, Awo omamma and surrounding towns important commercial centres of international trade mainly for oil palm. Oguta Lake also served as a Biafran army marine base during the Nigerian Civil War (Neff, 2002).

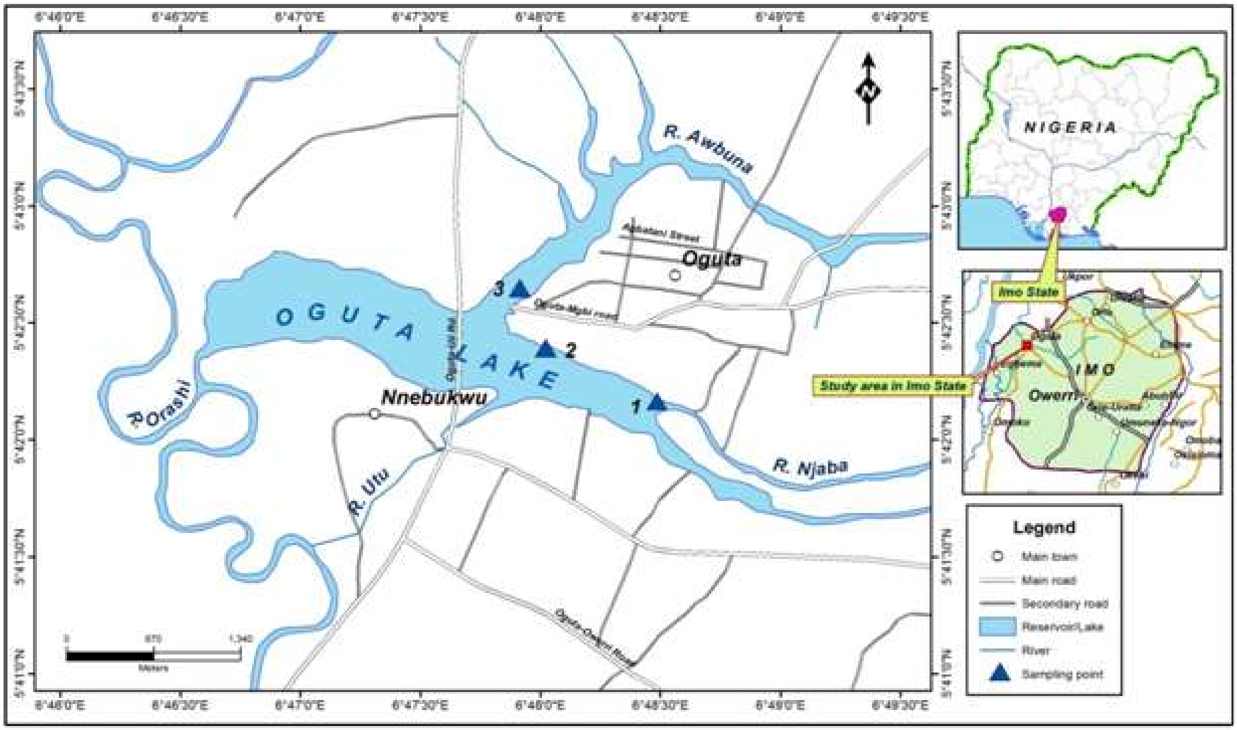

Figure 3.1: Map of Oguta Lake (Ogueri *et al*, 2018)

3.2 SAMPLE COLLECTION

3.2.1 SEDIMENT SAMPLES

The sediment samples were collected using the method described by Achionye-Nzeh & Isimaikaiye (2010). Surface sediment samples were collected at low tide by the grab method using Eckman grab. Samples from three (3) points at each location were collected. Grab bottom sediment samples were collected and kept in plastic containers that were previously treated with 10% nitric acid for 24 hours and rinsed with de-ionized water. The samples were transported to the laboratory and stored frozen. The samples were later oven-dried to a constant weight at 105°C, ground to powder, and then sieved through a 650μm stainless sieve to remove ungrounded matter. 10grams of the sieved sediments were weighed into an acid-washed plastic polythene bottle and digested in a 100ml solution of conc. HNO_3 and HCl acids (1:1 ratio). The mixture was vigorously shaken in a mechanical shaker and then filtered through No. 42 Whatman filter paper (Idodo-Umeh and

Oronsaye, 2006). Standard solutions of the metals were prepared from their 1000 ppm stock solutions for calibration.

3.2.2 FISH SAMPLES

Three (3) fish samples of spotted tilapia (*Tilapia mariae*), aged between 1.5 to 2 years and weighing between 250 to 300 grams, were collected for a period of 6 months with the services of local fishermen operating within the lake, using cast and gill nets. The samples were transported to the Laboratory and stored frozen. The frozen fishes were thawed and dried at 105 °C until they reach a constant weight. The dried samples were homogenized and digested with 10 ml tri-acid mixture (HNO_3: $HClO_4$:H_2SO_4), and then the digested samples were diluted to 100 ml with deionized water and kept for further analysis.

Plate 1: Sample of the spotted tilapia (*Tilapia mariae*) collected

3.2.3 WATER SAMPLES

Water samples were collected using high-density polyethylene (HDPE) bottles of 1 L each, prewashed using 10% v/v HNO_3, and rinsed several times with distilled water. During sampling, each prewashed sampling bottle was rinsed three to four times with stream water fetched at each corresponding site. Samples were collected at varying depths from 0 to 15 cm below the water surface by submerging uncapped sampling bottles upside down into the water stream. Immediately after the samples were collected, they were acidified to $pH < 2$ by two drops of HNO_3 and capped before being stored in an ice-cooled container. The sampling procedures, pretreatment, storage, and transportation protocols were followed as per standard guidelines (APHA 2017).

3.2.4 INSECT SAMPLES

Three one-minute kick samples were collected from approximately $3m^2$ of streambed to a depth of 5 cm, with a net (25 cm × 20 cm × 30 cm with 1 mm mesh) held vertically and the frame at right angles to the current. Samples were decanted into 1100 ml polypropylene bottles with just enough water to keep the sample damp to reduce damage and retard the activities of carnivores during transportation.

Insect species were preserved within five hours of collection using 95 percent ethanol and were sorted within a month, following the recommended standard procedure for RIVPACS (River Invertebrate Prediction and Classification System) (Environment Agency, 1997). The samples were first placed in large white trays to ease sorting since many water striders also inhabited those sample sites surveyed. Specimens were placed in petri dishes for identification to family level.

3.2.5 SNAIL SAMPLES

Snails were collected using a standard scoop net with a mesh size of 300 µm supported by a metal frame (Opisa et. al 2011). At each sampling site, all substrates were thoroughly searched to collect snails. Sampling time was fixed at 30 min per site. Sampling area per site was approximately 5 m^2. Afterwards, snails collected from each sampling site were transferred to plastic vials containing 80% ethanol to transport to the laboratory for identification. In the laboratory, each snail was identified to species level according to the shell morphology using the field guide to African freshwater snails (Mandahl-Barth G 1962) and only individuals identified to be *Lanistes lybicus* were counted to determine the number of each snail species collected per sampling site (Ede & Williams, 2008).

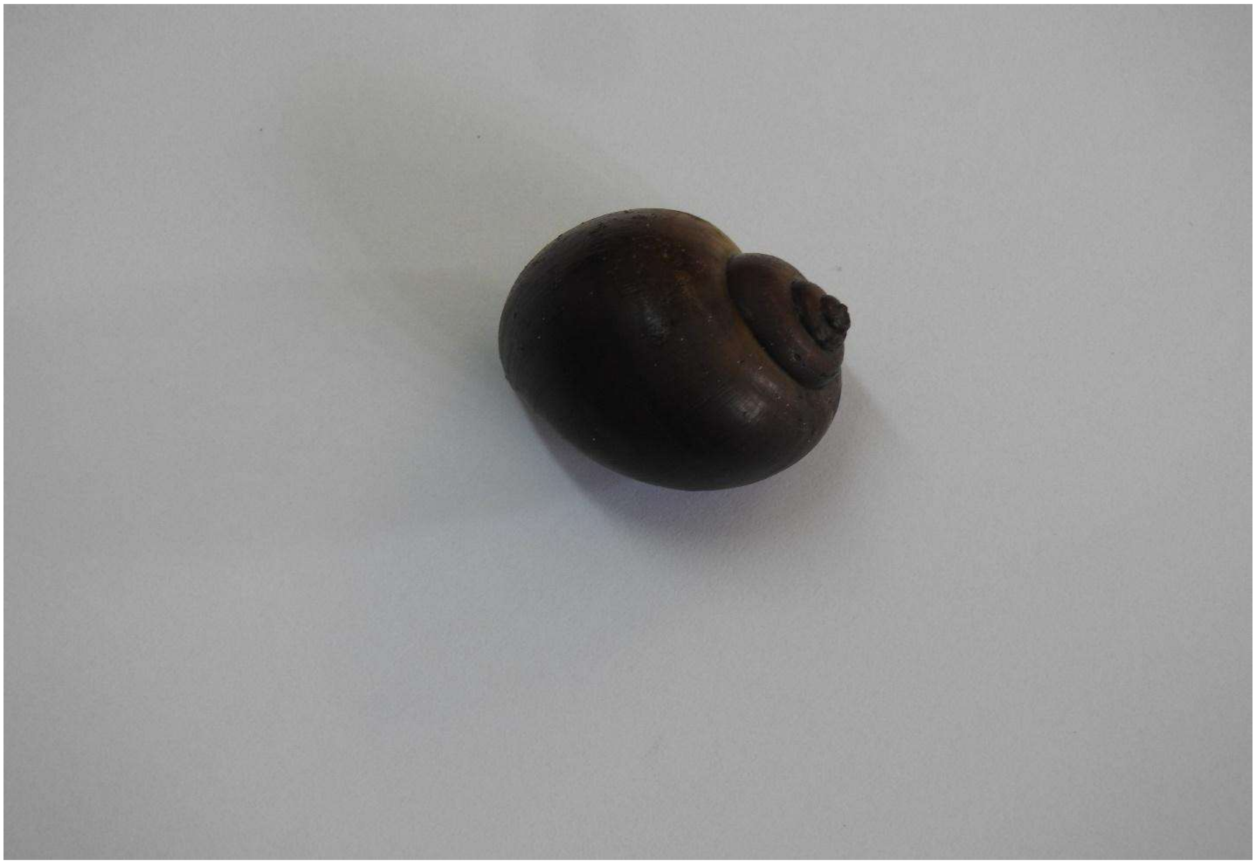

Plate 2: Sample of the Water snail (*Lanistes lybicus*) collected

3.3 SAMPLE ANALYSIS

3.3.1 PHYSICOCHEMICAL PARAMETER

Important physicochemical parameters like turbidity, pH, conductivity, Total Dissolved Solid, dissolved and temperature of the water sample was tested before and after treatment according to the drinking water guidelines. Turbidity was tested using turbidimeter, pH was tested using pH meter, conductivity using conductivity meter, Total dissolved solids (TDS) by using Digital Conductometer, Dissolved Oxygen was determined by titration using modified Winkler's method as given by (Adoni *et.al.*,1985) and temperature using basic thermometer. All these parameters were tested accordingly

3.3.2 HEAVY METALS

The concentrations of the heavy metals (Pb, Cd, As, Ni, Mn, Cu and Hg) in the study samples were determined using a Varian Atomic Absorption Spectrophotometer (Perkin Elmer Analyst AA 200 equipped with a high sensitivity nebulizer) as described by Ayeloja *et al*., (2014).

3.3.3 HEALTH RISK ASSOCIATED WITH THE CONSUMPTION OF THESE HEAVY METALS

This was carried out using a standard mathematical model as described by USEPAIRIS, (2011); Wongsasuluk *et al*., (2014); Lim *et al*., (2008). The average daily dose (ADD) of heavy metals and hazard quotient (HQ) was calculated using the formula below

$$\mathrm{ADD} = \frac{\mathrm{Ci} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}$$

$$\text{Hazard Quotients (HQ)} = \frac{\mathrm{ADD}}{\mathrm{RfD}}$$

Where –

- **Ci** is metal concentration in the vegetable,
- **IR** is ingestion rate,
- **EF** is exposure frequency,
- **ED** is exposure duration,
- **BW** is body weight of consumer and

- **AT** is average time.

3.4 STATISTICAL ANALYSIS

The data generated from the study was analyzed using tables, charts, and one-way analysis of variance.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 PHYSICOCHEMICAL PARAMETERS OF WATER SAMPLES COLLECTED FROM OGUTA LAKE

The physicochemical properties of water samples collected from Oguta Lake is shown in Table 4.1. Results obtained from sample analysis revealed Temperature range of between 26.04-29.35 which falls within WHO (2019) standard for drinking water. The mean pH value of the Lake was 7.32±1.77. The values indicated neutral level with which ranged from 7.17-7.77 across the sampling points. pH values were observed to be below 7.00 - 8.50 benchmark stipulated by the WHO. Mean values of Free CO_2 (ppm) were observed to be 10.11±1.02 which ranged between 9.78-10.34. The result obtained from the study indicated biochemical oxygen demand (BOD) values ranging from 10.14-10.42 mg/L which was below WHO set values of <10.00. The value of total dissolved solids ranged between 14.0 – 28. 22.23-28.04 mg/L with an overall mean of 250.00 Mg/L. Electrical conductivity varied from 0.30-0.49 µs/cm with a mean value of 0.46±0.14. Dissolved oxygen content of the study areas/locations ranged from 5.69-5.86 mg/L with an overall mean value of 5.91±0.48. However, values obtained for DO was below > 5.00 benchmark by the WHO permissible limit. The measured values of total hardness in the river water samples ranged from 18.49-21.00 with a mean value of 19.46±2.20. The concentrations of TD in the Lake were observed to be within 150.00 stipulated by the WHO. Concentration of Turbidity, Alkalinity (Mg/L), Sulphate (Mg/L), and Ammonium (Mg/L) (NTU) ranged between 15.03-17.76; 15.64-16.66; 2.19-2.55 and 0.26-0.40 NTU respectively.

Table 4.1: Physicochemical parameters of water samples collected from Oguta Lake

Parameters	WHO LIMIT	Oguta Lake	Range
Temperature (ºC)	30.00 - 32.00	26.16±2.89	26.04-29.35
pH	7.00 - 8.50	7.32±1.77	7.17-7.77
Free CO_2 (ppm)	<10.00	10.11±1.02	9.78-10.34
BOD (Mg/L)	< 10.00	10.29±1.27	10.14-10.42
TDS (Mg/L)	250.00	25.43±2.41	22.23-28.04
EC (µs/CM)	100.00	0.46±0.14	0.30-0.49
DO (Mg/L)	> 5.00	5.91±0.48	5.69-5.86
Total Hardness (ppm)	150.00	19.46±2.20	18.49-21.00
Turbidity (NTU)	150.00	17.16±2.12	15.03-17.76
Alkalinity (Mg/L)	200.00	16.35±1.2	15.64-16.66
Sulphate (Mg/L)	250.00	2.25± 0.29	2.19-2.55
Ammonium (Mg/L)	-	0.37 ± 0.18	0.26-0.40

4.1.2: HEAVY METAL CONCENTRATIONS IN WATER AND SEDIMENT SAMPLES COLLECTED FROM OGUTA LAKE

The mean concentration of heavy metals from water and sediment samples in Oguta Lake is depicted in Table 4.2. Results obtained revealed variation in heavy contents in both water and sediment samples. Mean concentrations of Pb, Cd, As, Ni, Mn, and Cu in water ranged between; 0.18-0.20; 0.38 - 0.44; 0.01 -0.02; 0.53 -0.68; 0.01-0.03; and 2.18 - 2.37 respectively. The level of Pb, Cd, As, Ni, Mn, and Cu in sediment were ranged as follows: 0.22-0.27; 1.01-1.16; 1.00-1.05; 1.18-1.29; 1.44- 2.88; and 1.53 - 2.04. No values of Hg were detected in both water and sediment samples.

Table 4.2: Heavy metal concentrations in water and sediment samples collected from Oguta Lake

Parameters	Oguta Lake	Range
Pbw (Mg/l)	0.19±0.05	0.18-0.20
Cdw (Mg/l)	0.41±0.07	0.38 - 0.44
Asw (Mg/l)	0.01±0.001	0.01 -0.02
Hgw (Mg/l)	ND	-
Niw (Mg/l)	0.59 ±0.1	0.53 -0.68
Mnw (Mg/l)	0.02±0.006	0.01-0.03
Cuw (Mg/l)	2.24 ± 0.31	2.18 - 2.37
Pbs (Mg/g)	0.26±0.04	0.22-0.27
Cds (Mg/g)	1.04±0.15	1.01-1.16
Ass (Mg/g)	1.02±0.16	1.00-1.05
Hgs (Mg/g)	ND	-
Nis (Mg/g)	1.22± 0.24	1.18-1.29
Mns (Mg/g)	1.98±1.68	1.44- 2.88
Cus (Mg/g)	1.87 ± 0.58	1.53 - 2.04

4.1.3: CORRELATION OF HEAVY METALS IN WATER AND SEDIMENT SAMPLES IN OGUTA LAKE

The interrelationship between heavy metals in water and sediment samples from Lake Oguta, were analyzed using Pearson's correction matrix to see if some of the heavy metals are interrelated with each other and the results are presented in Tables 4.11. Results obtained showed a strong positive correlation was observed at $P < 0.05$ for metals in water and sediment samples meaning that there was a strong association between these pairs, and common sources for the pairs of polluting substances. Positive correlations were observed for the following pairs of metals in water and sediments: Pb_w and Ni_s ($r = 0.356$), Cd and Ni ($r = 0.237$), Cu_w and Mn_s ($r = 0.325$), Cd_w and Pb_s ($r = 0.969$*), As_w and As_s ($r = 0.967$) at $p< 0.05$.

Table 4.5: Correlation of heavy metals in water and sediment samples in Oguta lake

	Pb_w	Cd_w	As_w	Hg_w	Ni_w	Mn_w	Cu_w	Pb_s	Cd_s	As_s	Hg_s	Ni_s	Mn_s	Cu_s
Pb_w	1													
Cd_w	0.034	1												
As_w	0.012	0.043	1											
Hg_w	0.009	0.012	0.017	1										
Ni_w	0.356	0.237	0.110	0.365	1									
Mn_w	0.144	0.124	0.116	0.178	0.264	1								
Cu_w	0.121	0.135	0.152	0.175	0.248	0.325	1							
Pb_s	0.969*	0.453	0.179	0.321	0.035	0.243	0.547	1						
Cd_s	0.078	0.917*	0.433	0.412	0.446	0.077	0.784	0.033	1					
As_s	0.022	0.039	0.967*	0.078	0.276	0.218	0.163	0.023	0.322	1				
Hg_s	0.009	0.014	0.012	0.000	0.023	0.015	0.017	0.009	0.005	0.010	1			
Ni_s	0.142	0.173	0.278	0.104	0.978*	0.287	0.423	0.034	0.066	0.076	0.013	1		
Mn_s	0.136	0.152	0.367	0.289	0.255	0.965*	0.752	0.061	0.034	0.092	0.021	0.078	1	
Cu_s	0.134	0.140	0.342	0.163	0.367	0.431	0.958*	0.032	0.078	0.022	0.011	0.034	0.025	1

* = Significant at $P < 0.05$ level

Legend

Where: Pb_w = lead in water, Cd_w = Cadmium in water, As_w = Arsenic in water, Hg_w = Mercury in water, Ni_w = Nickel in water, Mn_w = Manganese in water, and Cu_w = copper in water.

Pb_s = lead in sediment, Cd_s = cadmium in sediment, As_s = Arsenic in sediment, Hg_s = Mercury in sediment, Ni_s = Nickel in sediment, Mn_s = Manganese in sediment, and Cu_s = copper in sediment.

4.1.4: ACCUMULATION OF HEAVY METAL INTAKE IN FISH, INSECT, SNAIL AND ALGAE COLLECTED FROM OGUTA LAKE

Concentrations of Pb, Cd, As, Ni, Hg, Mn, and Cu in fish, insect, snail, and Algae along with the WHO Benchmark is shown in Table 4.3. Results obtained showed that highest value of Pb was gotten from fish samples (1.45±0.23ug/g) while the least value of Pb was obtained from Algae (0.17±0.02ug/g). However, these values were well below 2.0 permissible limits by the WHO. Concentration of Cd was observed to be higher in fish samples (0.54± 0.07ug/g) with a range of between 0.38-0.69 while the least value of Cd was obtained from Algae (0.04±0.01), similar trend was observed for Arsenic with the highest concentration in fish (1.41±0.13) and least value for Algae (0.17 ± 0.04). No values of Hg were recorded from the Lake. Concentrations of Ni, Mn and Cu were higher in fish samples with mean values of 0.39± 0.06; 0.83 ± 0.17 and 2.87 ± 0.41 while the least values were gotten from Algae 0.1±0.01; 0.09 ± 0.01 and 1.37 ± 0.22 respectively. Values obtained for each of the metals assayed were below WHO permissible limits.

Table 4.3: Accumulation of heavy metal intake in fish, insect, snail, and algae collected from Oguta lake

Heavy metals (µg/g)	**Sample Organisms**	WHO Permissible Limit	**Values obtained(µg/g)**	**Range (µg/g)**
Pb	Fish	2.0	1.45±0.23	1.34 - 1.69
	Insect		0.21±0.03	0.17-0.43
	Snail		1.33 ±0.12	1.24-1.45
	Algae		0.17±0.02	0.13-0.28
Cd	Fish	1.0	0.54± 0.07	0.38-0.69
	Insect		0.07 ±0.02	0.05-0.11
	Snail		0.23±0.09	0.18-0.28
	Algae		0.04±0.01	0.03-0.07
As	Fish	2.0	1.41±0.13	1.33-1.62
	Insect		0.34±0.08	0.24-0.47
	Snail		1.07 ± 0.10	1.01 - 1.12
	Algae		0.17 ± 0.04	0.03 - 0.07
Hg	Fish	0.3	ND	0.00
	Insect		ND	0.00
	Snail		ND	0.00
	Algae		ND	0.00
Ni	Fish	0.5	0.39± 0.06	0.33 - 0.61
	Insect		0.14 ± 0.02	0.11 - 0.23
	Snail		0.24 ± 0.04	0.18 - 0.37
	Algae		0.1 ±0.01	0.09 - 1.01
Mn	Fish	1.0	0.83 ± 0.17	0.62 - 0.91
	Insect		0.19 ± 0.03	0.12 - 0.26
	Snail		0.34 ± 0.05	0.27 - 0.42
	Algae		0.09 ± 0.01	0.06 - 0.14
Cu	Fish	3.0	2.87 ± 0.41	2.53 - 2.99
	Insect		1.67 ± 0.28	1.34 - 1.77
	Snail		2.03 ± 0.39	1.98 - 2.19
	Algae		1.37 ± 0.22	1.28 - 1.54

ND = not detected

4.1.5: ESTIMATION OF HEAVY METAL DAILY INTAKE AND TARGET CANCER RISK IN OGUTA LAKE

The estimated heavy metal daily intake (EDI), Target hazard quotient, Hazardous index (HI), Target cancer risk and Reference dose (RfDs) of heavy metals through the ingestion of fishes, Insects, Snails, and Algae in Oguta Lake is shown in Table 4.4. The results of these parameters that were above accepted limit (reference dose) are indicated in bold fonts. Among the heavy metals assayed, none was observed to be higher than the recommended reference dose across the sampling points.

Table 4.4: Estimation of heavy metal daily intake and target cancer risk in Oguta lake

Heavy metals	Species	EDI	THQ	HI	CR	RfDs
Pb	Fish	0.005	0.005	0.075	5.456E - 04	0.002
	Insect	0.002	0.002	0.017	2.272E - 02	
	Snail	0.003	0.003	0.034	3.745E - 03	
	Algae	0.001	0.001	0.012	1.472E - 02	
Cd	Fish	0.001	0.002	0.036	3.218E - 02	0.001
	Insect	0.0003	0.001	0.013	1.117E - 01	

	Snail	0.001	0.001	0.025	2.551E - 02	
	Algae	0.0002	0.001	0.010	1.221E - 01	
As	Fish	0.0004	0.0004	0.027	1.236E - 02	0.0003
	Insect	0.0002	0.0001	0.008	1.101E - 01	
	Snail	0.0003	0.0002	0.016	1.132E - 01	
	Algae	0.0001	0.0001	0.004	1.002E - 01	
Hg	Fish	0.000	0.0000	0.000	0.000E- 00	0.0003
	Insect	0.000	0.0000	0.000	0.000E- 00	
	Snail	0.000	0.0000	0.000	0.000E- 00	
	Algae	0.000	0.0000	0.000	0.000E- 00	
Ni	Fish	0.05	0.02	0.073	5.721E - 04	0.02
	Insect	0.01	0.01	0.024	2.348E -02	
	Snail	0.03	0.02	0.049	3.906E - 03	
	Algae	0.01	0.01	0.015	1.489E - 02	
Mn	Fish	0.12	0.13	0.067	2.432E - 03	0.14
	Insect	0.08	0.07	0.020	1.222E -01	
	Snail	0.10	0.10	0.036	2.111E - 02	
	Algae	0.06	0.04	0.013	1.023E -01	
Cu	Fish	0.3	0.30	0.073	3.873E - 03	0.3
	Insect	0.1	0.04	0.029	1.231E - 01	
	Snail	0.2	0.14	0.058	2.099E - 02	
	Algae	0.1	0.02	0.019	1.142E -01	

EDI = Estimated daily intake, THQ = Target hazard quotient, HI = Hazardous index, CR = Carcinogenic risk, RfDs = Reference dose. HI value<1 and CR < 10^{-6}= a non-significant effect. HI value > 1 and CR > 10^{-4}= significant effect.

4.1.6: BIOACCUMULATION FACTOR (BAF) OF FISH, INSECT, SNAIL, AND ALGAE FROM OGUTA LAKE

Bioaccumulation factor (BAF) values of toxic metals in fish, insect, snail, and algae from Oguta lake is presented in Figure 4.1. Bioaccumulation factor values were highest in the fish (2654.65) and Snail (1895.34) indicating that these species have the potentials to bioaccumulate metals in their body tissues compared to Insect (1267.48) and Algae (1085.37) respectively.

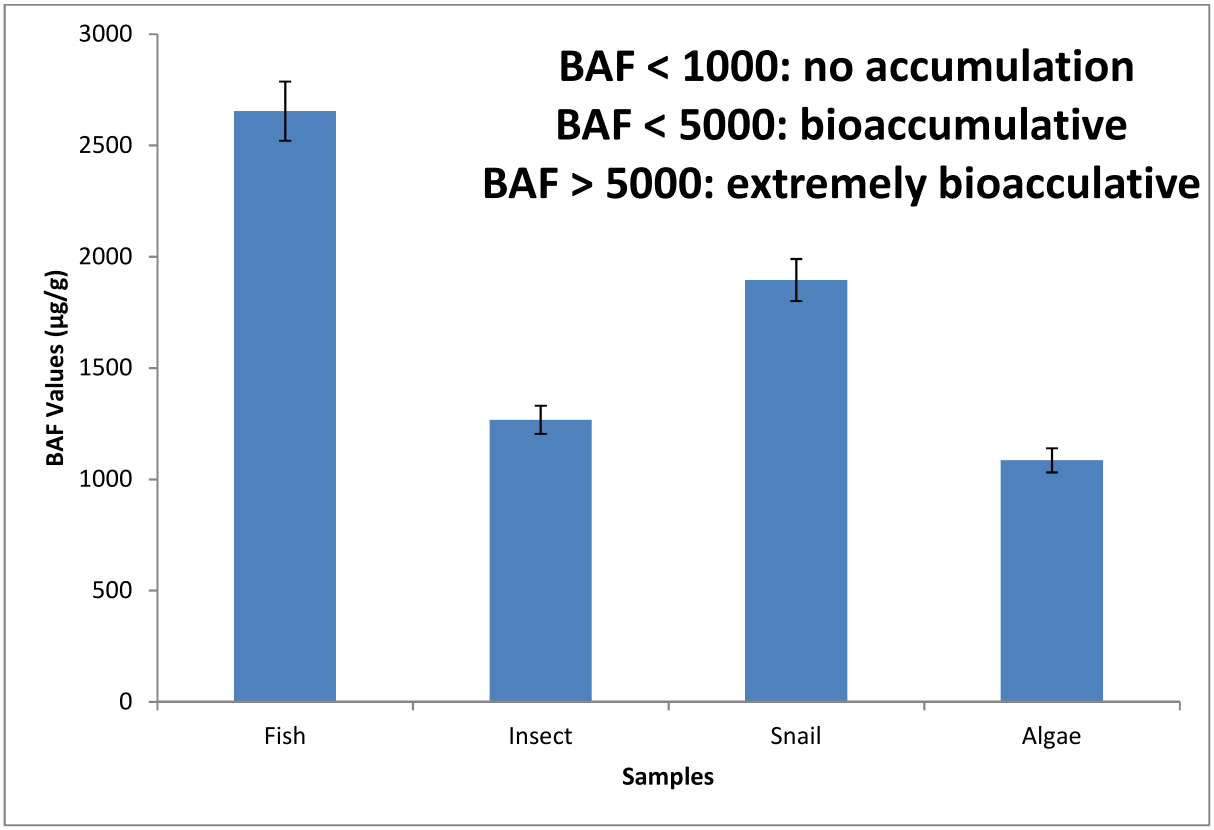

Figure 4.1: Bioaccumulation factor (BAF) of fish, insect, snail, and algae from Oguta lake

4.1.7: MONTHLY CONCENTRATION OF HEAVY METALS IN FISH, INSECT, SNAIL AND ALGAE FROM OGUTA LAKE

Figures 4.2 – 4.7 illustrate the monthly variations of each heavy metal (Pb, Cd, As, Ni, Mn, and Cu) observed for fish, insect, snail, and algae from Oguta lake in this study. The highest of Pb (0.417 mg/kg) was recorded in Fish during the dry season (February) while the minimum value of 0.01 mg/kg was recorded in Algae during the wet season (July). Cd, As, Ni, Mn and Cu seasonal accumulation was higher in fish samples compared to insect, snail, and algae respectively.

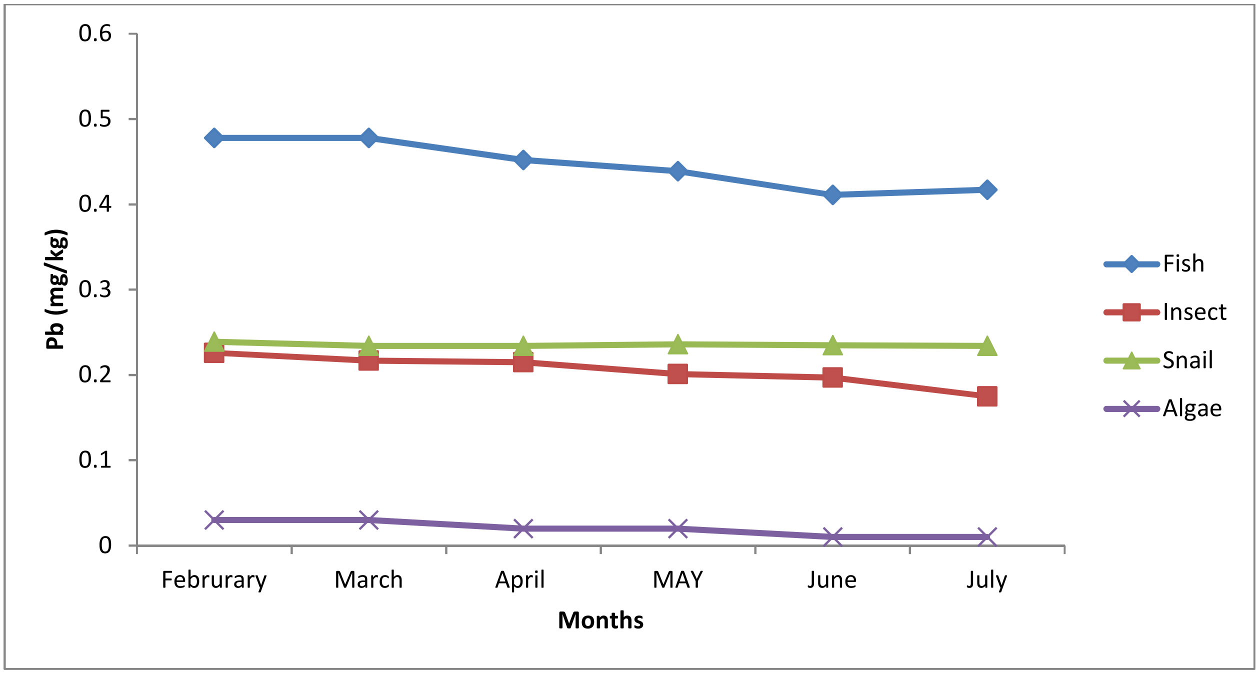

Figure 4.2: Monthly concentration of Pb in fish, insect, snail, and algae from Oguta lake

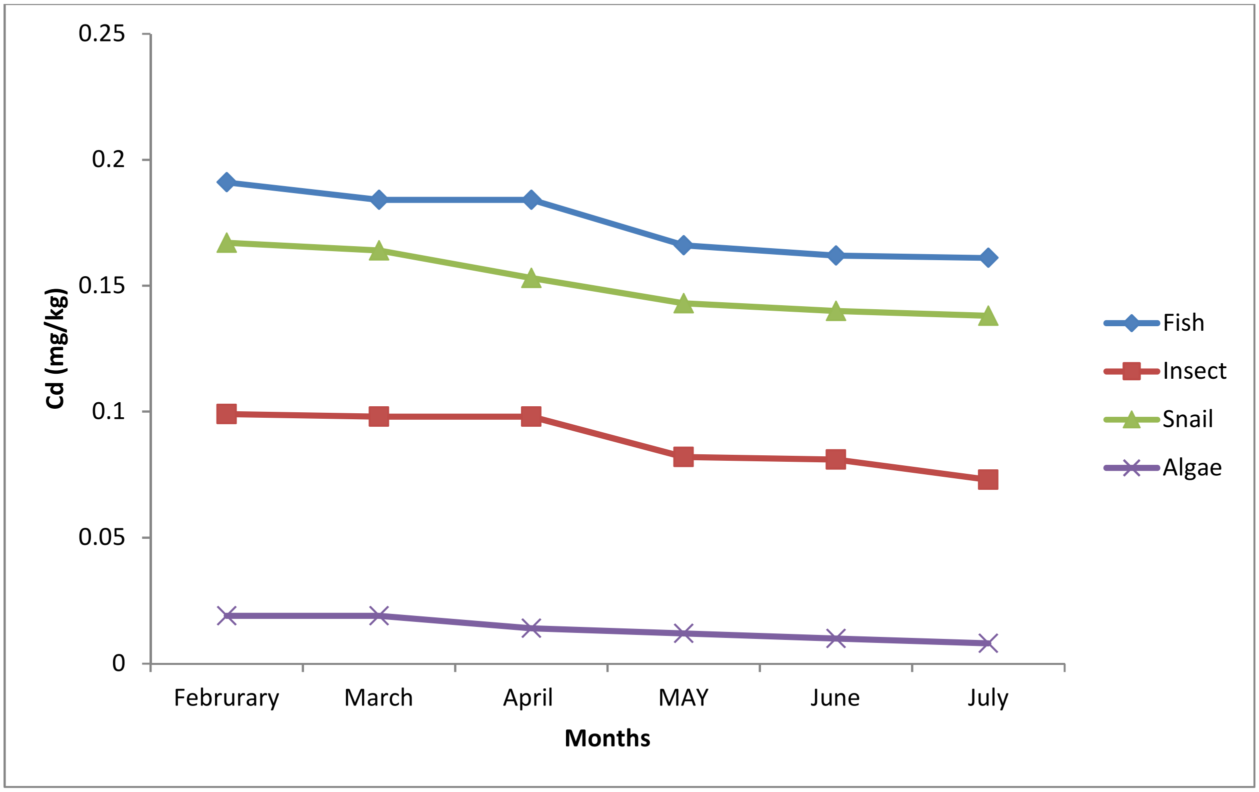

Figure 4.3: Monthly concentration of Cd in fish, insect, snail, and algae from Oguta lake

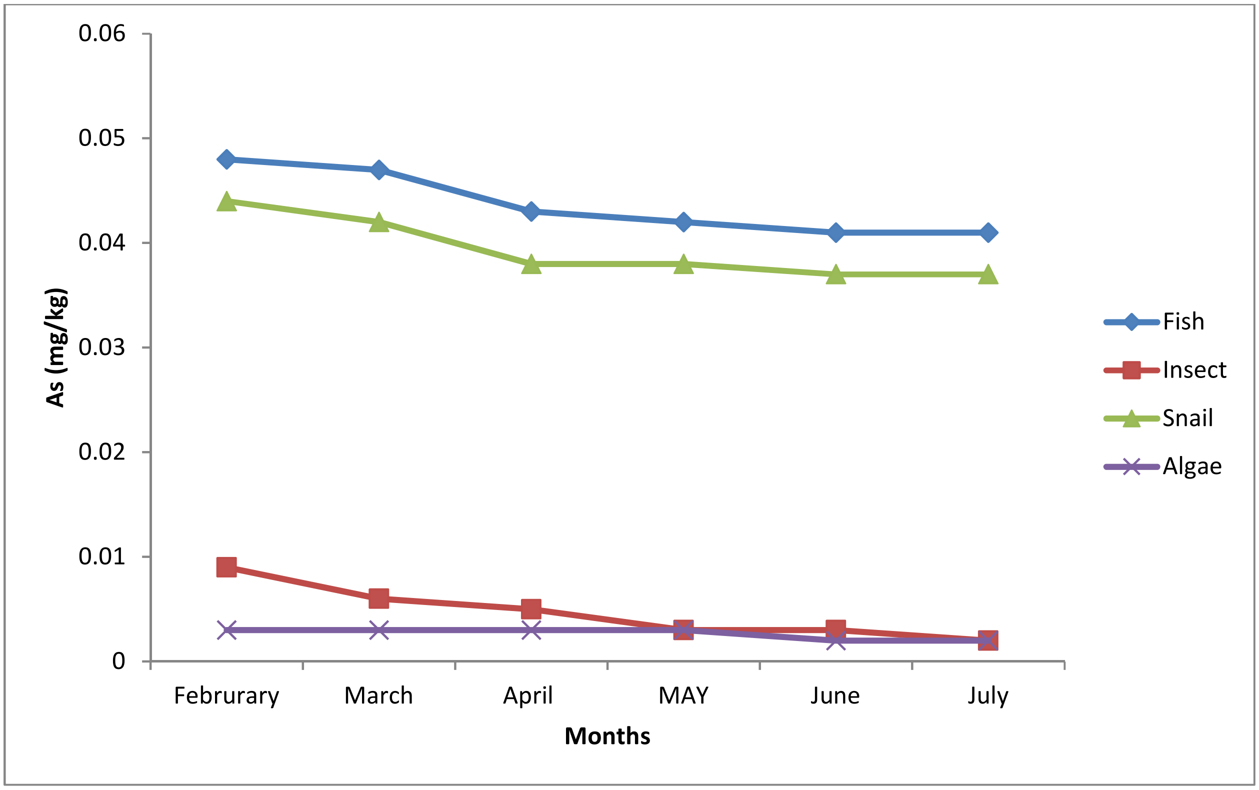

Figure 4.4: Monthly concentration of As in fish, insect, snail, and algae from Oguta lake

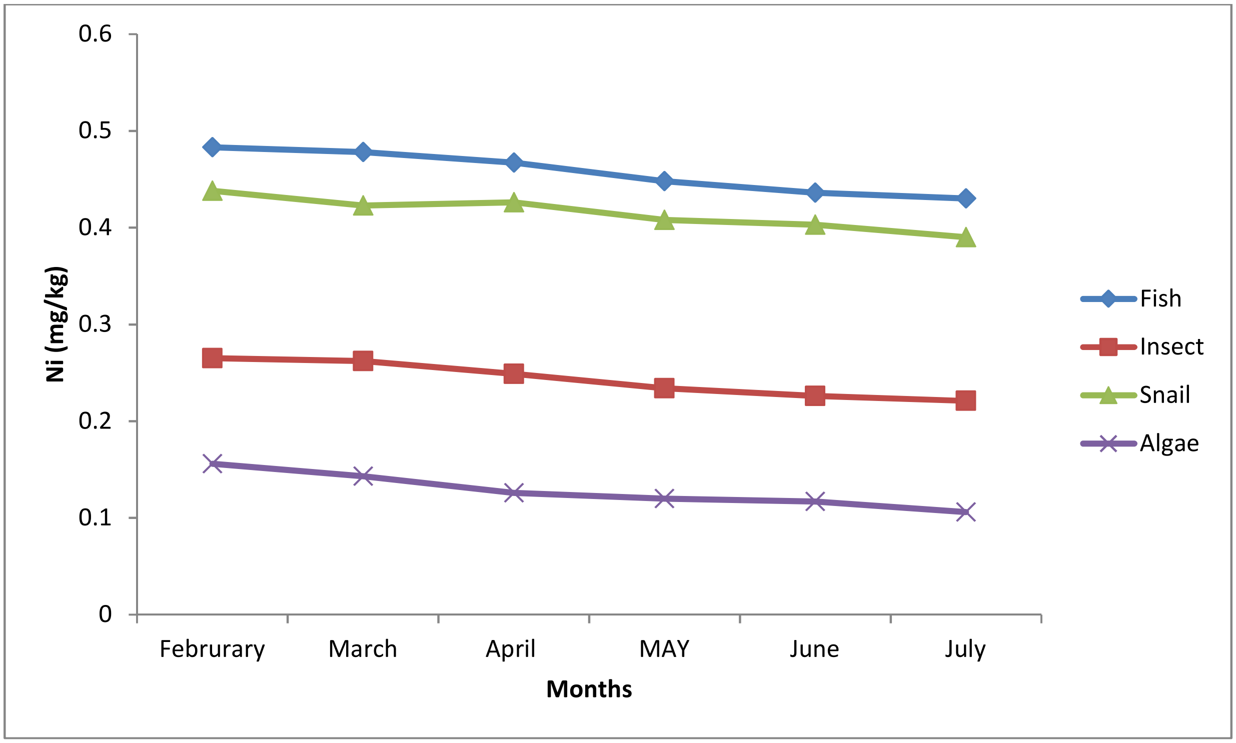

Figure 4.5: Monthly concentration of Ni in fish, insect, snail, and algae from Oguta lake

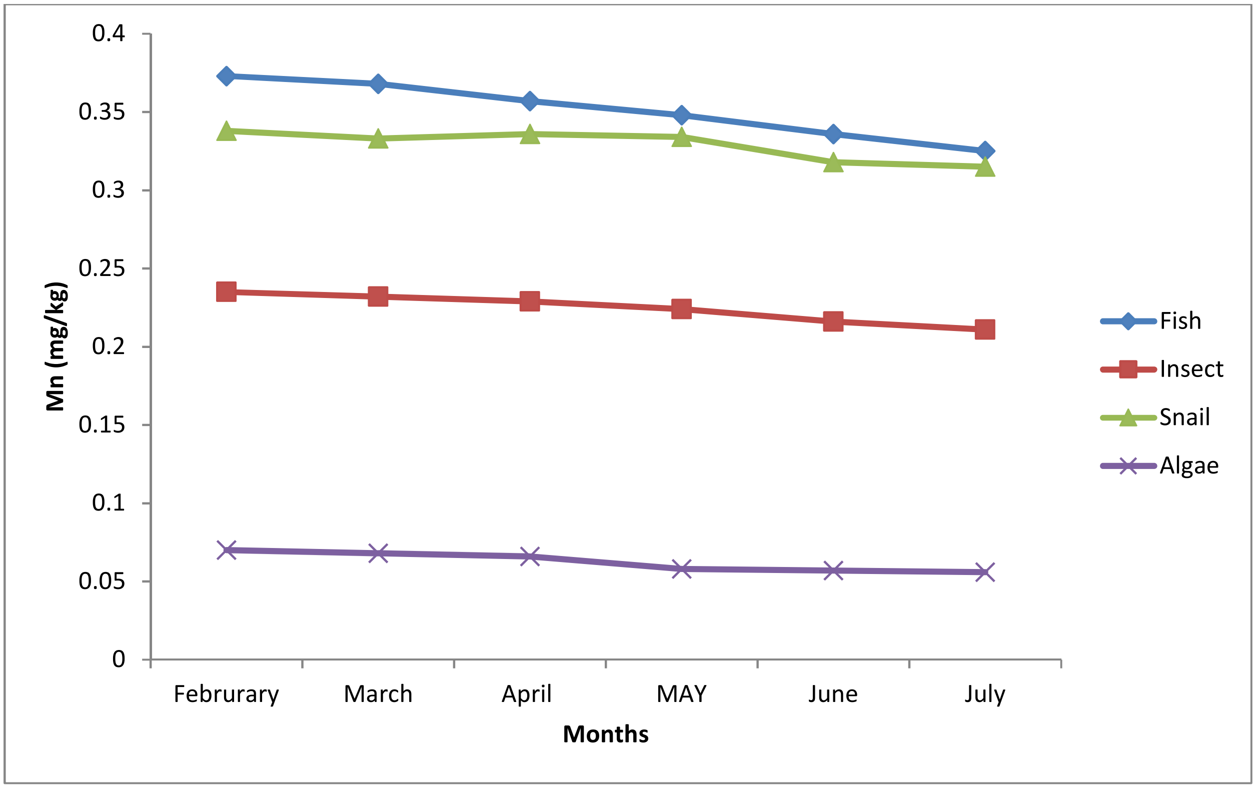

Figure 4.6: Monthly concentration of Mn in fish, insect, snail, and algae from Oguta lake

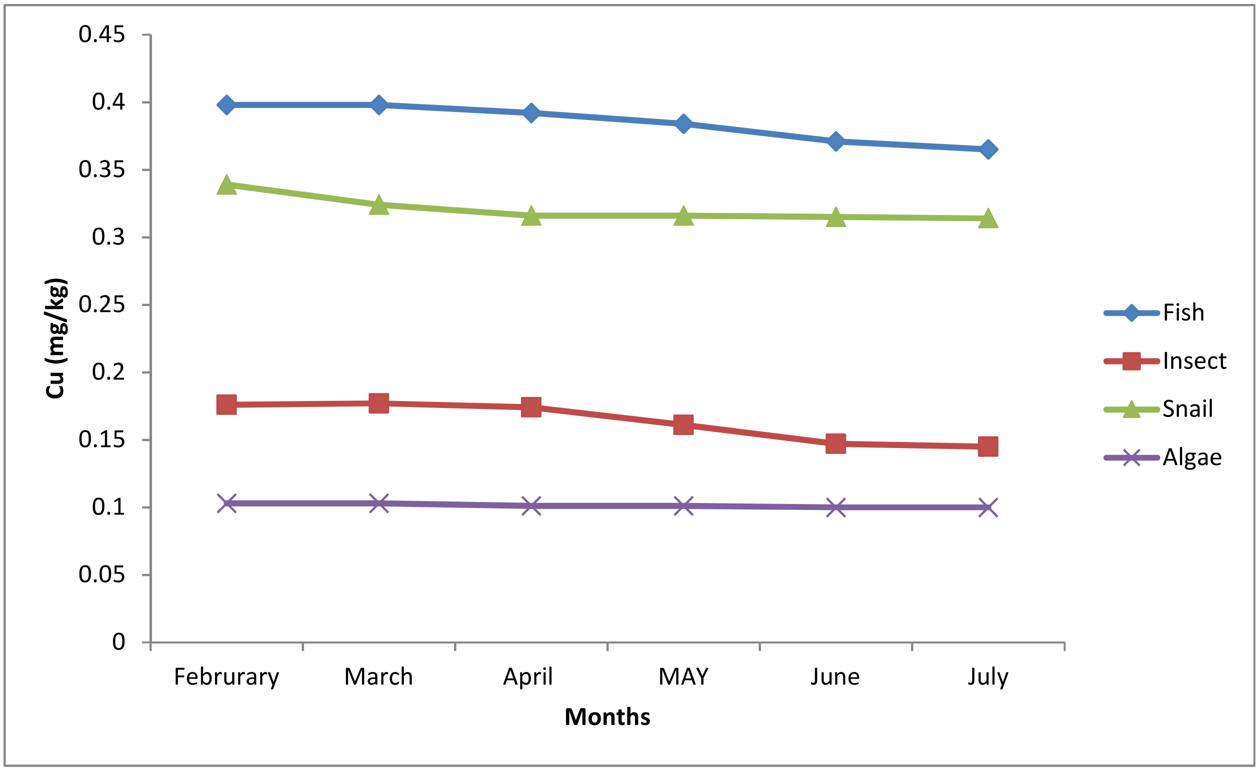

Figure 4.7: Monthly concentration of Cu in fish, insect, snail, and algae from Oguta lake

4.2 DISCUSSION

The results of this study showed the mean physicochemical parameters of water samples collected from Oguta Lake. The temperature range (26.04-29.35ºC) of Oguta Lake falls within WHO (2016) standard for drinking water. The temperature values obtained in this study compare favorably with those reported by earlier workers in Imo River water. These earlier works include Duru & Akubugwo (2019), (25.10 –26.11ºC), Duru, Adindu, Odike, Amadi, & Okezi (2021), (26 – 30oC), Adebisi (2020) (25.10 – 27.8ºC), and Aleleye Wokoma (2018) (26 – 30ºC). There was no significant difference in the temperature of all sampling stations, and this is also similar to the report of Ezeonye (2009) who attributed minimal variation in temperature between stations to the absence of micro climatic variations in temperature.

The mean pH value of the Lake was slightly neutral. This variation might be due to high level of pollution. The overall pH range of 7.17-7.77 was almost within the range for inland water (pH 6.5 – 8.5) as reported by Antoine & Al-Saadi (2020). Boyd and Lickkoppler (2000) reported pH range of 6.09 – 8.45 as being ideal for supporting aquatic life including fish. The pH range obtained in this study is within the acceptable level of 7.00 - 8.50 by the WHO.

The result obtained from the study indicated biochemical oxygen demand (BOD) values ranging from 10.14-10.42. The general high BOD values observed during in this study may be due to increased urban runoff which carried wastes from streets and sidewalks, nutrients from loan fertilizers, laces, games, chippings and paper from residential areas into the river. The results from this study agreed with the finding of Olawale (2021). Akubugwo *et al*., (2018) in his finding in assessment of water quality of Njaba River obtained BOD values 2.4 – 8.3 which disagrees with this study values but agrees with the results of Ijeh (2020).

Total dissolved solids test provides a quantitative measure of the number of dissolved ions. It is used as indicator test to determine the general quality of water Abowei (2021). The values of total dissolved solids were within the range of values reported by Olawale (2021), Duru & Nwanekwu (2019). Conductance qualitatively reflects the status of inorganic pollution and is a measure of total dissolved solid and ionized species in the water. Electrical conductivity varied from 0.30-0.49 µs/cm. The lower electrical conductivity recorded in this study might be due to water dilution. Ovie & Adeniji (2019) as well as Kolo & Oladineji (2020) observed a similar trend for Shiroro lake. Wide variations were observed in the sampling points. The wide variations suggest that considerable amount of dissolved ionic substances enter the river due to indiscriminate dumping of waste in the Lake. Conductivity value of 148 was observed by Ebigwai, Imemdimfen, Bright, Olowu, & Ekanem (2021) in Kwa River, Calabar which is higher than the values obtained in this study.

Dissolved oxygen content of the study area ranged from 5.69-5.86 mg/L. It agreed with the values obtained by Olawale (2021) in the study of physiochemical analysis of water from Asa river that ranged from 4.80 – 9.30. Domestic, agricultural, industrial effluent and waste discharge into rivers is a usual practice in Imo state and their environs and is the main reason for the pollution of the river. The findings agreed with the report of Okeke & Adinna (2018) where the dissolved oxygen of dry season fell within the range of 3.4 – 5.1. These findings agreed with the findings of Duru & Nwanekwu (2019) with DO values of 4.60 – 5.60. DO is one of the most important parameters in agriculture. It is needed by fish to respire and perform metabolic activities. These low levels of dissolved oxygen are often linked to fish kill incidents.

Total hardness is due to presence of bicarbonate, sulphate, chlorides and nitrates of calcium and magnesium. Hard water requires more soap and synthetic detergents for laundry and washing and contributes to scaling in boilers and industrial equipment (Ajayi & Osibunji, 2022). The result of hardness indicated low hardness values may probably be due to high dilution during wet season (18.49-21.00). Duru *et al.,* (2020) in the study of physio-chemical status of Nworie River found out that the total hardness in the water ranged from 10.6mg/L to 50.87. The results of this study agreed with the finding of Olawale (2019) in their study of Asa River water.

Turbidity is an important operation parameter in process control and can indicate problems with treatment processes, particularly coagulation, sedimentation, and filtration. It causes undesired taste and odours which affects the process of photosynthesis for algal growth. In this study, turbidity values of 15.03-17.76 (NTU) were recorded indicating that biological process had little effect on the material in the water column. The variation observed could be attributed to the release of suspended particles because of sand mining activities in the area and this is in line with the report of Nkwoji *et al* (2018) and the work of Ezekwe *et al.,* (2020) who recorded turbidity of 14.6 in pond water at Imo River Basin area sampled.

The total alkalinity ranged from 15.64-16.66 mg/L with mean value of 16.35±1.2. Since alkalinity is pH dependent and a reversal of acidity, the higher value recorded in this study is expected. The alkalinity agreed with the range value of 16.25 – 16.66 with overall mean of 15.9.10 as documented by Olawale (2016). The mean value of sulphate was 2.25± 0.29. The sulphate values for the sampling points and location ranged from 2.19-2.55. Significant amount of sulphate is introduced into the river as a result of industrial, agricultural and domestic activities. Concentration of Ammonium obtained in this study agrees with the report of Nwadinigwe, Udo, & Nwadinigwe, (2019).

Concentration of Heavy Metals (Pb, Cu, Cd, As, Hg, Ni, and Mn) in Water and sediment samples from the study area also varied. Results revealed a gradual build-up of heavy metals in the study points. Generally, higher levels of heavy metals were detected in water samples than sediment samples. Similar trend in heavy metal levels had been reported (Antoine, & Al-Saadi, 2020).

Findings in this study showed that there were variations in ability of Fish, Insect, Snail and Algae species to bioaccumulate heavy metals. Fish can take up heavy metals in their diets and bioaccumulate them at different rates in their organs. The concentrations of the metals in the species were in the order of fish > Algae > Snail > Insects. The result indicated higher bioaccumulation in the fishes across the sampling points. Similar observation had been documented by Bakan & Ozkoc, (2020).

The estimated daily intake of heavy metals from the mean concentration values of heavy metals via ingestion of Fish, Insect, Snail and Algae were used to determine the hazard quotient, cancer risk, total hazard index and cancer risk index. The hazard quotient of the heavy metals in fish samples showed no risks to the ecosystem of the water in the study areas with reference dose not exceeding permissible limit of each of the metals. Though other heavy metals (Pb, Cd, As, Hg, and Ni) showed concentration values that were below set limit and therefore showed hazard quotient that were below reference dose, its concentration values in Fish, Insect, Snail and Algae are a major source of concern. The consumption of these metals in excess could impact health hazards to the aquatic ecosystem and to human. Results of this study agree with report of Adakole, Abulode, & Balarabe (2020); Abdulahi, Taweel, Huhaim, & Ahmad (2019).

The mean concentration values of the heavy metals in water and sediment were subjected to correlation analysis to understand if there is any hidden trend between the data from the study areas. Correlation analysis provides information about associations between sites and between individual metal compounds to determine common origin. The table of the correlation matrix showed varying correlation between the various heavy metals in water and sediment at 0.05 and 0.01 level of significance. Correlated heavy metal in water and sediment connotes that the metals may have similar behavior and implies they could have common origin. Essiett, Effiong, Ogbemudia, & Bruno (2022) reported that two compounds with strong positive correlation between their concentrations are likely to have a common source. This observation aligns with the result of this study.

Seasonally, there were differences occurring in the sampled species (Fish, Insect, Snail and Algae) with respect to heavy metals. Elevated values of metals were observed during the dry season than in the wet period in all the study area. The metals are absorbed and get concentrated because there is no rain to wash them away. Wind can also be a major factor in aerial deposition of heavy metals on Fish, Insect, Snail and Algae. This suggests that Fish, Insect, Snail and Algae can uptake these metals in sediment through the waste discharged into the river by some anthropogenic activities such as industrialization, erosion, and domestic activities. This outcome, however, agrees with the findings of Onuoha, Nwankwo, & Chikwu (2021) who recorded higher values of metals in dry season than wet season in Ikpa River.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study was carried out to evaluate accumulation of heavy metals in fish, water, and sediment samples by studying the physicochemical properties of surface water, sediments from Oguta Lake. Water quality characteristics, which include physicochemical parameters and seven heavy metals, were analyzed. The study established alteration of physicochemical parameters in Oguta Lake and gradual build-up of heavy metals because of prevailing anthropogenic activities in the vicinity of the Lake. These findings gave valuable information on physicochemical properties and heavy metals concentrations in water, sediment and three selected species (Fish, Insect, and Snail) and algae. As a result of urbanization and civilization, water and its management will continue to be a major issue, which will have profound impact on our lives and that of our planet Earth than ever before. Indeed, water is life. Everyday water systems all over the world receive polluting runoffs of industrial processes, fertilizers, pesticides, sewage, and mining drainage. The investigations carried out in this study have inferred that the overall mean concentrations obtained for surface water parameters indicate levels that were within the water quality guidelines by the WHO. However, some of the heavy metals assayed showed presence of heavy metals at marginal level. This was due to discharge of waste entering the river and its tributaries from homes and industries. Although, the levels of heavy metals were found to be within permissible limits, bioaccumulation and magnification is capable of leading to toxic level of these metals in fish, Insect, Snail and Algae even when exposure is high. The result revealed that this discharge could pose significant health and environmental risk to those who rely on Oguta Lake as their source of domestic water without treatment. A look at these Lake physically shows that the Lake is not healthy. Seasonally, Oguta Lake shows more significant pollution during the dry seasons for most of the parameters studied, due to low flow rates and volumes of most of the rivers which helps to increase the concentration of contaminants. Results obtained from the estimation of daily intake and target cancer risk in the fish, insects, snail, and Algae showed that all sampling points had low risk in terms of heavy metals. Thus, the continuous daily intake of fish is a potential health concern as long term exposure to low activity concentrations is likely to activate bio-toxicity. According to the results obtained from the work, people should always purify and sterilize the water from this Lake before usage to free it from contaminants. Thus, Oguta Lake can be classified as moderately polluted from the findings of this study. Constant routine monitoring should be ensured to guide against ignorant consumption of excess pollutants (heavy metals) should the level of the heavy metals in the media increase to intolerable limit.

5.2 RECOMMENDATIONS

- Regular monitoring of the water and sediment qualities of the Oguta Lake should be carried out.
- Appropriate regulatory and enforcement agencies should ensure that effluents are properly treated before discharge into the Oguta Lake.
- Government should inform the populace around the Oguta Lake channel of the non-potability of the raw water.
- Periodic monitoring of heavy metal in the study area should be done since the water serves as a source of drinking water, fish and for all year-round irrigational farming.
- Constant routine monitoring should be ensured to guide against ignorant consumption of excess pollutants (heavy metals) should the level of the heavy metals in the media increase to intolerable limit.
- Further research on some other water pollutants (not considered in this study) affecting Oguta Lake, should be conducted.
- More studies on heavy metal metabolism rates in organs of fish species should be conducted.
- Public awareness and education about sources and health effects of heavy metals should be improved

5.2.1 CONTRIBUTIONS TO KNOWLEDGE

The research has provided information on the environmental status of Oguta Lake, with respect to sediment and Fish quality and has therefore increased existing knowledge and can be used as baseline data for heavy metal pollution in Nigerian Lakes generally. The study has established public health alert for accumulation and effects on consumers in the vicinity of this Lake. Hence, exposed fish to high-risk health status, which will resultantly become of public concern to man; pose risk to fish and other aquatic fauna in this study

REFERENCES

Abdallah, M. A. M. (2017). Bioaccumulation of hydrocarbons in freshwater fish species cultured in a shallow Coastal Lagoon, Egypt. *Earth Syst. Environ*., 1(2): 1- 7.

Abdulahi, K. A., Taweel, M. S., Huhaim, O., & Ahmad, A.K. (2019). Analysis of heavy metals concentrations in Tilapia fish from Lake Chini, Peninsuler Malaysia. *Malaysia journal of Analytical Science*. 10:91-92.

Abowei, J. F. N. (2021). Salinity dissolved oxygen, pH and surface water temperature conditions in Nkoro River Niger Delta, Nigeria: *Advanced Journal of Food Science and Technology,* 2(1):36-40

Achieche, O. Njoku, O. Duru, M. & Nwachukwu. O. (2020). Assessment of Physicochemical Properties and Heavy Metal Load in Soils of Ebocha Gas Flaring Site in Rivers State, Nigeria. *Asian Soil Research Journal*. 1-9.

Achionye-Nzeh, C. G. and Isimaikaiye A. (2010). Fauna and flora composition and water quality of a reservoir in Ilorin, Nigeria. *International Journal of Lakes and Rivers* 3 (1): 7-15.

Adakole, J. A., Abulode, D. S. & Balarabe, M. L. (2020). Assesssment of water quality of man-made lake in Zaria, Nigeria. *Proceedings of Taa/2007: The 12th World Lake Conference*. 1373 – 1382.

Adebisi, A.A. (2020). The physicochemical properties and hydrology of a tropical seasonal concentrations in Tilapia fish from Lake Chini, Peninsuler *Malaysia. Malaysia Journal of Analytical Science,* 10: 91-92.

Afzal, M. S., Ashraf, A., & Nabeel, M. (2018). “Characterization of industrial effluents and groundwater of Hattar industrial estate, Haripur,” Advances in Agriculture and Environmental Science: *Open Access (AAEOA),*1(2): 70–77

Ahmed, M. K., Parvin, E., Islam, M. M., Akter, M. S., Khan, S., & Al-Mamun, M. H. (2014). “Lead- and cadmium-induced histopathological changes in gill, kidney and liver tissue of freshwater climbing perch *Anabas testudineus* (Bloch, 1792),” *Chemistry and Ecology*, 30(6): 532–540

Ajayi, S.O. & Osibunji, O. (2022). Pollution studies on Nigeria Rivers, Water quality of some Nigerian Rivers. *Environmental Pollution*, 2, 87 – 95.

Akpoborie, I. E., Ekakite, O. A. & Adaikpoh, E. O. (2000) The Quality of Groundwater from Wells in Part of the Western Niger Delta. *Journal of NAFAK*, 5: 72-79.

Akubuguo, E.I., Nwachukwu, M., Odiki, P.C. and Duru, M. (2018). Water Quality Assessment of Njaba River. *Journal of Enviromenttal Science, Toxicology and Food Technolgy*. 4(6): 157 – 165.

Albretsen J. (2016). The toxicity of iron, an essential element; *Veterinary medicine*; Pp. 82–90.

American Public Health Authority (APHA) (1992). Standard methods for the examination of water and wastewater, 18th Edition. American Public Health Association, Washington DC, USA. Pp 76.

Antoine, S. E., & Al-Saadi, H. A. (2020). Limnological studies on the polluted Ashar canal at Basra (Iraq). city, western Kenya. *Parasitic Vectors*. 4: 226

American Public Health Authority (APHA). (2017). Standard methods for the examination of water and wastewater. 23rd ed. Washington DC American Public Health Association; 2017. p. 1–1546.

Appenroth, K. J. (2010). “What are “heavy metals” in Plant Sciences?” *Acta Physiologiae Plantarum*, 32(4): 615–619

Athar, M, Vohora. S.B, 2018, Heavy Metals and Environment, New Delhi, *New Age International Publisher*, 3–40.

Ayeloja, A. A., George, F. O. A., Shorinmade, A. Y., Jimoh, W. A., Afolabi, Q. O. and Olawepo K. D. (2014). Heavy metal concentration in selected fish species from Eleyele reservoir Ibadan Oyo State South-western Nigeria. *African Journal of Environmental Science and Technology* 8(7): 422 – 427.

Bagul, V. R., Shinde, D. N., Chavan, R. P., Patil, C. L. & Pawar, R. K. (2015). "New perspective on heavy metal pollution of water", *Journal. Chem. Pharma. Res*., 7(12): 700-705

Bakan, G. & Ozkoc, H. B. (2020). An ecological risk assessment of the mid-black sea coast of Turkey. chemistry and benthic macroinvertebrates of a south western, Lagoon Lagos, Nigeria. *Journal of American Science*, 6(3), 85 – 92.

Barabaszl W, Albinska D, Jaskowska M. & Lipiec J. (2015). Ecotoxicology of Aluminium. *Pol J Environ Stud.* 11(3):199–203.

Begum, A., HariKrishna, S., Khan & I., (2016). Analysis of Heavy metals in Water, Sediments and Fish samples of Madivala Lakes of Bangalore, Karnataka: *International Journal of ChemTech Research*, V.1(2), p. 245-249.

Bernard, A. (2018). Cadmium & its adverse effects on human health. *Indian Journal of Medical Resources* 128(4): 557–564.

Bezak-Mazur E, Widiak M, Ciupa T. A. (2001). Speciation analysis of aluminium in the River Silnica. *Pol Journal of Environmental Studies.* 10(4): 263–268.

Bhumpander, K. & Mukherjee, D. P. (2012). Distribution of heavy metals in valuable coastal fishes from North east coast of India. *Torkish Journal of Fisheries and aquatic science. Reveges hydrobiologia*. 67, 405-418.

Castagnetto, J. M., Hennessy, S. W., Roberts, V. A., Getzoff, E. D., Tainer, J. A. Pique, M. E. (2002). MDB: the metalloprotein database and browser at the Scripps Research Institute. *Nucleic Acids Res.* 30(1): 379–382.

Chen, C. W., Chen, C. F. and Dong, C. D. (2012). Distribution and Accumulation of Mercury in Sediments of Kaohsiung River Mouth, Taiwan. *APCBEE Procedia.*1: 153–158.

Clarkson, T. W. (2017). Human toxicology of mercury. *Journal of Trace. Element. Exp. Med.,* 11(2-3): 303-317.

Çoğun, H. Y. & Şahin, M. (2012). Nil Tilapia (*Oreochromis niloticus* Linnaeus, 1758)'da Kurşun Toksisitesinin Azaltılmasında Zeolitin Etkisi. *Kafkas Univ Vet Fak Derg*. 18(1): 135-140.

Daei, S., Jamili, S., Mashinchian, A. & Ramin, M., (2019). Effect of Pb and Cd on the iron solute in blood (*Chalcalburnus chalcoides*), *Journal of fisheries and aquatic science*, 4(6): 323-329.

Decena, S. C., Arguilles, M., & Robel, L. (2018). "Assessing heavy metal contamination in surface sediments in an urban river in the Philippines," Polish *Journal of Environmental Studies*, 27(5): 1983–1995

Dickman, M. D & Leung, K. M. (2018). Mercury and organo chlorine exposure from fish consumption in Hong Kong. *Chemosphere*, 37(5): 991-1015.

Dissanayake, C. B. & Chandrajith, R. (2019). Phosphate mineral fertilizers, trace metals and human health," *Journal of the National Science Foundation of Sri Lanka,* 37(3): 153–165.

Duan N, Wang XL, Liu XD, Lin C. and Hou J. (2010). Effect of anaerobic fermentation residues on a chromium-contaminated soil-vegetable system. *Procedia Environmental Sciences.* 2:1585–1597.

Duffus, J. H. (2002). ""Heavy metals" a meaningless term? (IUPAC Technical Report)," *Pure and Applied Chemistry*, 74(5): 793–807

Duru, M. K. C., Adindu, E. A., Odike, P. C., Amadi, B., & Okezi, C. E. R. (2021). Consequences of long-term consumption of water from the Nworie River (Owerri, Nigeria) on hematological, hepatic, and renal functions using a raw model. *Biokemistri Home Journal,* 24(1).

Duru, M. K. C. & Akuugwo, G. I. (2019). Biochemical implications of the consumption of water from Otamiri Owerri, Imo State. *Journal of emerging trends in engineering and applied sciences*. 4(3): 2-8.

Duru, M. & Nwanekwu, K. (2019). Physciochemical and microbial status of Nworie River, Imo State, Nigeria. *Asian Journal of Plant Science and Research*, 2(4): 433 – 436.

Duruibe, J. O., Ogwuegbu, M. O. C. & Egwurugwu, J. N. (2017). "Heavy metal pollution and human biotoxic effects", *International Journal Physical Sci.,* 2(5): 112-118.

Ebigwai, J. K., Imemdimfen, I. E., Bright, H. A., Olowu, C., & Ekanem, F. A. (2021). Physicochemical parameters and phytoplankton assemblages along spatial and temporal gradients in Kwa River, Calabar, Nigeria. *International Journal of Biological chemistry*. 8(1)1-20.

Ede, P. N. & Williams, I. (2008) Framework, Process and Effects of Dredging in the Niger Delta. Annual Workshop of the Nigerian Mining and Geosciences Society, Port Harcourt. Pp. 34.

Essiett, U. A., Effiong, G. S., Ogbemudia, F. O. & Bruno, E. J. (2022). Heavy metal concentrations in plants growing in crude oil contaminated soil in Akwa Ibom State, south-eastern Nigeria. *African Journal of Pharmacy and Pharmacology*. 4.7: 465-470.

Ezemonye, M. N. (2009). Surface and ground water quality Enugu, Urban Area, Unpublished Ph.D. Thesis. Department of Geology, University of Nigeria Nuskka. Pp 56-103.

Fernandes L. L. & Nayak, G. N. (2012). "Heavy metals contamination in mudflat and mangrove sediments (Mumbai, India)," *Chemistry and Ecology*, 28(5): 435–455

Flora, S. J. S., Mittal, M. and Mehta, A. (2008). Heavy metal induced oxidative stress & its possible reversal by chelation therapy. *Indian J Med Res.* 128:501–523.

Fu, J., Wang, Q., Wang, H., Yu, H. & Zhang, X. ((2014): Monitoring of non-destructive sampling strategies to assess the exposure of avian species in Jiangsu Province, China to heavy metals. *Environ Science Pollution Res,* 21(4): 2898-2906

Ghani A. (2011). Effect of chromium toxicity on growth, chlorophyll and some mineral nutrients of *Brassica juncea* L. *Egyptian Acad J Biol Sci.* 2(1):9–15.

Godwin, J., Vaikosen, N. E., Njoku, C. J. & Sebye, J. (2011). Evaluation of some heavy metals in tilapia nicolitica found in selected rivers in Bayelsa state. *EJEAFChe*, 10(7): 2451-2459

Grant, C. A. & Sheppard, S. C. (2008). "Fertilizer impacts on cadmium availability in agricultural soils and crops," Human and Ecological Risk Assessment: *An International Journal*, 14(2): 210–228

Grazuleviciene R, Nadisauskiene R, Buinauskiene J, Grazulevicius T. (2019). Effects of Elevated Levels of Manganese and Iron in Drinking Water on Birth Outcomes. *Polish J of Environ Stud.* 18(5): 819–825

Habashi, F. (1992). Environmental Issues in the Metallurgical Industry – Progress and Problems, Environmental Issues and Waste Management in Energy and Mineral Production. *Balkama, Rotherdam*, 1143 -1153.

Healey, N. (2019). Lead toxicity, vulnerable subpopulations and emergency preparedness. *Rad. Prot. Dosim*. 134: 143-151.

Hughes, J. P., Polissar, L. and Van Belle, G. (1988). Evaluation and synthesis of health effects studies of communities surrounding arsenic producing industries. *Int J Epidemiol.* 17: 407–413.

Idodo-Umeh, G. & Oronsaye, J. A. O. (2006). Heavy metal pollution of the sediments from Eriora River in Olomoro town, Niger Delta, Nigeria. *Journal of Sustain. Trop. Agric. Res.* 21: 74-81

Ihenyen, A. E. & Aghimien, A. E. (2002). A Study of Trace Heavy Metal Levels in Warri Soils and Vegetables, Southern Nigeria. *African Journal of Environmental Pollution Health*, I: 72–82.

Ijeh, B. I. & Onu, N. N. (2020). Assessment of pollution levels of groundwater in parts of Imo River Basin South Eastern Nigeria. *Egyptian Journal of petroleum*, 25(1): 107-123.

Ikpe, E. Nnawuike, J. Kelechi, S. Kelechi, J. Ukeje, K. Chinecherem, Chukwuebuka, D. & Nwachukwu. O. (2020). Assessment of Physicochemical Characteristics and Heavy Metal Concentration in Soils and Plants in Selected Refuse Dumpsites within Nkwerre L.G.A., of Imo State, Southeast Nigeria. 26-36.

Irfan, M., Hayat, S., Ahmad, A., and Alyemeni, M. N. (2013). Soil cadmium enrichment: Allocation and plant physiological manifestations. *Saudi J Biol Sci.* 20(1): 1–10.

Islam, M. S., Proshad, R., & Ahmed, S. (2018). "Ecological risk of heavy metals in sediment of an urban river in Bangladesh," Human and Ecological Risk Assessment: *An International Journal*, 24(3), 699–720

Jaishankar, M. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary toxicology*, 7 (2): 60-72

Kieber, R. J., Willey, J. D. & Zvalaren, S. D. (2017). "Chromium speciation in rainwater: temporal variability and atmospheric deposition," *Environmental Science & Technology,* 36(24): 5321–5327.

Kolo, A. U. & Oladimeji, T. D. (2020). An assessment of the physicochemical parameters of Shiroro lake, Kentagora, Niger State. *Journal environ. research*, 4, 55-66.

Lim, H. S., Lee, J. S., Chon, H. T. & Sager, M. (2008). Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon au–ag mine in Korea. *Journal Geochem Explor*, 96: 223–30.

Lindholmer, C. (2016). “Toxicity of zinc ions to human spermatozoa and the influence of albumin,” *Andrologia*, 6(1): 7–16

Mandahl-Barth, G. (1962). Key to the identification of east and central African freshwater snails of medical and veterinary importance. Bull World Health Organ. 1962; 27:135–50.

Mathew, B. B., Tiwari, A. and Jatawa, S. K. (2011). Free radicals and antioxidants: A review. *Journal of Pharmacy Research.* 4(12): 4340–4343.

Mazumder, G. (2018). Chronic arsenic toxicity & human health. *Indian J Med Res.* 128(4): 436–447.

Mohanty, M. and Kumar, P. H. (2013). Effect of ionic and chelate assisted hexavalent chromium on mung bean seedlings (Vigna Radiata l. Wilczek. Var k-851) during seedling growth. *JSPB.* 9(2):232–241.

Muawiya M. A., Edward O. D. & Sanusi B. M. (2017). Bioaccumulation of heavy metals in some tissues of croaker fish from oil spilled rivers of Niger Delta region, Nigeria. *Asian Pacific Journal of Tropical Biomedicine*. 7(6): 563-568

Mustafa, A. D., Juahir, H., Yunus, K., Amran, M. A., Che Hasnam, C. N. Azaman, F. (2015). Oil spill related heavy metal: a review. *Malays Journal Anal Science,* 19(6): 1348-1360

Mutlu, A., Lee, B. K., Park, G. H., Yu, B. G. and Lee, C. H. (2012). Long-term concentrations of airborne cadmium in metropolitan cities in Korea and potential health risks. *Atmos Environ.* 47: 164–173.

Najeeb, U., Ahmad, W., Zia, M. H., Malik, Z. and Zhou, W. (2014). Enhancing the lead phytostabilization in wetland plant *Juncus effusus* L. through somaclonal manipulation and EDTA enrichment. *Arab J Chem.* Pp 34.

Neff, J. M. (2002). Bioaccumulation in Marine Organisms: Effect of Contaminations from Well Produced Water. Amsterdam: Elsevier Science Publisher. https://doi.org/10.1016/B978-008043716-3/50002-6 September 3, 2021

Njoku, G. & Acho, O. (2010) Nworie River Dredging Controversy: Reducing the Overload Dallas. Texas, USA. Pp 54.

Nkwoji, J., Yakub, A.S., Ajani, G. & Bellow, B.O. (2018). Seasonal variations in the water chemistry and benthic macroinvertebrates of a south western, Lagoon Lagos, Nigeria. *Journal of American Science*, 6(3), 85 – 92.

Nowrouzi, M., Mansouri, B., Nabizadeh, S., & Pourkhabbaz, A. (2014). "Analysis of heavy metals concentration in water and sediment in the Hara biosphere reserve, southern Iran," *Toxicology and Industrial Health*, 30(1): 64–72.

Nwadinigwe, C. A., Udo, G. J. & Nwadinigwe, A. O. (2019). Seasonal variations of heavy metal concentration in sediment samples around major tributaries in Ibeno coastal area. *International Journal of Scientific Research*,3(11), 254 – 265.

Nwankwoala P. O. & Ekpewerechi P. O. (2007). Human Activities and Heavy Metal Concentrations in Aba River, Abia State, Nigeria. *British Journal Earth Sciences Research,* 5(1): 26-36

Ogbuagu, D. H., Idewele, M. O., & Nzekwue, K. P. (2019). Bioaccumulation of Persistent Environmental Pollutants (PEPs) in the mud catfishes (*Clarias gariepinus* and *Heterobranchus longifilis*) from the Ogu Creek, Rivers State, Nigeria, *International Journal of Marine Science*, 9(7): 54-65.

Okeke, P.N. & Adinna, E.N. (2018). Water quality study of Otammiri River in Owerri Nigeria. *Universal Journal of Environmental Research and Technology*.3, 641-649.

Olajire, A. A. & Kparia, I. (2000) A Study of the Water Quality of the Osun River: Metal Monitoring and Geochemistry. *Bulletin of the Chemical Society of Ethiopia*, 14: 1-8

Olaniran AO, Balgobind A, Pillay B. (2013). Bioavailability of heavy metals in soil: impact on microbial biodegradation of organic compounds and possible improvement strategies. *Int J Mol Sci.* 14(5):10197–10228.

Olawale, S. A. (2021). Assessment of heavy metal concentration in fish, surficial sediments and water. *Imperial Journal of Interdisciplinary Research*. 3(3): 122 – 123.

Omoregie, I. P., Thadeus, I. T. O., Idowu, I. J. & Freeman, O. E. (2016). Assessment of some heavy metals and total hydrocarbons in *Clarias gariepinus* fish of Osse River, Edo State, Nigeria. *IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT),* 10(9): 144-151

Onuoha, P. C. Nwankwo, D.I., & Chikwu, L.O. (2021). Spatio-temporal variation in Phytoplanktan biomass and diversity in a tropical eutotropic lagion, Nigeria. *Journal of American Science* 10, 94-106.

Ovie, S. I., & Adeniji, H.A. (2019). Zooplankton and environmental characteristics of shiroro parameters and phytoplankton assemblages along spatial and temporal gradients in Kwa River, Calabar, Nigeria. International Journal of Biological chemistry. 8(1)1-20.

Patrick, L. (2014). Mercury toxicity and antioxidants: Part 1: role of glutathione and alpha-lipoic acid in the treatment of mercury toxicity. *Altern Med Rev.* 7(6): 456–471.

Phippen B, Horvath C, Nordin R, Nagpal N. (2018). Ambient water quality guidelines for iron: overview; Ministry of Environment Province of British Columbia. Pp.45

Rahim, M., Ullah, I., Khan, A., & Haris, M. H. (2016). “Health risk from heavy metals via consumption of food crops in the vicinity of District Shangla,” *Journal of the Chemical Society of Pakistan,* 38(1): 177–185

Rajaei, G., Mansouri, B., Jahantigh, H., & Hamidian, A. H. (2012). “Metal concentrations in the water of Chahnimeh reservoirs in Zabol, Iran,” *Bulletin of Environmental Contamination and Toxicology*, 89(3): 495–500

Rajeev, K. (2015). “A Review on the detection of heavy metals in water bodies, fish organs, sediment river beds”, *International Journal Cur. Res. Rev.,* 05(18): 89-95.

Ram´ırez, R. (2013). “The gastropod *Osilinus atrata* as a bioindicator of Cd, Cu, Pb and Zn contamination in the coastal waters of the Canary Islands,” *Chemistry and Ecology*, 29(3): 208–220

Rezania, S., Taib, M. S., Md Din, M. F., Dahalan, F. A., & Kamyab, H. (2016). “Comprehensive review on phytotechnology: heavy metals removal by diverse aquatic plants speciesfrom wastewater,” *Journal of Hazardous Materials*, 318: 587–599

River.*Hydrobiology*,79:157 – 165.

Rosseland B. O, Eldhuset T. D, Staurnes M. (1990). Environmental effects of aluminium. *Environ Geochem Health.* 12(1–2): 17–27

Sanyal, T., Kaviraj, A., & Saha, S. (2015). “Depositionofchromium in aquatic ecosystem from effluents of handloom textile industries in Ranaghat-Fulia region of West Bengal, India,” *Journal of Advanced Research*, 6(6): 995–1002

Satarug, S., Garrett, S. H., Sens, M. A. & Sens D. A. (2011). Cadmium, environmental exposure, and health outcomes. *Ciência & Saúde Coletiva.* 16(5): 2587–2602.

Sekabira, K., Oryem O. H., Basamba T. A., Mutumba G. & Kakudidi E. (2010): Assessment of Heavy Metal Pollution in the Urban Stream Sediments and Its Tributaries. *International Journal of Environmental Science & Technology,* 7: 435-446

Sharma, P. & Dubey, R. S. (2015). Lead toxicity in plants. *Brazilian Journal of Plant Physiology,* 17(1): 35–52.

Singh, N., Kumar, D. & Sahu, A. (2017). Arsenic in the environment: effects on human health and possible prevention. *J Environ Biol.* 28(2): 359–365.

Stohs, S. J. & Bagchi, D. (1995). Oxidative mechanisms in the toxicity of metal ions. *Free Radic Biol Med.* 18(2):321–336.

Thomas I. H. L., Francisco B., Fredy R. C. R., Maria D. C. D., Patricia Q. O., Daniel A., & Avto G. (2015). Concentration of toxic elements in topsoil of the metropolitan area of Mexico city: Spatial analysis using ordinary kriging and indicator kriging. Rev. *Int. Contam. Ambie*. 31(1): 47-62

Thürmer, K., Williams, E. & Reutt-Robey, J. (2017). Autocatalytic oxidation of lead crystallite surfaces. *Science.* 297(5589): 2033–2035.

Titilayo AO, Olufemi AO (2014). Bioaccumulation of Heavy Metals in Fish (*Clarias gariepinus*) Organs from Selected Streams in South Western Nigeria. 2nd Inter. Conference Sustain. *Environ. Agric*. 76: 47 – 50.

Trasande, L., Landrigan, P. J. and Schechter, C. (2015). Public health and economic consequences of methyl mercury toxicity to the developing brain. *Environ Health Perspect.*113 (5): 590–596.

Trueby, P. (2013). Impact of Heavy Metals on Forest Trees From Mining Areas. In: International Conference on Mining And The Environment III, Sudbury, Ontario, Canada. Pp 34.

Tu¨rkmen, M., Tu¨rkmen, Y., Tepe, Y., & Ate A. (2009). "Determination of metals in fish species from Aegean and Mediterranean seas," *Food Chemistry*, 113(1): 233–237

Uma K. O. (2009). Water resources of Owerri and its environs, Imo State, Nigeria, *Journal of Mining and Geology,* 22(91): 57-64

US Environmental Protection Agency (USEPA) (1993). Environmental Criteria and Assessment Office: EPA 600/8-83-028, U. S. Environmental Protection Agency. Air Quality Criteria for Lead, Washington, DC, USA. Pp 39.

US Environmental Protection Agency's integrated risk information system (USEPA IRIS). (2011). Environmental protection agency region I, Washington DC 20460. US EPA. Pp 40.

Valko M. M. H. C. M, Morris, H, and Cronin M. T. D. (2005). Metals, toxicity and oxidative stress. *Curr Med Chem.* 12(10):1161–1208.

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

Wadhwa, N., Mathew, B. B., Jatawa, S. and Tiwari, A. (2012). Lipid peroxidation: mechanism, models and significance. *Int J Curr Sci.* 3: 29–38.

Wang, D., Dang, Z., Feng, H, & Wang, R. (2015). "Distribution of anthropogenic cadmium and arsenic in arable land soils of Hainan, China," *Toxicological & Environmental Chemistry,* 97(3-4): 402–408.

World Health Organization (WHO). (1997). Aluminium; Geneva: World Health Organization, International Programme on Chemical Safety Environmental Health Criteria. Pp 43.

World Health Organization (WHO). (2016). Guidelines for drinking water quality (electronic resource) 3rd edition in water. *Imperial Journal of Interdisciplinary Research*. 3(3): 122 – 123.

Wolińska, A., Stępniewska, Z. & Włosek, R. (2013). The influence of old leather tannery district on chromium contamination of soils, water and plants. *Nat Sci.* 5(2A): 253–258.

Wongsasuluk, P., Chotpantarat, S., Siriwong, W. & Robson, M. (2014). Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in Ubon Ratchathani province, Thailand. *Environ Geochem Health*. 36: 169–182.

Yongsheng, W., Qihui, L., & Qian T. (2016). Effect of Pb on growth, accumulation and quality component of tea plant. *Procedia Engineering.* 18: 214–219.

Zahra, A., Hashmi, M. Z., Malik, R. N., & Ahmed, Z. (2014). "Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah-Feeding tributary of the Rawal Lake Reservoir, Pakistan," *Science of the Total Environment,* 470-471: 925–933

Zayed A. M and Terry, N. (2017). Chromium in the environment: factors affecting biological remediation. *Plant Soil.* 249(1): 139–156.

Zhao, S., Shi, X., Li, C., Zhang, H., & Wu, Y. (2014). "Seasonal variation of heavy metals in sediment of Lake Ulansuhai, China,"*Chemistry and Ecolog*y, 30(1):.1–14

Zhuang, P., McBride, M. B., Zou, B. & Wang, G. (2013). "Health risk assessment for consumption of fish originating from ponds near Dabaoshan mine, South China," *Environmental Science and Pollution Research*, 20(8) 5844–5854.

APPENDIX

Appendix 1: One way ANOVA showing variation in heavy metals concentrations in *Tilapia mariae* (Fish), water boatman (insect), snail (mollusc), and algae.

Heavy metals	Source	Df	F	P
Pb	Location	2		
	Fish	2	0.283	≥ 0.01
	Insect	2	0.034	≥ 0.01
	Snail	2	0.107	≥ 0.01
	Algae	2	0.042	≥ 0.01
Cd	Location	2		
	Fish	2	0.103	≥ 0.01
	Insect	2	0.021	≥ 0.01
	Snail	2	0.094	≥ 0.01
	Algae	2	0.028	≥ 0.01
As	Location	2		
	Fish	2	0.076	≥ 0.01
	Insect	2	0.015	≥ 0.01
	Snail	2	0.031	≥ 0.01
	Algae	2	0.009	≥ 0.01
Hg	Location	2		
	Fish	2	0.000	≥ 0.01
	Insect	2	0.000	≥ 0.01
	Snail	2	0.000	≥ 0.01
	Algae	2	0.000	≥ 0.01
Ni	Location	2		
	Fish	2	3.784	≥ 0.01
	Insect	2	1.935	≥ 0.01
	Snail	2	2.452	≥ 0.01
	Algae	2	1.011	≥ 0.01
Mn	Location	2		
	Fish	2	2.456	≥ 0.01
	Insect	2	1.056	≥ 0.01
	Snail	2	1.123	≥ 0.01
	Algae	2	0.324	≥ 0.01
Cu	Location	2		
	Fish	2	2.078	≥ 0.01

	Insect	2	1.567	≥ 0.01
	Snail	2	1.245	≥ 0.01
	Algae	2	0.456	≥ 0.01