

**ASSESSMENT OF HEAVY METALS AND POLYCYCLIC AROMATIC
HYDROCARBONS IN WATER, FISH AND SEDIMENTS OF RIVERS NIGER
AND BENUE CONFLUENCE, IN LOKOJA, KOGI STATE, CENTRAL
NIGERIA.**

BY

YAKUBU NEWMAN MONDAY

PG/M.Sc./13/65471

**A THESIS SUBMITTED TO THE
DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY
UNIVERSITY OF NIGERIA, NSUKKA.**

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**DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY
UNIVERSITY OF NIGERIA, NSUKKA.**

**IN FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE
DEGREE OF MASTER OF SCIENCE IN CHEMISTRY**

SUPERVISOR: DR. EKERE N R.

January 2016

CERTIFICATION

I, Yakubu Newman Monday, a Postgraduate student in the department of Pure and industrial Chemistry with Registration number PG/MSC/13/65471 has satisfactorily completed the requirements for coursework and research work for the degree of Master of Science in Analytical Chemistry. The work embodied in this thesis is original and has not been submitted in part or in full for any Diploma or degree of this or any other University.

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DEDICATION

I dedicate this work to Jehovah my creator who designed my life and destiny the I am, who supplied all my needs and provided me with favor and protection for the fulfilment and accomplishment of this program and this research work in particular, which is an integral part of my destiny.

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Thank you all.

Yakubu Newman Monday

ABSTRACT

The concentration of six heavy metals and six of sixteen (16) US EPA priority polycyclic aromatic hydrocarbons (PAHs) in water, fish and sediment samples of the confluence of rivers Niger and Benue were investigated in triplicates using atomic absorption spectrophotometer (AAS) for the heavy metals determination and gas chromatography coupled with mass spectrometer detector for the PAHs after acid digestion of the samples for heavy metals, liquid-liquid and solid-liquid extraction for the PAHs samples. The heavy metals were profiled for dry and rainy seasons whereas, the PAHs concentration in the samples were profiled for only rainy season in five sample locations. The concentration of the metals in water across the locations ranged from Cd (0.038 to 0.089), Cr(0.106 to 0.240), Cu(0.092 to 0.0164), Fe(0.682 to 0.878), Pb(0.058 to 0.309) mg/L with distribution pattern of Zn>Fe>Pb>Cr>Cu>Cd for the dry season water samples and Cd(ND to 0.027), Cr(ND), Cu(ND to 0.021), Fe(2.236 to 13.634), Pb(0.119 to 0.205) and Zn(0.121 to 0.216) mg/L with distribution pattern of Fe>Zn>Pb>Cd>Cu>Cr during the rainy season. The sediments' metals concentration across locations ranged from Cd(2.189 to 2.893), Cr(4.367 to 9.927), Cu(3.433 to 6.780), Fe(233.210 to 254.160), Pb(8.967 to 17.420) and Zn(6.027 to 20.380) mg/kg with distribution pattern of Fe>Zn>Pb>Cr>Cu>Cd during the dry season and Cd (0.321 to 1.024), Cr(0.456 to 2.662), Cu(ND to 8.599), Fe(1.234 to 2.062), Pb(8.721 to 17.737) and Zn(12.350 to 66.343) mg/kg with distribution pattern of Zn>Pb>Cu>Cr>Fe>Cd for the rainy season samples. The mean concentration of the metals in Catfish during the dry and rainy seasons were Cd(3.367 and 0.666) Cr(- and 0.293), Cu(7.050 and 4.952), Fe(44.775 and 1.230), Pb(3.842 and 8.683) and Zn(63.625 and 85.266) mg/kg and the Tilapia mean concentration values for dry and rainy seasons were as follows Cd(4.850 and 0.453), Cr(- and 0.164), Cu(8.042 and 1.658), Fe(44.108 and 0.198), Pb(4.717 and 6.704), Zn(63.742 and 40.680) mg/kg. The concentrations of the PAHs in water across locations ranged from Nap(ND to 0.543), Ph(ND to 0.083) Ant (ND to 0.083), BbF(0.080 to 0.093), BkF(0.083 to 0.093) and BaP(0.083 to 0.113) mg/L with distribution pattern of Nap>BaP>BbF=BkF>Ant=Ph. The concentration of PAHs in sediment across the locations ranged as follows Nap(ND to 2.210), Ph(ND to 0.053), Ant(ND to 0.053), BbF(0.053 to 0.383), BkF(0.053 to 0.110) and BaP(ND to 0.053) mg/kg with distribution pattern of Nap>BbF>BkF>Ph=Ant=BaP. The mean concentration value of PAHs in Catfish and Tilapia were Nap(2.383 and 1.947), Ph(0.050 and 0.057), Ant(0.057 and 0.057), BbF(0.043 and ND), BkF(0.043 and ND) and BaP(0.050 and ND). The result of the heavy metals in water and fish samples were tested for non-carcinogenic and carcinogenic health risk using health risk assessment models such as hazard quotient (HQ), Total hazard index (THI) cancer risk (CR) and cancer risk index (CRI). The health risk assessment showed that Cd and Pb are of great concern. The ecological risk factors for the concentration of heavy metal and PAHs in sediment were estimated using ecological risk models such as geo-accumulation index (I_{geo}), contamination factor (CF), single ecological risk factor (ER), ecological risk index (RI), pollution load index (PLI) and polycyclic aromatic hydrocarbons pollution index (PPI). The results showed that sediment pollution ranged from no heavy metals pollution, low risk and very high risk pollution. The heavy metals and PAHs data were subjected to ANOVA at probability values less than 0.05 ($P < 0.05$) level of significance. The heavy metals concentration in sediment were significantly different but, HMs and PAHs were all not different significantly in the water and fish respectively. The data generated for HMs and PAHs were correlated for source identification and the correlation showed that the majority of the pollutants were from the same source.

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LIST OF ABBREVIATION

HMs	Heavy Metals
PAHs	Polycyclic Aromatic Hydrocarbons
NAP	Naphthalene
Ph	Rhenanthnene
Ant	Anthracene
Bbf	Benzo[b]Fluoranthene
Bkf	Benzo[k]Fluoranthene
Bap	Benzo[a]Pynene
TF	Tranfer Factor
BAf	Bioaccumulation Factor
GEMS	Gas Chromatography Coupled with Mass Spectrography
AAS	Atomic Absirption Spectrophotometer
CEC	Cation Exchange Capacity
ICP/AES	Inductively Coupled Plasma/Atomic Emission Spectrometry
ICP/MS	Industively Coupled Plasma/Mass Spectrometry
GC/FID	Gas Chrometography Coupled with Flame Ionization Detector
HQ	Hazard Quotient
THI	Total Hazard Index
CR	Cancer Risk Index
CRI	Cancer Risk

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Water pollution is any form of damage to the physical, chemical and biological characteristics of water which then affect the quality and suitability for any designated use or purpose^{1, 2}. Hence, it is an issue of great importance to protect the water sources from faecal, agricultural and industrial contamination or pollution which is continually threatening terrestrial and aquatic ecosystem due to increasing exposure of untreated wastes and chemical agents that are capable of causing damage to the environment³⁻⁵. For example, it has been reported that storm water runoff from urban areas contains numerous pollutants like polycyclic aromatic hydrocarbons (PAHs), heavy metals (HMs), biocides and suspended solids which are toxic or harmful to the aquatic environment and also have potential negative ecological impacts on receiving waters⁶. The negative impacts include eutrophication, oxygen depletion and chronic toxic effect towards aquatic flora and Fauna. The contamination of the environment, particularly the aquatic ecosystems by harmful waste indicators such as heavy metals and polycyclic aromatic hydrocarbons is a serious problem in the society because the environment is a direct receptacle for waste products generated in the space within the environment^{7, 8}.

Here, however, heavy metals and polycyclic aromatic hydrocarbons are of particular concern due to their prevalent toxicity to aquatic organisms and are persistent in the environment^{9, 10}. The toxicity of the aquatic environment poses threat to man for the fact that safe and suitable potable water supply for drinking and other uses are lacking especially in the rural settlement in Nigeria which makes rural dwellers to depend on rivers, streams, natural ponds, Lakes, shallow hand dug wells and

collection of rainfalls to meet their water needs as well as depending on aquatic animals which are capable of bio-accumulating pollutants like Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) as sources of food¹¹⁻¹³.

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) have been reported to have very carcinogenic, mutagenic and teratogenic effect on aquatic animals and humans who consume them or have direct encounter with the pollutants, especially with occupational exposure^{8, 14-19}, therefore it is consequential to take the environmental study of Heavy metals and polycyclic aromatic hydrocarbons very seriously to avert their possible effect and costly consequence of their contamination effects if not checked.

By definition, heavy metals (HMs) are loosely defined as members of a subset of elements that have density above 5.0 gcm^{-3} , exhibiting metallic properties and are chemically toxic to plants and animals²⁰⁻²². Examples of heavy metals include Mercury (Hg), lead (Pb), Iron (Fe), Cadmium (Cd), Copper (Cu), Arsenic (As), Thallium (TI), Manganese (Mn), Nickel (Ni), Vanadium (V) and Selenium (Se). The most important metals with regards to potential toxic effects are As, Cd, Cr, Hg, Pb and Zn; and Metals which in small quantities are essential for healthy growth but when in excess become hazardous include Co, Cu, Mn, Ni and Se respectively²³. Whereas, Polycyclic aromatic hydrocarbons (PAHs) on the other hand are large group of compounds containing two or more fused aromatic rings in linear, angular or clustered arrangement which sixteen of them are classified by the U.S environmental protection agency as pollutant of high priority having characteristics of persistence in the environment^{24,25}. The sixteen (16) priority polycyclic aromatic hydrocarbons (PAHs) include Naphthalene (NA), Acenaphthylene (ACY), Acenaphthene (ACE), fluorene (FL), phenanthrene (PH), Anthracene (AN), Fluoranthene (Flu), Pyrene (PY), Benzo[a] anthracene (BaA), Chrysene (CH), Benzo[b] fluoranthene (BbF), Benzo[K] fluoranthene (BKF), Benzo[a] pyrene

(BaP), Indeno[1,2,3 - Cd] pyrene (IP), Dibenzo[ah] anthracene (DA) and Benzo [g,h,i] Perylene (BP)^{25, 26}.

Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in nature and are daily being leached into rivers, lakes and oceans from natural and anthropogenic sources like rock weathering, waste water, industrial effluents, and incomplete combustion of organic materials, fossil fuel and petroleum. The pollutants are distributed in the rivers water, sediments and are bio-accumulated by the fishes and other aquatic animals in the water and this leads to bio-magnification of these pollutants in the food chain^{7, 12, 26-29}.

The toxicity of heavy metals depends on the physical and chemical conditions which also affect the mobility and bioavailability. These conditions include pH, temperature, water hardness salinity, organic matter, redox, complexing ligands and ion strength. Polycyclic aromatic hydrocarbons (PAHs) toxicity is also enhanced by dissolved oxygen, hardness and are often found attracted to stable particles in the water which settles in the sediment and not in the water phase because PAHs is hydrophobic and lipophilic in character. Because of the above mentioned characteristics of these pollutants, several studies have shown that the sediment is usually highly toxic than the water component of aquatic environment hence, sediments are seen to be repository for these pollutants (PAHs and HMs)^{6, 29-31}.

Therefore, this research work is focused on the determination or assessment of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in water, fish and sediments of the confluence of rivers Niger and Benue, in Lokoja, Kogi state, Nigeria.

1.2 Statement of the Problem

The main sources of heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) in the rivers and lakes are precipitation and urban runoff which leached these pollutants from both natural and anthropogenic sources into the water environment³². Five countries in the west-African region including Guinea, Mali, Niger, Benin and Nigeria have River Niger passed through their landmark and share in the usage of river Niger which originated from the Guinea highland in southern Guinea with Nigeria being the last country before the outpouring of the river into the Atlantic Ocean³³⁻³⁴. There is this belief around Lokoja that river Niger is more polluted than the river Benue because river Benue is only share in usage between Cameroon where it originates from and Nigeria where it joins the river Niger in Lokoja, Kogi State³⁵. But, it has been reported that the high rate of untreated effluent discharged into River Benue at Makurdi is alarming and that the rural dwellers uses this river as toilet as well as means of getting rid of their solid waste, and this water is the main source of drinking water to some of them as well as source of the fish they eat and export for their income³⁶ and the degradation of water quality is a significant problem for the River Niger because of the growth of large cities along the river's banks which has not been accompanied by development of wastewater collection and treatment plants, whether for domestic or industrial wastewater³³. Therefore, it becomes pertinent to check the effect of pollution on the river body and the aquatic lives in the river respectively to avoid the effect of the pollution in man who depends on the fishes of this river for food.

Lokoja is a community located at the bank of river Niger at the confluence of rivers Niger and Benue in Kogi state central Nigeria. The native people of Lokoja are predominantly farmers and fishermen. In recent times, the city is experiencing unusually high temperatures, problems of desertification and change in local vegetation, excessive deforestation, erosion and siltation of the river leading to

reduced fish catches and reduced fish catches is reported to be a result of pollution from various discharge of municipal wastes/sewage and other pollution³⁷⁻³⁹. It was also established that toxic effects are also experienced due to detergents, petroleum products and domestic factories⁴⁰. River Niger at the Lokoja axis, upstream from the confluence do experience inflow of pollutants from solid wastes from the two major markets opposite the river bank and domestic wastes from the residents of the community. Also contributing chemical pollutants are agrochemicals from the agricultural activities taking place on the river bank especially the agricultural scheme launched by the Kogi state government. Similarly, pollutants are added to the waters by all other countries and states that share in the usage of the rivers Niger and Benue before getting to Lokoja, Kogi State.

1.3 Aim and Objectives of the Research

The aim of this research study is to ascertain the level of pollution of the confluence of rivers, Niger and Benue, and the objectives are as follows: to

- a) Evaluate the levels of PAHs in water, fish and sediments samples from the rivers confluence.
- b) Assess the total levels of Heavy Metals in the water, sediments and fish samples selected.
- c) Determine Transfer factor (TF) of HMs from sediment to fish and therefore determine the bioaccumulation of the pollutants.
- d) Assess the possible health hazard posed by ingestion of fish and use of the river waters studied
- e) Determine the ecological risk index (ERI), Index of geo-accumulation, Contamination factor and Pollution load index posed by the heavy metals in the sediments and

- f) Compare the results with the set standards for water and fish by regulatory agencies.

1.4 Purpose of the study

The purpose of this research study is to understand and ascertain the different level or quantity of polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) that goes into the different rivers from the natural and anthropogenic sources and the contribution of the pollutants by the two rivers (Niger and Benue) to the downstream of the confluence in addition to the aim of the study, in order to ascertain the level of danger posed by these rivers based on the level of pollutants contributed by the rivers. Also, the level of the pollutants in the different rivers is of significance to the determination of the ^{river} that contributes more pollutants to the fish and other aquatic animals in the river, downstream of the confluence.

1.5 Significance of the Study

Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) pollution studies have been conducted in other areas downstream of River Niger but none is yet conducted at the confluence of rivers, Niger and Benue even though large numbers of fishes are caught from this axis and sold to the Nigerian people for consumption and export. Hence, the work will:

- a) for the first time, provide baseline data on heavy metals (HM) and polycyclic aromatic hydrocarbons (PAHs) for this area of study.
- b) generate data to be used to assess the impact of these heavy metals (HM) and polycyclic aromatic hydrocarbons (PAHs) in water and fish consuming populace in the area of study.

- c) therefore, the result could be used by the Kogi State and Nigerian governments in Legislation as regards to waste disposal and waste management.
- d) the result will be of use to Health management practitioners in the diagnoses of certain diseases prevalent in the area of study which could be caused by heavy metals.

1.6 Scope of the Study

The study was designed to assess and evaluate the level of Heavy Metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) contamination in the water, fish and sediments of rivers Niger and Benue confluence in Lokoja, Kogi State, central Nigeria using atomic absorption spectrophotometer for the heavy metals determination and gas chromatography coupled with mass spectrometry (GC-MS) techniques for the determination of the polycyclic aromatic hydrocarbons (PAHs) respectively^{41, 42}. The physico-chemical characteristics of the media were also measured using appropriate probes since they are the factors responsible for the environmental mobility and bioavailability of the pollutants. The work was limited to a dry and rainy season for HMs analysis and a rainy season for PAHs analysis and to the confluence of rivers Niger and Benue and three kilometers (3 km) upstream and downstream of the confluence respectively.

CHAPTER TWO

LITERATURE REVIEW

2.1 General Overview

Sediments have been reported to be an important sink and repository for heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) emitted from natural and anthropogenic sources as well as potential non-point pollution sources which may directly affect overlying waters and aquatic organisms^{43,44}. The concentration of heavy metals depends on the amount of heavy metal waste entering the waters. The more the waste entering the water, the higher the concentration found in the water. The heavy metals which enter water body will undergo sedimentation, dilution, dispersion, and then they will be absorbed by the organisms living in the water and the heavy metals which settles at the bottom will be stored in the sediment⁴⁴. Therefore, the profile of trace contaminants in undisturbed sediment cores can be utilized to estimate the extent and history of pollution in aquatic environment⁴⁵⁻⁴⁷. Apart from sediments, river water and even the aquatic animals (Fishes) have been used to determine pollution in the environment in order to assess the impact of pollution in the surrounding environment⁴⁸⁻⁵⁰. The chemical contaminants causing toxicity in aquatic environment and aquatic animals as a result of their accumulation, high stability and non-degradable or non-biodegradable nature include among others, heavy metals and polycyclic aromatic hydrocarbons (PAHs)³⁰. Therefore, this research work and particularly, this literature review is aimed at discussing the sources of heavy metals and polycyclic aromatic hydrocarbons as well as the impact of these two hazardous pollutants (Heavy metals and polycyclic aromatic hydrocarbons) on the aquatic organism and by implication man who depends on the aquatic organisms for survival. In addition, a brief discussion on the principles behind the operation of the techniques used to determine this pollutants

namely Atomic Absorption spectrophotometry for the heavy metals determination and Gas Chromatography for the PAHs determination were established respectively.

2.2 Heavy Metals

The term heavy metals have been previously defined as members of a loosely defined subset of elements that have density above 4.0 gcm^{-3} ; exhibiting metallic properties and can be chemically toxic to plants and animals which include: Hg, Pb, Fe, Cd, Cu, As, Tl, Mn, Ni, V and Se²⁰⁻²³. In natural environments, they occur at low concentrations but at high concentrations in contaminated environments, where they impact on public health.

Heavy metals are released into the environment from metal smelting and refining industries, scrap metals, plastic and rubber industries, various consumer products and from burning of waste containing these elements. The metals volatilize on burning and is released into the air. These volatilized metals become mobile and travel for large distances and are deposited on the soil, vegetation and water depending on their density. Once deposited, the metals are not degradable, they persist in the environment for many years poisoning humans through inhalation, ingestion and skin absorption. Acute exposure to these toxic metals leads to nausea, anorexia, vomiting, gastrointestinal abnormalities, dermatitis and many fatalities as those that occurred among a fishing community in Minamata Bay Japan, due to consumption of fish polluted by methylmercury in 1950, and in Ghana in 1967⁵¹⁻⁵⁵. In 1968, the Japanese government traced the causes of Itai-Itai disease - a very unusual and painful disease due to chronic cadmium poisoning resulting from consumed poisoned fish and recently in Nigeria, lead poisoning in Zamfara state killed several children caused by illegal mining activities^{51, 56-57}.

2.3 Review on Heavy Metals in Water, Sediment and Fish

Several studies have shown heavy metals presence, pollution or contamination of soil, water, fish and sediment in Nigeria. Studies of heavy metals pollution in Agricultural soil of Adogo in Ajaokuta L.G.A of Kogi state showed that the concentration of Cd, Cu, Mg, Ni, Pb and Zn were Cd<0.01, Cu: 0.89 ± 0.25 , Mg: 0.07 ± 0.001 , Ni 0.18 ± 0.03 , Pb 0.44 ± 0.16 and Zn 0.04 ± 0.03 µg/g, implying that the soil was not polluted since the metal content levels conformed to the world-wide background content of metals range in soil⁵⁸. Another study aimed at ascertaining the dispersion of contaminated heavy metals (notably Zn, Ni, Cr, Hg and Pb) within the soil profile in the vicinities of reclaimed auto-repair workshops, found significantly high levels of contamination. The general trend of dispersion of metal contaminants within the soil profile studied was Pb>>Ni>Hg>Cr>>Zn⁵⁹. The accumulation of heavy metals in soil and vegetable investigated in the vicinity of Gungulon Agricultural site showed that the soil heavy metals content suggested anthropogenic sources of contamination. The sequence of heavy metals in the cultivated soil samples from Gungulon Agricultural sit was in the order of Zn>Mn>Cd>Pb>Cu>Cr>Fe>Co>As>Ni⁶⁰. Heavy metals investigated in soil dust of industrial market in Enugu, south east Nigeria showed variation with some of the metals levels higher than the recommended allowable limit for such metals in soil by regulating agency. The results showed that Fe>Cu>Pb>Cd>Ni⁶¹. In the study of health risk assessment in relation to heavy metals in water sources in rural regions of South East Nigeria, it was investigated that the heavy metals in water samples collected from the major water sources in the study area; streams ponds/lake and shallow hand dug wells were found to contain heavy metals as such: Hg(0.00-0.01ppm), As (0.010 - 2.01 ppm), Cd(0.00-0.25ppm), Pd(0.38-3.04ppm) Cr(0.01-0.65 ppm), Cu (0.21 - 2.65ppm) and Fe(0.75 - 15.01ppm) with the risk assessment result indicated that while the hazard Quotient (HQ) of As, Cd, Cr and Pb were of moderate risk, (HQ>1), the total

hazard index (THI) of all the water bodies assessed were of high risk except one river⁴¹. Also, in a study, it was reported that the concentration of heavy metals investigated in Ikpoba reservoir - Benin City where of the concentration profile in descending order of Zn(116.59 mg/L) > Fe(5.60 mg/L) > Cu(0.24 mg/L) > Pb(0.07 mg/L) > Cr(0.033 mg/L) > Ni(0.03 mg/L) > Mn(0.026 mg/L) > Cd(0.02 mg/L). They researchers stressed that the values for Cd, Fe, Pb, Ni and Zn exceeded the world health organization (WHO) maximum permissible level for drinking water⁶². Heavy metal concentration in surface water and Bioaccumulation in fish of river Owan, Edo state Nigeria was investigated, they researchers found out that the concentration of the metal in water and fish where in the order: Fe> Ni> Zn and Fe> Zn> Mn> Ni. While Fe and Ni had higher concentration in water above WHO and FEPA recommended benchmarks for drinking water, Fe and Zn were found high in fish above the recommended benchmarks for fish consumption, therefore, they recommended that the metal concentration be monitored constantly⁶³. In the study to evaluate the concentration of heavy metals in sediments of river Ethiope, Delta state, Nigeria, the sources of the heavy metals according to the researchers were mainly due to anthropogenic effect, the concentration posed no imminent danger to the living organisms in the environment since the low levels observed do not pose any environmental contamination risk. The levels of the metals were reported to have an abundance ratio in the order of Zn> Pb> Cu> Mn> Ni> Cr⁶⁴. Interrelationship of heavy metals concentrations in water, sediment and fish samples from Owena multipurpose Dam was investigated and the results showed that the concentrations of heavy metals levels (mg/kg) in sediment and fish samples were far lower than their probable effect concentration (PEC) and ranged within the acceptable international standard in Fish for human consumption, and also, the concentration of the metals in sediment and fish samples were found to be several orders of magnitude greater than their corresponding values in water¹.

2.4 Sources of Heavy Metals in Aquatic Ecosystem.

Basically, there are two ways surface water bodies can be polluted. They are point sources and nonpoint sources of pollution. Nonpoint pollution sources can be hard to locate, quantify, and/or regulate. Locating nonpoint sources of pollution to surface water bodies is challenging because the sources may be located within the entire watershed area^{64, 65}. The nonpoint pollution sources, whether within or far from within the watershed are been helped to contaminate the aquatic ecosystem by leaching of pollutants via storm water runoff into the water body which PAHs and HMs were focused in this study⁶.

2.4.1 Point Sources of Pollution.

Point sources of water pollution refer to contaminants entering a waterway or river from a single source such as a pipe or ditch including discharges of harmful substances emitted directly into the water body like effluent sewage treatment works or waste from factories⁶⁶. Point sources of pollution include any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft, from which pollutants are or may be discharged. This term does not include agricultural storm water discharges and return flows from irrigated agriculture⁶⁷.

2.4.2 Nonpoint Sources of Pollution:

In this process of pollution, pollutants are not directly introduced into the water body from a point source but from a diffuse sources or several point sources that travels over a long distances to pollute the water body. Water runoff which travels over various land uses within a watershed is a major

source of non-point source of pollution leaching fertilizer, herbicide, agrochemicals, solid mineral deposit, crude oil, metal scrap and refuse dump into the water body^{63, 66-72}. Nonpoint sources of pollution majorly comes from many diffuse sources such as motor oil and grease left on streets from motor vehicles, and loose dirt and sediment from construction activities and new developments. As runoff from rainfall or irrigation water moves over the ground, it picks up and carries away natural and human-made pollutants and deposits them into lakes, rivers, wetlands, groundwater, and inland and coastal waters including Rivers Niger and Benue. Nonpoint sources, including natural sources, are the major contributors of pollutants to streams, lakes, wetlands, estuaries, marine waters, and groundwater basins in the world over and are important contributors of pollution to Rivers including Rivers Niger and Benue⁶⁶. Summarily, contaminants that are continuously being introduced into the aquatic environment are mainly due to leaching of pollutants or wastes by runoffs from polluted sources due to increasing activities of industrialization, technological development, growing human population, oil exploration and exploitation, agricultural and domestic residents. Among these contaminants, heavy metals constitute one of the most dangerous groups because of their persistent nature, toxicity, tendency to accumulate in organisms and undergo food chain amplification or magnification and more still, they are non-degradable or bio-degradable^{63, 72, 73}. Sources of some of the heavy metals are summarized as shown in the Table 2.1 below⁷⁴⁻⁷⁶:

Table 2.1 Heavy metals and their different sources^{74, 76}.

S/No	Heavy metals	Sources
1.	As	From its use in herbicides, cattle and sheep dips and insecticides. Also as a desiccant for cotton crop to facilitate the mechanical harvesting of the crop. Semiconductors, petroleum refining, wood preservatives, animal feed additives, coal power plants, volcanic, mining and smelting.
2.	Cu	Electroplating industry, smelting and refining, mining, biosolids
3.	Cd	From the application of phosphate fertilizers (Containing 2-200 mg Cd/kg) domestic and sewage sludge, wear of automobile tyres, lubricants and mining as well as metallurgical activities (metal smelting and refining) fossil fuel burning.
4.	Cr	Wastewater and sludge from dyeing and tanning industries (tanneries) are the major sources of chromium pollution to the environment. Also, waste from Electroplating industry and solid waste.
5.	Pb	Major sources of Pb pollution are burning of leaded gasoline in gasoline engine to emit exhaust gases via exhaust pipe, which account for nearly 80% of the total Pb in the air. Soils located near Pb mines may contain as high as 0.5% Pb content. Apart from minerals, sources of Pb are pesticides, fertilizer impurities, and emissions from mining and smelting operations, atmospheric fallout from the combustion of fossil fuels. Municipal sewage and industrial wastes enriched in Pb, paints.
6.	Hg	Major contaminating sources of Hg are: Hg based fungicides, sewage sludge and atmospheric fall out resulting from combustion of fossil fuels and industrial processes. Improper disposal of mercury containing equipment like thermometer. Volcano eruptions, forest fire, emissions from industries producing caustic soda, coal, peat and wood burning
7.	Se	Coal mining, oil refining, combustion of fossil fuels, glass manufacturing industry, chemical synthesis (e.g. Varnish, pigment formulation)
8.	Ni	Sources of Ni pollution, are: metal refining, smelting, and burning of coal and industrial sewage sludge. Volcanic eruptions, land fill, forest fires, bubble busting and gas exchange in ocean, weathering of soils and geological materials.
9.	Zn	Electroplating industry, smelting and refining mining, bio-solids.

2.5 Factors Affecting Mobility, Bioavailability and Bio-toxicity of Heavy Metals

Heavy metal toxicity is the degree to which heavy metal can damage an organ or a whole organism. The mobility of heavy metals, bioavailability and related bio-toxicity to organisms depend on their specific chemical forms or ways of binding rather than the total metal concentration obtained after strong acid digestion. The mobility and bioavailability of metals in water and sediment is a self-motivated process that depends on unambiguous combination of biochemical and environmental parameters. These include parameters such as pH, organic matter content, redox potential, cation exchange capacity (CEC), sulfate, carbonate, hydroxide, soil texture and clay content. The term bioavailability of any element is used to indicate that part of its total concentration which is readily soluble in water and considered to be easily available to organisms or fraction of heavy metal in water and sediments that is accessible to the food Chain via plants and animals. The water soluble fraction of heavy metals is the heavy metals's form that has the highest potential for food chain contamination⁷⁶⁻⁸². However, the concentration of heavy metals in terrestrial and aquatic ecosystem or organism is determined by the size of the source, precipitation and adsorption processes in the water and sediment whether the source of the metals is natural or anthropogenic. The extent of adsorption depends on the metal, the absorbent, the physicochemical characteristics of the environment and the concentration of other metals and complex chemicals present in the sediment and water body^[82]. Whereas the mobility of heavy metals is referred to the potential of transferring the metals through soil profile down to ground water aquifer or via plant-root uptake, that is,

transferring the metals from one point to another which is depended on the availability of the metals for such transfer⁷⁶. However, the following factors are known to be responsible as well as affecting the mobility and bioavailability of heavy metals in water and sediments.

2.5.1 Temperature:

This is a scientific physical quantity which corresponds to primary sensation or measure of the degree of hotness and coldness of a body⁸³. Higher temperature enhances the degradation of organic matter in media (water and sediments) thereby releasing organic acids, which increase the availability and mobility of heavy metal ions in the media, also, the decay of the organic matter leaves the heavy metals which are not biodegradable behind and thereby increasing the availability of the metal ions⁷⁶. Heavy metals and other pollutants are adsorbed more rapidly at higher temperatures than low temperature because at low temperatures, metals are more soluble in the media than at high temperature⁸⁴.

2.5.2 pH

The importance of pH in metal solubility is well-known to influence heavy metal adsorption, retention and movement. pH and Ca concentration affect Cd, Cu, Pb and Zn mobility in soils by competing on adsorption sites⁸⁵. The pH value of the sediment solution is the master variable that oversees the adsorption of metal ions at surfaces⁸⁶. High pH values promote adsorption while low pH can actually prevent the retention of metals by sediment⁸⁷. The effect of pH on metal sorption to soil surface can be found when pH increases. Usually, the electrostatic attraction between metals and soil constituents is enhanced by increased pH. Therefore, at high pH, metals are predominantly found as insoluble metal mineral phosphates and carbonates. When soil pH decreases, soluble metals increases. Therefore, in low pH soil, it is common to find free ionic species or soluble organometals

in there⁸⁸. This is due to precipitation of hydroxides, Carbonates or formation of insoluble organic complexes⁶⁰ and most metal hydroxide minerals have very low solubility under high pH conditions in natural water⁸⁹. At a pH below 3, many of the heavy metals exist as ions in the solution⁹⁰. The dominant effect of a decrease in pH will be to increase metal availability⁹¹.

2.5.3 Cation Exchange Capacity (CEC)

Cation exchange capacity or CEC is the number of exchangeable cations per dry weight that a soil is capable of holding, at a given pH value, and available for exchange with the soil water solution. Most sediments colloids are negatively charged so they tend to attract cations which carry opposite charge to their surfaces. These cations are called exchangeable cations, and in most sediment, they are dominated by Ca^{2+} , Mg^{2+} , K^+ , Na^+ , H^+ and Al^{3+} . Cation exchange capacities of sediments/soils increase as pH increases. As the rate of supply of dissociated hydrogen ions increases in sediment water from acid precipitation, the rate of cations exchange is increased: cations such as Na^+ K^+ and Mg^{2+} are displaced from exchangeable site on sediment particles. These can then be moved through the sediment, provided that the mobile ions are present to transport them and acid precipitation provides these in form of SO_2^{-4} , although Nitrate (NO_3^-) could serve the same purpose⁹¹. Soils and sludges with higher cation exchange capacities have greater tendency for retaining metals. For example, cadmium retention has been observed to be higher in soils with higher cation exchange capacity and Cd retention was greater in fine textured soils with high cation exchange capacity (CEC) compared to coarse-textured soils with lower⁸⁹.

2.5.4 Moisture

The effects of increasing the moisture content in soil are that it displaces metals from adsorbed sites, thereby releasing them into the soil solution. It was illustrated that the solubility level of Cu, Cd, Ni, Mn, Zn, Pb, Fe and Cr were higher in the rainy season than in the dry season due to enhanced desorption of the metals from the sediments. As soil dries, metals are held closer to soil surfaces^{92, 93}.

2.5.5 Redox potential

Metal bioavailability changes in response to changing redox conditions under oxidizing or aerobic conditions, metals are usually found in soluble cationic forms. In contrast, reduced or anaerobic conditions such as those found in sediments or saturated soils, often was relevant to metal precipitation⁸⁹. It is also reported that Sediments that are formed under waterlogged conditions contain iron sulfide minerals (predominantly as the mineral pyrite) or their oxidation products in an undisturbed state below the water table and are benign in that state but, when the sediments are drained, excavated or exposed to air by a lowering of the water table like the flooding experienced recently along the bank of rivers Niger and Benue, the sulfides react with oxygen to form sulfuric acid which then releases sulfuric acid from the sediments as well as iron, aluminium, and other heavy metals (particularly arsenic) within the sediments. Once mobilized in this way, the metals becomes available and can create a variety of adverse impacts^{94,95}.

2.5.6 Partition coefficient

The affinity of a metal to associate with particulate matter is quantified by its partition coefficient, K_d . The K_d for metals varies in response to changes in salinity and the nature of the particulate matter present. High K_d values signify stronger association of metals to solid phase. It has been shown by

many authors, that large amounts of heavy metals are bound in the fine grain fraction of sediments, mainly because of its high surface area to grain size ratio^{85, 96}.

2.5.7 Organic matter

Organic matter is another important sediments component that influences metal availability. It has a nutritional function by serving as a source of N, P, and S and has a high binding capacity for cations and organic contaminants^{86, 97}. It has been reported that Organic matter of sediments immobilizes metal at weakly acidic to alkaline reactions by forming insoluble or soluble organic metal complexes respectively. It has been demonstrated that for Cu and Pb, sediments organic matter decrease the solution concentration of Cu and Pb at pH value 4 and on the other hand at pH 6 to 8 higher concentration of Zn and Cd were measured for sediments samples with higher content of organic matter because of a complexation of heavy metals by soluble organic matter substances. Therefore, sediments organic matter can reduce toxicity or toxic effects of heavy metals at some certain pH values⁹⁸.

2.6 Environmental Health Impact of Heavy Metals

As pointed out earlier, heavy metals are ubiquitous because they volatilize and become mobile and travels for large distances and are deposited on the soil, vegetation and water depending on their density hence, they become cosmopolitan. Once deposited, the metals are not degradable, they persist in the environment for many years poisoning humans through inhalation, ingestion and skin absorption. Acute exposure to these toxic metals leads to nausea, anorexia, vomiting, gastrointestinal abnormalities, dermatitis and many fatalities⁵⁰⁻⁵⁶.

2.6.1 Arsenic (As)

It is a poisonous metal that its inorganic form is a dangerous carcinogen and can cause cancer of the skin, lungs, liver and bladder, ingestion of high levels may result in death⁹⁹ and soluble inorganic arsenic is acutely toxic that its intake over a long period can lead to chronic arsenic poisoning (arsenicosis). Effects, which can take years to develop depending on the level of exposure, include skin lesions, peripheral neuropathy, gastrointestinal symptoms, diabetes, renal system effects, cardiovascular disease and cancer. Organic arsenic compounds, which are abundant in seafood, are less harmful to health and are rapidly eliminated by the body. Human exposure to elevated levels of inorganic arsenic occurs mainly through the consumption of groundwater containing naturally high levels of inorganic arsenic, food prepared with this water and food crops irrigated with high-arsenic water sources¹⁰⁰.

2.6.2 Copper (Cu)

Copper is an essential micro-nutrient required in the growth of both plants and animals. It helps in the production of blood haemoglobin in human and in plants, it help in regulation of water and disease resistance but, in high dose, it can cause anemia, liver and kidney damage and stomach and intestinal irritation in animals. At higher concentration, Cu causes yellowish of plant leaves and inhibits various cellular metabolic processes and root growth and also produces toxic effect on chromosomal morphology. Industrially copper is used in producing a wide range of important alloys such as bronze (Cu, Sn), brass (Cu, Zn), cupronickel (Cu, Ni) and it is used in making electric wires and roofing sheets^{82, 84, 100}.

2.6.3 Cadmium (Cd)

The most significant use of cadmium is in nicked/cadmium batteries as rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and

electrical stress. Cadmium is produced as an inevitable by - product of zinc refining because they occur together naturally within the raw ore. Cadmium coatings provide good corrosion resistance, in high stress environments such as marine and aerospace applications where protection from sea high saltiness is required. It is also used as pigments, stabilizer for PVC, in alloys and electronic components. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products⁸². Japan was host to the first reported case of cadmium poisoning in the environment when doctors reported Itai-Itai in 1955, a disease characterized by several back and joint pains, kidney lesions, protein and sugar in the urine and decalcification of the bones, sometimes heading to multiple⁹¹.

2.6.4 Lead (Pb)

Lead arises in the environment from both natural and anthropogenic source. Exposure can be through drinking water, food, air, soil and even dust from old paint containing lead. Lead is used in the manufacturing, construction and chemical industries. It is used in batteries, petrol additives, rolled and extruded products alloys, pigments, cable sheathing and in guns and ammunition. Exposure to lead in humans can result in a wide range of biological effects depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn causes problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tracts, joints and reproductive systems and acute or chronic damage to the nervous system⁸².

2.6.5 Mercury (Hg)

Mercury (Hg) occurs naturally as a mineral and is distributed throughout the environment by both natural and anthropogenic processes and human activities. Inorganic mercury occurs naturally due to

its presence in rocks and soils. It is slowly released through erosion and weathering into surface waters¹⁰¹. Mercury is rather unique among metals in that it is readily volatilized. Industrial processes which heat mercury-containing materials easily release it into the air. Once in the air, it can travel far from its source. Ore roasting associated with gold mining, along with coal-fired power plants, cement kilns, and waste incinerators are known sources that release mercury into the air. Some of this airborne mercury makes its way into waters through atmospheric circulation and eventual deposition. Almost all the mercury making its way into surface waters is inorganic. Some of the inorganic mercury is converted into the organic form methylmercury (Me-Hg) in environments conducive to such conversion (low pH, low dissolved oxygen, and high organic matter, such as are found in the bottoms of lakes, marshes, and wetlands)¹⁰²⁻¹⁰⁴. In addition to being much more toxic than inorganic mercury, methylmercury readily biomagnifies, increasing several thousand-fold in concentration in aquatic food chains—algae to plankton to fish and so on—culminating with much higher concentrations in varieties of fish often sought for sport. It is known that methylmercury concentrations and bioaccumulation factors increase higher in the aquatic food chain. Piscivorous fish (e.g., bass, walleye, and lake trout) are at the top of most aquatic food chains and often contain the highest concentrations of methylmercury^{101, 105}. The use of mercury is widespread in industries and in various products. Much goes into electrical apparatus and into the chlor-alkali industry, which produces chlorine and sodium hydroxide electrolytically; Mercury is also used as a slimicide; in paints, pharmaceuticals, dental applications and precision instruments⁹¹. Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organism. Apart from its vapour form, it rarely occurs free in nature and is found in Cinnabar ore (HgS) in Spain and Italy⁸⁴. Inorganic mercury poisoning is associated with tremors, gingivitis and minor psychological changes, together with spontaneous absorption and congenital

malformation and development changes in young children. Natural biological process can cause methylated forms of mercury to form which bioaccumulate over a million fold and concentrate in living organisms, especially in fish^{76, 82}. Exposure to high levels of Mercury can permanently damage the brain, kidneys, and developing fetuses¹⁰⁰. Concern over mercury in the environment arises from these extremely toxic forms in which inorganic Mercury can be transformed into monomethyl mercury (CH_3Hg^+) and dimethyl mercury ($(\text{CH}_3)_2\text{Hg}$) which are highly toxic form of mercury causing neurotoxicological disorders⁸². Clinically, low concentration as little as $0.2\text{-}0.5\mu\text{g/L}$ in the blood of an adult show observable effect that may be consider potentially harmful to human¹⁰⁶.

2.6.6 Iron (Fe)

Iron is the most abundant metal and is believed to be the tenth most abundant element in the universe. It is extracted from its ore and hardly found in the free elemental state. Its combination of low cost and high strength makes it indispensable, especially in its applications. Like automobile, the hulls of large ships and structural components for buildings. Steel is the best known alloy of iron. Physiologically, it is essential to all organisms except few and excess iron in the body causes liver and kidney damage (haemochromatosis)⁸⁴.

2.6.7 Vanadium (V)

Vanadium is an abundant element in crude oil and is considered to be a toxic element in the environment. Vanadium causes the inhibition of certain enzymes in animals, which has several neurological effects. Next to the neurological effect, vanadium can cause breathing disorders, paralysis and negative effects on the liver and kidney. Vanadium can also cause harm to the

reproductive organ of female placenta. It can cause DNA alteration in some cases but not cancer in animals⁸⁴.

2.6.8 Zinc (Zn)

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unusually, due to addition of zinc through human activities. Most zinc is added during industrial activities such as coal mining and waste combustion and steel processing. Many foodstuffs contain certain concentration of zinc. Drinking water also contains amounts of zinc, which may be high when it is stored in metal tanks. Zinc is a trace element that is essential for human health and Zinc shortages can cause birth defect. Excess of Zinc can increase acidity of waters. Fish can accumulate and bio-magnify zinc in the food chain⁸⁴.

2.6.9 Nickel (Ni)

Nickel ions are non-biodegradable toxic heavy metals and may cause dermatitis and allergic sensitization. The tolerance limit of nickel in drinking water is 0.01 mg/L, and for industrial wastewater it is 2.0 mg/L. The parameter set for tolerance limit of inland surface waters subjected to nickel pollution is 3.0 mg/L, according to Indian Standard, the major sources of nickel contamination to water comes from industrial process such as electroplating, batteries manufacturing, mining, metal finishing and forging¹⁰⁷.

2.7 Techniques for Heavy Metals Determination

Myriad of analytical techniques exist for the determination of heavy metals in substances viz: Atomic Absorption Spectrophotometry (AAS), a well-recognized and an attractive technique to users for its sensitivity, reliability, versatility, accuracy and precision. Some other methods employed

in simultaneous determination of metals include Inductively Coupled Plasma-atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), Polarography, Voltammetry, Liquid Chromatography (LC) and UV-Visible Spectrophotometry¹⁰⁸.

2.7.1 Atomic Absorption Spectrometry (AAS)

In chemical analysis, Atomic Absorption Spectrometry (AAS) is one of the most common techniques used for the determination of the concentration of a particular metallic element within a sample. AAS can be used to analyze the concentration of over 62-70 different metals in a solution. This is possible because atoms absorb quantized or specific amount of ultraviolet or visible light to undergo transitions to higher energy levels (a process called excitation) and the spectra produced when the sample is excited by this absorbed radiation is read. The Atomic absorption methods measure the amount of energy in the form of photons of light that are absorbed by the sample¹⁰⁹. A series of samples containing known concentrations of the compound of interest are analyzed, and the corresponding absorbance, which is the inverse percentage of light transmitted, is recorded. The measured absorption at each concentration is then plotted, so that a straight line can then be drawn between the resulting points. From this line, the concentration of the substance under investigation is extrapolated from the substance's absorbance. The use of special light sources (hollow-cathode lamp) and the selection of specific wavelengths allow for the quantitative determination of individual components in a multi-elements mixture because the lamp is made with the metal of interest or contains the salt of the metal which produces radiation that can only be absorbed by the metal in solution^{110, 111}.

2.7.2 Inductively Coupled Plasma Atomic Emission Spectrometry

Like atomic absorption spectrometry (AAS), the use of inductive coupled plasma atomic emission spectrometry (ICP/AES) in the determination of heavy metals is principled upon the same

interaction of molecules with electromagnetic radiation whereby atoms are promoted or excited to higher electronic energy states or levels when heated to high temperature ¹¹¹. But, unlike AAS that uses flame based systems whose temperature (1700-2800) °C is used to atomize the metals before electromagnetic excitation by the excitation sources (for example, Hollowed cathode lamp), ICP/AES uses plasma which is a hot, partially ionized Argon gas consisting of cations and electrons capable of absorbing sufficient power from an external source by its further ionization to maintain high temperature of (5000-10000) °C. This hot temperature is sufficient to ionize and excite most atoms which leaves the zone of this high temperature and energy state and releases ultraviolet and visible photons as they return to their ground electronic state. This emitted photons intensity are measured as a function of the concentration of the metal of interest. ICP/AES determines up to 70 elements even simultaneously^{110, 112}.

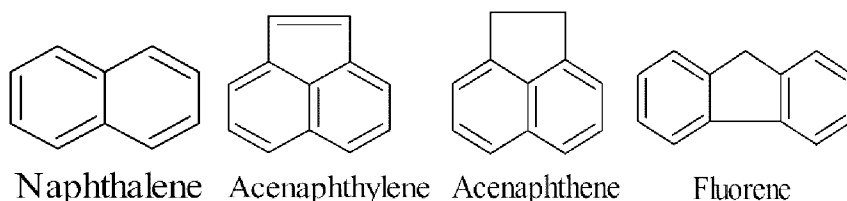
2.7.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) consist of an argon plasma that dries samples introduced into it as aerosol droplets, dissociates the molecules, and then removes an electron from the components, thereby forming singly-charged ions, which are directed into a mass filtering device known as the mass spectrometer. The aerosol produced via nebulization enters this high temperature plasma, where it is first dried to a solid, and then heated to a gas, referred to as atomization. These atoms will continue to travel through the plasma, absorbing energy until they release an electron, becoming ionized, referred to as ionization. These newly formed ions then travel out of the torch and pass through an interface that leads to the detector. Most commercial ICP-MS systems employ a quadrupole mass spectrometer which rapidly scans the mass range. At any given time, only one mass-to-charge ratio will be allowed to pass through the mass spectrometer from the

entrance to the exit. If, for example, the quadrupole was set to allow ions with a mass to charge ratio of 23/1 to pass through, we would find that sodium (Na) ions will be the only ions that passes while all other singly charged ions would not. Upon exiting the mass spectrometer, ions strike the first dynode of an electron multiplier, which serves as a detector. The impact of the ions releases a cascade of electrons, which are amplified until they become a measureable pulse. The software compares the intensities of the measured pulses to those from standards, which make up the calibration curve, to determine the concentration of the element^{113, 114}.

2.8 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are compounds containing two or more fused aromatic rings in linear, angular or clustered arrangement with Sixteen of them been classified by the U.S environmental protection agency as pollutant of high priority having characteristics of persistence in the environment^{24, 25}. Examples of polycyclic aromatic hydrocarbons (PAHs) include Naphthalene (NA), Acenaphthylene (ACY), Acenaphthene (ACE), fluorene (FL), phenanthrene (PH), Anthracene (AN), Fluoranthene (Flu), pyrene (PY), Benzo[a] anthracene (BaA), chrysene (CH), Benzo[b] fluoranthene (BbF), Benzo[K] fluoranthene (BKF), Benzo[a] pyrene (BaP), Indeno[1,2,3 - Cd] pyrene (IP), Dibenzo[ah] anthracene (DA) and Benzo [g,h,i] Perylene (BP)^{25, 26}. The sixteen PAHs classified by the U.S. Environmental protection agency as pollutant of high priority having characteristics of persistence in the environment include the following chemical structures in figure 1 below:



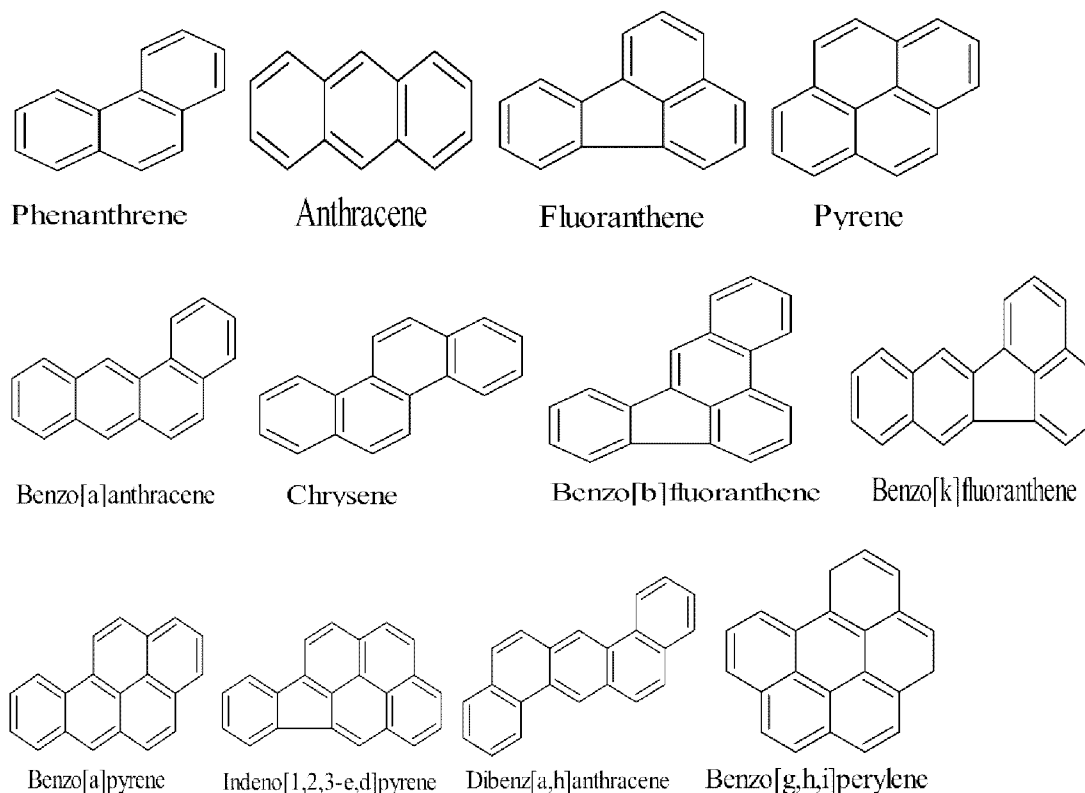
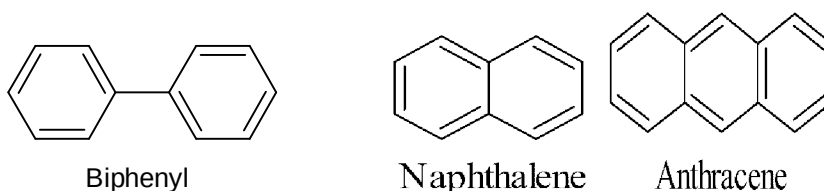


Figure 2.1 US EPA high priority PAHs¹¹⁵.

2.8.1 Nomenclature of Polycyclic Aromatic Hydrocarbon (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) has been defined earlier as compounds containing two or more fused aromatic rings in linear, angular or clustered arrangement. Based on the arrangement, there are three groups of PAHs, Polyaryls PAHs, Ortho-fused PAHs and Ortho and Peri-fused PAHs.



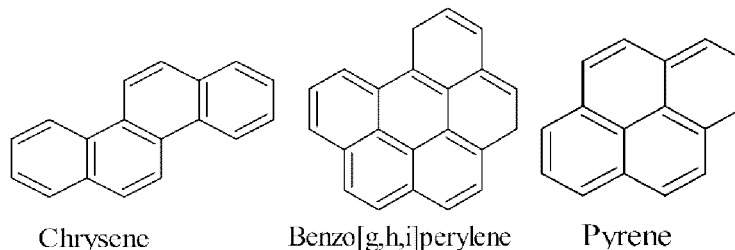


Figure 2.2 Linear, angular, clustered, Polyaryl, Ortho - and Peri-fused PAHS

When two rings are connected together by a single bond as in biphenyl above, it is called a polyaryls linked PAHs, when two rings share a common C-C bond, as in Naphthalene and Anthracene above, it is Ortho-fused linked PAHs and when three rings share a common C-C bond and a common central C- atom, as in Benzo[g,h,i]perylene and pyrene, it is called Ortho- and Peri-fused linked PAHs¹¹⁵. Discrepancies in nomenclature of PAHs do exist among the European and American scientist which makes names of PAHs undoubtedly confusing, however, the IUPAC nomenclature of polycyclic aromatic hydrocarbons is first based on the largest fragment of the rings with a trivial name and the simplest attachments are then selected for naming. The structures are typically oriented such that firstly, the greatest number of rings in a row are aligned horizontally, secondly, the maximum number of rings are positioned in the upper right quadrant (of the horizontal row) and thirdly, the least number of rings are positioned in the lowest left quadrant. Numbering of the rings begins with the uppermost ring furthest to the right, with the most counterclockwise carbon atom not involved with ring fusion. The numbering begins with or proceeds clockwise around the structure with hydrogenated carbon atoms as shown in figure 3 below^{116, 117}.

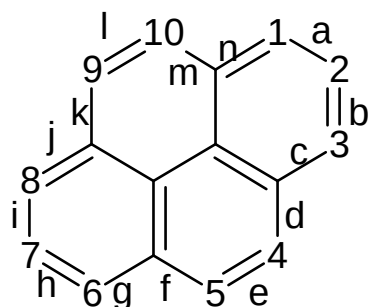
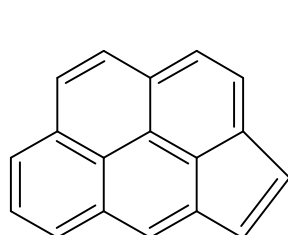
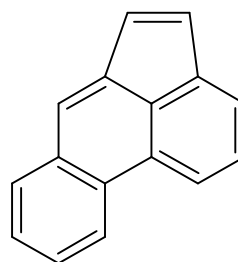


Figure 2.3 Structure of Pyrene showing numbering system in PAHs.

PAHs which has no accepted trivial names are named by prefixing to the name of a component ring designation of the other components. For example, the prefixes cyclopenta and ace in cyclopenta[cd]pyrene and acephenanthrylene indicates the presence of a five-membered ring as shown below.



Cyclopenta[cd]pyrene



Acephenanthrylene

Figure 2.4 Cyclopenta[cd]pyrene and Acephenanthrylene with their five member ring.

ñ-eneò indicates the compound is in an oxidized state and contains the maximum number of conjugated double bonds. Compounds ending in ñ-aceneò are linearly fused and those ending in ñ-pheneò angularly fused. Common abbreviated prefixes include: acenaphtho-, anthra-, benzo-, naphtho-, and phenanthro-. The ñoò is dropped when it prefixes another vowel, for example, it is benz[a]anthracene and NOT benzo[a]anthracene¹¹⁸.

2.8.2 Review of works on PAHs in water sediment and fish

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous¹¹⁹ and are hydrophobic and lipophilic substances which have low solubility in water¹²⁰ and their hydrophobicity and lipophilicity increase with increase in molecular weight as well as its persistent ability in the environment. Basically, PAHs are grouped into low molecular weight (LMW) if they have two or three fused rings and high molecular weight (HMW) if they have four or more fused rings¹¹⁸. PAHs having low vapor pressures and their compounds having five or more aromatic rings exist and are mainly adsorbed to airborne particulate matter, such as fly ash and soot. Those with four or fewer rings will occur both in the vapor phase and adsorbed to particles. PAHs are adsorbed strongly to the organic fraction of sediments and soil and it can be concluded that sediments and soil are usually considered as the main sink for PAHs in the environment. PAHs with four or more aromatic rings are persistent in the environment¹²¹. The best known PAHs is benzo[a] pyrene and it serves as a representative of the PAHs. Since PAHs occur as variable mixture, there has been criticism of this selection by the panel on contaminants in food chain at the European Food Safety Authority (EFSA) who submitted a report on PAHs in foodstuffs in 2008 and concluded that benzo[a] pyrene alone is not a suitable marker for the presence of PAHs in Foodstuffs and selected four specific PAH which include Benzo[a] Pyrene, Benz[a] anthracene, Benzo[b] fluoranthene and chrysene as marker for the presence of PAHs in Foodstuffs^{119, 120}.

Study on Polycyclic aromatic hydrocarbons in the coastal sea water, the surface sediment and Biota (Mudskipper *Boleophthalmus dussumieri*) from coastal areas of the Persian Gulf with source investigation, composition pattern and spatial distribution examined or measured using HPLC method showed that total PAHs concentrations in the sea water, the sediments, the liver and the gill tissues ranged between 0.80-18.34 $\mu\text{g/l}$, 113.50-3384.34 ng g^{-1} (d w), 3.99-46.64 ng g^{-1} (d w) and 3.11-17.76 ng g^{-1} (d w), respectively. PAHs distribution patterns in the sediment and the liver tissue

samples were dominated by three-and four-ring structures whereas two-and three-rings were dominated in the water and the gill, leading to the conclusion that a negative eco-risk effects occasionally occur in this area. The higher presence of low condensate ring structures reflected a predominant origin of petrogenic and some cases of pyrolytic sources the researchers said¹²¹. Polycyclic aromatic hydrocarbons (PAHs) and Polychlorinated biphenyls (PCBs) in soils of Agbabu, Nigeria were investigated, PAHs in the samples were quantified using gas chromatography - mass spectrometer, while gas chromatograph y- flame ionization detector was used for PCBs analysis. The maximum sum of concentrations of PAHs (ΣPAH) was 0.07 ± 0.036 ppm in the dry season, and 0.69 ± 0.19 ppm in the rainy season. Apart from three stations in both seasons where PAHs were not detected, other ΣPAH concentrations obtained were higher than 1-10 $\mu\text{g/kg}$, indicating anthropogenic sources. Most of the PAH concentrations obtained were within the expected limits for a rural environment. However, in the rainy season, 0.20 ± 0.04 ppm for Benzo(b)fluoranthene, 0.21 ± 0.05 ppm for Benzo (g, h, i) perylene and 0.32 ± 0.04 ppm for Indenol (1, 2, 3 ÿ cd) pyrene exceeded the expected limit. In the dry season, there was no significant relationship ($r^2 = 0.002$) between mean concentrations and percentage soil organic carbon while there was significant correlation ($r^2 = 0.57$) in this relationship in the rainy season. The predominance of 4 - 6 ring PAHs and the ratios between pairs of individual PAHs showed that the PAHs were from pyrolytic sources⁸. In the research; Polycyclic Aromatic Hydrocarbons (PAHs) in Freshwater Media: Factorial Effects and Human Dietary Exposure Risk Assessment, the researchers quantified Polycyclic aromatic hydrocarbons (PAHs) present in water column and preponderant fish species of Anambra River. Eight PAHs (naphthalene, acenaphthene, fluorine, phenanthrene, anthracene, pyrene, fluoranthene and benzo [a] pyrene) classified as priority pollutants by the United States Environmental Protection Agency and World Health Organisation were measured in the media following solid-phase

extraction and gas chromatographic procedures on three factorial experimental model designs. Season was tested at two levels: rainy and dry; fish species at two levels: *Synodontisclarias* and *Tilapia nilotica*; and location factor at five levels: Enugu Otu, Ezi-Aguleri, Otuocha, Otu-Nsugbe, and Onono. The human PAH exposure risk was assessed and daily intake through fish consumption determined. Polycyclic aromatic hydrocarbons were found preponderant in the water and fish species for both rainy and dry seasons at the five distinct locations. Concentrations detected in these principal media were generally low compared to earlier studies and unaffected by the season, location and fish species, including all the factorial level interaction effects. However, the dietary intakes of the contaminant through fish consumption were a subject of public health concern on continuous daily exposure as the PAH concentrations in the examined fish sourced from some of the locations in different seasons were higher than stipulated values by Environment Canada for edible tissues of fish and/or shellfish for human consumptions. Effective and continued monitoring of the quality conditions of the river needs to be sustained and compared with baseline catchment data for quality deviation as crude oil production is expected to commence at this delicate site. Further quantifications of these organic substances in other fauna and investigation in entire flora of the river, and modelling of its trophodynamics would practically underpin sound management strategies and sustainability of the aquatic resources¹²². Analysis of 16 polycyclic aromatic hydrocarbons (PAHs) of the US Environmental Protection Agency priority pollutant list was carried out in sediment samples of an industrial port in the southern Kaohsiung Harbor of Taiwan which is supposed to be extensively polluted by industrial wastewater discharges. The determination and quantification of the PAHs in the sediment samples were performed using gas chromatography coupled with mass spectrometry (GC-MS). The total concentrations of the 16 PAHs varied from 4,425 to 51,261 ng/g dw, with a mean concentration of 13,196 ng/g dw. The PAHs concentration is

relatively high in the river mouth region, and gradually diminishes toward the harbor region. Diagnostic ratios showed that the possible source of PAHs in the industrial port area could be coal combustion. As compared with the US Sediment Quality Guidelines (SQGs), the various observed levels of PAHs exceeded the effects range median (ERM), and could thus cause acute biological damages. The results can be used for regular monitoring, and future pollution prevention and management should target the various industries in this region for reducing pollution²⁵. The determination of the 16 US EPA priority polycyclic aromatic hydrocarbons (PAHs) in abiotic environmental matrices or superficial water and sediment of Tecocomulco Lake, Hidalgo, Mexico was evaluated and the analyses were made using a gas chromatograph connected to a mass spectrophotometer (GC-MS), the highest concentration of PAH in water was for acenaphthylene (2.400 mgL^{-1}), anthracene (1.1770 mgL^{-1}) and phenanthrene ($1,500 \text{ mgL}^{-1}$); in sediment the highest concentrations corresponded to naphthalene (2.155 mgL^{-1}), benzo[g,h,i]perylene (4.940 mgL^{-1}), and fluoranthene (2.240 mgL^{-1}). The EPAHs showed a noticeable difference between matrices, a concentration of 6.658 mgL^{-1} in water and 10.927 mgL^{-1} in sediment, with a total EPAHs of 17.585 mg/L ²⁶. A Study to examine the presence of polynuclear aromatic hydrocarbons in groundwater sources of the coastal settlement of Okrika Mainland where Port Harcourt Refinery Company is situated and discharges its effluent was carried out. Analysis using GC-FID showed that high concentrations of PAHs which exceeded the WHO maximum permissible limit for the PAHs in drinking water (0.002 mg/L) were re-corded from the borehole samples. Acenaphthene had the highest concentration of $0.88317 (0.202494 \pm 0.0652) \text{ mg/L}$, while acenaphthylene had the least maximum concentration of $0.18837 (0.04978 \pm 0.0123)$. However, naphthalene re-corded concentrations of between 0.00058 and $0.52510 (0.0874576 \pm 0.03472) \text{ mg/L}$, fluorene 0.00018 and $0.20438 (0.0527435 \pm 0.01564) \text{ mg/L}$, phenanthrene 0.00041 and $0.26732 (0.0603780 \pm 0.018634)$

mg/L, and anthracene between 0.00029 and 0.25084 (0.0692785 ± 0.0176569) mg/L¹²³. In a study of the Distribution, Levels, and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Some Water Bodies along the Coastal Belt of Ghana, the levels and distribution of 24 polycyclic aromatic hydrocarbons (PAHs) were determined in six water bodies along the coastal belt of Ghana using gas chromatography with flame-ionization detection (GC/FID). The average total PAHs recorded are from the Pra estuary, 6.3 $\mu\text{g/L}$; Benya lagoon, 7.5 $\mu\text{g/L}$; Sakumono lagoon, 10.1 $\mu\text{g/L}$; lower Volta estuary, 26.3 $\mu\text{g/L}$; Keta lagoon, 10.6 $\mu\text{g/L}$; and Narkwa lagoon, 16.1 $\mu\text{g/L}$. The 12 PAHs that were well distributed in all the coastal waters analyzed include naphthalene, pyrene, fluorene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, acenaphthalene, acenaphthene, 1-methylphenanthrene, 2,3,5-trimethylnaphthalene, chrysene, biphenyl, and phenanthrene. The presence of benzo(b)fluoranthene, benzo(a)anthracene and benzo(j,k)fluoranthene in some of the water bodies is a source of concern as they have been classified by the International Agency for Research on Cancer (IARC) and U.S. Environmental Protection Agency (EPA) as probable human carcinogens and these water bodies are used for fishing and for some domestic purposes by the people living around them, thereby exposing them to some dangers and the risk of getting cancer¹²⁴. The determination of PAHs concentration in *Penaeus monodon*, one of the most valued biota in the Niger Delta due to its nutritive and economic benefits to the people was carried out first by extraction using Soxhlet extractor with dichloromethane while Gas Chromatography equipped with Flame Ionization Detector was used to determine the concentrations of the PAHs in the extract and the results of the concentration of individual PAHs in the biota ranged between 0.943 mg/kg and 2.347 mg/kg (dry wt.). From the results of the investigation, it was observed that *Penaeus monodon* bioaccumulated PAHs to high levels and the concentration of individual PAHs in the organism when compared to the national and international recommended limits, was also high, an indication that the

consumption of this organism portends health risk. It is therefore the opinion of the researchers that the consumption of this organism from the environment be stopped forthwith pending when a remediation programme is carried out¹²⁵.

2.8.3 Sources of PAHs in the Environment

Source of PAH in the aquatic environment are via three major processes: Pyrogenic, Petrogenic and Diagenic PAH sources. Pyrogenic (based on combustion origin) PAHs sources result from an incomplete but high temperature and short-duration combustions of organic matters including fossil fuels and biomass and the pyrogenic inputs are largely prevalent in aquatic environments. Petrogenic (likely to originate from petroleum) input is closely related to petroleum products (e.g., oil spills, road construction materials). The PAHs are formed from this source by biogenic processes at a relatively low temperature over geological time scale, leading to the formation of petroleum and other fossil fuels containing PAHs, whereas, Diagenic PAHs sources refer to PAHs from biogenic precursors, like plant terpenes. The first two types of sources may be both natural and anthropogenic sources. Petrogenic PAH dominates oil-polluted samples, while Pyrogenic PAH tends to dominate the samples from industrial areas^{122, 126}. Therefore, polycyclic aromatic hydrocarbons (PAHs) as priority organic pollutants (POPs) have in recent times steadily increased and are widespread in the environment, occurring in food, air, water, soil, and sediments¹²⁷. Generally, PAHs are produced in incomplete combustion of organic matter such as wood, coal or oil. As a rule, the lower the temperature of the fire and the less oxygen is available, the more incomplete do materials burn and the more PAHs are produced¹¹⁹. This implies that different types of PAHs are formed based on combustion temperatures. The burning of materials without flame and little smoke or smoldering results in complex PAHs¹¹⁸. PAHs of biogenic origin such as perylene and retene are almost produced entirely from organic matter and are good markers for terrestrial organic inputs. However,

existence of larger levels of lower molecular weight (LMW) PAHs; PAHs with up to four benzene ring such as fluorene and acenaphthene in environmental media implies natural or petrogenic PAH contamination; while prominent concentrations of higher molecular weight (HMW) PAHs; PAHs with more than four benzene ring (e.g., fluoranthene, phenanthrene, pyrene) and fewer low molecular weight PAHs demonstrate combustion or pyrolytic origins¹²⁷. PAHs are released from natural sources which include, volcanoes and forest fires and anthropogenic sources which include: combustion of fossil fuels (motor vehicle emission and power generation), wood burning, municipal and industrial waste incineration, coal tar, coke, asphalt, crude oil, creosote, asphalt roads, roofing tar, discharges from industrial plants and waste water treatment plants, hazardous waste, smoke houses, aluminium production plants, atmospheric contamination of leafy plants, cigarette smoke and charbroiled meat¹¹⁸.

2.8.4 Environmental Health Impact of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in nature and are daily being leached into rivers, lakes and oceans from natural and anthropogenic sources like rock weathering, waste water, industrial effluents, and incomplete combustion of organic materials, fossil fuel, petroleum and ambient air. Human beings are exposed to PAH vapor or PAHs contained in dust and other particulate matter outdoors or indoors at the home or workplace through cigarette smoke, vehicle exhaust, residential heating, agricultural burnings, waste incineration, and emissions from industrial processes. PAHs can also enter the body via food and water consumption or skin contact^{26, 27, 128}. PAHs are transported into all tissues of the human body containing fat. They can be stored in fat, liver and kidneys and can accumulate by repeated and long-term exposures. Smaller amounts are also stored in the spleen, adrenal glands, and ovaries.^{26, 27, 128}. PAHs causes many adverse effects on different types of organisms, including plants, birds, and mammals. Some studies^{8, 25, 128, 129} have

reported that there is a significant positive correlation between mortality by lung cancer in humans and exposure to PAHs from exhaust from coke ovens, roofing-tar, and cigarette smoke. Some PAHs have been demonstrated to be carcinogenic, mutagenic and teratogenic in humans and experimental animals, and they are classified as carcinogenic materials by many organizations, including the United States Agency for Toxic Substances and Disease Registry (ATSDR), the International Agency for Research on Cancer (IARC), the Department of Health and Human Services (DHHS), the National Occupational Safety and Health Administration (OSHA), and the US-EPA¹²⁸. PAHs have resulted in symptoms such as eye irritation, nausea, vomiting, diarrhea and confusion, skin irritation and inflammation. Long term exposure are known to cause cataracts, kidney and liver damage and Jaundice as well¹²⁹. They are mutagenic, carcinogenic and tartogenic to man due to their highly toxicity or toxic nature^{8, 25}. Other bio-effects of PAHs properly noted and documented are interactive effects on DNA and RNA; haematological parameters; hepatic lesions and changes; reproductive abnormalities; immune-suppression; and developmental toxicity¹²⁷.

2.9 Gas chromatograph: Technique for PAHs determination

Other methods for the determination of PAHs such as Fluorescence methods which are capable of measuring subnanogram quantities of PAHs producing intense spectra with poor resolution and tend to be fairly non-selective exist. To overcome the non-selectivity problem, the use of ultraviolet (UV) absorption spectroscopy as the detection method coupled with pre-specified techniques involving liquid chromatography (LC) and thin layer chromatography (TLC) to isolate specific PAHs, particularly B[a]P were introduced, nevertheless, the more sensitive high performance liquid chromatography (HPLC) with UV/fluorescence detection or highly sensitive and specific gas chromatography/mass spectrometry (GC/MS) for detection was introduced. The choice of GC/MS as the recommended procedure for analysis of PAHs was influenced by its sensitivity and selectivity, along with its ability to analyze

complex samples¹³⁰. Gas chromatography involves the separation of mixtures by passage of the vaporized sample in a gas stream through a column containing a stationary phase. Components migrate at different rates due to differences in boiling point, solubility or adsorption. In gas chromatography the mobile phase is a gas. It comprises gas-liquid chromatography (GLC) and gas-solid chromatography (GSC). In GLC, the stationary phase is a high boiling liquid and the sorption process is principally that of partition. In GSC, the stationary phase is a solid and adsorption plays the major role. Samples, which must be volatile and thermally stable at the operating temperature, are introduced into the gas flow via an injection port located at the top of the column. A continuous flow of gas elutes the components from the column in order of increasing distribution ratio from where they pass through a detector¹³¹.

2.9.1 Gas chromatograph coupled with mass spectrometer (GC-MS)

GC-MS is one of the most frequently used analytical method for the identification and determination of PAHs in samples. The gas chromatograph utilizes a capillary column which depends on the column's dimensions and phase properties. The difference in the chemical properties between different molecules in a mixture separates the molecules as the sample travels the length of the column. The molecules take different retention time to elute from the gas chromatograph, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio. Combining these two processes reduces the possibility of an analytical error, as it is extremely unlikely that two different molecules will behave in the same way in both a gas chromatograph and a mass spectrometer. The most common GC-MS instruments for environmental analysis are those with electron impact ion sources and quadrupole mass analyzers. In the electron impact mass

spectrometer, analyte molecules bombarded in the ion source with a flow of electrons, produce charged fragments. The negatively charged ions are deflected and removed from the system, whereas the positively charged fragments are accelerated into the quadrupole mass analyzer. The fragments are separated by mass and velocity under the effects of a direct electrical current and a radio frequency applied to the quadrupoles. Only the ions with a single charge are retained in the mass analyzer. Each group of ions with the same m/z value has its own trajectory as it reaches the detector. As ion beams of different m/z values enter the electron multiplier of the detector, they are recorded as a change in the electrical signal. Every organic chemical has a mass spectrum, which is a combination of ions with different masses and different intensities. To identify a compound, its mass spectrum is compared to the mass spectra of standards, analyzed under the same instrument settings and to the mass spectra library. Compound identification in GS/MS is based on the retention time and the mass spectra interpretation while the quantitation is based on the abundance of a primary ion. For a compound to be positively identified, all of the ions in the spectrum must be detected at one and the same retention time, which corresponds to the retention time of the compound in the calibration standard¹³¹.

CHAPTER THREE

EXPERIMENTAL

3.1 Materials

The following Chemical materials, apparatus and instruments were used during this research work and all chemicals used were of analytical grade. The chemicals used were: Deionized water (H_2O), (65%) Nitric acid (HNO_3), (30%) Hydrogen Peroxide (H_2O_2), Hydrochloric acid (HCl), Hydrofluoric acid (HF), Dichloromethane (CH_2Cl_2) (JHD China), Anhydrous Sodium Sulphate (Na_2SO_4) (BDH Chemicals, Poole, England), 60-120 mesh Silica gel (Qualikems fine Chemicals, India), Potassium silicate (K_2SiO_3), Hexane (C_6H_{14}) (JHD China), Acetone (CH_3COCH_3), Standards of the sixteen priority PAHs (New Haven, USA) and Helium gas (Air liquid gas company, France).

The apparatus and instrument used were polyethylene bags and containers, Refrigerator, ice-cooler box, hand trowel, standard flask, plastic knife and plastic sieve, oven, fume cupboard, whatman filter paper, mortar and pestle, weighing balance, conical flask heating mantle or hot plate, Glass funnel, measuring cylinder Rotary vacuum evaporator (Seno technology, China), column chromatographic set, Soxhlet extractor (Quick fit, England), Magnetic stirrer, Porcelain basin, Evaporating dish, Desiccator, AAS (PG-900 and Sensa PS-270), and GCi MS (Agilen 7890, series A, USA)

3.2 Description of Study Area

The study area is the confluence of rivers Niger and Benue in Lokoja Kogi State, Central Nigeria. The state lies between the coordinate of latitude $7^{\circ}30'\text{N}$ / $6^{\circ}42'\text{E}$ and longitude 7.500°N / 6.700°E and Lokoja lies between $7^{\circ}45'\text{N}$, $7^{\circ}52'\text{N}$ of the equator and longitude $6^{\circ}45'\text{E}$ of the Greenwich meridian. Lokoja is bounded in the west by the river Niger at an altitude of 45 - 125 meters above sea level.

The climate is tropical wet and dry climate characterized by wet (raining) season between May to October and dry season between December to April, with an annual rainfall of about 1000mm^{132, 133}. Lokoja is the headquarters of Lokoja L.G.A. and the capital of Kogi State, having an area of 3180 km² land and a population of 196,643 people at the 2006 census with majority of the local indigene involving in farming and fishing^{134, 135}.

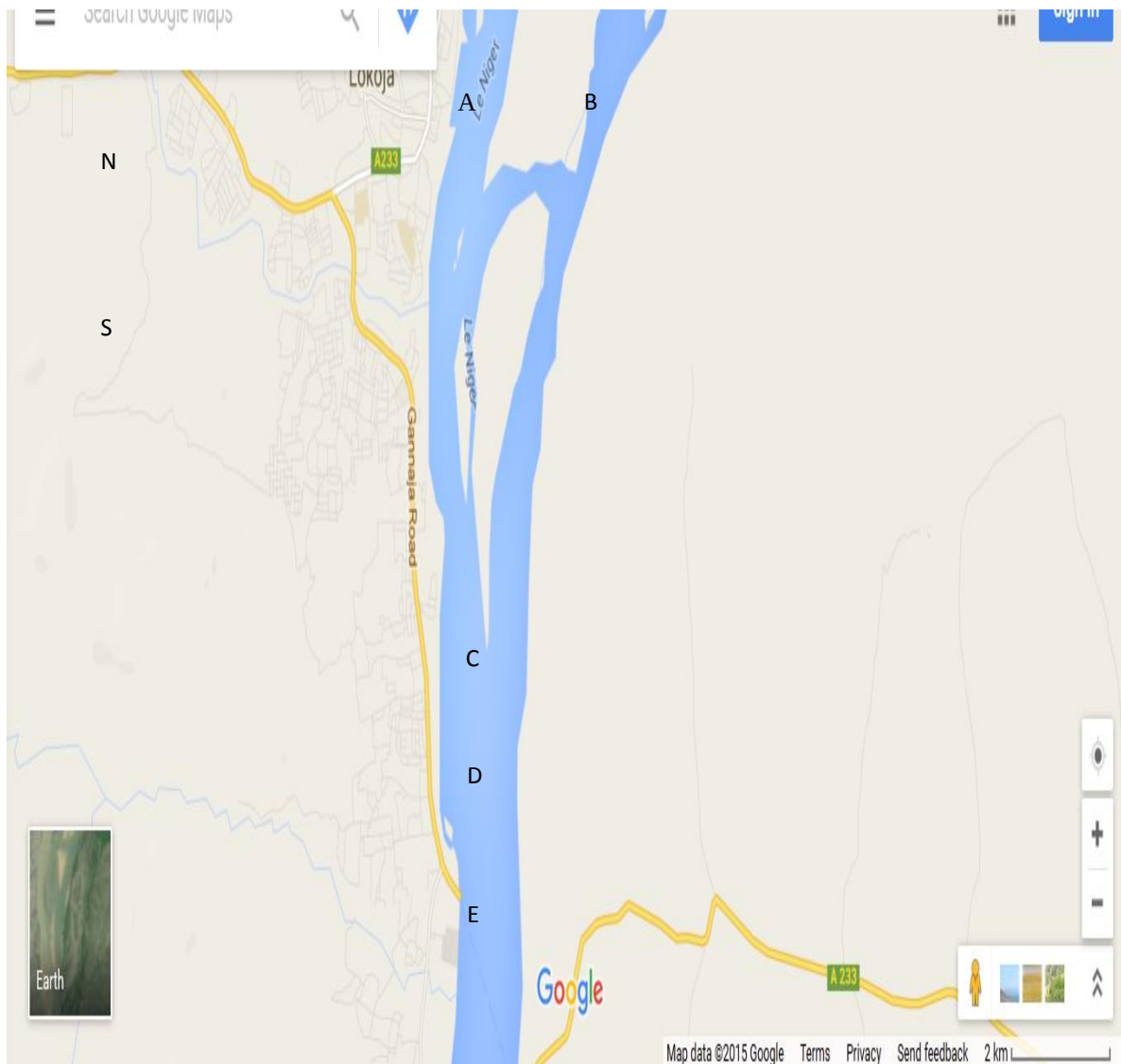


Figure 3.1: Map of Kogi State showing the Confluence of Rivers Niger and Benue. Source¹³⁶.

3.3 Samples and Sampling Technique

All polyethylene containers used for the collection of water samples, polyethylene bags for fish and sediments samples analyzed for heavy metals were washed with detergent, treated with dilute Nitric acid (10% HNO_3) and thoroughly rinsed with distilled-deionized water^{137, 138}.

Water and sediments of the confluence of rivers Niger and Benue were sampled as well as the upstream and downstream of the confluence 2 km apart during the dry and rainy season (March and August). The samples were collected randomly from twenty sample points made into five composite samples [A], [B], [C], [D] and [E]. Sampling of samples for the heavy metals determination were differently done from the samples for the PAHs determination and the heavy metals samples were added 5 mL con HNO_3 to preserve the sample to minimize the adsorption of metals onto the container walls and were taken in an Ice-cooler box with ice-block to the laboratory and also preserved in a refrigerator below 4°C prior to analysis. Some physico-chemical parameters were analyzed in the water samples using appropriate digital readout meters in situ, these parameters include temperature, pH, electrical conductivity and total dissolved solids. The water was collected with polyethylene containers by dipping the sampler below the water surface to minimize the contamination of water sample by surface films and cocked below water surface to avoid air entrapment¹³⁷⁻¹⁴⁰.

The fish samples A (Catfish) and B(Tilapias) were purchased and collected from the fishermen at the bank of the river and put in a polyethylene bags and transported in the ice-cooler box to the laboratory and stored below 4°C in a refrigerator prior to analysis. The sediment were collected using stainless hand trowel pre-cleaned with detergents, dilute HNO_3 , and de-ionized water and

transferred into the polyethylene bags and transported to the laboratory and stored in the refrigerator prior to analysis^{139, 140}.

3.4 Physical Parameters

The physical parameters: temperature, pH, electrical conductivity and total dissolved solids of the water were determined in situ on the field at the sampling points using hand held devices shown in the table below.

Table 3.1: Instrument for in Situ Determination of Physical Parameters

Parameters	Equipment used
Temperature	Thermometer
pH	pH meter (pHep®+ HI 98108 pH Meter)
Electrical conductivity	Electrical conductivity meter (TDS-EZ)
Total dissolved solids	Electrical conductivity meter (TDS-EZ)

3.5. Sample Preparation for Heavy Metals Determination

3.5.1 Water samples preparation for Heavy Metals Determination

The water samples were digested at 95 °C. 5 mL 1:1 Conc. HNO₃/H₂O₂ was added to 50 mL of the water samples, continuously until the completion of the digestion process. The digested samples were washed with deionized water, filtered and made up to 50 mL mark in a standard flask. Deionized water was used to prepare blank the same way as the samples and Heavy metals [Cr, Cu, Zn, Cd, Pb, Al and Fe] were analyzed using AAS in triplicates^{137, 141}. Heavy metals concentration in

water samples were estimated with equation (1), below from the results obtained from the AAS concentration in mg/L¹⁴²:

$$\text{Heavy metal concentration (mg/L)} = \text{reading of AAS} \times \frac{\text{Concentration of standard solution (mg/L)}}{\text{Absorbance of standard solution}} \quad (1)$$

AAS = Atomic Absorption Spectroscopy.

3.5.2 Fish samples Processing and Digestion for Heavy Metals Determination

The deep frozen fish samples, Catfish and Tilapia were thawed at ambient laboratory temperature overnight. The fish gills and muscle were carefully removed with a plastic knife and were put in a pre-acid washed and oven-dried crucibles and then dried in the oven to a constant weight at a temperature of 105 °C and the dried fish samples were cooled in desiccators at room temperature. After cooling, 2g of fish muscles and Gills was accurately weighed using an electronic weighing balance and transferred into a clean mortar and pestle and were homogenized and then transferred to a clean beaker. 1 g of the homogenized samples each were digested in a digestion flask in triplicates. The digestions were carried out by adding freshly prepared 1:1 HNO₃/H₂O₂ to the 1 g and heated for 1hr in a fume cupboard at 160 °C until the solution was clear. Whatman filter paper was used to filter the solution into a 25 mL standard flask and diluted to the mark with distilled-deionised water. Distilled-deionised water was used to prepare blanks the same way as the samples and analysis were carried out using AAS in triplicates^{41, 143-145}. Heavy metals concentration in fish samples were estimated with equation (2), below from the results obtained from the AAS concentration in mg/L¹⁴²:

$$\text{Heavy metal concentration (mg/kg)} = \text{reading of AS} \times \frac{\text{Concentration of standard solution (mg/L)}}{\text{Absorbance of standard solution}} \quad (2)$$

AS = Atomic Absorption.

3.5.3 Sediment samples preparation for Heavy Metals Determination

The samples were air dried, grounded with mortar and sieved through 0.5 mm sieve to remove coarse materials; 5 g of each sample was weighed and kept in a dried clean conical flask. The samples were digested using 5:3:2 mixtures of HNO₃, HCl and HF. The mixtures were covered with watch glass and heated on a hot plat to near boiling for one hour and was filtered and the filtrate made up to the mark with distilled-deionized water in 100 mL volumetric flask and stored at 4⁰C for analyses¹⁴³⁻¹⁴⁷. Heavy metals concentration in sediment samples were estimated with equation é é (1) below¹⁴²:

$$\text{Heavy metal concentration (mg/kg)} = \text{reading of AS} \times \frac{22222 \text{ } 2 \text{ } 22 \text{ } 222222 \text{ } 22222222}{2 \text{ } 22222222 \text{ } 222 \text{ } 222} \text{ é ..(3)}$$

AS = Atomic Absorption.

3.5.4 Atomic Absorption Spectrophotometry Conditions for analysis

Table 3.2 Atomic Absorption Spectrophotometer (AAS) Measurement, Instrument and Flam Mode Parameters.

Measurement Parameters	Instrument Parameters	Flam Mode Parameters
AAS (PG-900) use for the dry season heavy metals determination		

Signal process:	Serial	Measure method: Flame absorption	Fuel flow rate (mL/min): 2000
Integration time (sec):	0.1	Slit (nm): 0.4	Burner height (mm): 6
Range Expand:	1.0	High voltage (V): 300.00	Burner Location (mm): 0.0
Filter Factor:	0.30	Lamp Current (mA): 3.0	Lamp current 6.00 mA
Repeat number of standard:	3	Lamp Element: Lamp for each elements determined	
Repeat number of sample:	3	Background correction: No	

Table 3.2 continue

(Sensa PS-270) use for the rainy season heavy metals determination			
Measurement mode	Integration	Instrument type	Flam
		Slit width	0.20 nm
Sample introduction	Manual	Slit height	Normal
Read time	3.00 s		
			Lamp current 6.00 mA

The above information in table 3.2 above are the AAS condition that was used in the determination of the heavy metals [Cr, Cu, Zn, Cd, Pb, Al and Fe].

3.6 Sample Preparation for PAHs Quantification

3.6.1 Water Samples Preparation for PAHs Quantification

The analytes (PAHs) in the water samples were extracted, purified and analysed according to the United State Environmental Protection Agency (US EPA) Method 3510C. One liter (1 L) of water sample was extracted three times using 100 mL dichloromethane. The dichloromethane extracts (lower layer) were recombined and was drained into a funnel containing anhydrous sodium sulphate.

The dichloromethane extract was evaporated to 2-3 ml on the rotary vacuum evaporator. Extract were cleaned using silica gel/potassium silicate column chromatography consisting of 2 cm anhydrous sodium sulphate (approx.2.0 g) overlaid with 10 cm of activated silica gel (approx 10.0 g) and topped with another 2 cm of anhydrous sodium sulphate. Once the column was pre-rinsed with 30 mL of Hexane, the sample was added and a 50 mL mixture of hexane and dichloromethane (1:1v/v), the eluted extract was concentrated using a rotatory vacuum evaporator to 2.0 mL for the analysis of PAHs using GC-MS^{131, 148, 149}.

3.6.2 Fish Samples Preparation for PAHs Quantification

10 gram of the Gill and muscles samples of the dissected fishes were homogenized with 100 g of anhydrous sodium sulfate using a mortar and pestle and were transferred into the thimble of the Soxhlet apparatus and extracted using 300 ml of acetone and *n*-hexane (1:1, V/V) in a water bath for 8 hours. Extracts were reduced on a rotary evaporator to 1 ml and then passed through a silica gel column to remove lipids and interfering compounds as cleanup process as done above in water extract cleanup. The fraction (containing PAHs) was eluted with 100 ml of acetone: hexane (3:2 V/V). The extracts were then rotoevaporated to a volume of less than 1 mL and was made up to a final volume of 1 mL for GC-MS analysis¹⁴⁹⁻¹⁵².

3.6.3 Sediment Samples Preparation for PAHs Quantification

10 g of sediment samples were combined with 100 g of NaSO₄ and each sample was extracted using a soxhlet extractor for 16 hrs with acetone: hexane (1:1 V/V). The extracts were then rotoevaporated

to 5 mL. Sediment extracts were cleaned up using the same method described for water samples. All analysis of PAHs was done using GC – MS^{149, 151}.

3.6.4 Gas Chromatography-Mass Spectrometry Conditions

Polycyclic aromatic hydrocarbons analysis was conducted using an Agilen 7890, series A, gas chromatography (Agilent, Avondale, USA) interfaced to a mas selective detector (5975 series MSD, Agilent, Avondale,USA). Separation of PAHs were performed using a 5% Phenyl-methylsilicone (DB-5MS) bonded-phase fused-silica capillary column (30 m X 250 µm ID, film thicknes 0.25 µm) (Agilent, USA) with part number 19019J_413 and a temperature limit of -60 to 350 °C. The injector port was run in splitless mode. The oven temperature program was 65 °C for 1 min, and raised finally to 290 °C at a rate of 10 °C/min and maintained at this temperature for 11 min. The transfer line was maintained at 300 °C. Stock solutions were used to establish the retention time of each PAHs analyte. Detection of PAHs was carried out using scan mode, which is designed for preselected ion peaks, non-selected peaks are not identified and quantified. Helium was used as the GC carrier gas. The carrier gas helium was maintained at a constant pressure of 9.0855 Psi with a linear flow rate of 37.604 cm/sec.

3.7 Statistical Data Analysis and Quality Control studies

3.7.1 Statistical Data Analysis and Precision

All heavy metals and polycyclic aromatic hydrocarbons determinations were carried out in triplicates and the results reported as mean ± standard deviation to check the equipment precision which is the degree of nearness of results of replicate samples or an indication of the reproducibility of results of replicate samples measured under the same condition^{110, 153}. SPSS version 20 software package was

used to estimate the mean values from the triplicate results, to estimate the standard deviation, to run analysis of variance (ANOVA) at value less than 0.05 ($P < 0.05$) level of significant, Principal Component Analysis (PCA) base on the Pearson Correlation matrix analysis and component plot in rotated space statistics were carried out.

3.7.2 Quality Control studies/Spike and Recoveries

Recovery is used to denote the ratio of observed value, obtained from an analytical process via a calibration graph, divided by a reference value. The reference value is the increased amount of analyte observed from the addition of a known amount of analyte to the test sample, therefore, in the determination of HMs, a known concentration of standard solutions for metals were used to spike samples and were analyzed following the same procedure and conditions of determination of samples in order to carry out recovery experiments for the Heavy metals with equation (4) below:

$$\%R = \frac{F - I}{A} \times 100 \quad (4)$$

Where %R is the percentage recovery, F is the spiked samples, I is the unspiked samples and A is the concentration of the analyte added to the spiked portion^{153, 154}. Standard reference materials for the 16 priority PAHs and the six heavy metals were also obtained and analyzed to check the instrument recovery, consistency and efficiency.

3.7.3 The Limit of detection (LOD) and quantitation (LOQ)

Limit of detection is the minimum detectable value of appropriate chemical variable or detection limit is defines as the smallest amount or concentration of analyte in test sample that can be reliably distinguished from zero while limit of quantitation is the minimum quantifiable limit or quantification limit, which is the concentration or amount below which analytical method cannot

operate with an acceptable precision. LOD is expressed as the analyte concentration corresponding to the sample mean blanks value plus three standard deviation of the blanks values and LOQ is the analyte concentration corresponding to the sample mean blanks value plus ten standard deviations of the blanks values as shown in the following equations:

$$\text{LOD} = \bar{X}_{b1} + 3S_{b1},$$

$$\text{LOQ} = \bar{X}_{b1} + 10S_{b1},$$

Where $\bar{X}_{b1}$ is the mean concentration of the blank and S_{b1} is the standard deviation of the blank^{11,155}.

3.8 Risk Assessment models for Carcinogenic and Non-Carcinogenic Risk factors

Hazard Quotient (HQ), total hazard index (THI), bioaccumulation factor (BAF) and pollution index (PI) of Heavy metals and PAHs were used to assess human risk posed by the water and fish ingestion. The risk assessment model follows the methodology recommended by the U. S. Environmental protection Agency (1997a) which categories risk into non-carcinogenic and carcinogenic risk effect respectively¹⁵⁶. The non-carcinogenic risk is associated with long term exposure to contaminants such as heavy metals in food like in fish and water whereas, the carcinogenic risk is the use of slope factor to estimate the upper-bound lifetime probability of an individual developing cancer as a result of exposure to a particular level of potential carcinogen (Carcinogenic metals PAHs)^{157, 158}.

3.8.1 The non-carcinogenic risk: Hazard Quotient (HQ)

The hazard quotient (HQ) is a non-carcinogenic risk estimator that estimates hazards from the ratio of daily intake (EDI) of pollutant and the oral reference dose (RfD) of that pollutant. It is an exceedance of ingested pollutant when ingested exposure dose is compared with the oral reference

dose. If the value of HQ is less than 1, then, the exposed population (consumers) is said to be safe but, if HQ is equal to or higher than 1, it then mean that the human health is not safe, therefore potential health risk occurred, and related interventions for protective measures are required. However, HQ parameter does not estimate the risks; it only indicates a risk level associated with pollutants exposure. The non-carcinogenic risk was estimated using HQ calculated for heavy metals the non-carcinogenic PAHs using equationé é é (5) below:

$$\text{Health Hazard Quotient (HQ)} = \text{HQ} = \frac{\text{EDI}}{\text{RfD}} \dots\dots\dots (5)$$

Where, EDI is daily intake exposure dose and RfD is the oral reference dose. The oral reference dose is the dose of a substance that can be taken in daily without identifiable risk for lifetime exposure or the daily oral exposure for the human population, which does not cause deleterious effects during a lifetime ^{41, 155}. To calculate EDI, the daily intake exposure dose, multiple pathway exposure model developed by the National Institute of Public Health and Environmental Protection agencies (EPAs) was used to estimate the exposure dose of ingesting surface water and contaminated fish as the most important contributor routes to risk and hazards in humans in the area of study. The quantification and estimation of daily intake or exposure dose of each heavy metals from fish and water were done using the equations 6 and 7 bellow ^{41, 42, 159-165}.

$$\text{EDI}_f = \frac{\text{CM}_f \times \text{IR}_f \times \text{C}_f \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \dots\dots\dots (6)$$

Where EDI_f = Estimated daily intake or exposure dose from ingestion of Fish (mg/kg/day), CM_f is the heavy metals concentration in fish (mg/kg), IR_f is the daily fish food ingestion rate (mg /day/person), C_f if the conversion fscor of fish from fresh weight to dry weight = 0.208, EF = the exposure frequency (365 days/year), ED = the exposure duration and it is equivalent to average life time of 70 years, BW = Body weight (Kg) and Averaging time for non-carcinogens = $\text{AT} = \text{EF} \times \text{ED}$.

$$EDI_w = \frac{CM_w \times IR_w \times EF \times ED}{BW \times AT} \quad (7)$$

Where EDI_w = Estimated daily intake or exposure dose from ingestion of water (mg/kg/day), CM_w is the heavy metals concentration in water (mg/L.), IR_w is the daily water ingestion rate (mg/L/day/person), EF = the exposure frequency (365 days/year), ED = the exposure duration and it is equivalent to average life time of 70 years, BW = Body weight (Kg) and Averaging time for non-carcinogens $AT = EF \times ED$.

Table 3.3 Parameters used in the Calculation of exposure model for Heavy

Parameter	Child	Adult	Reference
Ingestion rate of fish (IRf) (kg/person/ day)	0.0163	0.049	This Study
Body weight (BW) (kg)	15.00	70.00	41
Ingestion rate of surface water (IRw) (liter/exposure/day)	50×10^{-3}	50×10^{-3}	41
Conversion fctor of fish from fresh weight to dry weight (Cf)	0.208	0.208	162

Metals

The average rate of intake of fish for one hundred and sixty five persons were used to estimate rate of intake of fish by an adult and one quarter of it was used as the estimate for a child. Descriptive response from the interview conducted on the quantity of fish consumed by people of the research areawere used for the IRf estimation because of their low illiteracy level and lack of interest to volunteer formal written information.

3.8.2 Total Hazard Index (THI)

Total hazard index (THI) has been developed by US EPA, 1989 to estimate the risk posed on human health due to ingestion of pollutants such as HMs. Total hazard index is the sum of the hazard quotients for all HMs and was calculated with Eqn 8

$$THI = \sum HQ = HQ_{M1} + HQ_{M2} + HQ_{M3} \dots HQ_M \text{ or } \sum HQ = HQ_{Fe} + HQ_{Zn} + HQ_{Cu} + HQ_{Pb} + HQ_{Mn} + HQ_{Cr} \dots (8)$$

It assumes that the magnitude of the adverse effect will be proportional to the sum of the multiple metal exposures.^{41, 159, 166}. The total hazard index (THI) parameter does not estimate the risks; it only indicates the risk level associated with pollutants exposure but the carcinogenic health effect estimated with the cancer risk does¹⁵⁷.

3.8.3 Carcinogenic Health Effect

The carcinogenic health effect is the probability of an individual developing cancer over a lifetime as a result of exposure to a contaminant, it was estimated by the multiplication of the pollutant oral slope factor (SF) with EDI, daily exposure doses averaged over a life time shown in equation 9 below:

$$\text{Cancer risk} = EDI \times SF \dots (9)$$

Where SF = oral slope factor and it is the percent increase in the risk of getting cancer associated with a dose of a toxin (in mg of toxin per kg of body weight) every day for a lifetime. The environmental protection agency had proved that when the level of carcinogenic health effects is at 10^{-6} for a pollutant, this will result in a relatively negligible cancer risks of one additional case of cancer during a lifetime in a population of a million persons^{157, 166}.

The water (EDI_w) or fish (EDI_f) ingestion per day or estimated daily intake of PAHs were calculated using the following equations⁴²,

$$EDI_w = \frac{CM_w \times IR_w \times EF \times BW}{BW} \quad (8)$$

$$EDI_f = \frac{CM_f \times IR_f \times EF \times BW}{BW} \quad (9)$$

Where CM_w is the PAHs concentration in water (mg/L.), IR_w is the daily water ingestion rate (mg /L/day/person), CM_f is the PAHs concentration in fish (mg/kg), IR_f is the daily fish food ingestion rate (mg /day/person) EF = the exposure factor = 1(unitless) and BW is the Body weight (Kg) of the individual. Therefore, the PAHs Cancer Risk for ingestion of water or fish were estimated using the equation,

$$\text{Cancer Risk} = \frac{EDI_w \times SF}{10^{-6}} \quad (10)$$

$$\text{Cancer Risk} = \frac{EDI_f \times SF}{10^{-6}} \quad (11)$$

Where SF is the oral slope factor for the PAHs. US EPA has proved that when the level of carcinogenic health risk is estimated to be $1.0E-6$ for individual toxic metal or pollutant, it will result to negligible cancer risk of a person per one million persons^{157 158}. The ease of comparing the calculated cancer risk with the standard carcinogenic health risk, cancer risk index (CRI) is introduce. It is the ratio of the calculated cancer risk and the US EPA standard acceptable standard risk of $1.0E-6$ ¹⁶⁷.

Table 3.4 Values of Oral reference dose and Cancer slope factor for heavy metals and PAHs used for risk assessment.

Metals	ORF	CSF	PAHs	ORF	CSF
Cd	1.0E-3	1.8E-3	Nap	2.0E-2	-
Cr	1.5	-	Ph	3.0E-1	-
Cu	4.0E-2	-	An	3.0E-1	-

Fe	7.0E-1	-	B[b]F	-	7.3E-1
Pb	4.0E-3	8.5E-3	B[k]F	-	7.3E-2
Zn	3.0E-1	-	B[a]P	-	7.3
Ref.		167		168	168

3.8.4 Bioaccumulation factor and Transfer factor

Transfer factor is the ratio between the concentration of a chemical pollutants measured in an organism and the concentration of the same chemical in water or sediment in an aquatic environment or it is the average metal concentration in a trophic level and it indicates that heavy metal bio-magnification takes place through a trophic chain with a value greater than 1 and it underlines bio-accumulation and it potent risk for consumers of such fish. This ratio is derived from field-collected samples of organisms and water. It is a simple model that estimates the magnitude of accumulation of heavy metal concentration from water or sediment into biota or fish in particular here¹⁷⁰. Transfer factor (TF) of the Heavy metals in fish tissues from the aquatic ecosystem which includes the water and sediments where determined thus:

$$\text{Transfer factor (TF) L/kg} = \frac{C_{\text{Fish}}}{C_{\text{water}}}$$

Where C_{Fish} = Concentration of metals in Fish in (mg/kg), C_{water} = Concentration of metals in water in (mg/L) and C_{Sediment} = Concentration of metals in Sediments in (mg/kg)¹⁶⁹⁻¹⁷².

K = Numbers of PAHs under consideration.

3.9 Ecological RiskAssessment of HMs in the Rivers' sediments

The potential ecological risk organisms (plants and animals) in the environment are likely to face due to heavy metals contamination of sediments are accessed by estimating the ecological risk index

(RI), geo-accumulation index (I_{geo}), Pollution load index using contamination factor and PAHs pollution index (PPI)^{7, 173-175}.

3.9.1 PAHs pollution index (PPI)

To compare the total content of PAHs at the different sampling sites, PAHs Pollution Index (PPI) were estimated^{7, 173}. PPI are potent tools in PAHs pollution evaluation, PPI values higher than 1 indicates the samples have been polluted and while the PPI value less than 1 indicates no pollution occurred:

$$\text{PAHs Pollution Index (PPI)} = (\text{Ch}_1 \times \text{Ch}_2 \times \dots \times \text{Ch}_k)^{1/k}$$

where,

Ch_1 = concentration value of the first PAH.

Ch_2 = concentration value of the second PAH.

Ch_k = concentration value of the kth PAH.

3.9.2 Potential Ecological Risk Index (RI)

The Potential Ecological Risk Index (RI) model of assessing risk of heavy metals is proposed by Hakanson (1980) to estimate the synergistic, concentration, toxic level and ecological sensitivity of the heavy metals. Potential ecological risk index (RI) can be calculated as follows using the following equations¹⁷³:

$$E_r^i = \frac{C_i}{C_n} \times T_r^i \quad (1)$$

$$E_r^i = \frac{C_i}{C_n} \times T_r^i \quad (2)$$

$$RI = \sum_{i=1}^n E_r^i \quad (3)$$

Where E_{ij} is the single potential ecological risk factor, TR_i is the heavy metal toxic response factor, P_{ij} is the single heavy metals pollution index, C_{ij} is the concentration of individuals heavy metals in samples and B_n is the reference value for heavy metals defined by the Martin & Meybeck (1979) (Pre-industrial background values (B_n) of the individual metals concentration values.

Table 3.5 Pre-industrial background value and Toxic response factor value of heavy metals.

Heavy Metals						
Parameter	Cd	Cr	Cu	Pb	Zn	Reference.
$B_n = E_{ij}$	0.2	97	32	20	129	173
TR_i	30	2	5	5	1	172

Based on the value of RI and E_{ij} , heavy metals risk is categorize as shown in the table below.

Table 3.6 RI and E_{ij} values and their corresponding pollution levels and risk characterization.

Classification Grade	RI	Grades of potential ecological risk of the environment	E_{ij} Value	Grades of ecological risk of single metal
A	$RI < 150$	Very low (0-1)	$E_{ij} < 40$	Very low (0-1)
B	$150 \leq RI < 300$	Low (2-3)	$40 \leq E_{ij} < 80$	Low (2-3)
C	$300 \leq RI < 600$	Medium (4-5)	$80 \leq E_{ij} < 160$	Medium (4-5)
D	$RI \geq 600$	High (6-7)	$160 \leq E_{ij} < 320$	High (6-7)

E			$\sum_{i=1}^n C_i \geq 320$	2022 2 22 2022 (22 2)
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Source¹⁷⁶.

3.9.3 Geo-accumulation index (I_{geo})

The Geo-accumulation index (I_{geo}) is used in characterization of the Pollution levels of heavy metals in sediments by comparing the differences between current and preindustrial concentrations values.

It is estimated using the following equation:

$$I_{\text{geo}} = \text{Log}_2 \frac{C_n}{1.5 B_n} = \frac{\text{Log}_{10} \left(\frac{C_n}{1.5 B_n} \right)}{\text{Log}_{10}(2)}$$

Where C_n is the concentration of the individual heavy metal in the sediments; the constant 1.5 is used due to minimize variations in the background data and B_n is the background value of individual heavy metal. The geo-accumulation index is classified heavy metal in degree of pollution based on the following classification: uncontaminated (UC, $I_{\text{geo}} \leq 0$); uncontaminated to moderately contaminated (UMC, $0 < I_{\text{geo}} \leq 1$); moderately contaminated (MC, $1 < I_{\text{geo}} \leq 2$); moderately to heavily contaminated (MHC, $2 < I_{\text{geo}} \leq 3$); heavily contaminated (HC, $3 < I_{\text{geo}} \leq 4$); heavily to extremely contaminated (HEC, $4 < I_{\text{geo}} \leq 5$); extremely contaminated (EC, $I_{\text{geo}} > 5$)^{176, 177}.

3.9.4 Pollution Load Index (PLI) and Contamination Factor (CF)

The pollution load index (PLI) is defined as the nth root of the multiplication of the concentration factors (CF_{metal}) of the individual heavy metals in the samples. It is estimated using the following equation:

$$\text{PLI} = (\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \dots \times \text{CF}_n)^{1/n}$$

where CF_1 is the contamination factor of the first heavy metal, CF_2 the second metal, CF_3 the third and CF_n the nth metal. The values of $PLI > 1$ imply that heavy metal pollution exists, otherwise, if $PLI < 1$, there is no heavy metal pollution¹⁷⁵.

While the degree of contamination (Cd) is simply defined as the sum of all contamination factors (CF).

3.9.5 Contamination factor (CF)

Contamination factor (CF) is used to determine the contamination status of sediment, it is the ratio of measured mean concentration value of heavy metals in samples and the background values of the metals calculated with the following equation:

$$CF = \frac{C_{Metal}}{C_{Background}}$$

Where C_{Metal} is the heavy metal content in samples and $C_{Background}$ is the pre industrial concentration of individual metals which is the background value of metals. Contamination factor can be used to differentiate between the metals originating from anthropogenic activities and those from natural processes and to assess the degree of anthropogenic influence. Four contamination categories of contamination factor are recognized as shown in Table 3.7. High Contamination values suggest strong anthropogenic influence^{177 - 181}.

Table 3.7 Terminologies used to describe the contamination factor.

CF	Description
$CF < 1$	Low degree of contamination

$$1 < CF < 3$$

Moderate degree of
contamination

$$3 < CF < 6$$

Considerable degree of
contamination

$$CF > 6$$

Very high degree of
contamination

Source¹⁷⁷.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS OF PHYSICOCHEMICAL PARAMETERS

The physicochemical characteristics of the water of rivers Niger and Benue confluence were determined in situ using hand held probes shown in Table 3.1(Chapter Three) during the dry and rainy season sampling for the determination of heavy metals and polycyclic aromatic hydrocarbons and the results of the physicochemical parameters were as shown in table 4.1 below. The table shows the values of temperature in degree Celsius, electrical conductivity in micro Siemen per centimeter and total dissolved solids in milligram per liter in station A to E.

Table 4.1 Results of Physicochemical parameters reported as mean $\pm$ Standard deviation.

Season	Parameters	Station					Max. Permissible
		A	B	C	D	E	Limit
DryLL	Temperature ($^{\circ}$ C)	29.97 $\pm$ 0.21	28.77 $\pm$ 0.81	30.57 $\pm$ 0.32	30.80 $\pm$ 0.10	31.47 $\pm$ 0.38	20-33
	pH	6.70 $\pm$ 0.26	6.73 $\pm$ 0.15	6.80 $\pm$ 0.10	6.73 $\pm$ 0.06	6.83 $\pm$ 0.06	6-8
	Elect. Cond. μ S/cm	15.15 $\pm$ 0.08	14.51 $\pm$ 0.38	14.58 $\pm$ 0.38	14.63 $\pm$ 0.26	15.07 $\pm$ 0.25	1000
	TDS (mg/L)	9.80 $\pm$ 0.61	9.50 $\pm$ 0.50	9.77 $\pm$ 0.25	9.80 $\pm$ 0.17	10.07 $\pm$ 0.15	500
Rainy	Temperature ($^{\circ}$ C)	23.77 $\pm$ 0.23	22.83 $\pm$ 0.06	24.40 $\pm$ 0.46	24.63 $\pm$ 0.46	26.40 $\pm$ 1.31	20-33
	pH	7.03 $\pm$ 0.15	7.30 $\pm$ 0.10	7.27 $\pm$ 0.31	7.29 $\pm$ 0.27	7.27 $\pm$ 0.12	6-8
	Elect. Cond. μ S/cm	13.02 $\pm$ 0.80	13.06 $\pm$ 0.76	13.31 $\pm$ 0.40	14.56 $\pm$ 0.90	13.56 $\pm$ 0.53	1000
	TDS (mg/L)	11.40 $\pm$ 0.53	11.43 $\pm$ 0.51	11.60 $\pm$ 0.26	12.43 $\pm$ 0.60	11.77 $\pm$ 0.35	500
	Ref						182-184

4.2 Results of quality control studies/Recovery Analysis

Analysis of standard reference materials of PAHs (SRM 822-275872-11) and HMs (ASTM D3557 for Cd, D1687 for Cr, D1688 for Cu, D1068 for Fe, D3559 for Pb and D1691 for Zn) were carried out as a measure of analytical quality assurance for the PAHs and HMs sort for in the samples of water, fish and sediments to obtain recovery of the method and to therefore ascertain the accuracy and precision of the method. The recovery of the results obtained ranged from 100.30 to 107.80 for the PAHs and 88.83 to 107.80 for the heavy metals as shown in table 4.2, 4.3 and 4.4 respectively.

Table 4.2: Results of Recovery analysis of standard reference material (SRM) for PAHs in ppm

PAHS	SRM Conc. (ppm)	Recovery Conc. (ppm)	%Recovery
Naphthalene	10.00	10.20	102.00
Phenanthrene	10.00	10.03	100.30
Anthracene	10.00	10.03	100.30
Benzo[b]fluoranthene	10.00	10.21	102.10
Benzo[k]fluoranthene	10.00	10.08	100.80
Benzo[a]pyrene	10.00	10.31	103.10

Table 4.3: Results of Recovery analysis of standard reference material for metals in ppm

Metals	SRM Conc. (ppm)	Recovery Conc. (ppm)	%Recovery
Cd	2.00	2.156	107.80
Cr	2.00	2.080	104.00
Cu	2.00	2.120	106.00
Fe	2.00	1.972	98.60
Pb	2.00	1.921	96.05
Zn	2.00	2.080	104.00

Table 4.4 Results of recovery of spiked samples with 12ppm Cd in percentage

Metal	Spiked Ppm	Conc.	Unspiked ppm	Conc.	% Recovery
Cd in Sediment	10.767		0.107		88.83
Cd in water	11.419		0.055		94.70
Cd in Water	10.797		0.021		89.80

Table 4.5 and 4.6 shows the results of the estimation of the limit of detection and limit of quantitation of the heavy metals and polycyclic aromatic hydrocarbons. While the replicates blanks ran for heavy metals and polycyclic aromatic hydrocarbons were used for the estimation of the limit of detection and quantitation, the GC detection limit of 0.0001 ppm were used for polycyclic aromatic hydrocarbons that produced zero blanks results and only the limit of detection and quantification of the PAHs detected by the instrument were presented below.

Table 4.5: Results of Limit of detection and Limit of quantitation of the heavy metals in ppm

Meals	Cd	Cr	Cu	Pb	Zn
LOD	0.003	0.005	0.004	0.012	0.003
LOQ	0.007	0.012	0.0093	0.029	0.007

Table 4.6: The Limit of detection (LOD) and Limit of quantitation (LOQ) of PAHs in mg/kg.

PAHs	Nap	PH	Ant	BbF	BkF	BaP
LOD	0.0001	0.0002	0.0002	0.0001	0.0001	0.0001
LOQ	0.0003	0.0007	0.0007	0.0003	0.0003	0.0003

4.3 Results of the concentration of heavy metals in water, Sediment and Fish.

Table 4.7 and 4.8 below shows the concentration values of six heavy metals (Cd, Cr, Cu, Fe, Pb and Zn) analyzed in mg/L for water samples collected from five sample station A, B, C, D and E. The results showed that the mean concentration values of the dry season heavy metals analysis slightly varied between the sample stations. Cadmium (Cd) mean concentration values were in the range of 0.038 to 0.089 across the sample station with station E showing the highest cadmium concentration value of 0.089 and station A showing the least concentration value of 0.038 mg/L. Results of the rainy season concentration values of metals showed that Cadmium was not detected at location A and C but showed lesser concentration values at location B (0.004) as the least rainy season concentration values and

Table 4.7: Results of Dry Season Heavy Metals concentration in water (mg/L) reported as Range and mean $\pm$ standard deviation ($\bar{x} \pm SD$)

Metals	Location					WHO/SON Max Limit
	A	B	C	D	E	
Cd	0.021-0.055	0.020-0.150	0.058-0.071	0.020-0.056	0.037-0.741	0.003
	0.038 ± 0.016	0.085 ± 0.065	0.066 ± 0.007	0.039 ± 0.018	0.089 ± 0.052	
Cr	0.096-0.116	0.106-0.220	0.209-0.215	0.196-0.214	0.224-0.255	0.002
	0.106 ± 0.010	0.163 ± 0.057	0.212 ± 0.003	0.203 ± 0.009	0.240 ± 0.016	
Cu	0.081-0.101	0.094-0.180	0.139-0.149	0.150-0.172	0.153-0.175	1.000
	0.092 ± 0.010	0.138 ± 0.043	0.145 ± 0.005	0.161 ± 0.011	0.164 ± 0.011	
Fe	0.720-0.750	0.854-0.876	0.692-0.728	0.876-0.880	0.681-0.684	0.300
	0.738 ± 0.016	0.867 ± 0.011	0.710 ± 0.018	0.878 ± 0.002	0.682 ± 0.002	
Pb	0.053-0.061	0.124-0.224	0.062-0.078	0.142-0.149	0.298-0.318	0.050
	0.058 ± 0.004	0.174 ± 0.050	0.071 ± 0.008	0.146 ± 0.004	0.309 ± 0.010	
Zn	0.097-0.295	0.193-0.353	0.235-0.274	0.0393-1.645	0.005-0.021	3.000
	0.227 ± 0.113	0.274 ± 0.080	0.251 ± 0.020	1.020 ± 0.626	0.015 ± 0.009	
Ref.						41, 171.

Fig. 4.1 Bar Chart of Dry Season Heavy Metals concentration in water (mg/L)

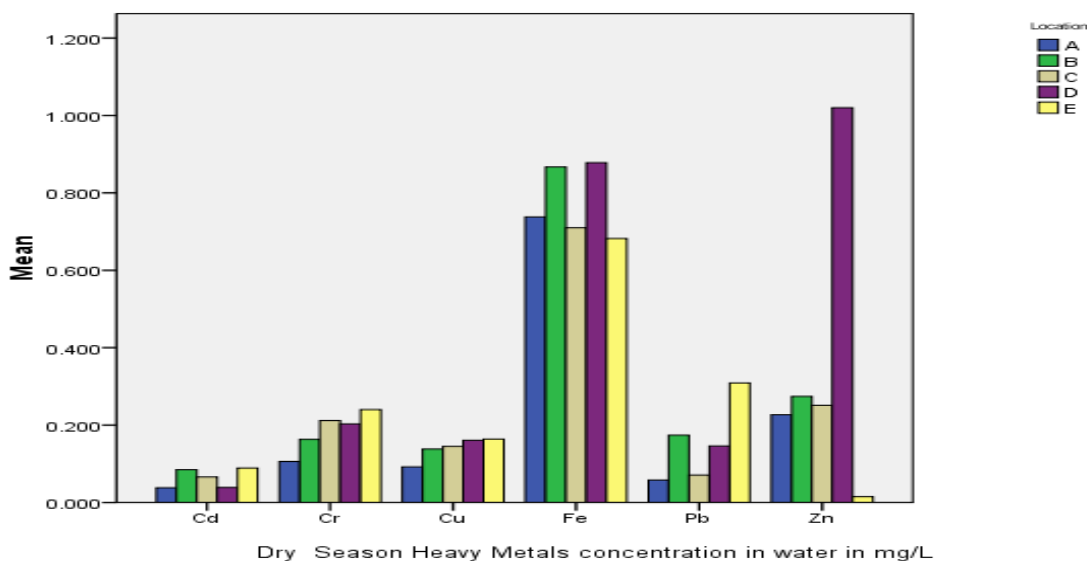
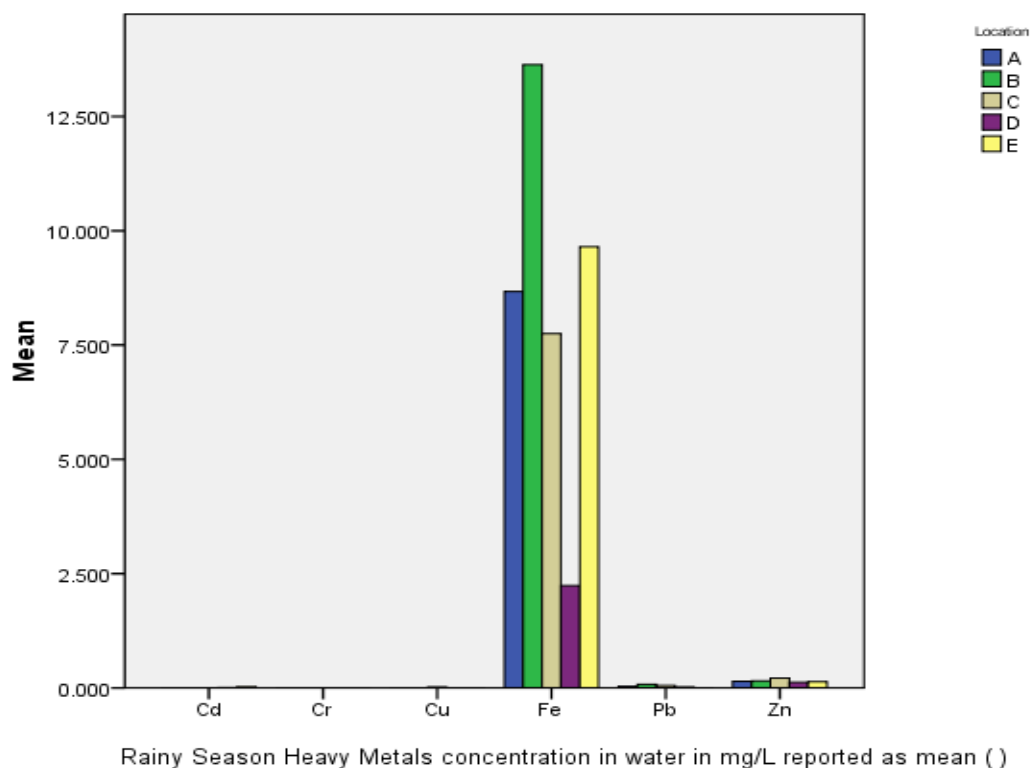


Table 4.8: Results of Rainy Season Heavy Metals concentration in water (mg/L) reported as Range and mean $\pm$ standard deviation ($\bar{x} \pm SD$)

Metals	Location					WHO/SON Max Limit
	A	B	C	D	E	
Cd		0.003-0.005	ND	0.006-0.007	0.023-0.031	0.003
	ND	0.004 $\pm$ 0.001		0.007 $\pm$ 0.001	0.027 $\pm$ 0.004	
Cr	ND	ND	ND	ND	ND	0.002
Cu	ND	ND	0.019-0.023	ND	ND	1.000
			0.021 $\pm$ 0.002			
Fe	8.552-8.599	13.607-13.664	7.654-7.896	2.031-2.500	9.578-9.770	0.300
	8.670 $\pm$ 0.165	13.634 $\pm$ 0.029	7.749 $\pm$ 0.129	2.236 $\pm$ 0.240	9.649 $\pm$ 0.105	
Pb	0.034-0.036	0.079-0.082	0.050-0.053	0.021-0.023	0.001-0.010	0.050
	0.035 $\pm$ 0.001	0.080 $\pm$ 0.002	0.051 $\pm$ 0.002	0.022 $\pm$ 0.001	0.004 $\pm$ 0.005	
Zn	0.144-0.149	0.154-0.157	0.205-0.232	0.119-0.122	0.136-0.140	3.000
	0.146 $\pm$ 0.003	0.155 $\pm$ 0.002	0.216 $\pm$ 0.014	0.121 $\pm$ 0.002	0.138 $\pm$ 0.002	
Ref.						41,171.

Fig. 4.2 Bar Chart of Rainy Season Heavy Metals concentration in water (mg/L)



0.027 mg/L at location E as the highest cadmium concentration value for the rainy season across the location A to E. The range of the mean concentration values for the dry and rainy season metals' concentrations were, Cr: 0.106 to 0.240 for the dry season and not detected for the rainy season, Cu: 0.092 to 0.164 for the dry season and 0.021 detection at only location C during the rainy season, Pb: 0.058 to 0.309 for the dry season and 0.004 to 0.080 for the rainy season, Zn: 0.015 to 1.020 for the dry season and 0.121 to 0.216 mg/L for the rainy season. The bar chart in figure 4.1 and 4.2 shows the dry and rainy season heavy metals mean concentration values in water. All the results print out for this research work was banded and will accompany this work as accompanying document because they are so much or many.

The mean metal concentration values were slightly higher in the dry season water analysis than the rainy season except for the rainy season iron (Fe) concentration with range values of 2.236 to 13.634 and were higher in all locations than the results of the dry season Fe concentration as shown by the bar graphs or bar charts in figure 4.1 and 4.2. Summarily, the heavy metals were profiled for dry and rainy seasons in five created sample locations. The concentration of the metals in water across the locations ranged from Cd (0.038 to 0.089), Cr(0.106 to 0.240), Cu(0.092 to 0.0164), Fe(0.682 to 0.878), Pb(0.058 to 0.309) mg/L with distribution pattern of $Zn > Fe > Pb > Cr > Cu > Cd$ for the dry season water samples and Cd(ND to 0.027), Cr(ND), Cu(ND to 0.021), Fe(2.236 to 13.634), Pb(0.119 to 0.205) and Zn(0.121 to 0.216) mg/L with distribution patter of $Fe > Zn > Pb > Cd > Cu > Cr$ during the rainy season.

The results of metals concentration values in sediment also varied from station A-E and between the seasons with the dry season heavy metals concentration values higher than the rainy season as shown in table 4.9 and 4.10. The range of the mean concentration values of the metals measured in mg/kg across stations and between seasons were 2.180 to 2.893 for dry season Cd and 0.321 to 1.024 for

rainy season, 4.367 to 9.927 for dry season Cr and 0.456 to 2.662 for rainy season, 3.433 to 6.780 for dry season Cu and 0.429 to 8.599 for rainy season with copper not detected at locations B and C, 233.210 to 254.160 for Fe dry season

Table 4.9: Results of Dry Season Heavy Metals concentration in Sediments (mg/kg) reported as Range and mean $\pm$ standard deviation ($\bar{x} \pm SD$)

Metals	Location				
	A	B	C	D	E
Cd	2.140-2.500	2.420-2.520	1.940-2.380	2.640-3.120	2.760-3.000
	2.313 $\pm$ 0.180	2.473 $\pm$ 0.050	2.180 $\pm$ 0.223	2.887 $\pm$ 0.240	2.893 $\pm$ 0.122
Cr	3.740-4.960	7.540-8.620	6.480-7.240	8.680-11.100	7.480-10.500
	4.367 $\pm$ 0.611	8.127 $\pm$ 0.546	6.873 $\pm$ 0.381	9.927 $\pm$ 1.212	8.993 $\pm$ 1.510
Cu	2.680-4.180	3.320-3.640	3.900-4.120	3.880-9.66	3.800-7.780
	3.433 $\pm$ 0.750	3.480 $\pm$ 0.160	4.007 $\pm$ 0.110	6.780 $\pm$ 2.890	5.793 $\pm$ 1.990
Fe	232.360-234.820	231.080-235.340	232.220-239.960	247.340-254.200	229.020-259.280
	233.590 $\pm$ 1.230	233.210 $\pm$ 2.130	237.360 $\pm$ 4.451	254.160 $\pm$ 6.800	244.170 $\pm$ 15.130
Pb	8.900-25.960	7.480-10.420	8.460-10.280	10.420-14.880	8.360-11.040
	17.420 $\pm$ 8.530	8.967 $\pm$ 1.470	9.380 $\pm$ 0.910	12.700 $\pm$ 2.232	9.700 $\pm$ 1.340
Zn	5.800-13.040	5.920-8.160	5.300-6.740	7.860-32.900	7.740-27.240
	10.080 $\pm$ 3.796	7.027 $\pm$ 1.120	6.027 $\pm$ 0.720	20.380 $\pm$ 12.520	17.493 $\pm$ 9.750

Fig. 4.3 Bar Chart of Dry Season Heavy Metals concentration in Sediments (mg/kg)

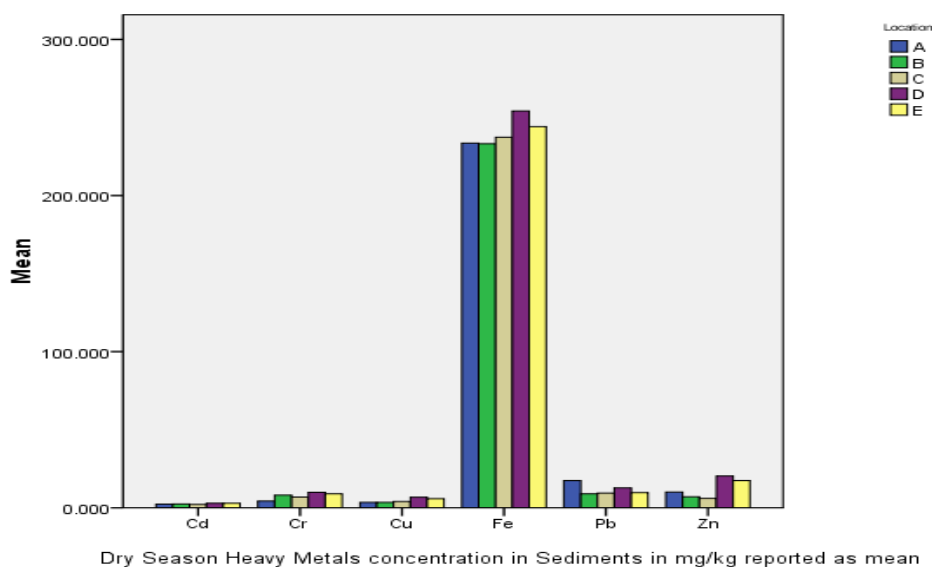
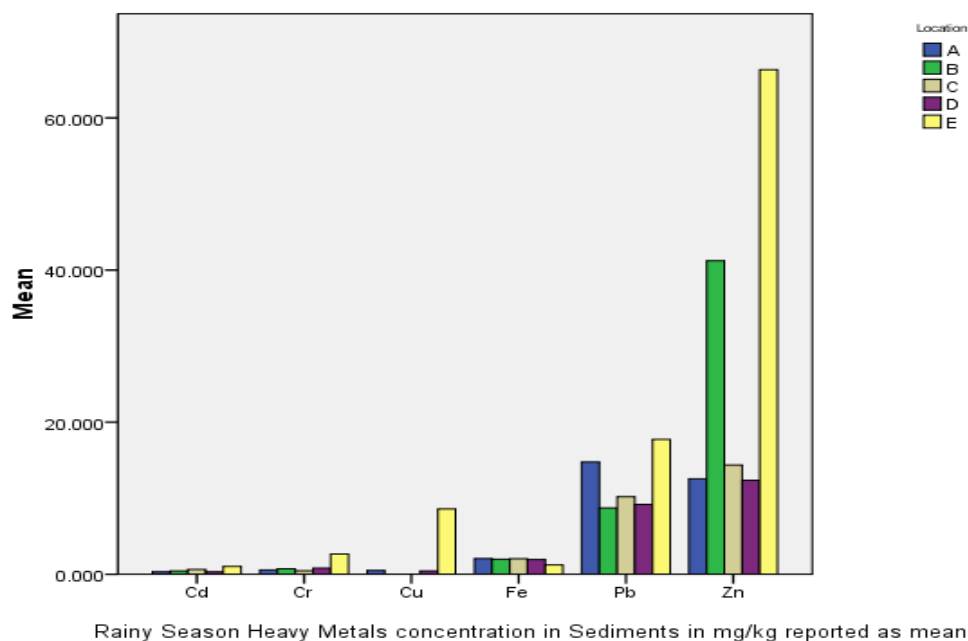


Table 4.10: Results of RainySeason Heavy Metals concentration in Sediment (mg/kg) reported as range and mean $\pm$ standard deviation ($\bar{x} \pm SD$)

Metals	Location				
	A	B	C	D	E
Cd	0.320-0.349	0.420-0.449	0.620-0.630	0.318-0.324	0.983-1.052
	0.332 $\pm$ 0.150	0.435 $\pm$ 0.015	0.626 $\pm$ 0.005	0.321 $\pm$ 0.003	1.024 $\pm$ 0.036
Cr	0.438-0.775	0.698-0.755	0.447-0.468	0.811-0.823	2.535-2.780
	0.566 $\pm$ 0.182	0.729 $\pm$ 0.029	0.456 $\pm$ 0.011	0.8190 $\pm$ 0.007	2.662 $\pm$ 0.123
Cu	0.506-0.511	ND	ND	0.422-0.428	8.495-8.713
	0.509 $\pm$ 0.003			0.426 $\pm$ 0.003	8.599 $\pm$ 0.109
Fe	2.014-2.153	1.952-2.024	2.020-2.059	1.932-1.957	1.215-1.262
	2.062 $\pm$ 0.786	1.979 $\pm$ 0.039	2.035 $\pm$ 0.021	1.941 $\pm$ 0.014	1.234 $\pm$ 0.025
Pb	14.570-14.947	8.633-8.871	10.107-10.276	9.165-9.198	17.603-17.852
	14.767 $\pm$ 0.189	8.721 $\pm$ 0.131	10.207 $\pm$ 0.088	9.183 $\pm$ 0.017	17.737 $\pm$ 0.126
Zn	12.304-12.861	41.113-41.284	14.317-14.385	12.218-12.461	66.225-66.431
	12.546 $\pm$ 0.285	41.216 $\pm$ 0.091	14.353 $\pm$ 0.034	12.350 $\pm$ 0.123	66.343 $\pm$ 0.106

Fig. 4.4 Bar Chart of Rainy Season Heavy Metals concentration in Sediments (mg/kg)



concentration value and 1.234 to 2.062 for the rainy season concentration values, 8.967 to 17.420 for dry season Pb and 8.721 to 17.737 for rainy season with undulating concentration values between the seasons and, 6.027 to 17.493 for dry season Zn and 12.350 to 66.343 for the rainy season concentration values with the rainy season Zn concentration higher than the dry season as depicted in figure 4.3 and 4.4 above. Summarily, the sediments' metals concentration across locations ranged from Cd(2.189 to 2.893), Cr(4.367 to 9.927), Cu(3.433 to 6.780), Fe(233.210 to 254.160), Pb(8.967 to 17.420) and Zn(6.027 to 20.380) mg/kg with distribution pattern of Fe>Zn>Pb>Cr>Cu>Cd during the dry season and Cd (0.321 to 1.024), Cr(0.456 to 2.662), Cu(ND to 8.599), Fe(1.234 to 2.062), Pb(8.721 to 17.737) and Zn(12.350 to 66.343) mg/kg with distribution pattern of Zn>Pb>Cu>Cr>Fe>Cd for the rainy season samples.

Table 4.11 summarizes the concentration values of heavy metals in range and mean $\pm$ standard deviation in dry and rainy season for two species of common fishes (Tilapia and Catfish) around the study area. The mean concentration values of metals in the two species of fishes during the dry and rainy seasons were (4.850 and 0.453), (3.367 and 0.666) for Cd dry and rainy season concentration values for Tilapia and Catfish. No determination was done for dry season Chromium metals in Tilapia and Catfish, but Cr concentration values for rainy season Tilapia and Catfish were (0.164 and 0.293). The dry and rainy season Cu concentration values for Tilapia and Catfish were (8.042 and 1.658) and (7.050 and 4.952). Also, (44.108 and 0.198) and (44.775 and 1.23) were the dry and rainy season Fe concentration values in Tilapia and Catfish. Pb content of the fishes were (4.717 and 6.704), (3.842 and 8.683) for dry and rainy season Tilapia and Catfish. Zn metals concentration values were (63.742 and 40.680), (63.625 and 85.266) for the dry and rainy season in Tilapia and Catfish. The concentration values of the metals varied between the species and between the seasons

slightly with the metals concentration values higher during the dry season than the rainy season except Pb in Tilapia that the

Table 4.11: Results of Dry and Rainy Season Metals Concentration in Tilapia and Catfish in mg/kg

	Dry Season		Rainy Season		
Metals	Tilapia	Catfish	Tilapia	Catfish	WHO/SON Max Limit
Cd	3.425-6.250	3.250-3.500	0.444-0.460	0.648-0.679	0.003
	4.850 ± 1.413	3.367 ± 0.126	0.453 ± 0.008	0.666 ± 0.016	
Cr	-	-	0.152-0.173	0.285-0.301	0.002
			0.164 ± 0.011	0.293 ± 0.008	
Cu	7.775-8.300	4.025-10.075	1.636-1.675	4.809-5.061	1.000
	8.042 ± 0.262	7.050 ± 3.025	1.658 ± 0.020	4.952 ± 0.130	
Fe	36.225-51.575	33.975-55.325	0.196-0.200	1.215-1.241	0.300
	44.108 ± 7.683	44.775 ± 10.677	0.198 ± 0.002	1.230 ± 0.013	
Pb	4.500-4.900	3.375-4.275	6.508-6.888	6.715-9.752	0.050
	4.717 ± 0.202	3.842 ± 0.451	6.704 ± 0.190	8.683 ± 1.706	
Zn	59.525-67.950	55.450-70.400	39.901-41.789	84.978-85.418	3.000
	63.742 ± 4.213	63.625 ± 7.573	40.680 ± 0.986	85.266 ± 0.250	
Ref			41,171.		

Figure 4.5 Bar graph of Dry and Rainy Season Heavy Metals Concentration in Tilapia (mg/Kg)

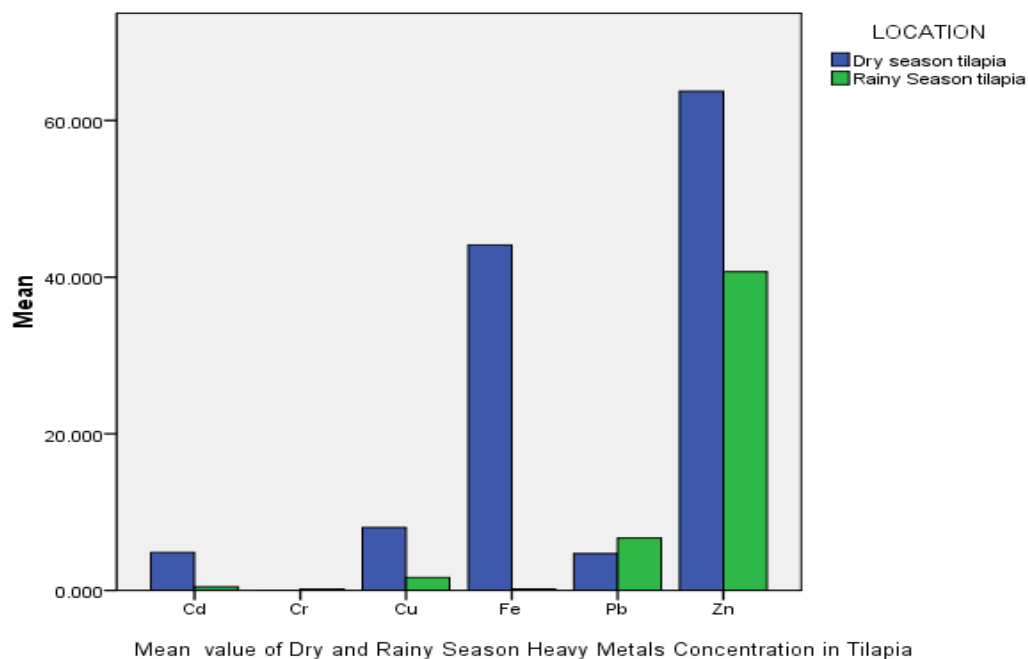
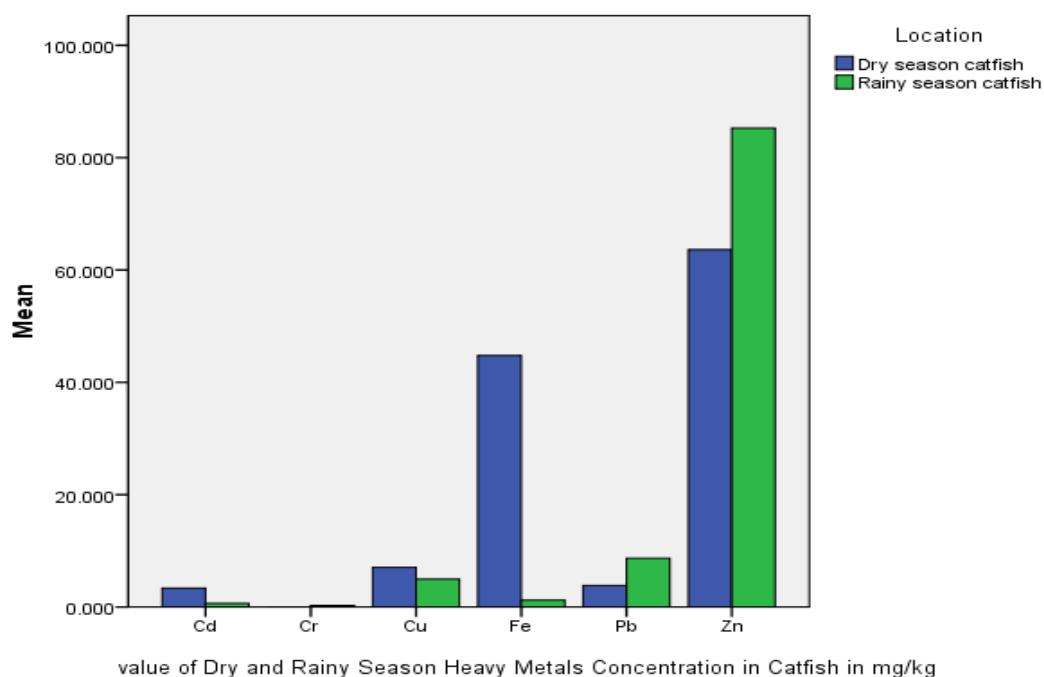


Figure 4.6 Bar graph of Dry and Rainy Season Heavy Metals Concentration in Catfish (mg/kg)



rainy season concentration value was higher than the dry season's whereas, Zn and Pb rainy season concentration values in Catfish were higher than the dry season concentration values as shown in

figure 4.5 and 4.6 as shown in figure 4.5 and 4.6 below. Summarily, The mean concentration of the metals in Catfish during dry and rainy seasons were Cd(3.367 and 0.666) Cr(- and 0.293), Cu(7.050 and 4.952), Fe(44.775 and 1.230), Pb(3.842 and 8.683) and Zn(63.625 and 85.266)mg/kg with distribution pattern of Zn>Fe>Cu>Pb>Cd and the Tilapia mean concentration values for dry and rainy seasons were as follows Cd(4.850 and 0.453), Cr(- and 0.164), Cu(8.042 and 1.658), Fe(44.108 and 0.198), Pb(4.717 and 6.704), Zn(63.742 and 40.680) mg/kg with the distribution pattern of Zn>Fe>Cu>Cd>Pb.

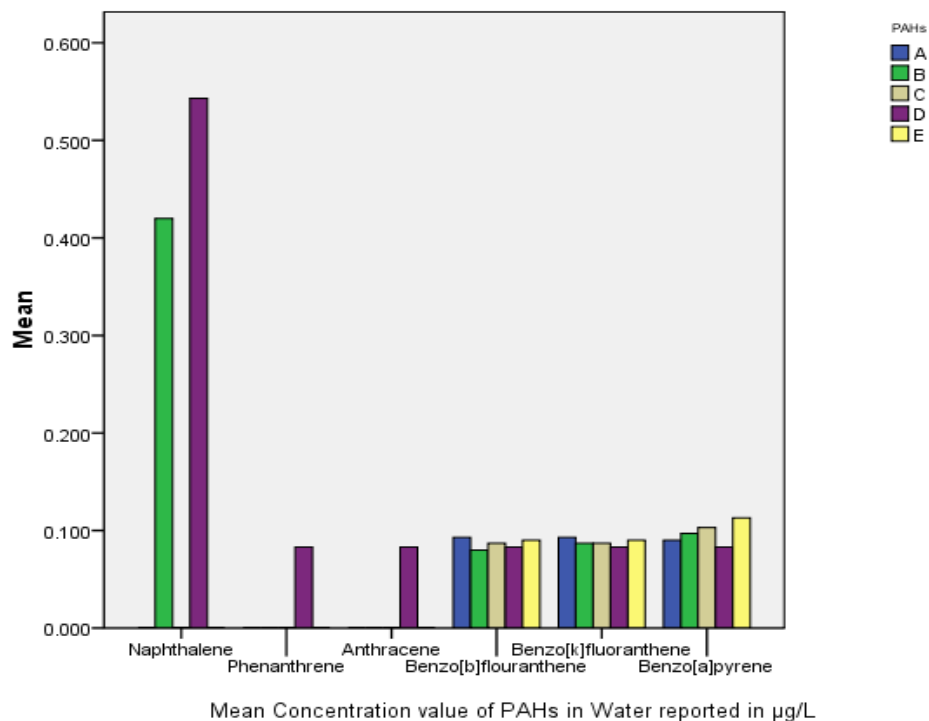
4.4 Results of the concentration of PAHs in Water, Fish and Sediment

Table 4.12, 4.13 and 4.14 shows six out of the sixteen United States Environmental Protection Agency (US EPA) priority polycyclic aromatic hydrocarbons sort for in the three media (Water, Sediment and Fish) in this research which were detected and determined respectively. The other PAHs may not have been detected not necessarily because they were not present but may be because they were present at a concentration below the detection limit of the GC. The PAHs detected and determined were Naphthalene, Phenanthrene, Anthracene, Benzo [b] fluoranthene, Benzo [k] fluoranthene and Benzo [a] pyrene.

4.12: Results of PAHs concentration in water (µg/L) reported as Range and ($\bar{x} \pm SD$)

PAHs	Location				
	A	B	C	D	E
Naphthalene	ND	0.380-0.440	ND	0.190-0.800	ND
		0.420 ± 0.035		0.543 ± 0.316	
Phenanthrene	ND	ND	ND	0.08-.009	ND
				0.083 ± 0.006	
Anthracene	ND	ND	ND	0.08-0.09	ND
				0.083 ± 0.006	
Benzo[b]fluoranthene	0.080-0.100	0.070-0.090	0.060-0.110	0.040-0.13	0.060-0.12
	0.093 ± 0.012	0.080± 0.010	0.087 ± 0.025	0.083 ± 0.045	0.090 ± 0.030
Benzo[k]fluoranthene	0.080-0.100	0.080-0.090	0.060-0.110	0.040-0.130	0.060-0.120
	0.093 ± 0.012	0.087 ± 0.006	0.087 ± 0.025	0.083 ± 0.045	0.090 ± 0.030
Benzo[a]pyrene	0.08-0.100	0.07-0.130	0.100-0.110	0.050-0.110	0.100-0.120
	0.090 ± 0.010	0.097 ± 0.031	0.103 ± 0.006	0.083 ± 0.031	0.113 ± 0.012

Figure 4.7 Bar graph of PAHs Concentration in water (µg/L)



The mean concentration values for the PAHs in water measured in µg/L from station A to E were Naphthalene: 0.420 to 0.543 µg/L but were not detected in stations A, C and E. The concentration values of Phenanthrene and Anthracene were 0.083 and were only detected in station D. Benzo[b]fluoranthene and Benzo[k] fluoranthene concentration values were 0.080 to 0.093 across station A to E and Benzo[a]pyrene had values that ranged from 0.083 to 0.113 µg/L with Benzo[a]pyrene having the highest value of concentration in station E. The results of the mean concentration values of the PAHs in the sediment were in the range of not detected at station D to 2.210 µg/kg at location A for Naphthalene across the station A to E and, not detected at station B, D and E to 0.053 µg/kg at location C for Phenanthrene across the station A to E. Anthracene mean concentration values were in the range of not detected to 0.053 µg/kg and Benzo[b]fluoranthene concentration were in the range of not detected to 0.050 µg/kg. Benzo[k]fluoranthene mean concentration values were in the range of not detected to 0.110 µg/kg and Benzo[a]pyrene showed mean concentration values of not detected to 0.053 µg/kg.

Table 4.13: Results of PAHs concentration in Sediments ($\mu\text{g/kg}$) reported as Range and mean $\pm$ standard deviation ($\bar{x} \pm \text{SD}$)

PAHs	Station				
	A	B	C	D	E
Naphthalene	2.120-2.270	0.050-0.060	1.740-1.960	ND	1.580-1.640
	2.210 ± 0.079	0.053 ± 0.006	1.850 ± 0.110		1.610 ± 0.030
Phenanthrene	0.040-0.050	ND	0.050-0.060	ND	ND
	0.047 ± 0.006		0.053 ± 0.006		
Anthracene	0.050-0.060	ND	0.050-0.060	ND	ND
	0.053 ± 0.006		0.053 ± 0.006		
Benzo[b]fluoranthene	0.040-0.110	0.040-0.96	0.050-0.060	0.04-0.060	ND
	0.100 ± 0.056	0.383 ± 0.494	0.053 ± 0.006	0.053 ± 0.011	
Benzo[k]fluoranthene	0.040-0.150	0.050-0.160	0.050-0.070	0.04-0.060	ND
	0.093 ± 0.055	0.110 ± 0.056	0.057 ± 0.012	0.053 ± 0.011	
Benzo[a]pyrene	ND	0.020-0.080	0.050-0.060	0.050-0.060	ND
		0.047 ± 0.031	0.053 ± 0.006	0.053 ± 0.006	

Naphthalene mean concentration value of $2.383 \mu\text{g/kg}$ in catfish was found higher than $1.947 \mu\text{g/kg}$ in Tilapia and the mean concentration value for Catfish and Tilapia for Phenanthrene were 0.050 and 0.057, the mean concentration values for Anthracene were $0.057 \mu\text{g/kg}$ for both fishes. While the mean concentration values of Benzo[b] fluoranthene, Benzo[k]fluoranthene for catfish were $0.043 \mu\text{g/kg}$ and Benzo[a]pyrene for Catfish was 0.05, Benzo[b] fluoranthene, Benzo[k]fluoranthene and Benzo[a]pyrene were not detected in the Tilapia, as shown also in figure 4.9 below. Summarily, The concentrations of the PAHs in water across locations ranged from Nap(ND to 0.543), Ph(ND to 0.083) Ant (ND to 0.083), BbF(0.080 to 0.093), BkF(0.083 to 0.093) and BaP(0.083 to 0.113) mg/L

with distribution pattern of Nap>BaP>BbF=BkF>Ant=Ph. The concentration of PAHs in sediment across the locations ranged as follows Nap(ND to 2.210), Ph(ND to 0.053), Ant(ND to 0.053), BbF(0.053 to 0.383), BkF(0.053 to 0.110) and BaP(ND to 0.053)mg/kg with distribution pattern of Nap>BbF>BkF>Ph=Ant=Bap. The mean concentration value of PAHs in Catfish and Tilapia were Nap(2.383 and 1.947), Ph(0.050 and 0.057), Ant(0.057 and 0.057), BbF(0.043 and ND), BkF(0.043 and ND) and BaP(0.050 and ND).

Figure 4.8 Bar graph of PAHs Concentration in Sediment (µg/kg)

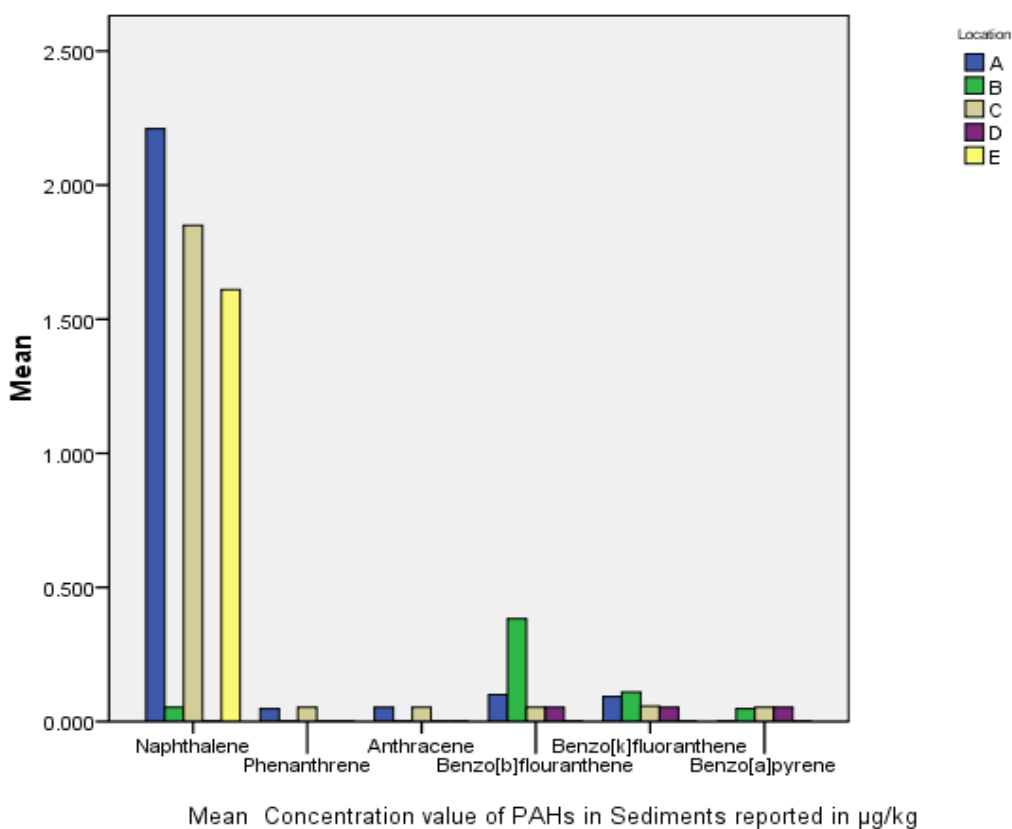
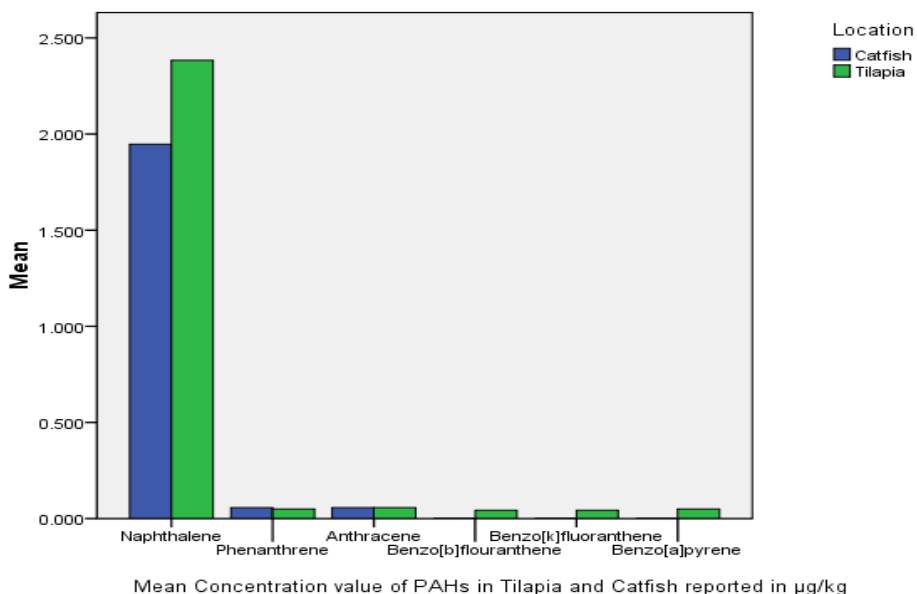


Table 4.14: Results of PAHs concentration in Fish (µg/kg) reported as Range and mean $\pm$ standard deviation ($\bar{x} \pm SD$)

PAHs	Catfish	Tilapia
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Naphthalene	2.340-2.420	1.200-2.310
	2.383 ± 0.040	1.947 ± 0.647
Phenanthrene	0.040-0.060	0.050-0.070
	0.050 ± 0.010	0.057 ± 0.012
Anthracene	0.040-0.080	0.050-0.070
	0.057 ± 0.021	0.057 ± 0.012
Benzo[b]fluoranthene	0.040-0.050	ND
	0.043 ± 0.006	
Benzo[k]fluoranthene	0.040-0.050	ND
	0.043 ± 0.006	
Benzo[a]pyrene	0.040-0.060	ND
	0.050 ± 0.010	

Figure 4.9 Bar graph showing the PAHs Concentration in Tilapia and Catfish ($\mu\text{g/kg}$)



4.5 Results of Estimated daily intake (EDI) of Heavy Metals and Polycyclic Aromatic Hydrocarbons through ingestion of water and Fish and Cancer risk (CR) for Adult and Child during the dry and rainy seasons

Table 4.15 and 4.16 display the results of the estimated daily intake (EDI) of heavy metals through the ingestion of water using the parameters in table 3.3 to compute the estimated daily intake for both dry and rainy seasons, the Hazard quotients and the cancer risk for the ingestion of Cadmium and Lead, metals known to be carcinogenic were also estimated and the results shown in the tables. The results of these parameters that were above the acceptable limits were indicated in bold fonts. Again, table 4.17 and 4.18 display the results of the estimated daily intake (EDI) of heavy metals through the ingestion of fish using the parameters in table 3.3 for both dry and rainy seasons and the Hazard quotients and the cancer risk for the ingestion of Cadmium and Lead were estimated and shown in the table for Tilapia and Catfish. The results of these parameters that were above accepted limit were indicate inbold fonts. The transfer factor (TF) of heavy metals from sediment to the two fish species were estimated and the results were shown in table 4.19 below. The results of the estimated daily intake (EDI) of polycyclic aromatic hydrocarbons through the ingestion of water and fish and the cancer risk were estimated and shown in table 4.20, 4.21 and 4.22. Only the cancer risk for Catfish were computed since there was no detections for the carcinogenic PAHs (Benzo[b]fluoranthene, Benzo[k]fluoranthene and Benzo[a]pyrene) in Tilapia.

Table 4.15 Estimated Daily Intake (EDI), Hazard Quotient (HQ), Cancer Risk Index (CRI) and Total Hazard Index (THI) of ingestion of Heavy Metals in water for Adult and Child during the dry season

	A	B	C	D	E	RfD ₀
Cd	EDI _{Adult} 2.7E-5	EDI _{Adult} 6.1E-5	EDI _{Adult} 4.7E-5	EDI _{Adult} 2.1E-3	EDI _{Adult} 2.1E-3	1.0 E-3
	EDI _{Child} 1.3E-4	EDI _{Child} 2.8E-4	EDI _{Child} 2.2E-4	EDI _{Child} 9.6E-3	EDI _{Child} 9.6E-3	
	HQ _{Adult} 2.7E-2	HQ _{Adult} 6.1E-2	HQ _{Adult} 4.7E-2	HQ_{Adult} 2.1	HQ_{Adult} 2.1	
	HQ _{Child} 1.3E-1	HQ _{Child} 2.8E-1	HQ _{Child} 2.2E-1	HQ_{Child} 9.6	HQ_{Child} 9.6	
	CR _{Adult} 4.9E-8	CR _{Adult} 1.1E-7	CR _{Adult} 8.5E-8	CR_{Adult} 3.8E-6	CR_{Adult} 3.8E-6	
	CR _{Child} 2.3E-7	CR _{Child} 5.0E-7	CR _{Child} 4.0E-7	CR_{Child} 17.3E-6	CR_{Child} 1.7E-5	
	RI _{Adult} 0.05	RI _{Adult} 0.11	RI _{Adult} 0.09	RI_{Adult} 3.8	RI_{Adult} 3.8	
	RI _{Child} 0.23	RI _{Child} 0.50	RI _{Child} 0.4	RI_{Child} 17.3	RI_{Child} 17.0	
Cr	EDI _{Adult} 7.6E-5	EDI _{Adult} 1.2E-4	EDI _{Adult} 1.5E-4	EDI _{Adult} 7.1E-3	EDI _{Adult} 6.4E-3	1.5
	EDI _{Child} 3.5E-4	EDI _{Child} 5.4E-4	EDI _{Child} 7.1E-4	EDI _{Child} 3.3E-2	EDI _{Child} 3.0E-3	
	HQ _{Adult} 5.1E-5	HQ _{Adult} 8.0E-5	HQ _{Adult} 1.0E-4	HQ _{Adult} 4.7E-3	HQ _{Adult} 4.3E-3	
	HQ _{Child} 2.3E-4	HQ _{Child} 3.6E-4	HQ _{Child} 4.7E-4	HQ _{Child} 2.2E-2	HQ _{Child} 2.0E-2	
Cu	EDI _{Adult} 6.6E-5	EDI _{Adult} 9.9E-5	EDI _{Adult} 1.0E-4	EDI _{Adult} 4.8E-3	EDI _{Adult} 4.1E-3	4.0 E-2
	EDI _{Child} 3.1E-4	EDI _{Child} 4.6E-4	EDI _{Child} 4.8E-4	EDI _{Child} 2.3E-2	EDI _{Child} 1.3E-2	
	HQ _{Adult} 1.6E-3	HQ _{Adult} 2.5E-3	HQ _{Adult} 2.5E-3	HQ _{Adult} 1.2E-1	HQ _{Adult} 1.0E-1	
	HQ _{Child} 7.7E-3	HQ _{Child} 1.2E-2	HQ _{Child} 1.2E-2	HQ _{Child} 5.7E-1	HQ _{Child} 4.7E-1	
Fe	EDI _{Adult} 5.2E-4	EDI _{Adult} 6.2E-4	EDI _{Adult} 5.1E-4	EDI _{Adult} 1.8E-1	EDI _{Adult} 1.7E-1	7.0 E-1
	EDI _{Child} 2.5E-3	EDI _{Child} 2.9E-3	EDI _{Child} 2.4E-3	EDI _{Child} 8.4E-1	EDI _{Child} 8.1E-1	
	HQ _{Adult} 7.4E-4	HQ _{Adult} 8.9E-4	HQ _{Adult} 7.3E-3	HQ _{Adult} 2.6E-1	HQ _{Adult} 2.4E-1	
	HQ _{Child} 3.4E-3	HQ _{Child} 4.1E-3	HQ _{Child} 3.4E-3	HQ_{Child} 1.2	HQ_{Child} 1.2	
Pb	EDI _{Adult} 4.1E-5	EDI _{Adult} 1.2E-4	EDI _{Adult} 5.1E-5	EDI _{Adult} 9.1E-3	EDI _{Adult} 6.9E-3	4.0 E-3
	EDI _{Child} 1.9E-4	EDI _{Child} 5.8E-4	EDI _{Child} 2.4E-4	EDI _{Child} 4.2E-2	EDI _{Child} 3.2E-2	
	HQ _{Adult} 1.0E-2	HQ _{Adult} 3.0E-2	HQ _{Adult} 1.3E-2	HQ_{Adult} 2.3	HQ_{Adult} 1.7	
	HQ _{Child} 4.7E-2	HQ _{Child} 1.5E-1	HQ _{Child} 1.8E-2	HQ_{Child} 10.5	HQ_{Child} 8	
	CR _{Adult} 3.5E-7	CR _{Adult} 1.0E-6	CR _{Adult} 4.3E-7	CR_{Adult} 7.7E-5	CR_{Adult} 5.9E-5	
	CR _{Child} 1.6E-6	CR _{Child} 4.9E-6	CR _{Child} 2.0E-6	CR_{Child} 3.6E-4	CR_{Child} 2.72E-4	
	RI _{Adult} 0.3	RI _{Adult} 1.0	RI _{Adult} 0.4	RI_{Adult} 77.4	RI_{Adult} 58.7	
	RI_{Child} 1.6	RI_{Child} 4.9	RI_{Child} 2.0	RI_{Child} 357	RI_{Child} 272	
Zn	EDI _{Adult} 1.6E-4	EDI _{Adult} 2.0E-4	EDI _{Adult} 1.7E-4	EDI _{Adult} 1.5E-2	EDI _{Adult} 1.2E-2	3.0 E-1
	EDI _{Child} 7.5E-4	EDI _{Child} 9.1E-4	EDI _{Child} 8.4E-4	EDI _{Child} 6.8E-2	EDI _{Child} 5.8E-2	
	HQ _{Adult} 5.3E-4	HQ _{Adult} 6.4E-4	HQ _{Adult} 5.7E-3	HQ _{Adult} 5.0E-2	HQ _{Adult} 4.0E-2	
	HQ _{Child} 2.5E-3	HQ _{Child} 6.7E-4	HQ _{Child} 2.8E-3	HQ _{Child} 2.3E-1	HQ _{Child} 1.9E-1	
THI_{Adult}	0.04	0.10	0.07	4.83	4.18	Table 4.16
THI_{Child}	0.20	0.45	0.26	22.12	19.48	

Daily Intake (EDI), Hazard Quotient (HQ), Cancer Risk Index (CRI) and Total Hazard Index (THI) of ingestion of Heavy Metals in water for Adult and Child during the rainy season

	A	B	C	D	E	RfD _O
Cd	ND	ND	EDI _{Adult} 2.9E-6	EDI _{Adult} 5.0E-6	EDI _{Adult} 1.9E-5	1.0 E-3
			EDI _{Child} 1.3E-5	EDI _{Child} 2.3E-5	EDI _{Child} 9.0E-5	
			HQ _{Adult} 2.9E-3	HQ _{Adult} 5.0E-3	HQ _{Adult} 1.9E-2	
			HQ _{Child} 1.3E-2	HQ _{Child} 2.3E-2	HQ _{Child} 9.0E-2	
			CR _{Adult} 5.2E-9	CR _{Adult} 9.0E-9	CR _{Adult} 3.4E-8	
			CR _{Child} 2.3E-8	CR _{Child} 4.1E-8	CR _{Child} 1.6E-7	
			RI _{Adult} 0.005	RI _{Adult} 0.009	RI _{Adult} 0.03	
			RI _{Child} 0.02	RI _{Child} 0.04	RI _{Child} 0.16	
Cr	ND	ND	ND	ND	ND	1.5
Cu	ND	ND	EDI _{Adult} 1.5E-5	EDI _{Adult} 1.5E-5	EDI _{Adult} 1.5E-5	4.0 E-2
			EDI _{Child} 7.0E-5	EDI _{Child} 7.0E-5	EDI _{Child} 7.0E-5	
			HQ _{Adult} 3.8E-4	HQ _{Adult} 3.8E-4	HQ _{Adult} 3.6E-4	
			HQ _{Child} 1.8E-3	HQ _{Child} 1.8E-3	HQ _{Child} 1.8E-3	
Fe	EDI _{Adult} 6.2E-3	EDI _{Adult} 9.7E-3	EDI _{Adult} 5.5E-3	EDI _{Adult} 1.6E-3	EDI _{Adult} 6.9E-3	7.0 E-1
	EDI _{Child} 2.9E-2	EDI _{Child} 4.5E-2	EDI _{Child} 2.6E-2	EDI _{Child} 7.4E-3	EDI _{Child} 3.2E-2	
	HQ _{Adult} 8.9E-3	HQ _{Adult} 1.4E-2	HQ _{Adult} 7.9E-3	HQ _{Adult} 2.3E-3	HQ _{Adult} 9.9E-3	
	HQ _{Child} 4.1E-2	HQ _{Child} 6.4E-2	HQ _{Child} 3.7E-2	HQ _{Child} 1.1E-2	HQ _{Child} 4.6E-2	
Pb	EDI _{Adult} 2.5E-5	EDI _{Adult} 5.7E-5	EDI _{Adult} 3.6E-5	EDI _{Adult} 1.6E-5	EDI _{Adult} 2.9E-6	4.0 E-3
	EDI _{Child} 1.2E-4	EDI _{Child} 2.7E-4	EDI _{Child} 1.7E-4	EDI _{Child} 7.3E-5	EDI _{Child} 1.3E-5	
	HQ _{Adult} 6.3E-3	HQ _{Adult} 1.4E-2	HQ _{Adult} 9.0E-3	HQ _{Adult} 4.0E-3	HQ _{Adult} 7.3E-4	
	HQ _{Child} 3.0E-2	HQ _{Child} 6.8E-2	HQ _{Child} 4.3E-2	HQ _{Child} 1.8E-2	HQ _{Child} 3.3E-3	
	CR _{Adult} 2.1E-7	CR _{Adult} 4.8E-7	CR _{Adult} 3.1E-7	CR _{Adult} 1.4E-7	CR _{Adult} 2.5E-8	
	CR _{Child} 1.0E-6	CR _{Child} 2.3E-6	CR _{Child} 1.4E-6	CR _{Child} 6.2E-6	CR _{Child} 1.1E-7	
	RI _{Adult} 0.2	RI _{Adult} 0.5	RI _{Adult} 0.3	RI _{Adult} 0.1	RI _{Adult} 0.02	
	RI _{Child} 1.0	RI _{Child} 2.3	RI _{Child} 1.4	RI _{Child} 6.2	RI _{Child} 0.1	
Zn	EDI _{Adult} 1.0E-4	EDI _{Adult} 1.1E-4	EDI _{Adult} 1.5E-4	EDI _{Adult} 8.6E-5	EDI _{Adult} 9.9E-5	3.0 E-1
	EDI _{Child} 4.9E-4	EDI _{Child} 5.2E-4	EDI _{Child} 7.2E-4	EDI _{Child} 4.0E-4	EDI _{Child} 4.6E-4	
	HQ _{Adult} 3.3E-4	HQ _{Adult} 3.7E-4	HQ _{Adult} 5.0E-4	HQ _{Adult} 2.9E-4	HQ _{Adult} 3.3E-4	
	HQ _{Child} 1.6E-3	HQ _{Child} 1.7E3	HQ _{Child} 2.4E-3	HQ _{Child} 1.3E-3	HQ _{Child} 1.5E-3	
THI _{Adult}	0.02	0.03	0.02	0.01	0.03	
THI _{Child}	0.07	0.13	0.10	0.06	0.14	

Table 4.17 Estimated daily intake (EDI) Hazard Quotient (HQ) and Cancer risk (CR) of HMs in Tilapia via ingestion for Adult and Child during the dry and rainy season

Season	Cd	Cr	Cu	Fe	Pb	Zn	THI
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Dry	EDI _{Adult} 7.1E-4					EDI _{Adult} 6.9E-4		
	EDI _{Child} 1.1E-3					EDI _{Child} 1.1E-3		
	HQ _{Adult} 7.1E-1		EDI _{Adult} 1.2E-3	EDI _{Adult} 6.4E-3	HQ _{Adult} 1.7E-1	EDI _{Adult} 9.3E-3		
	HQ_{Child} 1.1		EDI _{Child} 1.8E-3	EDI _{Child} 1.0E-2	HQ _{Child} 2.7E-1	EDI _{Child} 1.4E-2	THI _{Adult} 0.95	
	CR_{Adult} 1.3E-6		HQ _{Adult} 2.9E-2	HQ _{Adult} 9.2E-3	CR_{Adult} 5.9E-6	HQ _{Adult} 3.1E-2	THI _{Child} 1.5	
	CR_{Child} 8.5E-6		HQ _{Child} 4.5E-2	HQ _{Child} 1.4E-2	CR_{Child} 9.4E-6	HQ _{Child} 4.8E-2		
	RI_{Adult} 1.3					RI_{Adult} 5.9		
	RI_{Child} 8.5					RI_{Child} 9.4		
Rainy	EDI _{Adult} 6.6E-5					EDI _{Adult} 9.8E-4		
	EDI _{Child} 1.0E-4					EDI _{Child} 1.5E-3		
	HQ _{Adult} 6.6E-2	EDI _{Adult} 2.4E-5	EDI _{Adult} 2.4E-4	EDI _{Adult} 2.9E-5	HQ _{Adult} 2.4E-1	EDI _{Adult} 5.9E-3		
	HQ _{Child} 1.0E-1	EDI _{Child} 3.7E-5	EDI _{Child} 3.7E-4	EDI _{Child} 4.4E-5	HQ _{Child} 3.8E-1	EDI _{Child} 9.2E-3	THI _{Adult} 0.35	
	CR _{Adult} 1.2E-7	HQ _{Adult} 1.6E-2	HQ _{Adult} 6.0E-3	HQ _{Adult} 4.1E-5	CR_{Adult} 8.3E-6	HQ _{Adult} 2.0E-2	THI _{Child} 0.55	
	CR _{Child} 1.8E-7	HQ _{Child} 2.5E-2	HQ _{Child} 9.4E-3	HQ _{Child} 6.3E-5	CR_{Child} 1.3E-5	HQ _{Child} 3.1E-2		
	RI _{Adult} 0.12					RI_{Adult} 8.3		
	RI _{Child} 0.18					RI_{Child} 12.8		

Table 4.18 Estimated daily intake (EDI) Hazard Quotient (HQ) and Cancer risk (CR) of HMs in Catfish via ingestion for Adult and Child during the dry and rainy season

Season	Cd	Cr	Cu	Fe	Pb	Zn	
Dry	EDI _{Adult} 4.9E-4	ND			EDI _{Adult} 5.6E-4		
	EDI _{Child} 7.6E-4			EDI _{Child} 8.7E-4			
	HQ _{Adult} 4.9E-1		EDI _{Adult} 1.0E-3	EDI _{Adult} 6.5E-3	HQ _{Adult} 1.4E-1	EDI _{Adult} 9.3E-3	
	HQ _{Child} 7.6E-1		EDI _{Child} 1.6E-3	EDI _{Child} 1.0E-2	HQ _{Child} 2.2E-1	EDI _{Child} 1.4E-2	THI _{Adult} 0.70
	CR _{Adult} 8.8E-7		HQ _{Adult} 2.6E-2	HQ _{Adult} 9.3E-3	CR_{Adult} 4.8E-6	HQ _{Adult} 3.1E-2	THI _{Child} 1.10
	CR _{Child} 1.4E-6		HQ _{Child} 4.0E-2	HQ _{Child} 1.4E-2	CR_{Child} 7.4E-6	HQ _{Child} 4.8E-2	
	RI _{Adult} 0.88				RI_{Adult} 4.8		
	RI_{Child} 1.4				RI_{Child} 7.4		
Rainy	EDI _{Adult} 9.7E-5				EDI _{Adult} 1.3E-3		
	EDI _{Child} 1.5E-4				EDI _{Child} 2.0E-3		
	HQ _{Adult} 1.0E-1	EDI _{Adult} 4.3E-5	EDI _{Adult} 7.2E-4	EDI _{Adult} 1.8E-4	HQ _{Adult} 3.2E-1	EDI _{Adult} 1.2E-2	
	HQ _{Child} 1.5E-1	EDI _{Child} 6.6E-5	EDI _{Child} 1.1E-3	EDI _{Child} 2.8E-4	HQ _{Child} 4.9E-1	EDI _{Child} 1.9E-2	THI _{Adult} 0.51
	CR _{Adult} 1.7E-7	HQ _{Adult} 2.8E-2	HQ _{Adult} 1.8E-2	HQ _{Adult} 2.6E-4	CR_{Adult} 1.1E-5	HQ _{Adult} 4.1E-2	THI _{Child} 0.78
	CR _{Child} 2.7E-7	HQ _{Child} 4.4E-2	HQ _{Child} 2.8E-2	HQ _{Child} 4.0E-4	CR_{Child} 1.7E-5	HQ _{Child} 6.4E-2	
	RI _{Adult} 0.17				RI_{Adult} 11.1		
	RI _{Child} 0.27				RI_{Child} 17		

Table 4.19 Table Dryand Rainy Season Transfer Factor (TF) of Heavy Metals from Sediments to fish.

Season	Metals	Conc.	Tilapia	Catfish
Dry	Cd	2.549	1.9	1.3
	Cr	7.657	-	-
	Cu	4.699	1.7	1.5
	Fe	240.498	0.2	0.2
	Pb	11.633	0.4	0.3
	Zn	61.007	1.0	1.0
Rainy	Cd	0.548	0.8	1.2
	Cr	1.046	0.2	0.3
	Cu	3.178	0.5	1.6
	Fe	1.850	0.1	0.7
	Pb	12.123	0.6	0.7
	Zn	29.362	1.4	3.0

Table 4.20 Estimated daily intake (EDI) and Cancer risk (CR) of PAHs via ingestion of water for Adult and Child

Location	Nap	Ph	Ant	B[b]F	B[k]F	B[a]P
A	ND	ND	ND	EDI _{Adult} 6.6E-8	EDI _{Adult} 6.6E-8	EDI _{Adult} 6.4E-8
				EDI _{Child} 3.1E-7	EDI _{Child} 3.1E-7	EDI _{Child} 3.0E-7
				CR _{Adult} 4.8E-8	CR _{Adult} 4.8E-9	CR _{Adult} 4.8E-7
				CR _{Child} 2.3E-7	CR _{Child} 2.3E-8	CR_{Child} 2.2E-6
				RI _{Adult} 0.05	RI _{Adult} 0.005	RI _{Adult} 0.48
B	EDI _{Adult} 3.0E-7 EDI _{Child} 1.4E-6 HQ _{Adult} 1.5E-5 HQ _{Child} 7.0E-5	ND	ND	RI _{Child} 0.23	RI _{Child} 0.02	RI_{Child} 2.2
				EDI _{Adult} 5.7E-8	EDI _{Adult} 6.2E-8	EDI _{Adult} 6.9E-8
				EDI _{Child} 2.7E-6	EDI _{Child} 2.9E-7	EDI _{Child} 3.2E-7
				CR _{Adult} 4.2E-8	CR _{Adult} 4.5E-9	CR _{Adult} 5.1E-7
				CR_{Child} 1.9E-6	CR _{Child} 2.1E-8	CR_{Child} 2.4E-6
C	ND	ND	ND	RI _{Adult} 0.04	RI _{Adult} 0.05	RI _{Adult} 0.51
				RI_{Child} 1.9	RI _{Child} 0.02	RI_{Child} 2.4
				EDI _{Adult} 6.2E-8	EDI _{Adult} 6.2E-8	EDI _{Adult} 7.4E-8
				EDI _{Child} 2.9E-7	EDI _{Child} 2.9E-7	EDI _{Child} 3.4E-7
				CR _{Adult} 4.5E-8	CR _{Adult} 4.5E-9	CR _{Adult} 5.4E-7
D	EDI _{Adult} 3.9E-7 EDI _{Child} 1.8E-6 HQ _{Adult} 1.9E-5 HQ _{Child} 9.1E-5	EDI _{Adult} 5.9E-8 EDI _{Child} 2.8E-7 HQ _{Adult} 2.0E-7 HQ _{Child} 9.2E-7	EDI _{Adult} 5.9E-8 EDI _{Child} 2.8E-7 HQ _{Adult} 2.0E-7 HQ _{Child} 9.2E-7	CR _{Child} 2.1E-7	CR _{Child} 2.1E-8	CR_{Child} 2.5E-6
				RI _{Adult} 0.05	RI _{Adult} 0.005	RI _{Adult} 0.54
				RI _{Child} 0.21	RI _{Child} 0.02	RI_{Child} 2.5
				EDI _{Adult} 5.9E-8	EDI _{Adult} 5.9E-8	EDI _{Adult} 5.9E-8
				EDI _{Child} 2.8E-7	EDI _{Child} 2.8E-7	EDI _{Child} 2.8E-7
E	ND	ND	ND	CR _{Adult} 4.3E-8	CR _{Adult} 4.3E-9	CR _{Adult} 4.3E-7
				CR _{Child} 2.0E-7	CR _{Child} 2.0E-8	CR_{Child} 2.0E6
				RI _{Adult} 0.04	RI _{Adult} 0.004	RI _{Adult} 0.43
				RI _{Child} 0.2	RI _{Child} 0.02	RI_{Child} 2.0
				EDI _{Adult} 6.4E-8	EDI _{Adult} 6.4E-8	EDI _{Adult} 8.1E-8
	ND	ND	ND	EDI _{Child} 3.0E-7	EDI _{Child} 3.0E-7	EDI _{Child} 3.8E-7
				CR _{Adult} 4.7E-8	CR _{Adult} 4.7E-9	CR _{Adult} 5.9E-7
				CR _{Child} 2.2E-7	CR _{Child} 2.2E-8	CR_{Child} 2.7E-6
				RI _{Adult} 0.05	RI _{Adult} 0.005	RI _{Adult} 0.59
				RI _{Child} 0.22	RI _{Child} 0.02	RI_{Child} 2.7

Table 4.21 Estimated daily intake (EDI), Hazard Quotient and Cancer risk (CR) of PAHs in Catfish via ingestion for Adult and a Child

Location	Nap	Ph	Ant	B[b]F	B[k]F	B[a]P
Catfish				EDI _{Adult} 3.0E-8	EDI _{Adult} 3.0E-8	EDI _{Adult} 3.5E-8
	EDI _{Adult} 3.5E-7	EDI _{Adult} 7.3E-9	EDI _{Adult} 8.3E-9	EDI _{Child} 4.7E-8	EDI _{Child} 4.7E-8	EDI _{Child} 5.4E-8
	EDI _{Child} 5.4E-7	EDI _{Child} 1.1E-8	EDI _{Child} 1.3E-8	CR _{Adult} 2.2E-8	CR _{Adult} 2.2E-9	CR _{Adult} 2.6E-7
	HQ _{Adult} 1.7E-5	HQ _{Adult} 2.4E-8	HQ _{Adult} 2.8E-8	CR _{Child} 3.4E-8	CR _{Child} 3.4E-9	CR _{Child} 3.9E-7
	HQ _{Child} 2.7E-5	HQ _{Child} 3.8E-8	HQ _{Child} 4.3E-8	RI _{Adult} 0.02	RI _{Adult} 0.002	RI _{Adult} 0.26
				RI _{Child} 0.03	RI _{Child} 0.003	RI _{Child} 0.39

Table 4.22 Estimated daily intake (EDI), Hazard Quotient and Cancer risk (CR) of PAHs in Tilapia via ingestion for Adult and Child

Location	Nap	Ph	Ant	B[b]F	B[k]F	B[a]P
Tilapia	EDI _{Adult} 2.8E-7	EDI _{Adult} 8.3E-9	EDI _{Adult} 8.3E-9	ND	ND	ND
	EDI _{Child} 4.4E-7	EDI _{Child} 2.8E-9	EDI _{Child} 2.8E-9			
	HQ _{Adult} 1.4E-5	HQ _{Adult} 2.8E-8	HQ _{Adult} 2.8E-8			
	HQ _{Child} 2.2E-5	HQ _{Child} 9.3E-9	HQ _{Child} 9.3E-9			

4.6 The Results of the Ecological Risk Assessment of Heavy metals in Sediment.

The results of the ecological risk assessment of the heavy metals in the rivers sediments were determined and displayed in table 4.23 and 4.24. The ecological parameters that were used to estimate the pollution state of the sediments were Geo-accumulation index (I_{geo}), Contamination factor (CF), single potential ecological risk factor (P_{r_i}), risk index (RI), pollution load index and PAHs pollution index (PPI). The results of the estimation of the polycyclic aromatic hydrocarbons pollution index (PPI) were shown in table 4.25 below.

Table 4.23 Ecological Risk Assessment of Heavy metals in sediments for Dry season

Location	Item	Cd	Cr	Cu	Pb	Zn
A	I_{geo}	2.95	-5.06	-3.81	-0.78	-4.26
	CF	11.57	0.05	0.11	0.87	0.08
	$\sum \frac{I_i}{n}$	347	9.0E-2	5.4E-1	4.36	7.8E-2
	RI	352.07				
	PL	0.34				
B	I_{geo}	3.04	-4.16	-3.79	-1.74	-4.78
	CF	12.37	8.4E-2	1.1E-1	4.5E-1	5.4E-2
	$\sum \frac{I_i}{n}$	370.95	1.7E-1	5.0E-1	2.25	5.4E-2
	RI	373.92				
	PL	0.31				
C	I_{geo}	2.86	-4.40	-3.58	-1.68	-5.01
	CF	10.90	7.1E-2	1.3E-1	4.7E-1	4.7E-2
	$\sum \frac{I_i}{n}$	327	1.4E-1	6.5E-1	2.35	4.7E-2
	RI	330.02				
	PL	0.47				
D	I_{geo}	3.27	-3.87	-2.82	-1.24	1.10
	CF	14.44	1.0E-1	2.1E-1	6.4E-1	1.6E-1
	$\sum \frac{I_i}{n}$	433.05	2.0E-1	1.05	3.2	1.6E-1
	RI	437.66				
	PL	0.50				
E	I_{geo}	3.27	-4.02	-3.05	-1.63	-3.47
	CF	14.47	9.3E-2	1.8E-1	4.9E-1	1.4E-1
	$\sum \frac{I_i}{n}$	434.10	1.9E-1	9.0E-1	2.43	1.4E-1
	RI	437.76				
	PL	0.44				

Table 4.24 Ecological Risk Assessment of Heavy metals in sediments for Rainy season

Location	Item	Cd	Cr	Cu	Pb	Zn
A	I_{geo}	1.5E-1	-8.01	-6.56	-1.02	-3.95
	CF	1.6	5.8E-3	1.6E-2	7.4E-2	9.7E-2
	$\Sigma \frac{I}{n}$	49.80	1.2E-2	8.0E-2	3.69	9.7E-2
	RI	53.68				
	PL	0.064				
B	I_{geo}	0.54	-7.64	-6.56	-1.78	-2.23
	CF	2.18	7.5E-3	1.6E-2	0.44	3.2E-1
	$\Sigma \frac{I}{n}$	65.25	1.5E-2	8.0E-2	2.18	3.2E-1
	RI	67.85				
	PL	0.13				
C	I_{geo}	1.06	-8.32	-6.56	-1.56	-3.75
	CF	3.13	4.7E-3	1.6E-2	5.1E-1	1.1E-1
	$\Sigma \frac{I}{n}$	93.90	9.4E-3	8.0E-2	2.55	1.1E-1
	RI	96.65				
	PL	0.11				
D	I_{geo}	0.10	-7.47	-6.82	-1.71	-3.97
	CF	1.61	8.4E-3	1.3E-2	4.6E-1	9.6E-2
	$\Sigma \frac{I}{n}$	48.15	1.7E-2	6.7E-2	2.30	9.6E-2
	RI	50.63				
	PL	0.10				
E	I_{geo}	1.77	-5.77	-2.48	-0.76	-1.54
	CF	5.12	0.03	2.7E-1	8.9E-1	5.1E-1
	$\Sigma \frac{I}{n}$	153.60	5.5E-2	1.34	4.43	5.1E-1
	RI	159.94				
	PL	0.45				

Table 4.25 Polycyclic aromatic hydrocarbons Pollution index (PPI) of PAHs in water, sediment and fish

	A	B	C	D	E
PPI of Water	0.10	0.13	0.10	0.11	0.10
PPI of Sediment	0.14	0.10	0.10	0.05	-
PPI of Catfish			0.10		
PPI of Tilapia			0.10		

4.7 Statistical Correlation and Source Identification of HMs and PAHs.

The data generated for Heavy metals and PAHs were all subjected to Principal Component Analysis (PCA) based on the correlation matrix to understand the correlation and trends that exist between pollutants and therefore to understand if the pollutants have more than one source or origin^{185, 186}. Table 4.26 display the Correlation Matrix of PAHs in water, Sediment and Fish, Table 4.27 shows the Correlation matrix of dry and rainy season heavy metals in water, Table 4.28 display the Correlation matrix for dry and rainy season heavy metals in sediment, Table 4.29 shows the Correlation matrix for dry and rainy season heavy metals in Tilapia and Table 4.30 shows the Correlation matrix of dry and rainy Seasons heavy metals in Catfish samples respectively and figure 4.10 to 4.12 represent the Principal Component Analysis (PCA) under varimax rotation or component plots in rotated space for HMs in sediment, Tilapia and Catfish. The component plots in rotated space for PAHs and heavy metals in water could not be plotted because more than one of the variables were constant so, SPSS was prevented from computing the component plots in rotated space.

Table 4.26 Correlation Matrix of PAHs in water, Sediment and Fish samples

	NapW	PhW	ANw	BbFw	BkFw	BaPw	Naps	PHs	ANs	BbF s	BkFs	Baps	NaPf	PHf	ANf	BbFf	BkFf	BaPf
NapW	1																	
PhW	.632*	1																
ANw	.632*	1.000**	1															
BbFw	.143	-.110	-.110	1									.					
BkFw	.201	-.142	-.142	.976**	1													
BaPw	-.076	-.386	-.386	.478	.465	1												
Naps	-.870**	-.611*	-.611*	.202	.137	.233	1											
PHs	-.585*	-.403	-.403	.094	.048	.000	.758**	1										
ANs	-.588*	-.405	-.405	.107	.061	-.044	.763**	.972**	1									
BbFs	.265	-.148	-.148	.044	.025	.328	-.313	-.152	-.144	1								
BkFs	.206	-.125	-.125	.054	.041	-.316	-.163	.196	.214	.509	1							
Baps	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a						
NaPf	-.420	. ^a	. ^a	.327	.598	.529	.507	.506	.494	.064	-.578	. ^a	1					
PHf	.285	. ^a	. ^a	-.213	-.433	-.531	-.349	-.350	-.351	-.029	.872*	. ^a	-.800	1				
ANf	-.046	. ^a	. ^a	.146	.000	-.407	.016	.034	-.030	-.090	.853*	. ^a	-.423	.857*	1			
BbFf	-.984**	. ^a	. ^a	.642	.466	-.175	.992**	.989**	.971**	-.425	-.085	. ^a	.499	-.269	.129	1		
BkFf	-.984**	. ^a	. ^a	.642	.466	-.175	.992**	.989**	.971**	-.425	-.085	. ^a	.499	-.269	.129	1.000**	1	
BaPf	-.970**	. ^a	. ^a	.470	.239	-.241	.966**	.937**	.991**	-.417	-.106	. ^a	.479	-.276	.047	.963**	.963**	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.27 Correlation matrix of dry and rainy season heavy metals in water

	DS Cd	DS Cr	DS Cu	DS Fe	DS Pb	DS Zn	RS Cd	RS Cr	RS Cu	RS Fe	RS Pb	RS Zn
DS Cd	1	-.062	-.125	-.187	.496	-.154	.298	. ^a	.037	.397	.113	.138
DS Cr	-.062	1	.911 ^{**}	-.170	.482	-.037	.578 [*]	. ^a	.265	-.205	-.371	.077
DS Cu	-.125	.911 ^{**}	1	.108	.454	.197	.502	. ^a	.073	-.225	-.266	-.105
DS Fe	-.187	-.170	.108	1	-.130	.601 [*]	-.348	. ^a	-.393	-.156	.427	-.403
DS Pb	.496	.482	.454	-.130	1	-.181	.926 ^{**}	. ^a	-.434	.222	-.417	-.438
DS Zn	-.154	-.037	.197	.601 [*]	-.181	1	-.232	. ^a	-.129	-.657 ^{**}	-.076	-.317
RS Cd	.298	.578 [*]	.502	-.348	.926 ^{**}	-.232	1	. ^a	-.369	.074	-.647 ^{**}	-.423
RS Cr	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a
RS Cu	.037	.265	.073	-.393	-.434	-.129	-.369	. ^a	1	-.085	.243	.913 ^{**}
RS Fe	.397	-.205	-.225	-.156	.222	-.657 ^{**}	.074	. ^a	-.085	1	.565 [*]	.246
RS Pb	.113	-.371	-.266	.427	-.417	-.076	-.647 ^{**}	. ^a	.243	.565 [*]	1	.468
RS Zn	.138	.077	-.105	-.403	-.438	-.317	-.423	. ^a	.913 ^{**}	.246	.468	1

1 a. Cannot be computed because at least one of the variables is constant.

2 **. Correlation is significant at the 0.01 level (2-tailed).

3 *. Correlation is significant at the 0.05 level (2-tailed)

Table 4.28 Correlation matrix for dry and rainy season heavy metals in sediment

	DS Cd	DS Cr	DS Cu	DS Fe	DS Pb	DS Zn	RS Cd	RS Cr	RS Cu	RS Fe	RS Pb	RS Zn
Dry season Cd	1	.740**	.728**	.720**	-.205	.738**	.278	.613*	.544*	-.616*	.221	.444
Dry season Cr	.740**	1	.766**	.767**	-.303	.658**	.271	.408	.311	-.414	-.216	.374
Dry season Cu	.728**	.766**	1	.903**	.106	.964**	.178	.338	.308	-.333	.065	.111
Dry season Fe	.720**	.767**	.903**	1	-.011	.861**	.072	.231	.203	-.236	-.039	-.019
Dry season Pb	-.205	-.303	.106	-.011	1	.241	-.375	-.199	-.172	.295	.188	-.373
Dry season Zn	.738**	.658**	.964**	.861**	.241	1	.127	.374	.348	-.349	.201	.140
Rainy season Cd	.278	.271	.178	.072	-.375	.127	1	.847**	.884**	-.873**	.647**	.801**
Rainy season Cr	.613*	.408	.338	.231	-.199	.374	.847**	1	.983**	-.991**	.734**	.871**
Rainy season Cu	.544*	.311	.308	.203	-.172	.348	.884**	.983**	1	-.982**	.816**	.839**
Rainy season Fe	-.616*	-.414	-.333	-.236	.295	-.349	-.873**	-.991**	-.982**	1	-.714**	-.868**
Rainy season Pb	.221	-.216	.065	-.039	.188	.201	.647**	.734**	.816**	-.714**	1	.531*
Rainy season Zn	.444	.374	.111	-.019	-.373	.140	.801**	.871**	.839**	-.868**	.531*	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Component Plot in Rotated Space

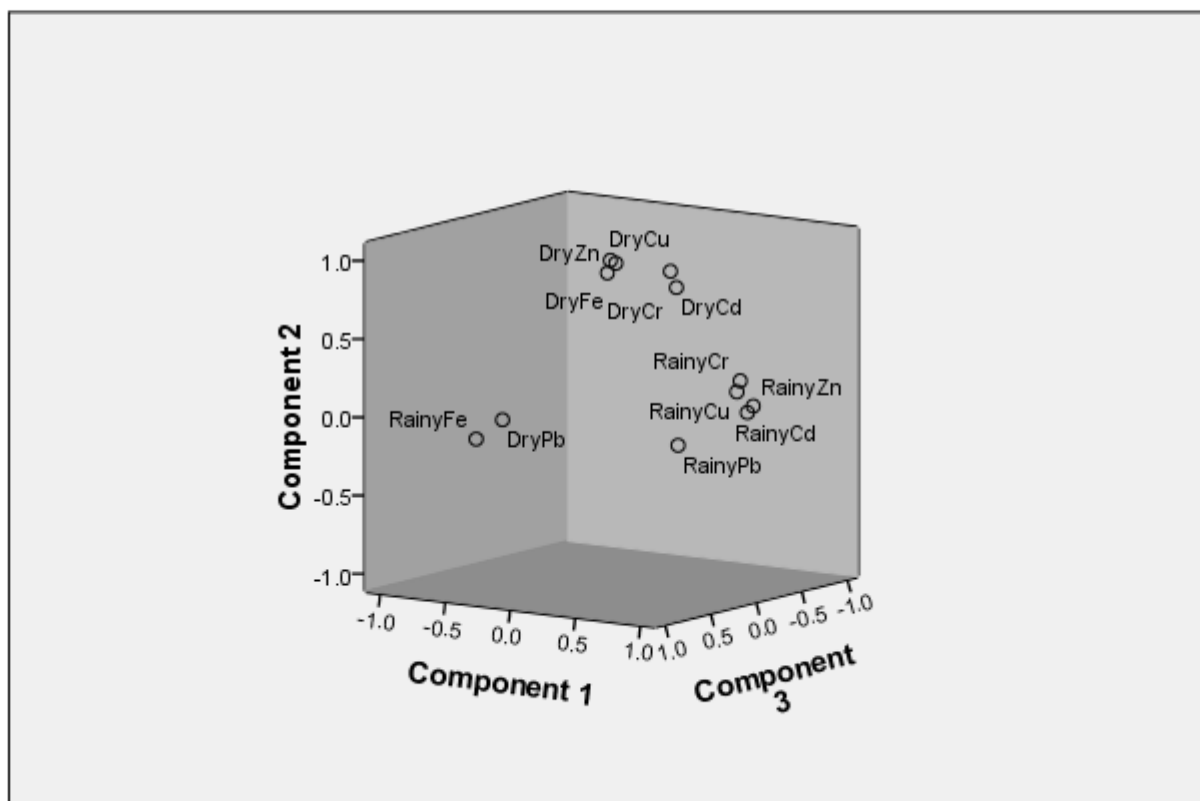


Figure 4.10 Component plot in rotated space of Principal Component Analysis (PCA) under varimax rotation for HMs in Sediments

Table 4.29 Correlation matrix for dry and rainy season heavy metals in Tilapia

	DS Cd	DS Cu	DS Fe	DS Pb	DS Zn	RS Cd	RS Cu	RS Fe	RS Pb	RS Zn	RS Cr
DS Cd	1	1.000**	-.998*	-.987	-1.000*	.683	-.292	.313	-.710	.557	.243
DS Cu	1.000**	1	-.997*	-.985	-1.000*	.692	-.304	.301	-.701	.567	.254
DS Fe	-.998*	-.997*	1	.995	.999*	-.636	.232	-.371	.752	-.504	-.182
DS Pb	-.987	-.985	.995	1	.990	-.559	.137	-.459	.812	-.419	-.086
DS Zn	-1.000*	-1.000*	.999*	.990	1	-.671	.276	-.329	.722	-.543	-.226
RS Cd	.683	.692	-.636	-.559	-.671	1	-.898	-.480	.029	.987	.874
RS Cu	-.292	-.304	.232	.137	.276	-.898	1	.817	-.466	-.957	-.999*
RS Fe	.313	.301	-.371	-.459	-.329	-.480	.817	1	-.891	-.615	-.846
RS Pb	-.710	-.701	.752	.812	.722	.029	-.466	-.891	1	.190	.511
RS Zn	.557	.567	-.504	-.419	-.543	.987	-.957	-.615	.190	1	.941
RS Cr	.243	.254	-.182	-.086	-.226	.874	-.999*	-.846	.511	.941	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed)

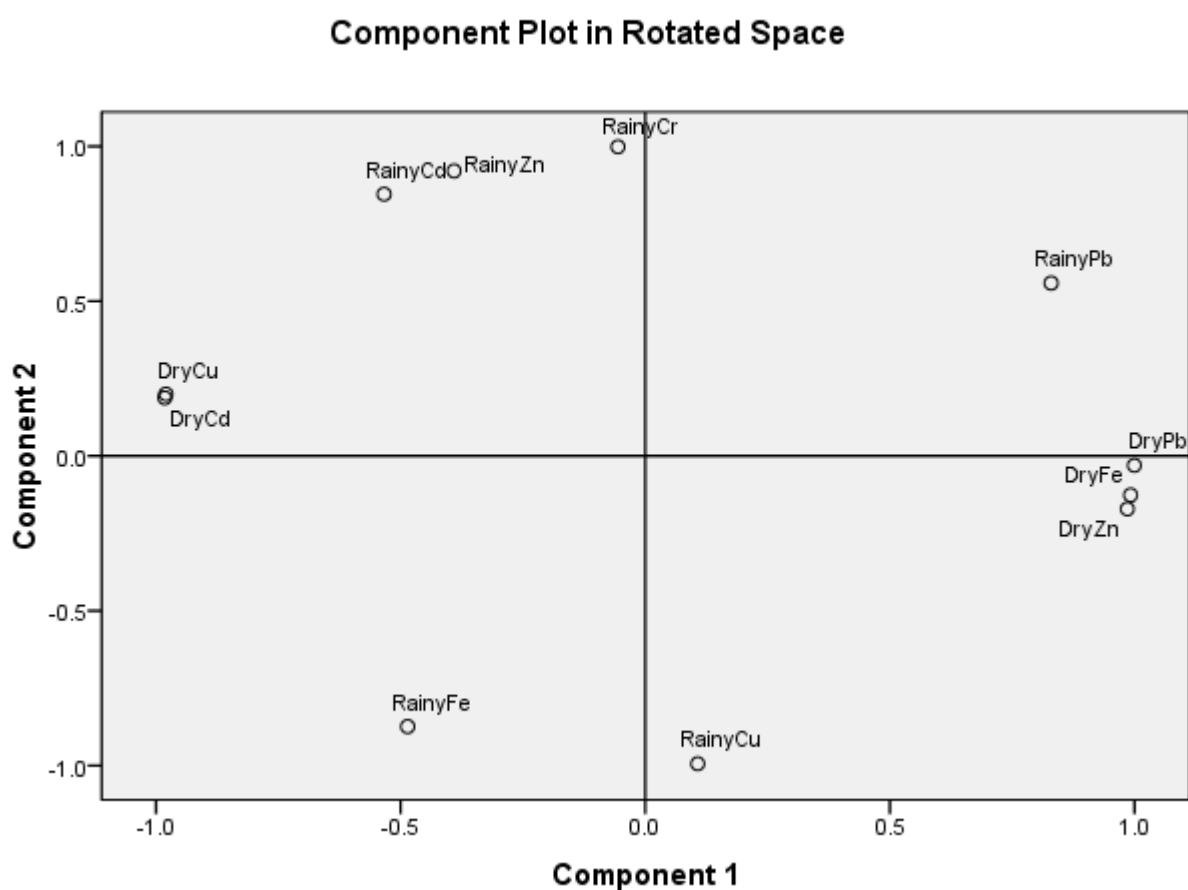
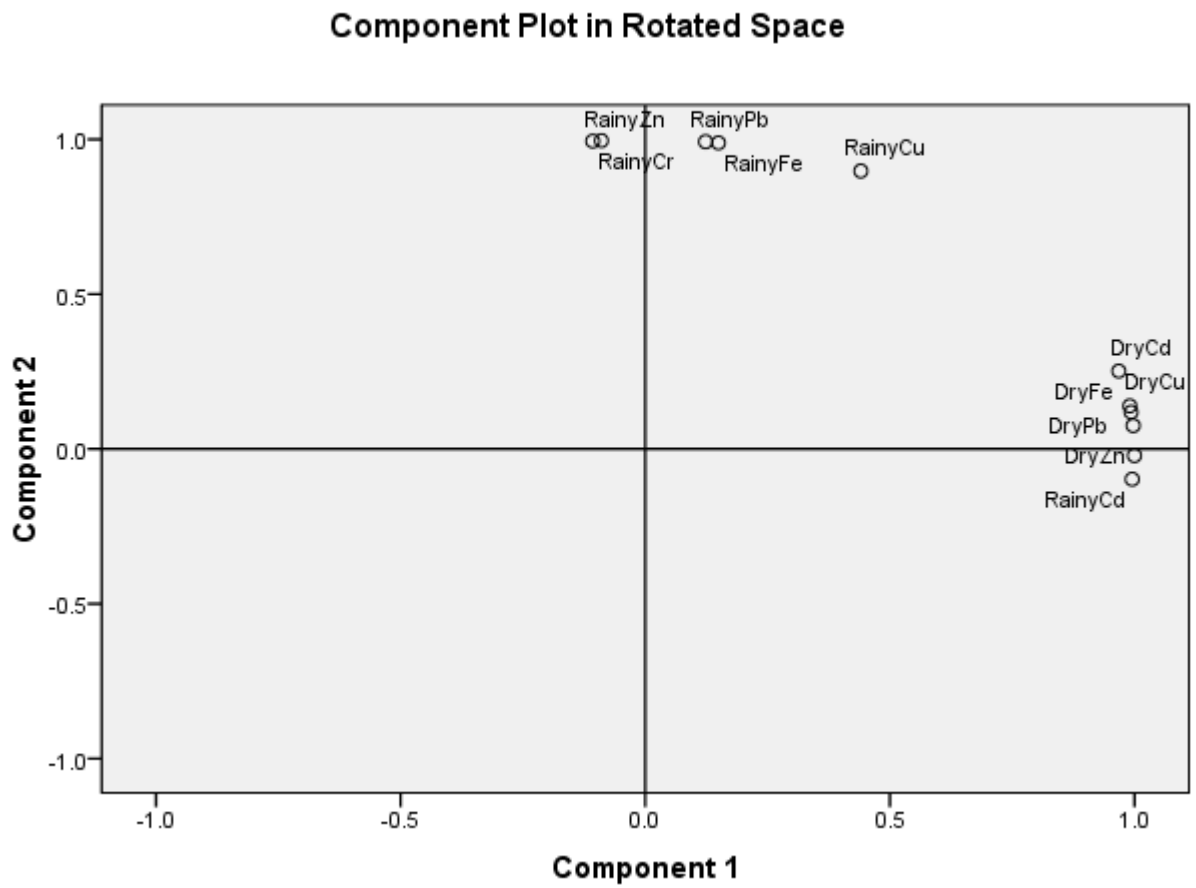


Figure 4.11 Component plot in rotated space of Principal Component Analysis (PCA) under varimax rotation for HMs in Tilapia

Table 4.30 Correlation matrix of dry and rainy Seasons heavy metal in catfish

	DS Cd	DS Cu	DS Fe	DS Pb	DS Zn	RS Cd	RS Cu	RS Fe	RS Pb	RS Zn	RS Cr
DS Cd	1	.993	.991	.984	.962	.939	.652	.394	.369	.164	.146
DS Cu	.993	1	1.000*	.998*	.987	.972	.561	.286	.260	.050	.032
DS Fe	.991	1.000*	1	.999*	.990	.976	.544	.266	.241	.030	.012
DS Pb	.984	.998*	.999*	1	.995	.985	.507	.224	.198	-.014	-.032
DS Zn	.962	.987	.990	.995	1	.997*	.421	.129	.102	-.111	-.128
RS Cd	.939	.972	.976	.985	.997*	1	.350	.052	.026	-.187	-.204
RS Cu	.652	.561	.544	.507	.421	.350	1	.954	.945	.855	.845
RS Fe	.394	.286	.266	.224	.129	.052	.954	1	1.000*	.971	.967
RS Pb	.369	.260	.241	.198	.102	.026	.945	1.000*	1	.977	.973
RS Zn	.164	.050	.030	-.014	-.111	-.187	.855	.971	.977	1	1.000*
RS Cr	.146	.032	.012	-.032	-.128	-.204	.845	.967	.973	1.000*	1

*. Correlation is significant at the 0.05 level (2-tailed).



4.12 Component plot in rotated space of Principal Component Analysis (PCA) under varimax rotation for HMs in Catfish

4.8 Discussion

4.8.1 Data Analysis: Analysis of Variance (ANOVA)

From the analysis of variance of the data generated from the heavy metals determination in water, sediment and fish samples at value less than 0.05 ($p < 0.05$) level of significance using mean concentration values of within and between groups, the results showed that there is no significant difference between the heavy metals concentration values within season and considering seasonal variation in the concentration values of heavy metals in the water and fish samples but showed that there is significant difference in the seasonal variation of the concentration values of heavy metals in sediments. The concentration values of PAHs in the three media (water, fish and sediments) showed no significant difference within and between the groups with values less than 0.05 ($p < 0.05$) level of significance as shown in the ANOVA table in appendix 1. The tables showed that the exact probability (Sig.) value of 0.338, 0.856 and 0.855 for the ANOVA generated from the analysis of water, sediment and fish for PAHs were greater than 0.05 ($p < 0.05$) significant level which means that the data were not different significantly.

4.8.2 Correlation Analysis and Source identification

The mean concentration values of the HMs and PAHs in water, sediment and fish were subjected to correlation analysis to reduce the data without any lost so as to understand if there is any hidden trends between the data. Correlation helps to identify and magnify for explanation any hidden relationship between

the data. The technique is the multivariate technique generally called Principle Component Analysis (PCA) that identifies the different group of heavy metals and polycyclic aromatic

hydrocarbons that correlates. Correlated HMs and PAHs connotes that the HMs and PAHs may have similar behavior and implies they could have common origin¹⁸⁶. Therefore, the correlation matrix of the PAHs display the relationship between the data variables as shown in table 4.26 above. The table of the correlation matrix showed varying correlation between the various PAHs in water, sediment and fish from -0.970 to 1.000 at 0.05 and 0.01 level of significance. At 0.05 level of significance, there is correlation between Phenanthrene in water and Naphthalene in water (0.632), Anthracene in water and Naphthalene in water (0.632) as well as a very strong, positive and perfect correlation with Phenanthrene in water (1.000) at 0.01 level of significance, there is also a very strong positive correlation between Benzo[k]fluoranthene in water and Benzo[b]fluoranthene in water (0.976) at 0.01 level of significance. Naphthalene in sediment showed strong negative correlation with Naphthalene in water (-0.870) at 0.01 level of significance, Phenanthrene and Anthracene in water (-0.611) at 0.05 level of significance, Phenanthrene in sediment showed moderate negative correlation with Naphthalene in water (-0.585) at 0.05 level of significance and positive correlation with Naphthalene in sediment (0.758) at 0.01 level of significance, Anthracene in sediment showed negative correlation with Naphthalene in water (-0.588) at 0.05 level of significance and positive correlation with Naphthalene in sediment (0.763) and a strong positive correlation with Phenanthrene in sediment (0.972) at 0.01 level of significance, while Phenanthrene in fish was positively correlated with Benzo[k]fluoranthene in sediment (0.872), Anthracene in fish was positively correlated with Bezo[k]fluoranthene in sediment (0.853) and Phenanthrene in fish (0.857) at 0.05 level of significance, Benzo[b]fluorantene, Benzo[k]fluorantene and Benzo[a]pyrene in fish showed strong negative correlations with Naphthalene in water (-0.984, -0.984 and -0.970) but strong positive correlation with Naphthalene in sediment, (0.992, 0.992 and 0.966), Phenanthrene in sediment (0.989, 0.989 and 0.937), Anthracene in sediment (0.971, 0.971 and 0.991) respectively at

0.01 level of significance, finally, while Benzo[a]pyrene in fish strongly positively correlated with Benzo[b]fluoranthene and Benzo[k]fluoranthene in fish (0.963), Benzo[k]fluoranthene was strongly positively and perfectly correlated to Benzo[b]fluoranthene at 0.01 level of significance. All these correlations show that these PAHs have similar behavior and are highly likely to have come from the same source or origin. Benzo[a]pyrene is a commonly used PAHs as marker for PAHs originating from combustion, the correlation of Benzo[a]pyrene with other PAHs is consistent with combustion being the primary source of the PAHs leached into the water body by water runoff¹⁸⁷.

Heavy metal concentration values in the water were also correlated at 0.01 and 0.05 level of significance as shown in table 4.27. The dry season Cu was strongly and positively correlated with dry season Cr at (0.911), dry season Zn was moderately correlated to the dry season Fe (0.601), rainy season Cd was moderately correlated to dry season Cr (0.578) and strongly correlated to dry season Pb (0.926), there is also a moderate negative correlation between rainy season Fe and dry season Zn (-0.657), while rainy season Pb was moderately negatively correlated to Rainy season Cd (-0.647) and moderately positively correlated to rainy season Fe (0.565), rainy season Zn was strongly positively correlated to rainy season Cu (0.913). The component plots in rotated space for PAHs and heavy metals in water could not be plotted because more than one of the variables were constant.

Table 4.28 shows the correlation matrix for dry and rainy season heavy metals concentration values in sediments samples, while the rainy season metals correlated with themselves, the dry season showed positive and negative correlation with themselves and the rainy season Cr, Cu and Fe were moderately correlated to the dry season Cd as supportively shown on the component plot in rotated space of PCA under varimax rotation for heavy metals in sediments in figure 4.8.

Unlike the heavy metals in water and sediments, the heavy metals in the Tilapia showed fewer correlation within and between seasons and the correlation matrix of the Catfish showed strong positive and perfect correlation within and between seasons, connoting that the metals in Catfish were likely to have come from the same source which may come from sediment's phytoplanktons and zooplanktons contaminated with metals brought into the river by water runoff or other source since catfish were known omnivore feeding on diverse plants and animals food substances that are found in the bottom of rivers¹⁸⁸ whereas Tilapia is mostly 60% herbivore¹⁸⁹.

However, a closer look at the mean concentration values of the PAHs and HMs reveals that the concentration values for heavy metals were generally higher in the sediments compare to the concentration in water but remarkable difference was not observed in the concentration values of the PAHs in the three media.

The measurement of the physicochemical parameters of water is of significance since the toxicity of heavy metals depends on the physical and chemical conditions of the water which also affect the mobility and bioavailability of the heavy metals and PAHs. These conditions amongst others include pH, temperature, electrical conductivity, total dissolved solids, water hardness, salinity, organic matter, redox, complexing ligands and ion strength. Polycyclic aromatic hydrocarbons (PAHs) toxicity is also enhanced by dissolved oxygen and water hardness^{6, 29-31}. The values of the water pH were only slightly acidic during the dry season and alkaline during the rainy season¹⁹⁰ due to seasonal variation but, were however within the acceptable limit for water set by the world health organization and other regulatory agencies^{191, 192} and therefore, the water sufficiently meet both drinking and fresh water quality requirement on these bases¹⁹³. Also, there were slight variation in the values of the other physicochemical parameters assessed which could definitely be due to seasonal variation.

4.8.3 Concentration of Heavy Metals in Water and Fish samples vis-a-vis Human Health Risk Assessment.

The estimated daily intake of HMs from the mean concentration values of HMs via ingestion of water and fish were used to determine the hazard quotient, cancer risk, total hazard index and cancer risk index. PAHs pollution index and metals bioaccumulation from sediment to fish were also assessed.

The hazard quotient of cadmium in dry season water samples showed that cadmium poses threat to the user of the water especially at location D and E where the $HQ > 1$ for both an adult and a child and the cancer risk for Cadmium in water and fish were more than the limit of one person per a million persons (1×10^{-6}). The application of phosphate fertilizers (Containing 2-200 mg Cd/kg), domestic and sewage sludge, wear of automobile tyres, lubricants and mining as well as metallurgical activities (metal smelting and refining) and fossil fuel burning were known source of cadmium that pollute aquatic environment^{74,76}. Cadmium is a dangerous metallic pollutant that is associated with chronic renal failure and skeletal damage⁴¹. Juxtaposing the permissible concentration value of 0.003 mg/kg for cadmium^{141, 171} with the concentration values in water and Fish samples showed that the concentration level of cadmium exceeds the average permissible limitvalue for Cadmium in the water and fish samples respectively. The transfer factor of cadmium was found to be above 1 ($TF > 1$) for Tilapia and Catfish, which means that both fish species were bio-accumulating Cadmium. The mean maximum and minimum concentration value of cadmium

during the dry season were 0.089 and 0.038 mg/kg and 0.027 and 0.004 mg/kg during the rainy season whereas, the mean concentration value of 0.05 ± 0.02 was obtained in a study conducted in 2012 around Ajaokuta steel company¹⁹³, a location that is about 25 km downstream of the confluence of rivers Niger and Benue. Long term exposure to cadmium could lead to carcinogenic occurrence in human kidney and lung damage, stomach irritation, vomiting as well as diarrhea¹⁹⁴.

Chromium concentration values in the dry season water samples exceed the limit of 0.002 mg/kg. Chromium and Copper showed hazard quotient (HQ), and transfer factor of less than 1 ($HQ < 1$, $TF < 1$) and indicates that they were both of less concern but, the chromium ions with concentration value more than the set limit could cause a deleterious effect on the long run. While Chromium concentration values in exceedance of set limit may increase the occurrence of goiter among humans and animals, copper, an essential micro-nutrient is required in the growth of both plants and animals. It helps in the production of blood hemoglobin in human and in plants, it helps in regulation of water and disease resistance but, in high dose, it can cause anemia, liver and kidney damage, stomach and intestinal irritation in animals. ^{41, 82, 84, 100}.

Zinc, though showed concentration values that were below set limit in water and therefore showed hazard quotient that were below one, its concentration values in fish were higher than the set limit and therefore showed transfer factor that were greater than 1 ($TF > 1$). Zinc occurs naturally in air, water and soil, but zinc concentrations may have unusually arisen, due to addition of zinc through human activities. Mostly zinc are been added to the environment during industrial activities such as coal mining and waste combustion and steel processing. Many foodstuffs contain certain concentration of zinc. Drinking water also contains amounts of zinc, which may be high when it is stored in metal tanks. Zinc is a trace element that is essential for human health and Zinc shortages

can cause birth defect. Excess of Zinc can increase acidity of waters. Fish can accumulate and bio-magnify zinc in the food chain⁸⁴ as observed.

The Iron (Fe) and Lead (Pb) hazard quotient in location D and E were above 1 (HQ>1). Lead is of environmental concern than Iron, Iron showed hazard quotient of a Child consumer of the water to be 9.6 and 1.2 for an adult and cancer risk index of 17.3 for a child and 3.8 for an adult against 1 chosen as standard. The rainy season pollutants concentration seem to pose no threat as all the values of the indices used to assess the hazard were all within or below acceptable limit except for Pb that showed cancer risk index of 2.3, 1.4 and 6.2 in location B, C and D. The hazard quotient of all the metals in Tilapia and Catfish were below the limits except for the dry season Cd concentration in Tilapia that the hazard quotient for a child was 1.3 and the Total hazard index of metals in Tilapia was 1.5 and 1.1 for Catfish. These result simply means that 17 children are likely to contact cancer in one million people for a life time against the recommended one person per million people (1×10^{-6}) from drinking of this water. The transfer factor of Iron and Lead were below 1 hence showed they were not been bio-accumulated. While Iron is the most abundant metal and is believed to be the tenth most abundant element in the universe. It is extracted from its ore and hardly found in the free elemental state. Its combination of low cost and high strength makes it indispensable, especially in its applications. Like automobile, the hulls of large ships and structural components for buildings. Steel is the best known alloy of iron. Physiologically, it is essential to all organisms except few and excess iron in the body causes liver and kidney damage (haemochromatosis)⁸⁴, Lead arises in the environment from both natural and anthropogenic source. Exposure can be through drinking water, food, air, soil and even dust from old paint containing lead. Lead is used in the manufacturing, construction and chemical industries. It is used in batteries, alloys, pigments, cable sheathing and in guns and ammunition. Exposure to lead in humans can result in a wide range of biological effects

depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn causes problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tracts, joints and reproductive systems and acute or chronic damage to the nervous system⁸².

4.8.4 Concentration of Heavy Metals and PAHs in Sediment samples vis-a-vis Ecological Risk Assessment.

The potential ecological risk of heavy metals and polycyclic aromatic hydrocarbons on organisms (plants and animals) in the environment may likely face due to contamination of sediments by HMs and PAHs were accessed by estimating the ecological risk index (RI), geo-accumulation index (I_{geo}), Pollution load index contamination factor and Polycyclic aromatic pollution index (PPI)^{7, 173-175}.

The Potential Ecological Risk Index (RI) model results showed that the sediments from all the locations poses threat with RI values falling within the considerable risk classification $300 < RI < 600$. Potential Ecological Risk Index (RI) model of assessing risk was proposed by Hakanson (1980) to estimate the synergistic, concentration, toxic level and ecological sensitivity of the heavy metals¹⁷⁵.

The single potential ecological risk factor r_i values for all the metals showed that Cadmium is the major contributor to the risk index of all the metals estimated above. Its values were all of ecological risk threatening, its values were within the very high risk classification ($r_i > 320$). All the other metals had values of r_i in the low risk classification ($r_i < 150$)¹⁷⁵.

The Geo-accumulation index (I_{geo}) was used to characterize the Pollution level of heavy metals in the sediments by comparing the differences between current and preindustrial concentrations values^{176, 177}. The geo-accumulation index of the element showed that the sediment were

uncontaminated by the metals except Cadmium that showed different degrees of contamination. Cadmium in location A and C showed moderate to heavily contamination (MHC, $2 < I_{geo} \leq 3$) and location B, D and E were showed to be heavily contaminated (HC, $3 < I_{geo} \leq 4$).

Contamination factor (CF) was used to determine the contamination status of sediment, it is the ratio of measured mean concentration value of heavy metals in samples and the background values of the metals. Contamination factor can be used to differentiate between the metals originating from anthropogenic activities and those from natural processes in order to assess the degree of anthropogenic influence. High Contamination values suggest strong anthropogenic influence^{177 - 181}. From the results of the contamination factor, all the other elements showed low degree of contamination ($CF < 1$) except Cadmium that showed very high degrees of contamination ($CF > 6$) in all the locations A to E. Lesser contamination factor values were observed with the rainy season sediment which showed moderate degrees of Cadmium contamination ($1 < CF < 3$) in location A, B and D but Considerable contamination in location C and E.

The pollution load index (PLI) was earlier defined as the n th root of the multiplication of the concentration factors (CF_{metal}) of the individual heavy metals in the samples. The values of ($PLI > 1$) imply that heavy metal pollution exists, otherwise, ($PLI < 1$), means there is no heavy metal pollution¹⁷⁵. From the results of the pollution load index, it appeared that the sediment were not polluted because all the values were below 1 ($PLI < 1$). The values were in the order of $B < A < E < C < D$ across location A to E.

Finally, the polycyclic hydrocarbons in the sediments were subjected to polycyclic aromatic hydrocarbons pollution index (PPI) test, the PPI showed that the sediments were not contaminated with PAHs. All the values of PPI were all below 1 ($PPI < 1$).

4.8.5 Polycyclic aromatic hydrocarbons in Water, fish and Sediments samples vis-a-vis Health and Ecological Risk Assessment.

The cancer risk model was used to estimate the health risk posed for the ingestion of carcinogenic PAHs classified by the US EPA as probable human carcinogen and these carcinogenic PAHs detected in the water, fish and sediments in this research include; Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF) and Benzo[a]pyrene (BaP) while hazard quotient model was used for the non-carcinogenic health risk estimation for the other PAHs termed non-carcinogenic which include Naphthalene, Phenanthrene, and Anthracene determined in this work¹⁹⁵.

The estimated daily intake of PAHs were determined and the cancer risk were therefore estimated for water and fish ingestion. The carcinogenic PAHs were assessed for cancer risk and cancer risk index, it appeared that the cancer risk and carcinogenic cancer risk of Benzo[b]fluoranthene, Benzo[k]fluoranthene Benzo[a]pyrene were observed to all fall within or below limit except the cancer risk value for Benzo[a]pyrene at location E that gave cancer risk value of 3 person per one million people and the cancer risk index of 2.7 which is above the limit of 1 per a million persons. The concentration of PAHs in cat fish showed cancer risk and cancer risk index value that all fell within the acceptable limit and the three carcinogenic PAHs (Benzo[b]fluoranthene, Benzo[k]fluoranthene Benzo[a]pyrene) were not detected in the Tilapia fishes. It was crystal clear that pollution is noticeably recorded at location D and E below location C, these observation could be because, between location C and D on the Lokoja bank opposite Shintaku bank, mini or local port exist where people from Shintaku in Bassa local government area as well as neighboring local government area of the state comes and goes out of Lokoja leading to high vehicular and boats movement and of course the use of petroleum products at this banks for the boat engines and the spilling of engine oil and other petroleum product where boats engines were repaired and maintained

on the banks. This observation is in tandem with a study in Ghana that asserted that canoe landing site is more polluted than the inner fishing harbor due to the numerous anthropogenic activities that go on there as well as the activities of fishmongers who smokes fish at the canoe landing site and therefore introducing more PAHs¹⁹⁶. Benzo[a]pyrene concentration values in water and Catfish stands high comparing with the concentration limit of 0.01 µg/L in water by Environment Canada⁴² and been a common marker for PAHs originating from combustion, its presence above the set limit indicates that threat of PAHs exist for the rivers Niger and Benue confluence.

CHAPTER FIVE

5.0 Conclusion and Recommendation

Health they say is wealth, therefore, man has always tried to know in order to avoid whatever is capable of causing deleterious effect on his health. Notable among the substance with the ability to damage the human health via diverse of human health issues are the heavy metals and PAHs which this research study seeks to evaluate at the outset of this study for the first time in the history of mankind in this research area of study. The research study was design to therefore profile and estimate the concentration of heavy metals and polycyclic aromatic hydrocarbons in the confluence of rivers Niger and Benue water, fish and sediment and to estimate the human health and ecological risk factors. The study has been able to clearly show that the concentration of heavy metals and PAHs in the water, fish and sediments are of moderate risk but begging for immediate attention, therefore good hygiene, measures against indiscriminate dumping of waste in the water as well as burning of tyres, organic and petroleum products that are the major sources of heavy metals and PAHs be ensured with the creation and implementation of stiffer laws to regulate bush burning and refuse disposal. Also, constant routine monitoring should be ensure in order to guide against ignorant consumption of excess pollutants (HMs and PAHs) should the level of the HMs and PAHs in the media increase to intolerable limit.

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APPENDIX 1

Rough Statistical Results from SPSS Version 20 Software Package

ANOVA showing seasonal variations of physiochemical parameters

[DataSet2] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\Data for PAHs ANOVA.sa

Descriptives

scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	20	46.2350	27.95144	6.25013	33.1533	59.3167	20.10	94.40
2	20	45.6500	19.91527	4.45319	36.3294	54.9706	21.10	79.20
Total	40	45.9425	23.95698	3.78793	38.2807	53.6043	20.10	94.40

ANOVA

scores					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3.422	1	3.422	.006	.940
Within Groups	22380.113	38	588.950		
Total	22383.535	39			

ANOVA for Dry season heavy metals concentration in water

[DataSet2] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

Scores

					95% Confidence Interval for Mean			
					Lower Bound	Upper Bound		
A	6	.63000	.801368	.327157	-.21098	1.47098	.115	2.215
B	6	.85038	.876864	.357978	-.06983	1.77060	.255	2.600
C	6	.72783	.721801	.294674	-.02965	1.48532	.199	2.130
D	6	1.22333	1.274563	.520338	-.11424	2.56091	.116	3.059
E	6	.74967	.708518	.289251	.00612	1.49321	.044	2.047
Total	30	.83624	.862312	.157436	.51425	1.15824	.044	3.059

ANOVA

Scores					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.271	4	.318	.391	.813
Within Groups	20.293	25	.812		
Total	21.564	29			

ANOVA for dry season heavy metals concentration in sediment

[DataSet2] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA2Scores

					95% Confidence Interval for Mean			
	N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
1	6	1.3560E2	277.39303	1.13245E2	-155.5028	426.7095	6.94	700.78
2	6	1.3164E2	278.35949	1.13640E2	-160.4804	423.7604	7.42	699.62
3	6	1.3291E2	283.82860	1.15873E2	-164.9465	430.7732	6.54	712.08
4	6	1.5342E2	298.90499	1.22027E2	-160.2649	467.0982	8.66	762.48
5	6	1.4452E2	288.42550	1.17749E2	-158.1640	447.2040	8.68	732.50
Total	30	1.3962E2	265.20325	48.41927	40.5901	238.6472	6.54	762.48

ANOVA

ANOVA2Scores					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2034.908	4	508.727	.006	1.000
Within Groups	2037615.188	25	81504.608		
Total	2039650.096	29			

ANOVA for dry season heavy metals concentratioin 2 fishes

[DataSet2] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA3scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	5	7.52750E1	81.760655	3.656448E1	-26.24426	176.79426	14.150	191.225
2	5	7.35950E1	83.781724	3.746833E1	-30.43375	177.62375	10.100	190.875
Total	10	7.44350E1	78.048264	2.468103E1	18.60264	130.26736	10.100	191.225

ANOVA

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	7.056	1	7.056	.001	.975
Within Groups	54816.728	8	6852.091		
Total	54823.784	9			

ANOVA for Rainy season heavy metals concentration in water

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA4Scores

					95% Confidence Interval for Mean			
	N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
1	6	4.42550	10.575079	4.317258	-6.67237	15.52337	.000	26.009
2	6	6.93700	16.640907	6.793622	-10.52656	24.40056	.000	40.903
3	6	4.01850	9.423167	3.846992	-5.87051	13.90751	.000	23.247
4	6	1.19233	2.705164	1.104379	-1.64656	4.03123	.000	6.707
5	6	4.90917	11.777644	4.808203	-7.45071	17.26905	.000	28.948
Total	30	4.29650	10.537878	1.923944	.36159	8.23141	.000	40.903

ANOVA

ANOVA4Scores					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	102.464	4	25.616	.205	.933
Within Groups	3117.895	25	124.716		
Total	3220.359	29			

ANOVA for Rainy season heavy metals in fishes

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA6scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	24.9283	48.15985	19.66118	-25.6123	75.4690	.49	122.04
2	6	50.5448	101.01643	41.23978	-55.4654	156.5551	.88	255.80
Total	12	37.7366	76.62605	22.12003	-10.9493	86.4225	.49	255.80

ANOVA

ANOVA6scores

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	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1968.615	1	1968.615	.314	.587
Within Groups	62618.448	10	6261.845		
Total	64587.064	11			

ONEWAY ANOVA5scores BY ANOVA5factors

/STATISTICS DESCRIPTIVES

/MISSING ANALYSIS.

ANOVA for Rainy heavy metals concentration in sediment

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA5scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	15.3912	20.01170	8.16974	-5.6098	36.3922	1.00	44.30
2	6	26.5400	48.55682	19.82324	-24.4173	77.4973	.00	123.65
3	6	13.8387	18.35962	7.49528	-5.4286	33.1059	.00	43.06

4	6	12.5190	15.70833	6.41290	-3.9659	29.0039	.96	37.05
5	6	48.7995	76.03723	31.04207	-30.9967	128.5957	3.07	199.03
Total	30	23.4177	42.01490	7.67084	7.7290	39.1063	.00	199.03

ANOVA

ANOVA5scores					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5573.696	4	1393.424	.764	.559
Within Groups	45618.603	25	1824.744		
Total	51192.299	29			

ANOVA showing difference between rainy season and dry season metal in water

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA7scores

					95% Confidence Interval for Mean			
	N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
1	30	.83624	.862312	.157436	.51425	1.15824	.044	3.059
2	30	4.29650	10.537878	1.923944	.36159	8.23141	.000	40.903
Total	60	2.56637	7.615243	.983124	.59915	4.53360	.000	40.903

ANOVA

ANOVA7scores

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	179.601	1	179.601	3.213	.078
Within Groups	3241.923	58	55.895		
Total	3421.524	59			

Difference between rainy season and dry season metals in sediment

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA8scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	30	1.39619E2	265.203246	4.841927E1	40.59015	238.64719	6.540	762.480
2	30	2.34177E1	42.014898	7.670836	7.72905	39.10629	.000	199.030
Total	60	8.15182E1	197.157017	2.545286E1	30.58711	132.44922	.000	762.480

ANOVA

ANOVA8scores					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	202540.086	1	202540.086	5.618	.021
Within Groups	2090842.394	58	36049.007		
Total	2293382.480	59			

Difference between rainy season and dry season metals in tilapia and catfishes

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA9scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	12	6.21834E1	76.175776	2.199005E1	13.78364	110.58320	.492	191.225
2	10	4.50988E1	82.552713	2.610546E1	-13.95585	104.15345	.595	255.798
Total	22	5.44177E1	77.691970	1.656398E1	19.97099	88.86437	.492	255.798

ANOVA

ANOVA9scores

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	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1592.095	1	1592.095	.254	.620
Within Groups	125164.791	20	6258.240		
Total	126756.886	21			

Difference in samples of PAHs in water

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA10scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	.13833	.151581	.061883	-.02074	.29741	.000	.280
2	6	.34167	.468291	.191179	-.14977	.83311	.000	1.260
3	6	.13833	.152632	.062312	-.02184	.29851	.000	.310
4	6	.48000	.563383	.230000	-.11123	1.07123	.250	1.630
5	6	.14667	.162686	.066416	-.02406	.31739	.000	.340
Total	30	.24900	.353732	.064582	.11691	.38109	.000	1.630

ANOVA

ANOVA10scores

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	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.581	4	.145	1.193	.338
Within Groups	3.047	25	.122		
Total	3.629	29			

Difference in samples of PAHs in sediment

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA11scores

					95% Confidence Interval for Mean			
	N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
1	6	1.2517	2.63706	1.07658	-1.5158	4.0191	.00	6.63
2	6	1.2517	2.63706	1.07658	-1.5158	4.0191	.00	6.63
3	6	1.0333	2.21366	.90372	-1.2898	3.3564	.00	5.55
4	6	.0500	.07746	.03162	-.0313	.1313	.00	.15
5	6	.8050	1.97184	.80500	-1.2643	2.8743	.00	4.83
Total	30	.8783	2.02977	.37058	.1204	1.6363	.00	6.63

ANOVA

ANOVA11scores

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	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5.966	4	1.491	.328	.856
Within Groups	113.513	25	4.541		
Total	119.479	29			

Difference in PAHs in tilapia and cat fishes

[DataSet1] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\ANOVA DATA.sav

Descriptives

ANOVA12scores

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	1.3133	2.85941	1.16735	-1.6874	4.3141	.13	7.15
2	6	1.0300	2.35788	.96260	-1.4444	3.5044	.00	5.84
Total	12	1.1717	2.50309	.72258	-.4187	2.7621	.00	7.15

ANOVA

ANOVA12scores

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a. Cannot be computed because at least one of the variables is constant.

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Principal component Analysis of dry and rainy seasons heavy metals in water

[DataSet0] C:\Users\Mkpoikankeotu\Desktop\Data analysis\Newman\New correlation data 2.sav

Warnings

There are fewer than two cases, at least one of the variables has zero variance, there is only one variable in the analysis, or correlation coefficients could not be computed for all pairs of variables. No further statistics will be computed.

Rainy season Fe	Pearson Correlation	.313	.301	-.371	-.459	-.329	-.480	.817	1	-.891	-.615	-.846
	Sig. (2-tailed)	.797	.805	.758	.696	.787	.681	.391		.300	.578	.358
	N	3	3	3	3	3	3	3	3	3	3	3
Rainy season Pb	Pearson Correlation	-.710	-.701	.752	.812	.722	.029	-.466	-.891	1	.190	.511
	Sig. (2-tailed)	.498	.505	.458	.396	.487	.981	.691	.300		.878	.658
	N	3	3	3	3	3	3	3	3	3	3	3
Rainy season Zn	Pearson Correlation	.557	.567	-.504	-.419	-.543	.987	-.957	-.615	.190	1	.941
	Sig. (2-tailed)	.624	.616	.664	.725	.635	.103	.187	.578	.878		.220
	N	3	3	3	3	3	3	3	3	3	3	3
Rainy season Cr	Pearson Correlation	.243	.254	-.182	-.086	-.226	.874	-.999*	-.846	.511	.941	1
	Sig. (2-tailed)	.844	.836	.884	.945	.855	.323	.033	.358	.658	.220	
	N	3	3	3	3	3	3	3	3	3	3	3

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Principal component Analysis for heavy dry and rainy season metals in tilapia

Communalities

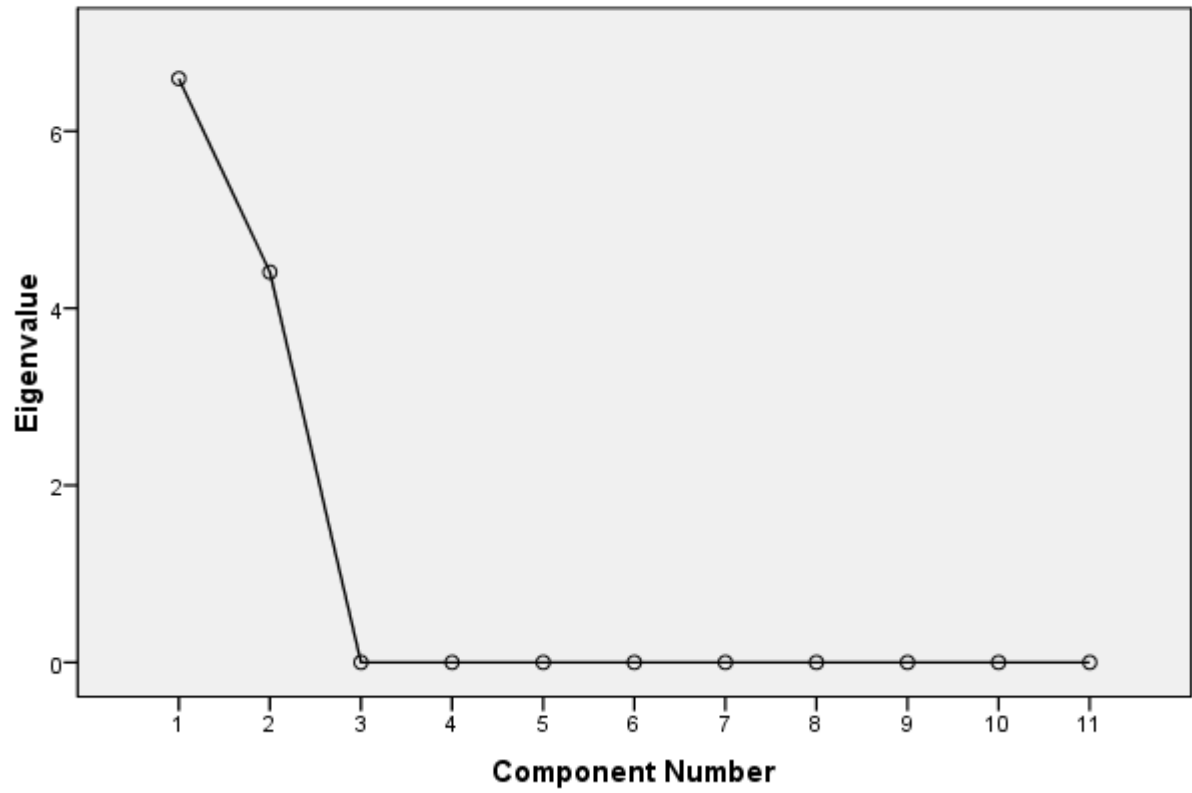
	Initial	Extraction
Dry season Cd	1.000	1.000
Dry season Cu	1.000	1.000
Dry season Fe	1.000	1.000
Dry season Pb	1.000	1.000
Dry season Zn	1.000	1.000
Rainy season Cd	1.000	1.000
Rainy season Cu	1.000	1.000
Rainy season Fe	1.000	1.000
Rainy season Pb	1.000	1.000
Rainy season Zn	1.000	1.000
Rainy season Cr	1.000	1.000

Extraction Method: Principal Component Analysis.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.593	59.936	59.936	6.593	59.936	59.936	6.255	56.863	56.863
2	4.407	40.064	100.000	4.407	40.064	100.000	4.745	43.137	100.000
3	4.799E-16	4.363E-15	100.000						
4	3.222E-16	2.929E-15	100.000						
5	1.270E-16	1.155E-15	100.000						
6	6.606E-17	6.005E-16	100.000						
7	-5.632E-17	-5.120E-16	100.000						
8	-1.591E-16	-1.446E-15	100.000						
9	-2.427E-16	-2.206E-15	100.000						
10	-5.131E-16	-4.664E-15	100.000						
11	-9.362E-16	-8.511E-15	100.000						

Extraction Method: Principal Component Analysis.

Scree Plot**Component Matrix^a**

	Component	
	1	2
Dry season Cd	.977	-.213
Dry season Cu	.979	-.202
Dry season Fe	-.962	.274
Dry season Pb	-.931	.365

Dry season Zn	-.973	.230
Rainy season Cd	.823	.568
Rainy season Cu	-.489	-.872
Rainy season Fe	.103	-.995
Rainy season Pb	-.543	.840
Rainy season Zn	.721	.693
Rainy season Cr	.444	.896

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

Rotated Component Matrix^a

	Component	
	1	2
Dry season Cd	-.982	.188
Dry season Cu	-.980	.200
Dry season Fe	.992	-.126
Dry season Pb	1.000	-.030
Dry season Zn	.985	-.171
Rainy season Cd	-.534	.846
Rainy season Cu	.107	-.994
Rainy season Fe	-.486	-.874

Rainy season Pb	.830	.558
Rainy season Zn	-.391	.920
Rainy season Cr	-.056	.998

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

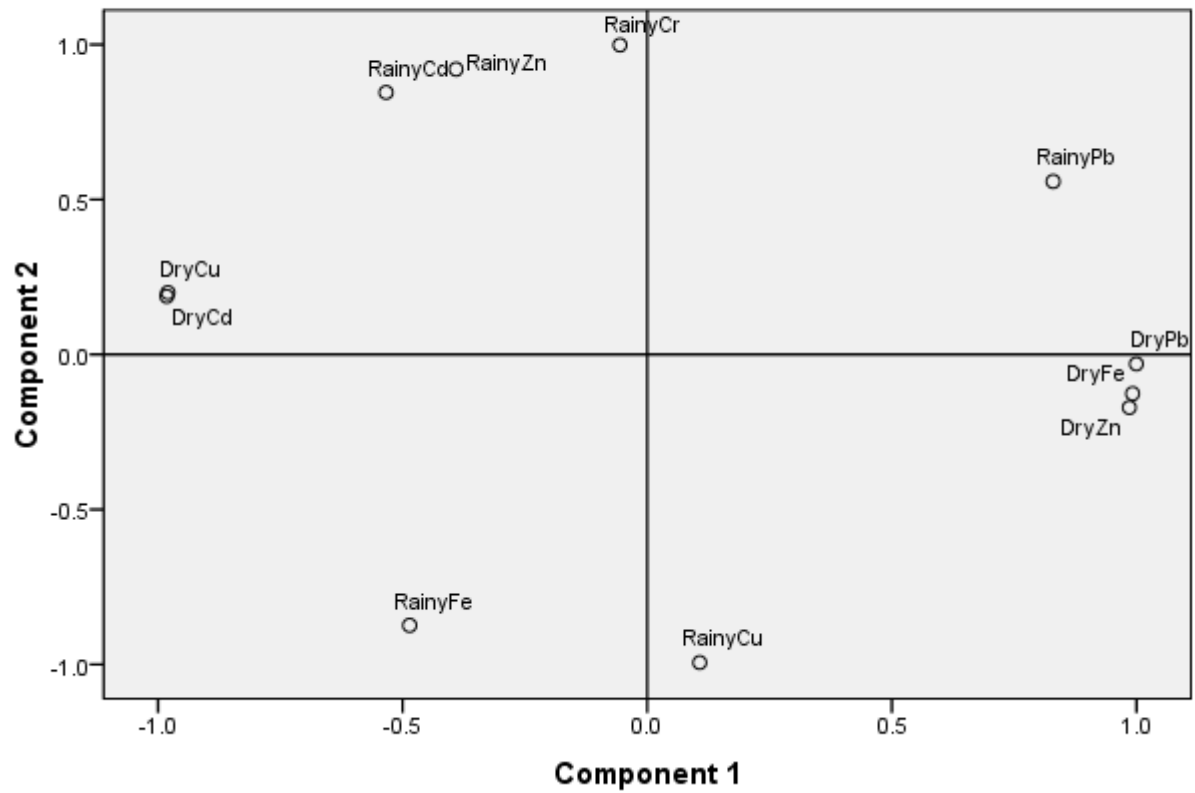
a. Rotation converged in 3 iterations.

Component Transformation Matrix

Component	1	2
1	-.919	.393
2	.393	.919

Extraction Method: Principal
Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Plot in Rotated Space**Component Score Coefficient Matrix**

	Component	
	1	2
Dry season Cd	-.155	.014
Dry season Cu	-.155	.016
Dry season Fe	.159	.000
Dry season Pb	.162	.021

Dry season Zn	.156	-.010
Rainy season Cd	-.064	.168
Rainy season Cu	-.010	-.211
Rainy season Fe	-.103	-.201
Rainy season Pb	.151	.143
Rainy season Zn	-.039	.188
Rainy season Cr	.018	.213

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Scores.

**Component Score Covariance
Matrix**

Compon ent	1	2
1	1.000	.000
2	.000	1.000

Extraction Method: Principal
Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Scores.

Correlation of dry and rainy seasons metal in catfish

		Dry season Cd	Dry season Cu	Dry season Fe	Dry season Pb	Dry season Zn	Rainy season Cd	Rainy season Cu	Rainy season Fe	Rainy season Pb	Rainy season Zn	Rainy season Cr
Dry season Cd	Pearson Correlation	1	.993	.991	.984	.962	.939	.652	.394	.369	.164	.146
	Sig. (2- tailed)		.073	.086	.114	.176	.224	.548	.742	.759	.895	.906
	N	3	3	3	3	3	3	3	3	3	3	3
Dry season Cu	Pearson Correlation	.993	1	1.000*	.998*	.987	.972	.561	.286	.260	.050	.032
	Sig. (2- tailed)	.073		.013	.041	.102	.151	.621	.816	.832	.968	.980
	N	3	3	3	3	3	3	3	3	3	3	3
Dry season Fe	Pearson Correlation	.991	1.000*	1	.999*	.990	.976	.544	.266	.241	.030	.012
	Sig. (2- tailed)	.086	.013		.028	.089	.138	.634	.828	.845	.981	.992
	N	3	3	3	3	3	3	3	3	3	3	3
Dry season Pb	Pearson Correlation	.984	.998*	.999*	1	.995	.985	.507	.224	.198	-.014	-.032
	Sig. (2- tailed)	.114	.041	.028		.062	.110	.662	.856	.873	.991	.980
	N	3	3	3	3	3	3	3	3	3	3	3
Dry season	Pearson Correlation	.962	.987	.990	.995	1	.997*	.421	.129	.102	-.111	-.128

Zn	Sig. (2-tailed)	.176	.102	.089	.062		.049	.723	.918	.935	.929	.918
N		3	3	3	3	3	3	3	3	3	3	3
Rainy season Cd	Pearson Correlation	.939	.972	.976	.985	.997 [*]	1	.350	.052	.026	-.187	-.204
	Sig. (2-tailed)	.224	.151	.138	.110	.049		.772	.967	.984	.880	.869
N		3	3	3	3	3	3	3	3	3	3	3
Rainy season Cu	Pearson Correlation	.652	.561	.544	.507	.421	.350	1	.954	.945	.855	.845
	Sig. (2-tailed)	.548	.621	.634	.662	.723	.772		.195	.212	.347	.359
N		3	3	3	3	3	3	3	3	3	3	3
Rainy season Fe	Pearson Correlation	.394	.286	.266	.224	.129	.052	.954	1	1.000 [*]	.971	.967
	Sig. (2-tailed)	.742	.816	.828	.856	.918	.967	.195		.017	.153	.164
N		3	3	3	3	3	3	3	3	3	3	3
Rainy season Pb	Pearson Correlation	.369	.260	.241	.198	.102	.026	.945	1.000 [*]	1	.977	.973
	Sig. (2-tailed)	.759	.832	.845	.873	.935	.984	.212	.017		.136	.147
N		3	3	3	3	3	3	3	3	3	3	3
Rainy season	Pearson Correlation	.164	.050	.030	-.014	-.111	-.187	.855	.971	.977	1	1.000 [*]

Zn	Sig. (2-tailed)	.895	.968	.981	.991	.929	.880	.347	.153	.136		.011
	N	3	3	3	3	3	3	3	3	3	3	3
Rainy season	Pearson Correlation	.146	.032	.012	-.032	-.128	-.204	.845	.967	.973	1.000*	1
Cr	Sig. (2-tailed)	.906	.980	.992	.980	.918	.869	.359	.164	.147	.011	
	N	3	3	3	3	3	3	3	3	3	3	3

*. Correlation is significant at the 0.05 level (2-tailed).

Principal component Analysis for dry and rainy seasons heavy metals in cat fish

Communalities

	Initial	Extraction
Dry season Cd	1.000	1.000
Dry season Cu	1.000	1.000
Dry season Fe	1.000	1.000
Dry season Pb	1.000	1.000
Dry season Zn	1.000	1.000
Rainy season Cd	1.000	1.000
Rainy season Cu	1.000	1.000
Rainy season Fe	1.000	1.000
Rainy season Pb	1.000	1.000
Rainy season Zn	1.000	1.000
Rainy season Cr	1.000	1.000

Communalities

	Initial	Extraction
Dry season Cd	1.000	1.000
Dry season Cu	1.000	1.000
Dry season Fe	1.000	1.000
Dry season Pb	1.000	1.000
Dry season Zn	1.000	1.000
Rainy season Cd	1.000	1.000
Rainy season Cu	1.000	1.000
Rainy season Fe	1.000	1.000
Rainy season Pb	1.000	1.000
Rainy season Zn	1.000	1.000
Rainy season Cr	1.000	1.000

Extraction Method: Principal Component Analysis.

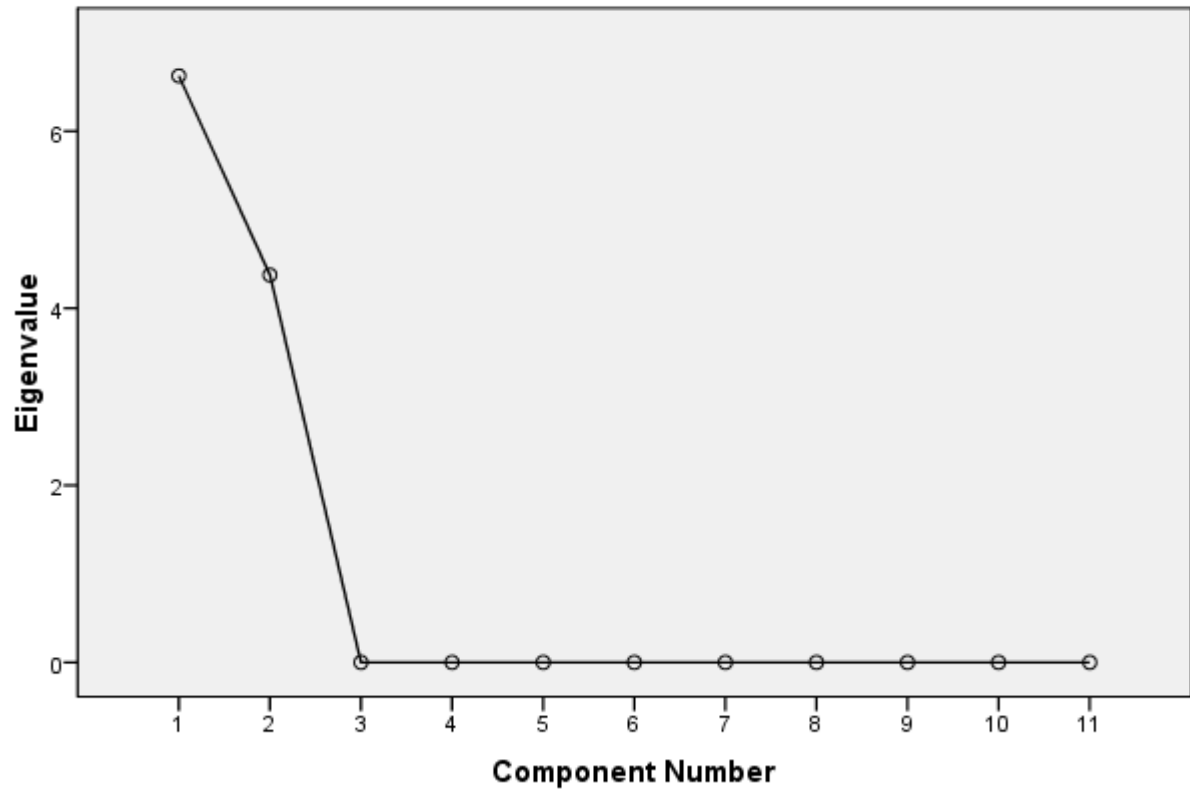
Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.625	60.225	60.225	6.625	60.225	60.225	6.139	55.805	55.805
2	4.375	39.775	100.000	4.375	39.775	100.000	4.861	44.195	100.000
3	3.907E-16	3.552E-15	100.000						
4	2.480E-16	2.255E-15	100.000						
5	1.766E-16	1.606E-15	100.000						
6	1.581E-16	1.437E-15	100.000						
7	6.842E-17	6.220E-16	100.000						
8	2.987E-17	2.715E-16	100.000						
9	-2.119E-16	-1.927E-15	100.000						
10	-2.733E-16	-2.484E-15	100.000						

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.625	60.225	60.225	6.625	60.225	60.225	6.139	55.805	55.805
2	4.375	39.775	100.000	4.375	39.775	100.000	4.861	44.195	100.000
3	3.907E-16	3.552E-15	100.000						
4	2.480E-16	2.255E-15	100.000						
5	1.766E-16	1.606E-15	100.000						
6	1.581E-16	1.437E-15	100.000						
7	6.842E-17	6.220E-16	100.000						
8	2.987E-17	2.715E-16	100.000						
9	-2.119E-16	-1.927E-15	100.000						
10	-2.733E-16	-2.484E-15	100.000						
11	-4.993E-16	-4.539E-15	100.000						

Extraction Method: Principal Component Analysis.

Scree Plot**Component Matrix^a**

	Component	
	1	2
Dry season Cd	.974	-.227
Dry season Cu	.941	-.337
Dry season Fe	.934	-.356
Dry season Pb	.918	-.397

Dry season Zn	.875	-.484
Rainy season Cd	.836	-.549
Rainy season Cu	.807	.590
Rainy season Fe	.592	.806
Rainy season Pb	.571	.821
Rainy season Zn	.384	.923
Rainy season Cr	.367	.930

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

Rotated Component Matrix^a

	Component	
	1	2
Dry season Cd	.968	.252
Dry season Cu	.990	.139
Dry season Fe	.993	.119
Dry season Pb	.997	.075
Dry season Zn	1.000	-.021
Rainy season Cd	.995	-.098
Rainy season Cu	.440	.898
Rainy season Fe	.150	.989

Rainy season Pb	.123	.992
Rainy season Zn	-.090	.996
Rainy season Cr	-.107	.994

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

a. Rotation converged in 3 iterations.

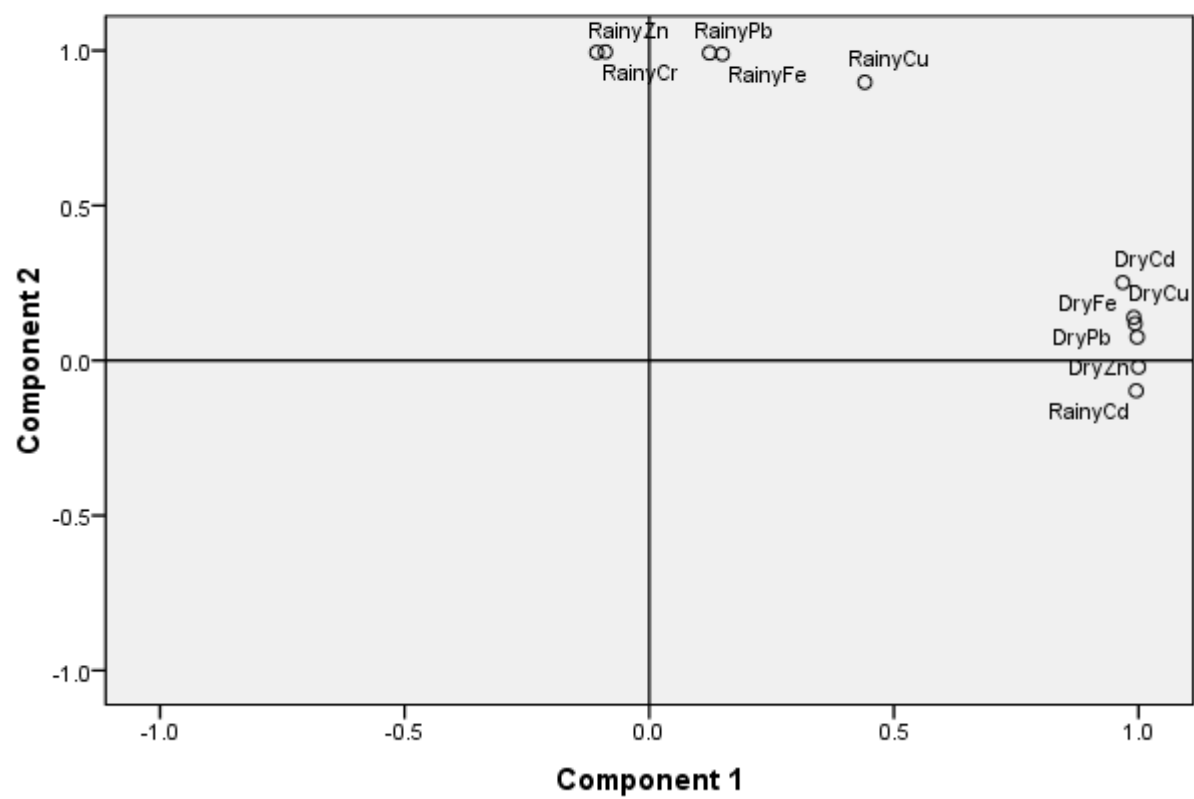
Component Transformation Matrix

Component	1	2
1	.885	.465
2	-.465	.885

Extraction Method: Principal
Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Plot in Rotated Space



Component Score Coefficient Matrix

	Component	
	1	2

Dry season Cd	.154	.022
Dry season Cu	.162	-.002
Dry season Fe	.163	-.007
Dry season Pb	.165	-.016
Dry season Zn	.168	-.036
Rainy season Cd	.170	-.053
Rainy season Cu	.045	.176
Rainy season Fe	-.006	.205
Rainy season Pb	-.011	.206
Rainy season Zn	-.047	.214
Rainy season Cr	-.050	.214

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Scores.

**Component Score Covariance
Matrix**

Component	1	2
1	1.000	.000
2	.000	1.000

**Component Score Covariance
Matrix**

Component	1	2
1	1.000	.000
2	.000	1.000

Extraction Method: Principal
Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Scores.

Correlation of dry and rainy seasons heavy metals in sediment

Correlations

	Dry season Cd	Dry season Cu	Dry season Fe	Dry season Pb	Dry season Zn	Rainy season Cd	Rainy season Cu	Rainy season Fe	Rainy season Pb	Rainy season Zn	DryCr	RainyCr
Dry season Pearson Correlation	1	.728**	.720**	-.205	.738**	.278	.544*	-.616*	.221	.444	.740**	.613*

Cd	Sig. (2-tailed)		.002	.002	.463	.002	.316	.036	.015	.428	.097	.002	.015
N		15	15	15	15	15	15	15	15	15	15	15	15
Dry season Cu	Pearson Correlation	.728**	1	.903**	.106	.964**	.178	.308	-.333	.065	.111	.766**	.338
	Sig. (2-tailed)	.002		.000	.706	.000	.525	.263	.225	.819	.694	.001	.218
N		15	15	15	15	15	15	15	15	15	15	15	15
Dry season Fe	Pearson Correlation	.720**	.903**	1	-.011	.861**	.072	.203	-.236	-.039	-.019	.767**	.231
	Sig. (2-tailed)	.002	.000		.969	.000	.799	.468	.398	.890	.948	.001	.406
N		15	15	15	15	15	15	15	15	15	15	15	15
Dry season Pb	Pearson Correlation	-.205	.106	-.011	1	.241	-.375	-.172	.295	.188	-.373	-.303	-.199
	Sig. (2-tailed)	.463	.706	.969		.386	.168	.539	.286	.502	.171	.273	.478
N		15	15	15	15	15	15	15	15	15	15	15	15
Dry season Zn	Pearson Correlation	.738**	.964**	.861**	.241	1	.127	.348	-.349	.201	.140	.658**	.374
	Sig. (2-tailed)	.002	.000	.000	.386		.651	.204	.202	.474	.620	.008	.170
N		15	15	15	15	15	15	15	15	15	15	15	15
Rainy season	Pearson Correlation	.278	.178	.072	-.375	.127	1	.884**	-.873**	.647**	.801**	.271	.847**

Cd	Sig. (2-tailed)	.316	.525	.799	.168	.651		.000	.000	.009	.000	.329	.000
	N	15	15	15	15	15	15	15	15	15	15	15	15
Rainy season Cu	Pearson Correlation	.544*	.308	.203	-.172	.348	.884**	1	-.982**	.816**	.839**	.311	.983**
	Sig. (2-tailed)	.036	.263	.468	.539	.204	.000		.000	.000	.000	.260	.000
	N	15	15	15	15	15	15	15	15	15	15	15	15
Rainy season Fe	Pearson Correlation	-.616*	-.333	-.236	.295	-.349	-.873**	-.982**	1	-.714**	-.868**	-.414	-.991**
	Sig. (2-tailed)	.015	.225	.398	.286	.202	.000	.000		.003	.000	.125	.000
	N	15	15	15	15	15	15	15	15	15	15	15	15
Rainy season Pb	Pearson Correlation	.221	.065	-.039	.188	.201	.647**	.816**	-.714**	1	.531*	-.216	.734**
	Sig. (2-tailed)	.428	.819	.890	.502	.474	.009	.000	.003		.042	.440	.002
	N	15	15	15	15	15	15	15	15	15	15	15	15
Rainy season Zn	Pearson Correlation	.444	.111	-.019	-.373	.140	.801**	.839**	-.868**	.531*	1	.374	.871**
	Sig. (2-tailed)	.097	.694	.948	.171	.620	.000	.000	.000	.042		.170	.000
	N	15	15	15	15	15	15	15	15	15	15	15	15
DryCr	Pearson Correlation	.740**	.766**	.767**	-.303	.658**	.271	.311	-.414	-.216	.374	1	.408

	Sig. (2-tailed)	.002	.001	.001	.273	.008	.329	.260	.125	.440	.170		.131
	N	15	15	15	15	15	15	15	15	15	15	15	15
RainyCr	Pearson Correlation	.613*	.338	.231	-.199	.374	.847**	.983**	-.991**	.734**	.871**	.408	1
	Sig. (2-tailed)	.015	.218	.406	.478	.170	.000	.000	.000	.002	.000	.131	
	N	15	15	15	15	15	15	15	15	15	15	15	15

** . Correlation is significant at the
0.01 level (2-tailed).

*. Correlation is significant at
the 0.05 level (2-tailed).

Principal component Analysis of dry and rainy seasons heavy metals in sediment

Communalities

	Initial	Extraction
Dry season Cd	1.000	.809
Dry season Cu	1.000	.949

Dry season Fe	1.000	.906
Dry season Pb	1.000	.882
Dry season Zn	1.000	.963
Rainy season Cd	1.000	.852
Rainy season Cu	1.000	.994
Rainy season Fe	1.000	.986
Rainy season Pb	1.000	.941
Rainy season Zn	1.000	.862
DryCr	1.000	.915
RainyCr	1.000	.978

Extraction Method: Principal Component Analysis.

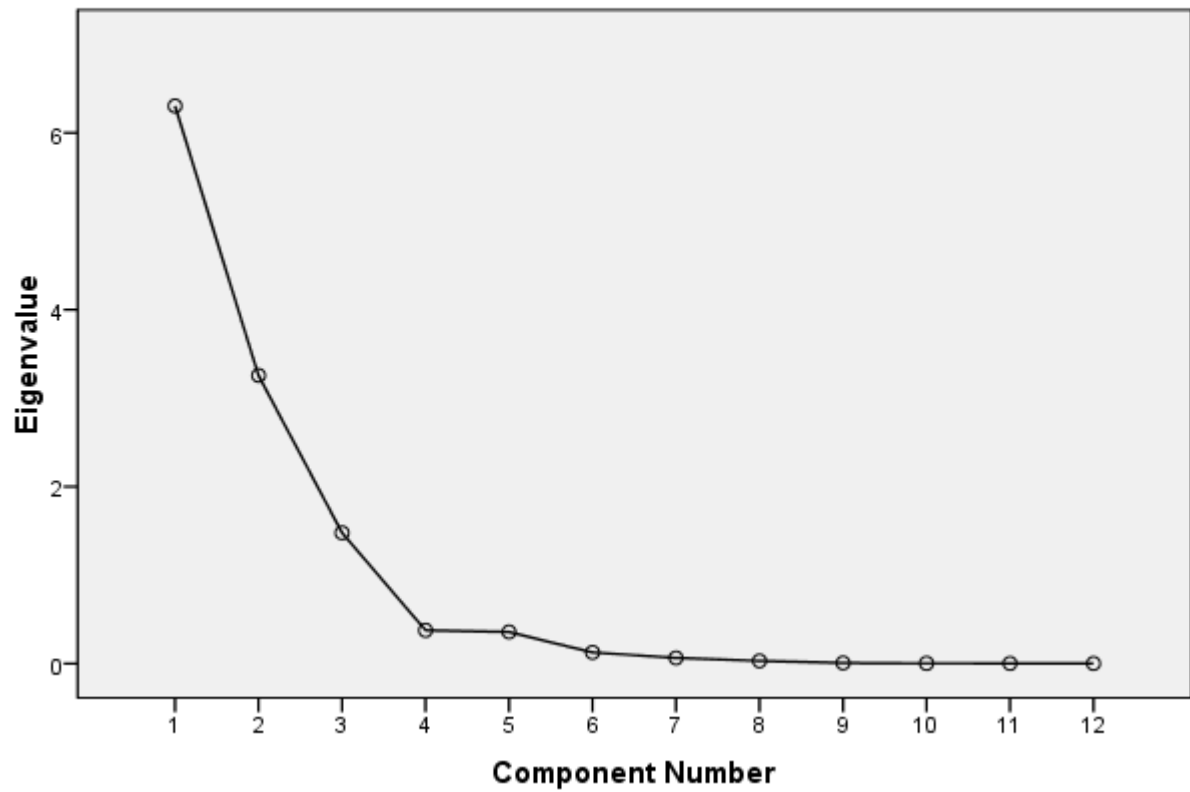
Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.304	52.530	52.530	6.304	52.530	52.530	5.270	43.915	43.915
2	3.257	27.143	79.673	3.257	27.143	79.673	4.229	35.245	79.161
3	1.478	12.313	91.986	1.478	12.313	91.986	1.539	12.826	91.986
4	.376	3.135	95.121						
5	.357	2.977	98.098						

6	.126	1.049	99.147								
7	.064	.530	99.677								
8	.029	.246	99.922								
9	.006	.050	99.972								
10	.002	.019	99.991								
11	.001	.008	99.999								
12	7.830E-5	.001	100.000								

Extraction Method: Principal Component
Analysis.

Scree Plot



Component Matrix^a

	Component		
	1	2	3
Dry season Cd	.784	.430	-.098
Dry season Cu	.620	.739	.136
Dry season Fe	.527	.793	.009
Dry season Pb	-.233	.198	.888
Dry season Zn	.625	.691	.307
Rainy season Cd	.781	-.482	-.101
Rainy season Cu	.916	-.371	.133
Rainy season Fe	-.939	.323	.015
Rainy season Pb	.597	-.511	.569
Rainy season Zn	.784	-.453	-.205
DryCr	.636	.585	-.410
RainyCr	.936	-.313	.060

Extraction Method: Principal Component Analysis.

a. 3 components extracted.

Rotated Component Matrix^a

	Component		
	1	2	3
Dry season Cd	.387	.796	-.160
Dry season Cu	.107	.963	.106
Dry season Fe	-.014	.952	-.007
Dry season Pb	-.196	.048	.917
Dry season Zn	.159	.929	.273
Rainy season Cd	.898	.042	-.210
Rainy season Cu	.974	.214	.014
Rainy season Fe	-.948	-.264	.133
Rainy season Pb	.843	-.074	.474
Rainy season Zn	.872	.066	-.312
DryCr	.142	.834	-.446
RainyCr	.949	.272	-.058

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 4 iterations.

Component Transformation Matrix

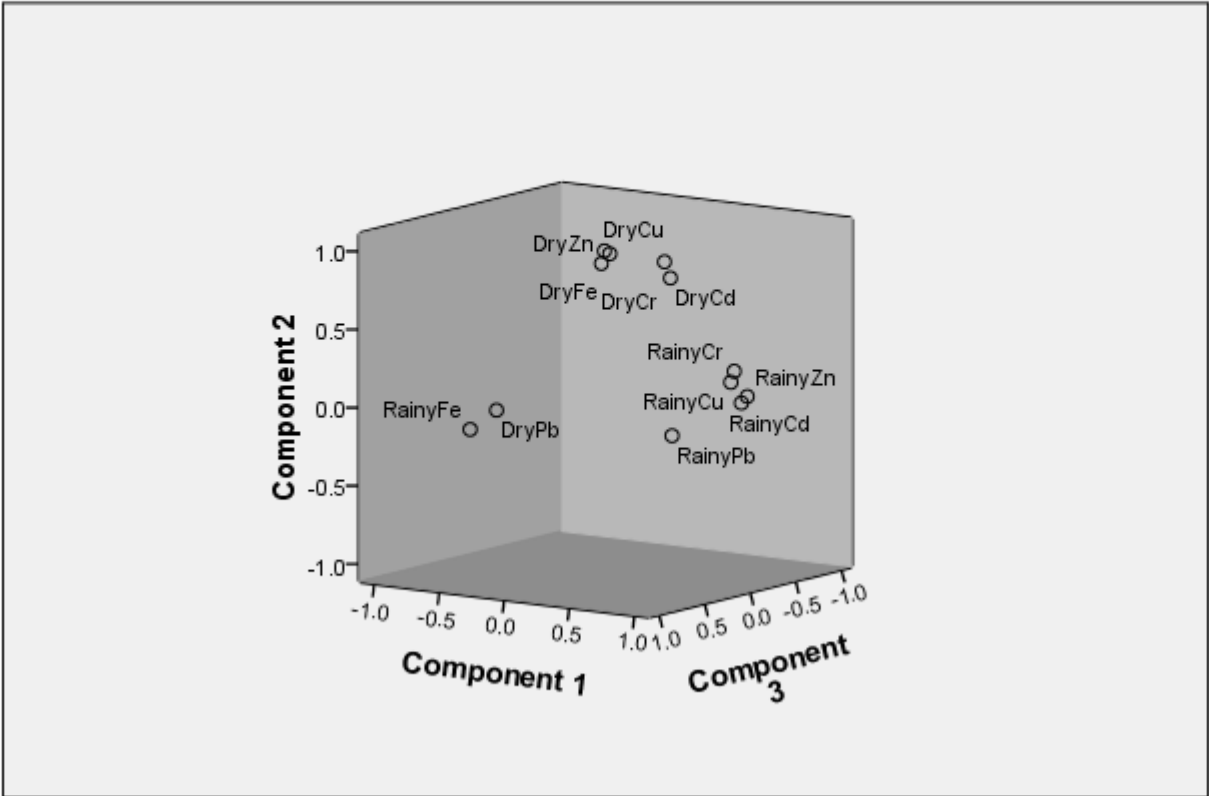
Component	1	2	3
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1	.818	.565	-.108
2	-.563	.825	.052
3	.119	.018	.993

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Plot in Rotated Space



Component Score Coefficient Matrix

	Component		
	1	2	3
Dry season Cd	.019	.178	-.073
Dry season Cu	-.036	.244	.093
Dry season Fe	-.068	.248	.009
Dry season Pb	.007	.040	.604
Dry season Zn	-.014	.235	.207
Rainy season Cd	.176	-.053	-.089
Rainy season Cu	.194	-.010	.068
Rainy season Fe	-.176	-.002	.031
Rainy season Pb	.212	-.069	.364
Rainy season Zn	.164	-.047	-.159
DryCr	-.052	.200	-.277
RainyCr	.180	.005	.019

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

Component Scores.

Component Score Covariance Matrix

Component	1	2	3

1	1.000	.000	.000
2	.000	1.000	.000
3	.000	.000	1.000

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser
Normalization.

Component Scores.

Correlation of PAHs in water, sediment and fishes

[DataSet1]

Correlations

		Nap W	PhW	ANw	BbF w	BkF w	BaP w	Naps	PHs	ANs	BbFs	BkF s	Baps	NaP f	PHf	ANf	BbFf	BkFf	BaP f
NapW	Pearson Correlation	1	.632*	.632*	.143	.201	-.076	-.870*	-.585*	-.588*	.265	.206	. ^a	-.420	.285	-.046	-.984**	-.984**	-.970**
	Sig. (2-tailed)		.012	.012	.611	.473	.788	.000	.022	.021	.340	.461	.	.407	.584	.931	.000	.000	.001
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6
PhW	Pearson Correlation	.632*	1	1.000**	-.110	-.142	-.386	-.611*	-.403	-.405	-.148	-.125	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a
	Sig. (2-tailed)	.012		.000	.697	.615	.155	.015	.136	.134	.599	.658	.	.000	.000	.000	.000	.000	.000
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6
ANw	Pearson Correlation	.632*	1.000**	1	-.110	-.142	-.386	-.611*	-.403	-.405	-.148	-.125	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a	. ^a
	Sig. (2-tailed)	.012	.000		.697	.615	.155	.015	.136	.134	.599	.658	.	.000	.000	.000	.000	.000	.000
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6
BbFw	Pearson Correlation	.143	-.110	-.110	1	.976*	.478	.202	.094	.107	.044	.054	. ^a	.327	-.213	.146	.642	.642	.470
	Sig. (2-tailed)	.611	.697	.697		.000	.072	.471	.740	.705	.876	.848	.	.527	.685	.782	.169	.169	.347
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6

BkFw	Pearson Correlation	.201	-.142	-.142	.976*	1	.465	.137	.048	.061	.025	.041	. ^a	.598	-.433	.000	.466	.466	.239
	Sig. (2-tailed)	.473	.615	.615	.000		.081	.627	.866	.830	.930	.886	.	.209	.391	1.000	.352	.352	.649
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6
BaPw	Pearson Correlation	-.076	-.386	-.386	.478	.465	1	.233	.000	-.044	.328	-.316	. ^a	.529	-.531	-.407	-.175	-.175	-.241
	Sig. (2-tailed)	.788	.155	.155	.072	.081		.404	1.000	.875	.232	.251	.	.281	.278	.423	.741	.741	.645
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6
Naps	Pearson Correlation	-.870*	-.611*	-.611*	.202	.137	.233	1	.758*	.763*	-.313	-.163	. ^a	.507	-.349	.016	.992**	.992**	.966**
	Sig. (2-tailed)	.000	.015	.015	.471	.627	.404		.001	.001	.257	.561	.	.305	.497	.976	.000	.000	.002
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6
PHs	Pearson Correlation	-.585*	-.403	-.403	.094	.048	.000	.758*	1	.972*	-.152	.196	. ^a	.506	-.350	.034	.989**	.989**	.937**
	Sig. (2-tailed)	.022	.136	.136	.740	.866	1.000	.001		.000	.590	.484	.	.306	.496	.949	.000	.000	.006
	N	15	15	15	15	15	15	15	15	15	15	15	15	6	6	6	6	6	6
ANs	Pearson Correlation	-.588*	-.405	-.405	.107	.061	-.044	.763*	.972*	1	-.144	.214	. ^a	.494	-.351	-.030	.971**	.971**	.991**

[illegible]

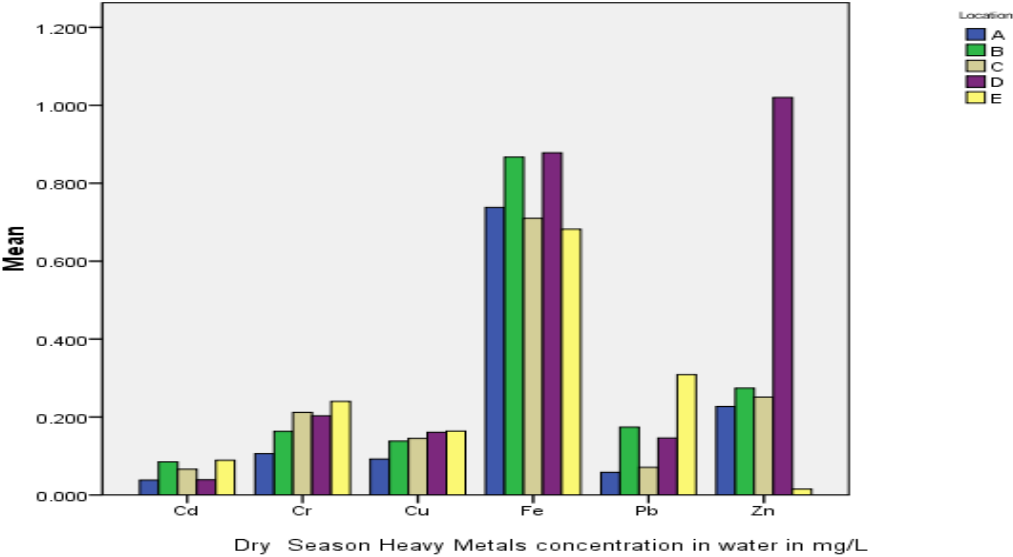
PHf	Pearson Correlation	.285	. ^a	. ^a	-.213	-.433	-. .531	-.349	-.350	-.351		-.029	.872 *	. ^a	-. .800	1	.857*	-.269	-.269	-.276
	Sig. (2-tailed)	.584	.000	.000	.685	.391	.278	.497	.496	.495		.956	.024	.	.056		.029	.607	.607	.597
	N	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
ANf	Pearson Correlation	-.046	. ^a	. ^a	.146	.000	-. .407	.016	.034	-.030		-.090	.853 *	. ^a	-. .423	.857 *	1	.129	.129	.047
	Sig. (2-tailed)	.931	.000	.000	.782	1.000	.423	.976	.949	.955		.866	.031	.	.404	.029		.807	.807	.929
	N	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
BbFf	Pearson Correlation	-. .984*	. ^a	. ^a	.642	.466	-. .175	.992* *	.989* *	.971* *		-.425	-. .085	. ^a	.499	-. .269	.129	1	1.000* *	.963**
	Sig. (2-tailed)	.000	.000	.000	.169	.352	.741	.000	.000	.001		.401	.872	.	.313	.607	.807	.000	.002	
	N	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
BkFf	Pearson Correlation	-. .984*	. ^a	. ^a	.642	.466	-. .175	.992* *	.989* *	.971* *		-.425	-. .085	. ^a	.499	-. .269	.129	1.000**	1	.963**
	Sig. (2-tailed)	.000	.000	.000	.169	.352	.741	.000	.000	.001		.401	.872	.	.313	.607	.807	.000	.002	
	N	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
BaPf	Pearson Correlation	-. .970*	. ^a	. ^a	.470	.239	-. .241	.966* *	.937* *	.991* *		-.417	-. .106	. ^a	.479	-. .276	.047	.963**	.963**	1
	Sig. (2-tailed)																			
	N																			

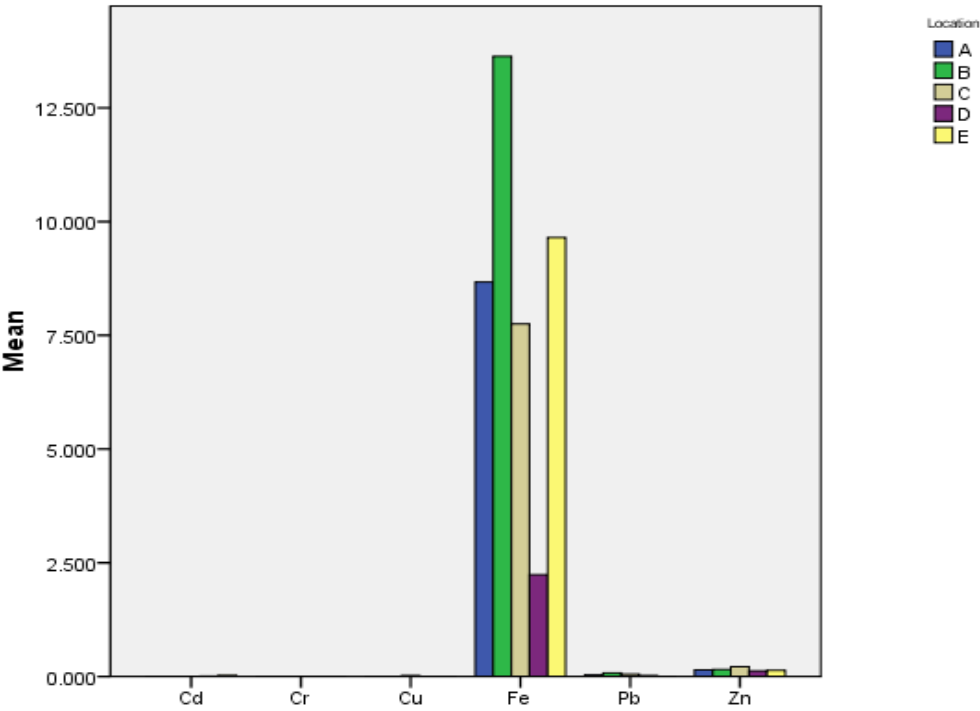
Sig. (2-tailed)	.001	.000	.000	.347	.649	.645	.002	.006	.000	.411	.842	.	.336	.597	.929	.002	.002	
N	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6

*. Correlation is significant at the 0.05 level (2-tailed).

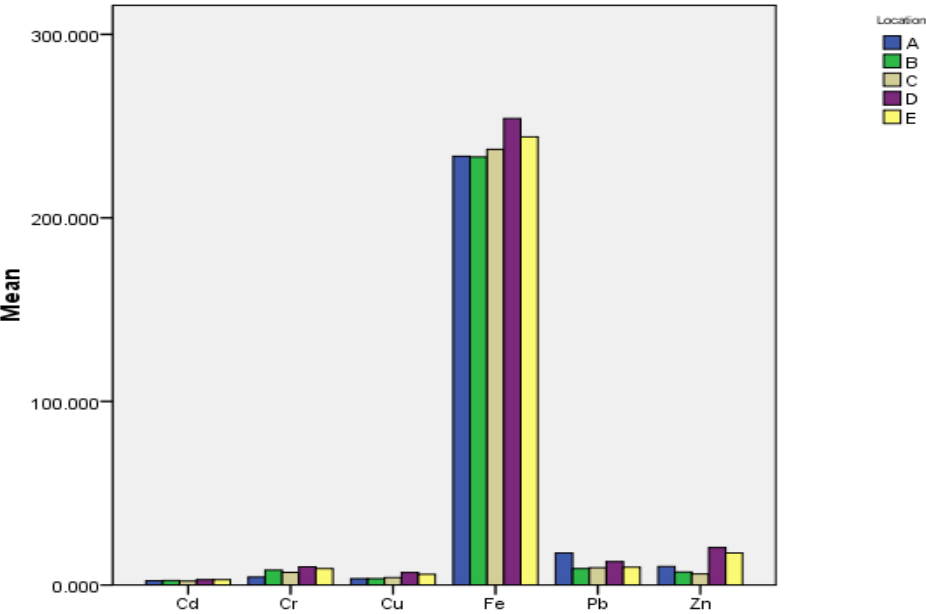
**. Correlation is significant at the 0.01 level (2-tailed).

a. Cannot be computed because at least one of the variables is constant.

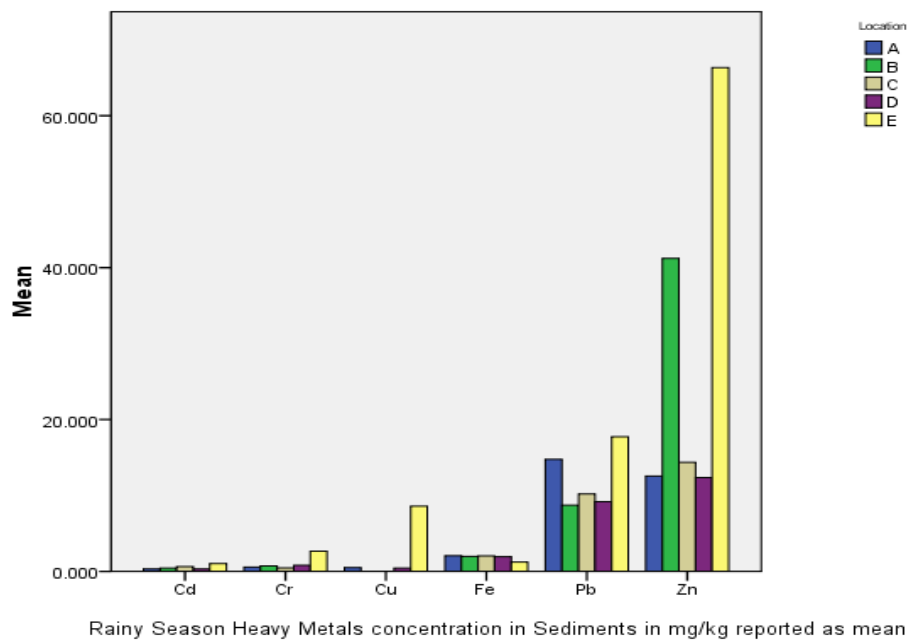


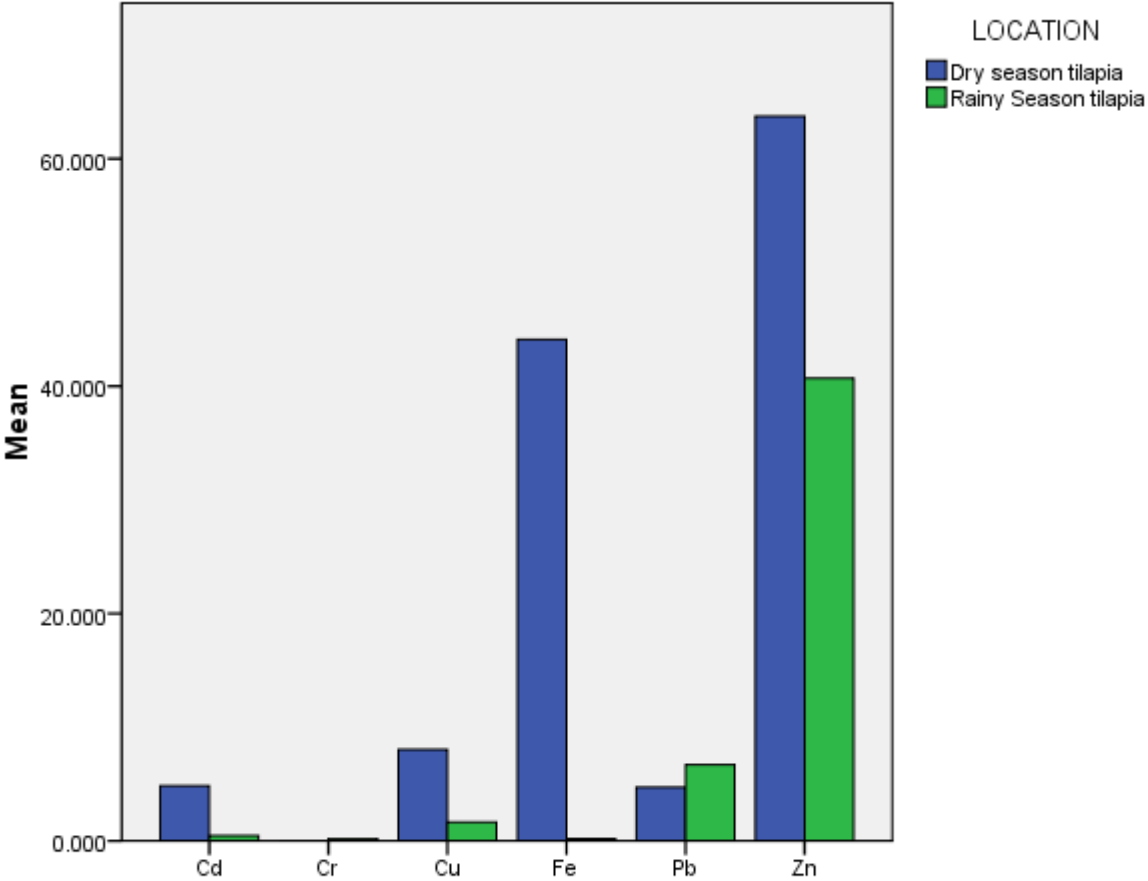


Rainy Season Heavy Metals concentration in water in mg/L reported as mean ()

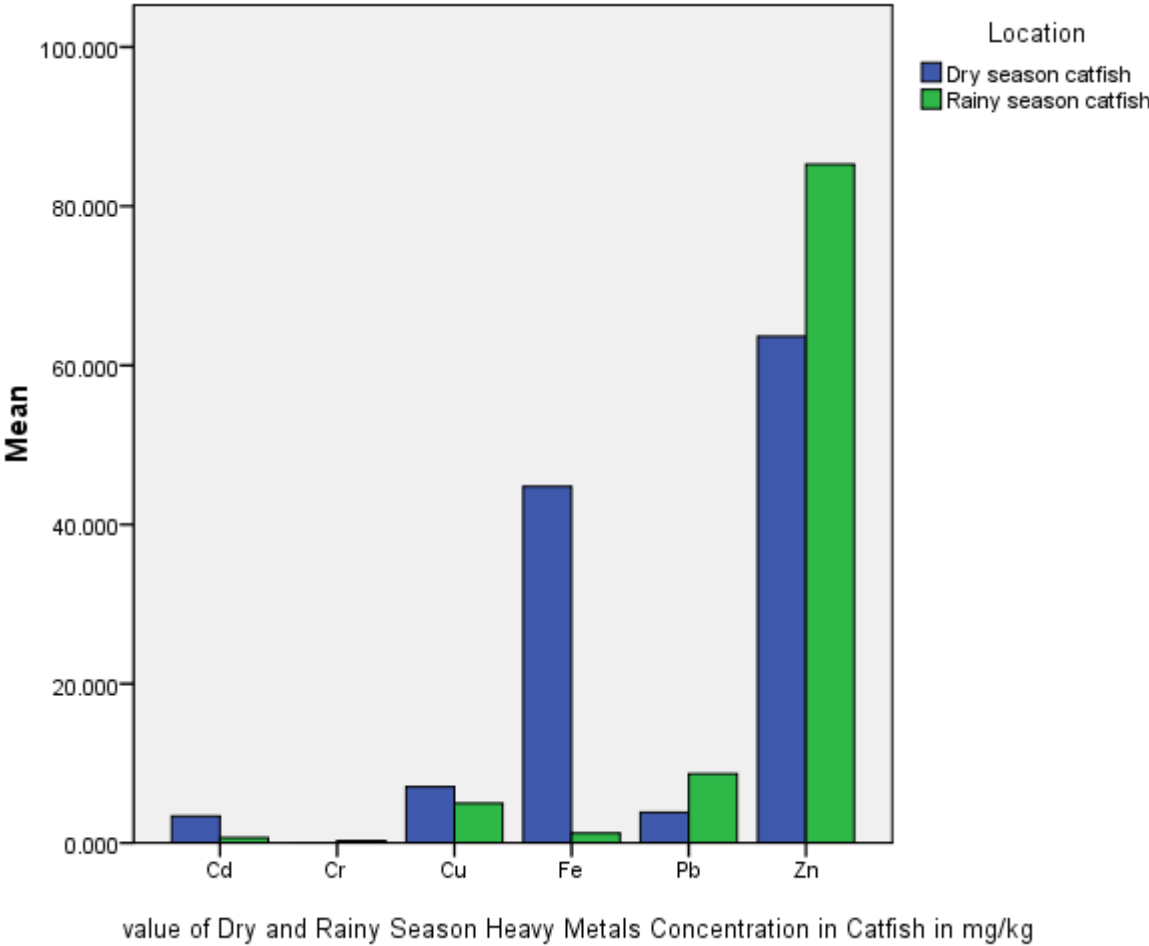


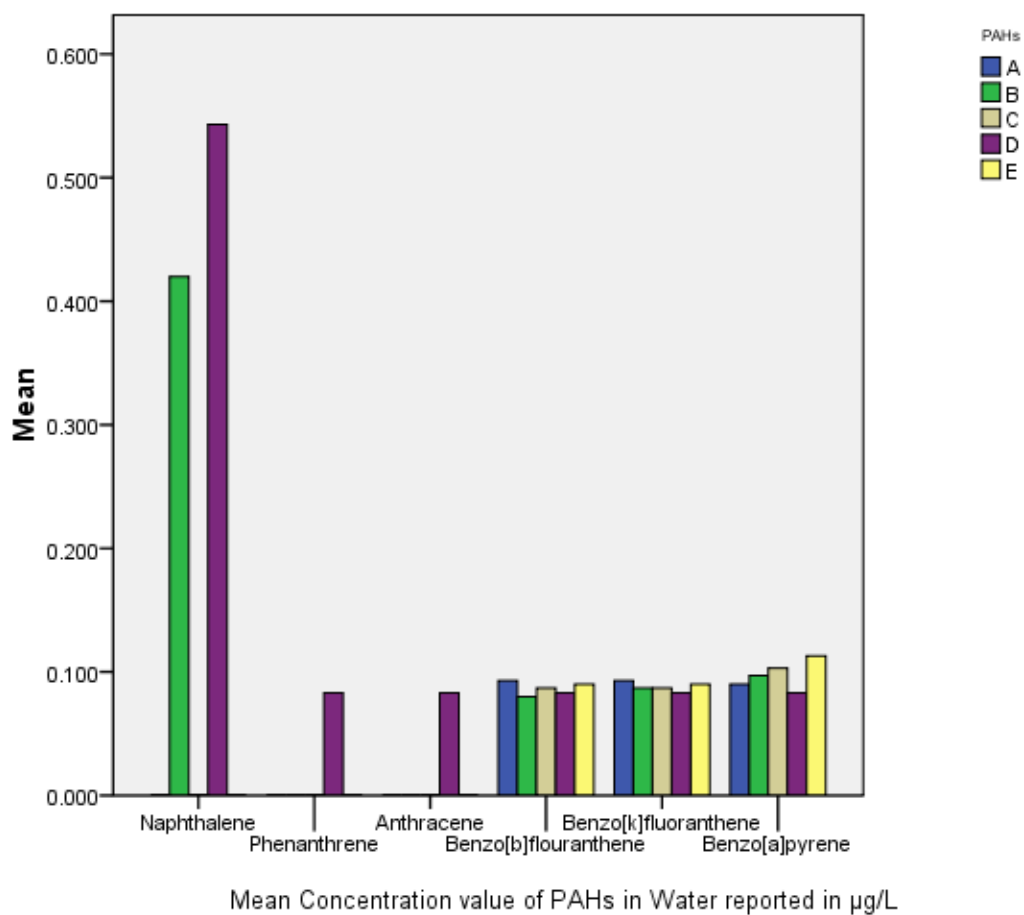
Dry Season Heavy Metals concentration in Sediments in mg/kg reported as mean

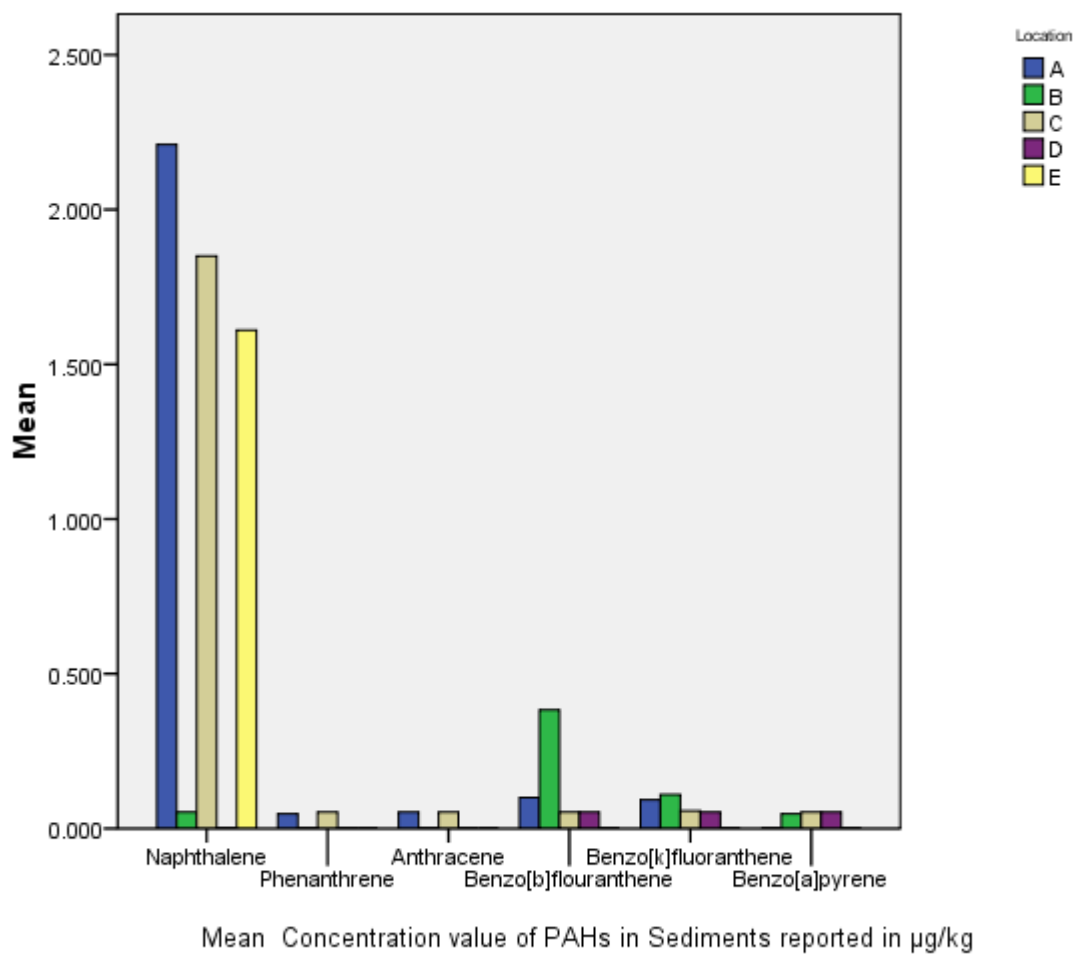


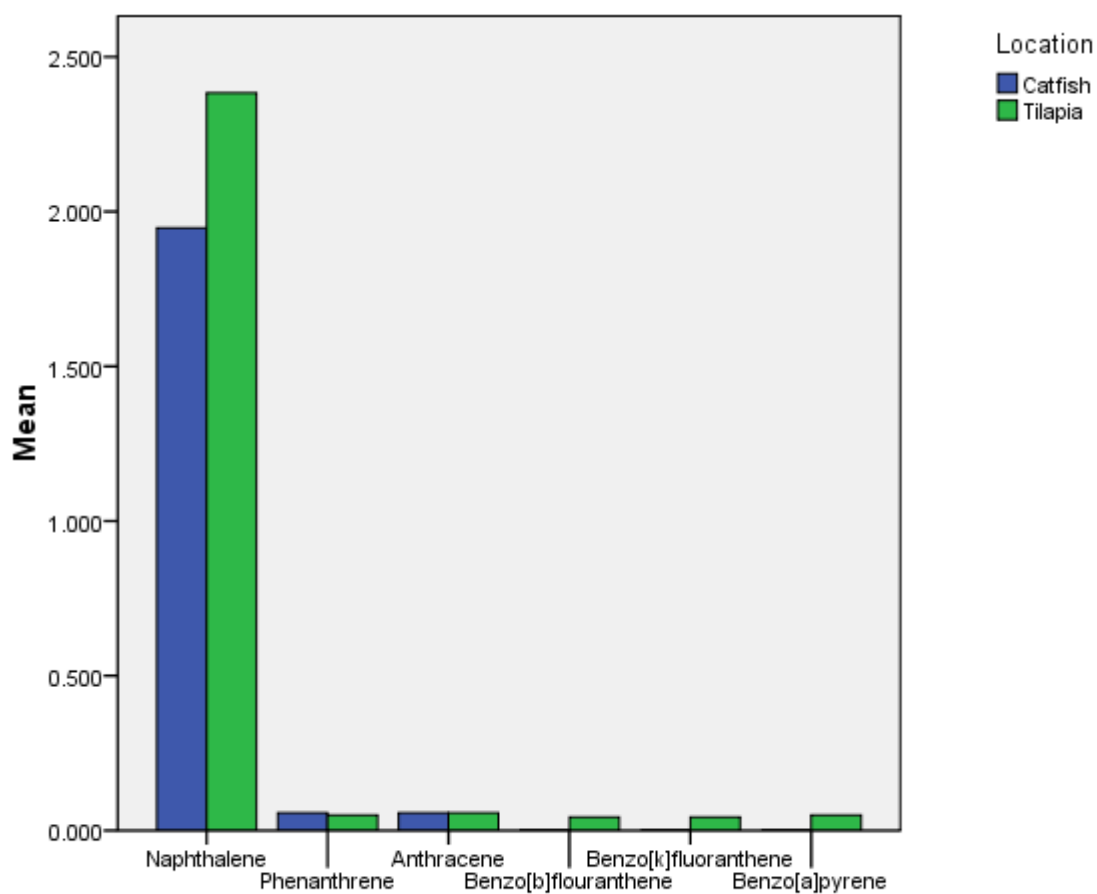


Mean value of Dry and Rainy Season Heavy Metals Concentration in Tilapia









Mean Concentration value of PAHs in Tilapia and Catfish reported in µg/kg