DETERMINATION OF SOME HEAVY METALS IN SELECTED FISHES IN THE VICINITY OF CONFLUENCE OF RIVERS NIGER AND BENUE IN LOKOJA, NIGERIA

BY

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A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER DEGREE OF SCIENCE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA

FEBRUARY, 2016

Declaration

I hereby declare that this Dissertation entitled "**Determination of some heavy metals in selected fishes in the vicinity of confluence of rivers Niger and Benue in Lokoja, Nigeria**" has been carried out by me in the Department of Chemistry under the meticulous supervision of Dr. P.A. Ekwumemgbo and Dr. K.I Omoniyi. All information used from other literatures has been duly acknowledged. I hereby attest that no part of this work has been presented or submitted elsewhere for the award of any degree or diploma in any other institution.

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Certification

This dissertation titled "**DETERMINATION OF SOME HEAVY METALS IN SELECTED FISHES IN THE VICINITY OF CONFLUENCE OF RIVER NIGER AND BENUE IN LOKOJA, NIGERIA**" by Isuwa BAWA meets the regulations governing the award of the degree of Master in Analytical Chemistry of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dedication

This work is dedicated to God Almighty and in lovely memory of my late mother Mrs. Tani Bawa and my aged father.

Acknowledgements

I am most grateful to God Almighty the author and finisher of our faith for his countless blessings and protection which led to the completion of this work.

My sincere appreciation goes to my able and caring supervisors Dr. P.A. Ekwumemgbo and Dr. K. I. Omoniyi, whose constructive criticisms and encouragement made it possible for the successful completion of this research. Your patience, cooperation and talented organizing ability that stimulated and guided me throughout the research period are highly commendable.

My gratitude goes to the Head of Department, Prof. V.O. Ajibola, former Postgraduate Coordinator of the Department, Dr. S.O. Idris, the Seminar Coordinator, Dr. I.A Bello, the present Departmental Postgraduate Coordinator, Dr. F.G. Okibe, Dr. J.D.F. Habila and all my lecturers who worked hard to facilitate the completion of the programme. My sincere appreciation goes to Mr. M. Sule and Mr. M. Bashir for their contribution and support.

I am also indebted to my Head of Department in my work place, Prof. A.B. Zarafi, Prof. O. Alabi, Mr. A. Kwanashe for always being by my side.

My utmost appreciation goes to my siblings Nuhu, Anthony, Paulina, Vincent, Moses, Dauda, Helen, Rhoda, Habila and my beloved younger brother, Simon for their moral support in the course of the research. History of this research would not be complete without mentioning Barr. Joseph Dabo, Dr. Alphonsus Cypril and his wife whose encouragement cannot be overemphasized. I wish to thank Felicia (Miria), Christiana, Thomas, Juliet and all my friends for being by my side.

Abstract

The study assessed the physicochemical parameters of the water and concentrations of Cd, Co, Cr, Cu, Pb and Zn in the water, sediments and organs (bones, brain and flesh) of *Clarias gariepinus, Oreochromis niloticus* and *Synodontis nigrita* obtained from River Niger, River Benue (close to their confluence) and after the confluence point at Lokoja, Nigeria during the months of March, June, September and December 2013. By using standard procedures, the chemical oxygen demand, dissolved oxygen, turbidity, biological oxygen demand, total dissolved solids, total hardness, conductivity and pH of the water were determined. The ranges of these parameters were 98.25 - 141.73 mg/L, 2.26 - 14.39 mg/L, 5.33 - 23.13 NTU, 5.56 - 15.59 mg/L, 457.91 - 781 mg/L, 48.85 - 245.83 mg/L, 65.61 - 233.39 µs/cm and 6.77 - 8.07 respectively. All the parameters were above the acceptable limits set by World Health Organisation (WHO), except pH. The concentrations (mg/L) of Cd, Co, Cr, Cu, Pb and Zn in the water samples were in the range of 0.0082 - 0.0276, 0.0042 - 0.0279, 0.0480 - 0.1391, 0.0979 - 1.8037, 0.0003 - 0.0047 and 0.7671 - 2.8510 respectively. Only Pb and Zn were in levels within the permissible limit set by WHO and the concentrations recorded between the rivers and across sampling periods were significantly different. The concentrations of Cd, Co, Cr, Cu, Pb and Zn in the sediments were in the range of 0.2026 - 2.0203, 2.1567 - 20.5421, 13.1767 - 33.0976, 7.0832 - 23.4040, 0.1054 - 2.5593 and 12.9263 - 32.8418 mg/kg respectively. The mean concentration of Cd in the sediment was above the ISQG (Interim Freshwater Standard Quality Guidelines) limit of 0.6000 mg/kg. The pollution load index for the heavy metals indicates low to moderate pollution state of the sediments while the geoaccumulation index for Cd, Co, Cr, Cu, Pb and Zn also suggest low to moderate

pollution of the sediments by Cd, Co and Cr. The organs of the three fish species bio-accumulate Cd, Co, Cr, Cu and Pb above their respective permissible limit. The bone accumulated the metals more than the brain and the level was least in the flesh for all the metals. However, Zn was below the acceptable limit in all the species and organs. Cd and Pb accumulate more in *O. niloticus* followed by *C. gariepinus* and least in S. *nigrita*. Generally, the parameters for the water samples obtained in March 2013 were the highest. The results indicate pollution of the rivers, so enforcement of environmental laws that will minimize anthropogenic activities is imperative.

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Abbreviations

AAS	-	Atomic Absorption Spectrophotometer
ANOVA	-	Analysis of Variance
BOD	-	Biochemical Oxygen Demand
Cd	-	Cadmium
Co	-	Cobalt
COD	-	Chemical Oxygen Demand
Conduct	-	Conductivity
Cr	-	Chromium
Cu	-	Copper
DO	-	Dissolved Oxygen
DPR	-	Department of petroleum resources
EC	-	Electrical Conductivity
EDTA	-	Ethylene-Diamine –Tetracetic acid
EPA	-	Environmental Protection Agency
FAO	-	Food and agriculture organization
Hd	-	Hardness

ISQG	-	Interim Freshwater Standard Quality Guidelines
MAFF	-	Ministry of agriculture, fisheries and forestry
mg/kg	-	Milligram per killogram
mg/L	-	Milligram per litre
NTU	-	Nephelometric turbidity unit
Pb	-	Lead
pH	-	Hydrogen ion activity
SON	-	Standard Organization of Nigeria
TDS	-	Total dissolved solids
Turb.	-	Turbidity
UNEP	-	United nation environmental programme
USEPA	-	United State Environmental Protection Agency
µS/cm	-	Microseconds per centimeter
WHO	-	World Health Organization
Zn	-	Zinc

CHAPTER ONE

1.0 INTRODUCTION

The most often polluted of part of the environmental is the aquatic systems, which include the water, sediments, fishes and other faunas. This is because contaminants in the air, soil or on land ultimately end up in the aquatic systems via local precipitation, water runoff and leaching of rocks and solid wastes (Osibanjo *et al*., 1998). Sewage, industrial wastes, and agricultural chemicals such as fertilizers and pesticides, mineral and petroleum exploration and exploitation are however, the main causes of pollution in aquatic system (Apina, 1999).

The aquatic environment with its water quality is considered the main factor controlling the state of health and disease in both cultured and wild fishes. Pollution of the aquatic environment by inorganic and organic chemicals is a major factor posing serious threat to the survival and quality of aquatic organism such as fish (Samir and Shaker, 2008).

Water pollution occurs when a body of water is adversely affected due to addition of large amounts of materials to the water thereby making it unfit for intended use. Two forms of water pollution exist; point sources (anthropogenic) and non-point source (natural processes). Point sources of pollution occur when harmful substances are emitted directly into a body of water. This includes effluent sewage treatment works, or waste from factories. While non-point source delivers pollutants indirectly through environmental conditions, for example fertilizer or herbicide application is carried into streams by rain in form of run-off which in turn affects aquatic life (Maitera *et al*., 2011). Pollution arising from non-point sources account for majority of contaminants in streams and lakes.

Water quality plays a role in the distribution of fish. The importance of measuring physical, chemical and biological variables was considered at the technical consultation on enhancement of fisheries of small water bodies in Harare (Aweke and Taddes, 2004). The physicochemical characteristics of water are important parameters as they may directly or indirectly affect its quality and consequently its suitability for the distribution and production of fish and other aquatic animals (George *et al*., 2010). Water pollution in Nigeria has been attributed to the following sources: municipal and agricultural waste, urban run-off, organic pollutants and sediment pollutants.

Environmental contaminants such as hydrocarbons, heavy metals and pesticides have been known to have direct toxic effects when released into the aquatic environment (Forstner *et al*., 1998). Over the last few decades, there has been growing interest in determining the levels of heavy metals in the marine environment; and attention was drawn to the measurement of contamination levels in public food supply, particularly fish, which serves as a major source of protein with low health implications (Kalay *et al*., 1999; Rose *et al*., 1999; Tariq *et al*., 1993). Heavy metals are non-biodegradable and once discharged into water bodies, can either be adsorbed on sediment particles or accumulated in aquatic organisms. Fish may absorb dissolved elements and heavy metals from surrounding water and food, which may accumulate in various tissues in significant amounts (Opaluwa and Umar, 2010) and elicit toxicological effects at critical targets. Also, fish may accumulate significant concentrations of metals in water even if those metals are below detection limit in routine water samples (Atolaye *et al*., 2006). Therefore, fish might prove a better indicator for detecting metals in freshwater contamination.

Sediments act as a sink and constant source of supply of pollutants that enter water bodies depending on physical, biological and chemical factors like temperature, pH, redox potential, ionic strength, anthropogenic input, type and concentration of organic and inorganic ligands and available surface area of adsorption (Jenneth *et al.*, 1980; Davies *et al.* 1991). According to Haan *et al.* (1994), sediment is composed of many materials including individual primary particles, aggregates, organic materials and associated chemicals and is considered to be fully characterized when its shape, size, density, composition, texture, mineralogy and stability are known.

There is a direct link between surface water and sediment contamination. Accumulated heavy metals or organic pollutants in sediment could be released back into the water with deleterious effects on human health. Sediments consist of sand, clay and silt components and since most anthropogenic contaminants (those associated with human activity) are also associated with clay and silt components, elevated concentrations of heavy metal in sediments can be a good indicator of man-induced pollution and the sources of pollution in aquatic systems (Forstner, *et al*., 1998).

Metal ions can be incorporated into the sediment as flood occurs. This can form a food chain with higher concentration in aquatic organisms to a level that affects their physiological state. Trace metals such as Zn, Cu and Fe play a biochemical role in the health conditions of all aquatic plants and animals; therefore, they are essential in the aquatic environment in trace amounts. However, the consequent high concentration of heavy metals that may accumulate in the aquatic phase is a threat to humanity (Mason, 2002).

The term "heavy metal" was in use as far back as 1817, when Gmelin divided the elements into non-metals, light metals and heavy metals. Heavy metals are those metals

whose densities fall within 5.308–22.000 g/cm^3 (Hawkes, 1997). Heavy metals are found naturally in the earth, and become concentrated as a result of human activities and are known to be non-biodegradable. Common sources are from mining and industrial wastes; vehicle emissions; lead-acid batteries; fertilizers, paints and treated woods. Lead is the most prevalent heavy metal contaminant. As a component of tetra-ethyl, it was used extensively in gasoline during the 1930s-1970s. Lead levels in the aquatic environments of industrialised societies have been estimated to be two to three times those of pre-industrial levels.

Heavy metals "can bind to vital cellular components, such as proteins, enzymes, and nucleic acids, and interfere with their functioning. Symptoms and effects can vary according to the metal or metal-compound, and the dose involved. Generally, long-term exposure to heavy metals can lead to carcinogenic, central and peripheral nervous system and circulatory effects (Neilen and Marvin, 2008).

1.1 Statement of Problem

Lokoja town generally is faced with poor disposal system in that, the bank of the confluence is used as dumping ground for waste. It was also reported by marketers that quantity of fish in Lokoja market has drop drastically as compared to past years due to reduced amount of fish in the confluence. Visibility study then led to oral interview of fishermen at the confluence in which they attested that fishes were dying in the water leading to shortfall in quantity. This then led to the presumption that the fishes were dying possibly due to poor water quality which could either results in mortality or reduced their reproductive viability.

1.2 Justification of the Study

As part of good environmental management, a periodical assessment of the environment is necessary considering the global warming of the world. Man's activities such as the use of chemicals in farm lands, discharge of sewage, use of chemicals for fishing etc, introduce pollutants to the aquatic system. Pollutants of high risk are heavy metals which are not biodegradable as such pose serious health implication when eventually consumed to a particular level. More so, the recent flood in the study area could also introduce some of these pollutants. In view of the above, this works is considered to be timely and relevant in investigating the pollution status of the rivers to enable policy makers come up with new management strategies of the rivers, and to also enlighten the public on the safety or otherwise of the water and fish from the study area within the time frame.

1.3 Aim and Objectives

This research work is aimed at determining the physicochemical parameter and some heavy metals in water, sediments and three species of fish from River Niger, River Benue in the vicinity of their confluence point at Lokoja, Nigeria in order to establish the pollution status and the safety or otherwise of the fishes for human consumption. This aim will be achieved through the following set of objectives:

1) To examine the levels of the following physicochemical parameters in the water: pH, hardness, conductivity, turbidity, dissolved oxygen, biochemical oxygen demand, total dissolved solids and chemical oxygen demand in each of the river for one year on a quarterly basis;

2) To determine the concentrations of Cd, Co, Cr, Cu, Pb and Zn in the water of each river for a period of one year on a quarterly basis;

3) To determine the concentrations of Cd, Co, Cr, Cu, Pb and Zn in the sediment of each river for a period of one year on a quarterly basis;

4) To determine the concentrations of Cd, Co, Cr, Cu, Pb and Zn in the bones, brain and flesh of *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia) and *Synodontis nigrita* collected at the study area for a period of one year in each of the sampling period;

5) To assess the pollution indices of the water, sediment and fish with respect to the river and seasonal variation.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Physicochemical Parameters of Water

2.1.1 Temperature

Temperature has long been recognized as an important environmental factor in both terrestrial and aquatic ecosystems in regard to its pivotal role over biological activity (development, growth and reproduction). Seasonal temperature differences strongly influence the biological activity of aquatic organisms and establish cyclical patterns that often mediate the scope of each activity. Changes in the thermal regime of the surrounding environment can affect the evolutionary, physiological and behavioural responses of individual organisms (Begon *et al.,* 1990). An increase in temperature decreases dissolved oxygen content, increases respiration and metabolic rate of aquatic biota, pathogen growth and toxicity of dissolved pollutants.

2.1.2 pH

pH is a measure of the relative amount of free hydrogen and hydroxyl ions in the water. Since pH can be affected by chemicals in the water, pH is an important indicator of water that is changing chemically (Andrew, 1990).

The pH of water determines the solubility and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (lead, copper, cadmium, etc.) and hence determines the survival chance of aquatic lives. In the case of heavy metals, the degree to which they are soluble determines their toxicity. Metals tend to be toxic at lower pH because they are more soluble. The optimum pH for freshwater fish is 6.5 to 9 (Garcia *et al*., 2009).

2.1.3 Dissolved oxygen

The measurement of dissolved oxygen (DO) gives a ready assessment of purity of water. DO levels decreases as temperature, salinity, decay of organic matter and respiration increases. Photosynthesis has also been reported to increase it. Warm water fish requires DO $\geq$ 5 mg/L for good growth and reproduction (Swingle, 1969). The oxygen dissolved in lakes, rivers and oceans is crucial for the organisms and creatures living in it. As the amount of dissolved oxygen drops below normal levels in water bodies, the water quality is harmed and creatures begin to die off due to insufficient oxygen caused by eutrophication (Fred and Ann, 2012). Low dissolved oxygen (generally under 3 mg/L) or "hypoxia" causes reduced cell functioning, disrupts circulatory fluid balance in aquatic species and can result in death of individual organisms as well as large dead zone (AALWQC, 2000). Hypoxic water can also release pollutants stored in sediment.

DO is essential to all forms of aquatic life including the organisms that break down man-made pollutants. Oxygen is soluble in water and the oxygen that is dissolved in water will equilibrate with the oxygen in atmosphere. Oxygen tends to be less soluble as temperature increases. The DO of fresh water at sea level will range from 15 mg/L to 8 mg/L at 25°C. Concentrations of unpolluted fresh water will be close to 10 mg/L. In general, the concentration of dissolved oxygen will be the result of biological activity. Photosynthesis of some aquatic plants will increase the DO during day light hours and the DO levels will fall during the nighttime hours. In natural waters, man-made contamination, or natural organic material will be consumed by microorganisms (Hanson and Leggett, 1982).

As this microbial activity increases, oxygen will be consumed out of the water by the organisms to facilitate their digestion process. In waters contaminated with fertilizers, suspended material or petroleum waste, microorganisms such as bacteria will break down the contaminants. The oxygen will be consumed and the water will become anaerobic. Typically DO levels less than 2 mg/L kill fish (Krenkel *et al*., 1979).

2.1.4 Biochemical oxygen demand

This represents the quantity of oxygen required by bacteria and other micro-organisms during the biochemical degradation and transformation of organic matter present in wastewater under aerobic conditions. BOD is considered as a major characteristic used in stream pollution control. It gives very valuable information regarding capacity of streams and serves as a guide-line for the Regulatory Authorities to check the quality of discharge into water bodies (Dara, 2002).

2.1.5 Chemical oxygen demand

This is a measure of oxygen equivalent to that portion of organic matter present in the waste water sample that is susceptible to oxidation by potassium dichromate. This is an important and quickly measure parameter for stream, sewage and industrial waste samples to determine their pollution strength. High COD levels decrease the amount of dissolved oxygen available for aquatic organisms (AALWQC, 2000).

2.1.6 Hardness and alkalinity

These are related to one another because the anions that cause alkalinity (CO_3^{2-}, HCO_3^-, OH^-) and the cations that cause hardness (Ca^{2+} and Mg^{2+}) are usually derived from solutions of carbonate minerals. Most water of high alkalinity also have high

hardness. Generally as hardness increases, heavy metal toxicity decreases (Ellis *et al*., 1989).

2.1.7 Turbidity

Turbidity is the measure of relative clarity of a liquid. It is an optical characteristic of water and is an expression of the amount of light that is scattered by material in the water when a light is shined through the water sample. Higher intensity of scattered light indicates higher turbidity. Therefore, high turbidity restricts light penetration and limits photosynthesis (Pillay, 1992). Material that causes water to be turbid includes clay, silt, finely divided inorganic and organic matter, algae, soluble coloured organic compounds, plankton and other microscopic organisms (Adefemi and Awokunmi, 2010).

Excessive turbidity, or cloudiness, in drinking water is aesthetically unappealing, and may also represent a health concern. Turbidity can provide food and shelter for pathogens. If not removed, turbidity can promote re-growth of pathogens in the distribution system, leading to the outbreak of waterborne diseases, which have caused significant cases of gastroenteritis throughout the United States and the world. Although turbidity is not a direct indicator of health risk, numerous studies show a strong relationship between removal of turbidity and removal of protozoa. The particles of turbidity provide "shelter" for microbes by reducing their exposure to attack by disinfectants. Microbial attachment to particulate material has been considered to aid in microbe survival. Fortunately, traditional water treatment processes have the ability to effectively remove turbidity when operated properly (EPA, 1998).

2.1.8 Total dissolved solids and electrical conductivity

Since electrical conductivity is a measure of the capacity of water to conduct electrical current, it is directly related to the concentration of salts dissolved in water, and therefore to the total dissolved solids (TDS). Since it is difficult to measure TDS in the field, the electrical conductivity of the water is used as a measure of TDS determination. The electrical conductivity of water can be determined in a quick and inexpensive way, using portable meter. Distilled water does not contain dissolved salts and, as a result, it does not conduct electricity and has an electrical conductivity of zero. Nevertheless, when the salt concentration reaches a certain level, electrical conductivity is no longer directly related to the salts concentration. This is because ion pairs are formed. Ion pairs weaken each other's charge, so that above this level, higher TDS will not result in equally higher electrical conductivity. The relationship between TDS and EC is shown in Figure 2.1 (Jenne *et al.*, 2011). EC can be converted to TDS using the following calculation:

$$\text{TDS (ppm)} = 0.64 \text{ X EC } (\mu\text{S/cm}) = 640 \text{ X EC (dS/m)} \quad 2.1$$

2.2 Heavy Metals and their Health Implications

2.2.1 Cadmium

Cadmium occurs in a few minerals and in small quantities in other ores, especially zinc ores, from which it is produced as a by-product. Some lead ores also contain small quantities of cadmium and if it is present in sufficient quantity, it is recovered by a cycle of operations similar to that used by zinc smelters (Rese, 1981). The concentrations of cadmium in water and sediment depend upon the amounts discharged into the aquatic environment, the amounts added in the form of fertilizers and soil amendments, the amounts deposited onto soils from the atmosphere and the amounts removed by harvested

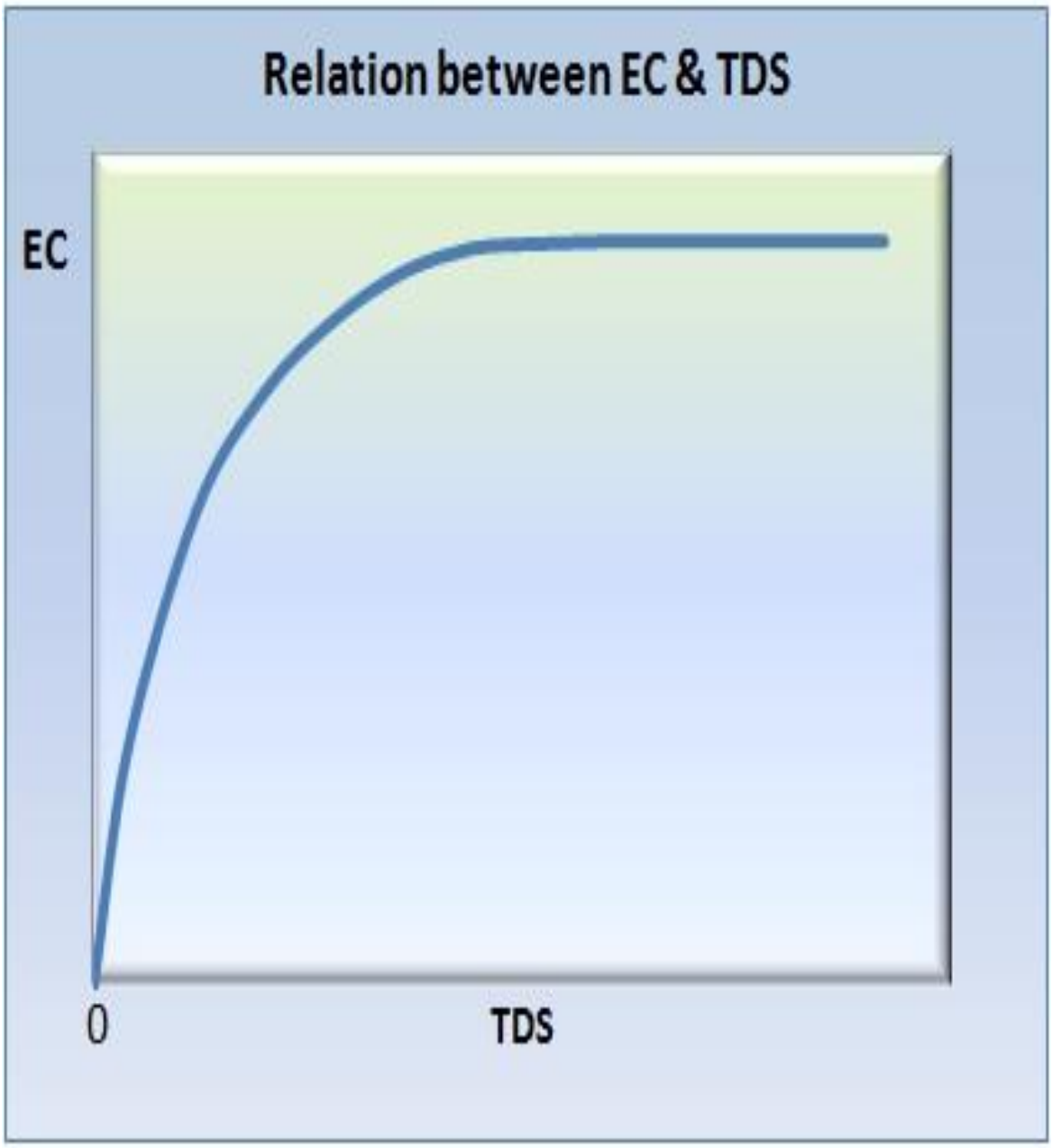


Figure 2.1: Relationship between EC and TDS

crops and by leaching. Among the commercial fertilizers, phosphorus fertilizers contain somewhat elevated levels of Cd. Results show that the long - term use of phosphorus fertilizers will slightly increase the concentration of Cd in the aquatic environment when eventually washed down into the river by rainfall (Wedelpohl, 1998).

In acute cadmium poisoning by ingestion, irritation of the gastrointestinal tract is the major toxicity, causing nausea, vomiting, diarrhea and abdominal cramps. With chronic exposure by inhalation, however, kidneys and lungs are the target organs. Cadmium compounds damage many organs. They cause skin lesions, decrease in heart contractility, blood vessel damage and injuries of the nervous system, kidney and liver. Cadmium compounds also produce skin and lung tumors in humans. The average daily intake for humans is estimated as 0.15µg from air and 1µg from water (Jenne *et al.*, 2011).

2.2.2 Cobalt

Approximately 0.0025% of the earth's crust is comprised of cobalt, which is often present in association with nickel, silver, lead, copper and iron ores. Cobalt occurs in mineral form as arsenides, sulphides and oxides, such as linnaeite (Co_3S_4), carrolite ($CuCo_2S_4$), safflorite ($CoAs_2$), skutterudite ($CoAs_3$), erythrite ($Co_3(AsO_4)_2.8H_2O$), and glaucodot (CoAsS) (Smith and Carson, 1981). Natural sources of cobalt to the environment include volcanic eruptions, seawater spray and forest fires. Anthropogenic sources of cobalt to the atmosphere include coal-fired power plants and incinerators, and exhaust from vehicles. Cobalt mining and processing activities, the production of alloys and chemicals containing cobalt, sewage effluents, urban run-off, and agricultural run-off are major anthropogenic contributors of cobalt to the aquatic environment (Morse, 1994).

2.2.3 Chromium

Chromium is an essential metal in the human body especially in enhancing insulin activity. However, Cr and its compounds are well known toxins especially Cr (VI) which due to its oxidizing potential, easily permeates biological membranes and causes renal damage, diseases of the central nervous system, cancer etc in man (Bae *et al.,* 2000).

2.2.4 Copper

The major portion of copper produced in the world is used by the electrical industries; most of the remainder is combined with other metals to form alloys (Prusty, 1983). Important series of alloys in which copper is the chief constituent are brasses (copper and zinc) and bronzes (copper and tin) (Morse, 1994). Copper is among heavy metals that are essential to life but could be toxic at elevated levels (Rogers *et al.,* 2009). It is toxic at low concentration in water and is known to cause brain damage in mammals.

Elevated levels of this metal has however, been found to be toxic (Hukabee *et al.,* 2011). High doses of copper can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk of health effects from overexposure to copper. Contribution of copper to environmental burden could be by atmospheric deposition from metal industries, dumpsites and power plants that burn fuels. Copper is an essential metal to both fish and man. However, symptoms of acute copper toxicity in man include hypotension, anaemia, and cardiovascular collapse while chronic toxicity leads to sporadic fever, vomiting, diarrhea and jaundice. Copper poisoning induces gill, liver and kidney damage in fish leading to fish mortalities (Baryla *et al.,* 2000).

2.2.5 Lead

Lead is present in several minerals but all are of minor significance except the sulphide, PbS (galena), which is the major source of lead production throughout the world. Lead is also found in anglesite, $PbSO_4$ and cerussite, $PbCO_3$ (Alaia, 1967). The elimination of lead from insecticides and paint pigments and the use of respirators and other protective devices in areas of exposure have reduced lead poisoning materially. The recognition that the use of tetraethyl lead [$Pb(C_2H_5)_4$] as an antiknock additive in gasoline was polluting the air and water led to the compound's elimination as a gasoline constituent in the 1980s (Taylor, 1995). In humans the main sources of lead are usually lead-based paint and drinking water carried through lead pipes; lead-based paints are especially harmful to children who chew on painted toys and furnishings and eat paint peelings from walls (Kersten *et al*., 2003).

Symptoms of lead poisoning include abdominal pain and diarrhea followed by constipation, nausea, vomiting, dizziness, headache and general weakness (Leonard *et al*., 1998). Lead is a well known toxic metal and after adsorption by the body, it is carried to soft tissues like the brain, lung, spleen and heart by the blood and finally deposited in the bone where about 90% of total body lead is found. Lead damages the liver, kidneys, brain, central nervous and reproductive systems of man and aquatic organisms causing all kinds of diseases (Kersten *et al.*, 2003). In some villages in Gummi and Bukkuyum Local Government area of Zamfara State, more than 400 deaths were reported due to lead poisoning. Heavy metals are potential threats to the environment and ecosystem due to their persistence and bio-accumulation in food chain (Galadima *et al.*, 2011).

Symptoms of lead poisoning vary. They may develop gradually or appear suddenly after chronic exposure. The poison affects the entire body especially the

nervous system, the gastrointestinal tract and the blood forming tissues. The victim usually becomes pallid, moody and irritable and may complain of a metallic taste. Digestion is deranged, the appetite fails and there may be severe abdominal pain, with spasms of the abdominal muscles and constipation. A black line (lead line) may appear at the base of the gums. There is often anaemia, in later stages, headache, dizziness, confusion and visual disturbances may be noted. Peripheral nerve involvement results in a paralysis (lead palsy) that generally first affects the fingers, hands and wrists (wrist drop) (Sahu *et al.,* 2008).

The most serious effects are seen in children under the age of six, in whom brain and nervous system development is still occurring. In these children, even a small amount of lead can result in permanent damage and loss of function of the affected area of the brain. Complications may occur, such as learning disabilities, slowed growth, blindness, deafness, and in extreme cases, convulsions and coma ending in death. Brain injury may also occur in adults after massive exposure. Exposure to lead can lead to a wide range of biological defects in human, depending on duration and level of exposure. The developing foetus and infants are far more sensitive than adults. High exposure can cause problems in the synthesis of haemoglobins, damage to the kidneys, gastrointestinal tract, joints, reproductive system and the nervous system. Studies have suggested that exposure to lead can cause up to a loss of 2 IQ points (Sahu *et al.,* 2008).

2.2.6 Zinc

The major uses of zinc metal are in galvanizing iron and steel against corrosion and in making brasses and alloys for die-casting. Zinc itself forms an impervious coating of its oxide on exposure to the atmosphere and hence the metal is more resistant to ordinary atmospheres than iron and corrodes at a much lower rate. Zinc is an essential

trace element in the human body, it is found in high concentration in the red blood cells as an essential part of the enzyme carbonic anhydrase, which promotes many reactions relating to carbon dioxide metabolism. The zinc present in the pancreas may aid in the storage of insulin. Zinc is a component of some enzymes that digest protein in the gastrointestinal tract (Noltze *et al.,* 2003).

The toxicity of zinc is low, in drinking water zinc can be detected by taste only when it reaches a concentration of 15 mg/kg; water containing 40 mg/kg zinc has a definite metallic taste. Vomiting is induced when the zinc content exceeds 800 mg/kg. Cases of fatal poisoning have resulted through the ingestion of zinc chloride or sulphide, but these are rare. Both zinc and zinc salts are well tolerated by the human skin. Excessive inhalation of zinc compounds can cause such toxic manifestations as fever, excessive salivation and a cough that may cause vomiting; but the effects are not permanent (Kline *et al.,* 2010).

2.3 Fish Species

Oreochromis niloticus (formally Tilapia niloticus) belongs to the family of Cichlidae. It is more elongated and less compressed than others. The colouration is brown olive with faint dark vertical bars on the flanks. The posterior part of the dorsal fin, the caudal fin and anal fins bears numerous dark vertical bars on a pale back ground, a characteristic which serves to distinguish it from all other species. It is mainly microphagus and abundant in many Nigerian rivers. Figure 2.2 shows a typical sample of *O. niloticus* (Reed *et al.,* 1967).

Synodontis nigrita fish specie is also known as *Synodontis schall* and it has a wide distribution with no known major widespread threats. It belongs to the family of

Mochokidae and is widely distributed in Africa. The genus *synodontis,* called 'Kurungu' in Hausa language, has about 110 species (Willoughby, 1974). They are easily recognized by their non-scaly bodies and bony shield on the top and sides of the head. According to Okoli (1988) adult specimen of the specie, have grayish or olive brown, ventrally white bodies while medium sized specimens have numerous dark spots on the body and fins while the young are handsomely marked with numerous spots.

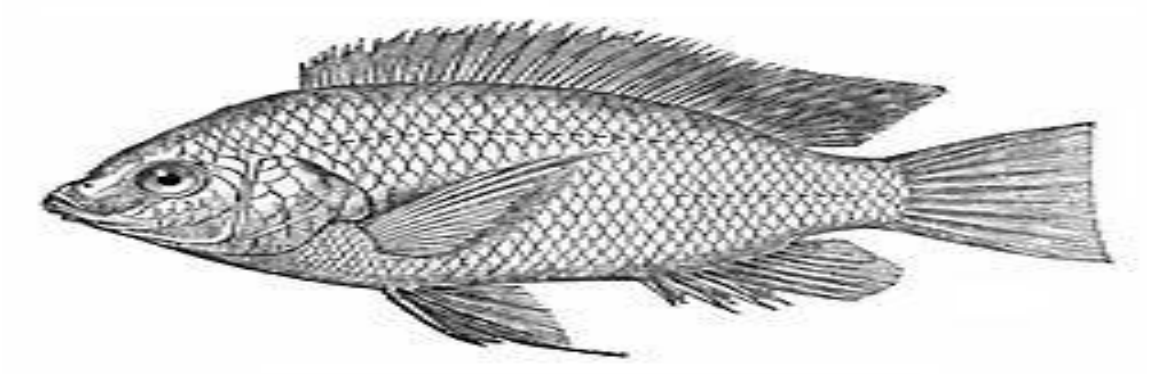
The African *Clarias gariepinus* (catfish) adapted from Skelton (2001) is a dominant freshwater fish. It can grow to between 1.4 and 2.0 m long and can weigh anything from 8 kg to 59 kg. Its body colouration varies from olive green, to brown and black with the flanks often uniform grey to olive-yellow with dark slate or greenish brown back. Underparts are pale olive to white and are mottled irregularly with dark brownish green, or uniformly silvery olive. It is a heavy boned, flat headed fish with premaxilla and lower joa pointed teeth arranged in several rows and four pairs of long trailing sensory organs known as ‘barbels’ around its mouth giving it a similar appearance to a cat, hence the name catfish. The body is elongated with long, low dorsal and anal fins and a smoothly rounded tail fin. It has a small but powerful pectoral fin set immediately in front of the anal fin which has a serrated spine. The eyes are small and set far forward in a flat and bony head (De Moor and Bruton, 1988; Bruton, 1977).

2.4 Pollution of River Water

River is one of the main sources of water to humanity and still unfortunate the most polluted source. Major contaminant of water is heavy metals; these pose serious threat to human health. The amount of cobalt in the Mississippi River water, USA was evaluated and the concentration of cobalt found to be 5.27 μg/L (Boyd and Walley, 1975). A review of the literature on the speciation of cobalt in freshwater revealed that



(a)



(b)



(c)

Plate 2.1: Fish Species (a)= *Clarias gariepinus*, (b)= *Oreochromis niloticus*, (c)= *Synodontis nigrita*

the proportion of the dissolved and suspended fractions of the metal in ambient water is highly variable (Smith and Carson, 1981). Surface water concentrations of cobalt measured in fresh surface water in the province of British Columbia range from non-detectable (detection limit 0.1 µg/L) to 27,000 µg/L. The total and dissolved cobalt concentrations in ambient, uncontaminated environments are generally low and adsorption becomes less efficient again (Theis *et al*., 1988).

The incidence of heavy metals (cadmium, copper, iron, nickel, lead, zinc and vanadium) in water samples from eight sampling points on six rivers in the Niger Delta region of Nigeria being investigated showed that all the metals except iron were extracted from water by solvent extraction. The mean metal contents were cadmium 1.62 µg/L; copper 11.29 µg/L; iron 383.73 µg/L; nickel 4.63 µg/L; lead 7.32 µg/L; vanadium 4.86 µg/L and zinc 15.21 µg/L. The study concluded that iron was the most abundant metal in the water from the rivers in the Niger Delta followed by zinc; and the metal concentrations were within international limits for rivers (Kakulu and Osibanjo, 1992).

Total suspended solid (TSS) could also act as a vector of nutrients such as phosphorus, and toxic compounds such as pesticides and herbicides from the land surface to the water body leading to proliferation of phytoplankton in rivers. In surface water, TSS could cause drift in invertebrate population. High TSS found in some rivers in Nigeria has tendency of reducing the light penetration into the river leading to a reduced photosynthesis with consequent effects on both phytoplankton and zooplankton populations of the aquatic environment. High TSS values have been reported in Asa River (Kwara state) and Rivers Ona and Alaro in Ibadan, Nigeria (Heathwaite, 1994).

Adakole (1995) collected water samples from three sampling points in River Kubanni, Zaria, Nigeria in dry and rainy seasons, digested them with HNO_3 and analyzed metal (copper, lead and zinc) concentrations with Flame Absorption Spectrophotometer. Copper was highest in dry season (mean 6.85 ppm) followed by zinc (mean 2.13 ppm) and lead (mean 0.53 ppm). Copper was also highest in the rainy season water (mean 1.46 ppm) followed by lead (mean 0.31 ppm) and zinc (mean O.l5 ppm). The study inferred that copper was the most abundant metal in the river water. However, sampling was done at only three sampling points along a small stretch of the river. Offiong and Edet (1996) reported that Fe concentrations in most Nigerian rivers are usually greater than World Health Organization (WHO) standard of 0.3 mgL^{-1} in drinking water.

Adakole *et al.* (1998) analyzed water samples from four sampling stations of Bindare Stream (which flows through the Chikaji industrial area and empties into River Galma) and one station on River Galma all in Zaria, Kaduna State, Nigeria and concluded that though there were signs of pollution, the river was still suitable for fish production. Onyilo (1999) analysed River Galma water from three sampling sites and found that levels of iron (mean 1.86 mg/L), copper (mean 0.46 mg/L), cadmium (mean 0.2 mg/L) and chromium (mean 0.54 mg/L) were higher than WHO standards in drinking water. He concluded that this was probably due to discharge of wastes from tobacco, textile, metal smelting industries; auto-mechanics and other artisans into the river. However, Onyilo (1999) collected samples from only three points on the river around the Sabon-Gari area of Zaria and found Fe, Cu, Cd and Cr to be within the acceptable range.

Nutrient enrichment is predominant in most rivers in Nigeria. The values of nitrates and phosphate have been reported to be low. But reports by other authors on some rivers indicated high nutrient load of most rivers in Nigeria. For instance, Olajire

and Imeokparia (2001) observed high concentrations of nitrate, ammonia and phosphate in Osun River, Nigeria. Human activities observed along the study area include agricultural land-use, anthropogenic activities and industrialization. Farming operations around the area were said to have contributed immensely to elevated values of ammonia and phosphate (Olajire and Imeokparia, 2001). The effect of urban run-off has been studied on the Epie Creek in the Niger Delta. The impact of human activities around the Creek was felt on the water body as low DO values were recorded during the wet season due to urban run-off (Izonfuo and Bariweni, 2001).

Water quality plays a role in the distribution of fish. The importance of measuring physical, chemical, and biological variables was considered at the Technical Consultation on Enhancement of Fisheries of small water bodies in Harare. The physicochemical characteristics of water are important parameters as they may directly or indirectly affect its quality and consequently its suitability for the distribution and production of fish and other aquatic animals (Aweke and Taddes, 2004).

The incidence of heavy metals in water of lake Kainji, Nigeria was evaluated and a general correlation between levels of cadmium, copper, cobalt, lead and zinc in three compartments was observed. Water samples from three sampling sites were collected, digested and determined heavy metals concentration using Flame Atomic Absorption Spectrophotometer. Zinc had the highest concentration in the water (0.13 ± 0.01 ppm) while cadmium had the lowest (0.007 ± 0.001 ppm). Metal content was highest in downstream water followed by upstream and then midstream water (Amoo *et al.*, 2005).

The impact of point source pollution from sewage treatment oxidation pond on a receiving stream was studied. The researchers observed significant elevation of water indices such as pH, BOD, nitrate, phosphate and TSS. It is well known that oxygen

depletion in water bodies could cause fish death while increase in BOD signifies high load of organic matter. Also, organic matter decomposition in surface water produced inorganic nutrients such as ammonia, nitrate and phosphorus with resultant effects of eutrophication and other serious ecological problems of such water body (Ogunfowokan *et al.,* 2005).

Furthermore, water samples collected from five sampling points in Ahmadu Bello University Dam (built on River Kubanni - a tributary of River Galma), digested with HNO_3 and analyzed for cadmium, chromuim, copper, lead and zinc. Lead content in the water was the highest (mean 2.66$\pm$1.6 mg/L) while cadmium content was lowest (mean 0.01 $\pm$0.00 mg/L) (Tukura *et al.,* 2005).

Metal pollution of some rivers in Nigeria may be due to industrial discharges, corrosion of iron, steel materials in building, leachates from dumpsites and exhaust from vehicles etc. High Pb concentration in some surface water samples have been attributed to the use of leaded petrol in vehicles (Jaji *et al*. 2007). Waste management is a major problem in most developing nations of the world including Nigeria. Indiscriminate disposal of municipal wastes remains a major threat to surface water pollution in Nigeria. In most cases, sewage and waste water from homes are routed into the rivers and streams. Jaji *et al.* (2007) found elevated water quality parameters in some sampling locations of Ogun River, Nigeria. These were partly attributed to the activities of abattoir located close to the river at a notable market in Abeokuta metropolis.

The work of Arimoro *et al.* (2007) on the impact of sawmill activities on the water quality of River Benin reported high BOD and low DO values at the discharge point of the wastes into the river. Another notable water quality characteristic of rivers in Nigeria is high turbidity. Turbidity values reported for most rivers in Nigeria were far

greater than 5.0 NTU limit given by WHO (2008). Wakawa *et al*. (2008) reported elevated turbidity values in rivers in Nigeria. This could be linked to run-off effects as well as domestic and industrial discharges on the rivers. Low BOD and COD values have been reported in New Calabar River and Kubanni River in Kaduna. However, a high BOD and COD values have been observed for Challawa River in Kano State with mean concentrations ranging between 10 to 30 mg L^{-1} and 170 to 260 mg L^{-1} respectively (Wakawa *et al.,* 2008). Research has shown that some of the water quality parameters of both ground and surface water often rise during the rainfall with high values of turbidity, solids and anionic species (Mustapha, 2008).

Edet and Worden (2009) assessed seasonal and tidal effects on the physical parameters of river and groundwater in Calabar, Nigeria. The researchers reported a significant seasonal effect on temperature, redox potential (Eh), and DO in the river water. They also observed that a significant tidal influence existed on DO in both river- and groundwater. Comparison between groundwater and river water showed statistically significant difference between EC, TDS, Eh, DO, Na, Cl^- and NO_3^-. The significant differences in EC, TDS, Na and Cl^- were attributed to tidal flushing; the difference in Eh was due to geology of the area while NO_3^- was as a result of anthropogenic pollution. The study concluded that tidal flushing, anthropogenic effects and oxygen supply during recharge contribute to the shaping of water chemistry in the area.

Elevated values of lead have been reported at a sampling site of Alakata stream in Abeokuta, Nigeria. High lead level in surface water may also be due to vehicular deposition. Dry deposition of particulate lead on water bodies is capable of increasing Pb level of surface water. Lead is a potential killer especially in children (Taiwo *et al*., 2010). Taiwo also observed high water quality parameters of a stream in Abeokuta due to

direct discharge of poultry wastes into the stream. The use of pesticides and fertilizer for bumper food production is a well known policy of several governments all over the world. However, agriculture remains the major source of nitrate and phosphate pollution of surface water. Nitrate in drinking water is detrimental to infant health due to the disease known as methemoglobineamia (Taiwo, 2010).

The determination of the physico-chemical characteristics of the lower River Niger and confluence water indicated that pH, turbidity, DO and BOD were 7.42, 42.75.60 NTU, 8.73 mg/L and 2.24 mg/L respectively for river Niger whereas, the confluence water recorded pH, turbidity, DO and BOD of 7.26, 90.25 NTU, 8.15 mg/L and 0.68 mg/L respectively (Zakariya *et al*., 2011). In a similar research, the physico-chemical characteristics of River Benue water at Makurdi was investigated by Akaahan *et al*. (2011) during which pH, TDS, turbidity, conductivity and copper were found to be 5.00 - 9.00, 6.81 - 521.33 mg/L, 3.00 - 258 NTU, 9.90 - 1071.00 µS/cm and 0.00 - 1.45 mg/L respectively.

Enokela and Salifu (2012) evaluated the quality of water at the bank of River Niger in the confluence town of Lokoja used for irrigation on Sarki-noma Fadama Farm. The pH obtained ranged from 6.9 – 7.2. They reported low level of salinity (ECw 250 to 385 s/m). Ions such as Na^{+}, Ca^{2+}, Mg^{2+}, Cl^{-} and SO_4^{2-} were found within the tolerable limit given by WHO. Mohammad *et al*. (2012) in their work in Balu River water Bangladash observed that cobalt concentration was only detectable in March and June. The maximum concentration of cobalt was 53.92 µg/L in March in the location of Kholapara which is higher than the Buriganga River.

A study on water collected at River Niger near the confluence point in Lokoja indicated that the concentration (mg/L) of heavy metals were in the range of: Mn 1.74 -

8.37 (mean 3.85 ± 0.93); Zn 0.98-4.82 (mean 2.72 ± 0.57); Cu 0.58 - 4.50 (mean 2.17 ± 0.73); Cr 0.53 - 4.09 (mean 2.08 ± 1.27); Ni 0.48 - 1.12 (mean 0.78 ± 0.12); Cd 0.02 - 0.13 (mean 0.05 ± 0.02); and Pb 0.01 -0.16 (mean 0.03 ± 0.02). The results showed fairly stable metal concentration in water, with distribution sequence in the order Mn > Zn > Cu > Cr > Ni > Cd > Pb. The mean surface water temperature was 29.35^{o}C with a standard deviation of 2.10. The highest average temperature for the segment of the river studied was 31^{o}C while the lowest average temperature was 21^{o}C. Analysis of variance reveals that there was no statistically significant variation in the water temperature between sampling stations and between months ($p > 0.05$). A circum-neutral pH was observed during the study period, with the highest average value of 7.50 and a lowest of 6.78. The mean ± SD for pH was 7.25 ± 0.23. This observed variation was statistically significant between months ($p < 0.05$) but not between stations ($p > 0.05$). Mean turbidity was highest in the month of March (101.60 NTU) and decreased steadily to June (the last month of the study), with a value of 24.80 NTU. The variations in turbidity varied statistically significant between months ($p < 0.05$) and not between the stations ($p > 0.05$). The mean DO value observed during the study was 8.2 mg/L with a SD of 0.55 mg/L. The highest and lowest DO values observed were 9.25 and 7.20 mg/L respectively. The BOD had a peak value of 2.5 mg/L, a lowest value of 0.10 mg/L and a mean of 1.27 ± 0.76 (Olatunde and Oladele, 2013).

2.5 Pollution of River Sediments

Sediments are composed of different phases (fractions) and metal ions partition between these fractions which include exchangeable, carbonatic, reducible (iron and manganese bound), oxidisable (organic matter bound) and residual fractions. Heavy metals tend to accumulate more in sediments than in water and aquatic organisms. The

incidence of heavy metals in water, bed and suspended sediments of Anyang River, Korea was reported to be more than 99% of the metals being associated with bed sediments. They collected sediments with stainless steel shovels from- eight sampling points on the river, air-dried, sieved and ground before metal determination with X-ray Fluorescence Spectrometer. It was concluded that metal concentrations were a function of particle size and organic matter content as metal concentrations were higher in sediments with higher organic matter content and clay content. More so, they divided sediments in aquatic systems into suspended and bed or bottom sediments which is called sediment in this study (Lee *et al.,* 2003).

Mansour and Sidkey (2003) worked on the heavy metals (cadmium, copper, chromium, lead, zinc etc) contamination of water, fish and sediments from Lake Qarun and Wadi El-Rayan wetland (both in Egypt). Samples of sediments were collected with hand from three points on the lake and two points on the Wadi, dried and digested and run the heavy metals concentrations. It was found that while total heavy metal content of Lake Qarun sediment was 1142 ppm, that of water and Tilapia were 1.42 ppm and 42.8 ppm respectively. Iron was the most abundant metal in the sediments and cadmium least. Biney *et al.* (2004) stated that heavy metals are partitioned between water, sediments, suspended solids and aquatic biota in water bodies. Allison and Allison (2005) reported that metals are partitioned between water and sediments according to a metal partition coefficient, K_d

$$K_d = \frac{\text{Sorbed metal concentrations (mg metal/kg of sorbing material)}}{\text{Dissolved metal concentration (mg metal/litre of solution)}} \qquad 2.2$$

The higher the K_d, the higher the metal concentration in sediments and vice versa.

Contamination of sediments and fauna in aquatic ecosystems of Niger Delta by a wide range of toxic and bio-accumulative metals and hydrocarbons have been reported severally by Ebong *et al.* (2006) and others. The heavy metal pollution of Asa River sediment in Ilorin, Kwara State, Nigeria showed that the metals were in the concentration range of: Mn (179.9 - 69.4 $mgkg^{-1}$), Fe (1998.4 - 4420.4 $mgkg^{-1}$) Cr (3.0 - 11.3 $mgkg^{-1}$), Zn (26.6 - 147.6 $mgkg^{-1}$) and Cu (1.9 - 13.3 $mgkg^{-1}$). Higher enrichment factors (EFs) were calculated for zinc, chromium, manganese and iron in the sediment samples. High values of EFs indicates anthropogenic source of contamination (Adekola and Eleta, 2007).

Elevated levels of Fe, Ni and V have been observed in the sediments of Iko River, a gas flaring station in the Niger Delta areas of Nigeria (Benson and Etesin, 2008). Garcia *et al*. (2009), in an experiment to analyze the distribution of lead, copper and zinc in size fractionated river bed sediments and observed that concentration and bioavailability of heavy metals in sediments increase with decreasing grain size of sediment (a function of particle size).

A study on sediment collected at River Niger near the Confluence point in Lokoja, found the concentrations (mg/kg) of heavy metals in the sediments to be within the ranges of: Zn 36.64 – 96.23 (70.70 ± 10.68); Mn 4.97 - 21.77 (13.24 ± 2.04); Pb 8.84 - 17.52 (12.35 ± 1.14); Ni 2.65 - 18.61 (9.67 ± 2.91) (Olatunde and Oladele, 2013).

2.6 Heavy Metal Accumulation in Fishes

According to Jobling (1994), bioaccumulation is the deposition and storage of toxic chemicals in the tissues of aquatic organisms such that tissue concentrations continue to rise with prolonged exposure to the chemicals. Sex, age, season, spawning periods, choice of food by younger and older fish and variations in pollutant exposures

across fish species may influence uptake, retention and bioaccumulation of contaminants in fish tissues. An experiment on a stretch River Kubanni, Zaria found that the accumulation of zinc and lead by *Oreochromis niloticus, Clarias* and *Alestes* were higher in the dry season than in the rainy season. Also the accumulation of zinc by all three fishes was high and that of lead low. He concluded that *Oreochromis niloticus* may be a better indicator species for monitoring heavy metal concentration in aquatic ecosystem than *Clarias* and *Aleste* (Adakole, 1995).

Tariq *et al.* (1996) reported a positive correlation between heavy metal content in fish and sediment. In an experiment to determine the pollution status of Indus River, Pakistan, they found that in some cases, metal content of fish was high at sites where metal content of sediment was also high. Also, static bioassay exposed *Clarias gariepinus* to two sub-lethal concentration levels (2% and 6% v/v) of tannery effluents. After eight weeks, samples of fish muscles and organs were ashed at $450^{o}C$ and digested with HNO_3 before being analyzed with FAAS. They concluded that metals concentrations were significantly higher in the liver ($P > 0.05$) than other tissues followed by the gill and the gut. The lowest concentrations were found in the muscles (Gbem *et al.*, 2001).

Toxicants enter fish through the body surface, the highly permeable gill epithelial membranes and through ingestion/gastrointestinal absorption. These toxicants are then metabolized and transported to the organs of the fish. The rate at which a chemical is metabolised, detoxified and cleared from the body is a major factor determining the level of bioaccumulation. Since fish bioaccumulate metals, their use as biomonitors has the advantage of allowing the comparison of metal concentrations among sites, where

water samples are near or below the detection limits of the atomic absorption technique (Ikem *et al.,* 2003).

Tukura *et al.* (2005) determined heavy metal concentrations in water, *Clarias gariepinus* and *Tilapia zilli* and found that except for chromium, metal levels were higher in water samples than in fish samples and that zinc and lead were the most bioavailable metals in the gills of both fish species. They concluded that apart from zinc, metal levels were higher in *Tilapia* than in *Clarias*.

Heavy metals accumulate more in the visceral tissues (liver, kidney, intestines etc) than in other organs and least in the muscles. The nutrient and heavy metal (zinc, chromium, copper, nickel and cadmium) concentrations in *Tilapia* and shrimps in tidal shrimp ponds was evaluated and conclusion drawn that all the metals studied accumulated more in the viscera *of Tilapia* but that wasn't the case in shrimp (Cheung *et al.*, 2006).

2.7 Limits for Heavy Metals in Rivers

Many national and international organizations have set standards for heavy metal concentration in river water, fish muscles and sediments. Values for the standards usually depend on what each country considers to be safe limits. However, United Nations bodies like FAO, UNEP and WHO have standards which are meant for worldwide application. Table 2.1 shows the limits set by UNEP, DPR, WHO, MAFF, FAO and USEPA for heavy metal concentration in river water, drinking water, fish muscle and river sediments. It is obvious that substantial differences exist in limits set by United Nations organizations like FAO and country organizations like MAFF. For instance, MAFF limit for Zinc in fish muscle is 50mg/kg while the limit set by FAO is 30mg/kg.

Table 2.1: Limits for Heavy metals in River water, fish muscle and sediments

Metal	Cadmium	Chromium	Copper	Lead	Zinc
UNEP(1999) limits in freshwater (mg/L)	-	<0.05 Total Cr	<1.0	<0.1	<0.5
DPR (1991) freshwater (mg/Lit)	-	-	1.0	0.05	1.0
SON (2003) drinking water (mg/L)	0.03		1.0	0.01	5.0
USEPA Drinking water (mg/L)	0.005	0.1	1.3	0.015	5.0
WHO(1987) Drinking water (mg/L) MDL	0.01	0.01 Cr(VI)	1.0	0.1	5.0 15.0
MAFF limits in fish muscle (mg/kg)	2.0	0.15-1.3	20	2.0	50
FAO(1983) Limits in fish muscle (mg/kg)	0.5		30	0.5	30
SEPA(1997) M limits in sediments (mg/kg) TEL	0.676	-	18.7	30.2	124

MDL= Maximum desirable limits. MPL= Maximum permissible limits. TEL= Threshold effects levels

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

All apparatus and equipment used are listed in appendix I.

3.2 Reagents

All reagents used in this research work were of high analytical grades and are listed in appendix I.

3.3 Preparation of Reagents

All reagents were prepared as described by APHA (1995), Ademoroti, 1996 and Government of India and Netherland Hydrology Project (1999).

3.3.1 Potassium hydrogen phthalate solution (0.05M)

The solution was prepared by dissolving 10.21 g $KHC_8H_4O_4$ in 50 cm^3 deionized water and thereafter diluted to 1000 cm^3 in a volumetric flask.

3.3.2 Borax buffer (0.01M)

This was prepared by dissolving 3.81 g of borax ($Na_2B_4O_7.10H_2O$) in 100 cm^3 freshly boiled and cooled deionized water and made up to 1000 ml with same deionized water in a volumetric flask.

3.3.3 Potassium chloride (0.01M)

The solution was prepared by dissolving 0.75 g of anhydrous potassium chloride in 100.00 cm^3 freshly boiled deionized water and made up to 1000 cm^3 in volumetric flask.

3.3.4 Hydrochloric acid (0.02M)

This was prepared by dissolving 8.30 cm^3 conc. HCl in 100 cm^3 deionized water and making it up to 1000 cm^3 in volumetric flak.

3.3.5 Methyl orange indicator (5%)

Accurately weighed 0.05 g methyl orange indicator was dissolved in 100 cm^3 deionized water.

3.3.6 Manganese sulphate solution

The solution was prepared by dissolving 480 g $MnSO_4.4H_2O$ in deionized water, filtered and diluted to 1000 cm^3.

3.3.7 Alkali-iodide-azide reagent

A 500.00 g NaOH was dissolved in deionized water and diluted to 1000 cm^3 in a volumetric flask. Then 10.00 g $NaNO_3$ was also dissolved in 40 cm^3 deionized water and the two solutions were then mixed together.

3.3.8 Primary standard of sodium thiosulphate solution (0.05M)

This was prepared by dissolving 24.82 g $Na_2S_3O_3.5H_2O$ in 200 cm^3 boiled and cooled deionized water and then made up to 1000 cm^3 with deionized water. Then 5 cm^3 trichloromethane was added as preservative.

3.3.9 Secondary standard of $NaS_2O_3.5H_2O$ (0.0125M)

This was prepared by diluting 250.00 cm^3 of the primary standard to 1000 cm^3 with distilled water.

3.3.10 Potassium dichromate solution (0.0125M)

The solution was prepared by dissolving 1.226 g of dry crystals of potassium dichromate in 100 cm^3 distilled water and made it up to 1000 cm^3 with distilled water in volumetric flask.

3.3.11 Starch solution

Exactly 5.00 g of soluble starch was dissolved in about 800 cm^3 of boiling water with stirring and was then diluted to 1000 cm^3 with distilled water. The mixture was allowed to boil for few minutes after which it was filtered. The solution was then preserved by the addition of 1.25 g salicylic acid.

3.3.12 Phosphate buffer solution

The solution was prepared by dissolving accurately weighed 8.50 g KH_2PO_4, 21.75 g K_2HPO_4, 33.40 g $Na_2HPO_4.7H_2O$ and 1.70 g NH_4Cl 500 cm^3 distilled water and then diluted to 1000 cm^3 with distilled water.

3.3.13 Magnesium sulphate solution

Exactly 22.50 g $MgSO_4.7H_20$ was dissolved in distilled water and made up to 1000 cm^3 with distilled water.

3.3.14 Calcium chloride solution

The solution was prepared by dissolving 27.5 g anhydrous $CaCl_2$ in about 200.00 cm^3 distilled water and finally made up to 1000.00 cm^3.

3.3.15 Cobalt stock solutions

Accurately 2.2032 g anhydrous $CoCl_2$ was dissolved in about 200.00 cm^3 distilled water in a beaker. The content was then transferred into 1000.00 cm^3 volumetric flask and made to mark with distilled water. 1.00 cm^3 =1 mg Co.

3.3.16 Chromium stock solutions

Exactly 2.8285 g of anhydrous $K_2Cr_2O_7$ was dissolved in distilled water and made up to 1000.00 cm^3 with distilled water in a volumetric flask.

3.3.17 Cadmium stock solutions

Exactly 1.6309 g $CdCl_2$ was weighed and dissolved in about 100.00 cm^3 of distilled water in a conical flask. The content was transferred into 1000.00 cm^3 volumetric flask and mark up with distilled water (APHA, 1992).

3.3.18 Lead stock solutions

Exactly 1.5985 g $Pb(NO_3)_2$ was weighed out into a beaker containing about 100.00 cm^3 distilled water. The mixture was shocked and transferred into a 1000.00 ml volumetric flask. Finally, it was made up to the mark with distilled water (Government and Netherland Hydrology Project, 1999).

3.3.18 Zinc stock solutions

This was prepared by dissolving 1.244 g of ZnO in 5.00 cm^3 of water then 25.00 cm^3 concentrated HNO_3 was added and the solution made up to 1000.00 cm^3 with distilled water giving 1000.00 mg/L.

3.3.19 Copper stock solutions

This was prepared by dissolving 3.803 g of $Cu(NO_3)_2.3H_2O$ in 5.00 cm^3 concentrated HNO_3 and made up to 1000.00 cm^3 with distilled water giving 1000.00 mg/L copper solution.

3.4 Study Area

The study area is located at Lokoja, the capital of Kogi State between latitude 7^o49'N to 7^o 8.89'N and longitude 6^o44'E to 6^o5.85'E. Kogi State shares

boundaries with Niger State to the north, Kwara State to the north-west, Nassarawa state to the north-east, Abuja to the north, Anambra to the south, Benue to the east, Ondo to the west, Edo to the south-west, Enugu to the south-east and Ekiti to the West respectively (Areola, 2004).

The annual rainfall of the area is between 1016 mm and 1524 mm with its mean annual temperature not falling below 27 ^{o}C. The rainy season lasts from April to October while the dry season lasts from November to March. The land rises from about 300 meters along the Niger-Benue confluence, to the heights of between 300 and 600 metres above the sea level in the uplands. The flood plains of the Niger and Benue river valleys in Lokoja have the morphic soils which contain a mixture of coarse alluvial and colluvial deposits (Areola, 2004).

The two rivers meet in a contentious partnership. It is commonly said by tourist guides that one of them has a darker shade of brown water and that they never agree. But then, it is a sight any day especially if you take a boat ride right into the meeting point. The confluence point take its water majorly from River Benue and River Niger as shown in Plate 3.1.

3.5 Sampling

The sampling was carried out in nine sampling points as indicated in Figure 3.1. The sampling points were 500 metres apart and the sampling was carried out four times on a quarterly basis for a period of one year. The first, second, third and fourth samplings were carried out in months of March, June, September and December 2013 respectively. Speed boat controlled by an experienced local was used as a means of movement on the water surface as shown in Plate 3.2.

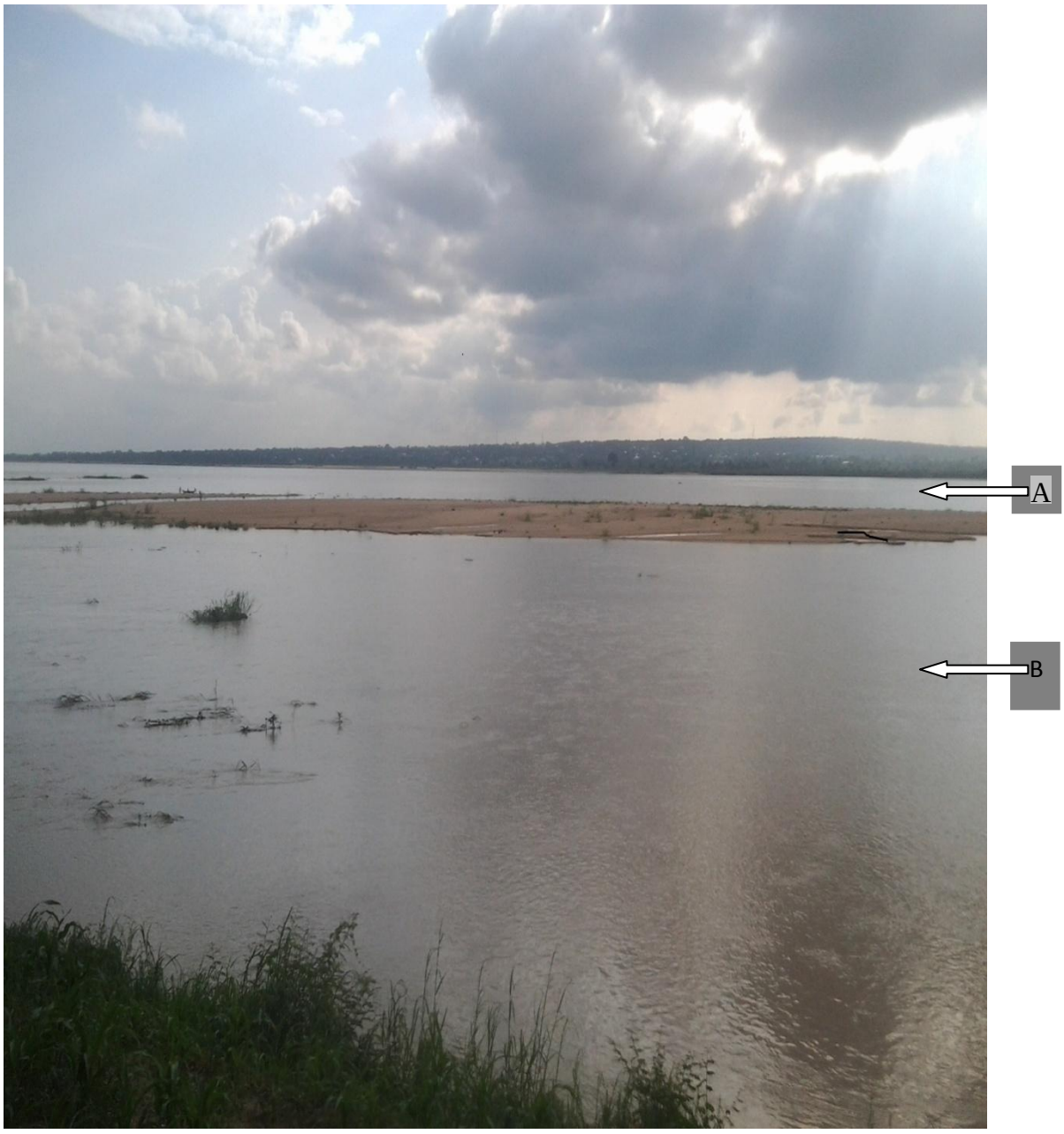


Plate 3.1: A= River Benue and B= River Niger

3.5.1 Water sampling and pretreatment

About 2000 cm^3 of water sample was collected in triplicates at the centre of the river in each of the sampling points. The samples were collected with the aid of an improvised sampler into plastic gallons earlier washed with 1.00M nitric acid and rinsed with deionised water and samples were coded as shown in appendix II.

For analysis of heavy metals, the samples were acidified with HNO_3 in order to keep the required specie and slow down biological change of the water. Typically addition of 20 cm^3 of 2.00M HNO_3 to 2000 cm^3 sample was done to achieve the required aim (Mustapha, 2008).

3.5.2 Sediment sampling and pre-treatment

The samples were collected in triplicates at intervals of 1.00 meter from each other at the banks of each of the sampling points thereby bringing a total of 27 samples and were immediately put in sterilised polythene bags, closed and coded as shown in appendix II. The samples were transported to the M.Sc Laboratory of the Department of Chemistry, Ahmadu Bello University, Zaria. These were later air-dried and stored at 40^oC in an oven prior to analysis.

3.5.3 Fish sampling and pre-treatment

Samples of *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia fish) and *Synodontis nigrita* were purchased at the point of fishing from locals at the sampling site. Fishes of approximate equal sizes for each of the specie were used for this research work. The samples collected were stored under ice bag and transported to the M.Sc Laboratory, Ahmadu Bello University Zaria where they were oven dried at 60^oC.

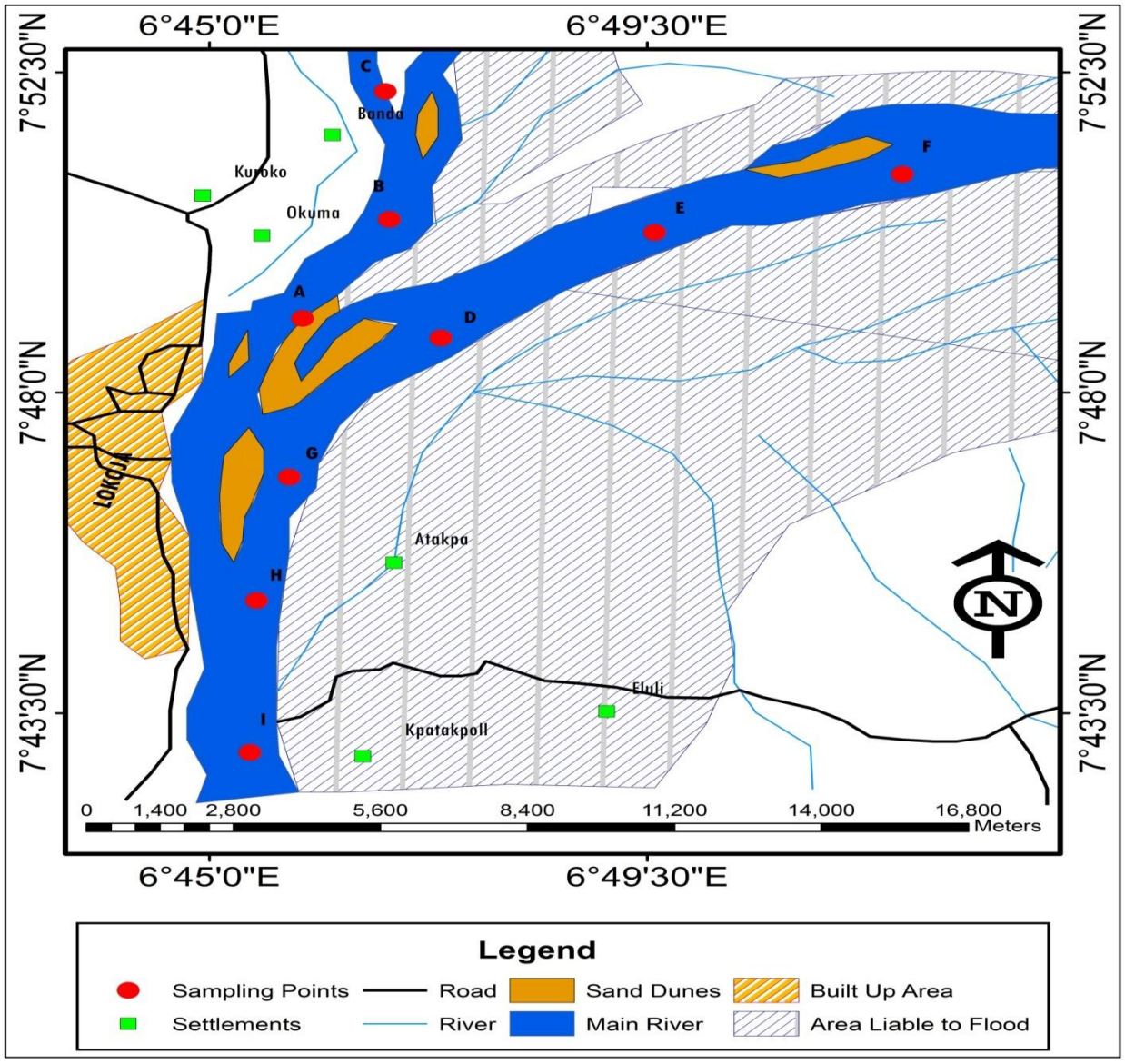


Figure 3.1: Abstract Map of Lokoja Showing Sampling Points

Source: Modified from Topograhic Map of Lokoja Sheet 247 N.E and N.W





Plate 3.2: Sampling Exercise

3.6 Determination of Physicochemical Parameters of Water

3.6.1 Turbidity

The turbidity of the water sample was determined using turbidimeter. About 10 cm^3 of the water sample was shaken thoroughly in order to disperse the solid contents. Air bubbles were allowed to disappear and the water was then poured into the turbidimeter tube and then read the turbidity directly after five minutes (APHA, 1992).

3.6.2 Total dissolved solids

Clean evaporating dish was dried at 103 – 105 ^oC in an oven until constant weight was achieved. The dish was cooled to room temperature in a desiccator. About 100 cm^3 of the water sample was evaporated to dryness using the dish on a steam bath. The outside of the dish was wiped and the residue in an oven was further heated for about 1 hour at 103 – 105^oC. The dish was then transferred into a desiccator, and the content cooled to constant weight. The weight of the dish was then subtracted from the constant weight of the mixture to obtain the weight of the total solid and TDS finally calculated using equation 1 (AOAC, 1998).

$$\text{Total dissolved solids (mg/L)} = \frac{mg\ total\ solids \times 1000}{100} \qquad 3.1$$

3.6.3 pH

The pH of the water sample was also determined *in-situ* with the help of HANNA portable pH meter. The pH meter was first standardised with potassium hydrogen phthatlates (pH 4.0) and borax buffer (pH 9.2) in order to check for proper instrument response. After the standardization, the electrodes of the meter were inserted into about 200 cm^3 of the water sample and allowed for about 5 minutes for stability. The pH of the water sample was then recorded (APHA, 1992).

3.6.4 Electrical conductivity

This was measured using a conductivity meter (ID: 1.10 version 2). The conductivity cell was rinsed with at least three portions of 20 cm^3 of 0.01M KCl solution and the resistance and temperature of the fourth portion was measured. The cell constant K_c was computed using the equation 2.

$$K_c = \frac{1412}{K_{KCl}} \times [0.0191(t - 25) + 1] \quad 3.2$$

where K_c is the cell constant, K_{KCl} is measured conductance and t is observed temperature of standard KCl solution.

The cell was thereafter rinsed with aliquot portions of sample. The temperature of the sample was then adjusted to about 25^0C and the sample conductivity recorded and EC finally calculated using equation 3.

$$\text{Electrical conductivity (mS/cm)} = \frac{C_M \text{ X Kc}}{0.0191\ (t-25)+1} \quad 3.3$$

where K_c is the cell constant, C_m is measured conductance of the sample (mS/cm) and t is observed temperature of sample (^{0}C) (APHA, 1992).

3.6.5 Hardness

About 25.00 cm^3 sample of water was diluted to 50.00 cm^3 with distilled water and 1.00 cm^3 of ammonium chloride buffer added to give a pH of 10.0 to 10.1. Thereafter, 2 drops of Eriochrome black T indicator was added and titrated with EDTA titrant to colour change from reddish tinge to blue. About 7.00 cm^3 of sample was added to the above mixture and completed titration within 5 minutes after buffer addition. The EDTA titrant was standardized against standard calcium solution using the above procedure and total hardness computed using equation below.

$$\text{Total hardness mg } CaCO_3/L = \frac{A\ x\ B \times 1000}{ml\ sample} \quad 3.4$$

where A is cm^3 EDTA titrated for sample and B is mg $CaCO_3$ equivalent to 1.00 cm^3 EDTA titrant (Indian and Netherlands Government, 1999).

3.6.6 Dissolve oxygen

The DO of the sample was determined using modified Winkler's method. About 200.00 cm^3 water sample was measured out into BOD bottle and Stoppard. The stopper was removed and added 1.00 cm^3 of $MnSO_4$ followed by the addition of 1.00 cm^3 alkali – azide reagent. The pipette tip was held just below the liquid surface touching the side of the bottle. The stopper was returned carefully and excluded air bubbles. The mixture was mixed by inverting the bottle a few times. The brown manganese hydroxide floc was allowed to settle to approximately half the bottle volume. Then, 1.00 cm^3 conc. H_2SO_4 was added and re-stoppered and mixed as above. About 201.00 cm^3 of the mixture was titrated with $Na_2S_2O_3$ solution using 2 drops of starch indicator and finally calculated the concentration of DO using equation 5 (AOAC, 1998)

$$\text{DO (mg/L)} = \frac{V \times M}{0.025} \qquad 3.5$$

where V is cm^3 of thiosuphate solution used and M is molarity of thiosuphate titrant.

3.6.7 Chemical oxygen demand

This was determined using titrimetric method. About 0.40 g $HgSO_4$ was placed in refluxing flask follow by the addition of 20.00 cm^3 of the water sample. About 10.00 cm^3 standard $K_2Cr_2O_7$ solution was added and 20 glass beads previously dried added at 600 ^0C for 1 hour. Slowly and with gentle swirling, 30.00 cm^3 Ag_2SO_4 - H_2SO_4 solution was added and connected the flask to a condenser. A blank mixture was prepared and thereafter refluxes the mixtures for 2 hours and cool. The condenser was rinsed with distilled water into the flask and diluted to about 150.00 cm^3. The cooled mixture was

titrated with standard ferrous ammonium sulphate (FAS) using 3 drops of ferroin as the indicator and COD computed using equation 6 (AOAC, 1998)

$$\text{COD (mg/L)} = \frac{(V_b - V_a) \times M \times 16{,}000}{ml\ sample} \quad 3.6$$

where V_b is cm^3 FAS used for blank, V_a is cm^3 FAS used for sample and M is Molarity of FAS.

3.6.8 Biological oxygen demand

Dilution water was prepared by adding 1.00 ml each of phosphate buffer, magnesium sulphate, calcium chloride and iron (III) chloride solution to about 200.00 cm^3 distilled water in order to saturate it with DO. The water sample was then treated by adding 1.00M NaOH solution to a pH of 7 follow by addition of 0.0125M Na_2SO_3 in order to decolourize the sample. Two sets of 30% of the sample were prepared using the dilution water earlier prepared. Each of the diluted samples was poured in BOD bottles in duplicates with the aid of a pipette. The initial DO of one of the sets was determined immediately and recorded as DO_o. The blank and the other set of the diluted sample were incubated for 5 days in an incubator at 20^oC. The DO of the incubated sample and the blank were determined thereafter and recorded as DO_d. The BOD of the sample was then computed using the equation 7 (APHA, 1992).

$$\text{BOD} = \frac{\text{DOo} - \text{DOd}}{\text{Dilution Factor}} \quad 3.7$$

where Dilution factor is number of days divided by ml of sample

3.8 Preparation of Calibration Curves

Six working standard solutions were prepared for each metal by serial dilution of stock solution. These standards and the blank solution were aspirated in VARIAN AAS

240FS, measured their absorbance. Then the calibration curves of absorbance versus concentrations of each heavy metal were plotted.

3.9 Digestion of Samples

3.9.1 Digestion of water sample

Exactly 100.00 cm^3 of water sample was measured into 250.00 cm^3 beaker and added 20.00 cm^3 conc. HNO_3 followed by few pieces of Chips to prevent splashing of mixture. The mixture was boiled slowly and evaporated on a hot plate to about 20.00 cm^3 in volume. Heating and addition of concentrated HNO_3 was continued until a light coloured, clear solution was obtained. The digest was removed and filtered hot into 100.00 cm^3 volumetric flask and finally made up to mark with distilled water. It was then poured into a plastic bottle and labeled appropriately for the heavy metal determination. Triplicate digestion of each sample was carried out together with the blank. The digestion was done in a fume cupboard as shown in Plate 3.3 (APHA, 1992).

3.9.2 Digestion of sediment samples

The dried sediment sample was ground into fine powder and sieved with 2 mm mesh sieve. 1.00 gram of the dried powered sediment sample was placed in a clean 100 cm^3 beaker followed by the addition of 20.00 cm^3 concentrated HCl, 5.00 cm^3 concentrated HNO_3 and 2.00 cm^3 con. HF. The mixture was then heated to boil for one hour, filtered hot and made up to the mark with distilled water in 50.00 cm^3 volumetric flask and finally transferred into 100.00 cm^3 plastic bottle and labeled appropriately for heavy metal determination. Triplicate digestion of each sample was carried out together with the blank (Maitera *et al*., 2011).

3.9.3 Digestion of fish sample

The dried fish samples were separated into organs (bones, flesh, and brain). About 10.00 g of each of the organ was pre-ashed with 5.00 cm^3 concentrated HNO_3 in a hot plate for 10 min. The pre-ashed sample was ashed in Murfle furnace overnight (16 hours) at a temperature of 525^oC and cool in a desiccator. The ash was dissolved in 10.00 cm^3 concentration HNO_3 and transferred into 100.00 cm^3 volumetric flask and diluted to the mark with de-ionized water. The digest was labeled and used for heavy metal measurement. Six samples for each of the organs of the fish species were prepared and read their concentrations in each of the sampling periods. A blank of same chemical composition but without the sample was prepared (Okafor and Opuene, 2006).

3.10 Wavelength, Current, Burner Height and Slit width of Measurement

The characteristic wavelength of absorption of each metal used in the analysis and other instrumental parameters are given in the Table 3.1

3.11 Statistical Analysis of Results

1. Data obtained were statistically analyzed using Statistical Analysis System (SAS) package in which their means were computed and their standard deviations separated using Duncan Multiple Range Test.
2. Analysis of Variance (ANOVA) was used to explain the discrepancies in the levels of heavy metals of water and sediments from the various rivers as well as organs of the three studied fish species.
3. Student t- test was used in ranking means of heavy metals in the water, sediment and fishes for levels of significant at 95% confident level







Plate 3.3: Digestion and AAS Measurement Exercise

Table 3.1: AAS Instrumental Parameters for Heavy Metals

Metal	Wavelength (nm)	Lamp Current (mA)	Gas mixture	Flow rate	Slit width (mm)	Burner Height (mm)
Cd	336.5	5	Acetylene	2.3	5	4
Co	324.8	3	Acetylene	2.3	3	4
Cr	228.8	4	Acetylene	4.0	4	4
Cu	279.5	8	Acetylene	2.3	3	4
Pb	283.3	5	Acetylene	1.5	7	5
Zn	213.9	3	Acetylene	2.4	5	4

4. Pearson Correlation Coefficient (r) was used to determine degree of linear relationship between two rivers and the confluence at the different sample collection periods as described by Uba *et al*. (2008). Where r is a dimensionless index that ranges from -1.0 to +1.0 inclusive. If there is a perfect linear relationship with positive slope between the two variables, a correlation coefficient of 1 is obtained and a correlation coefficient of -1 is obtained if there is an perfect inverse relationship the two variables. A correlation coefficient of 0 means that there is no linear relationship between the variables.
5. The pollution state of the sediments from the two rivers and the confluence were determined using Contamination/Pollution Load and Geoaccumulation indices as described by Tomlinson *et al*. (1980) and Boszke *et al*. (2004) respectively by the use of the equations below.

(a) Pollution Load Index (PLI) $= 6\sqrt{(CF1 \times CF2 \times CF3 \times CF4 \times CF5 \times CF6)}$ 3.8

where CF = Contamination factor which is concentration of metal divided by background value.

Background values are world average concentration of such metal. Background values used as reported for Shale by Bervoets and Blust (2003) are: Cd (0.3 mg/kg), Co (12.0 mg/kg), Cr (17.0 mg/kg), Cu (17.0 mg/kg), Pb (14.0 mg/L) and Zn (67 mg/kg).

(b) Geoaccumulation Index (I_{geo}) $= \log 2(Cn / 1.5 * Bn)$ 3.9

where C_n is the measured concentration of metal and B_n is the background value of the metal which is given in equation 3.8.

The classification of the degree of contamination as described by Hakanson (1980) is shown in Table 3.2.

Table 3.2 Degree of Contamination/Pollution Classification

Pollution Load Index		
Class	Range	Remark
1	<0 – 0	No pollution
2	0 – 1	Low degree of pollution
3	1 – 2	Moderate degree of pollution
4	2 – 4	High degree of pollution
5	4 – 8	Very high degree of pollution
6	8 – 16	Extremely high degree of pollution
Geoaccumulation Index		
0	$I_{geo} \leq 0$	Unpolluted
1	$0 < I_{geo} < 1$	low to moderately polluted
2	$1 < I_{geo} < 2$	Moderately polluted
3	$2 < I_{geo} < 3$	Moderately to highly polluted
4	$3 < I_{geo} < 4$	Highly polluted
5	$4 < I_{geo} < 5$	Highly to extremely polluted
6	$5 < I_{geo} < 6$	Extremely polluted

CHAPTER FOUR

4.0: RESULTS

4.1: Physicochemical Parameters of Water Samples

The plot of the mean values of BOD for water samples obtained from River Niger, Benue and after their Confluence point with respect to sampling periods is presented in Figure 4.1. The BOD ranges from 9.23-7.82, 10.34-7.01, 15.59-10.29 and 7.36-5.56 mg/kg for the months of March, June, September and December respectively. Figure 4.2 shows mean values of COD of water samples which ranges from 141.73-121.45, 134.18-112.72, 134.07-114.98 and 115.43-98.25 mg/kg for the months of March, June, September and December respectively. Conductivity of the water samples from the rivers as depicted in Figure 4.3 falls in the ranges of 131.16-109.69, 198.03-156.15, 233.39-291.41 and 88.19-65.61 µs/cm for the months of March, June, September and December respectively. Figure 4.4 shows the mean values of DO of the water samples for the months of March, June, September and December with corresponding ranges of 4.28-2.26, 7.49-5.23, 14.39-11.14 and 7.09-5.17 mg/kg respectively. Total hardness of the water samples is depicted in Figure 4.5 with means in the ranges of 189.07-158.57, 192.07-145.91, 245.83-221.30 and 57.06-48.85 mg/kg for the months of March, June, September and December respectively.

The mean values of pH of the water samples is displayed in Figure 4.6 and is found in the ranges of 8.07-6.85, 7.61-6.81, 7.64-6.77 and 7.71-6.88 for the months of March, June, September and December respectively. Similarly, the mean values of TDS are presented in Figure 4.7 with corresponding ranges of 591.35-509.49, 781.75-668.00, 721.61-682.18 and 486.19-457.91 mg/kg for the months of March, June, September and

December respectively. Furthermore, turbidity of the water samples obtained from River Niger, River Benue and after the Confluence point with respect to sampling periods are presented in Figure 4.8 and falls in the ranges of 12.38-10.02, 18.66-14.34 23.13-19.68 and 6.50-5.33 N.T.U for the months of March June September and December respectively. For further information, data for BOD, COD, conductivity, DO, total hardness, pH, TDS and turbidity are presented in Appendix III, IV, V, VI, VII, VIII, IX and X respectively.

4.2: Heavy Metal Concentrations in Water Samples

The concentrations of Cd for water samples obtained from River Niger, River Benue and after the Confluence point with respect to sampling periods are presented in Figure 4.9 with means in the ranges of 0.0276-0.0220 0.0191-0.0162, 0.0208-0.0154 and 0.0244-0.0082 mg/L for the months of March, June, September and December respectively. Figure 4.10 depicts the mean concentrations of Co in the water samples which falls within the ranges of 0.0179-0.0160, 0.0130-0.0104 0.0160-0.0081 and 0.0114-0.0042 mg/L for the months of March, June, September and December respectively. Similarly, the concentrations of Cr are shown in Figure 4.11 which had mean values in the ranges of 0.1391-0.1049, 0.0973-0.0693 0.0986-0.0650 and 0.0776-0.0376 mg/L for the months of March, June, September and December respectively. Figure 4.12 shows the mean concentrations of Cu in the water samples from the rivers with respect to sampling period. Cu is found to fall in the ranges of 1.8037-1.0533, 1.2311-0.7434, 1.0576-0.2068 and 1.1532-0.0979 mg/L during the month of March, June, September and December respectively. More so, Figure 4.13 shows the mean values of Pb in the water samples with respect to sampling period. During the months of March, June, September and December, Pb was found in the ranges of 0.0047-0.0003,

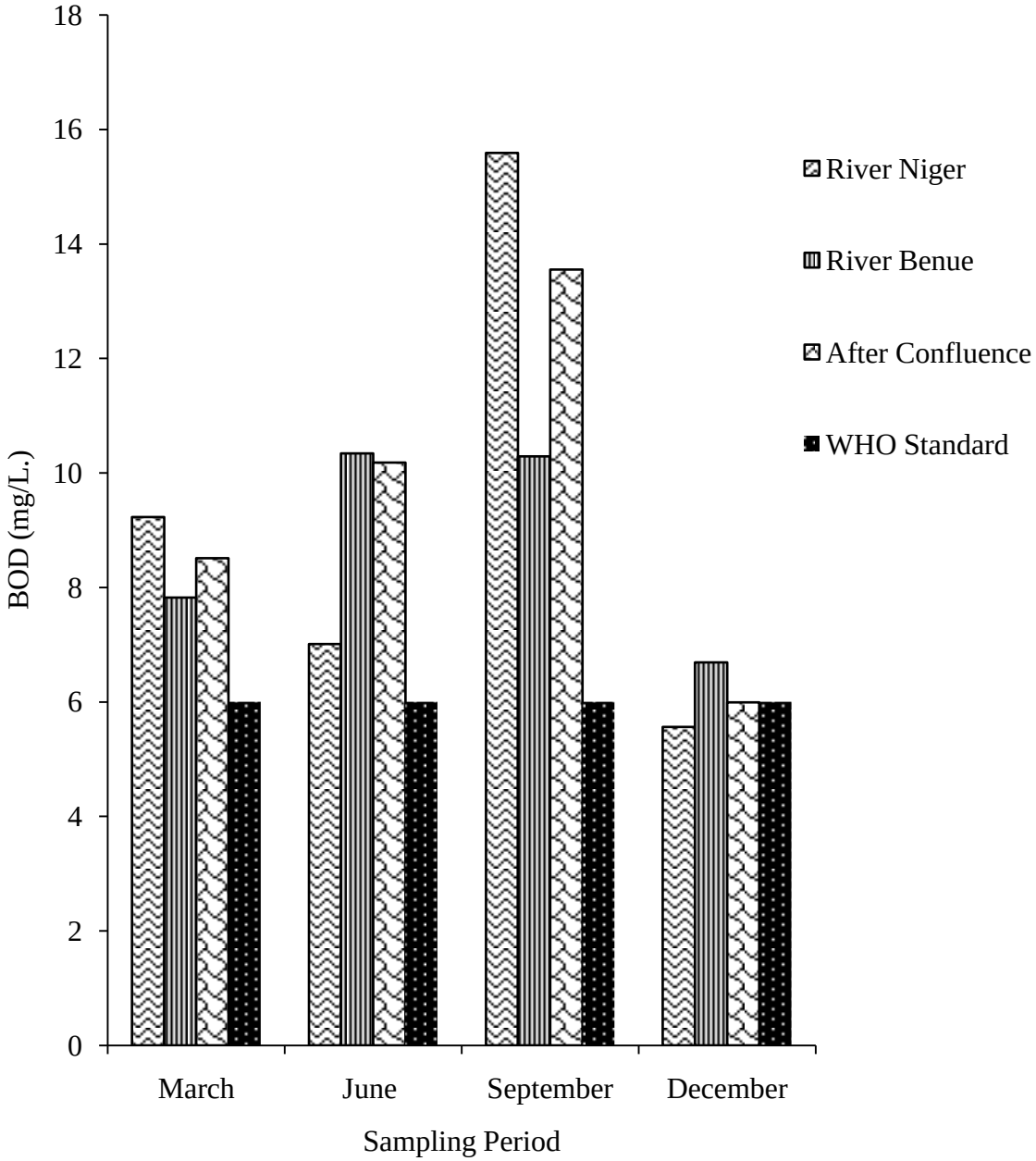


Figure 4.1: BOD of Water Samples from the Rivers with Respect to Sampling Period

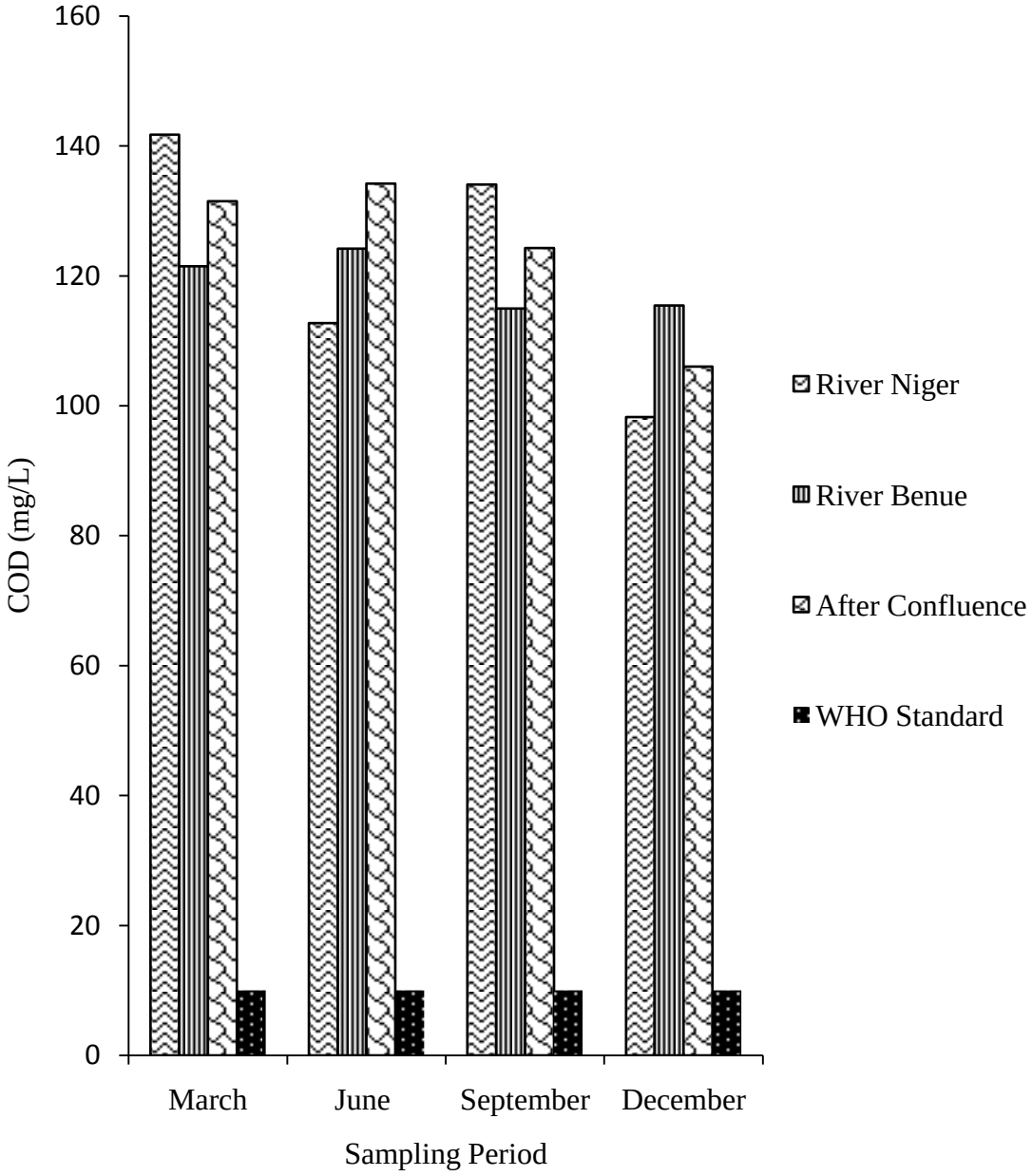


Figure 4.2: COD Values of Water Samples from the Rivers with Respect to Sampling Period

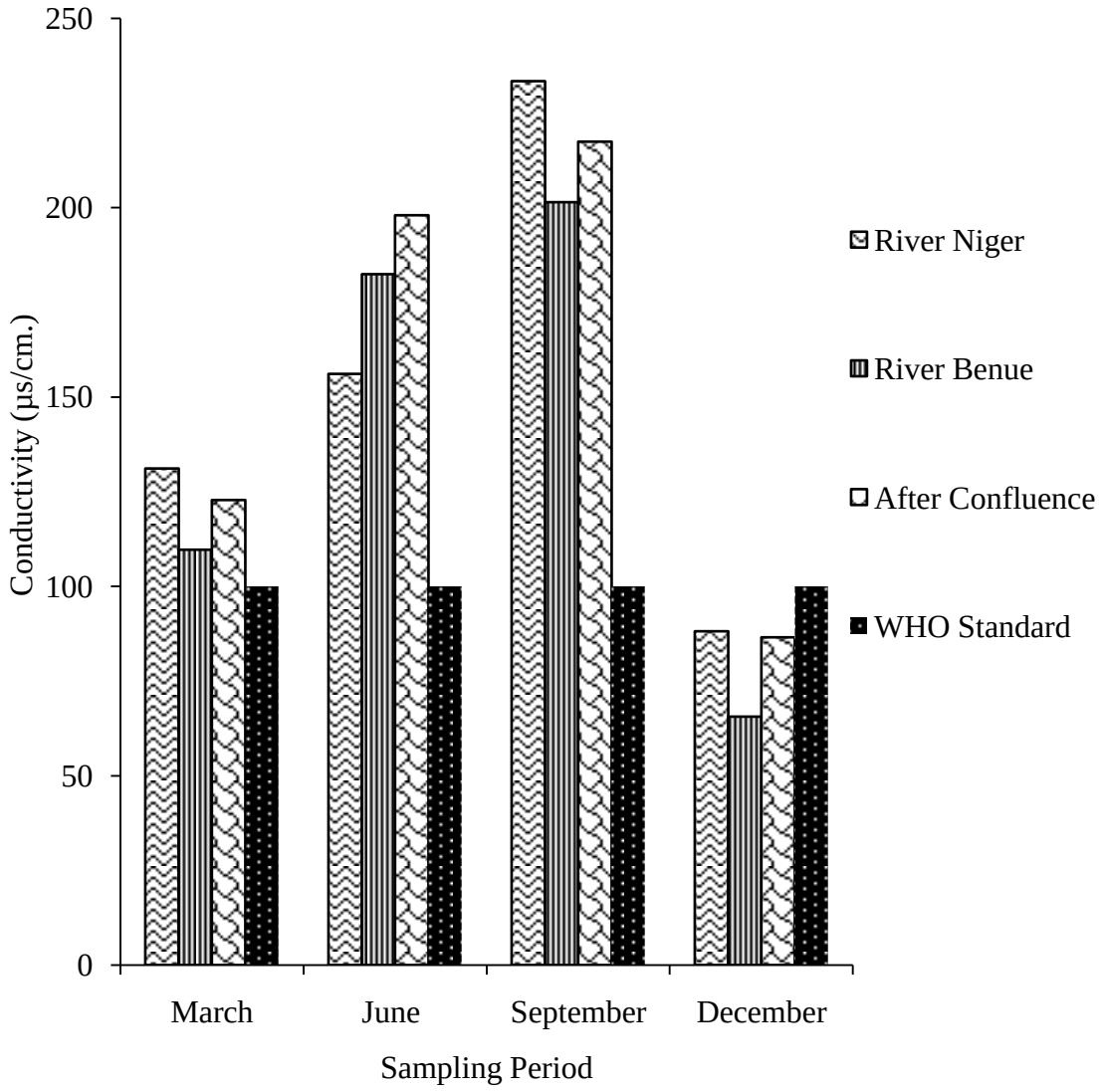


Figure 4.3: Conductivity Values of Water Samples from the Rivers with Respect to Sampling Period

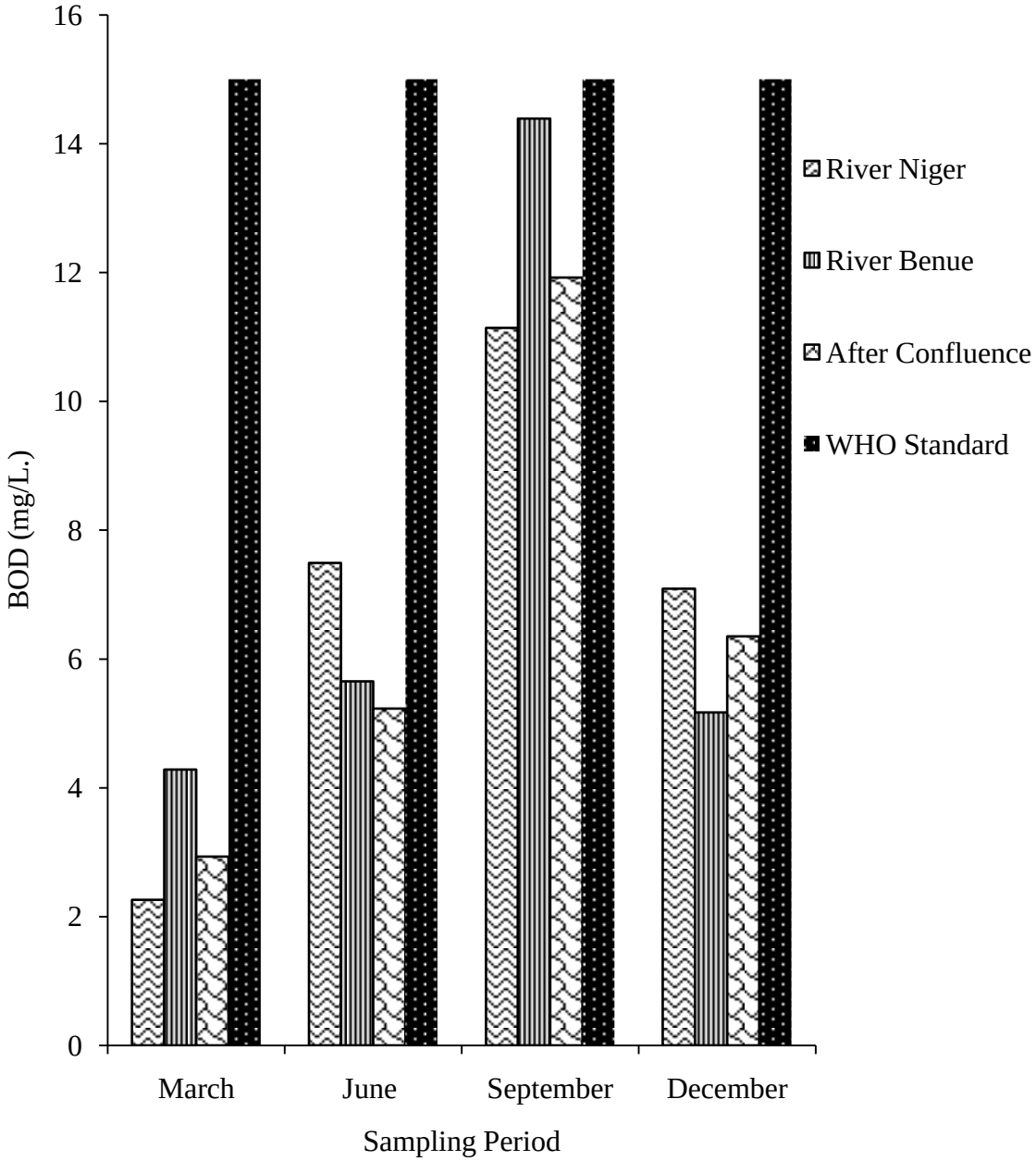


Figure 4.4: DO of Water Samples from the Rivers with Respect to Sampling Period

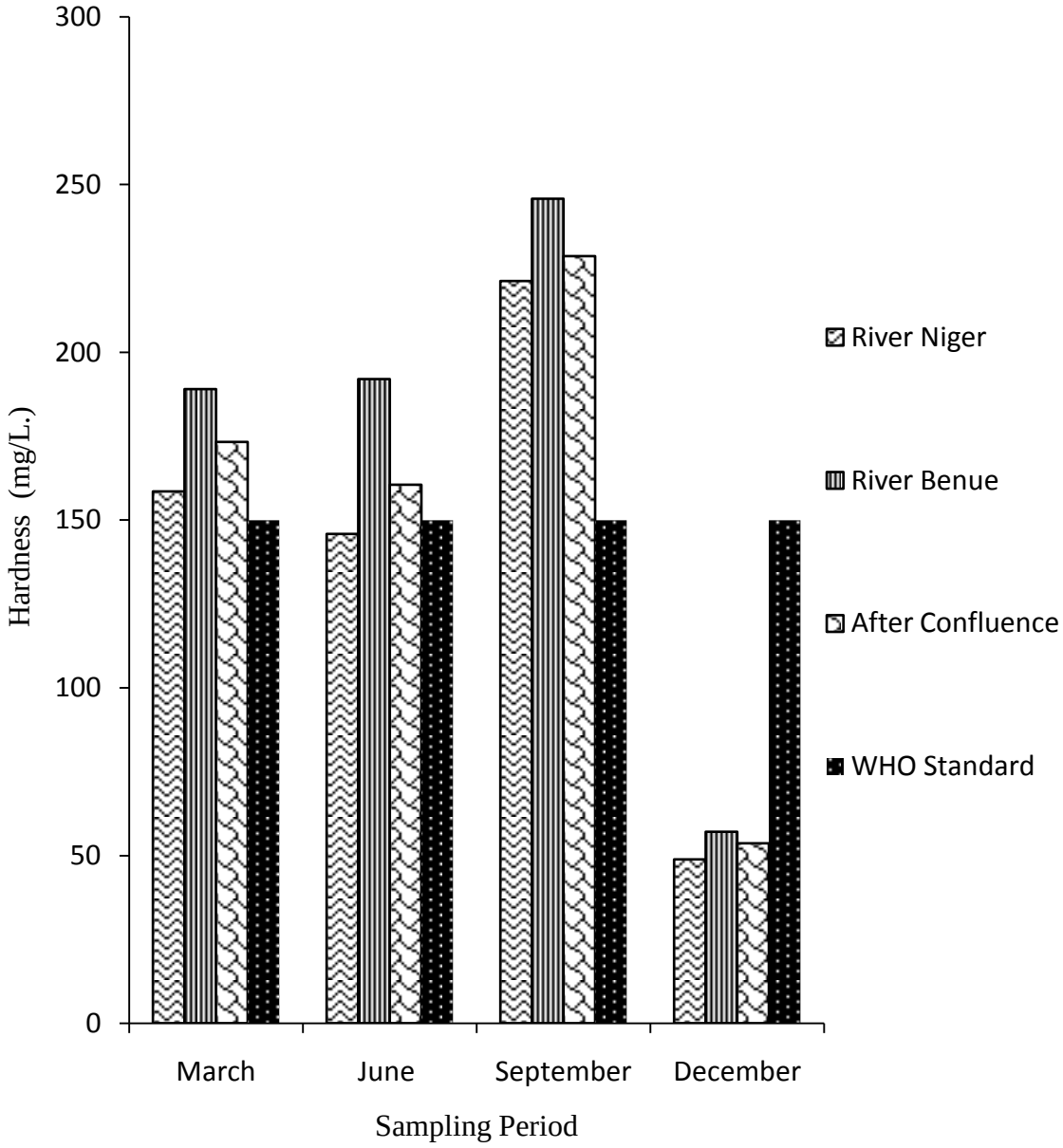


Figure 4.5: Hardness of Water Samples from the Rivers with Respect to Sampling Period

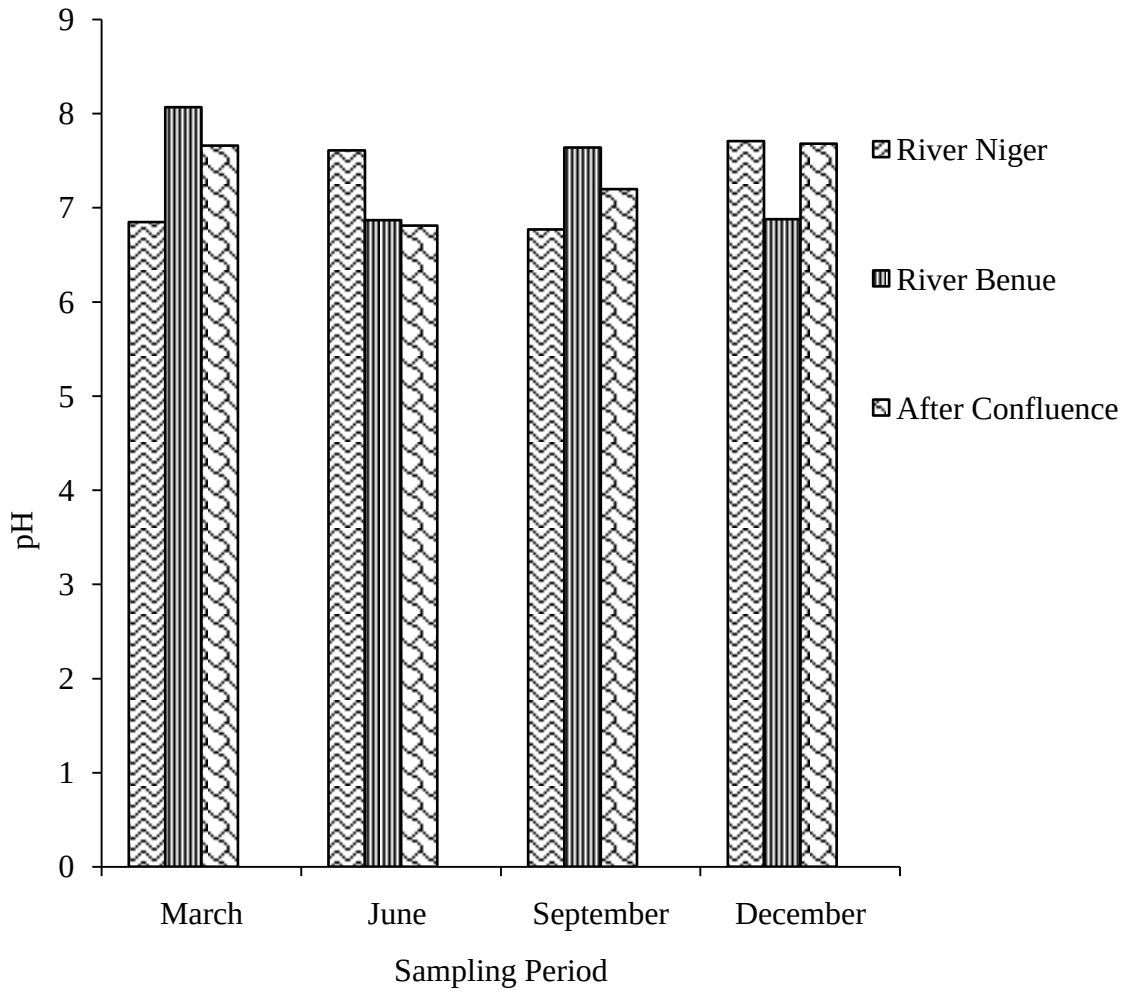


Figure 4.6: pH Values of Water Samples from the River with Respect to Sampling Period

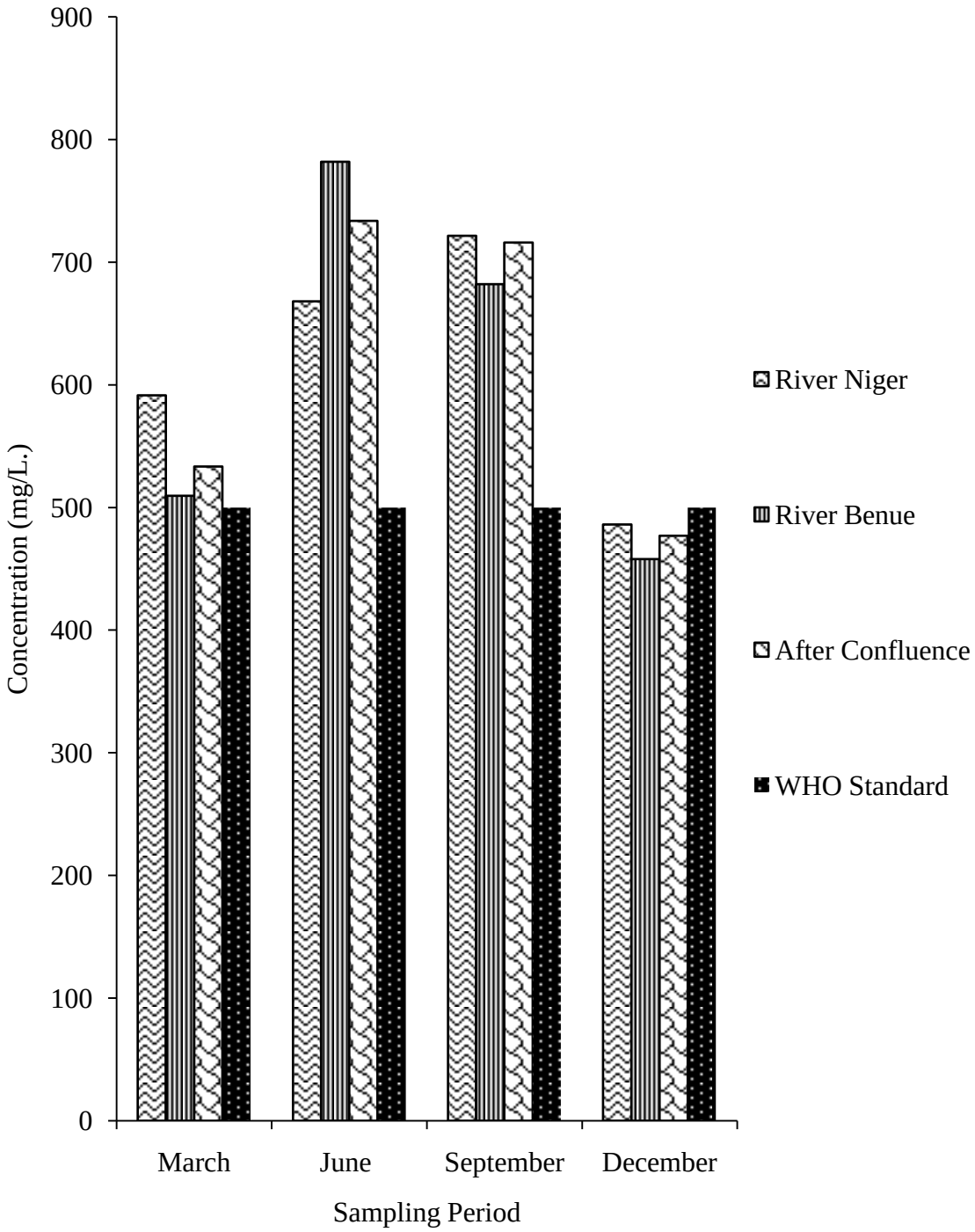


Figure 4.7: TDS of Water Samples from the Rivers with Respect to Sampling Period

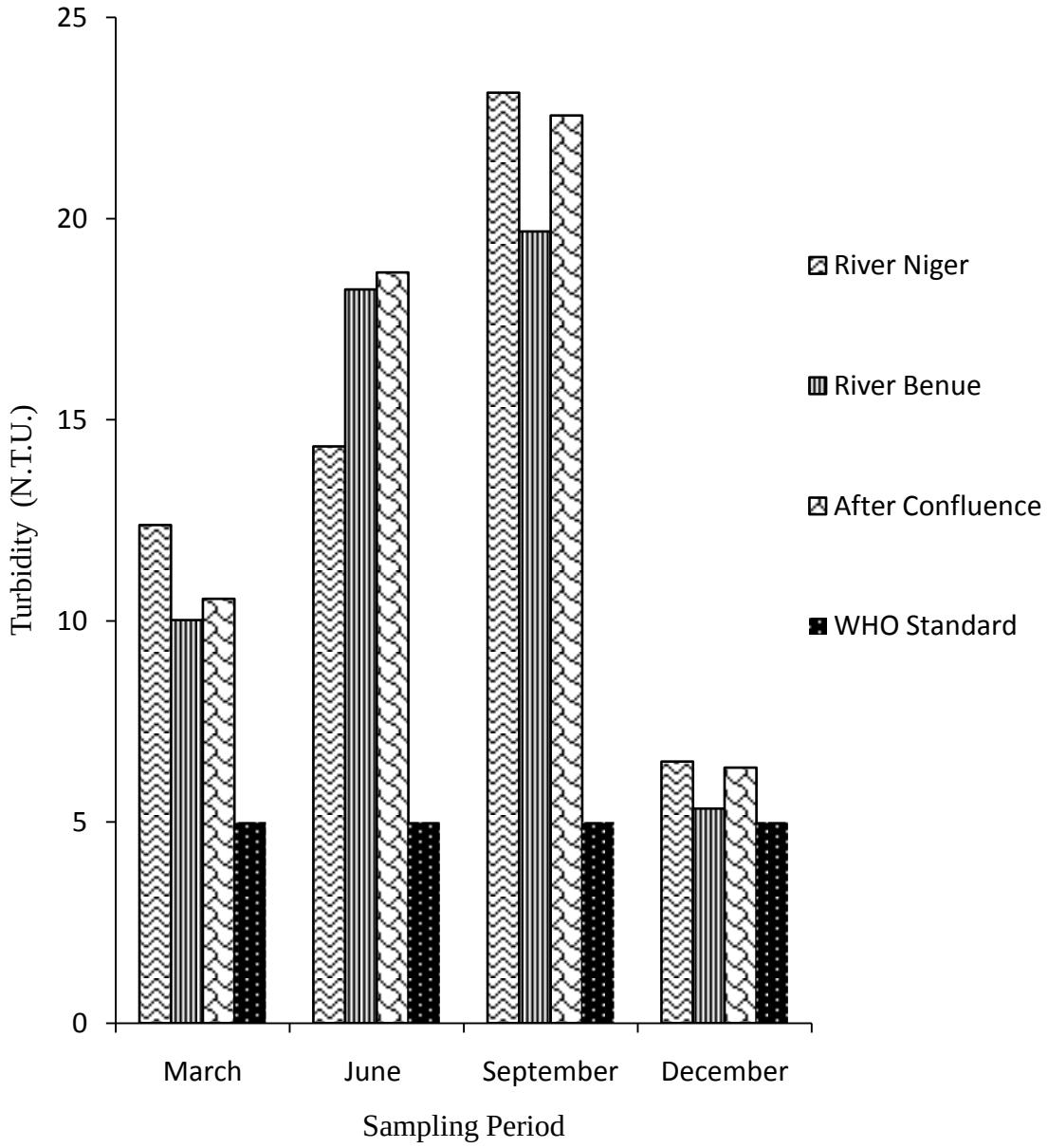


Figure 4.8: Turbidity of Water Samples from the Rivers with Respect to Sampling Period

0.0007-0.0003, 0.0014-0.0004 and 0.0007-0.0006 mg/L respectively. Lastly, Figure 4.14 shows the concentrations of zinc in the water samples which falls in the ranges of 2.8510-1.2850, 1.2136-1.0673, 1.0957-0.7671 and 0.9244-0.8054 mg/L for the months of March, June, September and December respectively. Data used for charts of Cd, Co, Cr, Cu, Pb and Zn are displayed in Appendix XI, XII, XIII, XIV, XV and XVI accordingly.

4.3: Pearson's Correlation Matrices of the Physicochemical Parameters with Heavy Metals in Water Samples

The Pearson correlation coefficients of the physicochemical parameters with the heavy metals in the water samples obtained from River Niger, River Benue and after the confluence point with respect to sampling periods are presented in Table 4.1, 4.2, 4.3 and 4.4 for the months of March, June, September and December 2013 respectively.

4.4: Heavy Metal Concentrations in the Sediment Samples from River Niger, Benue and after the Confluence Point

The concentrations of Cd for sediments obtained from River Niger, River Benue and after the Confluence point with respect to sampling periods are presented in Figure 4.15 with means in the ranges of 2.0203-1.3990, 1.1789-0.5502, 0.7883-0.4683 and 0.7944-0.2026 mg/kg for the months of March, June, September and December respectively. Figure 4.16 depicts the mean concentrations of Co in the sediments samples which falls within the ranges of 24.5330-3.1973, 18.7789-2.4426, 20.5421-2.2638 and 12.3172-2.1567 mg/kg for the months of March, June, September and December respectively. Similarly, the concentrations of Cr in the sediment samples are shown in Figure 4.17 which had mean values in the ranges of 33.0976-20.9292, 23.1660-14.9216, 27.4687-17.6063 and 22.9794-131767 mg/kg for the months of March, June, September and December respectively. Figure 4.18 shows the mean concentrations of Cu in the sediment samples from the rivers

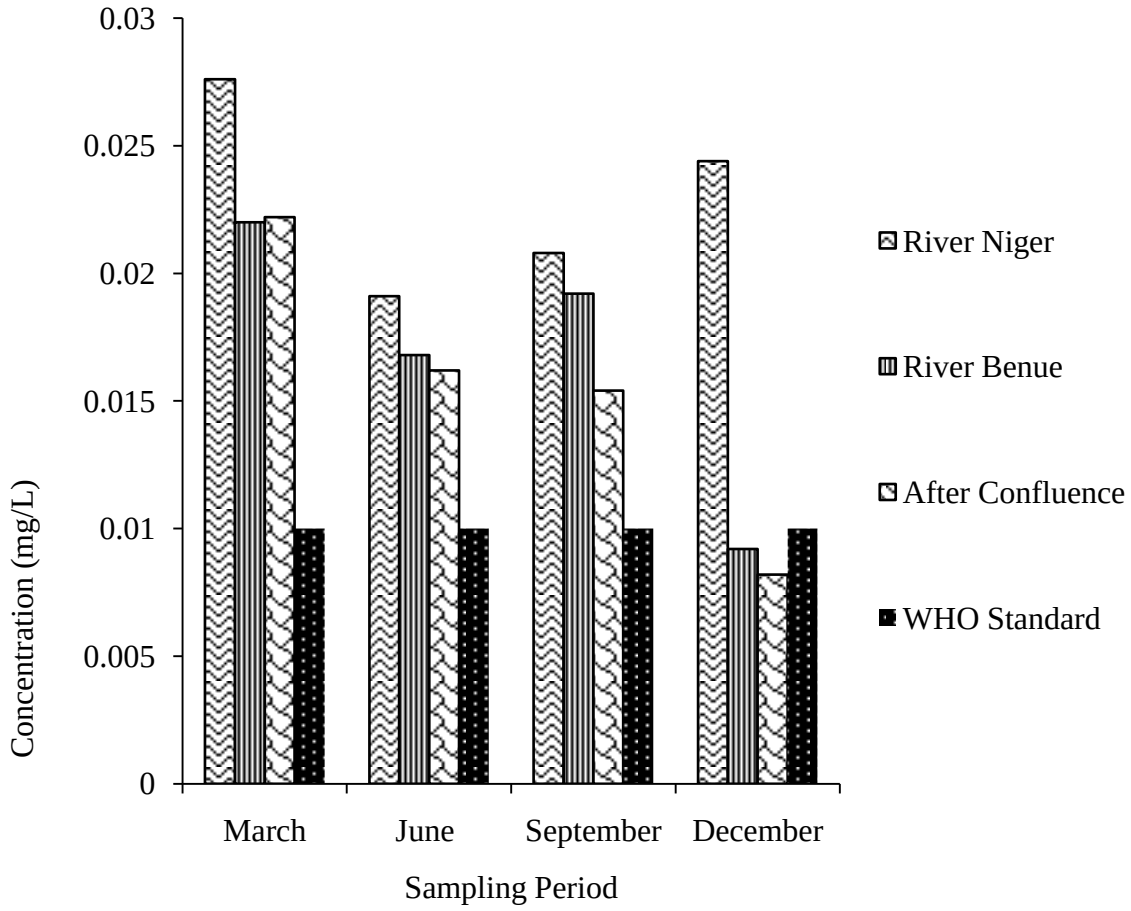


Figure 4.9: Concentrations of Cd in the Water from the River Versus Sampling Period

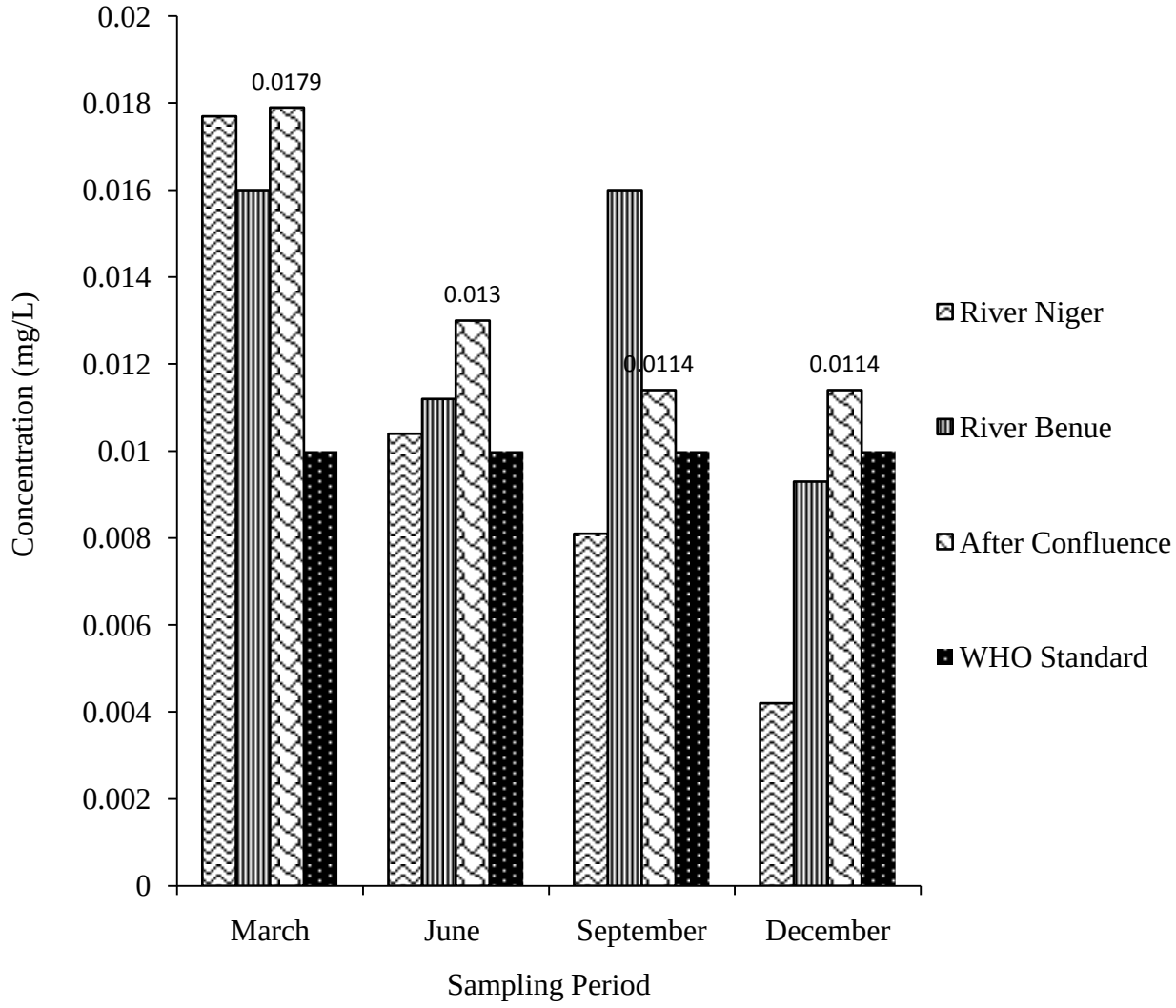


Figure 4.10: Concentrations of Co in Water Samples from the Rivers Versus Sampling Period

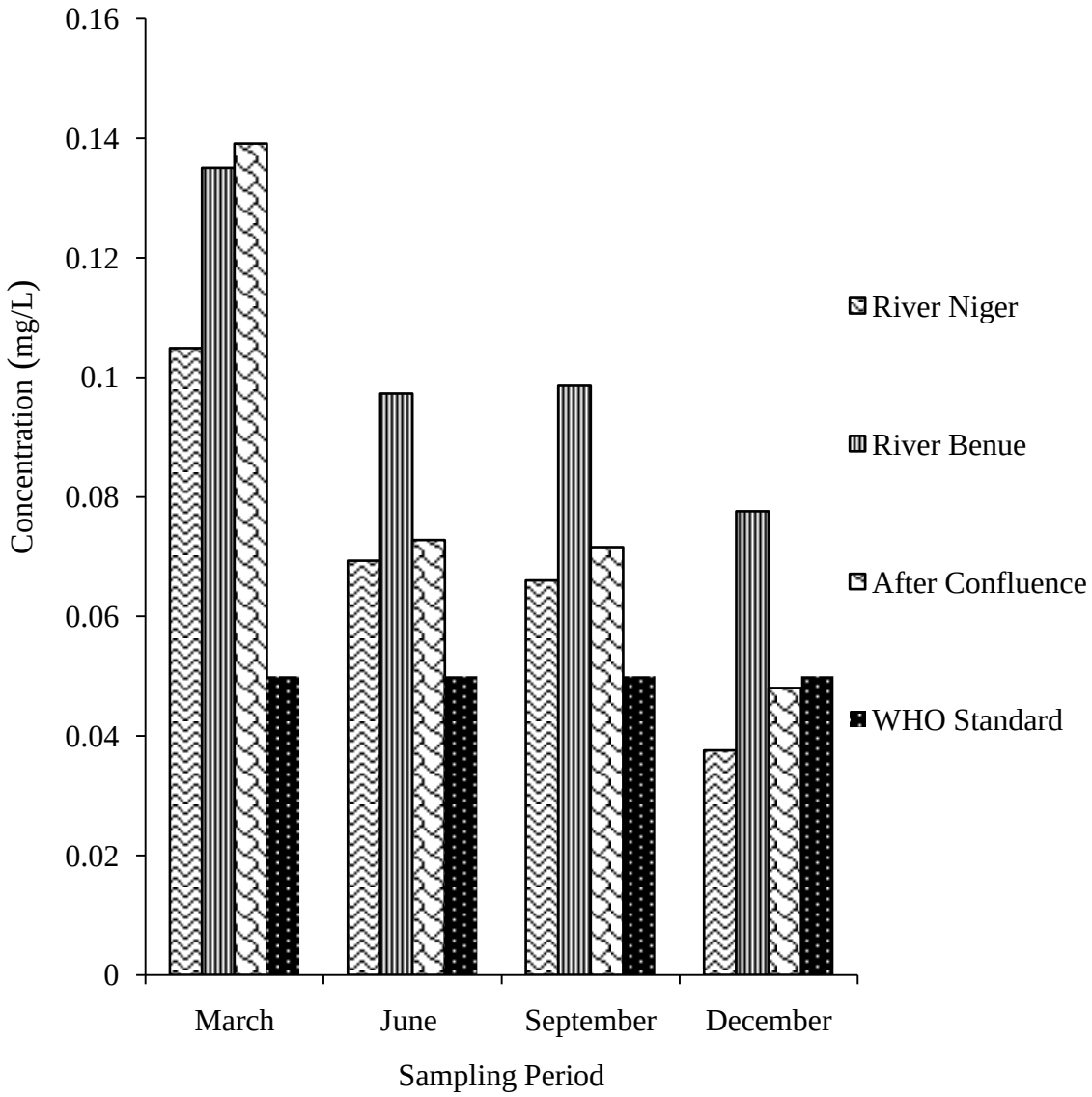


Figure 4.11: Concentrations of Cr in Water Samples from the Rivers Versus Sampling Period

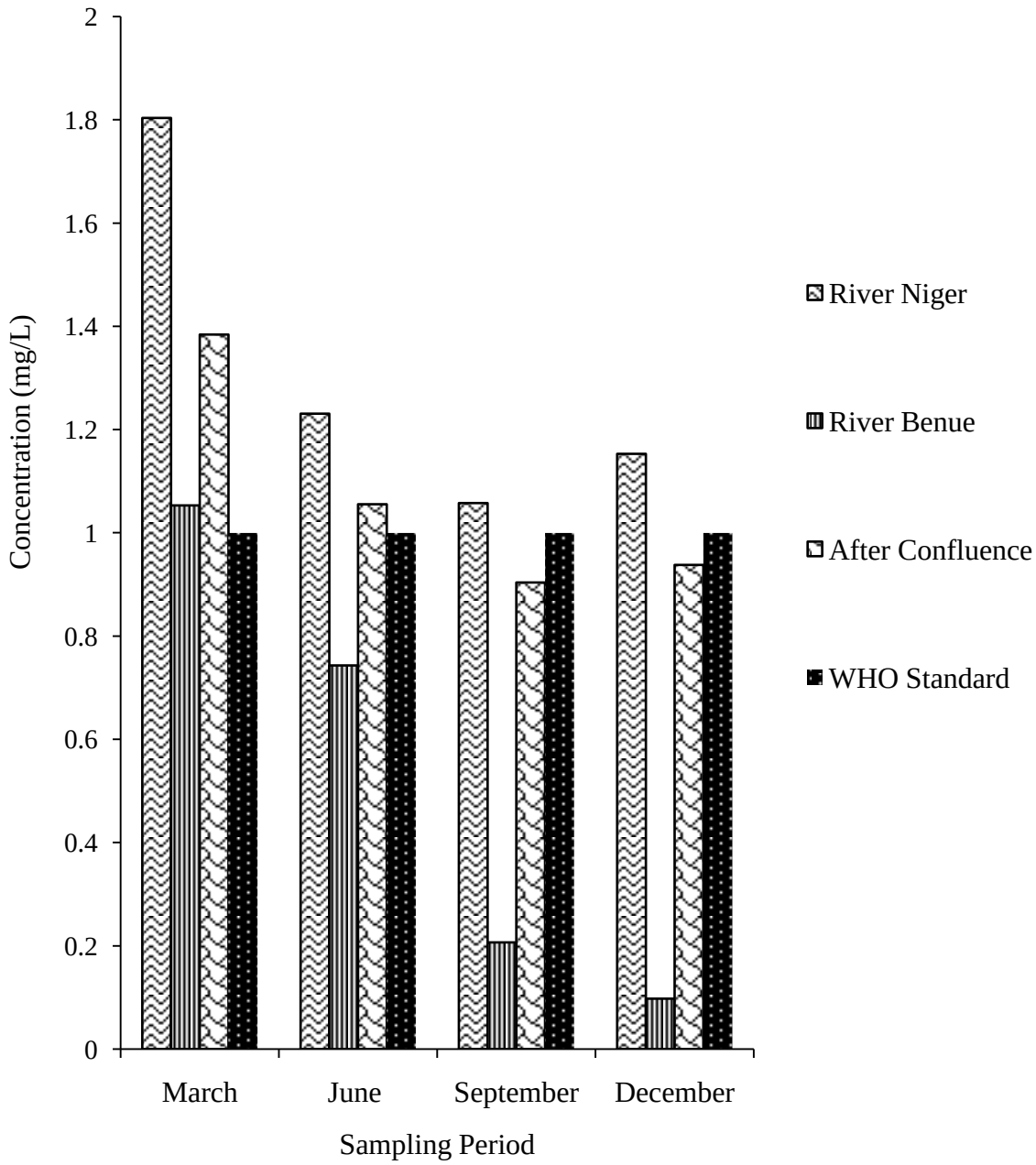


Figure 4.12: Concentrations of Cu in Water Samples from the Rivers Versus Sampling Period

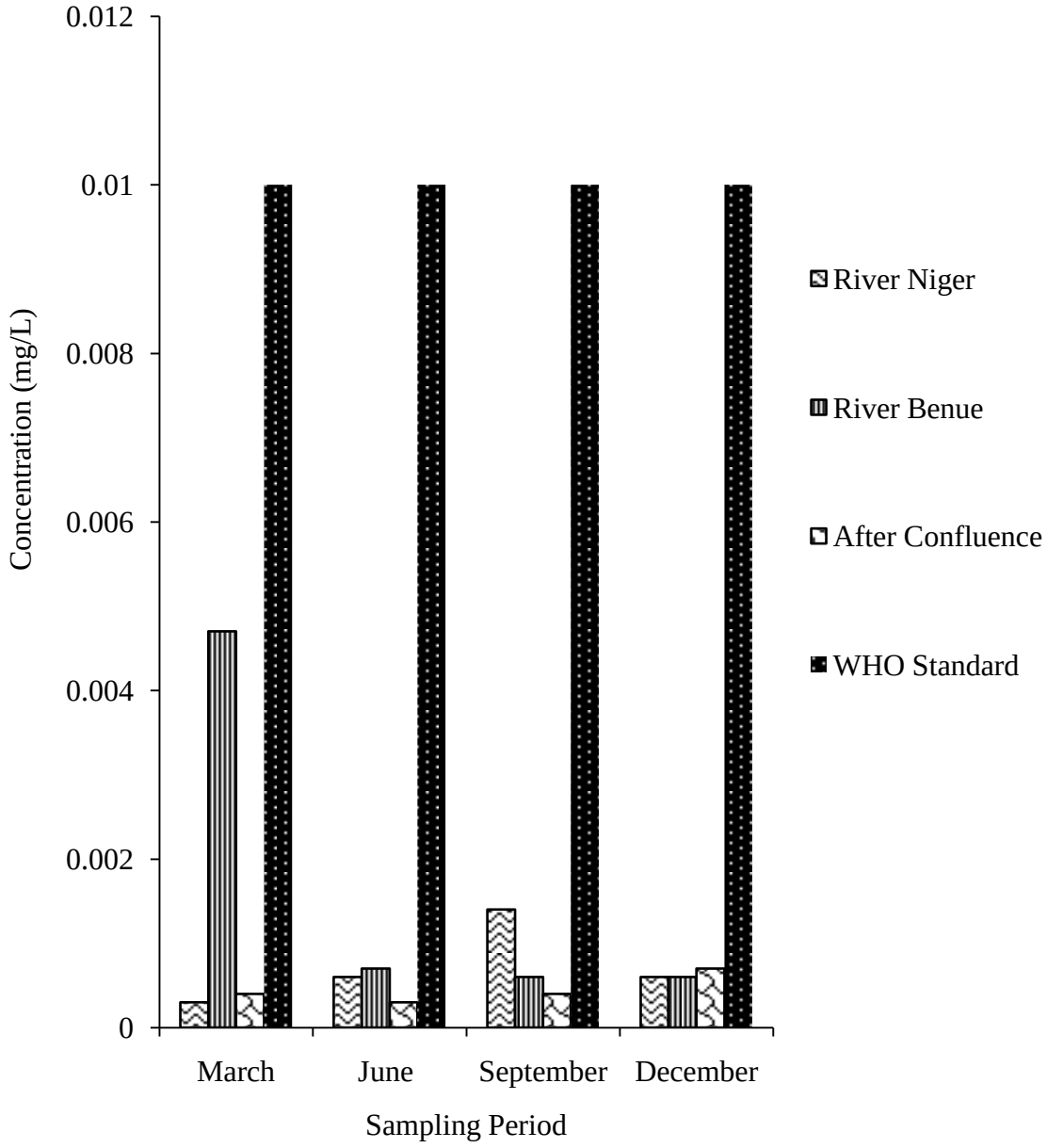


Figure 4.13: Concentrations of Pb in Water Samples from the Rivers Versus Sampling Period

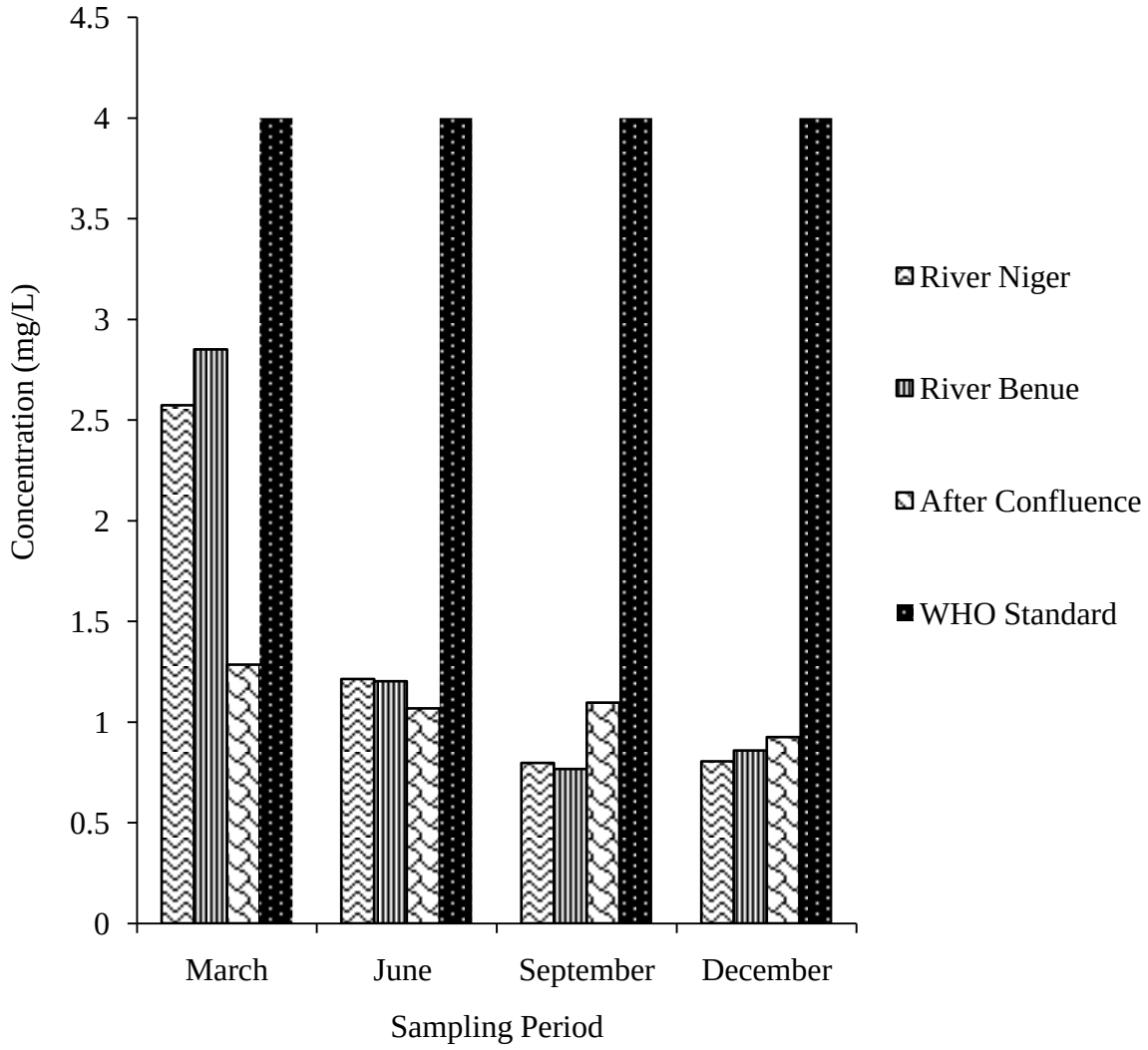


Figure 4.14: Concentration of Zn in Water Samples from the Rivers Versus Sampling Period

Table 4.1: Pearson Correlation Matrices of Physicochemical Parameters with Heavy Metals in Water Sample (March Sample)

	COD	DO	Turb	BOD	TDS	Hd	Ct	pH	Cd	Co	Cr	Cu	Pb	Zn
COD	1													
DO	-.947**	1												
Turb	.772**	-.713**	1											
BOD	.909**	-.884**	.817**	1										
TDS	.762**	-.667**	.868**	.739**	1									
Hd	- .592**	.473*	- .346	.509**	- .472*	1								
Ct	.714**	-.779**	.559**	.747	.508**	-.235	1							
pH	-.707**	.735**	-.638**	-.731**	-.563**	.197	-.902**	1						
Cd	-.360	.268	-.104	-.179	-.241	.330	-.169	.087	1					
Co	-.132	-.132	-.282	-.247	-.268	.111	-.029	.062	.141	1				
Cr	.205	-.279	.182	.188	.192	-.026	.207	-.218	-.103	-.227	1			
Cu	-.575**	.599**	-.527**	-.525**	-.507**	-.400*	-.333	.323	.065	-.024	-.264	1		
Pb	.703**	.703**	.748**	.663**	.785**	-.387*	.523**	-.684**	-.044	-.118	.062	-.551**	1	
Zn	.013	.020	.285	.092	.176	-.095	.048	-.172	.529	-.041	-.369	-.126	.367	1

**. Correlation is significant at 0.01 level (2-tailed) , *. Correlation is significant at 0.05 level (2-tailed)
Turb= Turbidity, Hd= Hardness, Ct= Conductivity

Table 4.2: Pearson Correlation Matrices of Physicochemical Parameters with Heavy Metals in Water Sample (June Sample)

	COD	DO	Turb	BOD	TDS	Hd	Ct	pH	Cd	Co	Cr	Cu	Pb	Zn
COD	1													
DO	-.710**	1												
Turb	.210	-.124	1											
BOD	.824**	-.835**	.198	1										
TDS	.330	-.232	.866**	.330	1									
Hd	-.026	-.159	.230	.140	.413*	1								
Ct	.224	-.186	.748**	.107	.700**	.328	1							
pH	-.249	.468*	-.234	-.413*	-.217	-.275	-.136	1						
Cd	.030	-.084	-.056	.036	.040	.152	-.013	-.436*	1					
Co	.409*	-.178	-.080	.265	-.091	-.229	.053	-.324	.354	1				
Cr	-.170	.424*	-.165	-.397*	-.173	-.568**	-.126	.415*	.071	.010	1			
Cu	.131	-.087	.468*	.199	.569**	.442*	.451*	-.238	.114	-.143	-.155	1		
Pb	.001	.026	-.193	-.074	-.086	-.130	-.181	.184	-.145	-.187	.337	-.082	1	
Zn	.083	-.094	.046	.064	.029	.032	.033	-.308	.643**	.168	-.010	.102	.207	1

**. Correlation is significant at 0.01 level (2-tailed) , *. Correlation is significant at 0.05 level (2-tailed)
Turb= Turbidity, Hd= Hardness, Ct= Conductivity

Table 4.3: Pearson Correlation Matrices of Physicochemical Parameters with Heavy Metals in Water Sample (September Sample)

	COD	DO	Turb	BOD	TDS	Hd	Ct	pH	Cd	Co	Cr	Cu	Pb	Zn
COD	1													
DO	-.898**	1												
Turb	.527**	-579**	1											
BOD	.813**	-.828**	.731**	1										
TDS	.471*	-.530**	.952**	.699**	1									
Hd	-.284	.476*	-.595**	-.561**	-.589**	1								
Ct	.605**	-.623**	.368	.734**	.368	-.378	1							
pH	-.606**	.645**	-.305	-.639**	-.326	.337	-.895**	1						
Cd	.156	.038	-.122	-.122	-.118	.251	.039	-.138	**1**					
Co	.297	-.305	.328	.403*	.210	-.402*	.305	-.358	.096	1				
Cr	.294	-.365	.245	.466*	.235	-.416*	.237	-.300	-.079	.337	1			
Cu	-.531**	.458*	-.598**	-.760**	-.552**	.437*	-.587**	.506**	.019	-.339	-.594**	1		
Pb	-.112	.118	-.112	-.159	-.186	-.105	-.319	.363	.134	.097	.001	.072	1	
Zn	.022	-.195	.235	.087	.214	-.232	.201	-.173	.044	.273	-.053	.178	.039	1

**. Correlation is significant at 0.01 level (2-tailed) , *. Correlation is significant at 0.05 level (2-tailed)
Turb= Turbidity, Hd= Hardness, Ct= Conductivity

Table 4.4: Correlation Matrices of Physicochemical Parameters with Heavy Metals in Water Sample (December Sample)

	COD	DO	Turb	BOD	TDS	Hd	Ct	pH	Cd	Co	Cr	Cu	Pb	Zn
COD	1													
DO	-.913**	1												
Turb	-.230	.241	1											
BOD	.675**	-.770**	-.770**	1										
TDS	-.177	.278	.416*	-.435*	1									
Hd	.144	-.054	-.150	.017	-.105	1								
Ct	-.298	.381	.699**	-.445*	.520**	-.303	1							
pH	-.134	.208	.347	-.373	.356	-.156	.616**	1						
Cd	.207	-.233	-.301	.125	-.312	.420*	-.505**	-.287	**1**					
Co	-.089	.093	.422*	-.167	.336	-.339	.534**	.522**	-.256	1				
Cr	-.433**	.427*	.222	-.396*	.301	-.565**	.637**	.474*	-.266	.423*	1			
Cu	.471*	-.516**	-.044	.498**	-.299	.345	-.481*	-.464*	.377	-.293	-.767	1		
Pb	.001	.058	.066	.171	-.208	-.277	.002	-.205	-.183	-.091	-.011	.073	1	
Zn	.062	.075	-.204	-.066	.022	.224	.100	.444*	-.078	.424*	.028	-.070	-.114	1

**. Correlation is significant at 0.01 level (2-tailed) , *. Correlation is significant at 0.05 level (2-tailed)
Turb= Turbidity, Hd= Hardness, Ct= Conductivity

with respect to sampling period. Cu is found to fall in the ranges of 23.4040-12.4617, 18.3080-8.5043, 14.4762-9.5483 and 10.2413-7.0832 mg/kg during the month of March, June, September and December respectively. More so, Figure 4.19 shows the mean values of Pb in the sediment samples with respect to sampling period. During the months of March, June, September and December, Pb was found in the ranges of 2.5593-0.7160, 0.8501-0.1914, 0.8980-0.1069 and 0.5089-0.1054 mg/kg respectively. Lastly, Figure 4.20 shows the concentrations of zinc in the sediment samples which falls in the ranges of 32.8418-22.4001, 24.0666-15.4673, 17.7769-14.1794 and 16.0028-13.6941 mg/kg for the months of March, June, September and December respectively. Data used for charts of Cd, Co, Cr, Cu, Pb and Zn are displayed in Appendix XVIII, XIX, XX, XXI, XXII and XXIII respectively. The charts also compare the values obtained with their respective standards recommended by regulatory bodies.

4.5: Pollution Load and Geoaccumulation Indices of Sediment

The pollution load index (PLI) of heavy metals in the sediment samples obtained from River Niger, River Benue and immediately after the Confluence point with respect to the sampling periods are presented in Table 4.5. River Niger had a pollution load index of 1.0248, 0.6967, 0.6423 and 0.4985 during the months of March, June, September and December respectively. River Benue in the other hand had pollution load index of 0.6094, 0.3051, 0.2631 and 0.2088 for the months of March, June, September and December respectively. The pollution load index of sediment at the Confluence for the months of March, June, September and December are 0.7213, 0.4428, 0.4141 and 0.2990 respectively.

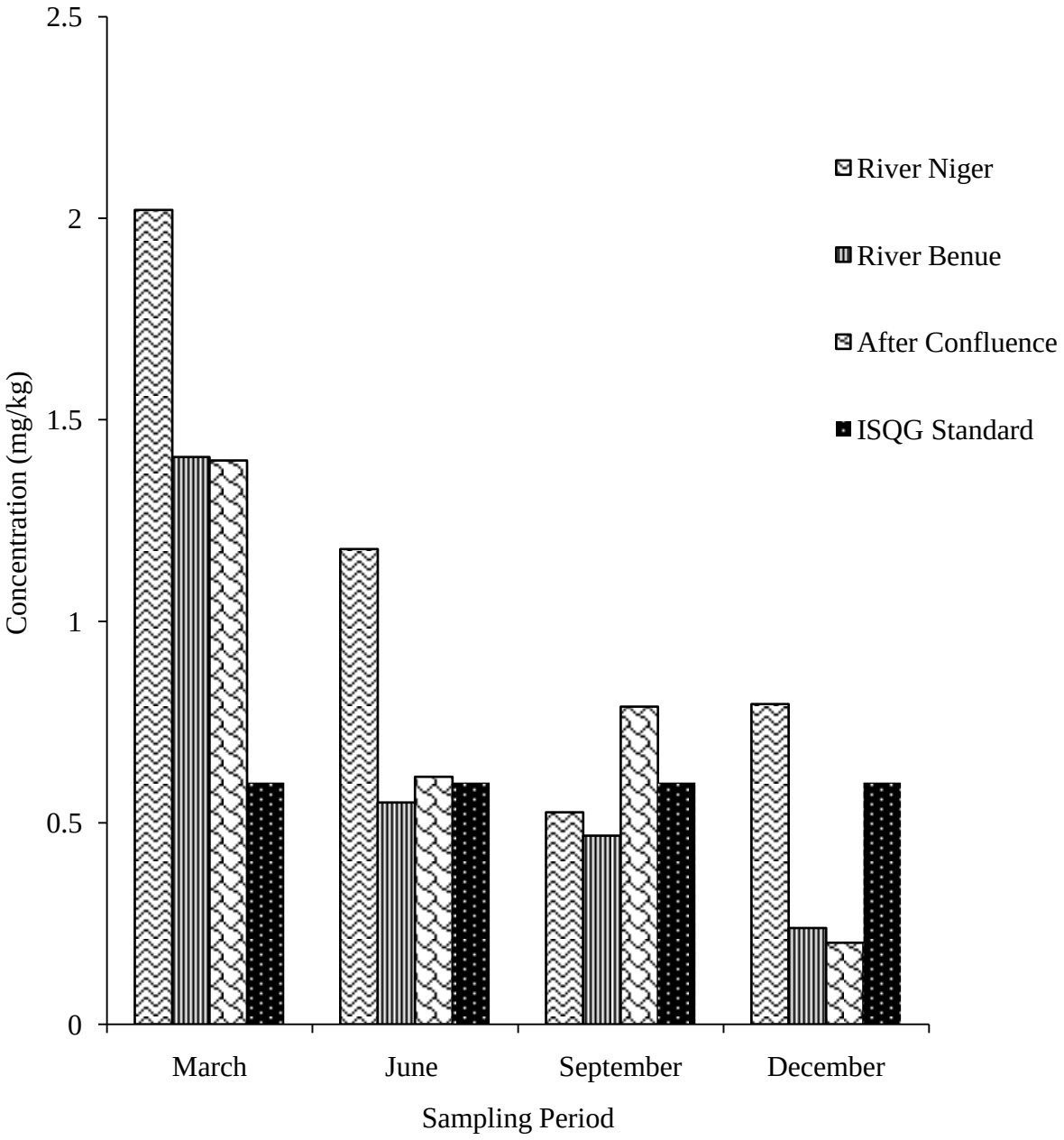


Figure 4.15: Concentrations of Cd in the Sediments from the Rivers Versus the Sampling Period

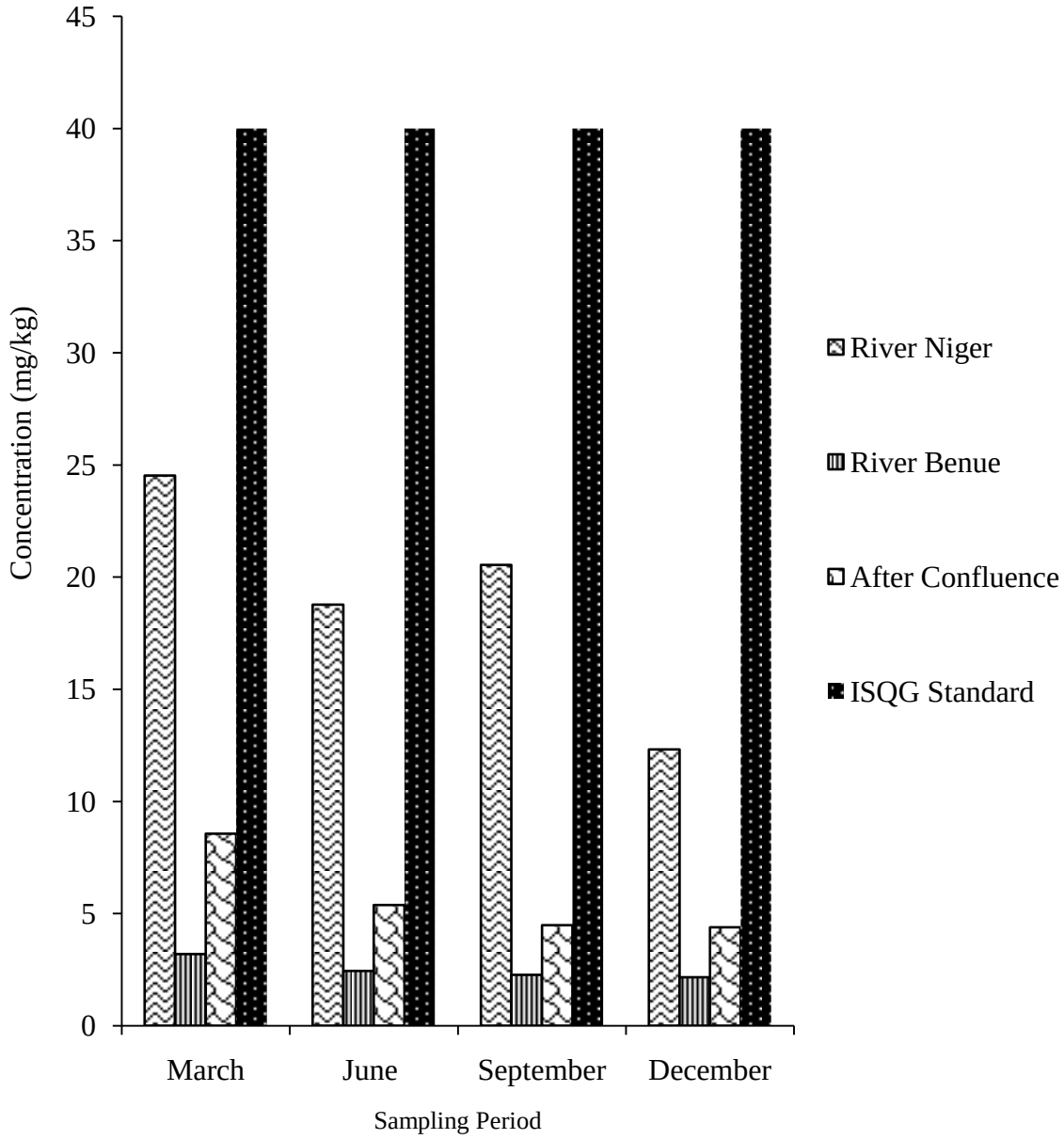


Figure 4.16: Concentrations of Co in Sediments from the Rivers Versus Sampling Period

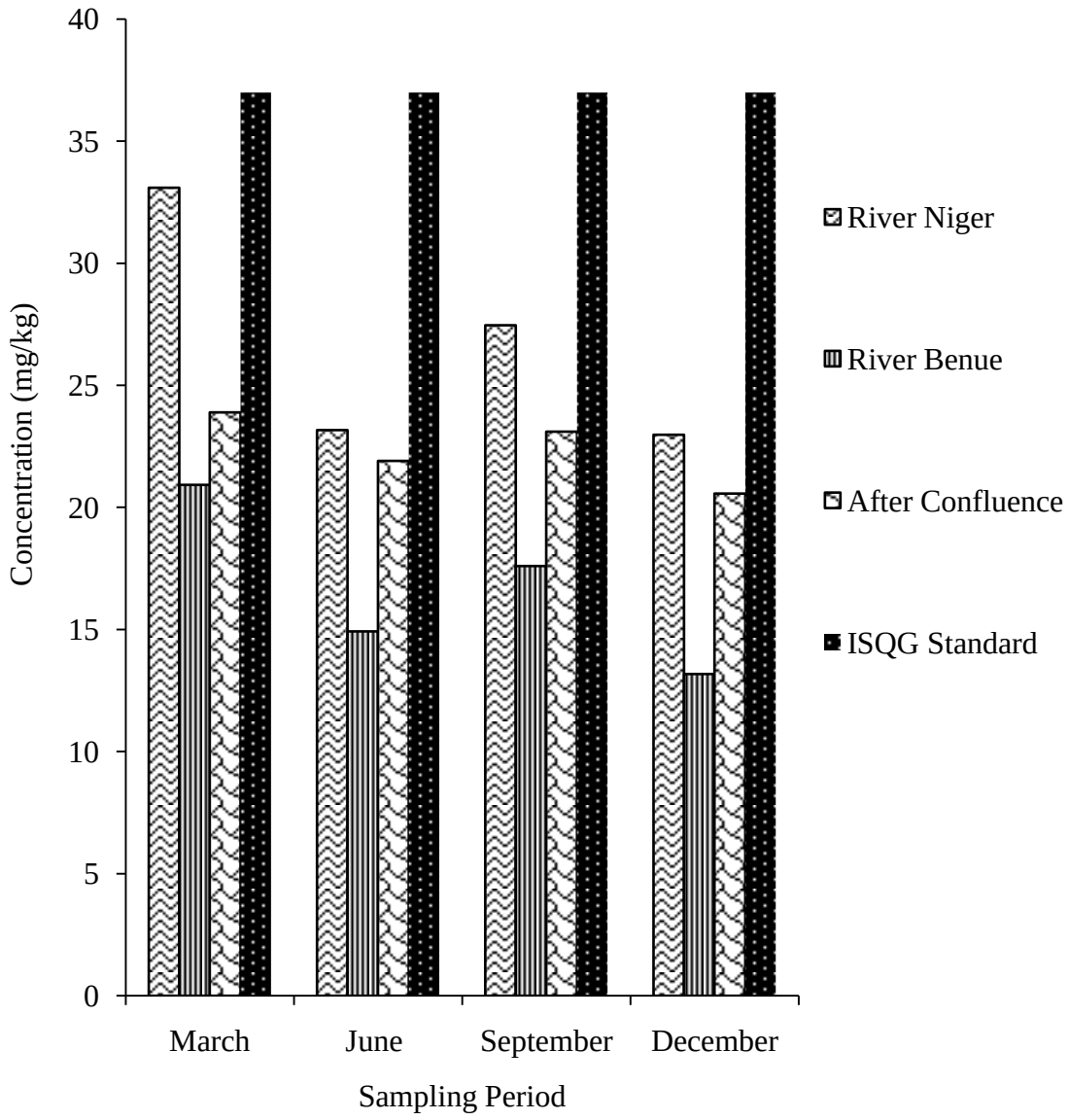


Figure 4.17: Concentrations of Cr in Sediments from the Rivers Versus Sampling Period

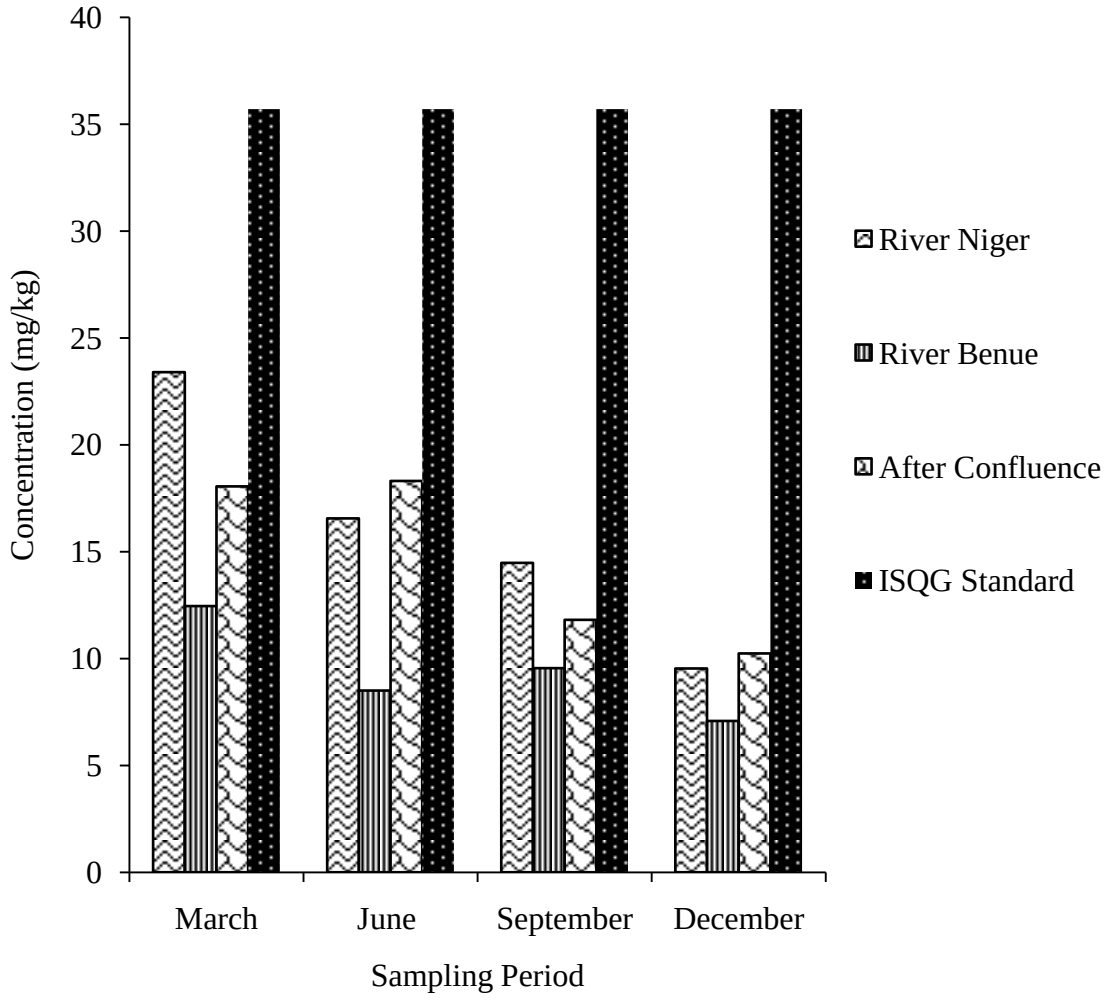


Figure 4.18: Concentrations of Cu in Sediments from the Rivers Versus sampling Period

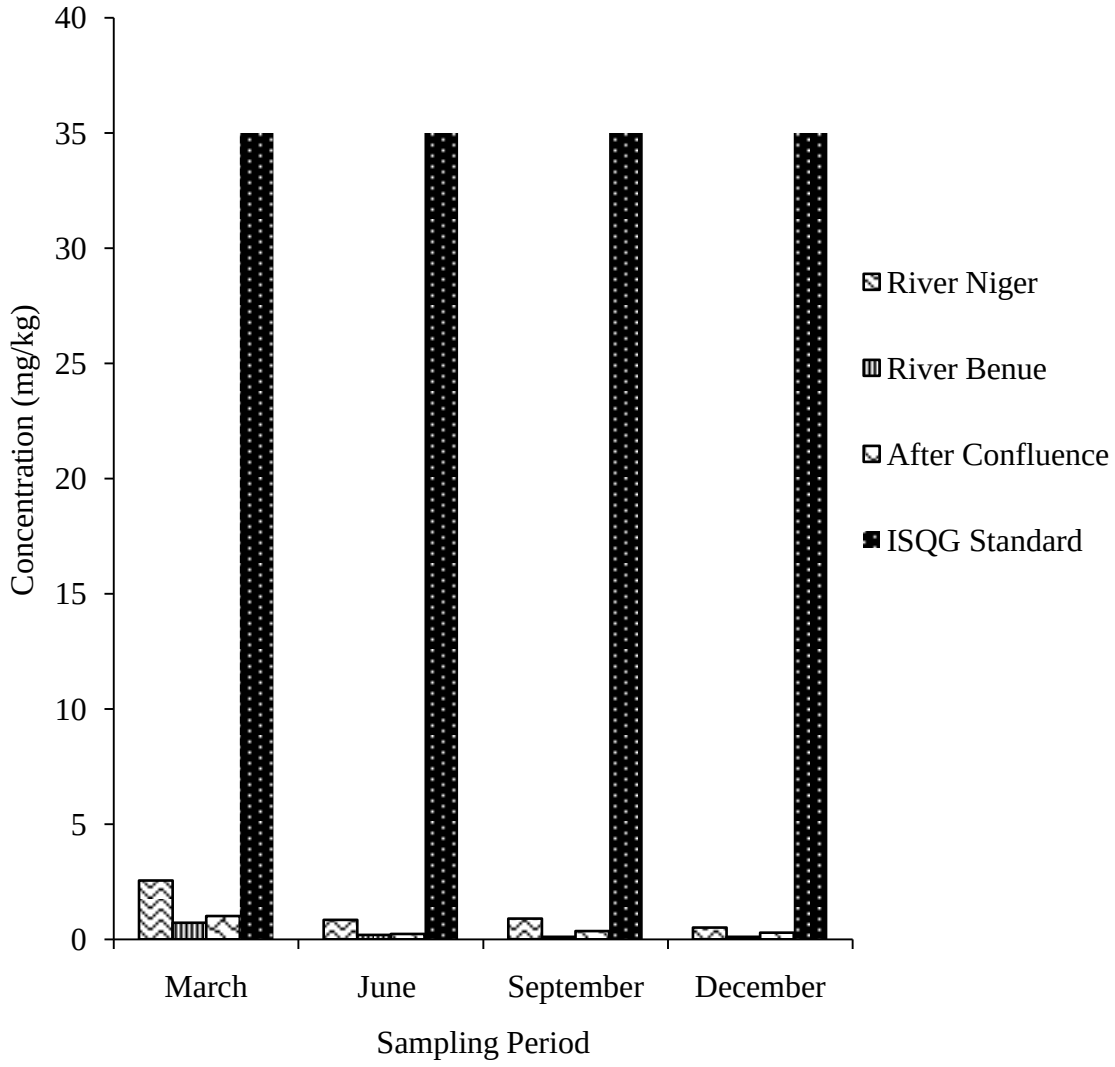


Figure 4.19: Concentrations of Pb in Sediments from the Rivers Versus Sampling Period

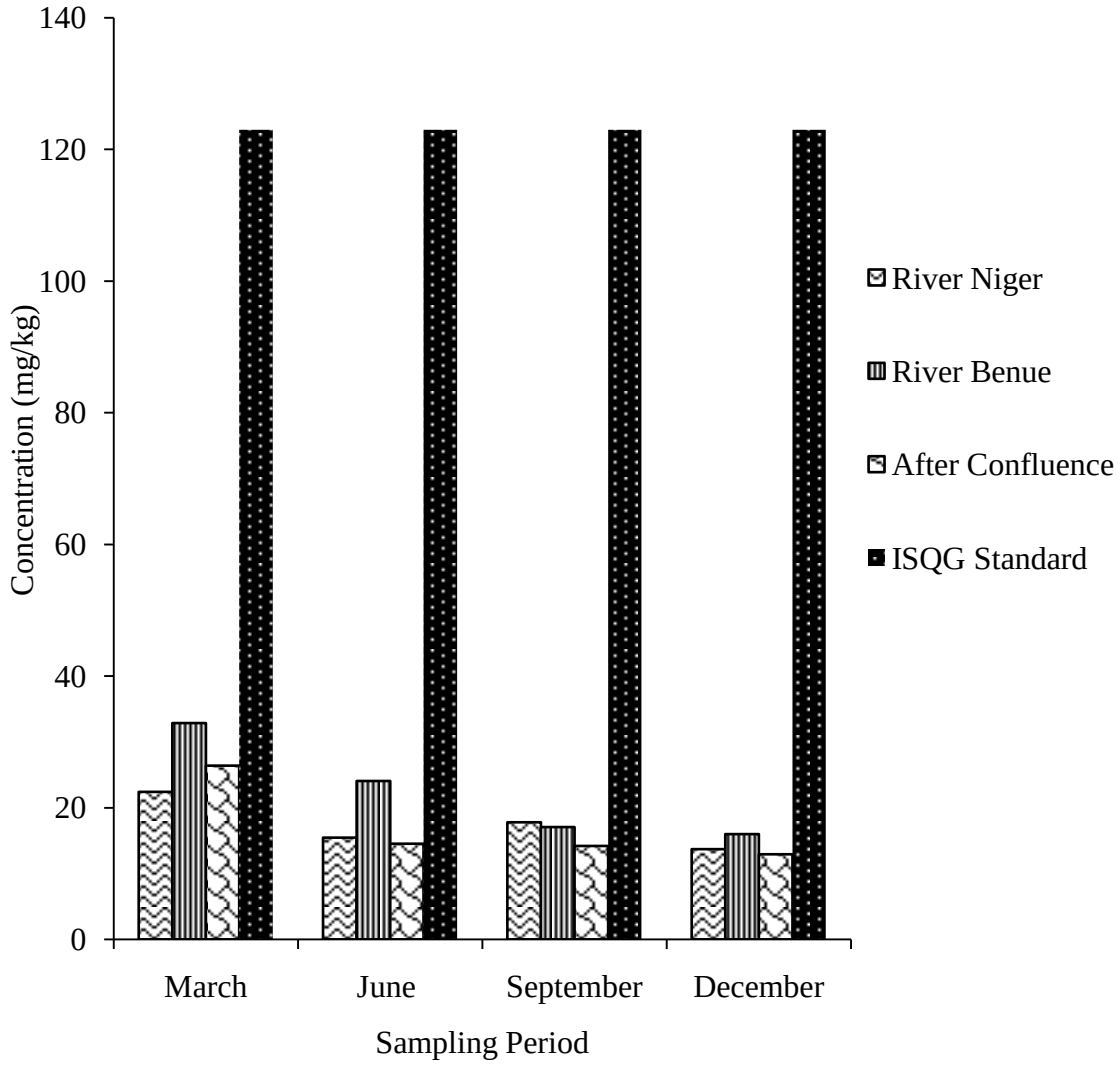


Figure 4.20: Concentrations of Zn in Sediments from the Rivers Versus Sampling Period

The geoaccumulation index (I_{geo}) of heavy metals in the sediments from the river Niger, River Benue and the Confluence point is presented in Table 4.6. During the study period, the I_{geo} of Cd, Co, Cr, Cu, Pb and Zn falls in the ranges of -0.6931 to 1.3056, -1.8430 to 0.2690, -0.5735 to 0.2265, -1.1126 to -0.0745, -4.5988 to -1.8282 and -1.7814 to -0.9715 respectively.

4.6: Heavy Metal Concentrations in Fishes from the Vicinity of the Confluence Point

The concentrations of Cd in the bones, brain and flesh of *C. gariepinus, O. niloticus and S.nigrita* collected at the vicinity of the confluence point with respect to the sampling periods are presented in Table 4.7. The results reveal Cd in the ranges of 1.508±0.212 – 0.643±0.089, 2.257±0.469 – 0.988±0.243 and 2.019±0.607 – 0.809±0.135 mg/kg respectively for *C. gariepinus, O. niloticus and S.nigrita*. The concentrations of cobalt in the bones, brain and flesh of the three species of fishes are presented in Table 4.8. Cobalt is found to fall in the ranges of 3.159±0.714 – 0.453, 2.664±0.871 – 0.655±0.133 and 2.541±0.916 – 0.481±0.210 mg/kg for *C. gariepinus, O. niloticus and S.nigrita* respectively and all values falls above the ITS (2000) recommended limit of 0.100 mg/kg. Chromium content in the fish organs (Table 4.9) falls within the ranges of 3.683±0.666 – 1.446±0.328, 3.603±0.774 – 1.609±0.485 and 3.315±0.508 – 1.858±0.371 mg/kg for *C. gariepinus, O. niloticus and S.nigrita* respectively and all values falls above the FOA (2003) recommended limit of 0.150 mg/kg.

Table 4.10 shows the concentrations of Cu in the bones, brain and flesh of *C. gariepinus, O. niloticus and S.nigrita* respectively. Cu is found in the ranges of 2.424±0.415-1.267±0.089, 3.002±0.105-1.259±0.510 and 2.564±0.398-1.112±0.252 mg/kg respectively for *C. gariepinus, O. niloticus and S.nigrita*. Similarly, Table 4.11

Table 4.5: Pollution Load Index (PLI) of Heavy Metals in Sediment Samples from River Niger, River Benue and after the Confluence Point

Period	River	CF_{Cd}	CF_{Co}	CF_{Cr}	CF_{Cu}	CF_{Pb}	CF_{Zn}	PLI
March	R. Benue	4.6930	0.2664	2.2311	0.7330	0.0511	0.4902	0.6094
	R. Niger	6.7343	2.0444	1.9469	1.3767	0.1828	0.3343	1.0248
	Confluence	4.6633	0.7138	1.4055	1.0624	0.0719	0.3940	0.7213
June	R. Benue	1.8340	0.2036	0.8777	0.5003	0.0137	0.3592	0.3051
	R. Niger	3.9297	1.5649	1.3627	0.9736	0.0607	0.2309	0.6967
	Confluence	2.0487	0.4484	1.2889	1.0769	0.0166	0.2169	0.4428
September	R. Benue	1.5610	0.1887	1.0357	0.5617	0.0076	0.2549	0.2631
	R. Niger	1.7530	1.7118	1.6158	0.8515	0.0641	0.2653	0.6423
	Confluence	2.6277	0.3736	1.3593	0.6945	0.0257	0.2116	0.4141
December	R. Benue	0.7963	0.1798	0.7751	0.4167	0.0075	0.2388	0.2088
	R. Niger	2.6480	1.0264	1.3517	0.5613	0.0364	0.2044	0.4985
	Confluence	0.6753	0.3654	1.2103	0.6024	0.0206	0.1929	0.2990

CF_{Cd} =Contamination factor of Cd, CF_{Co} =Contamination factor of Co, CF_{Cr} =Contamination factor of Cd, CF_{Cu} = Contamination factor of Cu, CF_{Pb} =Contamination factor of Pb and CF_{Zn} =Contamination factor of Zn

Table 4.6: Geoaccumulation Idex (I_{geo}) of Heavy Metals in Sediment Samples from River Niger, River Benue and after the Confluence Point

Period	River	I_{geo}Cd	I_{geo}Co	I_{geo}Cr	I_{geo}Cu	I_{geo}Pb	I_{geo}Zn
March	R. Benue	0.9907	-1.5010	-0.1716	-0.6219	-2.9346	-0.9715
	R. Niger	1.3056	0.2690	0.2265	-0.0745	-1.8282	-1.3038
	Confluence	0.9852	-0.6451	-0.0565	-0.2996	-2.6285	-1.1612
June	R. Benue	0.1746	-1.7348	-0.4654	-0.9499	-4.0896	-1.2415
	R. Niger	0.8365	0.0368	-0.0834	-0.3754	-2.7855	-1.6255
	Confluence	0.2708	-1.0488	-0.1318	-0.2878	-3.9108	-1.6796
September	R. Benue	0.0346	-1.8009	-0.3217	-0.8532	-4.5865	-1.5394
	R. Niger	0.1354	0.1147	0.0646	-0.4919	-2.7379	-1.5046
	Confluence	0.4870	-1.2074	0.0855	-0.6688	-3.5338	-1.7010
December	R. Benue	-0.5500	-1.8430	-0.5735	-1.1126	-4.5988	-1.5959
	R. Niger	0.4937	-0.3275	-0.0904	-0.8538	-3.2312	-1.7313
	Confluence	-0.6931	-1.2266	-0.1864	-0.7924	-3.7266	-1.7814

show the concentrations of Pb in the bones, brain and flesh of *C. gariepinus*, *O. niloticus and S.nigrita*. It is seen that that Pb falls within the ranges of 2.874±0.916-0.654±0.081, 2.964±0.315-0.664±0.421 and 2.674±0.925-0.831±0.755 mg/kg for *C. gariepinus, O. niloticus and S.nigrita* respectively. Finally, Zinc concentrations (Table 4.12) was found in the ranges of 5.460±1.069-1.954±0.290, 6.013±1.670-2.301±0.645 and 5.302±1.714-2.121±0.285 mg/kg for *C. gariepinus, O. niloticus and S.nigrita* respectively.

Table 4.7: Mean Concentrations of Cadmium (mg/kg) in Organs of Three Species of Fish Collected from the Vicinity of the Confluence Point

Specie	Organ	March Sampling	June Sampling	September Sampling	December Sampling
C.gariepinus	Bone	1.323±0.279	1.457±0.212	1.508±0.159	1.402±0.279
"	Brain	1.199±0.279	1.206±0.084	1.203±0.361	1.176±0.206
"	Flesh	0.649±0.232	0.643±0.089	0.894±0.164	0.654±0.021
O. niloticus	Bone	2.257±0.469	1.882±0.196	1.944±0.169	2.047±0.251
"	Brain	1.916±0.525	2.076±0.508	1.611±0.260	1.737±0.151
"	Flesh	1.072±0.229	0.988±0.243	1.014±0.298	1.063±0.217
S. nigrita	Bone	2.019±0.607	1.829±0.329	1.957±0.087	1.957±0.383
"	Brain	1.457±0.389	1.543±0.405	1.747±0.3131	1.613±0.395
"	Flesh	0.811±0.312	0.809±0.135	0.851±0.051	0.813±0.164

WHO (1998) limit for cadmium in fish = 0.500 mg/kg. Values are means replicate analysis of n=6

Table 4.8: Mean Concentrations of Cobalt (mg/kg) in Organs of Three Species of Fish Collected from the Vicinity of the Confluence Point

Specie	Organ	March Sampling	June Sampling	September Sampling	December Sampling
C. gariepinus	Bone	1.550±0.482	1.774±0.673	1.527±0.551	1.459±0.539
"	Brain	3.159±0.714	2.711±1.001	2.519±1.054	2.43±1.050
"	Flesh	0.630±0.308	0.570±0.117	0.800±0.192	0.453±0.192
O. niloticus	Bone	2.664±0.871	2.127±0.519	2.177±0.368	1.989±0.563
"	Brain	1.272±0.311	1.132±0.177	1.350±0.205	0.981±0.087
"	Flesh	0.919±0.114	0.768±0.169	0.887±0.014	0.655±0.133
S. nigrita	Bone	1.175±0.149	1.167±0.398	1.687±0.300	0.831±0.325
"	Brain	2.541±0.916	2.097±0.370	1.967±0.429	1.693±0.748
"	Flesh	0.753±0.232	0.755±0.135	0.872±0.161	0.481±0.210

Maximum permissible limit by ITS (2000)= 0.10 mg/kg. Values are means replicate analysis 0f n=6.

Table 4.9 Mean Concentrations of Chromium (mg/kg) in Organs of Three Species of Fish Collected from the Vicinity of the Confluence Point

Specie	Organ	March Sampling	June Sampling	September Sampling	December Sampling
C. gariepinus	Bone	3.683±0.666	2.843±0.604	2.792±0.347	2.957±0.508
"	Brain	3.322±0.370	2.463±0.338	2.385±0.248	1.897±0.940
"	Flesh	2.156±0.420	1.760±0.420	1.718±0.343	1.446±0.328
O. niloticus	Bone	3.603±0.774	3.542±0.360	2.914±0.230	2.903±0.327
"	Brain	2.814±0.592	2.590±0.326	2.460±0.065	2.226±0.082
"	Flesh	2.328±0.583	1.894±0.261	1.819±0.246	1.609±0.485
S. nigrita	Bone	3.315±0.508	3.073±0.421	2.949±0.485	2.585±0.276
"	Brain	2.793±0.270	2.371±0.258	2.134±0.807	2.043±0.030
"	Flesh	2.249±0.307	2.294±0.030	1.858±0.371	2.032±0.384

Maximum permissible limit of chromium in Fish by FOA (2003)= 0.15 mg/kg. Values are means replicate analysis of n=6

Table 4.10: Mean Concentrations of Copper (mg/kg) in Organs of Three Species of Fish Collected from the vicinity of the Confluence Point

Specie	Organ	March Sampling	June Sampling	September Sampling	December Sampling
C. gariepinus	Bone	2.122±0.069	2.279±0.143	2.391±0.357	2.424±0.415
"	Brain	1.744±0.147	1.766±0.270	1.667±0.176	1.852±0.112
"	Flesh	1.267±0.089	1.388±0.084	1.298±0.218	1.444±0.106
O. niloticus	Bone	3.002±0.105	2.870±0.074	2.780±0.241	2.959±0.160
"	Brain	2.256±0.237	2.545±0.166	2.572±0.124	2.539±0.248
"	Flesh	1.259±0.510	1.582±0.182	1.751±0.268	1.695±0.247
S. nigrita	Bone	2.255±0.153	2.496±0.220	2.564±0.398	2.416±0.020
"	Brain	1.750±0.240	1.915±0.544	1.882±0.348	1.940±0.534
"	Flesh	1.112±0.252	1.321±0.247	1.381±0.061	1.360±0.220

Maximum permissible limit of copper in fish by FEPA (2003) = 1.3 mg/kg. Values are means replicate analysis 0f n=6

Table 4.11: Mean Concentrations of Lead (mg/kg) in Organs of Three Species of Fish Collected from the vicinity of the Confluence Point

Specie	Organ	March Sampling	June Sampling	September Sampling	December Sampling
C. gariepinus	Bone	1.907±0.690	2.211±0.607	2.084±0.616	2.874±0.916
"	Brain	1.204±0.354	1.564±0.130	1.281±0.174	2.330±0.418
"	Flesh	0.654±0.081	1.284±0.495	1.138±0.300	1.044±0.151
O. niloticus	Bone	2.778±0.689	2.901±1.218	2.964±0.315	3.532±1.257
"	Brain	2.103±1.268	2.301±1.418	2.189±0.951	3.326±1.089
"	Flesh	0.664±0.421	0.823±0.668	0.902±0.500	1.451±0.608
S. nigrita	Bone	1.590±0.629	1.575±0.413	2.249±0.901	2.674±0.925
"	Brain	1.330±0.545	1.547±0.670	1.869±0.304	2.439±0.472
"	Flesh	0.831±0.755	1.029±0.572	0.888±0.345	1.046±0.425

WHO (1993), ITS (2000) Value for Pb=0.50 mg/kg. Values are means replicate analysis (n=6)

Table 4.12: Mean Concentrations of Zinc (mg/kg) in Organs of Three Species of Fish Collected from the vicinity of the Confluence Point

Specie	Organ	March Sampling	June Sampling	September Sampling	December Sampling
C. gariepinus	Bone	5.460±1.069	4.010±1.182	3.765±0.834	4.238±1.156
"	Brain	4.045±1.126	3.291±0.538	3.585±0.892	3.333±0.549
"	Flesh	3.236±1.086	2.100±0.658	1.954±0.290	1.965±0.706
O. niloticus	Bone	6.013±1.670	5.248±0.935	4.875±0.925	4.639±1.011
"	Brain	4.801±1.132	3.893±1.232	3.533±0.931	3.953±1.147
"	Flesh	3.151±0.977	2.301±0.645	2.522±0.818	2.660±0.794
S. nigrita	Bone	5.302±1.714	4.040±0.912	4.373±1.263	4.137±0.872
"	Brain	3.822±0.903	2.714±0.390	3.020±0.449	2.648±0.258
"	Flesh	2.781±0.362	2.139±0.488	2.121±0.285	2.211±0.509

Maximum permissible limit of zinc in fish by WHO (1999) = 40.0 mg/kg. Values are means replicate analysis 0f n=6

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physicochemical Properties of Water Samples from River Niger, River Benue and after the Confluence Point

5.1.1 Biochemical oxygen demand

Figure 4.1 depicts the levels of BOD in the water samples collected from River Niger, River Benue and after the confluence point all the vicinity of the confluence in Lokoja, Nigeria during the months March, June, September and December 2013, while the values obtained are presented in Appendix III. BOD of the water in River Niger ranged from 8.53 - 9.9, 4.87 - 9.00, 12.98 - 16.89 and 4.57 - 7.50 mg/L with the corresponding means of 9.23 ± 0.56, 7.01 ± 1.31, 15.59 ± 1.13 and 5.56 ± 1.106 mg/L for the month of March, June, September and December, 2013 respectively. The samples from River Benue recorded BOD in the ranges of 7.26 - 8.31, 7.79 - 17.06, 9.08 - 11.10 and 5.37 - 7.86 mg/L with means of 7.82 ± 0.36, 10.34 ± 2.88, 6.69 ± 0.87 and 5.99 ± 0.75 mg/L accordingly for the months of March, June, September and December 2013. Finally, water collected just after the confluence during March, June, September and December sampling recorded BOD within the ranges of 8.04 - 8.85 (mean 8.51±0.25), 6.73 -15.18 (mean 10.18 ± 3.29), 12.48 - 14.83 (mean 13.55 ± 0.68) and 5.23 - 7.43 (mean 5.99 ± 0.75) respectively. The results revealed that during the month of March, water from River Niger had the highest BOD level followed by that from the confluence and finally that from River Benue. An elevated level of BOD was observed in the month of June for the samples from River Benue and after the confluence, whereas that from River Niger had a drop in BOD level. Higher BOD values were recorded in September in

all the rivers and lastly, lower values were recorded in December 2013. This results showed that in March, June and September, all the rivers had BOD above the maximum limit set by WHO (6.00 mg/L), while in December, only the water samples from River Benue had BOD above the recommended limit. More so, the results indicated higher level of BOD during the wet season (June and September) compared to those of the dry season (March and December). This result indicates high influx of organic matter in the rivers during the study period except for the month of December in which River Niger and the confluence point recorded BOD below the acceptable limit. These outrageous values could likely be as a result of dumping of refuse at the banks of the rivers and possibly due to the preceded flood of 2012 in the study area, which was 5 months prior to this research. This result is far above the values recorded by Zakariya *et al.* (2011) with mean 2.24 and 0.68 mg/L for River Niger and the confluence respectively. The results obtained in this study is also above the BOD values reported by Olatunde and Oladele (5.58 ± 2.07 mg/L) during their investigation of River Niger water in early 2012. These high values could results into depletion of dissolved oxygen in the water and consequently affects aquatic faunas.

5.1.2 Chemical oxygen demand

The level of COD with respect to the rivers and sampling period is shown in Figure 4.2 whereas the values are displayed in Appendix IV. Water from River Niger had COD in the ranges of 137.03 - 145.97, 90.67 - 119.37, 112.87 - 154.09 and 71.12 - 113.23 mg/L for the months of March, June, September and December 2013 respectively; and had the corresponding means of 141.73 ± 2.98, 112.72 ± 8.58, 134.07 ± 12.98 and 98.25 ± 16.80 mg/L respectively. The samples from River Benue on the order hand

recorded COD in the range 117.84 - 128.04, 115.10 - 167.67, 109.65 - 125.87 and 104.88 - 131.80 for the months March, June, September and December 2013 respectively; however their corresponding means were 121.46 ± 3.08, 124.18 ± 16.52, 114.98 ± 5.43 and 115.43 ± 8.31 respectively for the sampling periods. Water at the confluence point also had COD between the ranges of 123.67 - 138.00, 114.40 - 205.67, 118.76 - 131.07 and 80.13 - 113.76 mg/L for the months March, June, September and December 2013 respectively; while the corresponding means were 131.51 ± 4.69, 134.18 ± 29.20, 124.26 ± 4.16 and 106.02 ± 11.59 mg/L respectively for the sampling periods. These values reveals that the COD content of the rivers is in the order River Niger > after confluence > River Benue for the month of March 2013. However, for June, September and December samples the trend was: after confluence > River Benue > River Niger, River Niger > after confluence>River Benue, and River Benue > after confluence > River Niger respectively.

The least COD values were found in the December samples while the March samples recorded the highest values. The study indicates that water after the confluence is more polluted with reference to COD followed by that from River Niger and lastly River Benue. Considering the values of COD of the water, the study indicates that the rivers had high influx of organic compounds and in comparison with the permissible limit set by WHO (10.00 mg/L), all the rivers had COD above the threshold value. However, this study reveals higher values compared to those reported by Osibanjo *et al.* (2011) and Olatunde and Oladele (2012) in their researches in River Ona and River Niger (23.54 - 95.32 and 18.52 - 22.46 mg L^{-1}) respectively. Similarly, results of this research are by far above those recorded by Zakariya *et al*, 2011. The high values thus recorded in this research could be due to human activities such as discharge of sewage by industries

(which might not necessary be point source), global worming such as flood (which took place in the study area prior to this studies) which might have washed organic pollutants from the environment down into the river. This result also implies a negative impact on the DO which could lead to oxygen depletion.

5.1.3 Conductivity

The EC of the water samples from the two rivers and after their confluence point during the sampling period are presented in Figure 4.3 and their corresponding values are as indicated in Appendix V. The study showed that in March, June, September and December 2013, the water samples from River Niger had EC in the ranges and means of 113.68 - 148.67 (131.16 ± 10.06), 137.67 - 176.33 (156.15±15.66), 210.62 - 257.03 (233.39 ± 15.40) and 83.00 - 104.33 (88.19 ± 8.30) µS/cm respectively. The water samples from River Benue recorded EC in the ranges and means of 95.00 - 128.02 (109.69 ± 11.77), 165.33 - 201.06 (182.44 ± 11.95), 174.08 - 226.87 (201.41 ± 17.09) and 56.00 - 73.71 (65.61 ± 6.00) µS/cm for the months March, June, September and December 2013 respectively. Finally, the water samples obtained from the confluence point had EC of 116.05 - 129.06 (122.80 ± 4.35), 154.53 - 283.67 (198.03 ± 49.42), 208.76 - 226.56 (217.43 ± 5.28) and 77.33 - 105.00 (86.56 ± 8.30) µS/cm for March, June, September and December respectively. In the months of March, June and September, the water from the three sampling sites had EC above the international standard set by WHO (100 µS/cm) while in December, values of EC were below the set limit. Gradual sedimentation of metal ions and precipitation as a result of low water current might account for the lower values recorded in March and December (dry season). More so, higher values recorded in June and September (wet season) is in

agreement with the claim of Olatunde and Oladele (2012) who suggested that during rainy season, more salts (compounds) are dissolved thereby increasing the ion levels of the water and hence increase in its EC; however, results of this research were higher, against those obtained by Olatunde and Oladele (2012). This implies likely hood of high total dissolve solids.

5.1.4 Dissolved oxygen

The level of DO in the water of the two rivers and just after the confluence point during the study period is presented in Figure 4.4, while the values are displayed in Appendix VI. DO in the water samples obtained from River Niger is found to be in the ranges and corresponding means of 1.73 - 2.64 (2.26 ± 0.37), 5.10 - 9.67 (7.49 ± 1.81), 9.36 - 13.56 (11.14 ± 1.44) and 5.20 - 8.80 (7.09 ± 1.28) mg/L for the months of March, June, September and December 2013 respectively. Similarly, River Benue recorded DO in the ranges of 3.63 - 4.96 (4.28 ± 0.54), 4.23 - 7.78 (5.65 ± 1.19), 11.93 - 16.89 (14.39) and 3.30 - 6.81 (5.17 ± 1.22) mg/L respectively for the months of March, June, September and December. Water samples after the confluence point on the other hand had DO in the ranges and means of 2.46 - 3.53 (2.93 ± 0.36), 2.63 - 7.70 (5.23 ± 1.91), 10.02 - 12.65 (11.92 ± 0.86) and 4.80 - 8.47 (6.35 ± 1.15) mg/L for March, June, September and December respectively. The highest values were observed in the samples collected in September followed by those of December, June and finally March 2013 samples. An inverse relationship was noticed between COD and DO signifying that, as much oxygen is used in the breaking down organic pollutants, the DO tend to reduce. These results show that the rivers had lower DO values in all the sampling periods compared to the minimum value of DO suggested by WHO (15.00 mg/L). Furthermore,

risk values (which could easily lead to death of aquatic faunas) were recorded in the samples collected in March 2013, as these values were below 3.00mg/L which is considered to be the critical DO value (Fred and Ann, 2012); though the results obtained for River Benue was an exception of. All the studied rivers had DO above the critical level in June, September and December 2013. Therefore, high risk of eutrophication is envisaged in all the rivers as values obtained were below the recommended limit of WHO (2008). The trend of this result is in conformity with the assertions of Osibanjo *et al.* (2011), Wakawa *et al.* (2008), Olatunde and Oladele (2012) and AALWQC (2000) who all asserted that as COD increases, DO tend to reduce. In addition, Zakariya *et al*. (2011) reported 8.73 - 8.15 mg/L of DO which are all above the values reported for the months of March, June and December 2013 in this study, though below those obtained for the samples of September 2013. This suggests that water of the study area prior to the flood had more DO as compared to after the flood.

5.1.5 Hardness

The hardness (amount of calcium and magnesium ions) in the water of River Niger, River Benue and the confluence point in Lokoja, Nigeria are pictorially presented in Figure 4.5 while their values are presented in Appendix VII. The results show that the water from River Niger had hardness in the ranges and corresponding means of 148.04 - 169.67 (158.57 ± 7.25), 115.33 - 167.00 (145.91 ± 19.09), 201.87 - 254.76 (221.30 ± 15.40) and 43.33 - 55.33 (48.85 ± 4.15) mg/L for the months of March, June, September and December 2013 respectively. River Benue recorded hardness in the ranges of 150.83 - 253.09 (189.07 ± 27.32), 175.67 - 241.67 (192.07 ± 19.98), 229.04 - 265.04 (245.83 ± 9.95) and 48.67 - 63.00 (57.06 ± 4.93) mg/L respectively for the months of March, June,

September and December. Finally, water from the confluence had hardness of 156.98 - 195.80 (173.31 ± 11.30), 98.05 - 177.67 (160.57 ± 49.43), 187.08 - 243.87 (228.69 ± 16.62) and 45.33 - 65.07 (53.63 ± 6.04) mg/L accordingly for the months of March, June, September and December. The high values noticed in September could be due to high water current which led to the washing and dissolution of rock materials from hills down to tributaries and finally to the studied rivers. Values were found to be above the tolerable limit (150 mg/L) in all the rivers in March, June and September with the exception of River Niger in June. Enokela and Salifu (2012) reported a normal hardness range (135-147 mg/L) in their evaluation of the quality of water at the bank of River Niger in Lokoja used for irrigation on Sarki-noma fadama farm. The results of this research suggest that a normal hardness range in the rivers was only found in December.

5.1.6 pH

The pH of the water from River Niger, River Benue and after the confluence point in Lokoja, Nigeria is depicted in Figure 4.6 and the data presented in Appendix VIII. The water samples from River Niger was found to have pH ranging from 6.10 - 7.89, 6.47 - 8.37, 6.37 - 7.68 and 7.17 - 8.27 for March, June, September and December 2013 respectively with corresponding means of 6.85 ± 0.66, 7.61 ± 0.63, 6.77 ± 0.47 and 7.71 ± 0.39. The ranges and means of the pH of water from River Benue for the months of March, June, September and December were 6.84 - 8.47 (8.07 ± 0.52), 6.15 - 7.77 (6.87 ± 0.64), 6.62 - 8.32 (7.64 ± 0.56) and 6.43 (6.88 ± 0.53) respectively. Water after the confluence recorded pH in the ranges and means of 7.04 - 8.04 (7.66 ± 0.29), 6.20 - 7.40 (6.81 ± 0.46), 6.79 - 7.50 (7.20 ± 0.23) and 6.83 - 8.87 (7.68) for the months of March, June, September and December 2013 respectively. In view of the result, water from the

rivers during the study period were either slightly acidic or slightly basic, as such posed no threat to aquatic faunas and flora; as all values obtained fall within the recommended pH range set by WHO for water body (6.5 - 9.5). This result is in agreement with the work of Adefemi *et al*. (2007) and Taiwo (2010) in the study of water from major Dams in Ekiti State and Alakata Stream in Abeakuta respectively.

5.1.7 Total dissolved solids

The levels of TDS as determined in the water from River Niger, River Benue and after the confluence point in Lokoja, Nigeria is depicted in Figure 4.7 and data displayed in Appendix IX. It is found that River Niger had TDS in the ranges of 563.47 - 605.87 (591.35 ± 14.51), 594.67 - 744.00 (668.00 ± 52.53), 684.65 - 736.06 (721.61 ± 16.15) and 469.00 - 505.33 (486.19 ± 12.52) for the months of March, June, September and December 2013 respectively. Similarly, water from River Benue was found to have TDS in the ranges and corresponding means of 480.67 - 531.06 (509.49 ± 17.39), 745.56 - 856.32 (781.75 ± 32.81), 648.02 - 713.03 (682.18 ± 7.06) and 407.00 - 535.54 (457.91 ± 43.79) for the months of March, June, September and December respectively. Water after the confluence on the other hand had TDS in the range of 487.08 - 576.02, 621.08 - 832.00, 703.02 - 725.65 and 431.67 - 521.00 with corresponding means of 533.31 ± 27.06, 733.65 ± 73.02, 716.26 ± 7.06 and 476.98 ± 23.98 for March, June, September and December respectively. The results reveal that TDS in the two rivers and after the confluence during the sampling periods follow the ranking: December < March < June < September. This therefore suggests high level in wet season (June and September) as against the dry season (March and December). The high values recorded in June and September could be as a result of rainfall which might have dissolved solid materials

from upland down to the rivers. In comparison with the set standard, the rivers recorded values lower to those of WHO (500.00 mg/L) only in December whereas in March, June, and September, all the rivers recorded values above the tolerable limit. The implication of this result is that conductivity will increase and chance of habitable environment for fishes reduced.

5.1.8 Turbidity

The turbidity of the water samples obtained from the three sampling sites during the sampling periods are shown pictorially in Figure 4.8 while the data are displayed in Appendix X. The results revealed that during March, June, September and December, the water from River Niger had turbidity in the ranges of 11.47 - 14.67, 12.60 - 18.10, 20.74 - 24.64 and 4.70 - 7.33 NTU with corresponding means of 12.38 ± 1.04, 14.34 ± 1.74, 23.13 ± 1.43 and 6.50 ± 0.77 NTU respectively. The samples from River Benue recorded turbidity in the ranges and corresponding means of 9.05 - 11.04 (10.02 ± 0.71), 16.06 - 25.76 (18.24 ± 2.93), 18.04 - 22.65 (19.68 ± 1.29) and 4.50 - 6.63 (5.33 ± 0.68) NTU for March, June, September and December respectively. The samples after the confluence on the other hand were turbid with ranges and means of 9.04 - 11.23 (10.55 ± 0.70), 12.09 - 27.33 (18.66 ± 5.41), 21.48 - 23.53 (22.56 ± 0.63) and 5.09 - 8.67 (7.36 ± 1.38) NTU for the months of March, June, September and December 2013 respectively. Higher turbidity values were recorded in the samples collected in September followed by June, March, while the ones collected in December had the least values. No regular pattern was recorded in the results of turbidity across the rivers with respect to sampling period. The higher values obtained in September could be due to rainfall effect which could wash all sort of environmental materials down into the river, thereby making it more turbid. More

so, high rainfall and possibly flood in the preceding year could account for the reason why the samples obtained in March was more turbid compared to the samples collected in December. The results revealed that the water of the three sampling sites had turbidity above the acceptable limit set by WHO (5.00 NTU). The implication for these high values is that, the water could provide food and shelter for pathogens and also limit photosynthesis by aquatic plants due to low light penetration into the water. This result is in agreement with the work of Ajibade (2004), Adefemi *et al*. (2007) and Wakawa *et al*. (2008) who all recorded turbidity values above 5.00 NTU in water from major Dams in Ekiti State and River Challawa, Kano State respectively.

5.2 Heavy Metals in Water Samples of River Niger, River Benue and after the Confluence Point in Lokoja

5.2.1 Cadmium

The concentrations of cadmium in the water samples during the study period are presented in Figure 4.9 and their data shown in Appendix XI. The results reveals that the level of Cd in water obtained from River Niger during the months of March, June, September and December ranged from 0.016 - 0.034, 0.011 - 0.026, 0.014 - 0.031 and 0.003 - 0.015 mg/L and corresponding means of 0.022 ± 0.007, 0.0168 ± 0.005, 0.019 ± 0.006 and 0.009 mg/L respectively. The samples obtained from River Benue showed high concentrations of Cd in March, June, September and December, with the ranges and corresponding means of 0.018 -.037 (0.028 ± 0.007), 0.012 - 0.028 (0.019 ± 0.06), 0.014 - 0.029 (0.021 ± 0.006) and 0.006 - 0.059 (0.024 ± 0.018) mg/L respectively. Finally, water samples after the confluence were found to contain Cd in the concentration ranges and means of 0.017 - 0.026 (0.022 ± 0.003), 0.020 - 0.023 (0.016 ± 0.004), 0.009 - 0.021

(0.015 ± 0.005) and 0.004 - 0.013 (0.008 ± 0.003) respectively for the months of March, June, September and December 2013. The results indicated that in March, there was a significant different in cadmium concentration of River Niger compared to the other sampling sites (River Benue and the confluence point) at $p < 0.05$ using ANOVA. Also, the results Cd obtained in September and December 2013, indicated a significant different between the two rivers and the confluence at $p < 0.05$ (Appendix XVII). Based on the results, River Benue is more polluted with Cd than the other sampling sites (River Niger and after the confluence point). In comparison to WHO limit (0.0100 mg/L) as shown in Figure 4.9, all the rivers recorded values above the acceptable limit in all the sampling occasions with the exception of the ones of December, in which the results obtained from River Benue and after the confluence were below the WHO value. The results obtained for the concentrations of Cd in the water samples agree with earlier work on the study area by Olatunde and Oladele (2013) in which Cd was found to be within the range of 0.02 - 0.13and the mean value was (0.05 ± 0.02) mg/L. Long exposure to this water by locals can lead to damage of vital organs such as kidney and lungs as reported by Jenne *at al*. 2011.

5.2.2 Cobalt

The variation of Co concentrations in the water obtained from River Niger, River Benue and after the confluence in Lokoja, Nigeria with respect to the sampling period is illustrated in Figure 4.10 and the data is presented in Appendix XII. The results showed that during the months of March, June, September and December 2013, River Niger had the level of Co in the ranges and corresponding means of 0.010 - 0.020 (0.016 ± 0.003), 0.008 - 0.015 (0.011 ± 0.003), 0.007 - 0.014 (0.016 ± 0.003) and 0.005 - 0.013 (0.009 ±

0.003) mg/L respectively. Similarly for the water samples obtained from River Benue, the concentration of Co ranged from 0.005 - 0.029 (0.018 ± 0.008), not detected (ND) - 0.026 (0.010 ± 0.008), ND - 0.016 (0.008 ± 0.005) and ND - 0.010 (0.004 ± 0.004) mg/L for the months of March, June, September and December 2013 accordingly. On the other hand, the water samples obtained after the confluence was found to contain Co in the ranges and corresponding means of 0.012 - 0.0224 (0.018 ± 0.004), 0.008 - 0.021 (0.013 ± 0.004), 0.007 - 0.016 (0.011 ± 0.003) and 0.005 - 0.018 (0.011 ± 0.004) mg/L for the months of March, June, September and December 2013 respectively. However, a decline in cobalt concentration was observed in June in both of the rivers studied. An increase in the concentration of cobalt was experienced in River Niger in September during which the peak of rainfall is often recorded in the area, whereas a decline in cobalt concentration was recorded in the samples obtained from River Benue and after the confluence. The same amount of Co (0.011 ± 0.004 mg/L) as obtained for the samples collected in September 2013 was recorded in the water collected at the confluence in the month of December; while River Niger and River Benue had a decline in the concentration of cadmium. By considering the variation of cobalt in the rivers and months, it is clearly shown that the rivers are polluted with respect to cobalt due to the elevated level recorded compared to WHO value (0.01 mg/L) as shown in Figure 4.10. The level of Co varied significantly between the three sampling sites at all the sampling months, as shown from the Analysis of Variance at $P < 0.005$ (Appendix XVII). This result is in agreement with the work reported by Mohammad *et al*. (2012), Hamilton (1994) and Smith (1999). The variation of this result with respect to sampling periods and rivers suggest anthropogenic

source of contamination and in view of the high values recorded; there could likely be deleterious effect on the biota.

5.2.3 Chromium

Figure 4.11 depicts the concentrations of chromium in the water samples collected from River Niger, River Benue and after the confluence in Lokoja, Nigeria, while Appendix XIII shows the data obtained. The level of Cr in the water from River Niger ranged from 0.098 - 1.187, 0.054 - 0.129, 0.065 - 0.130 and 0.058 - 0.091 mg/L respectively for the months of March, June, September and December 2015; while their corresponding means were 0.135 ± 0.031, 0.097 ± 0.024, 0.099 ± 0.024 and 0.078 ± 0.011 mg/L. In a similar manner, the samples obtained from River Benue during the months of March, June, September and December had the concentrations of Cr in the ranges and corresponding means of 0.063 - 0.143 (0.105 ± 0.002), 0.045 - 0.083 (0.069 ± 0.014), 0.042 - 0.083 (0.066 ± 0.012) and 0.021 - 0.046 (0.038 ± 0.007) mg/L respectively. The study indicated that the water samples after the confluence point was found to contain Cr within the ranges and corresponding means of 0.097 - 0.327 (0.139 ± 0.072), 0.054 - 0.087 (0.073 ± 0.012), 0.048 - 0.097 (0.072 ± 0.019) and 0.039 - 0.057 (0.048 ± 0.006) mg/L for the months of March, June, September and December respectively. Higher values of Cr in the water were recorded in March and the lowest values were recorded in December 2013. The results for Cr in the water by sampling period followed the trend: March > June > September > December for both rivers. In March, there was significant difference in the concentration of Cr in the water from River Benue compared to those of River Niger and the confluence at $p < 0.005$ (Appendix XVII) while in June, River Niger had the highest level of Cr and was significantly

elevated compared to the two other sampling sites (River Benue and the confluence). The level of Cr in the water obtained from the three sampling sites was significant different in September and December. Cr concentration in the water of the three sampling sites was above the recommended value by WHO (0.0500 mg/L) in March, June and September while in December, only River Niger had values that was above the WHO limit. This seasonal variation in Cr concentration suggest artificial source of contamination. However, the result is contrary to the results obtained by Olatunde and Oladele (2012) in the same study area, the range and mean of the values obtained were 0.53 - 4.09 mg/L and 2.08 ± 1.27 mg/L respectively. The outcome of this work however is in agreement with the work of Apeh and Ekenta (2012) which reported Cr concentration to be less than 0.05 mg/L in River Benue. High accumulation of this in human organs can pose threat to the central nervous system and also be cancerous (Bae *et al*. 2000).

5.2.4 Copper

The concentration of Cu in the water collected from the River Niger, River Benue and after the confluence point during the sampling periods is presented in Figure 4.12 and their corresponding values displayed in Appendix XIV. It was found that the water collected from River Niger had Cu in the ranges and corresponding means of 0.480 - 1.670 (1.053 ± 0.394), 0.340 - 1.010 (0.743 ± 0.210), 0.106 - 0.308 (0.207 ± 0.064) and ND - 0.277 (0.098 ± 0.092) mg/L for the months of March, June, September and December 2013. The water from River Benue on the other hand had the ranges and means of the concentrations of Cu being 1.030 - 2.330 (1.804 ± 0.359), 0.890 - 1.760 (1.231 ± 0.275), 0.867 - 1.209 (1.058 ± 0.130) and 0.769 - 1.601 (1.153 ± 0.290) respectively for the months of March, June, September and December 2013. Finally, the

water after the confluence point were found to contain Cu with the range and mean values of 0.986 - 2.033 (1.384 ± 0.398), 0.732 - 1.880 (1.056 ± 0.340), 0.675 - 1.263 (0.904 ± 0.182) and 0.432 -1.440 (0.938 ± 0.339) for the months of March, June, September and December respectively.

River Benue had the highest concentration in all the months followed by water after the confluence and lastly River Niger. Figure 4.12 indicates that in March, the value of Cu in water samples from all sites were above WHO limit of 1.000 mg/L while in June, only River Niger had the concentration of Cu below the recommended value. For the samples collected in September and December, the water from River Benue recorded higher value of Cu compared to the value set by WHO (2008). This result is in agreement with the work of Olatunde and Oladele (2012) on the water of River Niger near the confluence point in Lokoja, Nigeria, with the concentration of Cu in the range of 0.58 - 4.50 (2.17 ± 0.73) mg/L. Analysis of Variance (Appendix XVII) shows significant difference in the concentration Cu in the water of the two rivers and the confluence for all the sampling occasions at $p < 0.005$.

5.2.5 Lead

The concentrations of Pb in the water from the two rivers and after the confluence in Lokoja are presented in Figure 4.13 and values are shown in Appendix XV. The Figure reveals lower lead concentration in the water of River Niger which ranged from 0.002 - 0.007 (mean 0.0047±0.0007), ND - 0.002 (mean 0.0007 ± 0.0009), ND - 0.003 (mean 0.0006 ± 0.0010) and ND - 0.002 (mean 0.0006±0.0009) mg/L respectively for March, June, September and December 2013 samples. Similarly, the water from River Benue

recorded lower amount of Pb which ranged from ND - 0.002 (mean 0.0003 ± 0.0007), ND - 0.003 (mean 0.0006 ± 0.0011), ND - 0.007 (mean 0.0014 ± 0.0025) and ND - 0.003 (mean 0.0006 ± 0.0010) mg/L for the months of March, June, September and December 2013 respectively. Lastly, the water after the confluence had Pb in the ranges and corresponding means of ND - 0.002 (0.0004 ± 0.0007), ND - 0.002 (0.0003 ± 0.0007), ND - 0.003 (0.0006 ± 0.0009) and ND - 0.004 (0.0007 ± 0.00013) mg/L for the months of March, June, September and December 2013 respectively. The values of Pb obtained in this work were far below the WHO value (0.01 mg/L) as pictorially displayed in Figure 4.13. These low values could be due to the absence of industrial activities within the study area which is known to be a major source of lead to the environment as a result of their discharge; this could also be linked to the formation of insoluble salts of lead in the sediment and bedrock. In spite of the low concentration of Pb, there was significant difference in the levels of Pb in the two rivers and the confluence ($P < 0.005$). However, contrary to results of this work, Apeh and Ekenta (2012) reported Pb to be in the range 0.01 - 0.16 mg/L and mean 0.03 ± 0.02 mg/L for water obtained from River Benue..

5.2.6 Zinc

Figure 4.14 pictorially presents the mean concentrations of Zn in the water samples of the three sampling sites with respect to the sampling periods, and the data for Zn concentrations are presented in Appendix XVI. It was found that water obtained from River Niger during the months of March, June, September and December 2013 ranged from 1.225 - 6.740, 0.450 - 2.870, 0.376 - 1.038 and 0.067 - 1.830 mg/L while their means were 2.851 ± 2.224, 1.202 ± 0.731, 0.767 ± 0.254 and 0.858 ± 0.620 mg/L respectively. The study showed that the water obtained from River Benue in the months

of March, June, September and December 2013 had Zn in the ranges of 1.343 - 4.089 (mean 2.573 ± 1.075), 0.687 - 1.980 (mean 1.214 ± 0.444), 0.620 - 0.987 (mean 0.797 ± 0.126) and 0.232 - 1.432 (mean 0.805 ± 0.389) mg/L respectively. Finally, the water samples after the confluence was found to contain Zn in the ranges of 0.970 - 2.050 (mean 1.285 ± 0.361), 0.327 - 1.879 (mean 1.067), 0.765 - 1.565 (mean 1.096 ± 0.285) and 0.453 - 1.508 (mean 0.924 ± 0.352) mg/L respectively. A decline in the concentration Zn was generally observed in the water samples collected in September 2013. There was significant difference between the Zn concentrations obtained in the water samples during the four sampling periods at $p< 0.05$ as shown in Appendix XVII. The level of Zn in the water samples were however below the WHO recommended value (4.0000 mg/L) as shown in Figure 4.14, as such there is less risk of contamination of the water bodies and aquatic biota with Zn. Zinc in levels within the recommended limit generally improves the immune system, maintain taste, smell and protects the liver from chemical damage (Balch and Phyllis, 1990). The result of this work agrees with the values of Zinc reported by Olatunde and Oladele (2013) in River Niger, with range of 0.98 - 4.82 and mean 2.72 ± 0.57 mg/L.

5.3 Correlation Analysis of Water Parameters

Table 4.1 shows the correlation matrices of paired variable in the water samples collected in March 2013 from River Niger, River Benue and after the confluence point. Significant correlations at 0.01 and 0.05 levels of confidence are signified by ** and * respectively using 2-tailed ANOVA. From the analysis, BOD had high positive correlations with COD (0.909), turbidity (0.817), TDS (0.739), hardness (0.509) and lead (0.663); while strong negative correlation was observed with DO (-0.884), pH (-0.731)

and Cu (-0.525) respectively. There was also a strong positive correlation between COD with turbidity (0.772), TDS (0.762), conductivity (0.714) and Pb (0.703); while strong negative correlations were recorded with DO (-0.947), hardness (-0.592), pH (-0.707) and Cu (-0.575) respectively.

Similarly, the conductivity of the water samples recorded strong positive linear relationship with turbidity (0.559), TDS (0.508) and Pb (0.523) and strong negative relationship with DO (-0.779) and pH (-0.902) respectively. Also, DO recorded strong positive correlation with pH (0.735), hardness (0.473), Cu (0.599) and Pb (0.703); while DO negatively related to turbidity (-0.713) and TDS (-0.667). The analyses indicated that hardness negatively correlated with TDS (-0.472), Cu (-0.400) and Pb (-0.387). In addition, pH negatively correlated with turbidity with the correlation coefficient -0.638, TDS (-0.563) and Pb (-0.684). TDS shows strong positive relationship with turbidity (0.868) and Pb (0.785) and strong negative correlation with Cu (-0.507). Lastly, the only strong correlation recorded among the metals was between Pb and Cu (-0.551) which was an inverse relationship. The implication of this is that all variables with strong positive correlation indicates likely hood of same contamination and suggest anthropogenic activity.

From the result obtained in the water samples collected in June 2013 as presented in Table 4.2, BOD strongly correlated with only COD (0.824) and negatively correlated with DO (-0.835 at $p< 0.001$), BOD negatively correlated with pH and Cr (-0.413 and -0.397 respectively at $p< 0.005$). COD was also noticed to be positively correlated with Co (0.409) at $p< 0.005$ and it negatively correlated with DO (-0.710). Conductivity of the water had a strong positive correlation with turbidity, TDS (0.748 and 0.700 respectively

at p< 0.001) and Cu (0.451 at p< 0.005). DO also correlated positively with pH and Cr (0.468 and 0.424 respectively at p< 0.005.

Hardness was observed to have a positive linear relationship with TDS and Cu (0.413 and 0.442) respectively at p< 0.005 and had negative relationship with Cr (0.568) at p< 0.001. pH on the other hand recorded a positive relationship with Cr (0.415) and negatively for Cd (-0.436) all at p< 0.005. Similarly, TDS and turbidity were also strongly correlated with Cu (0.569 and 0.468) at 0.001 and 0.005 levels of significance respectively. Finally the only significant correlation among the metals was observed between Zn and Cd (0.643) which was a positive linear relationship.

Table 4.3 also shows a similar trend of correlation among the paired variable just as in March 2013, also for the samples collected in September 2013 with few exceptions. The exceptions during September were absence of significant correlation between Pb and BOD, COD, conductivity, DO, hardness, pH, TDS, turbidity and Cu. However, in contrast to the results for the March samples, a strong negative correlation was obtained between the level of Cu and Cr (-0.594) in the samples collected in September 2013.

Finally, Table 4.4 shows the correlation matrices of the parameters in the samples collected in December. The results indicated that BOD of the water samples had a positive correlation with COD (0.675) and Cu (0.498) and negative correlation with DO (-0.770), turbidity (-0.770), TDS (-0.435), conductivity (-0.445) and Cr (-0.396) respectively. COD was found to be negatively correlated with DO and Cr (-0.913 and -0.433) respectively. Conductivity of the water on the other hand correlated positively with turbidity, TDS, pH, Co, and Cr with the correlation coefficient 0.699, 0.520, 0.616,

0.534 and 0.637 respectively; and was negatively correlated to BOD, Cd and Cu (-0.445, -0.505 and -0.481). In addition, DO have positive relationship with Cr (0.427) and negative linearity with Cu (-0.516). Other paired parameters were observed to have similar trend like in the samples collected in June.

All positive correlations indicate that as one variable (parameter) increase, the other also increases and vice versa whereas negative correlation implies an inverse linear relationship (as one increase, the other decreases and vice versa). All correlation coefficient without * or ** indicates no significant linear relationship between the two set of parameters (Uba *et al*., 2008). Positive correlation also suggests that there is possibly same source of contamination for the two variables. The strong correlations were obtained at 0.01 levels of significance while moderate correlation was recorded at 0.05.

5.4 Heavy Metal Content in Sediment Samples (mg/kg) from River Niger and River Benue and after Confluence

5.4.1 Cadmium

Figure 4.15 depicts the concentrations of Cd in the sediment samples obtained from River Niger, River Benue and after the confluence point in Lokoja, Nigeria for the months of March, June, September and December 2013, while the data are displayed in Appendix XVIII. The amount of Cd in the sediment obtained from River Niger ranged from 0.620 - 3.786 (mean 2.020 ± 1.238), 0.344 - 2.103 (mean 1.179 ± 0.726), 0.396 - 0.685 (mean 0.526 ± 0.102) and ND - 1.932 (mean 0.7944 ± 0.639) mg/kg respectively for the samples collected in March, June, September and December 2013. On the other hand, the sediment obtained from River Benue recorded Cd in the ranges and means of

1.004 - 1.760 (mean 1.408 ± 0.271), ND - 1.023 (mean 0.550 ± 0.365), ND - 0.698 (mean 0.468 ± 0.209) and ND - 0.430 (mean 0.239±0.179) mg/kg for March, June, September and December samples respectively. Finally, the sediments obtained after the confluence were found to range from 0.894 - 2.003 (mean 1.399 ± 0.388), 0.212 - 0.976 (mean 0.615 ± 0.265), 0.408 - 0.964 (mean 0.788 ± 0.170) and ND - 0.480 (0.203±0.162) mg/kg respectively for the samples collected in the months March, June, September and December. From Analysis of Variance, Cd was found to follow the trend: March > June > September > December with respect to sampling period whereas with respect to the river type, the level of Cd in the sediment was found to follow the trend River Niger > River Benue > after confluence.

Analysis of variance (Appendix XXIV) shows that Cd content of the sediment from River Niger varied significantly compared to those of River Benue and the confluence for the samples obtained in March, June and December 2013; whereas for the samples collected in September, the Cd content of the sediment of confluence point was observed to vary significantly compared to those from River Niger and River Benue. The chart showed that the two rivers and the confluence point had Cd being above the permissible limit set by ISQG (0.6000 mg/kg) in March 2013. There were extremely high values of Cd in the sediment collected in June, September and December from River Niger, confluence and River Benue. This results is in conformity with that of Olatunde and Oladele, 2013 for Cd in the sediment from River Niger in Lokoja with the range of 0.3 - 3.4 mg/L.

5.4.2 Cobalt

The concentrations of Co in the sediments from River Niger, River Benue and after the confluence for all the sampling occasions are depicted in Figure 4.16 and the values are displayed in Appendix XIX. In the month of March, June, September and December 2013, the sediment from River Niger had Co in the ranges and means of 17.336 - 35.767 (24.533 ± 6.709), 9.575 - 24.651 (18.779 ± 4.498), 17.063 - 24.004 (20.542 ± 2.524) and 5.074 - 21.678 (12.317 ± 4.390) mg/kg respectively. River Benue on the other hand had Co with the range and mean 1.050 - 5.086 (3.197 ± 1.603), 1.008 - 3.652 (2.442 ± 0.978), 1.065 - 3.100 (2.264 ± 0.644) and 1.020 - 3.923 (2.157) mg/kg respectively for the samples collected in March, June, September and December 2013. Finally, the sediment obtained after the confluence point were found to contain cobalt in the ranges and corresponding means of 7.001 - 9.403 (8.565 ± 0.388), 3.656 - 6.673 (5.381 ± 0.265), 3.065 - 6.080 (4.483 ± 0.170) and 2.090 - 6.355 (4.385 ± 0.163) mg/kg respectively for the samples collected in the months of March, June, September and December 2013. The level of Co was observed to be higher in River Niger, followed by sediment after confluence point and then River Benue respectively in all the sampling months as shown in Figure 4.16. The samples collected in the month of March recorded the highest concentration of Co, while the ones collected in December 2013 had the least concentration. Analysis of variance (Appendix XXIV) shows that the Co content in sediment from the three sampling sites varied significantly at $p< 0.005$. Figure 4.16 showed that Co in the sediment from none of the rivers was above the ISQG standard of 40.00 mg/L. Cobalt content of the sediment was highest for River Niger, followed by that from the confluence and lowest in the sediment from River Benue for all the sampling

months. The low Co content recorded in the sediment could be related to the low relative abundance of Co in the earth crust which stands at 0.0025% (Smith and Carson, 1981) and this result is in agreement to that of Mohammad *et al*. (2012) for sediments of River Niger.

5.4.3 Chromium

The mean concentrations of Cr with respect to the sampling period are presented in Figure 4.17 and the values are presented in Appendix XX. From the results, sediment from River Niger have Cr concentration with the range and mean 29.133 - 39.650 (33.098 ± 3.543), 20.438 -27.508 (23.166 ± 2.555), 25.003 - 29.105 (27.469 ± 1.447) and 20.402 - 28.204 (22.979 ± 2.399) mg/kg respectively for the samples collected in March, June, September and December 2013.

Furthermore, the sediment from River Benue was found to have Cr in the ranges and corresponding means of 15.000 - 25.050 (20.929 ± 4.541), 10.602 - 18.349 (14.922 ± 2.816), 16.002 - 19.654 (17.606 ± 1.324) and 10.025 - 18.692 (13.177 ± 3.317) mg/kg for the months of March, June, September and December respectively. Similarly, the sediment after the confluence point contained Cr in the ranges of 17.881 - 29.840 (23.894 ± 4.355), 20.430 - 23.040 (21.911 ± 0.934), 20.976 - 25.657 (23.108 ± 2.117) and 18.007 - 22.770 (20.574 ± 1.513) accordingly for the samples collected in the months of March, June, September and December 2013. The level of Cr in the sediment is found to have an increasing trend thus: River Niger > after confluence > River Benue. However, with respect to sampling period, Cr in the sediment followed the ranking: March > September > June > December. Analysis of variance (Appendix XXIV) showed that Cr content of

the sediments from the two rivers and the confluence varied significantly at $P < 0.005$. The values of Cr in the sediments were all below the recommended limit (37.3000 mg/kg) as shown in 4.17. The values of Cr in the sediments obtained from this study exceed those reported by Adekola and Eleta (2007) in their work on the sediment from Asa River in Ilorin, Nigeria where Cr level was found to range from 3.0 - 11.3 mg/kg.

5.4.4 Copper

The mean concentrations of Cu in sediments of the two rivers are pictorially shown in 4.18 and the values are presented in Appendix XXI. The concentration of Cu in the sediment of River Niger was found to be in the ranges and corresponding means of 18.400 - 26.880 (23.404 ± 2.902), 14.990 - 18.434 (16.552 ± 1.2751), 12.856 - 15.050 (14.476 ± 0.980) and 8.202 - 11.290 (9.542 ± 1.131) mg/kg for the samples collected in March, June, September and December 2013 respectively. In the same manner, the sediment from River Benue recorded Cu with the concentration ranges of 11.407-13.680 (mean 12.462 ± 0.818), 8.044 - 10.003 (mean 8.504 ± 1.071), 8.076 - 10.640 (mean 9.558 ± 0.846) and 6.021 - 8.300 (mean 7.083 ± 0.752) mg/kg respectively for the samples collected in March, June, September and December 2013.

The sediments after the confluence on the hand had Cu with the concentration range of 17.043 - 19.000 (mean 18.060 ± 0.584), 16.567 - 19.654 (mean 18.308 ± 1.055), 10.045 - 12.987 (mean 11.807 ± 1.529) and 8.100 - 11.806 (mean 10.2413 ± 1.317) mg/kg for the months of March, June, September and December respectively. Analysis of Variance showed a significant difference in the Cu level of the sediment obtained from River Niger, River Benue and after the confluence point at $p < 0.005$. The highest content

of Cu in the sediment was recorded in River Niger for the samples collected in March 2013, and the least value was in the sediment from River Benue in the samples collected in December 2013.

From this study, the concentrations of Cu in the sediment were relatively low, compared to the ISQG standard of 35.7000 mg/kg (Figure 4.18). There was generally a decreasing trend in the Cu content of the sediments collected from March to December with the exception of the one from River Benue in June and September 2013.

5.4.5 Lead

The concentrations of Pb in the sediments collected in the three sampling sites at the respective sampling periods are presented in Figure 4.19 and the data is shown in Appendix XXII. From the results, the sediments of River Niger recorded Pb in the range of 1.902 - 5.061 (2.559 ± 0.991), ND - 1.446 (0.850 ± 0.501), ND - 1.456 (0.898 ± 0.567) and ND - 0.990 (0.509 ± 0.292) mg/kg respectively for the months of March, June, September and December 2013. In a similar manner, the sediments of River Benue had Pb in the ranges of ND - 1.700 (0.716 ± 0.606), ND - 0.705 (0.191 ± 0.263), ND - 0.400 (0.107 ± 0.147) and ND - 0.556 (0.105 ± 0.185) mg/kg accordingly for the months of March, June, September and December 2013. Finally, the sediment after the confluence had Pb in the ranges and corresponding means of ND - 1.970 (1.007 ± 0.689), ND - 0.452 (0.233 ± 0.183), ND - 0.657 (0.359 ± 0.194) and ND - 0.965 (0.288 ± 0.383) mg/kg for the months of March, June, September and December respectively. A sharp decline in Pb concentration in the sediment was observed from March to June, while moderate decrease was obtained in the sediment collected in June through to December 2013. The

results obtained indicated that the level of Pb in the sediments of the rivers vary significantly by sampling period at $p< 0.005$. However, the sediments from the three sampling sites were not polluted with respect to lead as the values obtained were far below the critical limit (35.00 mg/kg).

5.4.6 Zinc

Figure 4.20 shows the concentrations of Zn in the sediments obtained from the three sampling sites while the values are displayed in Appendix XXIII. Zn in the sediments obtained from River Niger was in the ranges of 23.455 - 27.417 (22.400 ± 8.114), 11.034 - 18.898 (15.467 ± 2.983), 14.376 - 20.380 (17.777 ± 2.047) and 10.006 - 19.074 (13.694 ± 3.718) mg/kg for the months of March, June, September and December 2013 respectively. Similarly, the sediment from River Benue had Zn in the ranges and corresponding means of 25.230 - 36.094 (32.842 ± 3.667), 19.001 - 29.030 (24.067 ± 3.400), 12.008 - 19.022 (17.079 ± 2.118) and 13.068 - 19.027 (16.003 ± 1.915) mg/kg for March, June, September and December samples respectively. Lastly, sediment after the confluence point were found to contain Zn in the ranges of 24.766 - 28.081 (26.399 ± 0.937), 11.076 - 19.093 (14.534 ± 3.018), 9.066 - 17.967 (14.179 ± 2.639) and 10.043 - 16.770 (12.926 ± 2.758) mg/kg respectively for the samples collected in March, June, September and December. The sediments from River Benue recorded the highest zinc content in March while the one from River Niger had the least value for the samples collected in December 2013. The values of Zn recorded for the sediments from River Niger, River Benue and the confluence were below the recommended limit (123.0000 mg/kg) by ISQG as depicted in Figure 4.20. There was significant difference (Appendix XXIV) in the Zn concentrations in the three sampling sites with the exception of River

Niger and the confluence in June, December and river Niger and Benue in the samples collected in September.

5.5. Pollution Load Index (PLI) of Heavy Metals in Sediment of River Niger, River Benue and the Confluence

Table 4.5 shows the contamination factors and pollution load index of heavy metals in the sediment samples. The result shows considerable contamination factors particularly for cadmium. Pollution severity and its variation along the sites were determined with the use of pollution load index. Results of this study show that the CF (Contamination factor) values of most of the metals such as Co, Cr, Cu, Pb and Zn in the sediments of the study areas are low (<1). However, CF for Cd in the sediment from the rivers recorded relatively high values. In spite of the low values of CF, the result suggests the influence of external discrete sources like industrial activities, agricultural runoff and other anthropogenic inputs. The values of Pollution Load Index in the last column were found to be generally low. According to Hakanson's degree of pollution classification, the sediment from River Benue and the confluence show low degree of pollution (0.6094 and 0.7213 respectively), while the sediment from River Niger shows moderate degree of contamination (1.0248) in the sample collected in March 2013, with respect to the analyzed heavy metals. For the sediment collected in June, September and December 2013 from the two rivers and the confluence point, there was low degree of pollution with reference to the six heavy metals analyzed as the values obtained were below 1. This result indicated low anthropogenic role as source of the heavy metal content of the sediment. This analysis conforms to those reported by Adel *et al*. (2011) and is higher than those reported by Anthony *et al*. (2014).

5.6 Geoaccumulation Index (I_{geo})

Table 4.6 shows the geoaccumulation index for the heavy metals studied in the sediment samples from River Niger, River Benue and the confluence in Lokoja, Nigeria with the sampling perriods. This index assesses the pollution status of each analysed heavy metal. The results indicate moderate pollution by cadmium in the two rivers in March, June and September 2013 whereas in December, only the sediment from River Niger recorded moderate pollution having 83.33% moderate pollution by Cd. The sediment from River Niger was observed to be moderately polluted in March, June and September with Co while the sediment from the two other sampling sites (Benue and confluence) were unpolluted resulting to only 25% moderate pollution of the entire study period. Cr on the other hand recorded moderate pollution in the sediment from River Niger during March and September and then the confluence in September which cumulatively gives 25% moderate pollution. The I_{geo} of Cu, Pb and Zn indicates no pollution of the sediment during the study period in all the sampling sites with respect to the studied heavy metals. The indices obtained for Cu, Pb and Zn is a product of the low values recorded visa vis their corresponding background values.

5.7 Heavy Metal Concentrations (mg/kg) in Organs of Fishes from the Vicinity of the Confluence of River Niger and River Benue in Lokoja

5.7.1 Cadmium

Table 4.7 shows the mean concentration of Cd in the bones, brain and flesh of *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (tilapia) and *Synodontis* nigrita (Kurungu in Hausa language) fishes collected at the study area during the sampling in March, June, September and December 2013. The bones of catfish, tilapia and S. *nigrita*

had cadmium in the ranges of 1.508±0.159-1.323±0.279, 1.882±0.196-2.257±0.469 and 1.829±0.329-2.019±0.607 mg/kg respectively. The brain contained Cd in the ranges of 1.203 ± 0.361 to 1.206 ± 0.084; 1.611 ± 0.260 to 2.076 ± 0.508 and 1.747±0.313 to 1.457 ± 0.389 mg/kg for catfish, tilapia and *S. nigrita* respectively. Lastly, the flesh had Cd ranging from 0.649 ± 0.232 to 0.894 ± 0.164; 0.988 ± 0.243 to 1.072 ± 0.229 and 0.809 ± 0.135 to 0.851 ± 0.051 mg/kg respectively for catfish, tilapia and *S. nigrita.* The result of the study reveals that *O. nilotocus* (tilapia fish) had the highest concentrations of Cd in all the studied organs and across sampling period compared to those of catfish and *S. nigrita*. Based on this result, Cd accumulates more in the bones followed by the brain and the flesh accumulated the least irrespective of the time of the year as well as the fish specie. This result is in agreement to those reported by Abraham *et al*. (2012) for Fishes of Hashenge Lake, Tigray, Northern Highlands of Ethiopia. By comparing this result with the WHO (1998) limit being 0.50 mg/kg for the level of Cd in the organs of fish, it could be seen that all the organs of the three species of fish are polluted with Cd, and therefore could pose deleterious effect to man on the long run by consuming the fish from these rivers.

5.7.2 Cobalt

The mean concentrations of cobalt in the three organs of the three species of fish studied are displayed in Table 4.8. The results reveal high accumulation of Co in the brain of catfish and *S. nigrita* while tilapia fish recorded its high values in the bone for all the samples collected with time. The flesh of the three fish species was found to contain the least concentrations of Co just like the report for Cd. The highest value (3.159 ± 0.714 mg/kg) was obtained in the brain of catfish in the samples collected in March 2013,

while the least value (0.453 ± 0.192 mg/kg) was recorded in the flesh of catfish collected in December 2013. This result shows high concentration of Co in both organs with respect to the Food and Agriculture Organization (FOA) (2003) set limit of 0.10 mg/kg. These results indicate that the long term consumption of the fish from River Niger and Benue could pose a threat to the health of the consumers, and thereby call for precautionary steps. High accumulation potential of Co by these organs could be attributed to the presence of anions and chelating agents in the body of these fish which led to formation of stable compounds (Jenne *et al.*, 2011). These results obtained for Co in the fish also agree with the report of Aweke and Taddese (2004) whose work reveals high concentration of Co in bones compared to liver and flesh of fish from Lakes Awassa and Ziway, Ethiopia.

5.7.3 Chromium

The mean concentrations of Cr in bones, brain and flesh of catfish, tilapia and *S. nigrita* is shown in Table 4.9. The result reveals the trend of the concentration of Cr in the organs to be bone > brain > flesh in all the fish species irrespective of the sampling period. About 91.67% of the results showed a decreasing trend from March to December while 8.33% shows an irregular pattern. The values of Cr recorded for all the three organs of the fish studied in this work exceeded the WHO set value of 0.15 mg/kg and therefore pose a serious threat to consumers of the fish from the study area. The work of Opaluwa *et al*., (2012) reported higher concentration of Cr (3.02 mg/kg) in bone of Nile Tilapia against 0.37 mg/kg of Cr in the flesh of the fish specie. Also a higher concentration of Cr in the bone compared to flesh was also reported by Aweke and Taddese (2004) in the study of fish from Lake Awassa and Ziway Ethiopia.

5.7.4 Copper

The mean concentrations of copper with respect to organs and fish species are displayed in Table 4.10. The data obtained in this analysis reveals that the bone accumulated copper more than the brain and flesh of the three species of fish studied. *O. niloticus* (tilapia) fish was found to contain the highest concentration of Cu with respect to other species (Catfish and *S. nigrita*). By comparing the values obtained to the limit specified by FEPA (1991) which is 1.3 mg/kg, it implies that almost 100% of the bones and brain of the three species of fish exceeded the limit, while about 12.5% of the flesh was within the tolerable limit, the other flesh samples were just slightly above the set limit. In view of this, a fair assertion that the flesh of the fishes is safe with respect to copper can be made considering its essential role in the body system. The variation of Cu in the organs of the three species of fish with respect to months is not significant. The variation of Cu in the studied organs agrees with the report of Adakole (1995) and Tukura *et al*. (2005) in their studies of *O. niloticus* fish from river Kubani, Zaria and Ahmadu Bello University Dam respectively.

5.7.5 Lead

The mean concentrations of Pb in the bones, brain and flesh of the three species of fish collected from River Niger and River Benue in Lokoja, Nigeria with the sampling periods in 2013 are presented in Table 4.11. The results reveals lead content in the ranges 1.907±0.690 – 2.874±0.916, 2.778±0.689 – 3.532±1.257 and 1.575±0.413 – 2.674±0.925 mg/kg for the bones of *C. gariepinus, O. niloticus* and *S. nigrita* respectively. Similarly, the brain of *C. gariepinus, O. niloticus* and *S. nigrita* had lead in the ranges of 1.204±0.354 – 2.330±0.418, 2.103±1.268 – 3.326±1.089 and 1.330±0.545 – 2.439±0.472

mg/kg respectively. The flesh recorded Pb in the ranges of 0.654±0.081 – 1.284±0.495, 0.664±0.421 – 1.451±0.608 and 0.831±0.755 – 1.043±0.425 mg/kg for *C. gariepinus, O. niloticus* and *S. nigrita* respectively. Lead was found to accumulate in the organs of the three species of fish studied, though there was low content of Pb in the water from the study area. This implies that the concentration of Pb in aquatic biota is not totally dependent on its concentration in the aquatic water. The results also indicates that the lead content the three organs were above the recommended value set by WHO (1993) which is 0.5 mg/kg. This implies that prolong accumulation of Pb in the body of consumers of the fish from the study area could pose serious threat of possible lead poisoning. The likely hood of different sources of lead to the organs other than just water could account to these high values recorded.

5.7.6 Zinc

Table 4.12 shows the mean concentration of Zn in the bone brain and flesh of *C. gariepinus, O. niloticus* and *S. nigrita* for the entire study period. Zinc in the bones of *C. gariepinus, O. niloticus* and *S. nigrita* were in the ranges of 5.460±1.069 - 3.765±0.834, 6.013±1.670 - 4.639±1.011 and 5.302±1.714 - 4.040±0.912 mg/kg respectively. The brain recorded Zn in the ranges of 4.045±1.126 - 3.291±0.538, 4.801±1.132 - 3.533±0.931 and 3.822±0.903 - 2.648±0.258 mg/kg for *C. gariepinus, O. niloticus* and *S. nigrita* respectively. Finally, the flesh of *C. gariepinus, O. niloticus* and *S. nigrita* had Zn in the ranges of 3.236±1.086 - 1.954±0.290, 3.151±0.977 - 2.301±0.645 and 2.781±0.362 - 2.121±0.285 mg/kg respectively. Zinc being one of the essential elements was found to fall below the permissible limit set by WHO (1999) which was 40.0 mg/L in all the organs of the three specie of fishes. Zinc in the organs was found to decrease in the order

bone > brain > flesh. The concentrations of Zn in the organs follow no regular pattern with respect to the sampling period. The levels of Zn in the organs reported in this work is below the values reported by Odoemelam (2005) in the study of organs of four species of fish collected from Oguta Lake in Nigeria as well as the report of Otitologbon (1995) in the study of organs of fish collected from ABU dam. This study indicates that the consumption of fish from River Niger and Benue could cause no health concern to the consumers in respect of Zn content.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

Water, sediments and three species of fish were collected from River Niger, River Benue and the confluence during the months of March, June September and December 2013. Selected physicochemical parameters of the water samples were determined. Six heavy metals (Cd, Co, Cr, Cu, Pb and Zn) were determined in the water, sediments and also in bones, brain and flesh of each of the three fish species. Standard methods by APHA and AOAC were used for the physicochemical analysis with appropriate equipment. VARIAN AAS (240FS) was used in assessing the concentrations of the heavy metals in the water, sediment and fish samples. Water samples from the two rivers and their confluence showed critical values of COD, DO, turbidity, BOD, TDS, hardness and conductivity in the months March, June and September while pH was within the permissible limit during the study period. Relatively low values of these physicochemical analytes were obtained in December 2013. Cd, Co, Cr and Cu were predominantly above the permissible limits in the water sample while Pb and Zn were below the tolerable limits in all the water samples.

All the sediment samples studied showed relative low values of Co, Cr, Cu, Pb and Zn, while Cd was in the sediment was above the acceptable limit in 58.3% of all the samples studied. Studies of the fish species reveals high bioaccumulation of Cd in all the organs of the fish species, with levels beyond the acceptable limit 0.500 mg/kg set by WHO (1998). Also, the level of Co and Cr also exceeded the threshold limit in all the fish samples irrespective of the organ or fish species. Only 4.69% of all the fish samples

had Cu within the acceptable limit while the remaining exceeded. Despite the low values of Pb recorded in the water and sediment samples, all the selected fish species studied accumulated Pb above the critical limit. Conclusively, the results indicated that bioaccumulation of Zn in all the samples of of the three species of fishes was low compared to the limits set by WHO (1999).

6.2 Conclusion

From the findings of this research, the following conclusions are being drawn:

1. Waters of River Niger, Benue and Confluence had high influx of organic substances during the study period as the COD, BOD and turbidity were above the acceptable limit set by WHO.

2. The water hardness for the samples collected in March, June and September 2013 was high except for the water from River Niger in June 2013. The water from River Niger, River Benue and the confluence had high electrical conductivity except for the samples collected in December 2013. Most of the parameters determined had the same source of pollution as indicated by the correlation matrices.

3. The water collected in the months of March, June and September 2013 was polluted with Cr, Co, Cr, and Cu but the water is in safe level with respect to Pb and Zn. There was significant difference in the levels of the heavy metals with respect to the three sampling sites. There was low pollution of the water samples with heavy metals in the month of December with the exception of Cu which recorded its lower values in September 2013.

4. From the results of the pollution load index the sediments have low degree of pollution with respect to the selected heavy metals. Geoaccumulation index indicated that the sediments from both rivers are lowly to moderately polluted with Cd and to some extent Co and Cr. No indication of pollution by Cu, Pb and Zn was recorded.

5. All the three organs of the fish studied were polluted with Cd, Co, Cr, Cu and Pb. However, the fleshes of the three fish species are lowly contaminated, whereas the bones have the highest contamination followed by the brain. The most threatening heavy metals (Cd and Pb) were found more in *Oreochromis niloticus* (Tilapia fish) followed by *Clarias gariepinus* specie.

6.3 Recommendations

1. Indiscriminate dumping of refuse close to river banks which could possibly be source pollutants to the rivers should be discouraged and the laws that ban such acts enforced, also punishments should be meted on defaulters.

2. Other tributaries of the rivers should be investigated with respect to their pollution status in order to ascertain the real source of pollutants to the rivers.

3. Further work should be carried out in the study area to investigate the fractionating pattern of the selected heavy metals in the sediments.

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Appendices

Appendix I: List of Apparatus and Equipments/ Reagents

1. Conical flasks
2. Beakers
3. Volumetric flask
4. Measuring cylinder
5. Plastic bottles for digest
6. Polythene bags
7. Wash bottles
8. Funnels
9. Forceps
10. Thermometer
11. BOD bottles
12. Incubator water bath
13. Reflux flasks
14. Hot plate
15. Nessler tubes
16. DO samplers
17. Siphon tubes
18. Conductivity meter
19. Magnetic stirrer
20. Nephelometric turbidimeter
21. Varian 240FS Atomic absorption spectrophotometer
22. Analytical balance

23. Muffle furnace

24. Oven

25. Hanna pH/Conductivity meter

26. Fume cupboard

27. Nose mask

28. Mortar and pestle

29. Filter paper

30. Crucibles

31. Glass rod

32. 2mm sieved

33. Spatula

List of Reagents and Chemicals Used (Analar Grade)

34. Sulphuric acid (H_2SO_4)

35. Nitric acid (HNO_3)

36. Standard ferrous ammonium sulphate

37. Potassium hydrogen phthalate ($KHC_8H_4O_4$)

38. Potassium dichromate solution

39. Sodium carbonate (Na_2CO_3)

40. Bromocresol green indicator

41. Phosphate buffer solution

42. Magnesium sulphate solution ($MnSO_4.4H_2O$)

43. Ferric chloride solution ($FeCl_2$)

44. Starch indicator

45. Eriochrometblack T sodium salt

46. Ammonium hydroxide solution

47. EDTA

48. Sodium thiosulphate solution ($Na_2S_3O_3.5H_2O$)

49. Ammonium acetate buffer solution

50. Sodium acetate

51. Ferrous ammonium sulphate

52. Hydroxylamine solution

53. Potassium dihydragen phosphate

54. Sodium borate decahydrate

55. Methyl orange indicator

56. Deinonised water

57. Borax Buffer ($Na_2B_2O_7.10H_2O$)

58. Sodium trioxonitrate ($NaNO_3$)

59. Cadmium chloride ($CdCl_2$)

60. Potassium heptachromate (v)

61. Copper sulphate pentehydrate

62. Cobalt (II) chloride

63. Pure lead Metal

64. Zinc sulphate

65. Mercury tetraoxosulphate VI ($HgSO_4$)

Appendix II: Sampling Points and Sample Coding for Water and Sediment from River Niger and Benue

River	Sampling Point	Water Sample Code	Sediment Sample Code
River Niger	A	1	S1
		2	S2
		3	S3
	B	4	S4
		5	S5
		6	S6
	C	7	S7
		8	S8
		9	S9
River Benue	D	10	S10
		11	S11
		12	S12
	E	13	S13
		14	S14
		15	S15
	F	16	S16
		17	S17
		18	S18
After Confluence	G	19	S19
		20	S20
		21	S21
	H	22	S22
		23	S23
		24	S24
	I	25	S25
		26	S26
		27	S27

Appendix III: Mean Values of B.O.D (mg/L) of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	9.50	7.48	15.87	5.83
	2	8.65	6.29	15.46	5.30
	3	9.72	6.84	12.98	4.80
	4	9.82	8.73	16.03	4.57
	5	9.93	7.26	15.89	5.02
	6	8.53	9.00	16.89	4.77
	7	8.79	5.80	14.87	5.13
	8	9.42	4.87	15.95	7.50
	9	8.68	6.85	16.37	7.13
	Mean	**9.23±0.56**	**7.01±1.31**	**15.59±1.13**	**5.56±1.106**
Benue	10	7.65	9.76	10.46	6.67
	11	7.36	7.79	10.67	7.83
	12	7.85	7.80	11.07	7.86
	13	7.94	11.53	9.25	7.47
	14	8.32	10.25	11.10	6.33
	15	8.24	9.43	9.08	6.43
	16	7.26	17.06	10.57	5.37
	17	7.85	11.56	9.78	5.78
	18	7.93	8.04	10.67	6.45
	Mean	**7.82±0.36**	**10.34±2.88**	**10.29±0.75**	**6.69±0.87**
After Confluence	19	8.04	14.43	13.08	5.80
	20	8.75	7.81	13.69	6.10
	21	8.56	6.73	12.96	7.00
	22	8.72	7.32	13.43	5.70
	23	8.85	15.18	14.83	7.43
	24	8.32	7.39	13.63	5.23
	25	8.43	10.79	13.85	5.57
	26	8.34	13.21	13.97	5.31
	27	8.58	8.93	12.48	5.76
	Mean	**8.51±0.25**	**10.18±3.29**	**13.55±0.68**	**5.99±0.75**

Appendix IV: Mean Values of C.O.D (mg/L) of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	141.50	115.50	125.43	112.44
	2	138.77	113.50	123.98	111.57
	3	145.97	114.87	112.87	90.25
	4	142.75	118.50	143.36	71.12
	5	143.87	115.57	138.07	83.41
	6	137.03	119.37	154.09	76.96
	7	141.05	111.97	125.87	94.72
	8	145.08	90.67	136.91	113.23
	9	139.57	114.50	146.01	112.57
	Mean	**141.73±2.98**	**112.72±8.58**	**134.07±12.78**	**98.25±16.80**
Benue	10	120.60	119.27	110.06	121.08
	11	118.33	115.83	115.76	114.55
	12	121.00	115.10	117.98	114.60
	13	128.04	123.50	108.45	131.80
	14	119.76	120.00	117.56	110.69
	15	123.74	118.07	125.87	111.65
	16	117.84	167.67	116.45	104.88
	17	121.75	121.09	109.65	107.70
	18	122.07	117.06	113.07	121.96
	Mean	**121.46±3.08**	**124.18±16.52**	**114.98±5.43**	**115.43±8.31**
After Confluence	19	123.67	131.67	125.06	80.13
	20	138.00	115.43	127.85	93.49
	21	127.33	114.40	119.56	113.48
	22	132.85	115.67	126.00	112.31
	23	137.08	203.77	131.07	113.76
	24	128.05	114.50	127.07	111.27
	25	132.48	124.83	121.36	112.60
	26	130.02	154.43	121.65	106.65
	27	134.08	132.90	118.76	110.50
	Mean	**131.51±4.69**	**134.18±29.20**	**124.26±4.16**	**106.02±11.59**

Appendix V: Means of Conductivity (µS/cm) of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	132.67	156.67	236.07	104.33
	2	134.68	146.33	221.98	99.00
	3	148.67	176.33	217.06	90.67
	4	135.43	142.00	243.96	86.33
	5	132.39	167.67	257.03	95.33
	6	127.00	137.67	248.63	86.67
	7	120.04	172.67	238.47	71.67
	8	135.87	137.33	210.62	83.00
	9	113.68	168.66	226.65	76.67
	Mean	**131.16±10.06**	**156.15±15.66**	**233.39±15.40**	**88.19±10.45**
Benue	10	104.68	201.06	211.83	73.71
	11	95.00	197.67	207.60	68.00
	12	128.00	176.65	215.87	63.33
	13	106.07	186.33	198.37	66.67
	14	101.38	165.33	178.04	56.00
	15	116.05	178.23	196.36	67.33
	16	102.03	187.98	174.08	73.67
	17	128.02	179.05	203.65	59.27
	18	105.94	169.67	226.87	62.47
	Mean	**109.69±11.77**	**182.44±11.95**	**201.41±17.09**	**65.61±6.00**
After Confluence	19	127.04	162.67	219.06	77.33
	20	129.06	154.53	208.76	83.67
	21	125.04	244.61	212.89	93.67
	22	120.05	283.67	215.38	85.00
	23	122.76	205.67	226.56	82.00
	24	126.06	164.33	216.98	85.67
	25	118.05	188.33	221.65	80.00
	26	121.06	176.67	220.87	105.0
	27	116.05	201.76	214.76	86.67
	Mean	**122.80±4.35**	**198.03±49.42**	**217.43±5.28**	**86.56±8.30**

Appendix VI: Mean Values of D.O (mg/L) of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	2.47	6.65	11.09	6.40
	2	2.61	7.88	12.78	6.77
	3	1.73	7.17	13.56	7.40
	4	1.93	5.42	9.87	8.53
	5	1.97	6.84	10.67	7.60
	6	2.64	5.10	9.36	8.80
	7	2.49	9.67	11.76	7.77
	8	1.89	10.63	11.58	5.30
	9	2.57	8.06	9.57	5.20
	Mean	**2.26±0.37**	**7.49±1.81**	**11.14±1.44**	**7.09±1.28**
Benue	10	4.72	5.52	14.76	4.24
	11	4.89	7.78	13.86	4.73
	12	4.27	6.23	13.87	4.92
	13	3.68	4.44	16.89	3.30
	14	4.67	5.47	13.58	6.43
	15	3.84	6.24	11.93	5.27
	16	4.96	4.23	14.07	6.81
	17	3.63	4.34	16.76	6.64
	18	3.82	6.56	13.75	4.21
	Mean	**4.28±0.54**	**5.65±1.19**	**14.39±1.57**	**5.17±1.22**
After Confluence	19	3.53	3.63	11.86	8.47
	20	2.70	6.74	11.59	7.43
	21	3.47	7.62	12.65	5.33
	22	2.87	6.39	11.89	4.80
	23	2.79	2.63	10.02	5.53
	24	3.02	7.70	11.46	6.20
	25	2.67	4.39	12.43	5.80
	26	2.86	4.53	12.62	6.87
	27	2.46	3.45	12.73	6.73
	Mean	**2.93±0.36**	**5.23±1.91**	**11.92±0.86**	**6.35±1.15**

Appendix VII: Mean Values of Hardness (mg/L) of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	155.10	124.00	201.87	47.67
	2	150.73	136.33	213.08	44.67
	3	155.13	115.33	208.64	48.00
	4	162.32	167.00	212.65	46.33
	5	162.03	156.00	231.06	55.33
	6	148.04	157.67	235.02	54.00
	7	157.03	156.22	219.63	52.33
	8	167.07	133.33	215.02	48.00
	9	169.67	167.33	254.76	43.33
	Mean	**158.57±7.25**	**145.91±19.09**	**221.30±15.40**	**48.85±4.15**
Benue	10	150.83	241.67	243.08	53.91
	11	190.53	194.00	247.02	48.67
	12	187.70	178.67	238.38	58.00
	13	191.06	175.67	265.04	62.33
	14	187.76	186.67	254.06	56.00
	15	176.36	195.49	243.01	63.00
	16	190.65	178.10	229.04	56.81
	17	253.09	185.30	245.76	62.32
	18	173.63	193.04	247.06	52.48
	Mean	**189.07±27.32**	**192.07±19.98**	**245.83±9.95**	**57.06±4.93**
After Confluence	19	195.80	166.67	231.65	56.00
	20	170.67	157.33	225.97	48.67
	21	175.57	176.33	230.95	52.33
	22	173.65	177.67	227.07	45.33
	23	164.07	168.67	187.08	49.33
	24	183.87	177.33	243.87	52.00
	25	172.06	167.00	236.97	54.00
	26	156.98	98.05	239.05	65.07
	27	167.09	156.06	235.56	59.87
	Mean	**173.31±11.30**	**160.57±49.43**	**228.69±16.62**	**53.63±6.04**

Appendix VIII: Means of pH of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	6.67	7.87	6.63	7.20
	2	6.30	8.33	6.87	8.20
	3	6.10	6.83	7.32	7.57
	4	6.50	7.53	6.43	7.70
	5	6.63	7.57	6.20	7.87
	6	7.04	6.47	6.37	7.87
	7	7.89	7.93	6.73	7.17
	8	6.54	7.63	7.68	7.50
	9	7.94	8.37	6.74	8.27
	Mean	**6.85±0.66**	**7.61±0.63**	**6.77±0.47**	**7.71±0.39**
Benue	10	8.47	6.32	7.65	7.98
	11	8.20	7.40	7.93	6.53
	12	7.77	7.50	7.56	6.43
	13	8.21	7.77	7.83	6.57
	14	8.45	7.43	8.32	6.87
	15	7.89	6.15	6.98	7.07
	16	8.43	6.56	8.32	6.47
	17	6.84	6.43	7.54	6.56
	18	8.34	6.23	6.62	7.42
	Mean	**8.07±0.52**	**6.87±0.64**	**7.64±0.56**	**6.88±0.53**
After Confluence	19	7.73	6.77	7.02	6.83
	20	7.43	7.33	7.43	7.40
	21	7.77	7.10	7.32	7.57
	22	7.83	7.40	7.24	7.33
	23	7.65	7.20	6.96	7.07
	24	7.04	6.20	7.50	7.40
	25	7.83	6.57	7.28	8.07
	26	7.63	6.43	6.79	8.54
	27	8.04	6.32	7.25	8.87
	Mean	**7.66±0.29**	**6.81±0.46**	**7.20±0.23**	**7.68±0.68**

Appendix IX: Mean Values of T.D.S (mg/L) of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	585.00	688.33	712.08	505.33
	2	579.00	645.67	732.05	501.33
	3	591.00	744.00	721.97	487.67
	4	605.87	622.33	737.76	478.00
	5	604.06	715.33	718.06	493.00
	6	586.07	605.67	725.77	483.67
	7	604.04	698.00	726.08	469.00
	8	563.47	594.67	736.07	487.00
	9	603.67	698.00	684.65	470.67
	Mean	**591.35±14.51**	**668.00±52.53**	**721.61±16.15**	**486.19±12.52**
Benue	10	527.33	856.32	675.04	467.87
	11	519.67	793.00	683.23	431.00
	12	480.67	767.33	648.02	420.33
	13	494.56	786.67	692.73	434.00
	14	521.06	757.67	690.02	407.00
	15	531.06	776.45	679.93	435.67
	16	503.00	795.32	713.03	476.37
	17	515.05	745.56	675.02	535.54
	18	492.98	757.43	682.56	513.43
	Mean	**509.49±17.39**	**781.75±32.81**	**682.18±17.32**	**457.91±43.79**
After Confluence	19	531.67	667.33	715.87	460.33
	20	527.00	684.67	725.65	477.67
	21	557.33	804.00	713.67	490.67
	22	576.02	832.00	703.02	479.33
	23	534.92	776.33	716.98	469.33
	24	524.08	676.67	723.65	486.00
	25	563.05	686.33	721.08	431.67
	26	487.08	821.08	717.17	521.00
	27	498.65	654.41	709.27	476.80
	Mean	**533.31±27.06**	**733.65±73.02**	**716.26±7.06**	**476.98±23.98**

Appendix X: Mean Values of Turbidity (N.T.U) of Water Samples with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	1	11.73	14.27	21.02	6.47
	2	11.60	13.57	24.38	6.73
	3	12.60	18.10	23.67	7.27
	4	14.67	12.60	24.38	7.33
	5	13.06	15.52	22.65	6.67
	6	11.53	12.67	23.63	6.23
	7	11.97	15.33	23.07	6.53
	8	11.47	13.00	24.64	6.60
	9	12.75	14.00	20.74	4.70
	Mean	**12.38±1.04**	**14.34±1.74**	**23.13±1.43**	**6.50±0.77**
Benue	10	10.03	25.76	19.03	5.98
	11	10.17	18.57	19.56	5.50
	12	9.67	17.23	18.67	4.83
	13	9.78	17.33	20.12	4.73
	14	10.65	16.33	20.04	4.50
	15	11.04	17.47	19.57	6.63
	16	9.05	18.36	22.65	5.32
	17	10.76	17.09	18.04	5.62
	18	9.06	16.06	19.46	4.87
	Mean	**10.02±0.71**	**18.24±2.93**	**19.68±1.29**	**5.33±0.68**
After Confluence	19	9.76	14.67	22.06	5.52
	20	10.88	15.47	23.06	7.63
	21	10.64	23.33	22.65	8.67
	22	11.04	27.33	21.48	7.87
	23	10.87	18.07	22.76	7.53
	24	10.67	15.00	23.04	7.57
	25	11.23	16.33	23.53	6.90
	26	9.04	25.67	22.43	9.43
	27	10.83	12.09	22.07	5.09
	Mean	**10.55±0.70**	**18.66±5.41**	**22.56±0.63**	**7.36±1.38**

Appendix XI: Mean Concentrations of Cadmium (mg/l) in Water Sample of River Niger, River Benue and the After the Confluence Point

River	Sample	March	June	September	December
Niger	1	0.017	0.012	0.015	0.007
	2	0.018	0.015	0.016	0.009
	3	0.018	0.016	0.016	0.010
	4	0.027	0.016	0.019	0.011
	5	0.034	0.023	0.027	0.014
	6	0.032	0.026	0.031	0.015
	7	0.016	0.011	0.014	0.003
	8	0.017	0.016	0.017	0.005
	9	0.019	0.016	0.018	0.009
	Mean	**0.022±0.007**	**0.017±0.005**	**0.019±0.006**	**0.009±0.004**
Benue	10	0.018	0.012	0.015	0.006
	11	0.023	0.013	0.018	0.008
	12	0.024	0.015	0.017	0.012
	13	0.019	0.013	0.014	0.024
	14	0.027	0.017	0.016	0.045
	15	0.037	0.025	0.025	0.059
	16	0.030	0.023	0.028	0.016
	17	0.033	0.026	0.029	0.018
	18	0.037	0.028	0.026	0.032
	Mean	**0.028±0.007**	**0.019±0.006**	**0.021±0.006**	**0.024±0.018**
After Confluence	19	0.020	0.010	0.009	0.004
	20	0.023	0.018	0.015	0.008
	21	0.024	0.023	0.020	0.013
	22	0.022	0.016	0.009	0.009
	23	0.023	0.016	0.013	0.009
	24	0.026	0.017	0.021	0.010
	25	0.017	0.011	0.014	0.005
	26	0.022	0.016	0.017	0.007
	27	0.023	0.019	0.021	0.009
	Mean	**0.022±0.003**	**0.016±0.004**	**0.015±0.005**	**0.008±0.003**

Appendix XII: Mean Concentration of Cobalt (mg/l) in Water Sample of River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	1	0.015	0.007	0.009	0.012
	2	0.018	0.010	0.013	0.007
	3	0.017	0.014	0.014	0.013
	4	0.017	0.013	0.015	0.009
	5	0.010	0.008	0.007	0.009
	6	0.015	0.010	0.012	0.008
	7	0.013	0.011	0.012	0.005
	8	0.019	0.013	0.013	0.009
	9	0.020	0.015	0.014	0.012
	Mean	**0.016±0.003**	**0.011±0.003**	**0.016±0.003**	**0.009±0.003**
Benue	10	0.015	0.005	ND	ND
	11	0.017	0.006	0.004	0.005
	12	0.021	0.013	0.016	0.007
	13	0.005	ND	0.004	ND
	14	0.08	0.003	0.005	0.001
	15	0.013	0.012	0.007	0.008
	16	0.028	0.026	0.010	0.002
	17	0.023	0.014	0.014	0.005
	18	0.029	0.015	0.013	0.010
	Mean	**0.018±0.008**	**0.010±0.008**	**0.008±0.005**	**0.004±0.004**
After Confluence	19	0.015	0.008	0.007	0.005
	20	0.021	0.012	0.009	0.009
	21	0.012	0.009	0.008	0.011
	22	0.017	0.012	0.013	0.017
	23	0.018	0.015	0.015	0.013
	24	0.012	0.011	0.009	0.009
	25	0.023	0.013	0.012	0.011
	26	0.024	0.016	0.014	0.010
	27	0.019	0.021	0.016	0.018
	Mean	**0.018±0.004**	**0.013±0.004**	**0.011±0.003**	**0.011±0.004**

Appendix XIII: Mean Concentration of Chromium (mg/l) in Water Sample of River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	1	0.129	0.126	0.130	0.087
	2	0.138	0.105	0.109	0.089
	3	0.138	0.129	0.127	0.091
	4	0.100	0.054	0.065	0.076
	5	0.106	0.080	0.085	0.078
	6	0.098	0.082	0.076	0.078
	7	0.154	0.087	0.082	0.058
	8	0.650	0.097	0.090	0.065
	9	0.187	0.116	0.123	0.076
	Mean	**0.135±0.031**	**0.097±0.024**	**0.099±0.024**	**0.078±0.011**
Benue	10	0.087	0.045	0.042	0.040
	11	0.063	0.054	0.057	0.043
	12	0.093	0.057	0.058	0.041
	13	0.112	0.078	0.067	0.036
	14	0.130	0.083	0.079	0.042
	15	0.143	0.082	0.083	0.046
	16	0.101	0.067	0.067	0.021
	17	0.107	0.076	0.069	0.034
	18	0.108	0.082	0.072	0.035
	Mean	**0.105±0.002**	**0.069±0.014**	**0.066±0.012**	**0.038±0.007**
After Confluence	19	0.100	0.056	0.048	0.043
	20	0.106	0.068	0.057	0.047
	21	0.132	0.087	0.058	0.046
	22	0.145	0.086	0.098	0.053
	23	0.104	0.085	0.097	0.049
	24	0.327	0.076	0.092	0.052
	25	0.121	0.054	0.062	0.039
	26	0.097	0.076	0.065	0.046
	27	0.120	0.067	0.067	0.057
	Mean	**0.139±0.072**	**0.073±0.012**	**0.072±0.019**	**0.048±0.006**

Appendix XIV: Mean Concentration of Copper (mg/l) in Water Sample of River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	1	1.040	0.980	0.143	0.067
	2	1.546	0.881	0.156	0.078
	3	1.670	1.010	0.106	0.180
	4	0.480	0.680	0.201	ND
	5	0.710	0.340	0.308	0.016
	6	0.899	0.704	0.210	0.015
	7	0.785	0.554	0.218	0.090
	8	1.330	0.772	0.254	0.277
	9	1.020	0.770	0.265	0.158
	Mean	**1.053±0.394**	**0.743±0.209**	**0.207±0.064**	**0.098±0.092**
Benue	10	2.021	1.300	1.046	1.400
	11	2.330	1.760	1.204	1.550
	12	1.550	1.030	0.965	0.769
	13	1.770	0.900	0.867	0.990
	14	1.851	1.220	0.976	1.040
	15	1.801	1.380	1.209	1.601
	16	1.030	1.200	0.942	1.022
	17	1.990	1.400	1.100	1.050
	18	1.890	0.890	1.209	0.957
	Mean	**1.804±0.359**	**1.231±0.275**	**1.058±0.130**	**1.153±0.290**
After Confluence	19	1.560	1.050	0.968	1.099
	20	1.980	1.000	1.263	1.000
	21	2.033	1.880	0.865	1.440
	22	1.300	0.996	0.894	1.003
	23	1.350	1.200	1.043	1.080
	24	1.029	0.980	0.954	1.231
	25	0.986	0.786	0.675	0.432
	26	1.187	0.876	0.764	0.610
	27	0.032	0.732	0.710	0.546
	Mean	**1.384±0.397**	**1.056±0.340**	**0.904±0.182**	**0.938±0.339**

Appendix XV: Mean Concentration of Lead (mg/l) in Water Sample of River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	1	0.005	0.002	0.003	0.002
	2	0.006	0.002	ND	0.001
	3	0.002	0.001	ND	ND
	4	0.005	ND	ND	ND
	5	0.007	ND	ND	ND
	6	0.005	ND	0.001	0.002
	7	0.003	0.001	ND	ND
	8	0.004	ND	0.001	ND
	9	0.005	ND	ND	ND
	Mean	**0.0047±0.0015**	**0.0007±0.0009**	**0.0006±0.0010**	**0.0006±0.0009**
Benue	10	ND	ND	ND	ND
	11	ND	ND	0.002	0.003
	12	ND	ND	0.004	0.001
	13	ND	ND	ND	ND
	14	ND	0.003	ND	0.001
	15	0.001	ND	ND	ND
	16	ND	ND	0.007	ND
	17	0.002	ND	ND	ND
	18	ND	0.002	ND	ND
	Mean	**0.0003±0.0007**	**0.0006±0.0011**	**0.0014±0.0025**	**0.0006±0.0010**
After Confluence	19	ND	ND	ND	ND
	20	ND	ND	ND	0.004
	21	0.001	ND	ND	0.001
	22	ND	ND	0.003	ND
	23	ND	0.001	ND	ND
	24	ND	ND	ND	ND
	25	0.002	0.002	ND	0.001
	26	0.001	ND	ND	ND
	27	ND	ND	0.001	ND
	Mean	**0.0004±0.0007**	**0.0003±0.0007**	**0.0004±0.0010**	**0.0007±0.0013**

ND – Not detected

Appendix XVI: Mean Concentration of Zinc (mg/l) in Water Sample of River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	1	1.225	0.970	0.843	0.749
	2	1.432	0.990	0.847	0.658
	3	1.560	1.450	0.910	0.985
	4	5.466	1.076	0.980	1.540
	5	5.030	1.650	0.965	1.340
	6	6.740	2.870	1.038	1.830
	7	1.139	0.450	0.467	0.067
	8	1.265	0.765	0.376	0.456
	9	1.802	0.600	0.478	0.100
	Mean	**2.851±2.224**	**1.202±0.731**	**0.767±0.254**	**0.858±0.620**
Benue	10	2.416	1.020	0.706	0.565
	11	4.041	1.097	0.796	0.676
	12	4.080	1.560	0.856	0.868
	13	1.519	0.687	0.659	0.232
	14	1.870	0.898	0.620	0.543
	15	1.890	1.050	0.785	0.599
	16	1.343	1.980	0.967	1.300
	17	2.349	0.870	0.798	1.034
	18	3.650	1.760	0.987	1.432
	Mean	**2.573±1.075**	**1.214±0.444**	**0.797±0.126**	**0.805±0.289**
After Confluence	19	1.146	1.001	0.875	0.453
	20	1.672	1.210	0.802	0.765
	21	2.050	1.879	0.765	1.345
	22	1.001	1.104	1.065	1.508
	23	1.300	1.030	1.435	1.074
	24	1.120	1.103	1.324	0.987
	25	0.970	0.327	1.565	0.566
	26	1.302	1.055	0.987	0.965
	27	1.003	0.897	1.043	0.657
	Mean	**1.285±0.361**	**1.067±0.398**	**1.096±0.285**	**0.924±0.352**

Appendix XVII: ANOVA Scores of Heavy Metals Concentration (mg/L) in Water Sample from River Niger and Benue

Sampling Period	River	Heavy Metal					
		Cd	**Co**	**Cr**	**Cu**	**Pb**	**Zn**
March	R. Benue	0.0276±0.0070[a]	0.0177±0.0084[a]	0.1049±0.00234[b]	1.8037±0.3593[a]	0.0003±0.0007[c]	2.5731±1.0750[b]
	R. Niger	0.0220±0.0070[b]	0.0160±0.0026[b]	0.1350±0.03052[a]	1.0533±0.3942[c]	0.0047±0.0015[a]	2.8510±2.2243[a]
	After Confluence	0.0222±0.0025[b]	0.0179±0.0043[a]	0.1391±0.0722[a]	1.3841±0.3973[b]	0.0004±0.0007[b]	1.2850±0.3608[c]
June	R. Benue	0.0191±0.0064[a]	0.0104±0.0079[c]	0.0693±0.0142[b]	1.2311±0.2745[a]	0.0006±0.0011[b]	1.2136±0.4442[a]
	R. Niger	0.0168±0.0048[b]	0.0112±0.0027[b]	0.0973±0.0244[a]	0.7434±0.2097[c]	0.0007±0.0009[a]	1.2023±0.7313[b]
	After Confluence	0.0162±0.0039[b]	0.0130±0.0039[a]	0.0728±0.0124[b]	1.0556±0.3396[b]	0.0003±0.0007[c]	1.0673±0.3976[c]
September	R. Benue	0.0208±0.0060[a]	0.0081±0.0054[c]	0.0660±0.0124[c]	1.0576±0.1295[a]	0.0014±0.0025[a]	0.7971±0.1261[b]
	R. Niger	0.0192±0.0058[b]	0.0160±0.0031[a]	0.0986±0.0242[a]	0.2068±0.0641[c]	0.0006±0.0010[b]	0.7671±0.2542[c]
	After Confluence	0.0154±0.0047[c]	0.0114±0.0033[b]	0.0716±0.0189[b]	0.9040±0.1824[b]	0.0004±0.0010[c]	1.0957±0.2845[a]
December	R. Benue	0.0244±0.0179[a]	0.0042±0.0037[c]	0.0376±0.0074[c]	1.1532±0.2899[a]	0.0006±0.0010[b]	0.8054±0.3886[c]
	R. Niger	0.0092±0.0039[b]	0.0093±0.0026[b]	0.0776±0.0109[a]	0.0979±0.0915[c]	0.0006±0.0009[b]	0.8583±0.6196[b]
	After Confluence	0.0082±0.0027[c]	0.0114±0.0041[a]	0.0480±0.0055[b]	0.9379±0.3391[b]	0.0007±0.0013[a]	0.9244±0.3523[a]
WHO limit		**0.0100**	**0.0100**	**0.0500**	**1.0000**	**0.0100**	**4.0000**

Letters differed in vertical rows within same sampling period refer to significant differences $P \leq 0.05$

Appendix XVIII: Mean Concentration of Cadmium (mg/kg) in Sediment Sample with Respect to Sampling Period

River	Sample	March	June	September	December
Niger	S1	0.620	0.432	0.506	ND
	S2	0.870	0.344	0.543	0.350
	S3	0.742	0.441	0.467	0.210
	S4	1.504	0.931	0.604	0.670
	S5	2.040	1.451	0.685	1.380
	S6	1.851	0.916	0.643	1.025
	S7	3.708	2.038	0.403	1.932
	S8	3.062	2.103	0.396	0.349
	S9	3.786	1.964	0.486	1.234
	Mean	**2.020±1.238**	**1.179±0.726**	**0.526±0.102**	**0.794±0.639**
Benue	S10	1.107	0.524	0.486	0.320
	S11	1.504	0.562	0.476	0.330
	S12	1.200	0.643	0.698	0.355
	S13	1.701	ND	0.589	ND
	S14	1.655	ND	0.367	0.011
	S15	1.760	0.504	0.386	0.430
	S16	1.004	0.693	0.543	0.340
	S17	1.307	1.003	ND	0.364
	S18	1.433	1.023	0.670	ND
	Mean	**1.408±0.271**	**0.550±0.365**	**0.468±0.209**	**0.239±0.179**
After Confluence	S19	1.702	0.548	0.876	ND
	S20	1.632	0.335	0.670	ND
	S21	1.185	0.212	0.408	0.132
	S22	2.003	0.976	0.876	0.203
	S23	1.578	0.896	0.894	0.362
	S24	1.600	0.922	0.964	0.105
	S25	0.993	0.556	0.895	0.480
	S26	1.004	0.524	0.767	0.309
	S27	0.894	0.562	0.745	0.232
	Mean	**1.399±0.388**	**0.615±0.265**	**0.788±0.170**	**0.203±0.162**

Appendix XIX: Mean Concentration of Cobalt (mg/kg) in Sediment Samples from River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	S1	34.008	23.420	24.004	12.201
	S2	35.767	20.055	23.648	12.764
	S3	24.042	21.772	23.196	21.678
	S4	21.230	16.209	18.375	13.023
	S5	24.490	17.860	20.754	9.044
	S6	27.059	24.651	19.547	11.966
	S7	17.336	18.407	19.663	5.074
	S8	17.992	9.575	17.063	11.445
	S9	18.873	17.061	18.629	13.660
	Mean	**24.533±6.709**	**18.779±4.498**	**20.542±2.524**	**12.317±4.390**
Benue	S10	3.303	3.051	2.765	2.542
	S11	2.075	3.652	2.654	3.923
	S12	3.971	3.070	3.100	2.544
	S13	2.500	2.465	2.678	1.983
	S14	1.050	1.008	1.989	1.020
	S15	1.086	1.073	1.065	1.032
	S16	4.654	2.050	1.578	1.325
	S17	5.086	3.541	2.105	2.950
	S18	5.051	2.073	2.440	2.081
	Mean	**3.197±1.603**	**2.443±0.978**	**2.264±0.644**	**2.157±0.958**
After Confluence	S19	9.403	5.827	6.080	3.025
	S20	8.987	6.673	6.054	3.086
	S21	9.861	5.080	5.843	2.090
	S22	8.340	6.033	4.065	4.876
	S23	9.344	6.076	4.611	3.554
	S24	7.980	6.330	3.065	4.930
	S25	8.300	4.876	3.865	6.355
	S26	7.870	3.656	4.105	5.654
	S27	7.001	3.879	2.657	5.897
	Mean	**8.565±0.388**	**5.381±0.265**	**4.483±0.169**	**4.385±0.163**

Appendix XX: Mean Concentration of Chromium (mg/kg) in Sediment Sample from River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	S1	30.750	21.154	29.043	20.830
	S2	31.004	22.005	25.003	21.402
	S3	30.766	20.438	26.086	23.887
	S4	32.800	27.508	28.065	24.425
	S5	31.002	26.734	29.105	23.333
	S6	29.133	22.373	28.560	28.204
	S7	39.650	23.705	28.065	21.325
	S8	36.776	23.923	26.225	22.850
	S9	35.997	20.654	27.066	20.559
	Mean	**33.098±3.543**	**23.166±2.555**	**27.469±1.447**	**22.979±2.299**
Benue	S10	24.650	15.955	19.065	13.551
	S11	25.050	16.558	18.076	18.692
	S12	27.880	11.581	19.654	10.025
	S13	20.400	10.602	16.087	11.406
	S14	22.450	14.906	17.942	14.988
	S15	20.882	12.434	16.002	8.086
	S16	16.050	18.308	17.645	16.503
	S17	16.001	18.349	17.921	14.016
	S18	15.000	15.601	16.065	11.323
	Mean	**20.929±4.541**	**14.922±2.816**	**17.606±1.324**	**13.177±3.317**
After Confluence	S19	25.350	21.425	25.065	20.951
	S20	25.974	22.699	24.004	22.770
	S21	17.881	21.091	24.432	22.303
	S22	28.549	21.490	25.657	18.007
	S23	26.431	21.453	20.976	19.650
	S24	29.840	20.430	22.002	19.000
	S25	21.007	23.040	22.665	20.991
	S26	19.089	22.970	24.076	20.430
	S27	20.112	22.600	19.098	21.067
	Mean	**23.894±4.355**	**21.911±0.934**	**23.108±2.117**	**20.574±1.513**

Appendix XXI: Mean Concentrations of Copper (mg/kg) in Sediment Sample from River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	S1	18.400	16.402	15.050	8.402
	S2	20.540	15.052	14.965	9.860
	S3	19.050	16.894	14.545	11.010
	S4	23.840	19.460	12.856	8.202
	S5	22.780	17.709	14.211	9.626
	S6	23.903	14.990	15.966	9.090
	S7	25.302	15.040	14.863	10.030
	S8	26.880	16.984	14.755	11.290
	S9	25.401	18.434	13.075	8.370
	Mean	**23.404±2.901**	**16.552±1.275**	**14.476±0.980**	**9.542±1.131**
Benue	S10	11.407	9.023	9.570	7.101
	S11	12.506	9.854	10.640	7.060
	S12	11.812	8.431	10.360	8.300
	S13	13.104	9.006	8.560	7.035
	S14	12.542	10.003	9.476	8.020
	S15	11.492	8.060	9.120	6.066
	S16	13.410	8.044	10.043	6.021
	S17	12.202	7.023	10.090	7.040
	S18	13.680	7.095	8.076	7.106
	Mean	**12.462±0.818**	**8.504±1.071**	**9.548±0.846**	**7.0832±0.752**
After Confluence	S19	18.200	16.567	12.056	10.897
	S20	18.450	18.909	10.765	11.403
	S21	19.000	18.043	11.645	11.806
	S22	17.043	19.045	12.987	9.001
	S23	17.578	18.565	10.045	8.100
	S24	18.001	19.321	11.655	10.218
	S25	18.037	17.545	10.088	11.643
	S26	17.670	17.123	12.056	10.102
	S27	18.562	19.654	14.966	9.002
	Mean	**18.060±0.584**	**18.308±1.055**	**11.807±1.529**	**10.241±1.317**

Appendix XXII: Mean Concentrations of Lead (mg/kg) in Sediment Sample from River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	S1	2.140	1.033	1.343	0.604
	S2	2.766	1.079	1.456	0.302
	S3	1.902	1.030	1.354	0.347
	S4	1.950	ND	0.864	0.705
	S5	2.300	ND	0.689	0.607
	S6	2.761	0.991	ND	ND
	S7	2.103	1.060	ND	0.695
	S8	2.051	1.012	1.076	0.990
	S9	5.061	1.446	1.300	0.330
	Mean	**2.559±0.991**	**0.850±0.501**	**0.898±0.567**	**0.509±0.292**
Benue	S10	1.700	0.705	ND	0.045
	S11	1.013	0.063	ND	0.076
	S12	ND	ND	0.023	ND
	S13	0.010	ND	0.400	ND
	S14	1.075	ND	0.306	ND
	S15	0.035	0.088	0.038	0.232
	S16	0.504	0.434	0.106	ND
	S17	1.077	ND	0.089	0.040
	S18	1.030	0.433	ND	0.556
	Mean	**0.716±0.606**	**0.191±0.263**	**0.107±0.147**	**0.105±0.185**
After Confluence	S19	1.104	0.134	0.238	0.064
	S20	1.902	ND	0.259	0.044
	S21	1.970	0.209	0.306	0.098
	S22	ND	ND	ND	ND
	S23	0.900	0.370	0.343	0.028
	S24	ND	0.454	0.546	0.014
	S25	1.108	0.365	0.657	0.800
	S26	1.002	0.110	0.498	0.965
	S27	1.076	0.452	0.386	0.576
	Mean	**1.007±0.689**	**0.233±0.183**	**0.359±0.194**	**0.288±0.383**

Appendix XXIII: Mean Concentrations of Zinc (mg/kg) in Sediment Sample from River Niger, River Benue and After the Confluence Point

River	Sample	March	June	September	December
Niger	S1	24.093	18.898	20.380	19.074
	S2	25.080	17.038	20.134	17.008
	S3	25.651	17.040	18.048	18.906
	S4	24.102	16.005	19.035	13.029
	S5	23.455	18.030	18.320	13.072
	S6	24.760	17.072	18.045	12.004
	S7	27.417	11.051	15.900	10.095
	S8	25.040	13.038	14.376	10.006
	S9	26.083	11.034	15.754	10.053
	Mean	**22.400±8.114**	**15.467±2.983**	**17.777±2.047**	**13.674±3.718**
Benue	S10	24.117	29.030	17.567	14.056
	S11	35.007	22.983	18.322	19.027
	S12	35.560	27.047	18.300	17.068
	S13	33.411	27.348	17.009	16.062
	S14	34.862	25.049	19.022	14.174
	S15	25.230	24.063	18.481	17.116
	S16	28.269	20.020	17.002	13.068
	S17	33.026	19.001	16.002	17.436
	S18	36.094	22.058	12.008	16.018
	Mean	**32.842±3.667**	**24.067±3.400**	**17.079±2.118**	**16.003±1.915**
After Confluence	S19	26.675	15.876	17.967	12.083
	S20	26.650	14.087	15.082	10.966
	S21	28.081	14.279	16.000	10.043
	S22	25.670	10.004	9.066	12.897
	S23	26.004	17.004	15.054	11.076
	S24	24.766	19.093	15.002	10.127
	S25	27.087	17.076	14.976	16.770
	S26	26.653	12.309	13.090	15.610
	S27	26.002	11.076	11.378	16.765
	Mean	**26.399±0.937**	**14.534±3.018**	**14.179±2.639**	**12.926±2.758**

Appendix XXIV: ANOVA Scores of Heavy Metals Concentration (mg/kg) in Sediment Samples with Respect to Sampling Period

Sampling Period	River	Element					
		Cd	Co	Cr	Cu	Pb	Zn
March	R. Niger	2.0203±1.2382 [a]	24.5330±6.7094 [a]	33.0976±3.5426 [a]	23.4040±2.9006 [a]	2.5593±0.9909 [a]	22.4001±8.1139 [c]
	R. Benue	1.4079±0.2711 [b]	3.1973±1.6027 [c]	20.9292±4.5412 [c]	12.4617±0.8175 [c]	0.7160±0.6056 [c]	32.8418±3.6669 [a]
	After Confluence	1.3990±0.3881 [b]	8.5651±0.3881 [b]	23.8937±4.3548 [b]	18.0601±0.5842 [b]	1.0069±0.6885 [b]	26.3987±0.9366 [b]
June	R. Niger	1.1789±0.7261 [a]	18.7789±4.4980 [a]	23.1660±2.5550 [a]	16.5518±1.2751 [b]	0.8501±0.5011 [a]	15.4673±2.9833 [b]
	R. Benue	0.5502±0.3650 [b]	2.4426±0.9784 [c]	14.9216±2.8158 [c]	8.5043±1.0714 [c]	0.1914±0.2633 [c]	24.0666±3.4003 [a]
	After Confluence	0.6146±0.2654 [b]	5.3811 ±0.2654 [b]	21.9109±0.9341 [b]	18.3080±1.0545 [a]	0.2327±0.1827 [bc]	14.5338±3.0175 [b]
September	R. Niger	0.5259±0.1018 [b]	20.5421±2.5235 [a]	27.4687±1.4473 [a]	14.4762±0.9797 [a]	0.8980±0.5666 [a]	17.7769±2.0474 [a]
	R. Benue	0.4683±0.2093 [b]	2.2638±0.6436 [c]	17.6063±1.3235 [c]	9.5483±0.8458 [c]	0.1069±0.1466 [b]	17.0792±2.1184 [a]
	After Confluence	0.7883±0.1695 [a]	4.4828 ±0.1695 [b]	23.1083±2.1173 [b]	11.8070±1.5285 [b]	0.3592±0.1938 [b]	14.1794±2.6394 [b]
	R. Niger	0.7944±0.6391 [a]	12.3172±4.3903 [a]	22.9794±2.3993 [a]	9.5422±1.1308 [a]	0.5089±0.2922 [a]	13.6941±3.7180 [b]
	R. Benue	0.2389±0.1792 [b]	2.1567±0.9584 [c]	13.1767±3.3171 [c]	7.0832±0.7522 [b]	0.1054±0.1845 [c]	16.0028±1.9146 [a]
	After Confluence	0.2026±0.1624 [b]	4.3852 ±0.1625 [b]	20.5743±1.5130 [b]	10.2413±1.3168 [a]	0.2877±0.3832 [bc]	12.9263±2.7577 [b]
ISQG STANDARD		0.6000	40.0000	37.3000	35.7000	35.0000	123.0000

Letters differed in vertical rows within same sampling period refer to significant differences $p \leq 0.05$. ISQG = Interim Freshwater Quality Guidelines as reported by Persaud *et al*. (199).