

**ASSESSMENT OF POLLUTION STATUS OFIMO RIVER,
SOUTH EASTERN NIGERIA**

A Ph.D. DISSERTATION

BY

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CERTIFICATION

This Ph.D. Dissertation on **Assessment of Pollution Status of Imo River, South Eastern Nigeria** was carried out by CHIKWE, OLUCHUKWU BENEDICTA, with Registration Number 2013547002F, in partial fulfillment of the requirements for the award of Doctor of Philosophy in Chemistry (Environmental Chemistry) in the Department of Pure & Industrial Chemistry, Faculty of Physical Sciences, Nnamdi Azikwe University Awka, Anambra State.

This work embodied in this dissertation is original and to the best of my knowledge has not been submitted for any other diploma or degree of this or any other university.

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DEDICATION

This Dissertation is dedicated to Almighty God and to my beloved parents Chief & Lolo Gabriel .I. Anaje (Ezekwesili 1 of Awka), for their love and support throughout my life.

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ABSTRACT

Globally the environment has been over the years faced with the challenge natural and anthropogenic waste management which affects water, sediment, fish and humans. These issues necessitated this work aimed at assessing the pollution status of upper part of Imo River, South Eastern Nigeria. This work was carried out using three parameters: physico-chemical, heavy metals concentration and PAHs analysis in three media namely: water, sediment and biota (fish). Triplicate batches of the samples were taken from three sampling points along the river coast and the physicochemical parameters analyzed in-situ and in the laboratory using gravimetric, titrimetric and spectrophotometric methods. The concentrations of heavy metals (Fe, Cd, Ni, Zn, Pb, Cu and V) in water, sediment and muscle of 2 fish species (Tilapia and Cat fish) from Imo River were analyzed using atomic absorption spectrophotometer. The results obtained were compared with both local and global standards for water, fish and sediments. The sixteen (16) priority polycyclic aromatic hydrocarbon (PAHs) were also investigated in water, sediment and fish (Tilapia and Cat fish) using gas chromatography coupled with mass spectrophotometer (GC-MS). Carcinogenic and non-carcinogenic risk models, Pearson correlation multivariate analysis of variance (MANOVA) were used to analyze the inter-relationship amongst water, sediment and fish. Seasonal variation and correlation matrix (ANOVA) of heavy metals were analyzed. The results showed that most of the parameters analyzed fall within the permissible limit except turbidity, conductivity, biochemical oxygen demand (BOD) and phosphate with mean values of 14.50NTU, 128 μ S/cm, 6.54mg/L and 0.5mg/L respectively which exceeded WHO and USEPA permissible limits of 5NTU, 100 μ S/cm, 5mg/L and 0.1mg/L. Sand was predominant in sediments with mean particle size distribution of 60.11% sand, 26.27% silt, 13.62% clay. The mean concentration of heavy metals in water from Imo River was Fe (0.019), Cd (0.0087), Pd (0.0188), Ni (0.149), Zn (0.0915), Cu (0.02) and V (0.017) while for sediment the values were Fe (1.005), Cd (0.0164), Pd (0.0575), Ni (0.055), Zn (3.185), Cu (0.99) and V (0.048)mg/kg. The mean values of heavy metals in the two fish samples were 3.925, 0.000415, 0.041, 0.055, 0.3615, 0.055, ND in Tilapia and 5.925, 0.057, 0.05, 0.0525, 0.685, 0.15 and ND in cat fish for Fe, Cd, Ni, Zn, Pb, Cu and V respectively. The mean values of LMW-PAHs in water, sediments and fishes were 0.0198, 0.1095 and 0.067 respectively while the mean values of HMW-PAHs in water, sediments and fishes were 0.072, 0.0128 and 0.006 respectively. Some of the PAHs concentration measured were within the WHO recommended limits while some PAHs such as naphthalene (0.0648), chrysene (0.0852), benzo (a) pyrene (0.300), and indeno (1, 2, 3, cd) pyrene (0.015), measured exceeded the recommended limit of (0.014), (0.000218), (0.005), and (0.0015) respectively. The cancer risk indices obtained from this study ranged from 10^{-2} to 10^{-4} . The questionnaire administered on the pollution status of Imo River showed no evidence of cholera outbreak but gastroenteritis. The results obtained from this study showed that Imo River was moderately polluted at the time of this investigation.

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LIST OF ABBREVIATIONS

AAS:	Atomic Absorption Spectrophotometer
ACE:	Acenaphtene
ACY:	Acenaphthylene
AF:	Adherence factor
ANOVA:	Analysis of Variances
ANT:	Anthracene
ANZECC:	Australian and New Zealand Environmental and Conservation Council
AOAC:	Association of Official Agricultural Chemists.
APHA:	American Public Health Association
AR:	Analytical Grade
ASTM:	American Standard Test and Method
AT:	Average Time
ATSDR:	Agency for Toxic Substances and Disease Registrar (ATSDR)
B(a)A:	Benzo(a) Anthracene
B(a)P:	Benzo (a) Pyrene
B(b)F:	Benzo(b) Fluoranthene
B(k)F:	Benzo(k) Fluoranthene
BOD:	Biochemical Oxygen Demand
BW:	Body Weight
Cd:	Cadmium
CDI:	Chronic Daily Intake
CF:	Contamination Factor
CHRG:	Chrysene
COD:	Chemical Oxygen Demand
CR:	Cancer Risk
CSF:	Cancer Slope Factor
Cu:	Copper
DB(ash) A:	Dibenzo(a,h) anthracene
DNA:	Deoxyribonucleic Acid
DO:	Dissolved Oxygen
DPR:	Department of Petroleum Resources
EC:	Electrical Conductivity
ED:	Exposure Duration

EDTA:	Ethylene diamine acetic Acid
EF:	Exposure Frequency
EI:	Estimated Intake
EU:	European Union
FE:	Fraction of Exposure
Fe:	Iron
FEPA:	Federal Environmental Protection Agency
FLT:	Fluoranthene
FLU:	Flourene
GCIFID:	Gas Chromatograph/Flame Ionization Director
GIS:	Geographic Information System
GPS:	Global Positioning System
GS-Ms:	(Gas Chromatograph-Mass Spectrometer.)
HCL:	Hydrochloric Acid
HMW:	Higher Molecular Weight
HNO ₃ :	Trioxonitrate (v) Acid
HPLC:	High Performance Liquid Chromatograph
HQ:	Hazard Quotient
IC:	Inorganic Carbon
IH:	Inhalation rate
IMR:	Imo River
Inden (1,2,3,cd)P:	Indeno (1,2,3,cd) Pyrene
IPCS:	International Programme in Chemical Safety
IR:	Injection rate
Igeo:	Geo accumulation Index
LMW:	Lower Molecular Weight
MANOVA:	Multivariate Analysis of Variance
Med:	Modified Degree of Contamination
MNAP:	Methylnapthlene
MPI:	Metal Pollution Index
MPN:	Most Probable Number
NAFDAC:	National Agency for Food Drug Administration and Control
NAP:	Naphthalene
NEMA:	National Emergency Management Agency

Ni:	Nickel
NIS:	Nigeria Industrial Standard
NOAA:	National Oceanic and Atmospheric Administration
NSDW:	National Standards for Drinking Water
NTU:	Nephelometric Turbidity Unit
PAHS:	Polycyclic aromatic Hydrocarbons.
Pb:	Lead
PCC:	Pearson Correlation Coefficient
PEF:	Particulate Emission factor
PHEN:	Phenanthrene
PLI:	Pollution Load Index
Pyr:	Pyrene
RFD:	Oral Reference Dose
SA:	Surface Area
SF:	Slope Factor
SON:	Standard Organization of Nigeria
TC:	Total Carbon
TDS:	Total Dissolved Solids
TEC:	Threshold Effect Concentration
TEF:	Total Equivalent Factor
TEL:	Threshold Effect Level
TF:	Transfer Factor
THQ:	Target Hazard Quotient
TOC:	Total Organic Carbon
TSS:	Total Suspended Solids
USEPA:	United State Environmental Protection Agency
UV/VIS:	Spectrophotometer, Ultra Violet/Visible Spectrophotometer
V:	Vanadium
WHO:	World Health Organizatio

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Water, sediment and (fish) and affected rivers are direct recipients of industrial waste and municipal sewage (Amadi, 2010). Changes in water chemistry of rivers are usually anthropogenic via domestic, industrial and agricultural discharges which may in turn result to degradation of aquatic ecosystems (Ugwu and Wakam, 2012). One of the most critical problems of developing countries is improper management of vast amount of wastes generated by various anthropogenic activities. More challenging is the unsafe disposal of these wastes into the ambient environment. Water bodies especially fresh water reservoir (rivers) is the most affected. This has often rendered these natural reservoirs unsuitable for both primary and secondary usage (Fakayode, 2005). Industrial effluent contamination of natural water bodies has emerged a major challenge in developing and densely populated countries like Nigeria. Estuaries and inland water bodies, which are major sources of drinking water, in Nigeria are often contaminated by the activities of adjoining populations and industrial establishments (Adesuji, 2016). River systems are the primary means for disposal of waste especially effluents from industries that are near them. These effluents from industries have a great deal of influence on the pollution of the water body. These effluents can alter the physical, chemical and biological nature of the receiving water bodies.

Increased industrial activities have led to pollution stress on surface water both from industrial, agricultural and domestic sources (Ajayi *et al.*, 1981). Water pollution refers to the introduction by man directly or indirectly of substance or energy into the marine environment (including estuaries) resulting in deleterious effects such as harm to living organisms, hazards to human health, hindrance to marine activities including fishing, impairment of quality use of river water and reduction of amenities (Dan *et al.*; 2014). Rivers drain urban, suburban and rural areas where they collect more pollutants. Rivers are by far the cheapest form of water supply compared to other sources like groundwater and sea water (Amadi *et al.*, 2010).

Meeting water quality expectations for streams and rivers is required to protect drinking water resources, encourage recreational activities and to provide a good environment for fish and wildlife. Therefore, assessment of pollution status of water (rivers) is of ecotoxicological importance. Of the aquatic ecosystem (Aiyesanmi *et al.*, 2012), water soluble wastes and other materials that are dumped, spilled or stored on the surface of the land or in sewage disposal pits can be dissolved by precipitation, irrigation. Water or liquid wastes can eventually seep through the well in the unsaturated zone to pollute the rivers. Thus constant monitoring of rivers quality /assessment is needed so as to record any alteration in the quality and outbreak of health disorder. Sediment sources in aquatic ecosystem include soil erosion, decomposition of plants and animals and discharge of effluents (USEPA, 2012). Wind and water help to carry these particles to rivers. Soil disturbance due to massive road construction and demolition of structures in Imo State and Abia State could significantly increase the load of sediments of Imo River. Sediments are contaminated with different pollution from effluent discharges and run off into the Imo River. (Ogwo and Okereke, 2014). The percentage of silt and clay in river sediments can have impact on the structure of the biotic assemblage. Heavy metals are wide spread pollutants of great environmental concern as they are non-degradable, toxic and persistent with serious ecological ramifications (Jumb and Nardin, 2009). Humans have always depended in aquatic resources for food, medicines and materials as well as recreational and commercial purposes such as fishes and tourism (Chopora *et al.*; 2009). Aquatic ecosystems are strongly influenced by long term discharge of untreated domestic and industrial wastewater, storm water runoff, accidental spill and direct solid waste dumping (Amadi, 2010). All these have a great ecological impact on the river quality and its surrounding food web (Uma, 1989). Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous anthropogenic pollutants that can be biologically amplified to high concentrations in food webs. Due to their lipophilic, persistence and high toxicity, these residues are readily accumulated in the tissues of non-target living organisms where they may cause detrimental effects. PAHs are toxic, carcinogenic and mutagenic to all organisms, including humans (Al-Kahtani, 2009). The main sources of these contaminants in the environment include forest fire, natural petroleum seeps,

combustion of fossil fuels, coal burning and use of oil for cooking and heating. Other sources include domestic and industrial waste waters and sewage. As a consequence, environmental contamination by PAHs has steadily increased in recent years (Ezekwee *et al.*, 2013).

Pollution of river bodies has become major and global problem due to inadequacy of surface water protection measures. Wastes are usually discharged into the rivers. Discharge of sewage, garbage, oil spills and industrial effluents are threats to the diluting capacity of rivers (UNESCO, 2006); hence constant assessments of the water quality conditions of receiving water bodies are very critical to effective planning and management. Pollution of water bodies (rivers) by heavy metals and polycyclic aromatic hydrocarbons (PAHs) is a major challenge facing both the developed and the developing nations. There is therefore, the need to carry out assessment of pollution status of Imo River in order to regulate this ugly trend. The three relevant parameters: physicochemical analysis, heavy metal concentration and analysis of polycyclic aromatic hydrocarbons (PAHs) will be used to assess the pollution status of upper part of Imo River, South Eastern Nigeria. Physicochemical parameters such as colour, pH, temperature, dissolved oxygen, turbidity, salinity, total dissolved solids, total suspended solids, biochemical oxygen demand, chemical oxygen demand, chemical oxygen demand, total hardness, alkalinity, acidity, phosphate, nitrate, sulphate, bacteriological analysis are necessary to ascertain the water quality index of Imo River which gives information on quality of the Rivers. The physicochemical characteristics of Imo River are important in the determination of its productive capacity and effect on the biota (Duru and Nwanekwu, 2012). Heavy metals and polycyclic aromatic hydrocarbons may enter the sediment and aquatic environments via industrial waste disposal, refuse, sewage, application of fertilizers and pesticides, atmospheric deposition (Amadi, 2010). Heavy metal concentrations analysis of water, sediment and fishes will be used to ascertain the mobility of the heavy metals, and the bioaccumulation and bio-magnification of these heavy metals in tilapia and cat fish and the adverse health risk these metals may pose on communities that use water from Imo River. The Environmental Protection Agency (EPA) concentrated on the sixteen polycyclic aromatic hydrocarbons that are included in their list of 126 priority pollutants. These compounds have been

chosen on the basis of frequency of occurrence at hazardous waste sites and toxicity potential for human exposure (Zhang *et al.*, 2011). Polycyclic aromatic hydrocarbons are mostly discharged into Imo River industrial effluents, domestic sewage, agricultural run-offs and vehicular emulsion. The concern is therefore that PAHs are detrimental to human beings (can impair survival and growth by causing abnormal reproduction and development). This study was carried out to assess the pollution status upper part of Imo River using water samples, sediment and biota (fishes).

1.2 Statement of Problem

Most of the available literature on the pollution status of Imo River deal more on physico-chemical parameters or concentration of heavy metals in water, sediment or biota. Literature available suggest that most studies conducted so far on pollution status of Imo River have not considered the sixteen(16) priority polycyclic aromatic hydrocarbons (PAHs) that are carcinogenic, mutagenic and tetragenetic. Hence this study will be useful in assessment of human health risk of pollutants, heavy-metals and polycyclic aromatic hydrocarbons in water, sediments and fish from upper part of Imo River.

1.3 Aim and Objectives of the Study

The aim of this work is to assess the pollution status of Imo River South Eastern Nigeria.

The specific objectives are to:

- (i) determine the physico-chemical parameters in water and sediment from Imo River.
- (ii) determine concentration of heavy metals in water, sediment and fish from Imo River.
- (iii) determine the level of some polycyclic aromatic hydrocarbons in water, sediments and fishes.
- (iv) correlate between heavy metals and polycyclic aromatic hydrocarbons in water, sediment and fish.

- (v) determine the potential health and ecological risk assesment of the above contaminants and pollutants using risk assessment models.

1.4 Scope of Study

The scope of study covered reconnaissance survey of the study area, mapping of sampling location, field sampling of water, sediment and biota (fish) from Imo River in-situ and laboratory analysis of samples. The analysis in the laboratory involved:

- i. determination of physico-chemical parameters of water, sediments and fish.
- ii. determination of heavy metals in water, sediments and fish.
- iii. determination of polyaromatic hydrocarbons in water, sediments and fish.
- iv. statistical analysis of data generated and interpretation with application of risk assessment models.

1.5 Significance of Study

The study is relevant to both the environmentalists and researchers as it will redound to knowledge of heavy metals contamination of Imo River. The findings of this study will be of immense benefit to the Federal Ministry of Environment in their plan to reduce pollution. This work will provide insight on the mobility and fate of heavy metal contaminants in the study area. Analysis of biota (fish) will give information on biological availability of the contaminants, its bioaccumulation and bio magnification along the food chain. The findings of this study will help to educate residents and those who depend largely on water and biota (fish) from the study area on dangers of heavy metals and polycyclic aromatic hydrocarbons toxicity. The inhabitants of the study area will benefit from this study, since the health risk assessment will help in predicting the level of human exposure to carcinogenic and non-carcinogenic effects. Finally, this study will serve as a future reference to health workers and researchers in the field of chemistry and environmental studies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Physicochemical Parameters in Water and Sediment

The use of agrochemicals especially fertilizers and pesticides have no doubt resulted in improvement in food production and control of disease but affect farmlands and domestic water supply sources (Egejuru *et al.*, 2014). In addition to these effects, they also modify the physicochemical properties and microbial diversity of affected sediment. Wyszkwaska and Kucharski (2000), Udosen and Benson(2003)., revealed that Imo River estuary is impacted with low contamination of trace metals largely influenced by both natural and anthropogenic input.

2.1.1 Colour

Amadi (2010) reported in his work that the colour of Oramiriukwa was clear. He stated thatthe colour of water sample can be reported as:

Apparent colour: is the colour of whole water sample and consists of colour from both dissolved and suspended material.

True colour: is measured after filtering the water sample to remove all suspended material.

Okeke *et al.*; (2013) in their study of water quality of Otamiri River in Owerri found that Otamiri River was colourless.

Testing for colour can be a quick and an easy test which often reflects the amount of organic material in the water, although certain inorganic components like iron or manganese can also impart colour (Oguzie, 2013). Dissolved and particulate material in water can cause discolouration. Slight discolouration is measured in Hazen units (HU). Impurities can be deeply coloured as well, for instance dissolved organic compounds called tenny can result in dark brown colours or algae floating in the water (particle) can impart a green colour.

Water colour can reveal physical, chemical and bacteriological conditions e.g. green indicates copper /lead from copper plumbing or algae growth. Blue can indicate copper or might be caused by back flowing. Reds can be signs of rust from iron pipes or air borne bacteria. Black water can indicate growth of sulphur indicating bacteria (WHO, 2008).

2.1.2 Temperature:

Ajayi and Osibanjo (2016) observed that temperature levels are higher in the dry season than in other seasons because of higher air temperature. Ezemonye (2009) found out that higher temperature makes metals more toxic to aquatic life and it affects the ability of water to hold oxygen. Also growth of micro organisms, taste, odour, colour and corrosion problems may increase. Okeke *et al.*, (2013) found out that temperature values of Otamiri along Imo River ranged from 30.6-32.2⁰C in dry season and 27.0-28.6⁰C in wet season. Water temperature is not only important to swimmers but also to industries, fish and algae. The temperature of water can affect downstream habitats.

2.1.3 pH

Ajayi and Osibanjo (2016) in his study revealed that Asa River is an anoxic estuarine ecosystem influenced by both fresh water characteristics and oceanic input. Ajayi and Osibanjo (2016) observed that temperature levels are higher in dry season than other seasons because of high air temperature along Imo river estuary. Okeke and Adinna (2013) assessed water quality of Otamiri River in Owerri along Imo River, Nigeria. They found out that the mean pH value of the dry season water samples (6.5) and rainy season (6.4) fell within the stipulated limits of 6.0-8.5 for drinking water. Although the dry period had slightly higher values, the difference between the two seasons was not significant. The lower pH values obtained in the study area could be linked to predominant soil type in the river (Adeniji, 2000). It is often useful to characterize an environment such as body of water by measuring its pH. pH is a measure of the acidity of the water or sediment based on its hydrogen ion concentration and it is mathematically defined as the negative logarithm of the hydrogen ion concentration or $\text{pH} = -\log [\text{H}^+]$; where the bracket around the H^+ symbolizes concentration. The pH of a media (soil or sediment/water) ranges on a logarithmic scale of 1-14, where pH 1-6 are acidic,

pH 7 is neutral and pH 8-14 are basic. Lower pH corresponds to higher H^+ , while higher pH is associated with lower $[H^+]$ (APHA, 1992).

2.1.4 Electrical Conductivity:

Onyegemeet *et al.*, (2016) observed electrical conductivity of 17.24-22.5 $\mu\text{S}/\text{cm}$ in Chokocho, Edegelem and Imeh rivers along Imo River. Duru *et al.*; (2012) in his assessment of Nworie River Owerri observed conductivity values of 100.0-193.2 $\mu\text{S}/\text{cm}$. Conductivity shows significant correlation with ten parameters such as temperature, pH value, alkalinity, total hardness, calcium total solids and total dissolved solids, chemical oxygen demand, chloride and iron concentration of water (Amadi, 2010). It is measured with the help of EC meter which measures resistance offered by the water between two platinized electrodes. The instrument is standardized with known values of conductance observed with standard KCl solution.

2.1.5 Total Dissolved Solids (TDS)

Okeke and Adinna (2013) found out that total dissolved solids varied spatially and temporarily. They found out that dry season concentrations were higher than the wet season values. It was found out that total dissolved solids concentration of Otamiri River water sample ranged from 18.6mg/L -217.3mg/L in dry season and 16.5-179.9 in rainy season. Olawale (2016) in his research on physicochemical analysis of water from Asa river, Ilorin Nigeria observed total dissolved solid (TDS) of 33.03 – 10.0 in wet season and TDS value of 33.03 – 135 in dry season. Alabaster and Lloyd (2000) reported that total dissolved solids (TDS) in excess of 1200 were not likely to support good fresh water organisms, while Namingo and Williams (2006) reported a TDS level not greater than 1000 for most industrial and domestic water requirements. Olorode (2016) observed that these physico-chemical parameters: temperature, pH, conductivity, total dissolved solids (TDS) for Imo River and Bonny river were high in dry season than in rainy season which was in correlation with the work of Amadi (2010). Total dissolved solid is a measure of the combined content of all inorganic and organic substances contained in liquid/water sample. Measurement of TDS helps in the study of water

quality for streams, rivers and lakes. It is used as an indication of aesthetic characteristics of drinking water. Primary sources for TDS in receiving waters are agricultural and residential runoffs, clay rich mountain waters, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants.

2.1.6 Total Suspended Solids

Olawale (2016) reported that the value of total suspended solids ranged between 16.13 – 152.3mg/L for the dry season analysis and 12.73 -244 for the wet season analysis with an overall mean of 119.32. He attributed the wet season increase in total suspended solid in Asa River to large amount of silt and debris held in suspension just before the rains.

Suspended sediment is the amount of soil moving along a stream. It depends on speed of water flow. Total suspended solids are differentiated from total dissolved solids in that the former cannot pass through a sieve of two micrometers and they are indefinitely suspended in solution.

2.1.7 Turbidity

Turbidity is an important operational parameter in process control and can indicate problems with treatment process particularly coagulation /sedimentation and it causes undesirable taste and affects the process of photosynthesis for algal growth (Nwadiaro, 2002). Turbidity reflects the materials dispersed or dissolved in the water column, be they living organisms or not, organic or inorganic. Ajibare (2013) found out that turbidity value of 41.95 NTU and 45.36NTU were recorded in Bijimi and Asumogbu rivers respectively. Reports of Amadi(2010) and Nkwoji (2010) showed that the salinity of coastal rivers of Imo State was between 16.35 and 16.50mg/L. Patnak (2010) observed that low pH values of a river indicate poor buffering capacity of total alkalinity and may also be as a result of organic matter decomposition. Amadi (2010) said that a river can self purify itself if BOD is below 4. Duru Majesty *et al*; ((2012) found at that low pH of 5.69-5.80 observed at Nworie River could lead to acidosis, which result in peptic ulcer. They also observed that some solids found in Nworie

river exist as total suspended or dissolved solids. Total solids were observed to be 64.29-320mg/L. Consumption of water with high solids could lead to gastro intestinal upset caused by gastro intestinal diseases (APHA,2005). Nworie River recorded colour of 8.33- 43.50 Pt/Co unit which could be attributed to solid waste dumped in the river (Ezemonye, 2009). Turbidity is the cloudiness or haziness of a water/fluid caused by large numbers of individual particles that are generally invisible to the naked eye. The measurement of turbidity is a key test of water quality. Nephelometer is used in measuring turbidity. (EPA,1993).

2.1.8 Nitrate

Nwosu (2013) in his study on physicochemical analysis of the upper reaches of Imo River reported that nitrate concentration was over two times above the recommended value for drinking water. Ijehet *al*; (2012) recorded nitrate values of 4.50, 4.10, 1.90 and 1.02 in Umuosu Umuduru, Amaigbo and Afara Umuahia respectively. He regarded that nitrate is an indicator of pollution in public water supply in Groundwater in parts of Imo River Basin, South Eastern Nigeria. Nitrate is commonly monitored for environmental protection purposes in agricultural, food control. Owing to the information of carcinogenic N-nitrosamines and being also essential to indicate organic pollution in water, many spectrophotometric methods are available for determination of nitrate (Mohammad, 2011). It is measured spectroscopically at 425nm radiation by making a colour complex with Nessler's reagent. The conditions of reaction are alkaline and cause severe interference from hardness in water.

2.1.9 Phosphate

Nwidu (2000) assessed water quality in Imo River at Oyigbo Local government area of Rivers State. In her study, she reported phosphate values of 0.07 – 0.11mg/L which exceeds WHO's permissible limit of 0.1. Phosphates enter water ways from human and animal waste, phosphorus rich bedrock, laundry, cleaning, industrial effluents and fertilizer runoffs.

These phosphates become detrimental when they over fertilize aquatic plants and cause stepped up eutrophication of 0.01-0.03level in uncontaminated lakes.

2.1.10 Sulphate

Okoro *et al.*; (2016) recorded sulphate values of 6.8 – 10.2mg/L in his investigation of surface water quality in Owerri Municipal. Ijeh (2012) recorded sulphate values of 0.02 – 12.50 in both seasons. Ejiogu *et al.* (2016) observed average sulphate concentration levels of water samples of Owerri dumpsite and environs of 74.00 was below the SON standard of 100 while the concentration levels of Orlu surface water was 567.50 and was above the WHO standard value of 400. It is measured by nephelometric method in which the concentration of turbidity is measured against the known concentration of synthetically prepared sulphate solution. Barium chloride is used for testing turbidity.

2.1.11 Dissolved Oxygen

The dissolved oxygen (DO) of water is an important environmental parameter for the survival of aquatic life. Dissolved oxygen affects the growth, distribution, behavior and physiology of fish and other aquatic organisms (Chindah, 2003). Dissolved oxygen concentration of 5.0mg/L and above are desirable for fish survival Abowei, (2010). Low dissolved oxygen concentrations are known to be one of the major problems of fauna and floral survival in the aquatic environment. This has been reported by (Erik *et al.*, 2016) in their study of Black and Baltic Sea. Numerous scientific studies suggest that 4-9 of DO is the optimal range that will support a large, diverse fish population. As a general rule concentration of DO above 5 is considered supportive of marine life, while concentrations below this are potentially harmful. At about 3mg/L, bottom fishes may start to leave the area and the growth of sensitive species such as crab larvae / juvenile is reduced (Ajibare, 2014). Ajibare (2014) found out that the quantity of mean dissolved oxygen in coastal river of Ondo state range from 7.53 -7.66 with a mean value of 7.58mg/L. The mean value agrees with the report of Boyd and Lich (2002) that dissolved oxygen of 5.0mg/L is desirable for fish survival.

Dissolved oxygen (DO): is a measure of the quantity of free oxygen molecules in water. The concentration of DO is an important indication of the health of an aquatic ecosystem because

oxygen is essential for almost all forms of life (Akpan, 2005). Ongoing low dissolved oxygen in a water body will harm most aquatic lives because there will not be enough oxygen to sustain life. DO is measured using dissolved oxygen meter or DO meter or electrochemical or optical sensor. The best method is to take the measurement in the field at the same time each day. DO concentrations can vary throughout a 24 hour periods. Dissolved oxygen testing equipment usually allows oxygen concentrations to be measured in both milligrams per litre (mg/L). There are three methods available for measuring dissolved oxygen concentrations. Modern Techniques involve either an electrochemical or optical sensor. The dissolved oxygen sensor is attached to a meter for spot sampling and laboratory application. In dry season, dissolved oxygen decreased due to increase in temperature and due to increased in microbial activity (Amadi, 2010).

2.1.12 Biochemical oxygen demand (BOD)

Arimoro *et al*; (2014) observed that biological oxygen demand fluctuated between 0.3 and 54.4mg/L in the assessment of Warri River. He found out that upstream station recorded lower values of BOD. Onuoha(2003) in his findings on impacts of anthropogenic activities on water quality of the Onuimo reported that BOD is a fair measure of the cleanliness of any water on the basis that values less than 2mg/L are clean, 3 – 5mg/L fairly clean and 10mg/L definitely bad one or polluted. Biochemical oxygen demand is the amount of dissolved oxygen needed by aerobic biological organism to break down organic material present in a given water sample at a certain temperature over a specific time period. The BOD value is most commonly expressed in milligrams of oxygen consumed per litre of sample during five days of incubation at 20°C (Clair, 2003). The method used in measuring BOD in water sample is incubation followed by titration. $BOD = \text{mgO}_2/\text{L}$. The modern technique is the use of biosensor BOD analyzer. The measurement of the BOD takes place in less than four minutes.

2.1.13 Chemical Oxygen Demand (COD)

Olaleye and Adeniji (2005) reported COD values of 20 -80mg/L in physical and chemical hydrology of water bodies. They noticed that chemical oxygen demand fluctuated between 10

and 80mg/L. Amadi (2010) found out that BOD turns out to be the most significant value that influences COD value. He also found out that phosphate concentration is the second factor that contributes to the COD value. Akpan- Itah (2005) observed COD values that ranged from 0.02-0.6mg/L. Chemical oxygen demand is another measure of organic material contamination in water specified in mg/L. COD is the amount of dissolved oxygen required to cause chemical oxidation of organic matter in water. The COD test only requires 2-3 hours. The COD test can be used to measure the strength of wastes that are too toxic for BOD test (Etim and Adie, 2012). It is commonly expressed in mass of oxygen consumed over volume of solution which is SI unit is milligrams per litre (mg/L). COD is useful in terms of water quality by providing a metric to determine the effect an effluent will have on the receiving body much like biochemical oxygen demand (BOD) (Clair *et al*; 2003). The clean method to determine chemical oxygen demand is the electrochemical oxidation using OH-radial using COD digester with focused microwave digestion method (Patnak, 2010)

2.1.14 Total Hardness

Akubugwo *et al.*, (2013) in their study of water quality of Njaba river Imo State observed total hardness of 60.00mg/L in Imo tributaries and total hardness of 50.00, 20.00 and 60.00 in confluence, upstream and downstream respectively. The values they obtained were below the permissible limit of 250 recommended by World Health Organization (WHO, 2003). Hardness is frequently used as an assessment of the quality of water samples (Table 2.1). The hardness of water is governed by the content of calcium and magnesium salts (temporary hardness), largely combined with bicarbonate and carbonate and with sulphate (Luo, 2016). Hardness can be measured by calculation of calcium and magnesium ions in the sample (Patnaik, 2010).

Table 2.1 Selected National and International Water Quality Standards

S/N		NAFDAC	SON	FEPA	NSDW	WHO	EU	USEPA
Conductivity		1000	1000	70	1000	-	-	-
Total dissolved solid		500	500	500	500	1000	-	500
pH		6.5-8.5	6.5-8.5	6.0-9.0	6.5-8.5	6.8	6.5-9.5	6.5-8.5
Total hardness		100	100	-	150	100	-	-
Total alkalinity		100	100	-	-	100	-	-
Nitrate		10	10	20	50	50	50	10
Total temperature		-	-	26	-	40	-	-
Dissolved oxygen		-	-	≥4	=	≥6	-	-

Source: Nigeria Industrial Standard NIS 554:2007

Table 2.2: Selected National and International Water Quality Standards

S/N	NAFDAC, 2007	SON, 2007	WHO,1983; 2008	EU, 1998	USEPA, 2005
Conductivity (us/cm⁻¹)	1000	1000	-	-	-
Total dissolve sol- ids(mg/L)	500	500	1000	-	500
pH	6.5-8.5	6.5-8.5	6.8	6.5-9.5	6.5-8.5
Total hard- ness(mg/L)	100	100	100-	-	-
Total alkalinity (mg/L)	100	100	100-	-	-
Chloride (mg/L)	100	100	250	250	250
Nitrate(mg/L)	10	10	50	50	10
Carbonate	-	-	-	-	-
Calcium	75	75	-	-	-
Biochemical oxygen demand	-	-	-	-	-

Source: Nigeria Industrial Standard NIS 554:2015

Table 2.3 Classification of Water Samples according to Hardness Level

Range(mg/L)	Hardness level
0.05	Soft
50 to 100	Moderately soft
100 to 150	Slightly hard
150 to 200	Moderately hard
Over 299	Hard
Over300	Very hard

Source: WHO Guidelines for Drinking Water Quality (2013).

2.1.15 Total Viable Bacteria

Okorundu (2015) reported that heterotrophic bacteria are found in water and could be from human/animal wastes, runoffs, pasture, natural soil or plant, sewage and other agricultural wastes. The WHO standard for total heterotrophic count is 1.0×10^2 in 100mL of count. They observed that all water samples from Oguta Lake water, Imo State were higher than WHO standard of zero (0) MPN in 100L for drinking and recreational water. According to WHO (2004) drinking water can be graded into four (4) categories depending on their most probable number (MPN) value. Water with MPN of zero (0) is excellent, MPN of 1-3 is satisfactory, MPN of 4-10 suspicious and MPN above 10 is unsatisfactory. Water MPN of 3 is not suitable for drinking WHO (2004).

2.1.16 Total Coliform Bacteria

Ndukwu *et al.*, (2016) observed that water samples from Otamiri River Imo State and its catchment communities in Rivers State have total coliform bacteria and faecal coliform bacteria between values of 0-10 MPN index 100mL^{-1} , which were higher than WHO (2004) accepted limit especially in all the stations. Akpan-Itah (2005) revealed the presence of coliform bacteria in Otamiri- Oche River. They stated that the presence of coliform bacteria in water makes it unfit for drinking.

2.1.17 Salinity

Arimoro (2008) found out that salinity varied between 13.65 and 52.05 in three different locations along Warri River. Amadi (2010) determined the salinity of eleven (11) rivers in Imo State with a view of classifying them for irrigation.

Salinity is the saltiness or amount of salt dissolved in a body of water. It is measured in parts per thousand (ppt). The salinity of water sample can be measured using a refractometer or by measuring the conductivity of a particular sample and total dissolve solids and correlating them (Akpan-Itah, 2005)

Methods of salinity determination include:

- i. Evaporation of sample
- ii. Conductivity of sample
- iii. Measurement of water density by hydrometer refraction of light.
- iv. Titration of the chloride ion (Cl^-)

Salinity = weight of salt/weight of water x 100%(2.1)

Determination of Salinity by Refractometer

A refractometer can precisely measure the amount of refraction that is caused by the density. The boundary between blue region and white region on the scale represents the sample's salinity. The titration method is accurate but complicated because chloride will be precipitated first using silver nitrate AgNO_3 (Arulananthan, 2000)

2.1.18 Acidity

Ejioguet *al.*, (2017) observed that acidity level within Imo River exceeded WHO permissible limit for drinking water. Acidity is an important parameter used to determine the quality of water. Acidity affects many things including chemical reaction rates, biological processes and corrosiveness (Adebisi, 1981). It can also be used to monitor pollution in water bodies (river). Acidity in water can be determined using acid base titration method.

Calculation:

$$\text{Acidity in mg/L as CaCO}_3 = A \times B \times 50,000 / V \quad (2.2)$$

A=mL of NaOH titrant

B= normality of NaOH

V=mL of sample

2.1.19 Alkalinity

Burugohain and Sarma (2012) in his work stated that the low level of alkalinity of water samples indicate that the underlying rocks which is the main source of natural alkalinity contains low carbonate, bicarbonate and hydroxide. Higher values of alkalinity reported by Amadi (2010) agreed with the findings of Geolink service limited on Etelebou field in southern Nigeria. Alkalinity is a measure of the capacity of water to neutralize acids. Alkalinity of water indicates the presence of biocarbonate (HCO_3^-) carbonate (CO_3^{2-}) and hydroxide ions (OH^-) in water. Alkalinity is a quality parameter to determine the amenability of waste water treatment processes (Patnak, 2010). Alkalinity acts as a stabilizer for pH. Alkalinity, pH and hardness affect the toxicity of many substances in the water samples. It is determined by simple dilute HCl titration in presence of phenolphthalein and methyl orange indicators. Olawale (2016) observed wide variations in the total hardness for all sampling points along Asa River, Ilorin for the two seasons (dry and wet seasons). Total hardness is due to the presence of bicarbonate, sulphate, chloride and nitrates of calcium and magnesium. Hard water requires more soap and synthetic detergents for home laundry and washing which contributes to scaling in boilers and industries equipments (EPA, 2011).

Water supplies with hardness greater than 200CaCO_3 are considered poor but can be taken by consumers. Those in excess of 500CaCO_3 are unacceptable for most domestic purposes (WHO, 2004). Njoku *et al.*, (2000) in his work on physicochemical properties of oil and some leguminous seeds observed that temperature; pH, dissolved solids, DO (dissolved oxygen) and BOD (biochemical oxygen demand) were all within WHO (World Health Organization)

standard. The physicochemical parameters (temperature, salinity, pH, total dissolve solids, electrical conductivity, dissolve oxygen and total suspended solids), also had seasonal effects in the absorption/dissolution and distribution of these substances in the surface water.

2.2.0 Physicochemical Parameters of Sediments

Sediments are considered as suitable medium to study the contamination of aquatic environment because they represent the multiple contaminant sources. Sproveriet *al.*, (2017) stated that apart from being a final reservoir for these contaminants, sediments act as their secondary sources in relation to changes in environmental physicochemical characteristics and response to human activities such as dredging. Eggleton and Thomas (2014) suggested that the Po River in Italy has suspended values from 220-270 (86% of this load being inorganic matter). Environmental programme under which water quality of rivers worldwide has been monitored at 240 stations since 1990 has drawn some interesting conclusion recently. It is found that most wide spread pollutant is the organic matter present in domestic sewage, the other important pollutants being nutrients, toxic metals, industrial and agricultural chemicals, (Sproveri *et al.*; 2007). Seiyaboh and Izah (2016) in their study of physicochemical characteristics of sediments from Epie creek Bayelsa State, Nigeria found out that the total hydrocarbon content and organic carbon % from Yenegoa, Onopa, Owom and Tombia rivers ranged from 1.20- 4.48 and 8.97- 22.54% respectively. They observed pH value of 6.66-6.77. Adesujiet *al.*, (2016) in their study of physiochemical characteristic of Nwaja Creek, Niger Delta reported % total organic carbon values of 10.22- 31.45%.

2.2.1 Total Organic Carbon

Total organic carbon is an index that measures the number of carbon containing compounds in a medium. It serves as a means of determining the level of organic contamination in a given environment (Adeyemo *et al.*, 2002). Ogbonna (2014) in their study on effect of abattoir waste water on physicochemical characteristics of soil and sediment in southern Nigeria observed TOC values of 0.0001mg/kg to 0.36mg/kg during wet season and dry season respectively which is within the WHO permissible limit. They attributed the presence of organic

carbon to the rapid decay and mineralization of animal wastes and sediments leading to the liberation of the mineral constituents of the animal wastes. Total Organic Carbon (TOC) is the amount of carbon found in an organic compound and is often used as a non – specific indicator of water quality or cleanliness. A typical analysis for TOC measures both the total carbon presented and so called inorganic carbon (IC). Total Organic Carbon (TOC) analyzers only measure total carbon (Dranin *et al.*, 2014). $TOC = TC - IC$ (EPA, 2006). TC =Total carbon and IC = Inorganic carbon. To determine the level of TOC, the organic carbons must be oxidized.

2.2.2 Total Organic Nitrogen

Total nitrogen is the sum of total kjeldah nitrogen (aminonia organic and reduced nitrogen) and nitrate – nitrite. Total organic nitrogen can be determined using kjeldah method, spectrophotometer or chromatography equipment.

2.2.2.3 Particle Size Determination % (silt, clay and sand)

Ezekiel *et al.*;(2011) found out in their study of physicochemical analysis of sediment from Sambreiro River, Niger Delta Nigeria that % silt, %sand and %clay of the River ranged from (1.72-6.28), (81.96-94.52) and (3.95-10.32) respectively. The result of sediment anslysis (particle size) in Sombreiro showed that sand was dominant across all stations. The texture of sediment is largely determined by the transportation process. The three important parameters used to assess the texture of sediment are size, rounding and sorting.

The ratio of sand, silt and clay in soil determines its ability to hold moistures and nutrients.

Sand, silt and clay are:

- i. **Sand:** is the material between 2mm and 0.06mm in size.
- ii. **Silt:** is any material which is finer than Sand but still feels gritty.

- iii. **Clay:** is the finest material of all and pure clay will feel smooth and will form a sticky ball when wet. % sand, silt and clay can be determined using a soil profile test and it uses sedimentation principle.

2.3 Heavy Metals in Aquatic System

Otitolaju (2002) reported different levels of heavy metals in water sediment and fishes from Oron, Abaloma and Ibu. They attributed the observed values to heavy metals pollution of terrestrial and aquatic environments as a result of increased urbanization, industrialization and crude oil exploration. The heavy metal pollution status of water and fish in Qua Ibo river estuary was investigated by Oze *et al.*, (2009). The mean values of the metals were Ni (0.21), Cr (0.53), Cd (0.03), Mn (0.14) and Pb (0.03). Based on WHO safety standard, the result indicates that the water was polluted with respect to all metals tested except Mn and Zn. The result for the bioaccumulation of the metals in fish was as follows: Ni (0.9mg/L), Cr (not detected), Cd (0.38), Mn (12.85) and Pb (25.88). When the result for bioaccumulation was compared with WHO standards, the fish was polluted with all the metals except Zn and Cr which were not detected. Since Cd, Mn, Pb, Zn and Ni are known to be neurotoxin, they can be passed to humans through the food chain. This may predispose water and fish consumers around Qua Iboe terminal community to possible neurotoxicity. The level of heavy metal in kidney, heart gills and liver of catfish from Ifiayong and Ibata beaches were analyzed using Atomic absorption spectrophotometry (AAS) by Akpanyong, *et al.*, (2014). The results showed that the levels of Zn and Cu were significantly higher than the maximum tolerable levels at both locations.

The bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of Wadi Hanifah, Saudi Arabia was determined using Shimadzu atomic absorption spectrophotometer by Abdel-Baki *et al.*, (2011). The concentrations of the heavy metals in water were within the international permissible limit. The results indicated that fish accumulated all metals in its tissues from water. Heavy metals under study in the edible parts of tilapia were within the safety permissible level for human use. Among environmental pollutants, metals are of particular concern, due to their potential toxic effect and ability to bioaccumulate in aquatic eco system (Lensi *et al.*; 2006). Heavy metal concentration in aquatic eco-systems are usually monitored by measuring their concentrations in water, sediments and biota (Al-Kahtani, 2009), which generally exist in low levels in water and attain considerable concentrations in sediments and biota.

Studies on heavy metals in Rivers, Lakes, fish and sediments (Ozman *et al.*, 2004; Ozturk *et al.*, 2009) have a major environmental focus especially during the last decade. Some heavy

metals (Cd, Cr, Cu, Fe, Ni, and Pb) were seasonally determined in water, sediment and some tissues of carpio from Avsar Dam Lake, which is an important water source for irrigation and drinking in Turkey. The results showed that the average values of Fe in water samples were higher than concentration of heavy metals such as Ni, Cu, Cr, Pb and Cd. Fe was maximally accumulated followed by Ni, Cu, Cr, Pb and Cd (Ozturk *et al.*, 2009). Heavy metals such as copper, iron, chromium and nickel are essential metals since they play an important role in biological systems, whereas cadmium and lead are non-essential metals as they are toxic, even in trace amounts (Ferandes *et al.*, 2008). For the normal metabolism of the fish, the essential metals must be taken up from water, food or sediment (Chindahet *et al.*, 2003). These essential metals can also produce toxic effects when the metal is excessively elevated.

Heavy metals contamination of Imo River was investigated by Ogwo and Okereke (2014) using heavy metal pollution index and the order of enrichment was Cd>As>Cr>Ni>Mn>Cu>Zn>Fe. It was found out that anthropogenic activities such as electroplating, discharge of industrial effluent and laundry waste that takes place along the river course are the likely sources of the heavy metals in the river water.

Sohand *et al.*, (2017) determined the transfer factors for Cu, Cr, Co, Fe, Mn and Zn from water and sediment in Nabber Lake in Egypt. The results indicated that only transfer factors from water for all metals were greater than one, which means that fish accumulated metals from water. The heavy metal distribution in fish tissues, sediments and water from Okumeshi River in Delta State, Nigeria was studied by Ekeanyanwu, *et al.*, (2010). Atomic absorption spectrophotometer was used to quantitatively analyze the presence of Pb, Ni, Cr, Mn and Cd in bottom sediment, tilapia, cat fish and water samples. The highest concentration of 0.62mg/kg was found in the muscle of tilapia while the lowest of 0.04mg/kg was found in tilapia bone. In most fish samples, the cadmium concentration was above the maximum tolerable values stipulated by international regularity authorities (APHA, 2005).

Pourang *et al.*, (2005) determined the concentration of trace elements in water sediment and fish from the Northern part of the Persian Gulf, inductively coupled plasma-mass spectrometer was used to determine the concentration of Cd, Pb, Ni and V in the above samples. There

was no significant difference among the sampling site in terms of Cd and Pb levels in sediment. The highest concentrations of Ni and V in sediments were found in the South - west of study area. The concentration of all metals except Vanadium was higher than the global baseline values. The determination of heavy metals in water, sediment and fish tissues from Epe and Badagry Lagoons, Lagos, Nigeria was reported by Olowu *et al.*, (2010). They analyzed quantitatively for the presence of Zn, Ni, Fe using Perking Elmer atomic absorption spectrometer. They found out that the sediments contained 13.30 Fe, 8.400 Fe in fishes and 7.30 Fe in water. In fish, it was 4.00u/g Ni on the head of Tilapia, 2.40 Ni in the intestine of cat fish. The highest concentration of 1.85 Zn was detected on the head of Cat fish while the lowest concentration value of 0.16ug/g was recorded in Tilapia head. The concentration of Zn in water was within the limit permitted by the Lagos state Environmental Agency (LASEPA) of 1.0 Zn recommended for water.

A study of the heavy metal levels and its risk assessment in some edible fishes from Bangshi River, Bangladesh was carried out by Rahman (2012). The concentration of the heavy metals Ni, Cr, Cu, Zn, Pb and Mn in two species collected from Banshi River were measured in two different seasons. Apart from Pb, the concentrations of studied metals were below the safe limit stipulated by international authorities for Carico Soberna.

Studies on the contamination from River Orogodu in Delta state, Nigeria by heavy metals were observed by Issa *et al.*, (2011). Sediment samples were collected for four months and analysed for heavy metals (Cd, Mn, Fe, Cu, Ni, Pb, Zn) using atomic absorption spectrophotometer. The result of the analysis indicated significant difference ($P < 0.05$) in Mn, Zn and Cr levels for the four months. The concentration of most heavy metals was low but the iron content was above the background value and Department of Petroleum Resources (DPR) standard for soil sediment which indicated significant contamination. The results of metal assessment indices revealed that Korean Coast sediments were moderately contaminated with the measured metals. The metal enrichment level decreased according to the order $Cu > Cd > Zn > Pb > Co > Cr > V$. The values and Zn when compared with sediment quality guide-

line indicated that 40% of the sediment samples exceeded TEL values (Threshold Effect Level) and can likely result in potential adverse effect on sediment-dwelling organisms (Harikumar and Nasir, 2010).

2.3.0 Heavy Metals

Heavy metal refers to any metallic chemical element that has a relatively high density and is toxic at low concentration. Examples of heavy metals: include Hg, Cd, Cr, Ni, V, As. However heavy metals such as copper, selenium, zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning (LEWTECH, 2016). Heavy metals are dangerous because they tend to bio accumulate. Heavy metals can enter a water supply by industrial and consumer waste or even from acidic rain breaking down soils and releasing heavy metals into stream, lake, rivers and ground water. When fish are exposed to heavy metals in aquatic ecosystem, they tend to take these metals up, which accumulate in various tissues.

Iron

Iron is believed to be the tenth most abundant element in the universe (Lenntech, 2017).

Iron is essential to almost living things, from micro – organisms to humans. The human body absorbs iron in the animal products faster than iron in products. Iron is essential part of haemoglobin. Iron may cause conjunctivitis choroiditis and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dust may result in development of a benign pneumoconiosis called siderosis. Iron (III)arsenite pentahydrate may be hazardous to the environment. Special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it persists in the environment.

Lead

Lead is a highly toxic metal whose wide spread use has caused extensive environmental contamination and health problems in many parts of the world (Rahman 2012). The sources of lead exposure include mainly industrial processes, food and smoking, drinking water and domestic sources. Lead metal causes toxicity in living cells by ionic mechanism and oxidative stress. High concentration of lead can affect protein kinase C which regulates neural excitation and memory storage (Flora *et al.*, 2012).

Cadmium

Cadmium is the seventh most toxic heavy metal as per Agency for Toxic substances and Disease Registrar (ATSDR) rating: It is a by – product of zinc production which humans or animals may get exposed to at work or in the environment. Once this metal gets into human, it will accumulate inside the body throughout life. It is used in rechargeable batteries; it is also being used in alkaline batteries as an electrode component. In coating, it is used as pigments and as a plastic stabilizer. It is used in production of alloys (Patnak, 2012). Cadmium is bio persistent and once absorbed by an organism, remains resident over decades in humans. Long term exposure is associated with renal dysfunction. Exposure to cadmium is commonly determined by measuring cadmium level in samples (blood, urine, water etc). Due to continue use of cadmium in industrial applications, the environmental contamination and human exposure to cadmium have dramatically increased during the past century (Cavan, 2017).

Nickel

Nickel is a metal of wide spread distribution in the environment. It is an essential constituent and which have many industrial and commercial uses. Although nickel (Ni) is omnipresent and is vital for the function of many organisms, concentrations in some areas from both anthropogenic release and naturally varying levels may be toxic to living organisms (Yapet *al.*, 2002). Nickel can be determined by electron thermal Atomic Absorption Spectrometry. Nickel is normally present in human tissues and under conditions of high exposure. These levels may increase significantly (Diagomanotin *et al.*, 2004). In the general population, con-

tributions to the body burden from inhalation of nickel in the air and from drinking water are generally of importance (Barceloux, 1999).

Zinc

Zinc is a very common substance that occurs naturally. Many foodstuffs contain certain concentrations of zinc. Drinking water also contains certain amounts of zinc which may be higher when it is stored in metal tanks. Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally due to addition of zinc through human activities such as mining, coal, waste combustion and steel processing (Patnak, 2010).

Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased senses of taste and smell, slow wound healing and skin sores. Too much concentration of zinc can cause health problems such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Zinc may also increase the acidity of water (Nwajeiet *al.*, 2007). Large quantities of zinc can be found in soil. When the soils are polluted with zinc, animals will absorb it. Some fish can accumulate zinc in their bodies, when they live in zinc accumulated water ways (Oguzie, 2003).

Copper

Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. Other examples are mining, metal production, wood production and phosphate fertilizer production. Copper is often found near mines, industrial settings, landfills and waste disposal (Jumbe and *Nandu*, 2009). Copper is a trace element that is essential for human health although human can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems (Duruibe *et al.*, 2007). Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomach aches.

Vanadium

Vanadium is a naturally occurring element. It is used in producing rust resisting spring and high-speed tool steels. Sources of vanadium are naturally and industrial. Vanadium is persistent in the environment (Duruibe *et al.*, 2007). Vanadium can cause DNA alternation in some

cases but it cannot cause cancer with animals and it can cause breathing disorder, paralyses and negative effects on liver and kidney. Vanadium can be found in the environment in algae, plant and fishes (Amadi, 2010).

Chromium

Chromium (Cr) is a naturally occurring element present in the earth's crust. Elemental chromium enters into various environmental matrices (air, water and soil (sediment) from a wide variety of natural and anthropogenic source with the largest coming from industrial establishment (metal processing, tannery facilities, stainless steel and chrome pigment production. (Rieuwerts,2015).

2.3.1 Heavy metals in Water

The pollution state of Ughoton stream water as of crude oil spillage in Ughoton stream in the Niger Delta was investigated by Uzoekwe and Achudume (2011). The surface water samples were collected at various distances 50m, 280, 400 and 500 downstream from an oil well. The concentrations of potential toxic elements such as Fe, Mn, Zn, Cu, Cr, Cd, Ni, Pb were below the threshold levels associated with toxicological effects and regulatory limits. The pollution status of the stream was further confirmed by its oil film coated environment.

The distribution of heavy metals and their rates of reactivity vary greatly between estuaries; depending on environmental factors such as hydrodynamic residence times, mixing patterns and transport processes. Therefore, there is no universal pattern of heavy metal behaviour in estuaries (Amadi, 2010).

The Department of Irrigation and drainage, West coast Malaysia reported higher concentration of heavy metals in the waters of West Coast of Peninsular Malaysia compared to other areas because of extensive land used and industrialization.

Censi *et al.*, (2006) carried out a geochemical survey on Thailand Gulf to define concentrations and distribution pattern of selected heavy metals in the water samples from coastal systems and estuarine area of Mae Klong River. The results indicated the presence of two different sources of heavy metals namely; sediments and suspended particulate matter in the studied environment.

Perez *et al.*, (1999) had studied heavy metal concentration in water of a Mexican reservoir. The results showed Lead, Chromium and Iron were the main metal contamination problem. In the same study, spatial and temporal distribution of total metal levels had also been identified. No organized pattern was detected for any particular metal concentration. The temporal variations of metal concentration showed evidence of the water self-cleaning capacity of the reservoir despite high level metal contamination being determined.

2.3.2 Heavy metals level in sediments

Sediment represents an important sink for heavy metals in aquatic system (Ogwo *et al.*, 2004). More than 90% of the heavy metal load in aquatic system is bound to the suspended particulate matter and sediment (Calmano *et al.*; 1993). The accumulation of heavy metals in mangrove sediments has been reported for a number of countries including Hong Kong, Brazil and Nigeria (Machado *et al.*, 2002; Liang *et al.*; 2003, Essien *et al.*; 2010). Although there have been investigations on the level of heavy metals in marine sediments of Malaysia (Yuet *et al.*, 2015). The metal contents in sediments are often used to describe the contamination of metal in different environment. For instance, Li *et al.*; (2007) studied heavy metals in coastal wetland sediments of the Pearl River Estuary, China.

The total concentrations of heavy metal such as Zn, Ni, Cr, Cu, Pb and Cu were investigated. The results significantly contaminated by Cd, Zn and Ni. Pb, Cd and Zn were strongly associated with exchangeable fractions while Cu, Ni and Cr were predominantly associated with organic fractions. Study done by Liet *et al.*, (2007) analysed total concentrations and fractions of selected heavy metals (Cd, Cr, Cu, Pb and Zn) in surface sediment from Dianchi Lake, Yuman Province China. It was found out that the concentration of the heavy metals decreased in the order Zn>Cu>Pb>Cr>Cd. These heavy metals except Cr were higher than the background levels, showing that the Dianchi Lake was polluted with Cd, Zn, Pb and Cu.

2.3.3 Heavy Metals Level in Fish

The bioaccumulation of some heavy metals in tilapia fish in Wali Hamidah, Saudi- Arabia was determined by Abdul- Baki et al., (2011). The result indicates that fish accumulated all metals in its tissue from water. Heavy metals under study in edible parts of tilapia were within the safety permissible level for human use. Pourang(2005) determined the concentration of heavy metals in fish from Northern part of the Persian Gulf. Inductively coupled plasma-mass spectrometer was used to determine the concentration of Cd, Pb, Ni, Fe and V in the above samples. There was no significant difference among the sampling sites in terms of Cd and Pb levels in the fish.

The determination of heavy metals in fish tissue from Epe and Badagry lagoons was reported by Ogundajo *et al*; (2010). The fish samples were analysed quantitatively for the presence of Zn, Ni and Fe using Perking - Elmer atomic absorption spectrophotometer. The highest concentration was recorded for Zn in the head of Cat fish while the lowest concentration was recorded for Zn in Tilapia head. All the heavy metals investigated were within the permissible limit set by world Health Organization (WHO, 2004). The concentration of heavy metals Cu, Cd, Zn Pb and Ni was determined in the liver, gills and muscles of tilapia fish from Langat River and Engineering Lake in Bangi, Malaysia. This analysis was conducted by (Taweel and Ahmad 2013).

Al-Yousof *et al*; (2000) had determined the influence of sex and body length on metal accumulation in fish. The results showed that the average metal concentration in liver, skin and muscle of a female fish were found to be higher than those found in male fish. The accumulation of zinc, copper manganese and cadmium in the liver tissue of *Lithrinus fistularius* was found high compared to skin and muscle tissues. Duruet *al.*, (2007) reported that the highest levels of Cd, Pb, Cu and Fe were found in the gills of fish species such as *Sparus aurata* and *murgil cephalus*.

The heavy metal pollution status of water, fish and sediments in Imo/Aba river was investigated by Amadi (2010). The study examined the degree of heavy metals such as Fe, Zn, Cu, Mn, Cr, Cd, As and Pb which were analyzed using Atomic Absorption Spectrophotometer and the result compared with the Nigerian standard for drinking water quality. The pollution index between the heavy metals in the river produced the following output: Fe>Zn>Cu>Mn>Ni>Cr>Pb>As>Cd. The metals exhibited a good linear correlation coefficient. The determination of heavy metals in fish tissues, water and sediment from Epe and badagry lagoons, Lagos - Nigeria was reported by Olowu (2010). The samples were analysed qualitatively for the presence of Zn, Ni, Fe using Perkins Elmer Atomic Absorption Spectroscopy. The highest concentration was recorded for Zn in the head of cat fish while the least concentration was recorded for Zn in tilapia head. All the trace metals investigated were within the permissible level set by world health organization (WHO).

The seasonal variation of heavy metal concentration in sediment samples around major tributaries in Ibeno coastal area, Niger delta, Nigeria was studied by Nwadinigwe et al; (2014). The concentrations of Mn, Ni, Pb and Zn in the dry season were above that of the wet season. The concentrations of all the metals were higher in the examined sites than the control but below WHO standard. The concentration of iron was abundant in both seasons while pH of sediment was slightly acidic and below WHO and the department of petroleum resource (DPR) standard. Ozturk (2009) analyzed heavy metal levels in water, sediment and fish samples from Avsar Dam Lake in Turkey using inductively coupled plasma spectroscopy. (ICP-AES). The result showed that the average values of Fe in water samples were higher than the stipulated values for fresh water. The analysis of heavy metals in sediments indicated that among the six heavy metals tested, Fe was maximally accumulated followed by Ni, Cu, Cr, Pb and Cd. The decrease in the level of heavy metals in tilapia muscle, stomach and intestine followed by the trend in the gill and heart Fe > Cu > Ni > Pb > Cd > Cr. In the fish samples the concentration of Cd, Cr, Ni and Pb were above the regulatory limit set by international agencies. Significant positive correlation between the heavy metals concentration in fish muscles were observed in both seasons while ANOVA analysis revealed that there was significant variation in heavy metal concentrations in different fish species in Bangshi River as reported by Rahman *et al.*, (2002).

2.4 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are hydrocarbons containing only carbon and hydrogen that are composed of multiple rings, Ujowundu *et al.*, (2004). Polycyclic aromatic hydrocarbons (PAHs) are mostly colourless, white or pale yellow solids. They are ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. Chemically the PAHs are comprised of two or more benzene rings bonded in linear, cluster or angular arrangements.

The major source of PAHs is the incomplete combustion of organic material such as coal, oil and wood. PAHs are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, thermo setting plastics lubricating materials and other chemical industries (Marce and Bornill, 2000). PAHs in water samples enter the water bodies/ rivers, lakes, ponds etc. from run-off water, human activities and effluents from industries. PAHs enter the environment by dry or wet deposition (Dike, 2008).

2.4.1 PAHs Level in Water

Adebayo *et al.*, (2012) Adeyemi, (2012) investigated 16 parent PAHs in water samples from Lagos Lagoon. The mean concentration of PAHs in 28% of samples were sufficiently high ($>0.001\mu\text{g/l}$) to cause acute toxicity to the exposed organisms. The outcome indicates the persistence and bio accumulative nature of chemicals in this aquatic environment and the need for regular monitoring of the lagoon to avert consequent health effect on exposed organisms and man.

It has also been found that certain plants and animal pigments are able to biosynthesize PAHs in a reducing condition in aquatic environment. This is an indirect biosynthesis of PAHs and it also adds to the bulk of the compound found in such aquatic ecosystem. Amadi (2010) in his study has shown that all aquatic organisms rapidly bio-concentrate in the ambient water.

Obayori *et al.*, (2010) have shown that biodegradation process which naturally reduces the level of organic pollutant in aquatic environment is mostly effective for the two or three rings PAHs (Naphthalene, Anthracene) while those with more condensed rings are relatively resis-

tant to biodegradation. A study on the levels of PAHs in water in Subamarekha River was investigated by Kumaret *al.*, (2012). It was found out that all sampling sites recorded Ant/Ant +Phen <0.1 and LMW/HMW >1 which indicated that the PAHs in Subamrekha River is of petrogenic source. Asaolu *et al.*, (1997) researched on the contamination of surface water by polycyclic hydrocarbons in two Nigeria coastal communities in eighteen sediments and indicated that PAHs contamination may not pose immediate threats to the organisms and people that utilize the stream for drinking and other domestic functions.

Obiakor *et al.*, (2014) determined eight priority PAHs present in water of Anambra River using gas chromatographic procedures on three experiment model design. It was found out that there was presence of seven PAHs: acenaphthene, fluorene, phenanthrene, anthracene, chrysene, benzo (a) pyrene, and benzo (ghi) perylene except naphthlene which was the only PAH compound not detected. PAHs occur as a mixture with two or more compounds and potent carcinogens that produce tumors in some organisms even at a single dose (Essumang *et al.*, 2009) exposure to water containins high levels of naphthalere via oral routes can result in health disorder, nausea, vomiting, and break down of red blood cells. Long term exposure to PAHs result in several health disorder such cataract, liver problem, breathing problem and dermal exposure may result to irritation and severe dermatitis (WHO, 2013). Benzo (a) pyrene, anthracene and naphthalene may cause allergic skin response in animals, humans (international programme in chemical safety (IPCS, 1998).

Law and Hil (2006), suggested that since most PAHs have similar mode of action, it is appropriate to compare their total PAH value with values of 2×10^4 [European Union (EU), 1998], since PAHs are carcinogenic and mutagenic in nature. The population (humans) located along the downstream of Imo River maybe exposed to PAH toxicity by drinking water from the river or using it to prepare meal/food. Humans accumulate these PAHs in it adipose tissues and since carcinogenic tendency is transgeneric, cancer prone genes may be inherited by the next filial generation (Ogbuagu *et al.*, 2011).

2.4.2 PAHs Level in Sediments

Studies have shown that PAHs degradation occurs at the water –sediment interface more than in deeper portion (Keith, 2015). This is because the top or surface sediments contain more

oxygen, rich in nutrient and more biological active degradation is therefore sped up by the healthy bacterial and fungal communities. Zhao *et al.*, (2006) believed that it is a measure of the presence of PAHs in soils and sediments would give an indication of the extent of this pollutant in the environment. This is probably due to readily ability of PAHs to absorb to dust particles, humic matter and settle in sediments. According to Neff (1999), the quantity of marine water is directly related to the quality of sediments because they are the final component of storage of large number of Xenobiotics (foreign compounds). Ekonomiuk *et al.*, (2006) in their study explained that soils and sediments have been found to be good environmental sinks for PAHs thereby reflecting their levels in the environment and could contain about 90% of these compounds with longer half- life in plants than in the atmosphere. Inengiteet *al.*, (2012) reported that during rainy season, it is expected that dissolution and washing –off of PAHs from the soil matrix could occur into the rivers thereby increasing their levels in sediments.

2.4.3 PAHs in Fishes

Adeogun *et al.*; (2015), Asagbara *et al.*; (2015) and Obiakor *et al.*; (2014) reported that enforcement of environmental laws, rapid industrial development, agricultural activities, urbanization among others have resulted in the discharge of wide range of environmental contaminants such as phthalates in fish from inland waters, sediments and open dump sites in Nigeria. Igwe *et al.*, (2015) assessed the polycyclic aromatic hydrocarbon content in smoked *C. garriepnus* and *T. guineans* fish species available in western Nigeria using gas chromatography (GC/FID). The results showed that Benzo (a) pyrene was not detected in all the fish samples except tilapia sample from Ibadan. 3 -ring PAHs were predominant in all the smoked samples of the two fish species. Phenanthrene to anthracene ratio showed that the PAHs are from combustion sources.

PAHs are deposited to the sedimentary environment by similar processes that govern the deposition to surface soils. Sediments also receive inputs of PAHs from storm, sanitary sewer effluents as well as road way runoff. PAHs are toxic, carcinogenic and mutagenic; some PAHs bind to cellular proteins and DNA (Obayori and Salam, 2010). Concentration of contaminants in fish is of considerable interest because of potential effects on the fish themselves

and top level organisms (such as man) that consume these contaminated fish (Alams, 2013). The heavier PAHs such as benzo (a) pyrene are potent carcinogens, while some of lighter compound such as naphthalene are more acutely toxic.

The EPA has concentrated on the sixteen polycyclic aromatic hydrocarbons that are included on their list of 126 primary pollutants. These compounds have been chosen on the basis of frequency of occurrence at hazardous waste site and toxicity, potential for human exposure Zhao *et al.*, (2008). The sixteen EPA (Environmental protection Agency) PAHs (Table 2.4) are as follows; naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), flourene (Flu), methylnaphthlene(MNap), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), chrysene (Chr), fluoranthene (Flt), benzo(a) anthracene (B(a)A), benzo(b) fluoranthene (B(b) fl), benzo(k) fluoranthene (B(k)fl), benzo(a) pyrene B(a)P, indeno (1, 2, 3, - cd) pyrene (InP), dibenzo (gh) anthracene(DB(gh)A).

Table 2.4 Compound Abbreviation Structure of PAHs (Rings/ Formula)

PAHs	Abbreviation	Ring No.	Molecular Formula
1 Naphthalene	Naph	2	C ₁₀ H ₈
2 Acenaphthylene	Acy	3	C ₁₂ H ₈
3 Acenaphthene	Ace	3	C ₁₂ H ₁₀
4 Flourene	Fl	3	C ₁₃ H ₁₀
5 Phenanthrene	Phen	3	C ₁₄ H ₁₀
6 Anthracene	Ant	3	C ₁₄ H ₁₀
7 Fluoranthene	Flt	4	C ₁₆ H ₁₀
8 Pyrene	Pyr	4	C ₁₆ H ₁₀
9 Benzo(a)anthracene	B[a]A	4	C ₁₈ H ₁₂
10 Chrysene	Chry	4	C ₁₈ H ₁₂
11 Benzo(b)fluoranthene	B(b)F	5	C ₂₀ H ₁₂
12 Benzo(k)fluoranthene	B(k)F	5	C ₂₀ H ₁₂
13 Benzo(g)pyrene	B(a)P	5	C ₂₀ H ₁₂
14 Dibenzo(a,h)anthracene	DB(a,h)A	6	C ₂₂ H ₁₄
15 Benzo[g,h,I]perylene	B(ghi)Per	6	C ₂₂ H ₁₂
16 Indeno[1,2,3,cd]pyrene	Ind(1,2,3-cd)P	6	C ₂₂ H ₁₂

Source: USEPA, 1993

Polycyclic aromatic hydrocarbons can be determined by various methods such as: GC- MS (Gas chromatography- mass spectrometer), high performance liquid chromatograpy (HPLC) method.

2.5.0 Determination of Cancer Risk Factor

The public cancer regarding exposure to PAHs is associated with its potential carcinogenicity in humans (WHO, 2004). The potential health risk of ingesting fish contaminated with carcinogenic contaminants were evaluated using the risk assessment guideline of USEPA (2005). The mean dietary intakes of the sixteen PAHs were considered probable human carcinogens by the USEPA (2005), and hence they are considered.

The general equation for estimating exposure, through ingestion of fish is as follows,

$$\text{Excess cancer risk} = \frac{\text{EL} \cdot \text{ED} \cdot \text{CSF}}{\text{BW} \cdot \text{AT}} \quad (2.3)$$

Where

EL: is the estimated intake (mg/kg)

ED: is the exposure duration.

CSF: is the oral cancer slope factor (mg/kg/d⁻¹),

BW: is the human body weight (assuming 60 weight or 70)

AT: is the average time for carcinogens assuming 70 years for adults

The CSF data for individual PAHS obtained from integrated risk information system reported by the USEPA are reported in the appendix VIII

Carcinogenic risk (CR) values of poly cyclic aromatic hydrocarbon in water via ingestion pathway was predicted from their chronic daily intake (CDI) obtained from the equation predicted by Caylak (2012) and USEPA(1997).

$$\text{CR} = \text{CDI} \cdot \text{SF} \quad (2.4)$$

Where CR=Cancer Risk

SF=Slope factor

CDI=Chronic daily intake ingestion pathway.

$$\text{CDI} = \text{C} \cdot \text{IR} \cdot \text{EF} \cdot \text{ED} / \text{BW} \cdot \text{AT} \quad (2.5)$$

Where CDI is the daily intake via ingestion (mg/kg/day)

C is the concentration of PAHs in mg/l. IR is the intake rate (2l per day for adults and 0.6/l for children)

BW is the body weight of the exposed person (70kg for normal adult and 30kg for children)

EF is i.e. exposure frequency (365 days/year)

ED: is the exposure duration over a life time (70 years for adult and 10 years for children).

AT is the averaging time in day (70 years *365 days) for adult and 3650 days for children.

Human carcinogenic risk assessment of polycyclic aromatic hydrocarbon in fresh water samples from Ogba/Egbema/Ndoni communities in Rivers State Nigeria was carried out by Essien *et al.*, (2014). The cancer risk due to certain ogenic PAHs (C-PAHs) from the ingestion of water was within the range of USEPA risk management criterion of 10^{-4} to 10^{-4} where management decision should be considered, the dominant PAHs were Benzo (b), flouranthene, Indeno (1,2,3-cd) pyrene, phenanthrene and benzo (k) fluoranthene.

Anyakora *et al.*, (2005) determined the presence of 16 priority poly cyclic aromatic hydrocarbons (PAHs) in fish, sediment and water samples of a fishing settlement in the Niger Delta region polluted by seepage from oil discharge terminal. The determination and quantification of PAHs was carried out with GC-MS and with the aid of isotopically labeled internal standards. The results revealed that the sixteen priority PAHs were present in significant amount in all the samples.

2.5.1.1 Identification and Quantification of PAHs in the Samples

Identity of PAHs in the samples was confirmed by the retention time and abundance of quantification/ confirmation ions and mass spectra match against the calibration standards in the authentic PAHs standards, confirmation of identity of the analytes were done using NIST/NIH Mass Spectral Library.

2.5.1.2 Human Health Risk Assessment Models

It involves the use of parameters approach based on water quality standard or toxicological data. It involved the use of Models software such as linear regression and accelerated life testing to predict no-effect and low-effect concentrations for chronic mortality

2.5.1.3 Determination of Human Health Risk Assessment

A human health risk assessment was used to estimate the nature and probability of adverse health effects on humans who may be exposed to chemicals in contaminated environment media (water, soil and biota) now or in future, using the following steps: planning, hazard identification, dose response assessment, exposure assessment and risk characterization.

2.5.1.4 Carcinogenic Risk Assessment

Carcinogenic risk (CR) values of polycyclic aromatic hydrocarbon in water via ingestion pathway was predicted from their chronic daily intake (CDI) obtained from the equation predicted by (Caylak 2012, and USEPA, 2009).

$$CR = CDI \times SF \quad (3.10)$$

Where CR = cancer risk

SF –slope factor, CDI – Chronic daily intake ingestion pathway.

*Slope factor for individual carcinogenic PAHs were used (Srouji, 2001)

Chronic daily intake (average daily intake) was calculated by equation 3.11 below:

$$CDI = \frac{C \times IR \times EF \times CF}{BW \times AT} \quad (3.11)$$

Where CDI is the chronic daily intake via ingestion (mg/kg/day)

C is the concentration of heavy metals/PAHs in mg or mg/kg for soil. IR in mg/day is the ingestion rate/intake rate (2L per day for adults and 0.61L for children), EF is the exposure frequency, ED is the exposure duration in years, BW is the body weight of the exposed individual in kg, AT is the average time or time period over which the dose is in days (70 years × 365 days/year) for adults and 3650 days for children. CF is the conversion factor in kg/mg of inhalation of heavy metals via soil particulates or thermal contact with soil.

$$ED/dems = \frac{C_s \times SA \times FE \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (3.12)$$

ED/dems: is the exposure dose via dermal contact in mg/kg. SA is exposed skin area in cm². FE is the fraction of the dermal exposure ratio to soil. AF is the soil adherence factor in mg/cm². ABS is the fraction of the applied dose absorbed across the skin. EF, ED, EW, CF are as defined earlier in equation 3.12. Table 2.5 shows the exposure parameters used for health risk assessment through different exposure pathways for soil.

Table 2.5 Exposure Parameters used for the Health Risk Assessment through different Exposure Pathways

Parameter	Unit	Child	Adult
Bodyweight(BW)	Kg	15	70
Exposure frequency (EF)	Days /years	350	350
Exposure duration (ED)	Years	6	30
Ingestion rate (IR)	mg/day	200	100
Inhalation rate (IR _{air})	m ³ / day	210	20
Skin surface area (SA)	cm ²	2100	5800
Soil adherence factor (AF)	mg/cm ²	0.2	0.07
Dermal absorption factor (ABS)	None	0.1	0.1
Dermal exposure ratio(FE)	None	0.61	0.61
Particulate emission factor (PEF)	m ³ /kg	1.3 × 10 ⁹	1.3 × 10 ⁹
Conversion factor (CF)	Kg/mg	10 ⁻⁶	10 ⁻⁶
Averaging time (AT)	DAYS	365 × ED	365 × ED

Source: USEPA (1997) and Caspah *et al.*, (2016).

2.5.1.5 Non Carcinogenic Risk Assessment

Non carcinogenic risk of heavy metals and PAHs in the environment was predicted from their target hazard quotient and hazard index (HI) indices.

2.5.1.6 Target Hazard Quotient.

$$THQ_i = CDI_i / RFD \quad (3.13)$$

THQ_i = target hazard quotient. CDI_i =chronic daily intake via ingestion

RFD = Oral reference dose of the contaminant (mg/kg/day). If the THQ and H1 exceed 1 there might be concern for non-carcinogenic risk; which indicates potential adverse effect on human health.

H1 is the sum of HQ's from all applicable pathways and pollutants. It is used to evaluate the total potential non-carcinogenic risk posed by more than one pathway (Amirah *et al.*, 2013; USEPA, 2011)

$$H1 = \text{THQ (toxicant 1)} + \text{THQ (toxicant 2)} + \dots + \text{THQ (toxicant n)} \quad (3.14)$$

For this study the equation (3.11) becomes

$$H1 = \text{THQ Zn} + \text{THQ Pb} + \text{THQ Cd} + \text{THQ Fe} + \text{THQ V} + \text{THQ Ni} + \text{THQ Cr} + \text{THQ Cu}$$

Target hazard quotient for dermal pathway THQd route was calculated as $\text{THQd} = \frac{\text{ED-Id}}{\text{RFD dermal}}$ (3.15)

RFD dermal+ dermal reference dose of the contaminant (mg/kg/day)

$$H1^* = \text{THQi} + \text{THQd}$$

H1*= sum of THQ from ingestion and dermal pathways.

$$\text{The estimated daily intake (EDI)} = \text{Cm} \times \text{FIR} / \text{BW} \quad (3.16)$$

Cm= concentration of the metal in food (mg/kg)

FIR= daily intake of food

BW= average body weight

2.5.2 Metal Pollution Index (MPI)

This was used to examine the overall heavy metal concentration in water, sediments and fish in the sampling locations.

This index was obtained by by calculating the geometrical mean of concentrations of all metals in water, sediment and fish (Caylak, 2012).

$$\text{MPI (mg/kg)} = (\text{Cf}_1 \times \text{Cf}_2 \dots \text{Cf}_n)^{1/n} \quad (3.17)$$

Where Cf i= concentration of the metal

N = The total number of metals

2.5.2.1 Transfer Factor (TF)

The transfer factor (TF) is the ratio of trace metal in the concentrating matrix to the concentration in the ambient matrix under equilibrium conditions. Sediment to fish transfer factor and water to fish transfer factor was computed using equation given by Muzyed (2011). Transfer factor = concentration of metal in fish muscle / concentration of metal in abiotic media. Where, the abiotic media represent water, sediment and food samples. If the transfer factor is greater than 1.0, then bioaccumulation for metal occurs by the fish samples.

2.5.2.2 Sediment Qualities Indices

Sediment quality indices such as contamination factor, enrichment factor, index of geo-accumulation, modified degree of contamination, pollution index and modified index were used to overcome inherent deficiencies in using a single index (Uwah *et al.*, 2013).

2.5.2.3 Contamination Factor

Contamination factor (CF) was calculated using the equation of (Uwah, *et al.*, 2013)

$$\text{CF} = \text{C}_o / \text{C}_n \quad (3.18)$$

C_o is the concentration of the examined element in the examined environment and C_n is the concentration of the examined element in the reference environment contamination.

$$\text{The degree of contamination } \text{Cd} = \sum \text{Cf} \quad (3.19)$$

2.5.2.4 Enrichment Factor

According to Nweke *et al.*, (2016) the metal enrichment factor (Ef) is defined by the equation:

$$EF = (X/Fe)_{\text{sediment}} / (X/Fe)_{\text{background(control)}}. \quad (3.20)$$

Where (X/Fe) sediment is the ratio of heavy metal (X) to Fe in the sediment samples from Imo River and (X/Fe) background (control) value of the metal –Fe ratio. Normalizing element Fe with natural background value of 232.7ug/g was used in the study.

2.5.2.5 Geoaccumulation Modified Degree

Geoaccumulation Index (Igeo)

The geoaccumulation (Igeo) was used to determine the extent of metal accumulation in the sediments and anthropogenic contribution to pollution in sediments (Uwah *et al.*, 2013). It was calculated using equation:

$$I_{\text{geo}} = \log_2 (C_n / 1.5 B_n). \quad (3.21)$$

C_n = the measured concentration of heavy metal (n).

B_n = the contamination of the metal in the environment and 1.5 accounts for possible variation in the background data due to lithogenic effects.

2.5.2.6 Modified Degree of Contamination

$$Med = Cd/n \quad (3.22)$$

Where n = number of pollutants

Cd = degree of contamination

2.5.2.7 Pollution Load Index (PLI)

This Index was calculated by the equation proposed by Tomilson *et al.*, (1980). Pollution load index provides a simple comparative means for assessing and comparing an estuary sediment quality.

$$PLI = (Cf_1 \times Cf_2 \times Cf_3 \times Cf_n)^{1/n}. \quad (3.23)$$

Where Cf = contamination factor

n = number of metals

2.5.2.8 Ecological Risk Assessment

The ecological risk of PAHs in surface sediments to benthic organisms was assessed using the threshold effect concentration-hazard quotient (TEC-HQ) and the mean effect range median quotient (m-ERM-Q) developed by Khairy *et al.*, (2012). This was obtained from the model in equation 3.24

$$m-ERM-Q = \Sigma[C_i/ERMi]/n \quad (3.24)$$

Where C_i = concentration of targets PAHs in sediment

$ERMi$ = ERM value for the same target PAHs

N = number of PAHs

$$TEC - HQ = C_i/TEC \quad (3.25)$$

Where C_i = concentration of target PAHs in sediment

TEC = Threshold effect concentration (sediment quality guideline).

2.5.2.9 Pearson Correlation Matrix Coefficient

Pearson Correlation Coefficient (PCC) is a bivariate correlation. It is a measure of the linear correlation between two variables X and Y . It has values between $+1$ and -1 where 1 is the total positive linear correlation (positive association). 0 is no linear correlation (there is no positive correlation between the variables). -1 is total negative linear correlation.

2.5.3.0 Multiple Linear Regression Model

A multivariate statistical regression model with one dependent variable and two explanatory variables was used in the study to predict the concentration of the contaminants in the fish when their concentration in water and sediment is known.

The model followed the general equation proposed by Gujarati and Porter (2009).

$$Y = B_0 + B_1X_1 + B_2X_2 + e \quad (3.26)$$

Where Y = dependent variable

X_1 and X_2 = predictor variable

B_0 = intercept term

e = error of regression model

2.6 Survey of Work done on Pollution of River in Nigeria and elsewhere in the World

Several studies have not only emphasized the pollution of rivers in Imo state/Nigeria but in other parts of the world. Ajibare (2014) in his work on assessment of physico-chemical parameters of water in Ilaje river, Ondo state found out that increasing anthropogenic activities around Ilaje area affected the water quality of Ilaje river. Dapam *et al.*, (2016), in the study of physicochemical parameters and heavy metal specification of water and sediment from Jiham River, Pankshi Plateau state observed that cadmium and lead are from anthropogenic source and that the river was moderately polluted. The results for physicochemical parameters and heavy metal concentrations in Jiham River, Pankshi were: 6.61 – 7.57 for pH, 24.5 – 24.2°C for temperature, 0.97 – 29.4 NTU for turbidity, 60 – 150 µS/cm for conductivity, 26.3 – 166.5 for total solids, 0.00 – 0.002 for nitrates, 37.35 – 78.5 for alkalinity, 11.71 – 19.17 for acidity, 0.02 – 0.11 for cadmium, 0.00 – 10 for lead and 0.00 – 0.03 for copper. Amareo (2005) evaluated the level of different physico-chemical parameter and heavy metals in terms of space and season in Awash River in Ethiopia and found out that there was significant spatial and seasonal variation in most of the physico-chemical parameters in Awash River. Asagbara *et al.*, (2015) investigated the levels of polycyclic aromatic hydrocarbons (PAHs) in water, sediment and the tissue of tilapia fishes from Warri River at Ubeji and he found out that there was predominance of lower molecular weight PAHs. Obiakor *et al.*, (2014) assessed the polycyclic aromatic hydrocarbons (PAHs) in fresh water media, factorial effects and human dietary exposure risk assessment at five different points along Anambra River.

Nwidu (2016) ascertained the water quality of Imo River in Oyigbo Local government by investigating the physico-chemical characteristics and microbial variability of the river during wet season. Cavin (2017) conducted a study on sediments in order to determine other anthropogenic sources of heavy metal and vertical transport of PAHs in sediments of lower river Nzola Ethiopia. Olawale (2016) evaluated the impact of pollution on Asa river segment and its biota *Clarias gariepinus* (African cat fish) in order to ascertain if Asa River is polluted and

if it's aromatic biota is bacteriologically contaminated and unsafe for human and animal consumption. Olawale 2016 in his study on physicochemical analysis of water from Asa River, Ilorin, Nigeria observed that temperature fall within the range of 24.03 – 25.5°C during dry and wet seasons, while turbidity, conductivity, pH, TSS, TDS, acidity and alkalinity were found to be between 8.06 (35 NTU), 66.45 – 275.13, 6.35 – 7.27, 12.75 – 244.10, 26.35 – 152.96, 22.80 – 55.40 and 86.23 – 302.33 respectively. Duru and Nwachukwu (2012) investigated the physical characteristics and microbial status of water samples of Nworie River in Owerri, Imo State Nigeria. The results obtained indicated that values of pH, temperature, dissolved oxygen, alkalinity, sulphate, nitrate and chloride all fall within the permissible limit except conductivity with mean value of 140 µS/cm which is above the safe limit of 100. Udosen *et al.*, (2016) in their study on distribution of trace metals (Zn, Cu, Ni, Mn, Fe, Co, V, Pb and Cd) in surface water and sediments from Imo River estuary attributed spatial and seasonal variations of surface water and sediments to both anthropogenic and natural processes in the environment. Enk *et al.*, (2016) observed that physicochemical characteristic and levels of 8 priority polycyclic aromatic hydrocarbon from water samples in Ngong River Nairobi Kenya fall were found to be within acceptable levels, but precaution was needed to be adhered to in the use of untreated water from River Ngong for fear of body accumulation of PAHs and their dangers. Dan *et al.*, (2014) investigated that seasonal variation of the distribution pattern, enrichment and contamination of some heavy metals (Cd, Cr, Fe, Pb, Zn, Ni and Cu) in surface water of Qua Iboe River and adjoining creeks using physicochemical parameters. The results obtained showed that salinity, pH and temperature among others played a significant role in the adsorption/dissolution of heavy metals in surface water. The enrichment factor analysis indicated that the metals (Cd, Cr, Cu, Fe, Pb, Zn and Ni) were more enriched in Qua Iboe River during wet season than dry season. The determination of heavy metals in fish tissue from Epe and Badagry was reported by Ogundajo *et al.*, (2010). The fish samples were analyzed quantitatively for the presence of Zn, Ni and Fe using atomic absorp-

tion spectrophotometer. The highest concentration was recorded in Zn. All heavy metals investigated were within the permissible limit set by World Health Organization (WHO, 2004). Asagbara (2015) in his study of Warri River in Ubeji, investigated eleven PAHs in sediment, fish and water. The results obtained showed total mean concentrations of 4.387.7, 0.1098.5 and 0.0198 in sediment, fish tissues and water respectively. Lower molecular weight PAHs were predominant in Warri River with naphthalene accounting for the highest concentration in all samples.

2.7 Literature Gap

From the reviewed literature, the following gaps were noticed:

1. There was no work that provided information on assessment of all the three parameters namely: physico-chemical parameters, heavy metals and polycyclic aromatic hydrocarbons (PAHs) in water, sediment and fishes (biota) along Imo River.
2. There was no information on cancer risk associated with carcinogenic heavy metals like Cd, Pb, Cr.
3. Most researchers excluded the investigation of sixteen (16) priority PAHs in all the three media (water, sediment and biota, (fishes).

This research was conducted to bridge these gaps.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 List of Apparatus and Instruments

Beakers, volumetric flasks, conical flasks, total dissolved solid meter, weighing balance, glass wares, oxygen sensitive membrane electrode, glass rod, nephelometer, nessler's tube, membrane electrode, burette, pipette, pH meter(Jenway3510/3520), hot plate, fume cupboard, water bath, plastic containers, sieve mesh, atomic absorption spectrometer(AAS) (LAAS320 Perkin Elmer), cuvettes, UV/VIS spectrophotometer(Hach PR6000), cuvettes, thermometer, dissolved oxygen analyser(HQ30D Model55, Pro20), COD digester(Model No. IPM-1915), gas chromatograph, mass spectrophotometer(Perkin Elmer HD 2010), Soxhlet extractor(Model 9903600), rotary vacuum evaporator, conductivity meter(Model LEC210), BOD bottle, Oximeter (HQ30D), Magnetic stirrer(Model HP15P), Teflon beaker, dissolved Oxygen meter, GC/MS(Model 7693 ALS/7890/240), Refractometer(DR60007), Incubators (BANN602) , Questionnaires.

3.1.2 List of Reagents

Nitric acid, hydrochloric acid, deionised water, dichloromethane, hexane, sodium hydroxide, anhydrous sodium sulphate, ethylene diaminetetracetic acid(EDTA) erichrome black T, stannouschloride, glycerol, ethyl alcohol, sodium chloride, silver nitrate, potassium chromate, ammonium hydroxide, ammonium chloride, magnesium salt of EDTA, distilled water, ammonium buffer, ammonium molybdate, phosphoric acid, stock nitrate solution, standard nitrate solution, glycerol, barium chloride, sodium sulphate, potassium dichromate indicator, sodium sulphate, isopropyl alcohol, phosphate buffer, magnesium sulphate, calcium chloride, ferric chloride, standards for metals (Fe, Pb, Zn, Ni, Cu, Cd, V). Every of these reagents used were of analytical grade.

3.1.3 Description of the Study Area

The Imo River is in the southern eastern Nigeria and flows 240 kilometers (150miles) from Onuimo into the Atlantic Ocean. Its estuary is around 40 kilometers (25miles) wide, (Afigbo-Adiele, 2005) and the river has an annual discharge of 4 cubic kilometers (1.0cu/ml) (Menally, 1980) with 26,000 hectares of wetland (Afigbo- Adiele, 2005). The Imo river tributaries are the Otamiri and Oramiriukwa (Russell, 1993). The Imo River was cleared under the British colonial administration of Nigeria in 1907-1908. The source location is Okigwe, Imo state. Its coordinates are $5^{\circ}50'56''\text{N}$, $7^{\circ}14'20''\text{W}$. It has an elevation of 0ft. Its length is 240km (150miles), (Afigbo-Adiele, 2005). The mouth is Atlantic oceans. Its location is eastern Obolo Akwa Ibom State. Its coordinates are $4^{\circ}28'14''\text{N}$, $7^{\circ}35'38''\text{W}$. The Imo River features an 830-meter (720ft) bridge at a crossing between Rivers state and Akwa Ibom. The coordinates of the study area are: (5.7788°N , 7.2329°E), (4.9637°N , 7.1851°E), (5.2542°N , 7.3220°E) for Onuimo, Asa-Owaza and Owerri-nta respectively.

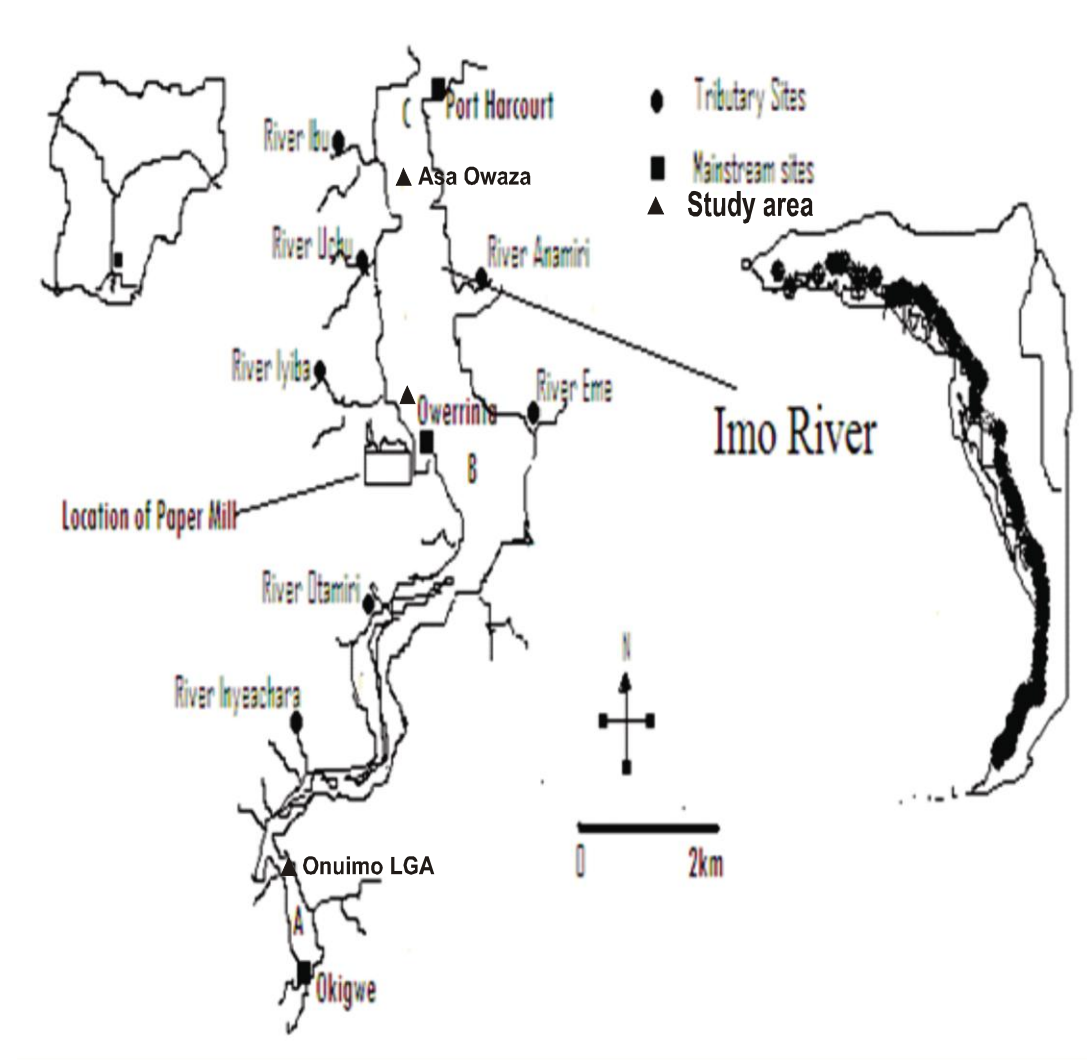
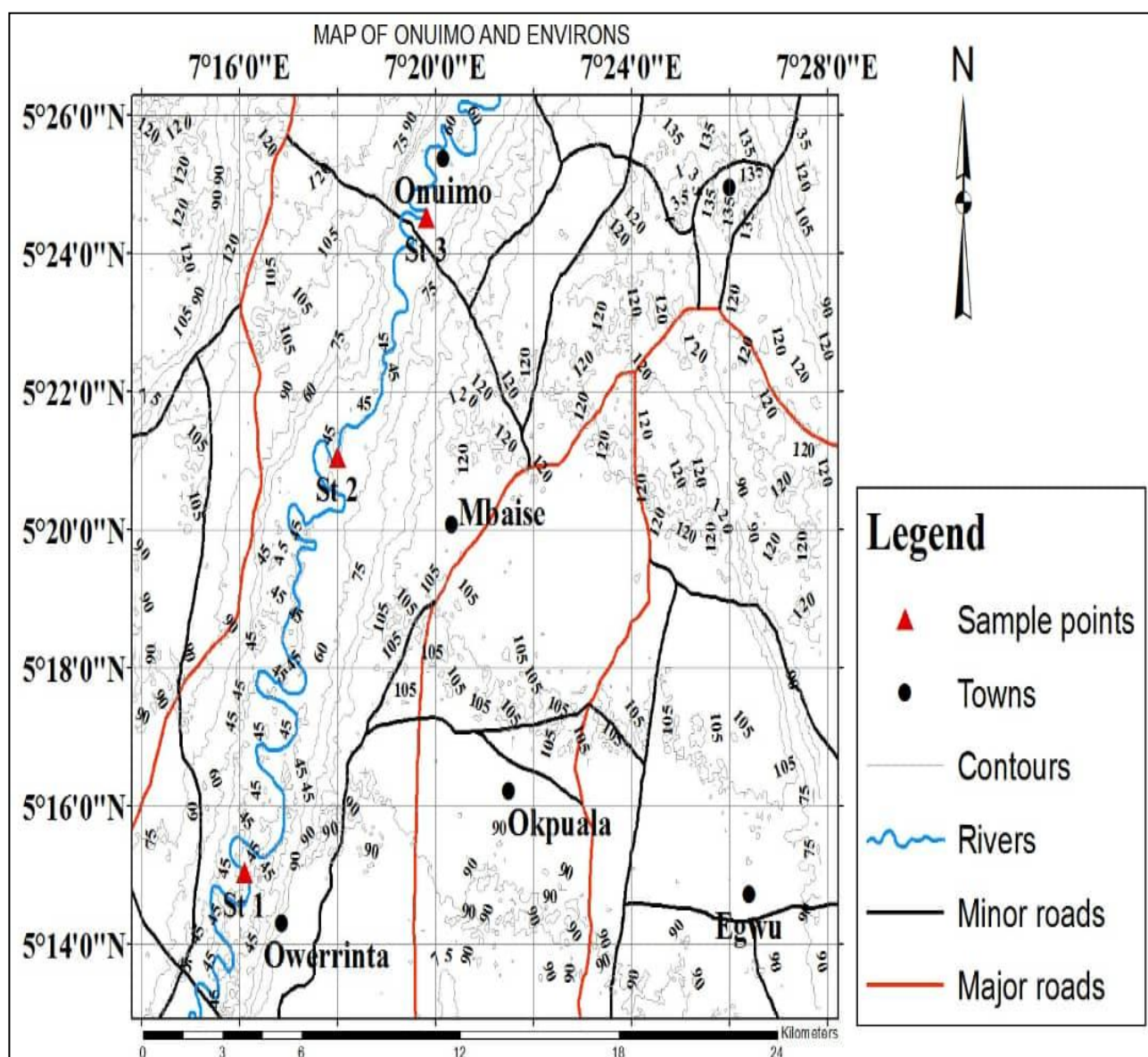


Fig. 1.1: Map of Imo River, showing Sampling Locations



3.2 Sampling

In this study, sampling was conducted monthly between January 2016 to December 2016 for both dry and wet season. Three locations were chosen at lower reaches of the river in Onuimo, Asa-Owaza and Owerri-nta. Three sub-samples per sampling site were homogenized to form a composite sample. Coordinates of the sampling location of the three stations were recorded using global positioning system (GPS) and plotted in geographic information system (GIS) to produce the pollution map. The GPS coordinates of different sampling stations are shown in fig 1.2.

In this study, typed questionnaires were administered to two hundred (200) people made of both sexes; ranging from 12 to 60 years living along the sampled areas.

3.3 Sample Collection, Treatment and Preservation

Using sterile bottle containers, water samples were collected from three (3) different points of river water upstream; midstream, downstream at three different locations within the study area. All sampling points were however geo-referenced. At every sampling point, the sampling containers were thoroughly washed with the water sample before final collection. Sample for different parameters were taken and preserved as prescribed by APHA (2005) and Aiyesanmi (2006).

3.3.1 Sample Collection, Treatment and Preservation for Physicochemical Parameters Analysis

Samples for general physiochemical parameters were stored in the pre-washed 2 litres keg.

Samples for heavy metals were stored in the prewashed 1 litre keg and fixed to a pH of <2 by the addition of 2mL analar grade concentration HNO_3 . Samples for COD were put separately in the pre-washed 250 mL brown bottle and fixed with analar grade H_2SO_4 . Samples for BOD determination were put in the BOD bottle and wrapped with aluminium foil.

3.3.2 Water Sampling, Treatment and Preservation for Heavy Metal Analysis

The sample bottles were conditioned by washing with metal-free non ionic detergent solution (citranox) and finally rinsed with distilled water. The pre-cleaned sampling bottles were immersed 10cm below the water surface and 0.5litre of water was taken at each sampling location. Samples were acidified with 10% HNO₃ placed in an ice bath and taken to the laboratory. The samples were filtered using whatman No1 filter paper and stored at 4°C in a refrigerator until time for physico-chemical and heavy metal analysis (Ozturk *et al.*, 2009).

3.3.3 Sample Collection, Treatment and Preservation for PAHs

Water, sediment and fish samples were collected every month from 3 points in each three location making a total of nine sampling points. The sampling bottles were pre-conditioned with 5% nitric acid and later rinsed thoroughly with distilled de ionized water. At each sampling site, the polyethylene sampling bottles were rinsed at least three times before sampling was done. Pre-cleaned polyethylene sampling bottle were immersed 10cm below the surface. 100mL of water samples were taken at each sampling site.

Samples were acidified with 10% HNO₃, placed in an ice bath and brought to the laboratory. The samples were filtered through a 0.5 µm microspore membrane filter and kept at 4°C until analysis. Sediment samples were transported to the laboratory and air dried in the laboratory at room temperature. Once air dried, sediment samples were powdered and passed through 2mm sieve. The samples packed in polyethylene bags and stored below 20°C prior to analysis. Sediments samples were weighed, placed into the digestion bomb with 10mL of HNO₃/HCl (1.3w/v) and digested in a micro wave digestion system. Sediment analysis were carried out according to the procedure described (USEPA, 1997). Fish samples were collected with nets by local fishermen. Fish samples were transported to laboratory in a thermos flask with ice on the same day. The mean length and weight of the fish were 303.6±12.4mm. Sample containers and glassware for PAHs analysis were rinsed with hexane and dich-

loromethane, to remove adhering polar and non-polar compounds. The water samples were collected using amber coloured borosilicate 1 litre capacity glass bottles with teflon-lined caps and 3 drops of 1M HCl placed to prevent photochemical and bacterial degradation of sample respectively (Amadi, 2010).

3.3.6 Sediment Sampling and Preservation

Sediment samples were collected using grab sample method from three locations and three sub-stations (nine sampling points for 12 months). Samples were transported to the laboratory in a cooler with crushed ice. In the laboratory the sediment samples were air dried. After drying, visible remains of organism and debris were crushed using pestle and mortar and passed through a 2mm sieve mesh. The samples were packed in polyethylene bags and stored at 4⁰C until further analysis. Sediments samples were weighed, placed into the digestion bombs with 10mL of HNO₃ / HCl (1:3 v/v) and digested in a micro wave digestion system. Sediments analysis was carried out according to the procedure described earlier (Binning and Braid, 2001).

3.4 Fish Sampling, Treatment and Preservation

The fish samples were obtained from the nine sampling points monthly using fishing net and local traps. The mean length and weight of the fish were 303.6± 12.4mm and 526.6 ± 32.15 for tilapia and cat fish respectively. The fish samples were washed with deionized water and collected into reclined polyethylene bags and were transported to the laboratory in a thermos flask with ice for identification and immediately preserved in a deep freezer at -18⁰C to avoid deterioration. The identification was done by Mrs. Alozie Chiemerem of Fishery Department of Imo State Polytechnic Umuagwo. The frozen samples were washed with distilled water after removing the scales and the muscle portion were removed by a stainless steel knife for further processing. The muscle tissue was oven-dried to a constant weight at 80⁰C in an acid-washed petridish. After cooling in a desiccator, the samples were ground using a mortal and

pestle to make powder and sieved through 1mm mesh. The homogenized powdered sample was stored in an air tight pre-cleaned dry plastic bottle and preserved for further analysis.

3.4.1 Digestion of Sample for Physico-Chemical Analysis

3.4.2 Physico-Chemical Analysis

Sample collection was done using sterile bottle container. Water samples were collected from the 3 different points of each location namely upstream, midstream and downstream. The water samples were labeled thus U(Onuimo), M(Owerrinta) and D(Asa-Owaza) indicating samples from the three different sampling points.

3.4.3 Sterilization of Materials

Glasswares were sterilized as described by USEPA (2005) and using an oven at 170°C for two (2) hours. Moist heat, dry heat, direct flames and chemical methods of sterilization were applied as described by Cruickshank *et al.*, (2002)

3.4.4 Digestion of Water for Heavy Metal Analysis

A 100mL of the water sample was filtered using a Whatman filter paper, the filtrate was acidified with 2mL of concentrated HNO₃ and 5mL of concentrated HCl. It was evaporated to near dryness on an electric hot plate. After cooling, the solution was transferred to a 100mL volumetric flask and made up to the mark with de-onised water and the metal determined by use of atomic adsorption spectrophotometer (USEPA, 2005).

3.4.5 Digestion of Sediment for Heavy Metal Analysis

The dried ground and sieved sample 1g was weighed into a 100mL beaker. The digestion of the metal was done using mixed method (Hseu, 2002). A mixture of conc. HClO₄ and HNO₃ (20mL) was added at a ratio 4:1 to the sample and 0.2% (v/v) HNO₃. The solution was filtered using an acid- washed filter paper (Whatman No.42) and filtrate was made up to 20mL with distilled water. A blank was prepared similarly with the omission of sample.

3.4.4 Digestion of Fish for Metal Analysis

Heavy metal analysis:

The digestion of the sample was performed as described by Bhumpander and Mukherjee (2001). The digestion took place after 0.5g homogenized powdered sample was placed in a Teflon beaker and digested with 10mL mixture (5:1) of concentrated HCl (70%) and concentrated nitric acid (65%) and heated on a hot plate. The digestion process lasted for six hours in a fume chamber and a clear solution was obtained. After complete digestion, the residue was dissolved and diluted with 0.2% v/v nitric acid to 20mL. The digested solution was filtered and used for the analysis. The digest was prepared in triplicates. The blank determination was also carried out in a similar way as described above except for the omission of the sample to authenticate the analytical quality.

3.5 Preparation of Stock Solution for Analysis

In order to obtain a calibration curve, it was necessary to use aliquots from stock solution. Using either the metal or a salt of the metal (APHA, 2005), each stock solution was prepared by dissolving one gram of the metal compound or its salt in different amount of aliquots of acid mixture and diluted to 1 liter with deionised water (Anwaret *al.*, 2014). Standard solution was prepared from stock solution usually of 1000ppm and the stock solution was stored in plastic bottles instead of glasswares to prevent contamination and adsorption.

3.5.1 Preparation of Stock Solution of Iron (1000ppm)

Iron granules (1.0g) was dissolved in 20mL of 5 HCl and 5mL of 1M HNO₃ was added to the mixture in 1dm³ flask and made up to mark with deionised water.

3.5.2 Preparation of Stock Solution of Cadmium (1000ppm)

Cadmium (1.0g) metal was dissolved in 50mL of 1M HCl and 2mL of 0.1M HNO₃ was added and the mixture was diluted to 1dm³ with deionised water in a volumetric flask.

3.5.3 Preparation of Stock Solution of Lead (1000ppm)

1.000g of lead metal was dissolved in 50mL of 2M HNO_3 and diluted to 1dm³ (1litre) in a volumetric flask with de-ionised water.

3.5.4 Preparation of Stock Solution of Nickel (1000ppm)

Nickel (1.0g) was dissolved in 50mL of 5M HNO_3 and diluted to 1dm³ with deionised water in a volumetric flask.

3.5.5 Preparation of Stock Solution of Zinc (1000ppm)

Zinc metal (1.0g) was dissolved in 50mL of 5M hydrochloric acid (HCl) and dilute to 1 litre in a volumetric flask with deionised water.

3.5.6 Preparation of Stock Solution of Copper (1000ppm)

Copper metal (1.0g) was dissolved in 50mL of 5M HNO_3 was added to the mixture and the solution was diluted to 1dm³ with ionized water.

3.5.7 Preparation of Vanadium (1000ppm)

Vanadium metal (1.0g) was dissolved in 25mL of HNO_3 and diluted to 1dm³ with deionised water.

3.6 DETERMINATION OF PHYSIOCHEMICAL PARAMETERS

3.6 .1 Temperature

The temperatures of water samples from Imo River were determined using a thermistor.

3.6.2 Electrical Conductivity

Conductivity meter was used to measure the electrical conductivity of various water samples from Imo River. The electrode of the conductivity meter was dipped into the sample and the reading was noted for stable value in $\mu\text{s}/\text{cm}$.

3.6.3 Odour

The odour was detected using physiological sense.

3.6.4 pH

The pH of water samples was determined using a pH meter. The pH meter was calibrated, then the pH of water sample was determined by pressing the on mode of the meter. The pH electrode was rinsed with distilled water to prevent water contamination of the tested solutions. Then the pH electrode was dipped into the testing solution (water samples), the solution was stirred with a magnetic bar. Readings were taken when it was stable.

3.6.5 Total Dissolved Solids

The total dissolved solids of the water samples were measured using total dissolved solid meter (TDS meter). Three buttons; on the, E.C were pressed on and the sensor in the total dissolve oxygen meter was inserted 2cm above water sample level. Then readings were taken when it was stabilized.

3.6.6 Total Dissolved Oxygen

Total dissolve oxygen was measured using dissolved oxygen meter. The instrument was calibrated using 7.5% potassium chloride and de-ionised water according to recommendation of the manufacturer. The dissolved oxygen meter was standardized using de-ionised water since it has standard amount of oxygen in it. The dissolved oxygen meter (D.O meter) had membrane electrode, silver anode and gold cathode. It had temperature probe. The dissolve oxygen probe was dipped in water sample, the solution was gently stirred until the reading is nearly stable, then the reading was taken.

3.6.7 Total Hardness

The total hardness was determined using complexometric titration. Carbonates and bicarbonates of calcium and magnesium cause temporary hardness. Sulphates and chloride cause permanent hardness. 5ml of water samples was piped in a conical flask 1ml of ammonium

buffer and 2-3drops of Erichrome black T indicator was added. The mixture was titrated against standard 0.01m EDTA until the wine red colour of the solution turns pale blue at the end point.

CALCULATIONS:

$$\text{Total hardness (mg/l)} = (T) (1000)/V \quad (3.1)$$

Where

T = volume of titrant

V = volume of sample

3.6.8 Phosphate

Phosphate was calculated by stannous chloride method, 50mL of sample, 4mL of ammonium molybdate reagent and 4-5 drops stannous chloride were mixed. After about 10minutes but before 12minutes, the colour developed was measured photometrically at 690nm.

3.6.9 Nitrates

Nitrates was measured using phenoldisulphonic method. 50ml of sample was pipette into a porcelain dish and evaporated to dryness on a hot water bath. 2mL of phenol disulphonic acid was added to dissolve the residue by constant stirring with a glass rod. Concentrated ammonium hydroxide and distilled water was added with stirring to make it alkaline. It was filtered into Nessler's tube. The absorbance was read at 410nm using a spectrometer.

3.6.10 Sulphate

Sulphate in water samples were determined by turbidometric method. 100mL of sample was filtered into a Nessler's tube containing 5mL of conditioning reagent, about 0.2g of barium crystal was added with continued stirring. A working standard is prepared by taking 1mL of the standard, 5mL of conditioning reagent and made up to 100mL to give 100NTU. The turbidity developed using a Nephelometer and the results got were tabulated.

3.6.11 Biochemical Oxygen Demand

Biochemical Oxygen Demand was measured in water samples using D.O meter and oximeter. The sample having a pH of 7 was determined for first day. D O of various dilutions (at least 3) were prepared to obtain 50% depletion of D.O using sample and dilution water. The samples were incubated at 20°C for 5 days and 5th day DO was noted using oximeter. A reagent blank was also prepared.

CALCULATION:

$$\text{BOD (in mg/l)} = \frac{(D1-D2)-(B1-B2) \times F}{P} \quad (3.3)$$

P

D1= 1st day D.O of diluted sample

D2 = 5th day of D.O of diluted sample

P = decimal volumetric fraction of sample used.

B1 = 1st day D.O of control

B2 = 5th day D.O of control

3.6.12 Chemical Oxygen Demand

Chemical oxygen demand was measured using open reflux method. 50mL of sample was homogenized at high speed for 2 minutes. The cap of COD digestion reagent vial was removed and held at 45⁰C. 2mL of the sample was pipette into the vial. The cap was replaced and tightened. The vial was placed in pre-heated COD reactor. A reagent blank was prepared by substituting 2ml of distilled water in place of sample. The vial was incubated for 2hrs. The COD reactor was turned off and the vial was allowed to cool at room temperature. Then the COD was measured using spectrophotometric method.

3.6.13 Total Viable Bacteria

Total viable bacteria of the water samples were determined using plate method.

3.6.14 Total Coliform Bacteria

The water sample was placed on a culture medium plate and incubated for 3 days. After incubation period, the number of colony was counted.

3.6.15 Salinity

The salinity of the samples were determined using refractometer. The face of the prism and cover lens of the refractometer were rinsed with de-ionized water and dried with a cloth or towel. The scale of the refractometer was zeroed using de-ionized water. A dropper was used to drop one or two drops of the sample into prism face. The prism was held towards light source. The reading was taken when an intersection occurred between the upper shaded portion and lower clear portion. The salinity is recorded to the nearest parts per thousand (ppt%).

3.6.16 Acidity

Acidity was determined using titrimetric method. 2.5mL of sample was pipetted into Erlenmeyer flask, 0.05ml / 1 drop of 0.1N thiosulphate solution were added to free the sample of residual chlorine. After this, 2 drops of methyl orange were added and the content titrated against 0.02N hydroxide solution. The end point was noted when colour changed from orange to yellow. Then 2 drops of phenolphthalein indicator were added and titration continued till a pink colour developed. Then the colour of the titrant used was noted.

3.6.18 Alkalinity

The alkalinity of the water samples was determined using titrimetric method. A clean delivery tube was inserted into 0.16N sulphuric acid titrant cartridge and the cartridge attached to titrator body. The delivery knob was turned to eject air and a few drops of titrant. The counter is reset to zero and the tip wiped. The delivery tube was inserted into the beaker containing the sample. The delivery knob was turned while magnetically stirring the beaker until the pH meter reads 4.5. The number of digits reached to get pH of 4.5 was recorded. The titration

was continued until a pH of 4.2 and the number of digits for this was also recorded. The alkalinity was obtained using the formula:

$$\text{Alkalinity}(\text{CaCO}_3\text{mg/L}) = (2a-b) \times 0.1 \quad (3.4)$$

Where a = digits of titrants to reach pH 4.5

b = digits of titrants to reach pH 4.2

3.6.19 Physiochemical Analysis of Sediment Samples from Imo River.

3.6.20 pH

The sediment samples (0.5g) was sieved through a 2mm mesh size sieve and weighed into 250mL conical flask and the pH was determined using pH meter.

3.6.21 Temperature

The temperature of the sediment sample was determined using thermister/thermometer.

3.6.22 Electrical Conductivity

Conductivity meter was used to measure the electrical conductivity of the various sediment samples from Imo River. The electrode of the conductivity meter was dipped into the sediments sample and the reading was noted for stable value in $\mu\text{S/cm}$.

3.6.23 Total Organic Carbon (TOC)

Sediment samples (0.5g each) were sieved through a 2mm size mesh sieve and weighed into 250mL conical flask. 10mL of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and 20mL H_2SO_4 were added and left to stand for 30mins after intermittent swirls, 100mL of distilled water was added, then 3 drops of ferrous indicator were added and the mixture was titrated with 0.5M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ using digital titrator. The solution went from green to light green and finally maroon red to brown and that was the end point.

$$\text{TOC} = \frac{\text{Blank titre value} - \text{Titre value} \times 0.195 (\text{Factor blank})}{\text{Weight of sediment in (g)}} \quad (3.5)$$

3.6.24 Nitrates

Nitrates in the sediment was analysed using APHA 450-NO₃ (1995). Sediment solution (10mL) was transferred into sample cuvette. Reagent powder pillow was added to complex. The colours and the reading in mg/L were taken on HACH spectrophotometer.

3.6.25 Total Hydrocarbon Content

The total hydrocarbon content of the sediment was determined using American Standard Tests and Method (ASTM,1995). Sediment sample (5.) after air-dried was sieved through a 2mm mesh-size sieve. The essence of sieving was to obtain particle sizes of almost uniform diameter, increase surface area so as to enhance the contact/spreading of organic solvent within the soil matrix. 25mL of chloroform was added to soil sample in the beaker, stirred carefully to allow for proper extraction of organic materials or extract. The organic extract was used to dehydrate the sample of any excessive moisture so as to avoid interference of moisture within the organic extract. Chloroform (CHCl₃) was used as blank and the organic extract as sample. The blank was inserted into the cell holder of the spectrophotometer. The blank was zeroed and removed from the cell holder. In turns the sample was inserted, the concentration was obtained on the digital read-out of the spectrophotometer when it was stable.

Total hydrocarbon content was calculated.

$$\text{THC} = \text{Dilution} \times \text{Spectrophotometer} \frac{\text{reading} \times \text{vol of solvent}}{\text{weight of soil (g)}} \quad (3.6)$$

3.6.26 Particle Size Distribution Determination

The particle size distribution of the sediment samples was determined by the hydrometer method as described by Gee and Bauder (1986) and AOAC (1990). The determination of particle size larger than 63µm was done by sieving first. The particle size was determined using hydrometer with calgon (sodium hexametaphosphate) as the displacing agent. The hydrome-

ter was calibrated so that the corrected reading gives the grammes of sediment materials in suspension. The sand settled to the bottom of the cylinder within 40s.

Therefore, the 40 seconds hydrometer reading gave the amount of silt and clay in suspension.

The weight of sand in the sample was obtained by subtracting the corrected hydrometer reading from the total weight of the sample.

$$\% \text{ sand} = \frac{\text{Wt. of sand in the sample}}{\text{Wt. of sample}} \times \frac{100}{1}. \quad (3.7)$$

To determine the percent clay in the sample, the suspension was re-shaken and hydrometer reading was taken at the end of 2 hours and corrected. The corrected hydrometer reading represents the gram of clay in the sample.

$$\% \text{ clay} = \frac{\text{Wt. of clay in the sample}}{\text{Wt. of sample}} \times \frac{100}{1}. \quad (3.8)$$

The percentage silt in the sample was obtained as follows:

$$\% \text{ silt} = 100 - \% (\text{clay} + \text{sand}). \quad (3.9)$$

3.6.27 Sulphate and Phosphate

Sulphates and Phosphate in the sediment were analyzed using APHA 4500 – SO₄ and APHA 4500 – PO₄ APHA (1995). 10mL of sediment solution was transferred into sample cuvette. To this was added the contents of the reagent powder pillow either for sulphates or phosphates to form complex ions. The colour was noted and the reading (mg/L) was taken on HACH 2400 spectrophotometer.

3.7 Heavy Metal Analysis Using Atomic Absorption Spectrophotometer (AAS)

The heavy metals were determined using atomic absorption spectrophotometer. The concentrations of the heavy metal were determined using standard solution of metal.

The sample was mixed thoroughly by shaking. 100mL of the sample was transferred into a glass beaker of 250 mL volume and 5mL of conc. Nitric acid was added and heated to boil till the volume was reduced to 20mL, then 5mL of nitric acid was added until the residue dissolved completely. The mixture was cooled, transferred and made up to 100mL using metal free distilled water. Then the sample was taken to AAS for analysis. The instrument was switched on and left to warm up for some minutes and when the instrument was stabilized the appropriate instrumental conditions were set for each heavy metal. These include the corresponding resonance, wavelength, flame type, fuel type and lamp current. The hollow cathode for each metal was used for the calibration of the instrument using the standard solutions. Each of the working standards was aspirated into the flame and corresponding absorbance for each concentration was recorded. The appropriate wavelength for the metal to be detected was selected, the slits were adjusted to get closest to the required wavelength to avoid excess light. The acetylene-air mixture was lit at recommended pressure, the burner level was adjusted. The samples were aspirated by feeding them through the capillary and the readings were noted.

3.8 Determination of PAHs Level

PAHs in water, sediment and fish samples from Imo River were determined using GC-MS (Gas Chromatography-Mass Spectrometer).

3.8.1 Determination of PAHs in Water

Water samples were filtered through whatman filter paper of 0.45 μ m diameter followed by liquid-liquid extraction using dichloromethane. 100ml of the water sample was measured into a separating funnel and 25mL of dichloromethane was added to the sample and shaken vigorously so as to extract all the available organic material. The separating funnel was left undisturbed on a retort stand for some time so that the mixture separated into the organic and water layers. After this extraction, another batch extraction was repeated with hexane and dichlo-

romethane mixture as solvent. The organic extract was collected into a receiving container and passed through chromatographic column containing glass-wool, silica-gel and anhydrous sodium sulphate which serve as a dehydrating agent. The extract was concentrated using water bath at 40°C. The concentrated extract was dissolved with 1mL of dichloromethane. The dissolved organic extract was injected by means of hypodermisyringe through a rubber septum into the capillary column of the gas chromatograph. The various fractions of the polycyclic aromatic hydrocarbon components were automatically detected as they emerged from the solution using mass spectrometer.

3.8.2 Determination of PAHs in Sediment and Fish

The grammes of the oven-dried ground samples of fish and air-dried samples sieved through 100-mesh stainless sieve were extracted using soxhlet extractor with hexane and dichloromethane(3:1v/v) as the extractor solvent for 6 hours Olawale (2016). The extracts were concentrated to a volume of 1mL at 60°C by a rotary vacuum evaporator. The purified aromatics were analysed by using an HP 6890 series GC system coupled to a mass spectrometer.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Physicochemical Analysis of Water Samples

The physicochemical analysis of Water samples for the period January 2016 to December 2016 are shown in appendices 1 to 12. The wet and dry season statistical variation are shown in Tables 4.1, 4.3 -4.13.

Table 4.1: Physicochemical Parameters of Water Samples from Imo River (IMR) During Dry Season

PHYSICOCHEMICAL PARAMETERS	ASA			ONUIMO			OWERRINTA		
	μ	\pm	CV%	μ	\pm	CV%	μ	\pm	CV%
Color	5.22	± 0.21	4.06	5.26	± 0.28	4.75	5.54	± 0.47	8.48
Temperature	27.8	± 0.70	2.5	28.1	± 0.58	0.58	28.8	± 0.68	2.44
pH	6.96	± 0.089	1.28	6.86	± 0.05	6.8	7	± 0.11	1.56
Conductivity $\mu\text{S/cm}$	134	± 11.40	8.5	132	± 9.70	7.34	154	± 11.40	7.4
Total Dissolved solid mg/l	27.8	± 1.17	4.2	27.76	± 0.90	3.2	29.1	± 0.75	2.58
Total suspended solid mg/l	17.8	± 2.53	14.2	17.3	± 3.6	20.9	19.3	± 5.70	29.52
Turbidity NTU	9.08	± 0.78	8.54	9.88	± 1.53	15.54	9.84	± 3.10	30.5
Nitrate mg/l	7.32	± 1.03	14.07	7.67	± 0.31	4.04	7.72	± 0.74	9.56
Phosphate mg/l	0.52	± 0.045	8.6	0.43	± 0.04	5.1	0.63	± 0.06	8.8
Sulphate mg/l	10.24	± 1.09	10.64	9.16	± 1.58	17.29	9.6	± 0.958	10.23
Dissolved Oxygen mg/l	11.54	± 4.68	40.51	16.2	± 6.68	41.23	13.4	± 5.9	44.2
Biochemical Oxygen mg/l	5.4	± 2.47	45.74	4.86	± 1.92	39.5	5.1	± 2.25	44.4
Chemical Oxygen Demand mg/l	22.8	± 7.43	32.63	23	± 5.92	25.8	22.3	± 7.54	33.8
Total Hardness mg/l	43.32	± 16.72	38.6	49.6	± 13.64	7.44	50.95	± 7.83	15.36
Total viable bacterial cfc/100ml	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total Coliform Bacteria cfu/100ml	ND	ND	ND	ND	ND	ND	ND	ND	ND
Salinity mg/l	0.48	± 0.34	69.85	0.52	± 0.28	54.81	0.612	± 0.11	31.16
Acidity mg/l	23.6	± 15.02	63.63	22.7	± 11.38	50.15	28.64	± 19.19	67.02
Alkalinity mg/l	44.6	± 24.31	54.6	48.6	± 28.6	57.9	55.62	± 28.95	52.04

ND: Not detected, μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for triplicate measurements.

Table 4.2: Physicochemical Parameters of Water Samples from Imo River (IMR) during Wet Season

PHYSICOCHEMICAL PARAMETERS	ASA			ONUIMO			OWERRI-NTA		
	μ	±	CV%	μ	±	CV%	μ	±	CV%
Color	4.62	±0.14	3.02	4.82	±0.13	2.79	5.4	±0.24	4.53
Temperature	26.7	±0.075	0.3	26.66	±0.15	0.6	27.01	±0.71	2.63
Ph	6.7	±0.12	1.72	6.77	±0.09	1.34	6.82	±0.10	1.47
Conductivity μs/cm	82.14	±24.80	30.19	90.9	±25.60	28.16	98.6	±24.70	25.05
Total Dissolved solid mg/l	23.34	±2.47	10.57	25.1	±1.82	7.25	24.81	±2.76	11.13
Total suspended solid mg/l	40.23	±9.94	24.71	36.8	±10.61	0.29	45.63	±18.30	0.4
Turbidity NTU	17.87	±6.66	0.37	16.67	±7.72	0.46	23.53	±8.90	0.38
Nitrate mg/l	10.23	±3.25	31.75	9.93	±2.70	27.22	11.41	±5.20	45.33
Phosphate mg/l	0.51	±0.16	30.62	0.51	±0.11	21.6	0.67	±0.14	21.23
Sulphate mg/l	27.28	±6.80	24.91	28.44	±10.79	37	34.96	±16.06	45.93
Dissolved Oxygen mg/l	32.74	±23.28	71.1	48.73	±29.76	61.08	43.16	±26.5	54.94
Biochemical Oxygen mg/l	6.71	±1.83	27.27	8.41	±4.39	52.19	8.81	±4.14	21.28
Chemical Oxygen Demand mg/l	27.71	±7.90	28.49	21.03	±53.10	14.26	23.44	±7.20	32.06
Total Hardness mg/l	24.5	±8.83	36.6	25.91	±10.17	35.18	31.9	±10.41	12.9
TOTAL VIABLE BACTERIAL cfc/100ml	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total Colifom Bacteria cfu/100ml	ND	ND	ND	ND	ND	ND	ND	ND	ND
Salinity mg/l	0.18	±0.106	59.3	0.26	±0.08	30.76	0.612	±0.08	35.8
Acidity mg/l	42.7	±13.47	31.6	39.6	±13.40	34.1	28.64	±9.83	22.81
Alkalinity mg/l	25.65	±12.55	48.93	48.62	±17.38	76.83	55.62	±20.05	75.95

ND: Not Detected, μ= Mean, ± = Standard deviation, Cv = Coefficient of variation for triplicate measurements.

4.1.1 Colour

The colour observed in dry season with highest value of 5.9 (Pt/Co) from Owerrinta sampling station and least value of 4.4 (Pt/Co) in wet season in Asa sampling station. The water was clear in wet season than in dry season as seen in appendices 1-12. The range of colour observed was 4.4 – 5.9 (Pt/Co) which is lower than WHO permissible limit of 15Pt/Co units.

4.1.2 Temperature

The temperature of water is important in terms of its intended use. For instance, drinking water should have temperature range of 20 – 30°C (Duru and Nwanekwu 2012). Temperature range (26.0 – 28.7°C) of Imo River falls within WHO (2013) standard for drinking water. The temperature values obtained in this study compare favourably with those reported by earlier workers in Imo River water. These earlier works include Duru and Akubugwo (2012), (25.10 – 26.11°C), Duru *et al.*, (2012), (26 – 30°C), Adebisi (1981) (25.10 – 27.8°C), and Aleleye – Wokoma (2007) (26 – 30°C). It compared favourably with Lagos Lagoon waters reported by Emmanuel and Onyema (2011) 23.5 – 30.8°C and Nkwoji (1998) (29 – 29.5°C). There was no significant difference in the temperature of all sampling stations and this is also similar to the report of Gamba (1987) who attributed minimal variation in temperature between stations to the absence of micro climatic variations in temperature.

4.1.3 pH

The mean pH value of the dry season water sample was 6.95 and that of wet was 6.76. The values ranged from slightly acidic value of 6.5 for Asa in wet season to a neutrally level of 7.0 for same location in the dry season. This variation might be due to high level of pollution. The overall pH range of 6.5 – 7.0 was almost within the range for inland water (pH 6.5 – 8.5) as reported by Antoine and Al-Saadi (2002). Boyd and Lickkoppler (2000) reported pH range of 6.09 – 8.45 as being ideal for supporting aquatic life including fish. The pH range obtained in this study is within the acceptable level of 6.0 – 8.5 for culturing tropical fish

species and for recommended levels for drinking water (WHO, 2005). Nigeria Industrial Standard (2007) recommended pH 6.5 – 8.0 for drinking and 6.0 – 9.0 for aquatic life. Although the dry season had slightly higher values, the difference between the two seasons is insignificant. The range of pH values observed in the study area was lower than the range reported for some Nigeria rivers: Kaduna (6.4 – 7.2), River Asa 8 – 8.9 (Olawale, 2016). However, it falls within the range values reported by Okeke and Adinna, (2013), for Otamiri River (6.4 – 6.9).

4.1.4 Conductivity

Conductance qualitatively reflects the status of inorganic pollution and is a measure of total dissolved solid and ionized species in the water. Electrical conductivity varied from 38 – 120 $\mu\text{S}/\text{cm}$ in wet season (appendices 1-12) and 130 – 180 $\mu\text{S}/\text{cm}$ in dry season (appendices 1-12) with an overall mean of 128 (appendix 25). There was seasonal variation in conductivity with a general trend of higher conductivity in dry season than the wet season. There was high significant difference ($P < 0.05$) in the seasons sampled. The lower electrical conductivity recorded in wet season might be due to water dilution, while the higher electrical conductivity recorded in dry season might be attributed to reduced water volume and high rate of evaporation. The dry season values for Asa-Owaza, Onuimo and Owerri-nta were higher than the standard limit of 100 $\mu\text{S}/\text{cm}$ for WHO (2004). This could be as result of the influence of season. Dry season is characterized by low precipitation, higher atmospheric temperature and evaporation (Duru *et al.*, 2005). Ovie and Adeniji (2003) as well as Kolo and Oladineji (2004) observed a similar trend for Shiroro lake. Wide variations were observed in the sampling stations. The wide variations suggest that considerable amount of dissolved ionic substances enter the river due to indiscriminate dumping of waste indownstream. Conductivity value of 148 was observed by Ebigwai *et al.*, (2001) in Kwa River, Calabar.

4.1.5 Total Dissolved Solid

The value of total dissolved solids ranged between 26 – 31.0mg/L in dry season and 20.8 – 28.0 in wet season (appendices 1-12) with an overall mean of 27.5. Total dissolved solids test provides a quantitative measure of the amount of dissolved ions. It is used as indicator test to determine the general quality of water Abowei (2010). Studies however have not shown any health effect associated with ingestion of water with high concentrations of total dissolved solids. The values of total dissolved solids were higher in the dry season than the wet season which is in agreement with the work of Olawale (2016), Duru and Nwanekwu (2012). Sikoki *et al.*, (2004) also acknowledged seasonal and daily changes in the concentration of substances present in water.

4.1.6 Total Suspended Solid

The value of total suspended solids ranged between 14.0 – 28.6mg/L (appendices 1- 12) in dry season and 24.8 – 702) for wet season (appendices 1-12) with an overall mean of 30.8. The values of 14.0 and 24.8 for Onuimo for dry & wet seasons analysis respectively were the lowest recorded for this study. The seasonal profile of total suspended solids in Imo River indicated that wet season levels were higher than dry season values. Ovie and Adeniji (2003) as well as Olawale (2016) observed a similar trend for Shiroro lake, Ogun River and Asa River. The wet season increase in total suspended solids in Imo River was probably due to large amount of silt and debris held in suspension just before the rains Amadi (2010). The dry season decrease in level of total suspended solids was probably due to sedimentation when the current velocity and water level reduced.

4.1.7 Turbidity

Is an important operation parameter in process control and can indicate problems with treatment processes; particularly coagulation, sedimentation and filtration. It causes undersired taste and odours which affects the process of photosynthesis for algal growth. In this work,

turbidity values of 8.0 – 33 (NTU) were recorded in tables (appendices 1-12), indicating that biological process had little effect on the material in the water column. The variation observed could be attributed to the release of suspended particles as a result of sand mining activities in the area and this is in line with the report of Nkwoji *et al.*, (2005) and the work of Ezekwe *et al.*, (2013) who recorded turbidity of 10 in pond water at Imo River Basin area sampled. The study revealed increase in turbidity downstream of the river channel with the least value of 8 at Owerri-nta during the dry season (appendices 1-12) and highest value of 33.4 at Onuimo during the wet season (appendices 1-12). The overall mean of the river turbidity was 14.50 which is well above guideline value of 5 for drinking water (EPA, 2001., WHO, 2008). Higher values were recorded during the wet season which may be due to the fact that river receives large volume of storm water which subsequently increased the volume and flow rate. The faster water flow, the more materials it picks up and the larger the size of the pieces carried along. As water slows down, the larger particles settle out while clay and silt remain suspended in water longest, because of their particle size and specific gravity (Aiyesanmi *et al.*, 2006, Tukura *et al.*, 2012;). This is confirmed by the higher total suspended solid recorded for the wet season's study (25.04 – 70.6). This also agrees with the work reported by Salaudeen Olawale (2015) in the study of physico-chemical analysis of water from Asa River, Ilorin with turbidity of 11.13 – 35.4 and total suspended solid of 12.27 – 244.00. It is note worthy that turbidity classification gives [< 10(excellent), 15 – 30 (fair), > 30 (poor) (EPA, 2001)].

4.1.8 Nitrate

Nitrate concentrations varied with sampling locations. It was below 10mg/L limit at various locations (Tables 4.1, 4.2). There was significant difference ($P=0.05$) between the seasonal values with wet seasons having higher values than dry season. This agreed with the findings of (Olawale, 2016). This is attributed to increase in farming activities during raining season with application of nitrate and phosphate fertilizers used in agriculture in the study area.

The implication of river waters having high nitrate concentration is the stimulation of the growth of planktons and water weeds that provide food for fish. If algae grow too widely, oxygen levels will be reduced and fish will die and eutrophication sets in Kilfoy *et al.*, (2011) added also that the guideline value for nitrate in drinking water is solely to prevent methemoglobinemia, which depends upon the conversion of nitrate to nitrite. The parametric one-way analysis of variance (ANOVA) indicated that anthropogenic activities such as deforestation, fishing, subsistence agriculture, bathing and washing and inputs from surface run-off associated with human settlement in the present study were not found to have significant impact on the physical and chemical characteristics of the Imo River. There were similarities between nitrates, phosphates and sulphate. Transparency/colour when correlated amongst nitrate, sulphate and phosphate has a significant value < 0.01 .

4.1.9 Phosphate

The phosphate level varied along the sampling locations with area close to upstream having low values than the mid-stream and downstream. The range of values obtained in this study agreed with the moderate to high levels of phosphate in southern Nigeria rivers for example (Egborge *et al.*, 2004), recorded a range of phosphate value of 0.01 – 7.40 mg/L for Yelwa River in southern Nigeria. Ugwu *et al.*, (2015) in their study of physicochemical parameters of water samples from Onuimo River Imo state recorded mean phosphate value of 0.017 with range of 0.01 – 0.03 mg/L. However, the phosphate values in this study were higher than the permissible limit of 0.1 mg/L. There was significant difference $p = 0.05$ between the means of dry and wet season values. Inputs of phosphate from detergents used in various car wash centres close to the river might have contributed to high phosphate value greater than the permissible limit. Although phosphates are not toxic and do not represent a direct threat to animals and other organisms, they do represent a serious indirect threat to water quality (Ijeh and Onu, 2013). The results obtained from this study agreed with the results obtained from analysis of pollution status of Asa River by (Olawale, 2016). He found out that value of phosphate

of Asa River water ranged from 1.90 – 12.40mg/L in wet season and 0.25 – 0.89 in dry season. Okorondue *et al.*, (2015), in his study found that the phosphate values of Oguta Lake water fall within the range of 0.02 – 0.50 with upstream having the highest value of 0.50 and mid stream, the least value of 0.02. Ijeh and Onu (2013) detected phosphate concentration of 0.36 – 0.89. However, typical phosphate concentrations in surface waters is 0.30 or more in nutrient enriched waters, although 0.10 is the recommended maximum concentration for rivers and stream (DWAF, 1996). Thus, the mean phosphate value recorded in Imo River was above the recommended maximum concentration 0.1. The significance of phosphates in river is principally, in regard to the phenomenon of eutrophication enrichment of lakes and rivers. Nitrites and phosphates promote the growth of algae and other plants leading to algae blooms, littoral shimes, diurnal dissolved oxygen variations of great magnitude and related problems (EPA, 2001).

4.1.10 Sulphate

From Tables 4.1 and 4.2, there was increase in values of sulphate from Imo River in wet season than in dry season. The mean value of sulphate in wet season was 30.25mg/L and 9.66mg/L for dry season. The sulphate values for the sampling points and location ranged from 7.2 to 58. Significant amount of sulphate is introduced into the river as a result of industrial agricultural and domestic activities.

4.1.11 Dissolved Oxygen (DO)

Dissolved oxygen content of the study areas/locations ranged from 8.6 – 82.7mg/L. It agreed with the values obtained by Olawale (2016) in the study of physiochemical analysis of water from Asa river that ranged from 4.80 – 9.30. Seasonal variations observed in DO content with higher value in wet season could be due to increased aeration due to rainfall. Domestic, agricultural, industrial effluent and waste discharge into rivers is a usual practice in Imo/Abia State and their environs and is the main reason for the pollution of the river. The coefficient

of variation of water samples from Imo River ranged from 40.51% in dry season to 71.10% in wet season. The dissolved oxygen of wet season was significantly higher than that of dry season, this probably was as a result of influence of temperature or oxygen dissolution. The findings agreed with the report of Okeke *et al.*, (2013) where the dissolved oxygen of dry season fell within the range of 3.4 – 5.1. These findings agreed with the findings of Duru and Nwanekwu (2012) with DO values of 1.60 – 5.60. Dissolved oxygen (DO) was also above limits in some of the locations. DO is one of the most important parameters in agriculture. It is needed by fish to respire and perform metabolic activities. These low levels of dissolved oxygen are often linked to fish kill incidents. In general, a saturation level of at least 5 is required, values lower than this can put undue stress on fish and levels below 2 may result in fish kills (USEPA, 2013).

4.1.12 Biochemical Oxygen Demand (BOD)

The result obtained from the study indicated biochemical oxygen demand (BOD) values ranging from 5.3 – 15.0mg/L for wet season and 3.2 – 7.8 for dry season (appendix 1-12). The variation in BOD was observed to be similar to that of DO. The general high BOD values observed during wet season may be due to increased urban runoff which carried wastes from streets and side walks; nutrients from loan fertilizers, laces, grames, chippings and paper from residential areas into the river. The results from this study agreed with the finding of Olawale (2016) where the BOD values ranged from 2.90 – 6.70 for wet season and 2.20 – 4.80 for dry season. The coefficient of variation for wet season and dry season were 27.27% and 45.74% respectively for Asa Owaza (Tables 4.1, 4.2).

Akubugwo *et al.*, (2013) in his finding in assessment of water quality of Njaba River obtained BOD values 2.4 – 8.3 which agreed with this study values. The results of Ijeh (2012) were similar to results of George *et al.*, (2010) where they obtained BOD values of 2 – 17 with mean value of 3.25 and 2 – 18 with mean value of 333 respectively which is similar to

the BOD mean value of obtained in this study. Olawale(2016) in their study of assessment of water quality in Asa river observed BOD values that ranged from 6.8 to 14.00. The high BOD values are indicative of the presence of organic and inorganic pollutants respectively in Imo river water. The mean BOD values of all samples exceeded the recommended maximum allowable concentration (RMC)/WHO set by the European Union for good quality water for fisheries and other aquatic life which is 3.0 – 6.0/ 3- 5(ppm). Unpolluted waters typically have BOD values of 2 or less whereas those receiving waste waters may have values up to 10mg/L or more (Amadi 2010).

The BOD values are high probably due to discharge of domestic waste especially defecation activities and poorly executed agricultural activities near river banks which was observed during survey of study site. Okeke and Adinna (2013) observed similar values, the BOD values they obtained from all locations were higher than 4.0 WHO standard limit except for values from location (upstream) which was within standard. The BOD of 2.3 – 18.2 (dry season) and 2.01 – 13.21 (wet season) were obtained from the study of Otamiri river, a tributary of Imo river. This agrees also with the report of Amadi, (2010) and Dike, (2002) that there were significant increases in organic and bacterial load after rain storm since BOD and COD levels exceeded the recommended limit of WHO (3.5 – 5), BOD and COD directly affect the river system.

4.1.13 Chemical Oxygen Demand

The level of COD in the sampling points exceeded the 10mg/L COD of WHO and EU maximum permissible level for drinking water and aquatic life (Chapman, 1996). The COD values varied between 13.6mg/L – 30.2mg/L in dry season and 11.2 – 38.0 in wet season. COD determines the amount of oxygen required for chemical oxidation of organic compounds. High COD levels lead can lead to the death of fish and can cause dysentery in human who use the polluted water. Amadi (2016), in his study on assessment of water quality index of Otamiri

and Oramiri-Ukwa along Imo River observed COD values of 10.20mg/L – 42.00mg/L with mean value of 31.82 which agreed with overall mean of COD 25.68mg/L obtained in this study (appendix 25).

4.1.14 Hardness (Total Hardness)

Wide variations were observed in the figures of total hardness at all sampling points for the two seasons. Total hardness is due to presence of bicarbonate, sulphate, chlorides and nitrates of calcium and magnesium. Hard water requires more soap and synthetic detergents for laundry and washing and contributes to scaling in boilers and industrial equipments (Ajayi *et al.*, 2003). The maximum permissible limit for total hardness for drinking water is 500mg/L as shown in appendix 13 (Kumar *and* Park, 2011). The result of hardness indicated low hardness values during wet season (appendix 25) and higher values during dry season (appendix 25) which may probably be due to high dilution during wet season. The measured values in the river water samples ranged from 10.4 – 46.2 in wet season and 30.7 – 70.2 in dry season. Duru *et al.*, (2012) in the study of physio-chemical status of Nworie River found out that the total hardness in the water ranged from 10.6mg/L to 50.87. The results of this study agreed with the finding of Olawale (2013) in his study of Asa River water. The measured values in the river water samples ranged from 38.20 – 128.2. Also the hardness recorded by Asomugha and Adeogba (2013) were not significantly different from each water. The variation in hardness observed in this study agreed with the result of Idowu *et al.*, (2011) and can be linked with the presence of Ca^{2+} and Mg^{2+} in the water system.

4.1.15 Total Viable Bacteria

Total viable bacteria was not detected in all the samples in various sampled locations in this study.

4.1.16 Total Coliform Bacteria

There were no coliform bacteria found in the samples investigated (Table 4.1 and 4.2)

4.1.17 Salinity

Salinity of surface water is relatively uniform as it is generally well mixed by waves, wind and tides. However, variation of surface water salinity is due to the effects of rainfall, evaporation, precipitation and other weather related factors that are often observed. From this study, the results of salinity values ranged from 0.40mg/L – 0.79mg/L in dry season and 0.1 – 0.40 in wet season. Salinity is considerably higher during the dry season when sea water penetrates far up the rivers, than in the wet season when rain water and flood from Niger and Benue rivers drive the salt water back towards the sea due to the movement of sea and ocean. The results in this study agreed with the report of Ajibare (2014) in his assessment of Ondo River with salinity of 9.93 – 17.49. Ramane and Schlieper (2013) opined that salinity is the major environmental factor restricting the distribution of marine and lacostre taxa, resulting in poverty of species in brackish and fresh water.

4.1.18 Acidity

In this study the acidity values in mg/L ranged from 13.2mg/L – 60.4mg/L with an increase in wet season over dry season values as reflected in the pH of the river water. The acidity values agreed with that reported by (Olawale, 2016), with acidity value of 28.80 – 55.4 in wet season and acidity value of 26.3 – 40.8 in dry season with range of 26.3 – 55.4. Also Okeke *et al.*, (2013) reported acidity value of 12.1 – 50.4 which agrees with the present study. Data from this study showed that the level of acidity of the water samples was within the stipulated limit by WHO despite the variation of pH in the water samples.

4.1.19 Alkalinity

The total alkalinity ranged from 93mg/L– 80.8mg/L(appendix25) with mean value of 49.6 in dry season and 24.89 in wet season. Since alkalinity is pH dependent and a reversal of acidi-

ty, the higher value recorded during the dry season is expected. The alkalinity values of Imo River was 9.3 – 70.0 in wet season with overall mean of 35.13. The alkalinity agreed with the range value of 86.25 – 205 with overall mean of 127.10 as documented by Olawale (2016). The alkalinity is higher in the dry season and lower in the wet season, when the dam had high water level. This could be due to low water level with its attendant concentration of salts and lower value in wet season as this could be due to dilution. Ufodike *et al* (2001) recorded similar result for Dokowa Lake. The high levels of alkalinity in the dry season agreed with the findings of Amadi (2010), on the correlation of seasonal fluctuation of water level and alkalinity. Similar observations have been made by Olawale (2016) in Rivers Sokoto in Asa River. The coefficient of variation of acidity in dry and wet seasons were 63.63% and 31.60% respectively (appendix 25) while that of alkalinity were 54.60% for dry season and 48.93% for wet season (appendix 25). Emmanuel (2016) in his study of physico-chemical parameters of Onuimo River in triplicate batches of samples observed alkalinity and acidity values of 40.6 and 25.9mg/L respectively which agreed with the findings of this study. Data from this study showed that the alkalinity of the water samples were within the stipulated limit 200mg/L, despite the temporary and spatial variation of the values. The low level of the alkalinity indicates that the underlying rock which is the main source of natural alkalinity probably contains low carbonate, bicarbonate and hydroxide (Burasohain and Sarma, 2012).

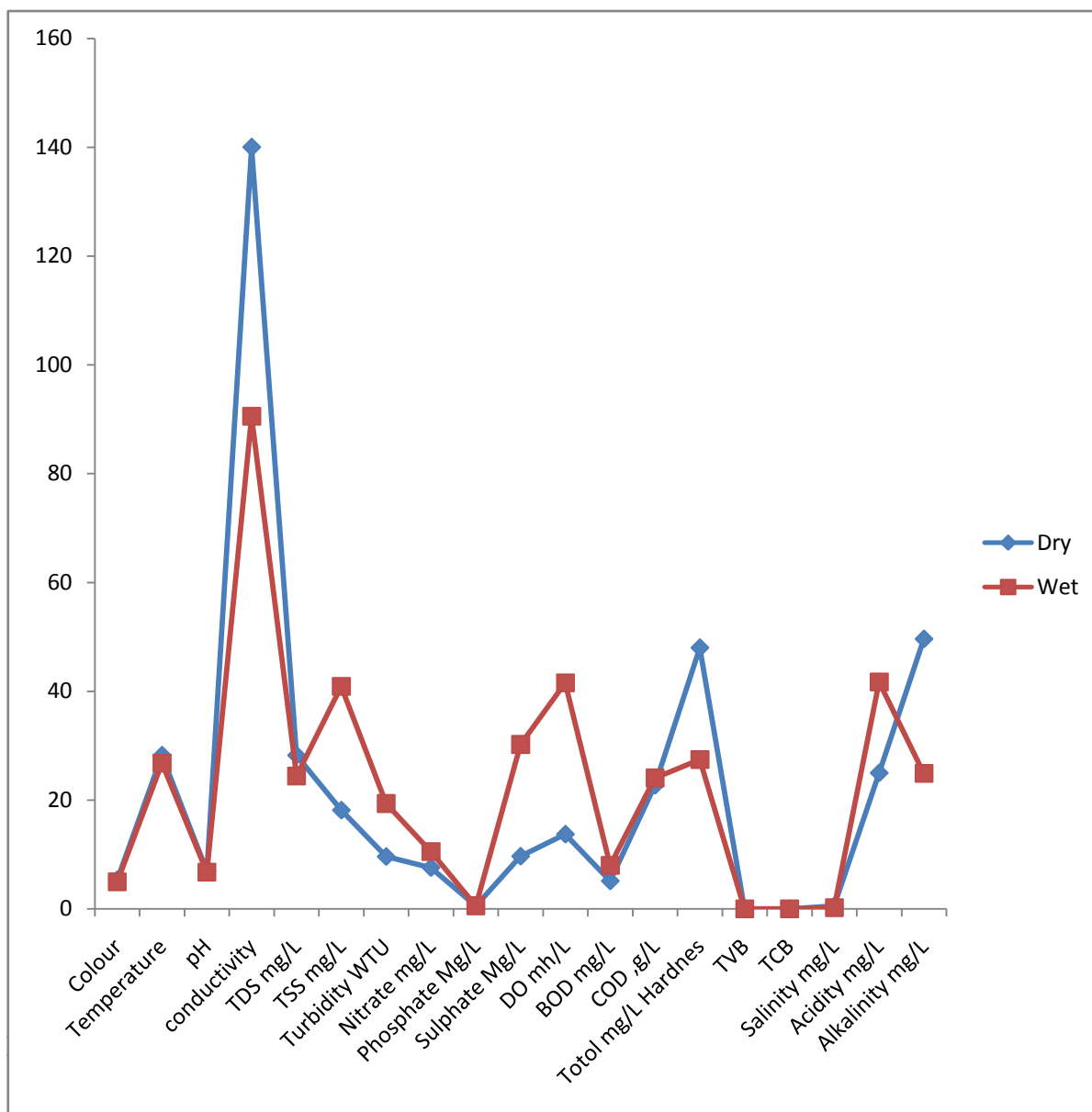


Figure 4.1: Seasonal Variation of Physi-cochemical Parameters in water samples from Imo River.

Fig.4.1 and Appendix 25 showed that conductivity, temperature, pH, TDS, COD, total hardness, alkalinity and salinity were higher in dry season than wet season. Acidity, TSS, Turbidity, DO and BOD were higher in wet season than dry season.

4.2 Physicochemical analysis of sediment in Imo River

The results of physicochemical analysis of sediment samples from Imo River are shown in Tables 4.3-4.4 and appendix 26.

Table 4.2: Physicochemical parameters of Sediment in Imo River during Dry season

S/N	PHYSICOCHEMICAL PARAMETERS	ASA-OWAZA			ONUIMO			OWERRI-NTA		
		μ	\pm	CV%	μ	\pm	CV%	μ	\pm	CV%
	pH	6.84	± 0.05	0.84	6.74	± 0.051	0.81	6.84	± 0.49	1.32
	Temperature	26.56	± 0.43	1.61	26.48	± 0.79	2.98	26.70	± 0.38	1.42
	Conductivity us/cm	82.6	± 11.13	13.5	75.8	± 7.09	9.35	11.10	± 25.9	23.4
	Total Organic Carbon	0.49	± 0.27	55.45	0.49	± 0.23	47.7	0.52	± 0.25	48.65
	Total Nitrogen	0.026	± 0.01	38.8	0.04	± 0.006	15.15	0.08	± 0.014	47.39
	Sand %	50.74	± 5.74	11.31	52.68	± 4.68	8.89	58.41	± 8.28	14.18
	Silk %	26.15	± 7.56	28.9	33.25	± 6.47	19.46	25.67	± 8.06	34.53
	Clay %	23.24	± 3.91	16.84	14.08	± 6.66	47.3	15.93	± 6.14	38.54

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for triplicate measurements

Table 4.3: Physicochemical Analysis Result of Sediment Samples from Imo River (IMR) during Wet Season

PHYSICOCHEMICAL PARAMETERS	ASA-OWAZA			ONUIMO			OWERRI-NTA		
	μ	\pm	CV%	μ	\pm	CV%	μ	\pm	CV%
pH	6.70	± 0.066	1.00	6.71	± 0.066	1.00	6.67	± 0.700	1.13
Temperature	26.5	± 0.21	0.79	26.63	± 0.226	0.773	26.35	± 0.18	0.68
Conductivity us/cm	52.14	± 9.94	19.00	68.00	± 4.62	6.8.0	75.00	± 6.14	8.5.00
Total Organic Carbon	0.683	± 0.24	34.00	0.765	± 0.25	32.00	0.77	± 0.23	29.00
Total Nitrogen	0.031	± 0.14	45.00	0.61	± 0.85	13.80	0.035	± 0.21	61.00
Sand %	65.86	± 8.6	13.00	63.93	± 3.00	4.70	68.72	± 6.68	13.18
Silk %	24.84	± 4.83	19.00	25.01	± 2.51	10.04	22.79	± 3.00	13.18
Clay %	9.5	± 5.57	58.6	8.215	± 3.49	42.40	8.59	± 6.7	78.00

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for triplicate measurements

4.2.1 pH

The pH values of sediments from Imo River in this study ranged from 6.5 – 6.90 which is slightly acidic within the permissible limit of WHO for drinking water and aquatic life. High pH value was observed during the dry season, there is a correlation between high pH and alkalinity in Tables 4.3-4.4. The results in this study agreed with the report of Ogwoet *al.*, (2014), in analysis of sediment and fauna of Osondu River in Okigwe with pH 6.4 – 7.2. Ezekiel *et al.*, (2011), reported pH value that ranged between 5.06 – 5.85 with a mean value of 5.59 in Sombrero river sediment. This indicated that the river sediment is acidic which does not compare favourably with the report of this study. However, Chindahet *al.*, (2004) reported alkaline range of 6.9 – 7.8 from fresh water stream of Minichida stream, Niger Delta. Minichida stream is alkaline while Imo River is slightly acidic. This difference may be attributed to the fact that Minichida stream is in urban location characterized by land drainage pollution arising from the presence of automobile workshops, photographic workshops and other commercial activities (Chindahet *al.*, 2004).

4.2.2 Temperature

The temperature of the sediment samples in the various locations along Imo River ranged from 26.04°C – 26.9°C (Appendices 13-24). Owerri-nta and Onuimo recorded the highest value of 26.9°C during dry season. The mean values of dry and wet seasons were 26.58°C and 26.49°C (Appendix 25) respectively. Umunnakweet *al.*, (2013), in their investigation on water quality of Imo River reported temperature values of 26.10°C, 26.3°C and 26.0°C for upstream, midstream and downstream respectively with mean value of 26.20°C. These results agreed with the mean value of this study.

4.2.3 Electrical Conductivity

Electrical conductance is a good measure of dissolved solids. Conductivity is a measurement used to determine mineralization of sediments. In this study the conductivity of sediment-sample in wet season ranged from 40 – 150 $\mu\text{S}/\text{cm}$ with mean value of 77.40 while in dry season it ranged from 64– 150. High conductivity was recorded in dry season due to water dilution, while low mean electrical conductivity might be due to reduced water volume and evaporation. This agreed with the findings of Ogwo *et al.*, (2014) in his study of physicochemical parameters of sediment of Vasai Creek Mumbai, India which reported conductivity values of 102 – 276 in dry season and 72 – 20 in wet season with mean value of 165 $\mu\text{S}/\text{cm}$. Tukura *et al.*, (2012) reported electrical conductivity of 4.98 – 7.46 in dry season and 3.60 – 4.53 in wet season in their study of Mada River, Nassarawa State.

4.2.4 Total Organic Carbon (TOC)

The total organic carbon content of the sediment in both seasons (Tables 4.3-4.4) were within an optimum value of 1.0%, indicating a moderate content of organic matter in Imo River (IMR) sediment. This agreed with the one observed by Etesinet *et al.* (2013). It also agreed with findings of USEPA (1999). The mean value of total organic carbon (TOC) value of Imo River (IMR) was 0.51% in dry and 0.73% in wet season which agreed with the one reported by Marcus *et al.*, (2013) of TOC of (1.14±0.40). Total organic carbon of sediments of Imo River ranged from values of (0.26 – 0.96%). This agreed with Marcus *et al.* (2013) results at Bonny Greeks with TOC values of 0.34 – 1.14%. TOC has been recognized as an analytical technique to measure water quality during the drinking water purification process. TOC in source waters comes from decaying natural organic matter (NOM) and from synthetic sources. Humic acid, fulvic acid, amines and urea are the types of NOM. Detergents, pesticides, fertilizers, herbicides, industrial chemicals and chlorinated organics are examples of synthetic sources (Jaoude *et al.*, 2016).

4.2.5 Total Nitrogen (TN)

The range of total Nitrogen (TN) was (0.008 – 0.068%) in the Imo River as shown in appendices 13-24 which is similar to those found off major rivers like Iko River;(Abia), Otammiri River, Nworie River (Imo), Okirika river (Rivers) and Amazon river. (Ramashang *et al.*,2008, Etesin *et al.*,2013, Marcus *et al.*,2013, Okeke *et al.*,2013,). The concentrations of total nitrogen in the study locations were quite low and similar. The results obtained revealed that there was no significant difference $P>0.05$ in the mean levels of total nitrogen in the locations during the wet and dry season. The levels observed in Imo River (IMR) were 0.012 – 0.05% (appendices13-24) in dry season and 0.008 – 0.068% in wet season (appendices 13-24). This agreed with the findings of Onyegeme-Okerenta (2016), who observed the total nitrogen (TN) levels in Imo River estuary with values of 0.12 – 0.47% and 0.11 – 0.30% during wet and dry seasons respectively.

4.2.6 Sediment Particle Size (%Sand, %Clay, %Silt)

The average results of the percentage composition of sand, silt and clay of the stations or locations of Imo River are presented in Tables 4.3-4.4 and appendices 13-24 and 26. The sand contents of the sediment were high across the locations. The percentage sand content ranged from 37.66% - 73.84%. Asa had the highest value of 73.84% and Onuimo had the lowest value of 37.66%(Fig 4.2 and 4.3). The percentage silt content ranged from 20.13% - 41.61%, with mean value of 28.30% in dry season and 24.20% in wet season (appendix 26). The percentage clay content ranged from 2.03% - 27.93%. The results of the sediment analysis showed that sand was dominant across the stations. This agreed with the report of Ezekiel *et al.*, (2011) in analysis of sediments from Sombreiro River (% sand of 60.12 – 90.68%) with mean value of 73.9%, (% silt of 13.46 – 38.63% with mean value of 27.14% and % clay of 18.6 – 30.98% with mean value of 20.0%. Ezekiel *et al.*, (2011) also reported that sand was dominant across the locations analyzed. Ogwo *et al.*, (2004) also concluded that sand dominates across the stations of Okpoka Creck. Allan (1995) reported that sediments depend on the parent material available and deposits of materials. The mean value of clay in wet season was 8.77% while in dry season the mean value was 17.80% (Appendix 26).

4.2.7 Seasonal Variations of Physicochemical Parameters Using Charts and Plots

The variations of physicochemical parameters for wet and dry seasons are showed in figures 4.2 to 4.4.

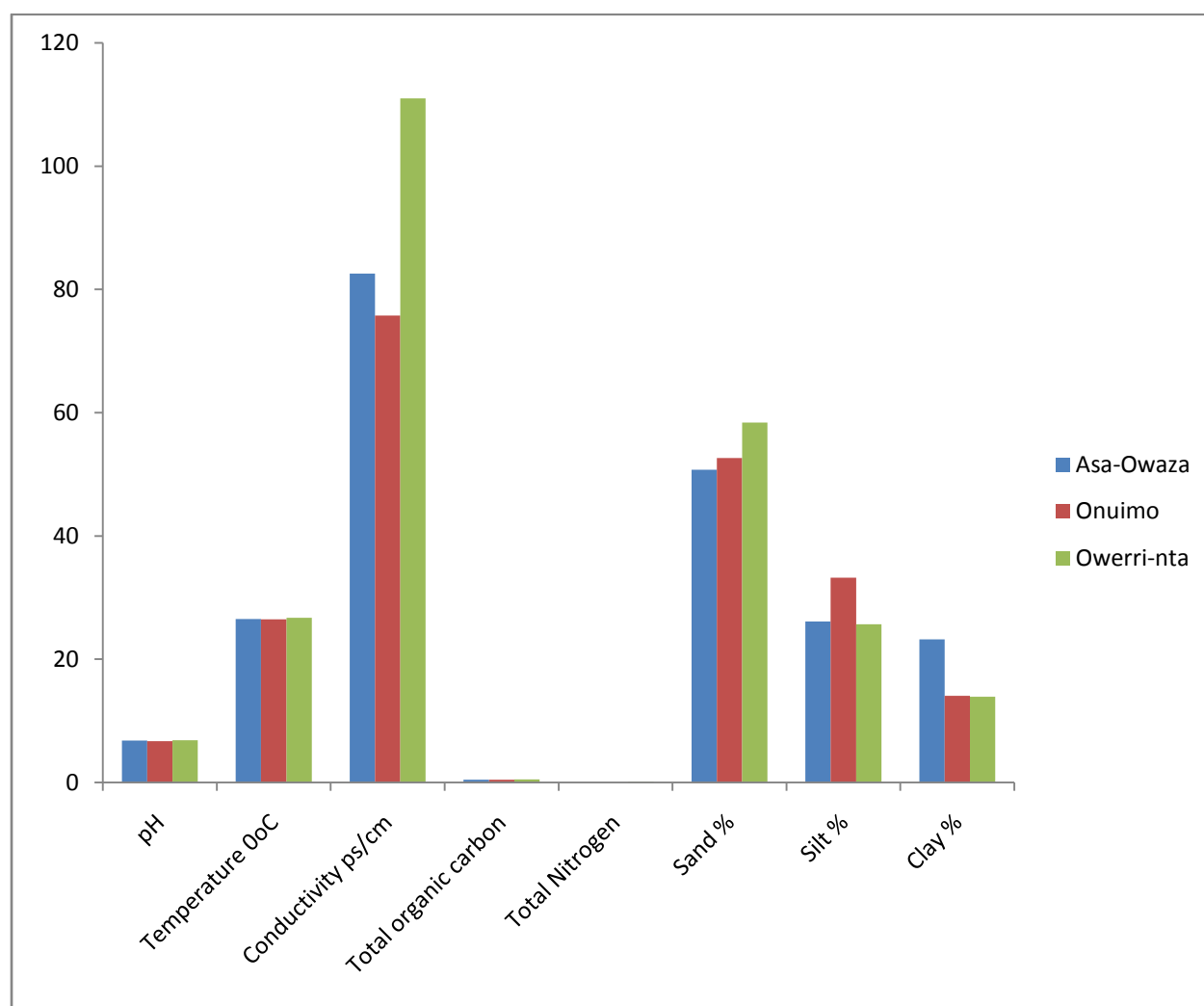


Fig 4.2: Physico-chemical analysis result of sediments from Imo River during dry season

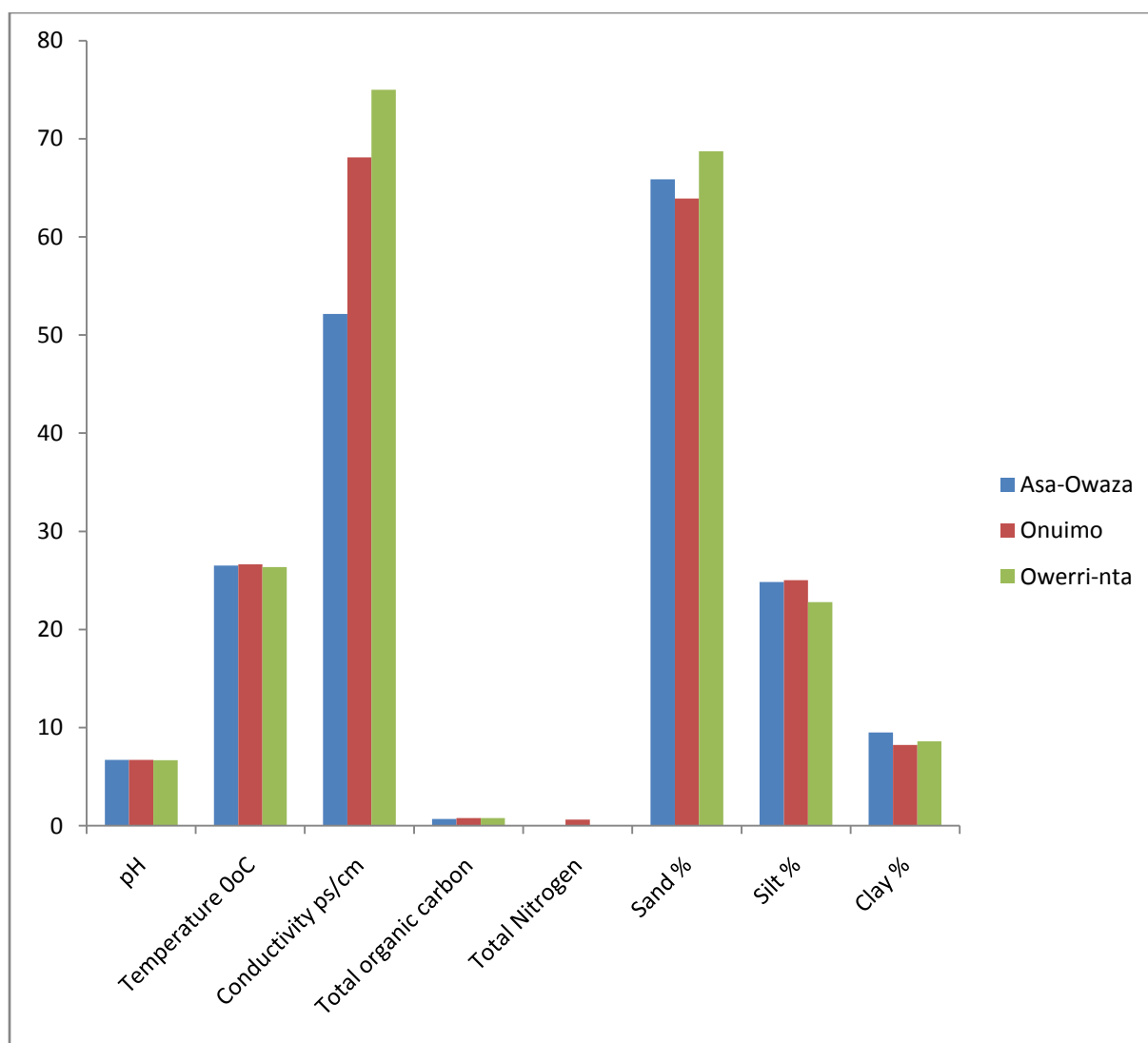


Fig 4.3: Physico-chemical analysis result of sediments from Imo River during wet season

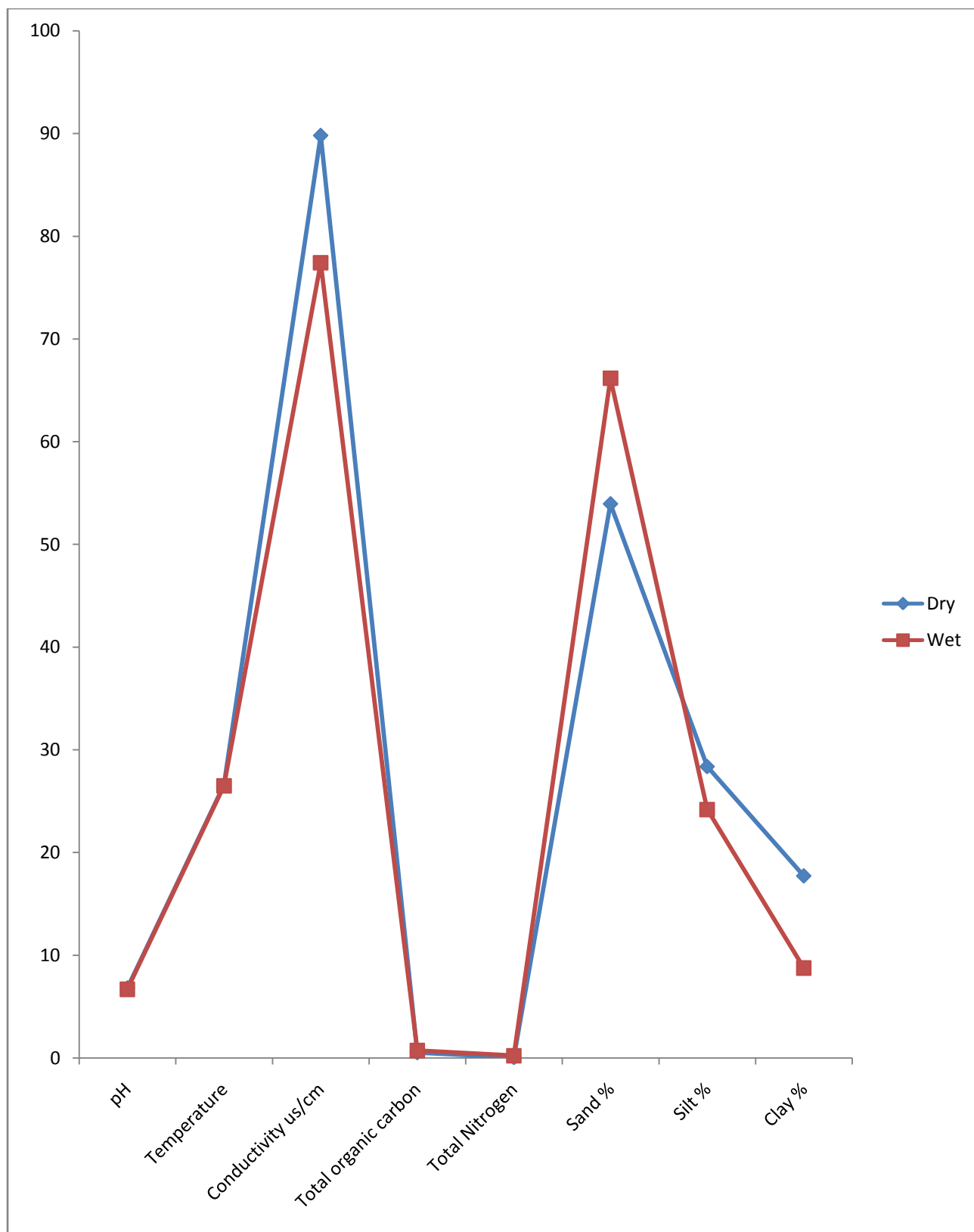


Fig 4.4: Seasonal variation of sediments from Imo River for both seasons (wet and dry).

pH of sediments of Imo River ranged from 6.67-6.84. This indicates that the pH of the river is slightly acidic. Organic matter in water body can be measured using TOC. Figures 4.2, 4.3, and 4.4 revealed that sediment materials are derived from mineral source, since the levels are less than 12% w/w of sediments;(levels above 12% suggest that the sediments materials are from decaying organic source). The figure 4.2 to 4.4 showed that Owerri-nta had the highest percentage of sand (68.72%). This may account for heavy sand mining activities going on in the station. The mean value of % sand obtained in the study were 65.86, 63.93 and 68.72 for Asa-Owaza, Onuimo and Owerri-nta respectively in wet season and that of dry season for Asa –Owaza, Onuimo and Owerri-nta were 50.74 52.68 and 58.41 respectively. The mean value clay in wet season for Imo River is 8.76% while in dry season the mean value for Imo River was 17.8%(appendix 26).

4.3 Heavy Metal Concentration in Water Samples from Imo River During Dry and Wet Season.

Table 4.5 – 4.6 showed the concentration of heavy metals in dry and wet seasons. Table 4.7 showed heavy metal comparison with standards.

Table 4.5: Heavy Metal Concentration in(mg/L) in Water from Imo River during Dry Season

	Fe		Cd		Pb		Ni		Zn		Cu		V		
Location	μ	±	CV(%)	μ	±	CV(%)	μ	±	CV (%)	μ	±	CV (%)	μ	±	CV (%)
Asa-	0.1247	+0.0	11.6	0.0018	+0.0	55.5	0.0615	+	48.8	0.0015	+0.00	66.7	0.015	+0.0	66.7
Owaza	14			01			0.03			15			1		
Onuimo	0.26	+0.02	7.6	0.018	+0.00	83.3	0.0980	+	51.0	0.0504	+0.03	59.5	0.215	+0.0	37.2
				15			0.05			8			5		
Owerri-	0.1623	+0.0	18.5	0.0013	+0.0	76.9	0.0421	+	47.5	0.0309	+0.02	64.7	0.05	+0.01	20.0
nta	3			01			0.02						5		

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for seven measurements

Table 4.6: Heavy Metal Concentration (mg/L) in Water from Imo River During Wet Season

	Fe		Cd		Pb		Ni		Zn		Cu		V		
Location	μ	±	CV(%)	μ	±	CV(%)	μ	±	CV(%)	μ	±	CV(%)	μ	±	CV(%)
Asa-Awaza	0.0247	+0.01	40.5	0.0014	+0.01	71.4	0.0553	+0.05	90	0.0013	+0.001	76.9	0.012	+0.06	50
Onuimo	0.036	+0.02	55.5	0.0014	+6.001	71.4	0.0814	+0.06	73	0.0500	+0.03	60	0.220	+0.10	45.5
Owerri-nta	0.0021	+0.001	50	0.0012	+0.002	60	0.0321	+0.01	31.15	0.0301	+0.02	66.5	0.03	+0.01	66.7

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for seven measurements

Table 4.7: Heavy Metal Concentrationin (mg/L) from Imo River (IM) in Comparison with Water Guidelines

Location/guideline	Fe	Cd	Pb	Ni	Zn	Cu	V
WHO	0.5 – 50	0.003	0.05	0.02	3.0	2	-
SON	-	0.005	0.01	0.02	-	-	-
WPCL	0.01	0.003	0.01	0.02	-	-	-
USEPA	1.0	0.01	0.05	-	1.0	-	-
IMR (Wet season)	0.020	0.0013	0.556	0.271	0.087	0.0165	0.014
Mean Value							
IMR (Dry season)	0.181	0.016	0.032	0.028	0.093	0.023	0.020

The mean concentrations of heavy metals ranged from 0.0015mg/L – 0.26mg/L in dry season. Nickel has the least value of 0.0015 in Asa – Owaza while concentration of Fe is 0.26 in Onuimo station. (Table 4.5). In wet season, the least value was recorded for Nickel (0.0013 in Asa-Awaza. While the highest mean value was recorded for Fe with value of 0.036 in Onuimo station. From Table 4.7, the heavy metal concentration of Pb (0.5) and Ni (0.22) in Imo river water along sampling points from Onuimo to Asa-Owaza axis in wet season were above the WHO, SON, USEPA, WPCL recommended limit of Pb (0.05, 0.01, 0.01, 0.05) and Ni (0.02, 0.02, 0.02, Nil) respectively. In dry season the heavy metal concentrations of Pb (0.016) and Ni (0.028) of the study area water samples are slightly above the WHO, SON, WPCL and USEPA standards. In this study, Table 4.7 and appendix 27 the mean values of heavy metals in dry season were Fe (0.183), Cd (0.0016), Pb (0.067), Ni (0.028), Zn (0.093), Cu (0.023), V (0.060) respectively. In wet season, the mean values of heavy metals were Fe (0.020), Cd (0.0013), Pb (0.056), Ni (0.0271), Zn (0.087), Cu (0.0163), and V (0.059) respectively. Concentrations of most of the heavy metals analyzed were below the WHO, NESREA, SON, WPCL and USEPA permissible limit as shown in Table 4.7 except concentration of Nickel in both seasons which was above WHO, SON and WPCL permissible limit. This could be attributed to effluents from industries and wastes from homes which enter the river system. Ozeet *al.* (2006) in their work observed that the mean values of metals were Ni (0.21), Cr (0.5), Cd (0.03), Mn (0.14) and Pb (0.3), based on WHO safety standard, the result indicated that the water were polluted with respect to all the metals except Mn and Zn.

The level of Fe in the dry season in this work varied as follows: Onuimo > Owerri-nta > Asa – Owaza while the trend for the wet season Onuimo > Owerri-nta > Asa – Owaza. The concentration of cadmium in this study ranged from 0.0013 – 0.0018 at Owerri-nta, (Asa Owaza) and Onuimo stations. The mean concentration of cadmium was 0.0016 in dry season. The

least variability for cadmium (55.5%) was obtained from Asa-Owaza during dry season while the highest variability was obtained at Onuimo and Asa-Owaza with CV=71.4%. The distribution pattern of lead revealed that Owerri-nta recorded the lowest concentration (0.0321) during wet season while Onuimo recorded the highest concentration of 0.0980 during dry season. The trend for dry season was Onuimo > Asa – Owaza > Owerri-nta. The order of decrease for lead in wet season was Onuimo > Asa-Owaza > Owerri-nta. The least of coefficient of variation for lead was obtained at Owerri-nta (CV = 31.15%) during wet season while the highest variability was obtained at Asa Owaza with CV = 90% during wet season. The values of Nickel in this study ranged from 0.0015 in Asa-Owaza station, 0.0501 in Onuimo during the dry season while the values of concentration of Nickel was 0.0013 to 0.0504 for wet seasons.

The result for the heavy metals investigated in this study is consistent with the report of Duru and Nwanekwu (2010) and Amadi (2010) while Ebong *et al.*, (2004) reported higher values in the wet season than in the dry season. Udosen *et al.*, (2008) also recorded higher values of iron in water from Nworie River compared to other heavy metals determined. The concentration of Lead, Iron, Cadmium and Vanadium in this study are comparable to the values reported by Ebong *et al.*, (2004) for Imo River while research conducted by Ekeanyanwu *et al.*, (2010) and Okeke and Adinna (2013) showed lower values for some heavy metals investigated in Tables 4.6 and 4.7. The concentration of heavy metals in this study at different stations /locations was compared with internal standards. The results revealed that with the exception of Pb, the concentrations of the metals were within the stipulated standards of WHO (2003). High level of heavy metals in dry season compared to wet season depends on several factors. Amadi (2010), suggested that higher level of heavy metals in dry season compared to wet season depends on several factors such as mechanism of deposition, transport of solute compounds during the wet season, ion exchange of metals with sea-salt cations which reduc-

es metals concentration in the wet season and growth of aquatic organisms. High coefficient of variation (CV) was recorded by some heavy metals at some stations which implied that the metals that have high variability are less stable. Ebong *et al.*, (2004) stated that the value of CV in an environment medium gives an indication of the distribution of the pollutants and their degree of variability. Udosen *et al.*, (2010) stated that lower the coefficient of variation of a heavy metal in an environment, the more stable the metal. More stable metals have the ability of persisting in the environment and this may result in higher pollution level and bio accumulation.

Ihedioha and Okoye (2013) reported that lead in marine environment is associated with oil exploration, pipeline transportation, corrosion inhibition as well as other processes. The results of lead obtained in this study agreed with the reports of Dan *et al.*, (2004) and Ayenimo *et al.* (2009). However, Dan *et al.*, (2004) Nduka and Obi (2010), Udosen *et al.*, (2010) recorded higher values of Pb than this study. Dan *et al.*, (2004) stated that high levels of nickel (Ni) are found in waste from petroleum industries and chronic discharge of such waste can result in Nickel accumulation in the aquatic system. Ebong *et al.*, (2004) linked nickel toxicity to cancer of the lungs, dermatitis (skin irritation) while Udosen *et al.*, (2010) postulated that long term exposure to nickel can result to decreased body weight, heart and liver damage. The level of vanadium in this study especially in some locations in the dry season is due to industrial effluents, discharge by oil tanker, oil drillings and platforms close to Imo River. There is possibility of ocean's tidal wave movement being involved in the transportation of this pollutant. The low concentration of vanadium in this study compared to other metals might be due to low level of vanadium in the earth's crust or soil along the course of Imo River. Health effects of vanadium include irritation of the respiratory tract, hemorrhage, coughing, nausea, vomiting and dizziness. However, the result of vanadium in this study was higher than result reported by Okeke and Adinna (2013), Ekeanyanwu *et al.*, (2010), and Dan

et al., (2014). Iron in this study was higher in dry season than wet season. When compared with other studies in Niger Delta, the result in this study is consistent with report of other authors (Ayenimo *et al.*, 2009, Nduka *et al.*, 2010, Dan *et al.*, 2014). High level of iron in water and food constitute health hazard to people. High level of iron results in gene mutation, haemochromatosis, heart disease, liver problems, streak of blood in stool, vomiting and stomach pains (Duru and Nwanekwu, 2012). The concentration of zinc in water from Imo River during dry season decreased according to the following trend Onuimo > Owerri > Asa-Owaza while the wet season trend was Onuimo > Owerri > Asa Owaza. The value of zinc in this study ranged from 0.0015 in Asa-Owaza during dry season to 0.22 in Onuimo during wet season. The highest variability in zinc CV=66.7% was recorded in Owerri during wet season and the least variability was recorded at Onuimo (CV= 45.5%) during the same season (wet season). The value of copper in this study ranged from 0.01 to 0.04. In Table 4.7 the mean values of copper for dry and wet season were 0.023 and 0.0163 respectively. The dry season's decrease followed the order: Owerri > Asa-Owaza > Onuimo. The concentration of vanadium in Asa-Owaza in this study ranged from 0.008 to 0.137 in Onuimo, with coefficient of variation CV of 25.00% - 81.10%.

4.3.1 Analysis of Heavy Metals in Water using Graphs

Figures 4.5 – 4.7. showed the variations of metals during rainy and dry seasons.

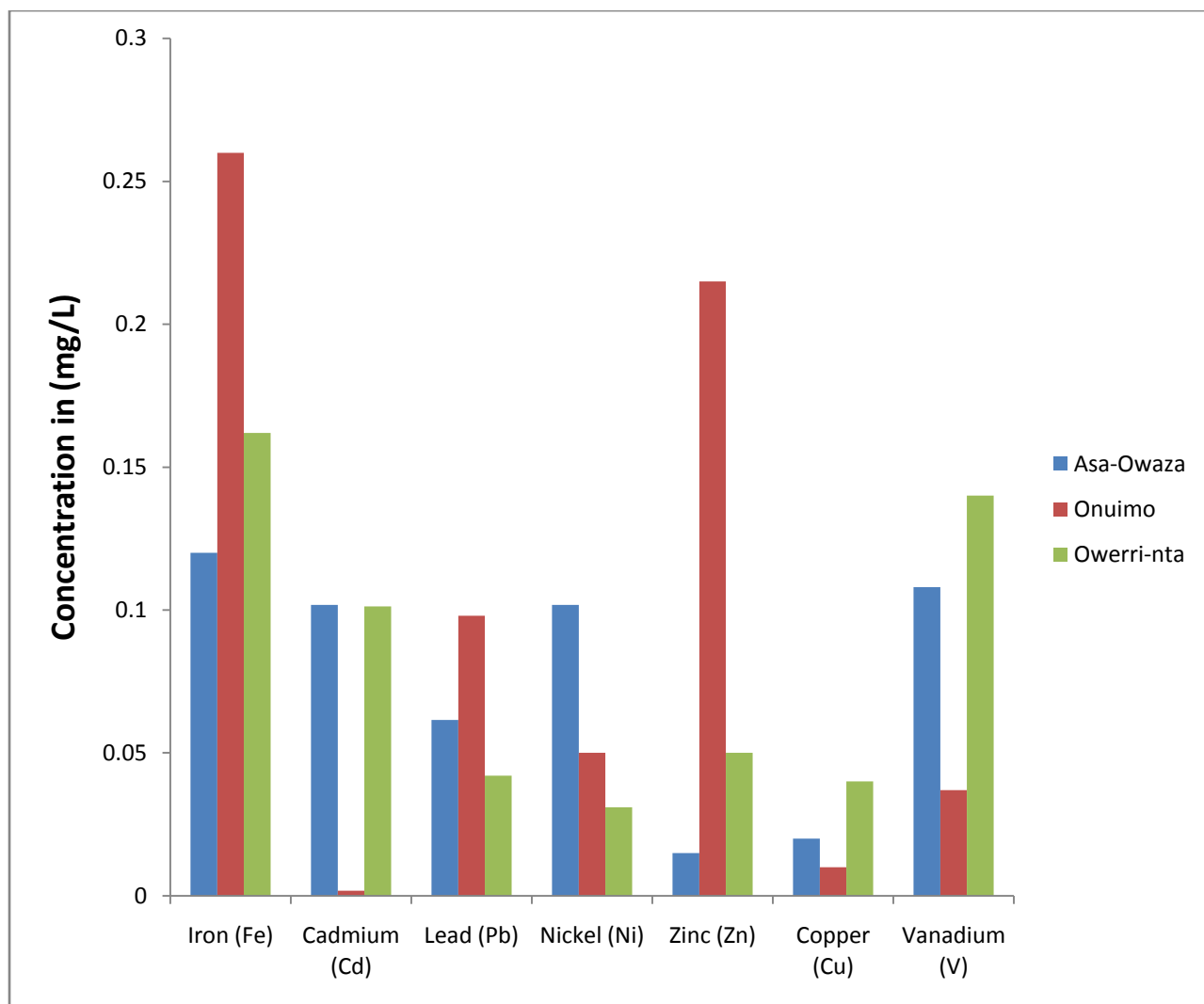


Fig. 4.5: Mean of heavy metal concentration in water from Imo River during dry season

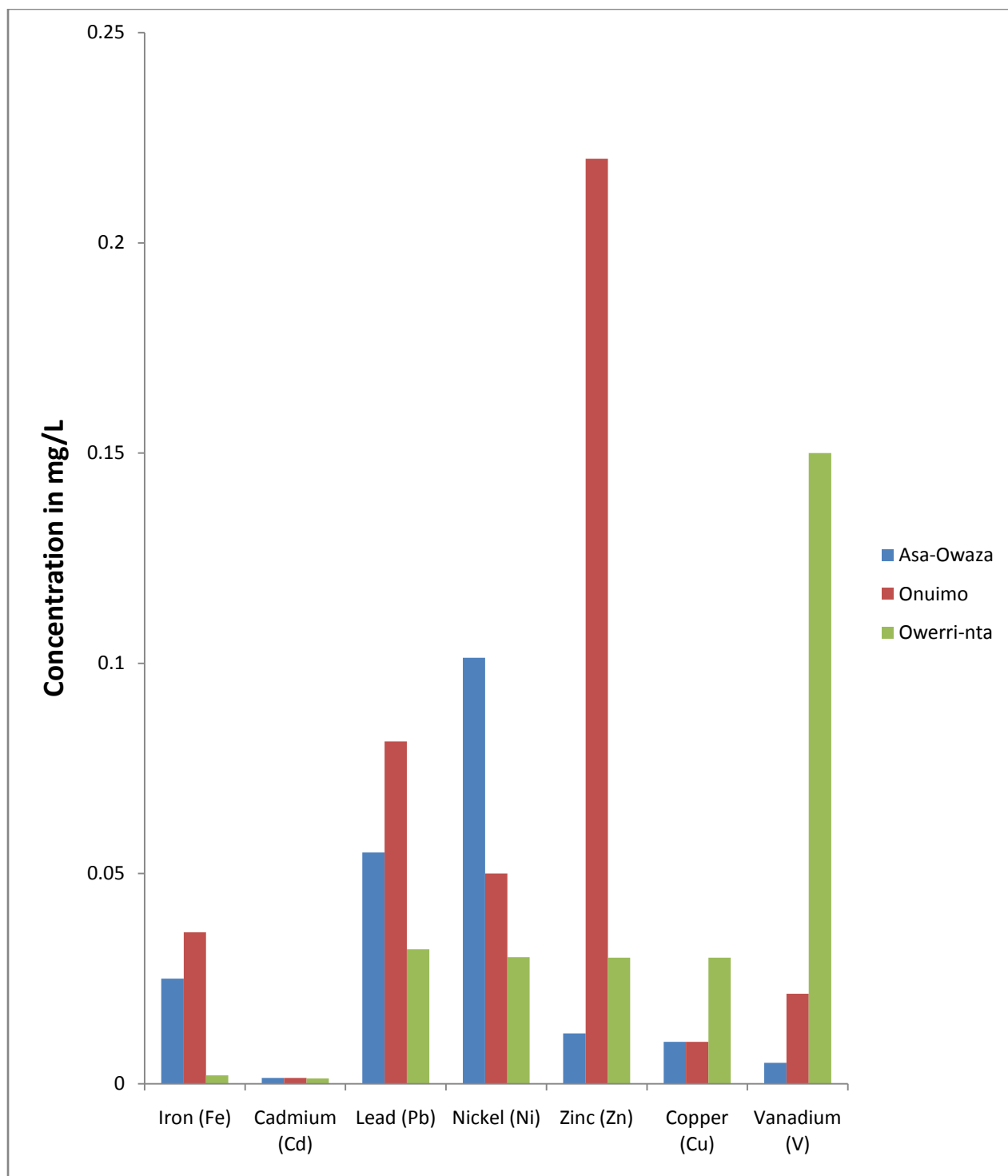


Fig. 4.6: Mean of heavy metal concentration in water from Imo River during wet season.

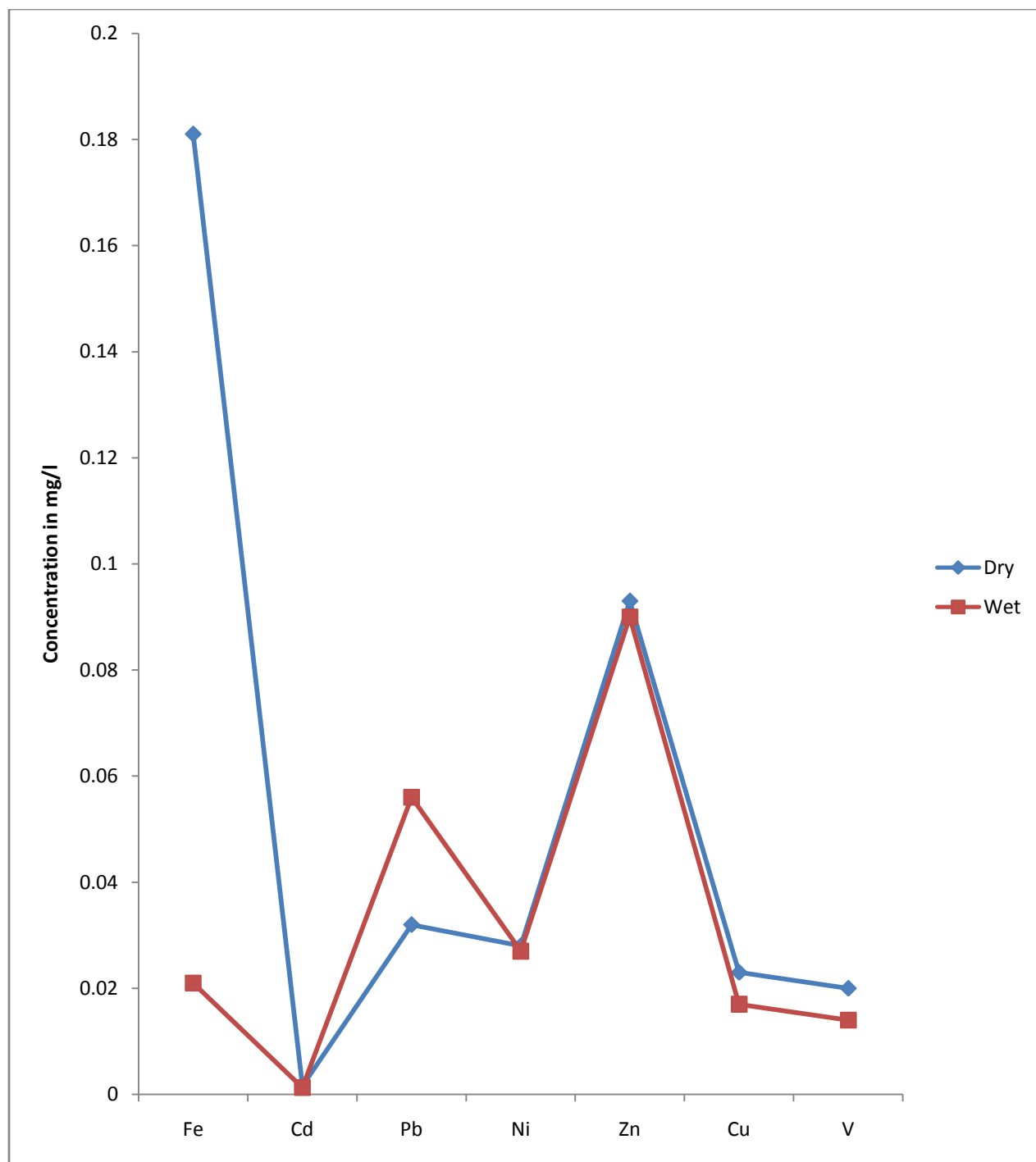


Fig.4.7: Seasonal variation of heavy metals in water from Imo River in both seasons.

The bar chart /plot for individual trace metals revealed that the origin of Fe is quite different from other metals (fig. 4.5 and 4.6). It was due to geological history of study area while other heavy metals investigated come from different anthropogenic or natural origin (Essien, 2006). The concentration of zinc is high in both seasons because zinc is a very common envi-

ronmental contaminant and it is commonly found in association with lead and cadmium. The major sources of zinc in the aquatic environment are the discharge of domestic waste waters, coal –burning power plants and manufacturing processes involving metals Amadi (2010).Ihedioha and Okoye (2013), studies on level of heavy metals in water and sediment of rivers in different part of Nigeria indicated that the concentration of these heavy metals depend on industrial and other human related activities such as industrial discharge/effluents, mining, vehicular emission, oil spills and petroleum exploitation.

4.3.2: Pearson Correlation Matrix for Heavy Metals in Water

Tables 4.8 and 4.9 showed the Pearson Correlation for the metals in dry and wet seasons respectively.

Table 4.8 Correlation Matrix for Heavy Metals in Water from IMR during dry season

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	0.25140	1					
Pb	0.814889	0.76586	1				
Ni	0.9215	-0.1161	0.549738	1			
Zn	0.99405	0.355135	0.871093	0.30531	1		
Cu	-0.55937	-0.94491	-0.93415	-0.21541	-0.6385	1	
V	-0.03448	-0.97598	-0.607370	0.329713	-0.138920	0.85089	1

Table 4.9 Correlation Matrix for Heavy Metals in Water from IMR during wet season

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	0.88	1					
Pb	0.997	0.848	1				
Ni	0.376	-0.104	0.437	1			
Zn	0.805	0.4301	0.843	0.852	1		
Cu	-0.881	-1	-0.848	-0.109	-0.430 1	1	
V	-0.828	-0.994	-0.789	-0.207	-0.335	-0.994	1

Pearson's correlation matrix for heavy metal pairs with strong positive correlation suggest that such metals maybe from same pollution source (crustal or anthropogenic) while metal pairs with significant negative correlation affect the occurrence or existence of each other. (Nduka *et al.*, 2010). Udosen and Benson (2006) reported that metals with significant positive correlation coefficient indicate co-accumulation relation of both metals in surface water while Ndukwu (2016) reported that significant positive correlation between heavy metals suggest possibility of common source or origin which may be anthropogenic. In this study in Table 4.8 and 4.9, Iron co-existed with Pb, Ni, Cd, Zn in the dry season and with Cd, Pb, Ni, and Zn in wet season. This maybe due to abundance of the metal in earth crust Ebong *et al.*, (2004) and Uwah *et al.*, (2013) stated that iron is used as a normalizer in the determination of metal enhancement in the environment. In dry season strong positive correlation was observed at $P < 0.05$ for the following metals pairs: Fe – Cd ($r = 0.251$), Cd – Pb ($r = 0.767$), Fe – Pb ($r = 0.815$), Fe – Ni ($r = 0.921$), Ni – Pb ($r = 0.550$), Zn – Pb ($r = 0.994$), Zn – Cd ($r = 0.355$), Zn – Pb ($r = 0.871$), Zn – Ni ($r = 0.305$), V – Cu ($r = 0.850$) which suggested that they are from the same source and are purely anthropogenic. Strong negative correlation was observed at $P < 0.05$ between Fe – Cu ($r = -0.560$), Cu – Cd ($r = -0.945$), Cu – Pb ($r = -0.93$), Cu – Ni ($r = -0.215$), V – Pb ($r = -0.607$), V – Ni ($r = -0.320$), V – Zn ($r = -0.139$) which suggested that they are not from the same source. During wet season significant positive correlation was observed between the following metal pairs: Cd – Fe ($r = 0.882$), Pb – Fe ($r = 0.998$), Pb – Cd ($r = 0.850$), Zn – Fe ($r = 0.810$), Zn – Ni ($r = 0.852$), while significant negative correlation was observed at $P < 0.05$ between Cu – Fe ($r = -0.881$), Cu – Pb ($r = -0.850$), V – Fe ($r = -0.83$), V – Cd ($r = -0.99$).

4.4 Heavy Metals in Sediment from Imo Rivers (IMR)

The concentrations of heavy metals in sediments from Imo River are presented in tables 4.10, 4.11 and 4.12.

Table 4.10 Heavy Metal concentration (mg/kg) in sediment from Imo River (IMR) during dry season.

Location	Fe			Cd			Pd			Ni			Zn			Cu			V		
	μ	\pm	CV(%)	μ	\pm	CV(%)	μ	\pm	CV(%)	μ	\pm	CV(%)	μ	\pm	CV(%)	μ	\pm	CV(%)	μ	\pm	CV(%)
Asa-Owaza	0.6271	± 0.2	31	0.0019	± 0.0007	36.8	0.0427	± 0.007	16.4	0.0267	± 0.005	27.0	3.520	± 0.95	27.0	0.775	± 0.02	12.9	0.052	± 0.0018	3.5
Onuimo	3.8395	± 0.5	13.02	0.006	± 0.002	3.33	0.0532	± 0.015	28	0.0443	± 0.006	13.5	2.160	± 0.6	27.7	0.720	± 0.05	6.94	0.054	± 0.0015	2.8
Owerri-Nta	0.2068	± 0.05	24.2	0.0006	± 0.00008	13.3	0.0615	± 0.0082	13.3	0.0412	± 0.009	21.8	4.401	± 0.88	20.0	0.805	± 0.09	11.18	0.059	± 0.001	1.7

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for seven measurements

Table 4.11 Heavy metal concentration (mg/kg) in sediment from Imo River (IMR) during wet Season

Location	Fe		Cd		Pd		Ni		Zn		Cu		V	
	$\mu \pm$	C(%)	$\mu \pm$	CV(%)	$\mu \pm$	CV(%)	$\mu \pm$	CV(%)	$\mu \pm$	CV(%)	$\mu \pm$	CV(%)	$\mu \pm$	CV(%)
Asa-Owaza	0.120 \pm 0.052	43.3	0.0015 \pm 0.0009	60	0.0320 \pm 0.006	18.8	0.0220 \pm 0.006	27.3	3.220 \pm 0.67	20.8	0.635 \pm 0.05	7.8	0.031 \pm 0.59	19
Onuimo	1.224 \pm 0.69	56.6	0.0014 \pm 0.0007	50	0.0485 \pm 0.007	14.4	0.0403 \pm 0.0042	10.4	2.023 \pm 0.92	45.5	0.600 \pm 0.03	5.0	0.034 \pm 0.001	29.4
Owerri-Nta	0.020 \pm 0.007	35.0	0.0013 \pm 0.0009	65.4	0.0530 \pm 0.001	18.9	0.0400 \pm 0.008	20	3.801 \pm 0.78	20.5	0.713 \pm 0.07	9.8	0.044 \pm 0.038	8.6

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for seven measurements

Table 4.12 Heavy Metal Concentration (mg/kg) in Sediment from Imo River and other Rivers in comparison with Sediment quality guidelines

Location / Guideline (mg/kg)	Fe	Cd	Pb	Ni	Zn	Cu	V	Cr	References
LEI (lowest element level)	10.38	0.6	31	16	120	-	-	26	NOAA (2009)
TEL (threshold effect level)	10.30	0.99	35.8	22.7	120	-	-	43.4	NOAA (2009)
PEC (probable effect concentra- tion)	20.03	4.95	12.8	48.6	111	-	-	111	NOAA (2009)
Sec (severe effect concentration)	35.30	10	250	75	820	-	-	110	Anornuet <i>al</i> (2012)
Canadian Interim sediment quali- ty guideline	-	0.6	35	-	123	20	-	37.30	Adekela and Scridu (2005)
USEPA Screening value	-	0.68	30.2	15.9	-	-	20	-	USEPA (2013)
Continental earth (background value)	20,000	0.2	2.5	75	70	-	135	110	Ahmed <i>et al</i> (2010)
Average shade (background val- ue)	47,200	0.3	20	68	95	-	30	90	Nduka <i>et al</i> (2010)
Anambra river (omambara river)	1.72	0.00	0.56	0.21	0.96	0.002	0.00	-	Izuchukwu Ujah <i>et al</i> (2016)
Imo river(IMR) dry season	1.5578	0.0028	0.053	0.037	3.36	0.99	0.06	-	This study
Imo river(IMR) wet season	0.454	0.03	0.045	0.033	3.01	0.99	0.55	-	This study
Control dry season	3.60	0.005	0.01	0.014	1.20	0.06	0.03	-	This study
Controlwet season	0.039	0.0012	0.052	0.032	3.62	0.61	0.04	-	This study

The highest value was recorded for Iron in Onuimo during dry season while the lowest value was recorded for vanadium at Owerri-nta during wet season. The variations of metal during dry season followed the trend Fe > Zn > Cu > V > Ni > Pd > Cd. The variation in levels of Iron (Fe) during the dry season was Onuimo > Asa-Owaza > Owerri-Nta (31.0%, 24.2%, 13.02%) while Onuimo > Asa-Owaza > Owerri-Nta (56.6%, 43.3% and 35.04%) while in wet season the variation for Fe was Onuimo > Asa-Owaza > Owerri-Nta. Cadmium according to the order of Onuimo = Owerri-Nta > Asa-Owaza. (Table 4.10) while that of wet season followed the trend Fe > Zn > Cu > V > Pd > Ni > Cd while the wet season variation was Owerri-Nta > Asa-Owaza.

The trend of variation for lead in dry season was Owerri-Nta > Onuimo > Asa-Owaza while in wet season the order for lead was Owerri-Nta > Onuimo > Asa-Owaza (table 4.11 and appendix 28). The stability of the metals in both seasons was predicted using their coefficient of variation values. The results revealed that Cd at Owerri-Nta during the wet season recorded the highest value (Cv=65.4%) being the least stable while the least Cv value for the heavy metals was recorded by vanadium in the same station during the wet season (CV=1.8%) Hence vanadium was the most stable metal in the Sediment in this study.

The mean value of heavy metal from Imo Rivers during dry season for Fe, Cd, Pd, Ni, Zn, Cu and V were 1.552, 0.0028, 0.053, 0.034, 3.36, 0.77 and 0.06 respectively while the mean values of heavy metals from this study during wet season for Fe, Cd, Pd, Ni, Zn, Cu and V were 0.455, 0.03, 0.042, 0.04, 3.01, 0.99 and 0.04 mg/kg respectively (tables 4.10 and 4.11). Higher values obtained from this study agreed with the findings of Ogwo and Okereke (2014) in their study of post impact analysis of sediment and macro bottom Fauna of Osondu River in Okigwe Imo State. They recorded high value of heavy metal concentration in dry season than wet season. In table 4.12, the values of mean concentration of heavy metals in sediments in this study were below the LEL, TEL and PEC values as recommended by NOAA (2009) while the values from this study were similar to the ones reported by Nduka *et al.* (2010) which implied that Imo River sediment is moderately polluted.

4.4.1 Pearson Correlation Matrix between Heavy Metals in Sediment from Imo River (IMR).

The interrelationship between heavy metals in sediment from Imo River during dry and wet season was analysed using Pearson's correlation matrix to see if some of the heavy metals are interrelated with each other and the results are presented in Tables 4.13 and 4.14.

Table 4.13 Correlation Matrix for Heavy Metals in Sediment from IMR during Dry Season

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	0.99119	1					
Pb	-0.03848	-0.16451	1				
Ni	0.55085	0.44090	0.812788	1			
Zn	-0.95684	-0.98590	0.327214	-0.28453	1		
Cu	-0.96905	-0.99249	0.283972	0.28397	0.99896	1	
V	-0.34150	-0.45759	0.955233	0.59631	0.59990	0.5629	1

Table 4.14 Correlation Matrix for Heavy Metals in Sediment from IMR during Wet Season.

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	-0.4286	1					
Pb	0.2413	-0.98034	1				
Ni	0.446641	-0.99978	0.976063	1			
Zn	-0.96859	0.18992	0.00751	-0.21016	1		
Cu	-0.96092	0.16115	0.036715	-0.18151	0.99957	1	
V	-0.31216	-0.7249	0.8465	0.7105	0.53857	0.56295	1

During the dry season strong positive correlation was observed at $P=0.01$ for

Fe –Cd ($r=0.99$), Pb-V ($r=0.955$), N-Zn ($r=0.99$), Zn-V ($r=0.59$), Cu-V ($r=0.56$) and this implied that the metals are from one source. In wet season, the significant positive correlations were observed at $P=0.01$ between Fe-Pb ($r=0.24$) Fe-N ($r=0.45$), Pb – Ni ($r=0.97$), Cd-Zn ($r=0.99$), Cu-V ($r=0.71$), V-Zn ($r=0.54$), Cu-V ($r=0.56$), which means that as one metal increases in concentration the other pair also increases. Significant negative correlation was observed between the following pairs during dry season at $P=0.01$ Cd-Zn ($r=-0.985$), Fe-Zn ($r=-0.34$), Fe-Cd ($r=-0.43$), Cd-V ($r=-0.724$) Fe-Cu ($r=-0.96$) while other metal pair recorded low negative correlation which means that they are not of the same source.

4.4.2 Distribution of Heavy Metals in Sediment from IMR.

Figures 4.8, 4.9 and 4.10 showed the distribution of heavy metals in Imo River sediments during dry and wet seasons.

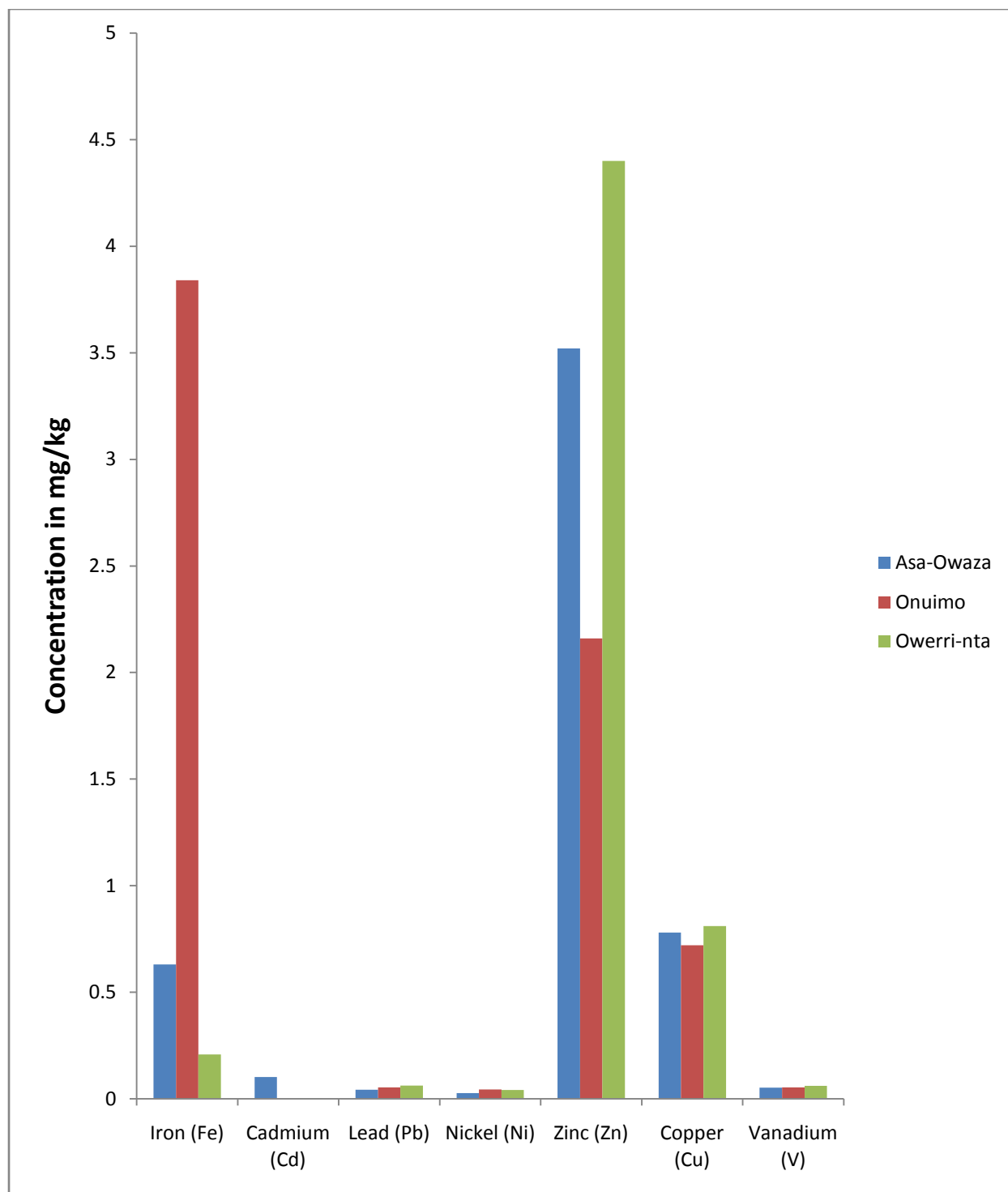


Fig. 4.8: Mean concentration of heavy metals in sediments from Imo River during dry season in mg/kg.

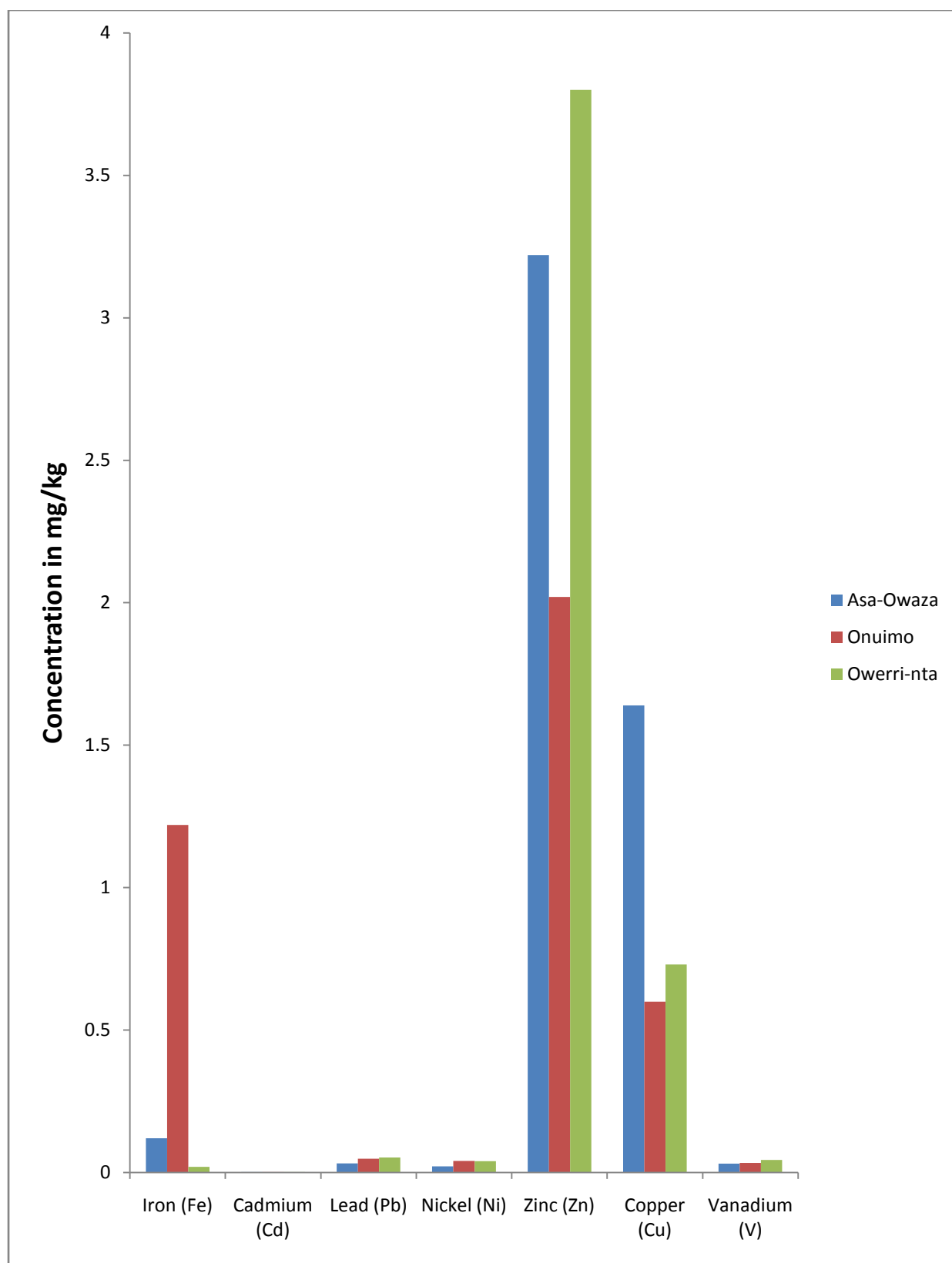


Fig. 4.9: Mean concentration of heavy metals in sediments from Imo River during wet season in mg/kg.

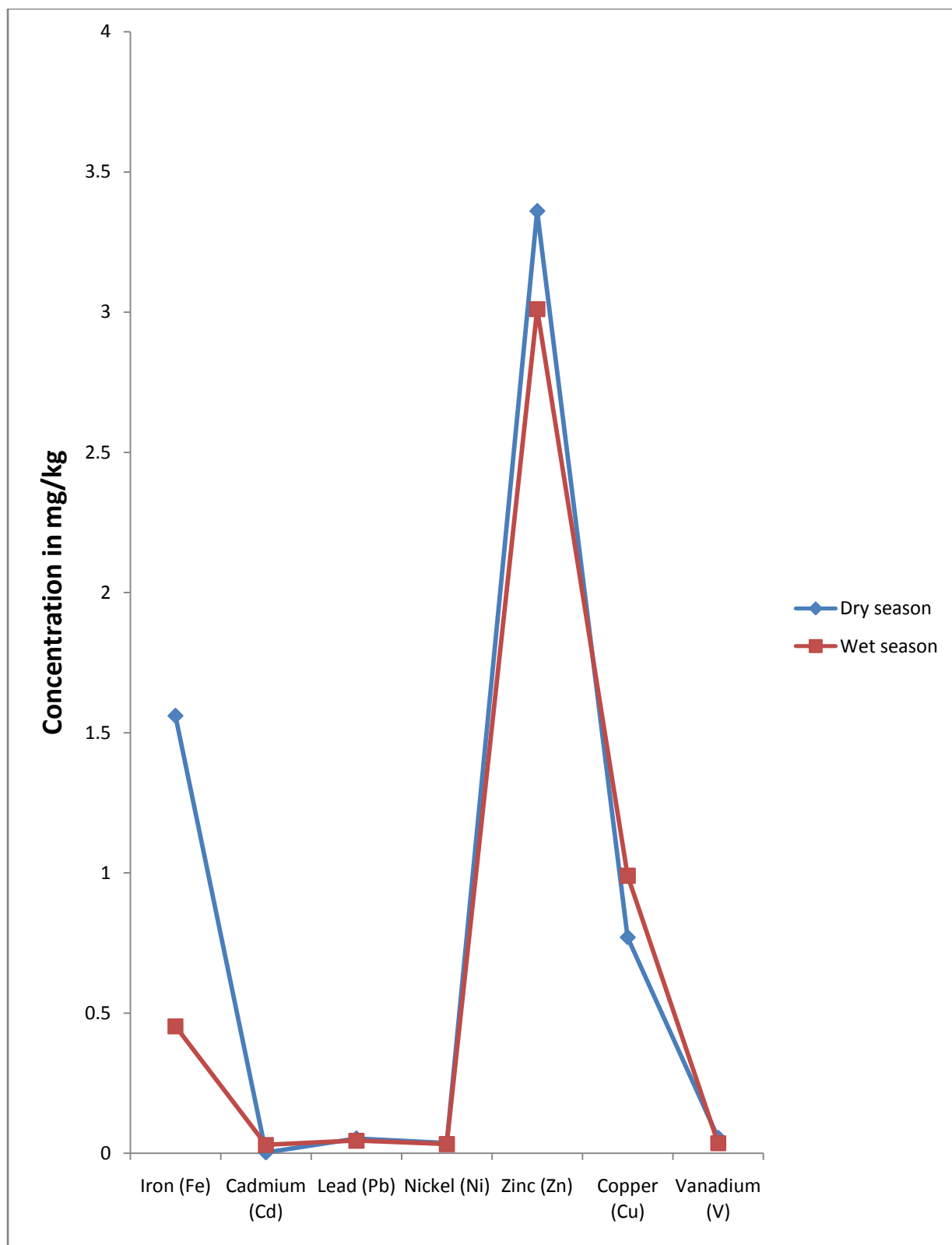


Fig. 4.10: Seasonal variation of heavy metals in sediments from Imo River in both season (wet and dry) mg/kg.

In fig 4.8, the mean concentration of heavy metals in sediments in dry season were Fe (0.62, 3.8, 0.21), Cd (0.009, 0.006, 0.0006) , Pd (0.042, 0.053, 0.062), Ni (0.026, 0.044, 0.041), Zn (3.32, 2.16 and 4.40), Cu (0.775, 0.720, 0.805), V (0.052, 0.054, 0.059) in Asa-Owaza, Onuimo and Owerri-nta respectively while in 4.9, the mean concentration of heavy in metals in sediments in wet seasons were Fe (0.12, 1.22, 0.02), Cd (0.0015, 0.0014, 0.0013), Pb (0.032, 0.0485, 0.053), Ni (0.02, 0.04, 0.04), and Zn (3.22, 2.02, 3.80). Nickel in dry seacon followed the trend Onuimo > Owerri-Nta > asa- Owaza while the wet season was Onuimo > Owerr-Nta > Asa- Owaza. The distribution pattern for zinc in the dry season was Owerri-Nta>Asa-Owaza > Onuimo. This pattern was almost similar in both seasons because they have a common source.

The distribution pattern for copper in dry season was Owerri-Nta > Asa-Owaza > Onuimo while in wet season the pattern was Owerri-Nta > Aza- Owaza> Onuimo. The distribution pattern for vanadium was Owerri-nta> Onuimo>Asa-Owaza for both seasons. In fig. 4.10, the average level of heavy metals in dry season was higher than that of wet season. The result in this study is similar to the findings of Amadi (2010) who reported higher dry season mean values in heavy metals than wet season values. This could be due to absorption of metals by sediment particles because of reduced water volume associated with increased evaporation rate in dry season. Nwadinigwe *et al.*, (2014) stated that seasonal variation in metal concentration could be as a result of slow water movement in the sediment and absorption ability of heavy metals by sediments. The results obtained in this study for heavy metals in both seasons agreed with the range reported by Obayori and Salam (2010), Udosen *et al.* (2007) and Eggleton *et al.*, (2014). In table 4.12, all the samples investigated in both seasons were below the sediment quality guidelines (Tables 4.12) such as lowest element level (LEL), Threshold effect level (TEL), Probable effect level (PEL) and Severe effect level (SEL) reported by National Oceanic and Quality Guideline (NOQG) and United State Environmental Protection Agency (USEPA) screening value.

TEL values are values below which adverse biological effect are unlikely to be observed while PEL values are values above which harmful biological effect would frequently occur Izu-chukwu *et al.*, (2004), when compared with other results recorded higher values. The high level of iron in sediment of this study is consistent with the report of other authors (Udosen *et al.*, 2007, Ozturk *et al.*, 2009 Issa *et al.*, 2011,). Most of the pipelines used in conveying oil from the platform to the treatment sites are made up of iron, ferro-chromium materials and alloys of zinc and iron which when corroded can result in the release of these metals into the aquatic ecosystem. Increase in level of heavy metals such as zinc, iron and chromium in sediment over water may be due to human activities such as discharge of untreated sewage, industrial materials that contain these materials as well as the ability of sediments to act as a sink. The source of zinc in the study area may be due to other anthropogenic activities apart from oil evaporation and production. Generally, elemental concentrations depend not only on anthropogenic and lithogenic sources but also on the textural characteristics such as organic matter, mineralogical composition and depositional environment of the sediments (Pourang *et al.*, 2005). Fine sediments (sand) predominate in IMR and heavy metals are believed to be more associated with smaller grain size particles in comparison with the average concentration of water in both seasons. The concentration of heavy metals in the sediment was higher than in water thus results are in agreement with reports from several authors (Anornu *et al.* 2012). Sediments are sinks to many chemical compounds such as heavy metals and organic compound from natural and anthropogenic sources.

4.4.3 Sediment Contamination Indices

Results for contamination indices are presented in Tables 4.15 and 4.16.

Table 4.15: Table of Contamination Factor (CF), Degree of Contamination (Cd), Modified Degree of Contamination (mCd), Pollution Load Index (PLI) in Dry Season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V	Cd	mCd	PLI
Asa	1.045	3.6	4.27	1.9	2.9	12.29	1.73	16.735	2.3	2.09
Onuimo	6.389	12	5.32	3.14	1.8	1.2	1.8	31.56	4.5	3.2
Owerri-nta	0.0034	12	6.15	2.21	3.6	1.42	1.3	26.68	3.8	1.2
Control/Obeche	1	1	1	1	1	1	1	1	1	1.1

Table 4.16: Table of Contamination Factor (CF), Degree of Contamination (Cd), Modified Degree of Contamination (mCd), Pollution Load Index (PLI) in Wet Season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V	Cd	mCd	PLI
Asa-Owaza	3.08	1.25	0.61	1.25	0.89	1.04	0.72	8.89	1.27	1.3
Onuimo	31.38	1.16	0.92	0.94	0.59	0.98	0.85	36.96	5.25	1.4
Owerri-nta	0.57	1.08	1.01	1.25	1.05	1.17	1.1	7.24	1.03	1.00
Control (Obeche)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

In the dry season, the results for the contamination factor ranged from 1.00 for the heavy metal at control station to 6.389 for iron at Onuimo while, for the wet season the range was 1.00 for all heavy metals at control station to 36.73 at Onuimo for cadmium (Cd). The range for degree of contamination Cd, modified degree of contamination (mCd) and pollution load index during the dry season were 7 – 31.56, 1 – 4.5 and 1 – 3.2 respectively. The highest value was recorded at Onuimo while the lowest value was recorded at control site. For the wet season, the range for degree of contamination (mCd) and pollution load index were 7 – 36.763, 1 – 5.25 and 1 – 1.46 respectively. The highest value for the wet season was recorded at Onuimo and the lowest value was recorded at the control site. Dapam (2006) recorded high

contamination factor (CF) for Pb, Co, Cd, Fe, low CF for As, Cr and moderate CF for Zn, Ni, Mn and Cu, while studying the level of heavy metal contamination in water and surface sediments of the River Jibam Plateau State. The CF values for Fe and Pb in this study may be due to pollution sources such as industrial waste from non-treatment of oil field, waste from homes and industries, agricultural run-off and other anthropogenic inputs. The highest CF value in this study was recorded for Fe (31.38) at Onuimo during the wet season while the least CF value was recorded for Zn (0.558) during the wet season.

According to Hakenson *et al.*, (2005), contamination factor (CF) of <1 points to low contamination, $3 < CF < 6$ points to moderate contamination while $CF > 6$ points to high contamination factor. On the basis of the above classifications, IMR sediments recorded high contamination factor for Fe (Onuimo), Pb Owerinta, Cd (Onuimo & Owerinta), in dry season and Fe (Onuimo) during wet season. However, the contamination of Vanadium was low for both seasons. Considerable contamination was recorded for Cu, Zn and Ni in dry season while Cd, Ni and Cu revealed moderate contamination in the wet season (Tables 4.15 and 4.16). According to the classification of Dapam (2006) (Appendix X), the degree of contamination of all the heavy metals investigated in the study was classified as very high. However, when the modified degree of contamination was adopted for the data analysis (Uwah *et al.*, 2013, Likuku *et al.*, 2013), all the station apart from the control site recorded moderate degree of contamination while Obeche (Control Site) recorded low degree of contamination.

In the dry season, the degree of contamination (Cd) of all heavy metals investigated in this study was classified as very high. However, when the modified degree of contamination mCd was adopted for the data analysis (Uwa *et al.*, 2013, Likuku *et al.*, 2013), all the stations recorded moderate modified degree of contamination. In the dry season, an extremely high degree of contamination of 16.735, 31.56 and 26.68 were recorded for Asa, Onuimo and Owerinta respectively and mCd values of 2.3, 4.5 and 3.8 respectively. These results confirmed

the previous assertion by Amadi *et al.*, (2016) that sediments from IMR were moderately contaminated with heavy metals. Human activities domiciled in the area are the major sources of these metals. Pollution load index (PLI) values less than one indicates no pollution while PLI value greater than one indicates pollution (Rabee *et al.*, and Nameer, 2011). Sahand *et al.*, (2017) postulated that a PLI value greater than one indicates an immediate intervention to ameliorate pollution. $PLI = O$ (background concentration) $0 < PLI < 1$ (unpolluted, $1 < PLI < 2$ (moderately to unpolluted) $2 < PI < 3$ (moderately polluted), $3 < PI < 4$ (moderately to highly polluted; $4 < PI < 5$ (highly polluted)). The degree of contamination and pollution load index are simple indices that can help the public and policy makers to ascertain the pollution status of an environment in order to take necessary remedial measures (Amadi *et al.*, 2016). From this study in Table 4.15 pollution load index of heavy metals in dry season ranged from 0 – 3.2 which indicated that in dry season, Imo River was moderately polluted. In wet season from Table 4.16 the pollution load index of heavy metals from Imo River was within the range of 1.0 – 1.46 which showed that in wet season, Imo River is moderately polluted. Pollution load index provides some understanding about the quality of a component of the environment and indicate the possible trend over time and area (Yongming *et al.*, 2006). The enrichment factor for Imo river sediment for the dry and wet seasons are outlined in Tables 4.17 and 4.18 respectively.

Table 4.17: The Enrichment Factor for Sediment from IMR in Dry Season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa-Owaza	1.00	0.34	4.08	1.82	2.80	1.23	1.70
Onuimo	1.00	0.19	0.83	0.50	0.28	0.19	0.28
Owerinta	1.00	3.4	2.90	6.4	10.63	4.11	3.80
Control (Obeche)	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Table 4.18: The Enrichment Factor for Sediment for IMR in Wet Season.

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa-Owaza	1.00	0.406	0.20	0.41	0.29	0.34	0.34
Onuimo	1.00	0.37	0.30	0.41	0.018	0.03	0.037
Oweri-nta	1.00	2.11	2.0	2.44	2.04	2.28	2.54
Control Ob-eche	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Enrichment factor (EF) is an important aspect of geochemical studies and enrichment factor measurement is used to differentiate between the metal originating from anthropogenic (non-crustal) source and geogenic (crustal) sources and to assess the degree of metal pollution (Dapam 2006; Uwah *et al.*, 2013; Ogundayo *et al* (2010), Amadiet *al.*, 2010; Youngminget *al.*, 2006). suggested that values of $0.5 < EF < 1.5$ indicate that the heavy metal concentration may come from natural source. However, an $E.F. > 1.5$ may come from other sources like point and non-point pollution. $EF < 2$ (Deficiency to minimal enrichment $EF. 3 - 5$ is

moderately enrichment, EF. 10 – 25 is highly enrichment. EF. > 40 is extremely high enrichment shown in appendix 11). However, in this study the EF. (enrichment factor) for heavy metals in sediments of Imo River from Onuimo to Asa fall within the values of 0.19 – 10.63 in dry seasons and values of 0.0018 – 2.54 during the wet season indicating that Imo River sediment during both seasons is moderately polluted and the heavy metal is from anthropogenic sources since EF. > 1.5 suggests the heavy metal concentration did not come from natural source. Enrichment factor values greater than one indicates minor sediment contamination from natural origin for instance soil or parent rock while those greater than 10 are considered to be from anthropogenic sources (Youngming *et al.*, 2006). For the studied locations, the enrichment factor for Cd in Asa-Owaza and Onuimo indicate natural source of contamination in dry season. The enrichment factor for all the metals in Onuimo that ranged from 0.19 – 0.83 indicate natural source while the enrichment factor for all the metals Cd, Pb, Ni, Cu, Zn, V in Owerri-Nta station indicate anthropogenic source of contamination for both dry and wet seasons.

Based on the classification of Borkin and Keller (2008); zinc, nickel, chromium and cadmium showed minor to moderate enrichment for both seasons. In this study, the enrichment factor for heavy metals in the dry season was higher than that of wet season. In addition, the finding in the study is consistent with the result of Uwah *at al.*, (2013). High enrichment of heavy metals in sediment from Imo River in dry season may be due to domestic wastes which are contained in batteries, pigment, paints, oil field waste and agricultural run-off. It may also be due to atmospheric deposition, domestic effluent discharges and extension use of paints along the study area or Pb – laden effluents discharged into the ecosystem. Lead in the environment is of great concern to scientists because it is a cumulative toxin in humans and also it is toxic to many aquatic organisms at a low concentration. When Pb is released into the environment it has long residence time compared with most other pollutants. It has low solubility and does not experience microbial degradation. Hence, it can accumulate in sediments for a long time

and become accessible to aquatic food chains (Davies *et al.*, 2010). Etim (2012) reported that vanadium originated from anthropogenic sources such as combustion of coal, crude oil, fossil fuel and atmospheric deposition. Vanadium is not degraded in the environment but can become attached to air borne particulates that may settle to the ground and are washed out of the air by rain into sediments. In this study, iron was used as a conservative tracer to differentiate natural from anthropogenic pollution source. According to Yap *et al* (2002), and Nwadinigwe *et al.*, (2014), determination of anomalous metal concentration and evaluation of metal abundance is achieved by geochemical normalization of the trace metal data to a conservative element e.g. Al, Fe, Si. Iron is chosen as normalization element because its origin is lithospheric. The Geoaccumulation indices for heavy metals in sediments are outlined in Tables 4.19 and 4.20 for dry and wet seasons respectively.

Table 4.19: Geoaccumulation Indices for Heavy Metals in Sediments from IMR During Dry Season.

Location	Fe	Cd	Pb	N1	Zn	Cu	V
Asa	0.207	0.11	0.85	0.383	0.590	0.260	0.34
Onuimo	1.28	0.24	1.07	0.634	0.36.1	0.241	1.00
Owerinta	0.07	0.24	1.23	0.4429	0.74	0.26	0.26

Table 4.20: Geoaccumulation Indices for Heavy Metal in Sediments from IMR During Wet Season.

Location	Fe	Cd	Pb	N1	Zn	Cu	V
Asa	0.617	0.025	0.123	0.140	0.178	0.209	0.195
Onuimo	6.297	0.23	0.190	0.304	0.112	0.190	0.213
Owerinta	0.1029	0.217	0.204	0.25	0.210	0.235	0.276

Geoaccumulation index (Igeo) of sediment was classified by Muller (1979), Taylor (1964), and Onyia *et al.*, (2008) and Likuku (2013) into 6 classes. Class 6 of sediment Igeo value $>>5$ (very highly polluted); class 5 of sediment Igeo value $>>4 - 5$ (highly polluted); class 4 of sediment Igeo value $>>3 - 4$ (moderately to highly polluted); class 3 of sediment Igeo value $>>2 - 3$ (moderately polluted); class 2 of sediment Igeo value $>>1 - 2$ (moderately polluted to unpolluted); class 1 of sediment Igeo value $>>0 - 1$ (unpolluted); class 0 of sediment Igeo value <0 (practically none as shown in Appendix 12). In this study, all heavy metals in sediment from Imo River during the dry season (Table 4.19) were moderately polluted while all other metals, Cd, Pb, Ni, Zn, Cu and V in wet season fall into unpolluted class (Table 4.20). The results in this study suggest possible pollution of Pb and background concentration for Cd, Zn, Ni, Cu and V in sediment from Imo River. Accumulation of trace metals in sediments tend to pose threats to aquatic life due to re-suspension into the water column from geochemical cycling, bioaccumulation in benthic organisms, biomagnification through the aquatic food web and remobilization (Ozturk *et al.*, 2009).

4.5. Heavy Metals in Fish from Imo River

Heavy metal concentrations in the 2 kinds of fishes: Tilapia zilli and Cat fish from Imo River are shown in Tables 4.21, 4.22, 4.23 and 4.24. Tables 4.21 and 4.22 showed the trace metals in Tilapia zilli in dry and wet season respectively. Tables 4.23 and 4.24 are the trace metals in catfish for dry and wet season respectively

4.5.1 Heavy metals in *Tilapia zilli* from Imo River

Table 4.21: Heavy Metal Concentration (mg/kg) in *Tilapia zilli* from Imo River (IMR) during Dry Season.

Location	Fe		Cd		Pb		Ni		Zn		Cu		V	
	$\mu \pm$	CV %	$\mu \pm$	CV %	$\mu \pm$	CV %	$\mu \pm$	CV %	$\mu \pm$	CV %	$\mu \pm$	CV %	$\mu \pm$	CV %
Asa	3.2722+1.24	37.80	0.0005	20.00	0.0219	6.80	0.0259	23.0	0.432	48.60	0.020	45.0	ND	-
					+0.0015		+0.006		+0.21		+0.009			
Onuimo	5.272	27.80	0.0004	25.00	0.0675	9.70	0.042	48.5	0.334	35.9	0.024	41.0	ND	-
	+1.59		+0.0001		+0.003		+0.02		+0.12		+0.01			
Owerrinta	5.374	22.39	0.0007	58.00	0.0519	8.70	0.0512	58.6	0.478	20.9	0.030	33.0	ND	-
	+2.40		+0.00012		+0.0042		+0.03		+0.10		+0.01			
FAO (mg/kg)	1.46		0.05		0.05		0.6		30		0.6			-
WHO (mg/kg)	3.00		2		2		0.4		40		6.04			

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for seven measurements

Table 4.22: Heavy Metal Concentration (mg/kg) in *Tilapia zilli* from Imo River (IMR) during Wet Season.

	Fe		Cd		Pb		Ni		Zn		Cu		V	
Location	$\mu \pm$	CV%	$\mu \pm$	CV%	$\mu \pm$	CV%	$\mu \pm$	CV%	$\mu \pm$	CV%	$\mu \pm$	CV%	$\mu \pm$	CV%
Asa	1.275	64.7	0.0004	25.0	0.019	47.37	0.0231	43.47	0.276	32.60	0.010	50	ND	-
	± 0.825		± 0.0001		± 0.009		± 0.01		± 0.09		± 0.005			
Onuimo	2.352	22.5	0.0002	50.00	0.0515	19.41	0.0300	16.6	0.288	17.36	0.013	7.6	ND	-
	± 0.527		± 0.0001		± 0.01		± 0.005		± 0.05		± 0.001			
Owerri-nta	4.370	28.6	0.0004	22.50	0.0418	71.80	0.0493	40.57	0.345	11.5	0.020	50	ND	-
	± 1.25		± 0.0009		± 0.03		± 0.002		± 0.04		± 0.011			

μ = Mean, \pm = Standard deviation, Cv = Coefficient of variation for seven measurements

Table 4.21 and Table 4.22 revealed the concentration of heavy metals in *Tilapia zilli* from three sampling points of Imo River in both seasons. Fe (iron) recorded the highest value for both seasons and vanadium recorded the least value. Similar distribution pattern was observed for heavy metals in water and sediment in the river system. The metals decreased according to order $Fe > Zn > Ni > Pb > Cu > Cd > V$ in dry season and the order for wet season was $Fe > Zn > Ni > Pb > Cu > Cd > V$. Higher mean values were recorded during the dry season for most heavy metals than in wet season (comparing the mean values of the two seasons using student's t-test). The result further revealed that the concentration of iron and zinc were significantly higher ($P < 0.05$) for fish samples in dry season than for wet season. During dry season the least variability study was observed for Pb (lead) at Asa- Owaza (CV = 6.8%) and highest variability was recorded at Owerri-nta for Ni (CV = 58.6%). During wet season, the least variability was observed for copper in Onuimo (CV = 7.6%) and highest variability was recorded in Owerrinta for Pb (CV = 71.80%).

4.5.2 Heavy Metal Distribution of *Tilapia Zilli* from IMR

Appendices 59-60, depicts the distribution of heavy metals in *tilapia Zilli*. Iron recorded the highest value in both seasons followed by Zinc while Vanadium recorded the least value. This may be attributed to the abundance of Iron in the earth crust. Seasonal variation of heavy metals in *tilapia* fish is shown in appendix 61. The heavy metal concentration in dry season is higher than that of wet season. This might be attributed to decrease in water level as a result of evaporation during dry season which will lead to metal adsorption. High concentration of Iron could be as result of dissolved oxygen which oxidized iron into insoluble forms. In dry season, Iron varied as followed Owerri-nta > Onuimo > Asa-Owaza (appendix 61). The distribution pattern was different for wet season where the concentration decreased as follows Owerri-Nta > Onuimo > Asa. In

both season, Asa-Owaza had the least concentration of iron Amadi, (2010) recorded the same value for Imo River along Otammiri. The trend in the wet season value of cadmium was Asa = Owerri-nta > Onuimo (appendix 60), while in dry season, the concentration of cadmium decreased as follows Owerri-nta > Asa-Owaza > Onuimo (app 59). The distribution pattern of Pb in the dry season was Onuimo > Owerri-nta > Asa-Owaza while the pattern for wet season was Onuimo > Owerri-nta > Asa-Owaza. In the dry season, Nickel (Ni) decrease trend was Onuimo > Asa-Owaza; while, the decrease in the wet season was Owerri-nta > Onuimo > Asa-Owaza. The distribution pattern for zinc in dry season was Owerri-nta > Asa-Owaza > Onuimo while the decrease in wet season was Owerri-nta > Onuimo > Asa-Owaza. In the dry season the decrease in copper followed the trend Owerri-nta > Onuimo > Asa.

4.5.3 Pearson's Correlation Matrix for Heavy Metals in *Tilapia Zilli* from Imo River (IMR)

The correlation for heavy metals in tilapia are shown in Tables 4.25 and 4.26 respectively

4.25: Correlation Between Heavy Metals in *Tilapia* Fish During Dry Season in Imo River

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	0.231065	1					
Pb	0.961728	-0.04437	1				
Ni	0.93583	0.559151	0.803441	1			
Zn	-0.16178	0.92274	-0.425986	0.196408	1		
Cu	0.827861	0.737043	0.642478	0.972439	0.419611	1	
V	ND	ND	ND	ND	ND	ND	1

ND = Not detected

4.26: Correlation Between Heavy Metals in *Tilapia* Fish During Wet Season in Imo River

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	0.173	1					
Pb	0.547	0.73	1				
Ni	0.994	0.281	0.45	1			
Zn	0.983	0.352	0.382	0.997	1		
Cu	0.998	0.225	0.501	0.998	0.991	1	
V	ND	ND	ND	ND	ND	ND	ND

ND = Not detected

The interrelationship between heavy metals in *Tilapia Zilli* fish was examined using Pearson correlation coefficient and the results are shown in Table 4.25 and 4.25. In the dry season strong negative correlation was observed at $P < 0.05$ between Pb – Cd ($r = -0.044$), Fe – Zn ($r = -0.161$) Pb – Zn ($r = -0.4259$). Significant positive correlation was observed at $P < 0.05$ for the following metal Pairs Fe – Cd ($r = 0.231$) Ni – Cd ($r = 0.559$) Cu – Zn ($r = 0.419$), Cu – Pb ($r = 0.6424$) Ni – Fe ($r = 0.935$), Zn – Cd ($r = 0.922$) Cu – Cd ($r = 0.737$), Fe – Cu ($r = 0.827$). This shows that the metals have common source. During the wet, significant positive correlation was observed between pairs, Fe-Ni ($r = 0.99$), Zn-Cu ($r = 0.99$), Ni-Zn ($r = 0.99$), Zn-Fe ($r = 0.98$) which showed that they have common source. In dry season, Iron varied as followed Owerri-nta > Onuimo > Asa-Owaza (Appendix 61). The distribution pattern was different for wet season where the concentration decreased as follows Owerri-Nta > Onuimo > Asa. In both season Asa-Owaza has the least concentration of iron, Amadi (2010) recorded the same value for Imo River along Otammiri. The trend in the wet season value of cadmium was Asa = Owerri-nta > Onuimo (Appendix 59), while in dry season, the concentration of cadmium decreased as follows: Owerri-nta > Asa-Owaza > Onuimo (appendix 59).

The distribution pattern of Pb in the dry season was Onuimo > Owerri-nta > Asa-Owaza while the pattern for wet season was Onuimo > Owerri-nta > Asa-Owaza. In the dry season, Nickel (Ni) decreased Onuimo > Asa-Owaza; while, the decrease in the wet season was Owerri-nta > Onuimo > Asa-Owaza. The distribution pattern for zinc in dry season was Owerri-nta > Asa-Owaza > Onuimo while the decrease in wet season was Owerri-nta > Onuimo > Asa-Owaza. In the dry season the decrease in copper followed the trend Owerri-nta > Onuimo > Asa-Owaza.

4.6 Heavy Metals in Cat Fish (*Clarias gariepinus*) from Imo River (IMR).

Table 4.25: Heavy metal concentration (mg/kg) in Cat Fish from Imo River during Dry Season.

	Fe		Cd		Pb		Ni		Zn		Cu		V	
Location	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%
Asa	5.3193±2.810	52.8	0.015±0.0085	53.3	0.0083±0.002	24	0.0332±0.001	3.0	0.700±0.05	7.14	0.121±0.01	8.21	ND	-
Onuimo	8.3193±1.930	23.2	0.0013±0.003	23.07	0.082±0.003	36.30	0.0309±0.001	3.20	0.756±0.02	2.64	0.11±0.01	9.0	ND	-
Owerrinta	9.319±2.570	26.9	0.004±0.0002	14.29	0.062±0.002	32.2	0.0400 ±0.01	5.68	0.678±0.03	4.42	0.130±0.01	7.69	ND	-

μ = Mean, δ = Standard deviation, Cv = Coefficient of variation for seven measurements

Table 4.26 Heavy Metal Concentration (mg/kg) of Cat fish from Imo River (IMR) during Wet Season

	Fe		Cd		Pb		Ni		Zn		Cu		V	
Location	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%	Mean	CV%
Asa	3.214±8.89	27.20	0.012±6.009	75	0.0183±0.105	27.3	0.0320±0.01	31.3	0.666±0.085	12.76	0.111±0.01	9.0	ND	-
Onuimo	3.106±1.23	24.10	0.0011±0.009	81.8	0.0627±0.002	3.18	0.0300±0.01	33.3	0.614±0.05	7.42	0.100±0.072	40.0	ND	-
Owerrinta	4.205±0.88	20.91	0.0013±0.009	50.0	1.0440±0.002	4.5	0.0333±0.01	28.3	0.600±0.69	15.0	0.120±0.01	8.3	ND	-

The concentration of heavy metals in Cat Fish (*Clarias gariepinus*) from the location of Imo River (IMR) in both seasons was shown in Tables 4.25 and 4.26, Fe recorded the highest value for the study in the dry season and vanadium recorded the least value in the same season. Similar distribution pattern (range) was observed for heavy metals in water and sediment in Imo River system. The metals concentration in cat fish decreased according to the order Fe > Zn > Cu > Pb > Ni > Cd > V in dry season and Fe > Zn > Cu > Pb > Ni > Cd > V in wet season. Higher mean values were recorded during the dry season for heavy metals (Fe, Pb, Zn) than in wet season (Appendix 30). Comparing the mean values of the two seasons using student's t-test the results further revealed that the concentration of iron and zinc measured were significantly higher ($P < 0.05$) for fish sampled in dry season than for wet season. The least variability in this study were observed at Onuimo for Zn (CV = 2.64%) during the dry season and highest variability was recorded at Onuimo during the wet season for cadmium (CV = 8.18%).

4.6.1 The Distribution Pattern of Heavy Metals in Cat Fish During Dry and Wet Seasons.

Appendices 62-64 showed the mean concentration and seasonal variation of heavy metals in Cat Fish from Imo River during dry and wet seasons respectively. The maximum level of most heavy metals was detected during dry season which is growth period of Cat fish while the minimum level during wet season which corresponds to breeding period in Cat fish. In all the metals analysed, Iron had the highest level, cadmium had the least value while vanadium was not detected.

4.6.2 Pearson's Correlation Matrix for Heavy Metals in Cat Fish (*Clarias gariepinus*) Imo River (IMR)

The interrelationship between heavy metals in Cat fish (*Clarias gariepinus*) was calculated and examined using Pearson correlation coefficient and the results are shown in Tables 4.27 and 4.28.

Table 4.27: Correlation Between Heavy Metals in Cat Fish from Imo River during Dry Season

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	-0.43717	1					
Pb	0.650132	-0.96661	1				
Ni	-0.92028	0.046586	-0.301006	1			
Zn	0.980907	-0.25020	0.489952	-0.97880	1		
Cu	-0.92695	0.063972	-0.317564	0.999848	-0.982216	1	
V	ND	ND	ND	ND	ND	ND	1

ND = Not detected

Table 4.28: Correlation Between Heavy Metals in Cat Fish from Imo River during Wet Season

	Fe	Cd	Pb	Ni	Zn	Cu	V
Fe	1						
Cd	-0.887	1					
Pb	-0.998	-1	1				
Ni	-0.353	0.205	-1	1			
Zn	0.828	-0.398	1	-0.817	1		
Cu	-0.474	0.074	-1	0.991	-0.886	1	
V	ND	ND	ND	ND	ND	ND	ND

ND = Not detected

In the dry season, strong negative correlation was observed at $P < 0.05$ between Fe – Cd ($r = -0.437$) Pb – Cd ($r = -0.967$), Ni – Fe ($r = 0.920$) Ni – Pb ($r = -0.301$), Zn – Ni ($r = -0.979$) Cu – Fe ($r = 0.927$), Cu – Pb ($r = -0.318$) Cu – Zn ($r = -0.982$), which showed that they do not have common source. Significant positive correlations was observed at $P < 0.05$ for the following metal pairs; Pb – Fe ($r = 0.650$) Ni – Cd ($r = 0.046$) Zn – Fe ($r = 0.980$), Zn – Pb ($r = 0.490$), Cu – Cd ($r = 0.0639$); Cu – Ni ($r = 0.999$), which showed that as one metal increases the other pair increases.

4.7 Transfer Factor (Bioaccumulation Factor) of Heavy Metals in *Tilapia Zilli* and Cat Fish.

Tables 4.29 to 4.34 show transfer factor of heavy metals in *Tilapia Zilli* and Cat fish.

Table 4.29 – Heavy Metal Transfer Factor in *Tilapia Zilli* from Sediment during Dry season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	5.218	0.263	0.5129	0.970	0.123	0.0258	ND
Onuimo	1.373	0.667	1.156	0.930	0.155	0.033	ND
Oweri-nta	25.98	1.167	1.218	1.657	0.1087	0.037	ND

ND = Not detected

Table 4.30: Heavy Metal Transfer Factor from Sediment during Wet Season (*Tilapia Zilli*)

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	10.63	0.26170	0.594	1.077	23.00	0.0157	ND
Onuimo	1.922	0.14291	1.062	0.744	1.309	0.0217	ND
Oweri-nta	28.44	0.3077	0.7887	1.233	11.50	0.281	ND

ND= Not detected

Table 4.31: Heavy Metal Transfer Factor from Water to Cat fish during Dry Season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	42.6	0.833	0.135	22.13	46.67	1.000	ND
Onuimo	31.83	0.722	0.0837	0.613	3.516	2.400	ND
Oweri-nta	58.67	0.5385	0.147	1.139	13.56	0.750	ND

ND= Not detected

Table 4.32: Heavy Metal Transfer Factor from Water to Cat Fish during Wet Season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	160.7	0.850	0.331	24.6	55.50	11.00	ND
Onuimo	141.80	0.786	0.770	0.600	3.061	10.00	ND
Oweri-nta	200.2	1.08	1.370	1.106	20.00	4.00	ND

ND = Not detected

Table 4.33: Heavy Metal Transfer Factor from Sediment to Cat fish during Dry Season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	8.482	0.789	1.945	1.240	0.1990	0.156	ND
Onuimo	2.167	0.217	1.540	0.698	0.350	0.156	ND
Oweri-nta	46.04	2.33	1.010	0.854	0.154	0.161	ND

ND = Not detected

Table 4.34: Heavy Metal Transfer from Sediment to Cat fish during Wet Season

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	26.78	8.000	0.572	1.455	0.207	0.175	ND
Onuimo	4.170	7.857	1.293	0.744	0.333	1.667	ND
Oweri-nta	210.0	1.000	0.830	0.833	0.158	0.168	ND

ND = Not detected

Transfer factor was calculated by Razek using the fomular $TF = m \text{ tissue}/m \text{ metal}$. In this study the order of these heavy metals in relation to the concentration of heavy metals in the organs of fish species is found as $Fe > Ni > Pb > Cd > Zn > Cu > V$ as shown in Table 4.29 in dry season. In a research by Canpolat et al., (2012), Fe, Mn, Cu, Zn, Cd, Cu and Pb accumulation in the organs and tissues of *Capoeta capoeta umbla* which lives in Takar Hazar, the order of these heavy metals in relation to their concentration in muscles, organs and tissues of fish was found as $Zn > Fe > Pd > Cd > Cu$. Mansour and Sickly (2012) investigated the accumulation of Zn, Cu, Cd, Pb and Sn in some species of fish caught in Fayoum government (*Tilapia* Sp, Cat fish Sp and Solea Sp). They foundout that the level of the heavy metal accumulation changes according to seasons. Canpolat *et al.*, (2012) found out that there is relationship between fish ages and heavy metal level in muscle tissue. He found out that the level of all metals analyzed increased with fish age. He found out that accumulation of heavy metals in the living organisms are related to some many factors such as pH, temperature, inorganic matter, process of ionic changes and microbial activities.

Tukura (2015) reported that the organs tend to accumulate high concentration of heavy metals with increase of fish size. From this study, it was found that heavy metals accumulation charges with seasons, kind of fish and size of fishes. Heavy metals accumulated higher in dry season than wet season because the activities of the fish rise in dry season .It was found out that Cat fish accumulated higher heavy metals than *Tilapia*. The results revealed that transfer factor values for all the heavy metal in *Tilapia Zilli* during dry season were lower than 1.000 except for transfer factor of some heavy metals Fe, Cd, Pb, Ni, Zn at Owerri-Nta, which indicated that the transfer factors of all metals in the two fish samples from water were greater than those of sediments.

4.8 Human Health Risk Assessment of Heavy Metals via Ingestion of Water from IMR.

The levels of estimated daily intake (EDI) of selected heavy metals in water during dry and wet season are summarized in Tables 4.35-4.38

Table 4.35: Estimated Daily Intake of Heavy Metals by Tilapia Zilli in Imo River during Dry Season (mg/kg)

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	1.52×10^{-1}	2.33×10^{-5}	1.018×10^{-3}	1.20×10^{-3}	2.00×10^{-2}	9.3×10^{-4}	ND
Onuimo	2.45×10^{-1}	1.86×10^{-5}	2.86×10^{-2}	2.00×10^{-3}	2.17×10^{-3}	1.11×10^{-3}	ND
Oweri-nta	2.49×10^{-1}	3.25×10^{-5}	2.4×10^{-3}	2.30×10^{-3}	2.22×10^{-2}	1.39×10^{-3}	ND

ND = Not detected

Table 4.36 Estimated Daily Intake of Heavy Metals by Tilapia Zilli in Imo River during Wet Season in (mg/kg)

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	5.93×10^{-2}	1.86×10^{-5}	8.835×10^{-4}	1.10×10^{-3}	1.28×10^{-2}	4.65×10^{-4}	ND
Onuimo	1.094×10^{-1}	9.3×10^{-6}	239×10^{-3}	1.395×10^{-3}	1.34×10^{-2}	6.045×10^{-4}	ND
Oweri-nta	2.017×10^{-1}	1.56×10^{-5}	2.29×10^{-3}	2.29×10^{-3}	1.6×10^{-2}	9.3×10^{-4}	ND

ND = Not detected

Table: 4.37 Estimated Daily Intake of Heavy Metals by Cat Fish in Imo River during Dry Season in (mg/kg)

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	2.47×10^{-1}	6.97×10^{-5}	3.88×10^{-3}	1.54×10^{-3}	3.26×10^{-2}	5.63×10^{-3}	ND
Onuimo	3.867×10^{-1}	6.045×10^{-5}	3.81×10^{-3}	1.44×10^{-3}	3.52×10^{-2}	2.11×10^{-3}	ND
Oweri-nta	4.42×10^{-1}	6.51×10^{-5}	2.88×10^{-3}	1.64×10^{-3}	3.15×10^{-2}	6.05×10^{-3}	ND

ND = Not detected.

Table: 4.38 Estimated Daily Intake of Heavy Metal by Cat Fish in Imo River during Wet Season (mg/kg)

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	1.49×10^{-1}	5.58×10^{-4}	3.85×10^{-3}	1.49×10^{-3}	3.1×10^{-2}	4.65×10^{-3}	ND
Onuimo	2.37×10^{-1}	5.16×10^{-3}	3.81×10^{-3}	1.40×10^{-3}	3.1×10^{-2}	4.60×10^{-3}	ND
Oweri-nta	1.95×10^{-1}	6.05×10^{-5}	2.05×10^{-2}	1.55×10^{-3}	2.79×10^{-2}	5.58×10^{-3}	ND

ND = Not detected

Table: 4.38 Estimated Daily Intake of Heavy Metal by humans via ingestion of water during drySeason (mg/kg)

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	3.56×10^{-3}	5.14×10^{-5}	1.76×10^{-3}	4.26×10^{-5}	5.71×10^{-4}	5.71×10^{-4}	ND
Onuimo	7.40×10^{-3}	5.16×10^{-5}	2.80×10^{-3}	1.47×10^{-3}	6.14×10^{-3}	2.85×10^{-4}	ND
Oweri-nta	1.79×10^{-1}	3.71×10^{-5}	1.20×10^{-3}	8.82×10^{-4}	1.40×10^{-3}	1.14×10^{-3}	ND

ND = Not detected

Table: 4.38 Estimated Daily Intake of Heavy Metal by humans via ingestion of water during wet Season (mg/kg)

Location	Fe	Cd	Pb	Ni	Zn	Cu	V
Asa	7.06×10^{-4}	4.00×10^{-4}	1.50×10^{-3}	1.49×10^{-3}	3.40×10^{-3}	2.86×10^{-4}	ND
Onuimo	1.02×10^{-2}	4.00×10^{-4}	2.30×10^{-3}	1.40×10^{-3}	6.29×10^{-3}	2.86×10^{-4}	ND
Oweri-nta	6.00×10^{-4}	3.43×10^{-6}	9.10×10^{-4}	8.50×10^{-4}	8.57×10^{-4}	8.57×10^{-4}	ND

ND = Not detected

The decrease in the level of EDI in *Tilapia Zilli* during the dry season followed the order Fe>Zn>Pb>Ni>Cd>Cu>V while the wet season decrease was Fe>Zn>Ni>Pb>Cu>Cd>V. The estimated daily intake of some heavy metals in water by Cat Fish from IMR followed the trend Fe>Zn>Ni>Cu>Pb>Cd>V in dry season and Fe>Zn>Pb>Cu>Ni>Cd>V in wet season. In all stations, the estimated daily intake of Fe was higher in dry season than the wet season. The values of Cu in all the station for both seasons were comparable. The concentration of Fe, Pb, Zn and Cd are toxic while Cd is known to be among the most toxic heavy metals to aquatic organisms. Cadmium (Cd) has a higher affinity for thiol (SH) groups in human physiology which may cause more health problems when enhanced concentration are taken in through the consumption of fishes.

Cd/Zn ratio of 0.0305 in cat fish in both seasons was greater than Cd/Zn in tilapia fish as shown in tables 4.35-4.38. Hence, the estimated daily intake of heavy metals by cat fish and tilapia fish during both seasons were below 0.5mg/kg maximum tolerable limit for shell fish and fish (Ogundayo *et al.*, 2010).

4.9 Concentration of PAHs in Water from Imo River

Tables 4.39 and 4.40 showed the concentration of the 16 priority PAHs in water from IMR in both dry and wet season while the summation of PAHs in water from IMR for both season was computed as shown in appendix 29.

Table 4.39: Concentration of PAHs in Water (mg/L) in Imo River during Dry Season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.12	0.07	0.9
Methylnapthylene	0.039	0.211	0.0349
Acenaptylene	0.44	0.45	0.02
Acenaphthlene	0.54	0.20	0.40
Fluorene	0.08	0.05	0.10
Phenanthrene	0.05	0.07	0.08
Anthracene	0.06	0.041	0.51
Pyrene	0.001	0.05	0.077
Chrysene	0.05	0.001	0.001
Fluoranthene	0.25	0.001	0.001
Benzo [a] Anthracene	0.005	0.007	0.08
Benzo [b] Fluoranthene	0.07	0.001	0.001
Benzo [k] Fluoranthene	0.01	0.02	0.01
Benzo [a] Pyrene	0.06	0.001	0.002
indenol [1,2,3, cd] pyrene	0.001	0.002	0.047
Dibenzo [ah] Anthracene	0.43	0.267	1.013

Table 4.40: Concentration of PAHs in Water(mg/L) in Imo River during Wet Season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.100	0.040	0.030
Methylnapthylene	0.101	0.001	0.001
Acenaptylene	0.450	0.120	0.010
Acenaphthlene	0.360	0.850	0.200
Fluorene	0.100	0.490	0.090
Phenanthrene	0.020	0.020	0.050
Anthracene	0.060	0.041	0.510
Pyrene	0.001	0.070	0.050
Chrysene	0.001	0.001	0.001
Fluoranthene	0.010	0.001	0.0008
Benzo [a] Anthracene	0.030	0.080	0.060
Benzo [b] Fluoranthene	0.060	0.003	0.0002
Benzo [k] Fluoranthene	0.000	0.00	ND
Benzo [a] Pyrene	0.010	0.001	0.0009
indenol [1,2,3, cd] pyrene	0.005	0.001	0.030
Dibenzo [ah] Anthracene	0.01	0.001	0.001

The highest value (0.85) for the individual PAHs was recorded for Acenaphthylene at Onui-mo in wet season while the least value (0.0009) was recorded for Benzo(a) pyrene at Owerri - Nta in wet season. The occurrence of low molecular weight PAHs (LMW-PAHs) ranged from 0.8% to 30.2% in the dry season and 0.09% to 3.1% in the wet season.

The occurrence of high molecular weight PAHs (HMW-PAHs) ranged from 7.7% to 98.2% in the dry season and 97.6% to 98.2% in wet season. The PAHs concentration in the Imo River provided comprehensive look at present water quality conditions. Polycyclic aromatic hydrocarbons were detected in various locations of the river but existed at very low concentrations in both seasons. Polycyclic aromatic hydrocarbon of low molecular weight (1-3 ringed) are usually lost due to microbial de-gradation and volatilization while larger molecular weight compounds (4-5 ringed) get lost as a result of photo-oxidation and may be attached to the underlying sediment (Obiakoret *et al.*, 2014). The values of individual PAHs reported in this study are lower than the range of values reported by other authors. Campolat (2012) reported values of PAHs that ranged from 0.0003 – 0.032 which is lower than the values in this study which is 0.0001 – 0.54 in IMO River water samples. The mean values of 16 PAHs reported by Gorlaky *et al.*, (2014) ranged from 33.2 – 34.5 while Imam *et al.*, (2014) reported individual range of 1.38 to 5.95 in water sample. Anyakora *et al.*, (2015) reported values that ranged from not detected (ND) – 2.355 for water in Silokolo fishing settlement. Low percentage of low molecular weight PAHs (LMW – PAHs) compared to high molecular weight PAHs (HMW – PAHs) was observed in this study as shown in Tables 4.41 and 4.42.

2 – 3 ring PAHs are more easily bio degraded and volatilized compared to 4 – 6 ring PAHs. Moreover, the high level of HMW – PAHs in this study may be due attachment on soot produced from gas flaring from an oil exploration industry. Anyakora and Cooker (2000) attributed the presence of HMW PAHs in water to the presence of dissolved solid that have these compounds attached to them because of their low solubility in water. In this study the 2 – 3 ring PAHs Naphthalene, Methylnaphthylene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene and Anthracene were 0.36mg/L, 0.095, 0.30, 0.38, 0.77, 0.067, 0.20 respectively in dry season as shown in the appendix 29.

Law *et al.*, (1997) stipulated PAHs standards of 0.012, 1.0 and 2.0 for Naphthalene, Anthracene and Phenanthrene. The mean concentration of PAHs in water samples from Imo River in wet season for 2 – 3 ring PAHs Naphthalene, Methynaphthylene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene were 0.057, 0.03, 0.19, 0.47, 0.23, 0.03, 0.20 respectively. The mean concentration for 4 – 6 ring PAHs, Pyr, Chy, Flt, B(a)A, B(b)F, B(k)F, B(a)P, Ind(1,2,3,c,d)P and DB(a,h)A in dry and wet season were 0.04, 0.01, 0.08, 0.03, 0.02, 0.01, 0.02, 0.02, 0.01 and 0.04, 0.001, 0.004, 0.06, 0.02, 0.00, 0.004, 0.01 and 0.004 respectively. Adokoh *et al.*, (2009) reported that pathways for PAHs to enter surface water include atmospheric fallout, urban run off, municipal effluents, industrial effluents and oil spillage. Amadi, (2010) stated that waste water from Imo-Abia environs contributed to higher PAHs level of 2.0×10^{-2} mg/l in Otammiri River along Imo River. In this study the carcinogenic PAHs are of lesser level than non-carcinogenic PAHs. It was observed that LMW-PAHs are more abundant in Imo River than HMW-PAHs. The level of PAHs in dry season was higher than that of wet season as shown in Tables 4.41 and 4.42 and Appendix 31.

Table 4.41 Summation of PAHs in Water from Imo River (IMR) Dry Season (mg/L)

PAHs mixture	Asa	Onuimo	Owerri-nta
LMW – PAHs	1.33	1.14	212
HMW – PAHs	8.76E – 01	3.0E01	1.15
Total PAHs	2.21	1.44	3.28
ΣC – PAHs	6.26E – 01	2.9E – 01	1.14
ΣNon C-PAHs	1.58	1.14	2.12
% 2 – 3 rings	60.18	96.53	62.29
% 4 – 6 rings	39.82	3.47	37.71

Table 4.42 Summation of PAHs in water from Imo River (IMR) Wet Season in (mg/L)

PAH mixture	Asa	Onuimo	Owerri-nta
LMW – PAHs	9.1E – 02	5.92E – 01	4.37E – 01
HMW – PAHs	1.05	3.13E – 01	9.1E – 03
Total PAHs	1.14	9.15E – 01	4.46E – 01
ΣC – PAHs	1.04	3.13E – 01	8.0E – 03
ΣNon C-PAHs	1.0E – 01	5.92E – 01	4.38E – 01
%2 – 3 rings	1.75	10.16	97.76
%4 – 6 rings	98.25	89.84	2.24

The concentrations of the carcinogenic PAHs (C-PAHs) in both seasons were higher than the non-carcinogenic PAHs (N-PAHs). The European Union permissible limit for total C – PAHs is 10^{-4} mg/L or 0.0001mg/L. The concentration of C – PAHs in water samples from all the examined sites in both seasons were higher than the standard. This may be due to increased anthropogenic activities at the examined site. It is worthy to note that those of Asa-Owaza were very high due to closeness to oil wells and flare stations. The results in this study are similar to the findings of Anyakora (2006). Al Kahtan (2009) postulated that C – PAHs can cause tumor in laboratory animals through different exposure routes. Coker *et al.*, (2006) reported that most carcinogenic PAHs show greater resistance to microbial degradation.

The standard for the sum of B(a)P, B(b)F, B(k)F and D(a, h)A was set at 2×10^{-4} mg/L (0.0002) while the standard for the sum of B(b) F, B(g,h,i)P, B(k)F and Ind (1,2,3 – cd)P was set at 1×10^{-4} mg/L (0.001) by European Union (1996). The sum of the seven mentioned C – PAHs was set at 0.0001 (10^{-4} mg/L by European Union (1996). The sum of the seven mentioned C – PAHs. (Chry, B(a)A, B(b)F, B(a)P, Ind (1,2,3, c, d)P, DB(a,h)A were above the stipulated standard in all stations in both seasons (Tables 4.41 and 4.42). The concentration of

B(a)P in water from all the stations were below the standard of 0.7 stipulated by Institute of Standards and Industrial Research of Iran (ISIRI) (2010) and WHO (2011) in both the dry and wet seasons. Marce and Bornil (2000) reported that PAHs concentration of 0.7 corresponds to an excess life time cancer risk of 10^{-5} .

4.9.1 Seasonal Variation of PAHs Using Plots

From the lineplot in appendix 65 the level of PAHs in dry season was higher than in wet season. Acenaphthylene recorded highest value and Benzo(a)Pyrene the least value in wet season.

4.9.2 PAHs Interrelationship in Water from Imo River

The results of correlation analysis conducted among the concentration of individual PAHs in water sample was used to assess PAHs interrelationship and their origin during dry and wet season as presented in tables 4.43 and 4.44. Strong positive significant correlation was observed between some individual PAHs in water during the dry season. B(a)P and D(a, h)A. showed the highest PAHs association with correlation coefficient of 0.99 for HMW-PAHs followed by Chy and Flt. During the wet season, significant positive correlation was observed between the following PAHs pairs: B(b)F and B(a)A, Chy and B(k)F. B(k)F, and Ind(1,2,3cd) p($r=0.99$), B(a) and B(k)F ($r=0.716$) which indicate that the PAHs have common source. However strong negative correlation were observed between individual PAHs Flt-Chy ($r=-0.563$), B(b)f –B(a)F ($r = 0.991$), B(a)- Ind(1,2,3cd)P, $r(=-0.99)$ which shows that the PAHs do not have common source.

Table 4.43: Correlation Between Low Molecular Weight PAHs in Water from IMR during Wet Season (mg/kg).

	Naph	Methyl	Ace	Acy	Fl	Phen	Ant	Pyr
Naph	1							
Methyl	-0.297	1						
Ace	-0.518	0.971	1					
Acy	-0.833	-0.281	-0.043	1				
Fl	-0.695	-0.481	-0.256	-0.977	1			
Phen	0.975	-0.5	-0.693	-0.690	-0.516	1		
Ant	0.983	-0.469	-0.667	-0.716	0.549	0.999	1	
Pyr	0.016	-0.959	-0.864	0.540	0.708	0.236	0.201	1

Table 4.44: Correlation between Low Molecular Weight PAHs in Water from IMR during Dry Season (mg/kg).

	Naph	Methyl	Ace	Acy	FI	Phen	Ant	Pyr
Naph	1							
Methyl	-0.563	1						
Ace	-0.999	0.535	1					
Acy	-0.991	0.669	0.986	1				
FI	0.999	-0.566	-0.999	-0.991	1			
Phen	0.719	0.169	-0.742	-0.619	0.716	1		
Ant	0.999	-0.548	-0.999	-0.988	0.999	0.732	1	
Pyr	0.736	-0.145	-0.759	-0.638	0.733	0.999	0.748	1

The result of the correlation analysis conducted among the concentration of individual PAHs in water samples to assess PAH interrelationship and their origin during the dry and wet season is presented in tables 4.45 &4.46.

Table 4.45: Correlation between High Molecular Weight PAHs in Water from IMR during Dry Season (mg/kg).

	Chy	Fit	B(a)A	B(b)F	B(k)F	B(a)P	Ind(1,2,3,CD)P	D B(ah)A
Chy	1							
Fit	-0.563	1						
B(a)A	-0.999	0.535	1					
B(b)F	-0.991	0.669	0.986	1				
B(k)F	0.999	-0.566	-0.999	-0.991	1			
B(a)P	0.719	0.169	-0.742	-0.619	0.716	1		
Ind (1,2,3,C,D)P	0.999	-0.548	-0.999	-0.988	0.999	0.732	1	
D B(ah)A	0.736	0.145	-0.759	-0.638	0.733	0.999	0.748	1

Table 4.46: Correlation between High Molecular Weight PAHs in Water from IMR during Wet Season (mg/kg).

	Chy	Fit	B(a)A	B(b)F	B(k)F	B(a)P	Ind (1,2,3,cd) P	D B(ah)A
Chy	1							
Fit	0.999	1						
B(a)A	-0.918	-0.909	1					
B(b)F	0.999	0.999	-0.900	1				
B(k)F	-	-	-	-	1			
B(a)P	0.999	0.999	0.914	0.999	-	1		
Ind (1,2,3,C,D)P	-0.386	-0.403	-0.013	-0.424	-	-0.395	1	
D B(ah)A	0.998	0.999	-0.898	-0.999	-	0.999	-0.428	1

Strong positive correlation was observed between some individual PAHs in water during the dry seasons and wet seasons as presented in Tables 4.65 to 4.68. Ind(1,2,3cd)P/B(k)P and DB(ah)A/B(a)P showed the highest PAHs association with correlation coefficient of 0.99 and 0.99 respectively. During the wet season, positive correlation was observed between Phen and Ant ($r = 0.99$) at 0.01 levels while some PAHs pairs recorded significant correlation of 0.05 levels. They are Flt/Chy, DB(a, h)A/Flt. Correlation analysis provides information about associations between sites and between individual PAHs compounds to determine common origin (Essumang *et al.*, 2009). The result for correlation analysis between individual PAHs in water from IMR revealed that compounds with strong positive correlation were derived from a common anthropogenic origin. Ezeronye and Ubalua (2005) reported that two compounds with strong positive correlation between their concentrations are likely to have a common source. Also the strong positive correlation between B(a)A and Chrysene observed in this study is due to close relatedness in molecular weight (Ogbuagu *et al.*, 2011).

4.10 PAHs in Sediments from Imo River

The results of the level of polycyclic aromatic hydrocarbon in sediment from Imo River in both seasons (dry and wet season) were summarized in Table 4.47 to 4.50.

Table 4.47: Concentration of PAHs(mg/kg) in Sediments in Imo River during Dry Season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.041	0.0349	0.0421
Methylnapthylene	0.039	0.001	0.001
Acenaptylene	0.001	0.076	0.007
Acenaphthlene	0.001	0.004	0.060
Fluorene	0.011	0.013	0.057
Phenanthrene	0.191	0.001	0.070
Anthracene	0.209	0.203	0.010
Pyrene	0.244	0.001	0.214
Chrysene	0.507	0.001	0.490
Fluoranthene	0.001	0.001	0.255
Benzo [a] Anthracene	0.413	0.205	0.255
Benzo [b] Fluoranthene	0.413	0.388	0.342
Benzo [k] Fluoranthene	0.000	0.000	ND
Benzo [a] Pyrene	0.001	0.002	0.001
indenol [1,2,3, cd] pyrene	0.001	0.147	0.196
Dibenzo [ah] Anthracene	0.000	0.001	0.002

ND – Not Detected

Table 4.48: Concentration of PAHs(mg/kg) in Sediments in Imo River during Wet Season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.002	0.001	0.0017
Methylnapthylene	0.001	0.0353	0.210
Acenaptylene	0.005	0.001	0.080
Acenaphthlene	0.006	0.008	0.004
Fluorene	0.001	0.012	0.130
Phenanthrene	0.002	0.0235	0.010
Anthracene	0.003	0.001	0.001
Pyrene	0.071	0.510	0.001
Chrysene	0.062	0.001	0.001
Fluoranthene	0.010	0.000	0.001
Benzo [a] Anthracene	0.452	0.001	0.001
Benzo [b] Fluoranthene	0.520	0.010	0.001
Benzo [k] Fluoranthene	0.000	ND	ND
Benzo [a] Pyrene	0.001	0.267	0.001
indenol [1,2,3, cd] pyrene	0.001	0.0330	0.001
Dibenzo [ah] Anthracene	0.001	0.001	0.002

ND - Not detected

Table 4.49: Summation of PAHs in Sediments from Imo River (IMR) during Wet Season (mg/kg).

PAH mixture	Asa	Onuimo	Owerri-nta
LMW – PAHs	9.10E – 02	5.9E – 01	4.37E – 01
HMW – PAHs	1.05	3.13E – 01	8.1E – 03
Total PAHs	1.14	9.03E – 01	4.5E – 01
ΣC – PAHs	1.04	2.99E – 01	7.0E – 03
ΣNonC PAHs	1.0E – 01	6.0E – 01	4.38E – 01
%2 – 3 rings	1.8	10.00	96.89
%4 – 6 rings	98.2	90.00	3.11

Table 4.50: Summation of PAHs in Sediments in Imo River (IMR) during Dry Season (mg/kg)

PAH mixture	Asa	Onuimo	Owerri-nta
LMW – PAHs	7.37E – 01	3.34E – 01	4.61E – 01
HMW – PAHs	1.40	7.54E – 01	1.54
Total PAHs	2.13	1.08	2.00
ΣC – PAHs	1.40	7.44E – 01	1.29
ΣNonC–PAHs	7.38E – 01	3.34E – 01	7.16E – 01
%2 – 3 rings	23.15	30.93	12.35
%4 – 6 rings	76.35	69.07	87.65

The results of the sum total concentration PAHs in sediment samples from Imo river for wet and dry seasons were 2.49 and 5.21 respectively. The least value was recorded for B(k)F while the highest value was recorded for Flt at Asa-owaza during the dry season and during the wet season the results ranged from 0.0001 to 0.52 while during the dry season the results ranged from 0.001 at Onuimo to 0.51 at Asa-Owaza. The decrease for total PAHs in both seasons was Asa-Owaza > Owerri-nta > Onuimo. The concentration of total PAHs in sediment in the dry season was higher in most locations than the value for wet season. When compared with student's test there was no significant difference between the two seasons at $p < 0.005$. The value of total carcinogenic PAHs (Σ C-PAHs) in this study ranged from 7.44×10^{-1} to 1.40 in dry season and 4.5×10^{-1} to 1.14 in wet season. The concentration of HMW-PAHs ranged from 0.0081 to 1.05 for wet season. The summation of non C-PAHs (non-carcinogenic) polycyclic aromatic hydrocarbon in this study ranged from 3.34×10^{-1} to 7.38×10^{-1} in dry season and 1.01×10^{-1} to 6.0×10^{-1} in wet season. The % of 2-3 rings ranged from 12.35 % to 30.93% in dry season and 1.8% to 96.89% in wet season. The % of 4-6 rings ranged from 69.07% to 87.65% and 3.11% to 98.2% in dry and wet seasons respectively.

Srogi (2007) reported that the concentration of individual C – PAHs stipulated by WHO in coastal and surface water was 5×10^{-5} mg/L (0.00005) (WHO, 1998). In this study the values of C – PAHs were above the WHO limit. Similarly Mandy and Presley (2011) recorded high values of B(b)F and (1,2,3 – cd)P for PAHs in water from Ogba/Egbema Ndoni communities in the Niger Delta of Nigeria. The results obtained from this study implied that the consumption of fish and other sea food from the above sites can be harmful to the consumers since the above C – PAHs may gain entry into man. Essumang *et al.* (2009) reported that PAHs occur as a mixture of low or more compounds and are potent carcinogens that produce tumors in some organisms even at a single dose. They also create advanced glycogen end-products which lead to an increased risk of coronary heart disease. Anware *et al.*, (2010) stated that la-

laboratory animals experience different forms of cancer depending on their pathway of entry into the body or route of administration. He also stated that ingestion of PAHs or application on the skin results in stomach and skin cancer respectively.

4.10.1 PAHs Interrelationship in Sediment in Imo River (IMR)

The interrelationship between individual PAHs (polycyclic aromatic hydrocarbons) in sediment during the dry and wet season are presented in the Tables 4.51 and 4.52. Tables 4.53 and 4.54

Tables 4.51: Correlation between Low Molecular Weight PAHs in Sediments from IMR during Dry Season (mg/kg).

	Naph	Methyl	Ace	Acy	Flt	Phen	Ant	Pyr
Naph	1							
Methyl	0.372	1						
Ace	-0.977	-0.567	1					
Acy	0.582	-0.538	-0.395	1				
Flt	0.587	-0.533	-0.401	0.999	1			
Phen	0.654	0.946	-0.799	-0.235	-0.228	1		
Ant	-0.596	0.523	0.412	-0.999	-0.999	0.217	1	
Pyr	0.967	0.595	-0.999	0.357	0.824	0.824	-0.374	1

Table 4.52: Correlation between Low Molecular Weight PAHs in Sediments from IMR during Wet Season (mg/kg).

	Naph	Methyl	Ace	Acy	Flt	Phen	Ant	Pyr
Naph	1							
Methyl	0.073	1						
Ace	0.269	0.980	1					
Acy	-0.682	-0.779	-0.888	1				
Flt	0.1484	0.997	0.993	-0.825	1			
Phen	-0.997	0.007	-0.190	0.621	-0.069	1		
Ant	0.731	-0.627	-0.461	0	-0.565	-0.784	1	
Pyr	-0.912	-0.477	-0.641	0.922	-0.543	0.876	-0.386	1

Table 4.53: Correlation between High Molecular Weight PAHs in Sediments from IMR during Dry Season (mg/kg).

	Chy	Flt	B(a)A	B(b)F	B(k)F	B(a)P	Ind(1,2,3,CD)P	D B(ah)A
Chy	1							
Flt	0.474	1						
B(a)A	-0.091	0.834	1					
B(b)F	-0.091	0.834	-0.973	1				
B(k)F	-	-	-	-	1			
B(a)P	-0.999	-0.5	0.062	0.168	-	1		
Ind (1,2,3,C,D)P	-0.304	-0.694	-0.976	-0.901	-	-	1	
						0.276		
D B(ah)A	-0.029	0.866	0.998	-0.986	-	0	0.961	1

Table 4.54: Correlation between High Molecular Weight PAHs in Sediments from IMR during Wet Season (mg/kg).

	Chy	Flt	B(a)A	B(b)F	B(k)F	B(a)P	Ind(1,2,3,CD)P	D B(ah)A
Chy	1							
Flt	0.996	1						
B(a)A	1	0.996	1					
B(b)F	0.999	0.982	0.999	1				
B(k)F	-	-	-	-	1			
B(a)P	-0.5	-0.578	0.5	-0.487	-	1		
Ind (1,2,3,C,D)P	-0.5	-0.577	-0.5	-	-	-	1	
				0.4868		0.432		
D B(ah)A	-0.5	-0.418	-0.5	-0.513	-	-0.5	-0.5	1

The Pearson's correlation matrix for the dry seasons revealed that correlation coefficients were mostly positive although few negative values were recorded in dry season. In wet season, significant positive correlation was recorded between the following PAHs pairs Ace/methyl ($r=0.98$) methyl/Fl ($r=0.997$) Ant/naph ($r=0.98$) methyl/Fl ($r=0.997$) Ant/Naph, ($r=0.73$) Pyr/Acy, ($r=0.92$) at $P = 0.01$. During dry season, significant positive correlation was recorded between the following PAHs pairs Naph/Phen ($r = 0.654$), Ant/methyl ($r = 0.52$), Phe/Methyl ($r = 0.59$), Pyr/Ant ($r = 0.824$), Pyr/Methyl ($r = 0.59$), Fit/Chy ($r = 0.99$), B(b)F/Chy ($r = 0.99$), B(a)A/fl ($r = 0.99$), B(b)/Fl ($r = 0.98$), [Pyr/Fl ($r = 0.72$), Phen/Nap ($r = 0.65$), while in wet session there were mostly negative correlation as shown in Tables 4.51-4.54. B(a)P / B(a)A except in Chy/ Fit ($r = 0.99$). The positive correlation implies that the PAHs are from same source while the negative PAHs imply that they are not of the same source.

4.10.2 Analysis of PAHs in Sediment from Imo River using graphs

From appendix the values of individual PAHs recorded in this study in all the station were lower than the sediment quality guideline stipules by Australian and New Zealand environmental conservation council ANZECC and ARMCANZ (2000) as shown in appendix 30. The high concentration of PAHs in sediment from Asa-Owaza is due to the fact that the sampling point receives direct discharge of effluents from a manufacturing industry and oil wells located closed to it. The values in the study are lower than values reported by Li *et al.*, (2009) for Aajiany River water way in Wenzhou, China. Yu *et al.*, (2014) reported higher total PAHs values in urban soil of Hangzhous, China, when compared with the standard proposed by ANZECC and ARMCANZ (2000). The total PAHs in this study was below the effect range low (ERL) standard of 4.022mg/kg. This implied that there is no possibility of acute adverse biological effect on the sediment dwelling organisms. Traven (2013) reported higher values for ΣC - PAHs that ranged from 25.6ng (0.02mg/lkg) to 50ng (5.0×10^{-1} mg/kg) with an average

concentration of 164mg/kg ($0.164\text{mg/kg} = 1.64 \times 10^{-1}\text{mg/kg}$). The values of individual PAHs in sediments in all sampling points/locations in both seasons were lower than the values for water except at some stations such as Asa-Owaza and Owerri-nta. This supports the findings of Zhao et al., (2014) that PAHs especially high molecular weight PAHs are usually adsorbed onto sediments. The level and percentage occurrence of HMW – PAHs in this study was higher than LMW-PAHs.

Epidermological study evidenced that > 4 – rings PAHs can penetrate deeply into lungs when inhaled resulting in greater bio-accessibility of Hmw-PAHs than Lmw-PAHs (Yu *et al.*, 2015). It was thus proposed that PAHs in the particulate phase can pose greater adverse health impact on human and thus are highly carcinogenic. This confirmed that Imo River from Owerri-nta to Asa-Owaga are highly polluted by HMW and can pose high health risk to man. Yu *et al.*, (2015) in the study of human exposure to PAHs in Beijing suggested that exposure of HMW-PAHs and LMW-PAHs took place mostly by oral ingestion and can pose adverse health impacts on human. He reported that LMW-PAHs have higher vapour pressure which tend to occur in gaseous phase whereas the high molecular weight (HMW-PAHs) component mostly bound with particulate. (Wei *et al.*, 2015) reported higher Σ HMW – PAH values for sediment from Kanarrey Bay 0.032 to 1.3 with an average concentration of 0.286mg/kg. Zhao *et al.*, (2016) stated that temperature is significance for the fate of PAHs on soil and sediment. Temperature controls solubility, bioavailability, volatilization and hydrophobic nature of PAHs. The higher percentage of HMW-PAHs compared to LMW-PAHs in this study is similar to the findings of other researchers on PAHs distribution in marine sediment (Tobiszewski and Namesink, 2012).

Polycyclic aromatic hydrocarbons (PAHs) are easily absorbed in the sediments, hardly biodegraded and volatilized and have higher octanol – water partition coefficient (Caylak 2012). This is why their concentration in this study is very important. Generally, the variation

of PAHs content in sediment from different sampling site that ranged from 0.001 to 0.53 may be due to physicochemical properties of sediments such as particulate organic matter. The sorption of PAHs in sediments tends to be higher in organic matrix and on fine particles of sediments (Yang, 2011). Yang (2011) attributed the sediment retention capacity of PAHs to physiochemical properties such as grain size, organic matter, colour while Zhao *et al.*, (2014) postulated that the level of PAHs in sediments is a function of photo-oxidation, chemical oxidation, microbial degradation, adsorption, leaching, bioaccumulation and volatilization.

4.10.3 Diagnostic Ratio for PAHs in Sediments from Imo River

Table 4.55 summarized the different diagnostic ratio of PAHs used in identification of possible source of PAHs in sediments from Imo River for both seasons.

Table 4.55 Diagnostic ratios of PAHs in sediments from Imo River during dry and wet season

Location	DRY	AN/AN + PH	WET	AN
	$\frac{\sum \text{LMW}}{\sum \text{HMW}}$		$\frac{\sum \text{LMW}}{\sum \text{HMW}}$	AN + PH
Asa- owaza	0.7373	0.52	0.091	0.06
Onuimo	0.336	0.208	0.5998	0.001
Owerrinta	0.449	0.01	0.437	0.001

The ratio of low molecular weight PAHs to high molecular weight PAHs has been used in the identification of pyrogenic and petrogenic sources of PAHs in sediments (Zhao *et al.*, 2014). Namesink and Tobiszewski (2012) reported that temperature process such as combustion emits high molecular weight PAHs. Atmospheric deposition and sedimentation are responsible for PAHs level in sediments. When the ratio of Anthracene/ Anthracene + Phenanthrene was used for identification of PAHs sources in sediment from Imo River. Mixed PAHs source (Petrogenic and Pyrogenic) was found at Asa-Owaza, Onuimo and Owerri-nta during both season. In this study pyrogenic source was recorded in all the stations during dry season while Petrogenic PAHs origin was recorded in some of the stations during the wet season. According to Nekhavhambe *et al.*, (2016), $\text{Ant}/\text{Ant} + \text{Phen} < 0.1$ indicated petrogenic source while $\text{Ant}/\text{Ant} + \text{Phen} > 0.1$ indicates pyrogenic source. In this study there is a mixed pattern of petrogenic and pyrogenic source. This result corroborates with the investigation of Joshua *et al.*, (2016) that reported a mixed pattern of petroleum and combustion sources of PAHs in sediment and waste water effluents in Xhembe Distrock South Africa.

If ratio LMW-PAHs/HMW-PAHs < 1 , the source is pyrogenic but if ratio of LMW PAHs/HMW PAHs is > 1 , the source is petrogenic. The results for some of the station indicated petrogenic source of PAHs in sediment and the predominance of petrogenic source of PAHs in this study is as a result of dry deposition and wet depositio, and combustion. In dry season as shown in the table 4.55 the diagnostic ratios, the ΣLMN and ΣHMW and $\text{AN}/\text{AN} + \text{PH}$ in most locations were < 1 or > 0.1 respectively which indicated pyrogenic source as shown in appendix 34. It means the PAHs originated from combustion. Essam *et al.*, (2013) reported diagnostic ratios between $\text{AN}/\text{AN} + \text{PH} = 0.52 - 1.0$, which suggested that the sources of PAHs at the majority station studied at Langkawi Island, Malaysia were derived primarily from pyrogenic sources, from incomplete fuel combustion of the boats and vehicle engines with lesser amounts of PAHs contributed from petrogenic source.

In wet season, the diagnostic ratios; $\frac{LMW}{HMW}$ for Asa -Owaza, Onuimo and Owerrinta were 0.087, 1.71 and 5.3 respectively while $\frac{AN}{AN+PH}$ for Asa-Owaza, Onuimo and Owerrinta were 0.06, 0.041 and 0.91 from appendix 34, it indicates petrogenic source which means that the PAHs originated from petroleum source. The result for the correlation matrix during the wet season suggested similar PAHs sources for all carcinogenic PAHs (Wei *et al.*, 2015). Correlations values give information on or identify PAHs that can co vary or coexist in the environment. Edokpanyi *et al.*, (2016) stated that the source of PAHs in sediment is atmospheric deposition followed by sedimentation.

4.11 PAHs in Fish

The level of sixteen (16) priority PAHs and their summation in *Tilapia Zilli* and Cat fish from IMR in both dry and wet season are shown in Tables 4.56 to 4.59.

Table 4.56: Concentration of PAHs (mg/kg) in *Tilapia Zilli* in Imo River during dry season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.028	0.026	0.030
Methylnapthylene	0.004	0.00	0.007
Acenaptylene	0.002	0.008	0.010
Acenaphthlene	0.0002	0.000	0.001
Fluorene	0.015	0.013	0.029
Phenanthrene	0.000	0.000	0.002
Anthracene	0.005	0.010	0.0012
Pyrene	0.007	0.008	0.006
Chrysene	0.001	0.001	0.004
Fluoranthene	0.000	0.000	0.009
Benzo [a] Anthracene	0.004	0.0420	0.0038
Benzo [b] Fluoranthene	0.0032	0.000	0.0058
Benzo [k] Fluoranthene	0.002	0.006	0.004
Benzo [a] Pyrene	0.010	0.003	0.0028
indenol [1,2,3, cd] pyrene	0.012	0.017	0.010
Dibenzo [ah] Anthracene	0.001	0.001	0.001

Table 4.57:Concentrationof PAHs(mg/kg)in *Tilapia Zilli*In Imo River During Wet Season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.0152	0.00127	0.00171
Methylnapthylene	0.003	0.003	0.009
Acenaptylene	0.001	0.003	0.008
Acenaphthlene	0.000	0.000	0. 000
Fluorene	0.009	0.006	0.012
Phenanthrene	0.000	0.000	0.000
Anthracene	0.010	0.011	0.015
Pyrene	0.013	0.018	0.008
Chrysene	0.000	0.003	0.000
Fluoranthene	0.028	0.038	0.054
Benzo [a] Anthracene	0.001	0.001	0.004
Benzo [b] Fluoranthene	0.000	0.000	0.003
Benzo [k] Fluoranthene	0.001	0.002	ND
Benzo [a] Pyrene	0.017	0.019	0.018
indenol [1,2,3, cd] pyrene	0.007	0.009	0.002
Dibenzo [ah] Anthracene	0.000	0.000	0.000

ND = Not Detected

Table 4.58: Concentration of PAHs(mg/kg)in Cat Fish in Imo River during Dry Season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.040	0.030	0.038
Methylnapthylene	0.050	0.008	0.070
Acenaptylene	0.020	0.06	0.070
Acenaphthlene	0.675	0.090	0.0825
Fluorene	0.010	0.010	0.037
Phenanthrene	0.024	0.027	0.030
Anthracene	0.00	ND	0.000
Pyrene	0.007	0.001	0.004
Chrysene	0.0012	0.002	0.0028
Fluoranthene	0.0016	0.0018	0.0015
Benzo [a] Anthracene	0.006	0.005	0.007
Benzo [b] Fluoranthene	0.002	0.009	0.003
Benzo [k] Fluoranthene	0.000	0.000	0.012
Benzo [a] Pyrene	0.005	0.006	0.004
indenol [1,2,3, cd] pyrene	0.010	0.025	0.0013
Dibenzo [ah] Anthracene	0.002	0.000	0.003

ND = Not Detected

Table 4.59: Concentration of PAHs(mg/kg) in Cat Fish in Imo River during Wet Season

Parameter	Asa-Owaza	Onuimo	Owerri Nta
Napthalene	0.018	0.170	0.050
Methylnapthylene	0.040	0.003	0.040
Acenaptylene	0.002	0.007	0.005
Acenaphthlene	0.006	0.007	0.007
Fluorene	0.010	0.0026	0.024
Phenanthrene	0.012	0.009	0.027
Anthracene	0.001	ND	ND
Pyrene	0.005	0.003	0.004
Chrysene	0.001	0.001	0.000
Fluoranthene	0.0008	0.009	0.010
Benzo [a] Anthracene	0.000	0.004	0.005
Benzo [b] Fluoranthene	0.002	0.002	0.008
Benzo [k] Fluoranthene	0.00125	0.0025	0.00175
Benzo [a] Pyrene	0.002	0.004	0.006
indenol [1,2,3, cd] pyrene	0.007	0.006	0.011
Dibenzo [ah] Anthracene	0.001	0.001	0.000

ND = Not Detected

The individual PAHs ranged from ND to 0.037 for *Tilapia* in both seasons. Σ PAHs values also exceeded EU limit in both species which attributed to high naphthalene concentration. Napthalene concentration was significantly higher ($p < 0.05$) than the concentration of other PAHs. Nnaji and Ekwe (2017) reported total PAHs (Σ PAHs) value of 1.8E-02 and 1.4E-02 in fish Cat fish and Tilapia fish respectively. Akpanbonget *al.*, (2009) reported values less than the values obtained in this study. They obtained a BaP concentration of 6.48E-05 and 5.21E-04 mg/kg in fleshy and smoked fish.

Factorial effects of season and location were not observed in the current work. However, season has been known to affect the concentration of PAHs in aquatic ecosystem and spatial location confirmed to play essential role in PAHs level variation and distribution (Nnaji and Ekwe, 2017). The trend for the individual PAHs in different sampling locations decreased as follows Owerinta > Asa -Owaza > Onuimo. The total PAHs in dry season was compared with total PAHs concentration in the wet season using student t-test and no significant difference in the mean value of the seasons was observed. Summation of PAHs in fish from IMR during both seasons is computed in Appendix 33. All the sixteen (16) targeted PAHs were detected in all the two kinds of fishes except Anthracene in Onuimo sampling station.

4.11.1 Analysis of PAHs in Fish using Graph

From appendix 67, there were higher values of PAHs in tissues and muscles of fish in wet season than in dry season. The trend in PAHs in fish in this study were as follows fluorene > methylnaphthene > fluoranthene > others in both season while B(k)F recorded the least value for both season.

4.11.2 Pearson correlation Matrix for PAHs in Tilapia and Cat fish from Imo River

The relationship between individual PAHs in *Tilapia zilli* and Cat fish during both season are presented in Tables 4.60 to 4.65.

Table 4.60: Correlation between Low Molecular Weight PAHs in *Tillapia Zilli* from IMR during Wet Season (mg/kg).

	Naph	Methyl	Ace	Acy	Flt	Phen	Ant	Pry
Naph	1							
Methyl	-0.476	1						
Ace	-0.401	0.961	1					
Acy	-	-	-	1				
Flt	0.775	-0.924	-0.994	-	1			
Phen	-0.633	0.982	0.996	-	-0.979	1		
Ant	-0.028	-0.867	-0.693	-	0.609	-0.756	1	
Pry	-1	-	1	-	-9	1	1	1

Table 4.61: Correlation between High Molecular Weight PAHs in *Tilapia Zilli* from 1MR during Dry Season (mg/kg).

	Chy	Fit B(a)A	B(b)F	B(k)F	B(a)P	Ind(1,2,3,C, D)P	D B(ah)A
Chy	1						
Flt	0.812	1					
B(a)A	-0.866	-0.866	1				
B(b)F	0.835	0.835	-0.998	1			
B(k)F	0	0	0.5	-0.551	1		
B(a)P	-0.521	-0.521	0.024	0.035	0.854	1	
Ind(1,2,3, C,D)P	-0.721	-0.721	-0.971	-0.983	0.693	-0.216	1
D B(ah)A	-	-	-	-	-	-	1

Table 4.62: Correlation between High Molecular Weight PAHs in *Tillapia Zilli* from IMR during Wet Season (mg/kg).

	Chy	Flt	B(a)A	B(b)F	B(k)F	B(a)P	Ind(1,2,3,CD)P	D B(ah)A
Chy	1							
Flt	-	1						
B(a)A	-	0.924	1					
B(b)F	-	0.924	0.948	1				
B(k)F	-	-	-	-	1			
B(a)P	-	0.187	0.547	0.547	-1	1		
Ind (1,2,3,C,D)P	-	0.782	-0.961	-0.961	-0.721	-0.758	1	
D B(ah)A	-	-	-	-	-	-	-	1

Table 4.63: Correlation between High Molecular Weight PAHs in Cat Fish from IMR during Wet Season (mg/kg).

	Naph	Methyl	Ace	Acy	FI	Phen	Ant	Pyr
Naph	1							
Methyl	0.327	1						
Ace	-0.5	0.655	1					
Acy	0.646	-0.509	-0.984	1				
FI	0.327	0.930	0.886	-0.789	1			
Phen	-0.189	0.866	0.945	-0.871	0.989	1		
Ant	-	-	-	-	-	-	1	
Pyr	0.673	-0.478	-0.977	0.999	-0.767	-0.853		1

Table 4.64: Correlation between High Molecular Weight PAHs in Cat Fish from IMR during Dry Season (mg/kg).

	Chy	Flt	B(a)A	B(b)F	B(k)F	B(a)P	Ind(1,2,3, CD)P	D B(ah)A
Chy	1							
Flt	-0.327	1						
B(a)A	0.500	-0.982	1					
B(b)F	0.132	0.893	-0.792	1				
B(k)F	0.866	-0.756	0.866	-0.381	1			
B(a)P	-0.500	0.982	-1	0.792	-0.866	1		
Ind (1,2,3,C,D)P	0.189	0.866	-0.756	0.998	-0.327	0.756	1	
D B(ah)A	-0.687	-0.462	0.286	-0.812	-0.231	-0.286	-0.844	1

Table 4.65: Correlation between High Molecular Weight PAHs in Cat Fish from IMR during Wet Season (mg/kg).

	Chy	Flt	B(a)A	B(b)F	B(k)F	B(a)P	Ind(1,2,3,C D)P	D B(ah)A
Chy	1							
Flt	-	1						
B(a)A	-	0.8707	1					
B(b)F	-	0.999	0.867	1				
B(k)F	-	0.999	-0.8605	0.999	1			
B(a)P	-	0.8707	0.5	0.0	0.0108	1		
Ind (1,2,3,C,D)P	-	0.9801	-0.945	-0.982	0.979	-0.189	1	
D B(ah)A	-	-0.492	-0.866	-0.5	-0.491	0.866	0.654	1

During the dry season, positive correlation was recorded between Ace/methyl ($r=0.9617$), Phe/Ace ($r=0.996$). Methyl/Phen ($r=0.9617$) for LMW-PAHs in Tilapia Zilli during wet season while for HMW-PAHs during same season, there were positive correlation between the following PAH pairs in the wet season: B(a)A/Flt, B(b)F/B(a)A, at 0.924 and 0.928 respectively. For Cat fish, there were strong negative correlations in both seasons. Also during dry season, strong positive correlation was found between the following PAHs pairs for HMW-PAHs in both rainy and wet season: B(a)P /Ind(1,2,3,cd)P ($r=0.979$) and DB(g, h)A and Ind(1,2,3,cd)P ($r=0.86$). It showed that the PAHs pairs had common source.

4.12 Carcinogenic Health Risk Induced by PAHs via Ingestion of Water from Imo River

Table 4.67: - Cancer Risk (CR) values of HMW PAHs in Water from IMR

Tables 4.66 and 4.67 summarized the result obtained from the computation of the carcinogenic risk assessment induced by PAHs through the ingestion of water from IMR (Imo River) in both dry and wet seasons.

Table 4.66: Cancer Risk (CR) values of HMW PAHs in Water from IMR during the Dry Season for Children and Adults

Carcinogenic PAHs	Asa Children		Onuimo		Owerrinta	
		Adult	Children	Adult	Children	Adult
Chry	1.00E -04	1.428E -04	2.00E -06	2.85E -06	2.00E -06	2.85E -05
Fluo	4.00E -04	5.714E -04	1.6E -06	2.28E -06	1.60E -07	2.28E -06
B(a)A	2.00E -05	2.86E -05	2.80E -05	3.98E -05	3.20E -05	2.28E -05
B(b)F	6.0E -04	8.55E -04	1.2E -04	2.28E -03	1.60E -05	2.28E -05
B(k)F	6.0E -04	8.55E -04	1.2E -04	1.70E -04	6.0E -05	8.55E -05
B(a)P	1.2E -03	1.71E -03	2.00E -05	2.85E -05	4.10E -05	5.70E -05
Ind(c,d)P	1.4E -06	1.995E -06	2.8E -06	3.9E -06	6.58E -06	9.38E -05
DB(a,h)A	8.6E -02	1.23E -01	5.34E -02	7.32E -02	2.026E -01	2.89E -01

Table 4.67: Cancer Risk (CR) values of HMW PAHs in Water from IMR during the Wet Season for Children and Adult

Carcinogenic PAHs	Asa	Child-	Onuimo		Owerrinta	
	ren	Adult	Children	Adult	Children	Adult
Chry	2.10E – 06	2.85E – 06	2.00E – 06	2.85E – 06	2.00E – 06	2.85E – 05
Fluo	1.6E – 05	2.286E – 05	1.6E – 06	2.285E – 06	1.28E – 06	1.82E – 06
B(a)A	1.2E – 04	1.71E – 04	3.20E – 04	4.36E – 04	2.4E – 04	3.42E – 04
B(b)F	9.6E – 04	1.21E – 03	4.8E – 05	6.90E – 05	3.2E – 06	4.57E – 06
B(k)F	0.00	0.00	0.00	ND	ND	ND
B(a)P	2.00E – 04	2.85E – 04	2.00E – 05	2.85E – 05	1.8E – 05	2.86E – 05
Ind(c,d)P	7.00E – 06	1.00E – 05	1.4E – 05	1.995E – 05	4.20E – 05	6.00E – 05
DB(a,h)A	2.22E – 03	2.86E – 03	2.00E – 04	2.86E – 04	2.10E – 04	2.86E – 04

The carcinogenic risk values in dry season for adults ranged from 1.60E-06 to 2.89E-01 with Onuimo recording the lowest value and Owerri-nta recoding the highest value for HMW PAHs. The range for the carcinogenic risk for children during dry season was 1.60E-07 to 2.03E-01. In wet season the range for children was 2.00E-06 to 0.00, while the range for adults was 1.28E-06 to 0.00. For both children and adult the lowest result was recorded at Onuimo while the highest value was recorded at Asa-Owaza.

Table4.68: Chronic Intake (exposure dose) values via Ingestion of HMW PAHs in Fish from IMR during the dry Season for Children and Adult

Carcinogenic PAHs	Asa Children		Onuimo		Owerrina	
		Adult	Children	Adult	Children	Adult
Chry	1.00E – 03	1.4.28E – 03	2.00E – 05	2.85E – 05	200E – 05	2.85E – 05
Fluo	5.00E – 03	7.143E – 03	2.00E – 05	2.85E – 05	2.00E – 05	2.85E – 05
B(a)A	1.00E – 04	1.43E – 04	1.40E – 04	1.99E – 04	1.60E – 03	2.28E – 03
B(b)F	1.40E – 03	2.0E – 03	2.00E – 05	2.85E – 05	2.00E – 05	2.85E – 05
B(k)F	2.0E – 03	2.85E – 03	4.00E – 04	5.70E – 04	2.00E – 04	2.85E – 04
B(a)P	1.2E – 03	1.71E – 03	2.10E – 05	2.85E – 05	4.00E – 05	5.70E – 05
Ind(c,d)P	2.0E – 05	2.85E – 05	4.00E – 05	5.70E – 05	9.4E – 04	1.34E – 03
DB(a,h)A	8.6E – 03	1.23E – 02	5.34E – 03	7.32E – 03	2.026E – 02	2.89E – 02
Total	1.93E – 02	2.7E – 02	9.96E – 03	1.39E – 02	2.146E – 02	3.089E – 02

Table 4.69: Chronic Daily Intake (exposure dose) values via Ingestion of HMW PAHs in Fish from IMR during Wet Season

Carcinogenic PAHs	Asa children		Onuimo		Owerrinta	
		Adult	children	Adult	children	Adult
Cry	2.00E – 0.5	2.85E – 05	2.00e – 05	2.85E – 05	2.00E – 05	2.85E – 05
Fluo	2.00E – 04	2.857E – 04	2.00E – 05	2.85E – 05	1.60E – 05	2.28E – 05
B(a)A	6.00E – 04	8.857E – 04	1.60E – 03	2.85E – 03	1.20E – 03	1.71E – 03
B(b)F	1.20E – 0	1.55E – 03	6.00E – 05	8.57E – 05	4.00E – 06	5.71E – 06
B(k)F	0.00	0.00	-	-	-	-
B(a)P	2.10E – 04	2.85E – 04	2.00E – 05	2.85E - 05	1.8E – 05	2.857E – 05
Ind(1,2,3,c,d)P	1.0E – 04	1.43E – 04	2.00E – 05	2.85E – 05	6.00E – 04	8.57E – 04
DB(a,h)A	2.0E – 04	2.86E – 04	2.10e – 05	2.86E – 05	2.00E – 05	2.857E – 05
Total	2.52E – 03	3.41E – 03	1.71E – 03	2.51E – 03	1.88E – 03	4.29E – 03

Table 4.68 and 4.69 show the chronic daily intakes (daily exposure doses) through ingestion of HMW-PAHs from Imo River for both seasons for children and adults. The values ranges from 4.00E-06 (B(a)f to 2.026E-02 (DB (a, h) A in children and 5.716E-06(B(b)F) to 2.89E-02 DB (a, h) A. However, some results were above the USEPA acceptable limit of 1×10^{-6} to 1.10×10^{-6} (via ingestion) in the water column suggesting possible carcinogenic effects to humans (children and adults) with children being the most vulnerable Cancer Risk (CR) between 10^{-6} and 10^{-4} indicates potential risk while CR greater than 10^{-4} denotes potential high risk and CR of 10^{-6} or less denotes virtual safety. However, result of risk of cancer (Table 4.66 and 4.67) due to human exposure to PAHs at Onuimo, Owerri-nta and Asa-Owaza ranged from 10^{-2} to 10^{-4} . That means any community that makes use of Imo River are at potential high risk

4.13 Multiple Linear Regression Analysis (R)

This analysis was done to investigate the relationship between PAHs in water, sediment and fish in Imo River. It attempts to assess the individual contribution of the predictor variables (C-PAHs) concentration in water and sediment to the outcome variable (C-PAHs in fish). The result is summarized in Tables 4.70 and 4.71 and Appendices 43-58. The result for R and R^2 values varied from one PAHs to another as shown in Tables 4.72 and 4.73 and Appendices 43-58. This result was obtained using statistical software IBM SPSS Statistics Version 21.

Table 4.70 Multiple Linear Regression for Low Molecular Weight (Non- Carcinogenic) PAHs in Water, Sediment and Fish from IMR in both Seasons.

	PAHs	R	R ²
	Napthalene	0.625	0.391
	Methylnapthalene	0.341	0.117
	Acenapthalene	0.150	.023
	Acenapthylene	0.263	0.069
	Fluorene	0.375	0.140
	Phenanthrene	0.947	0.888
	Anthracene	0.519	0.270
	Pyrene	0.741	0.540

Table 4.71: Multiple Linear Regressions for High Molecular Weight (Carcinogenic) PAHs in Water, Sediment and Fish from IMR in both Seasons.

N	PAHs	R	R ²
	Chrysene	0.747	0.558
	Fluoranthene	0.708	0.502
	Benzo(a)anthracene	0.287	0.082
	Benzo(b)fluoranthene	0.591	0.348
	Benzo(k)fluoranthene	0.018	0.000
	Benzo(a)pyrene	0.160	0.026
	Indenol(123c,d)pyrene	0.600	0.367
	Dibenzo(a,h)anthracene	0.587	0.345

Table 4.72 Multiple Linear Regression for Low Molecular Weight (Non- Carcinogenic) PAHs in Water, Sediment and Fish from IMR in both Seasons.

PAHs	R	R ²
Napthalene	0.625	0.391
Methylnapthalene	0.341	0.117
Acenapthalene	0.150	0.023
Acenapthylene	0.263	0.069
Fluorene	0.375	0.140
Phenanthrene	0.947	0.888
Anthracene	0.519	0.270
Pyrene	0.741	0.540

Table 4.73 Multiple Linear Regression for High Molecular Weight (Carcinogenic) PAHs in Water, Sediment and Fish from IMR in both Seasons.

PAHs	R	R ²
Fluoranthene	0.747	0.558
Chrysene	0.708	0.502
Benzo(a)anthracene	0.287	0.082
Benzo(b)fluoranthene	0.591	0.348
Benzo(k)fluoranthene	0.018	0.000
Benzo(a)pyrene	0.160	0.026
Indenol(123c,d)pyrene	0.600	0.367
Dibenzo(a,h)anthracene	0.587	0.345

Multiple Linear Regression Model involves a single dependent variable (fish) and two independent variables (sediment and water). It develops a relationship between water, sediment and fish. Neff (1999) reported the use of regression to analyze the accumulation of hydrocarbon by biota from their immediate environment. The result obtained from multiple linear regression models in this study confirmed that the uptake of C-PAHs from the exposure environment is more from water than sediment. This is due to mixed sources of PAHs (pyrogenic or petrogenic) and higher availability of PAHs in water compared to sediment. According to Inergrite *et al.*, (1992); HMW – PAHs are more hydrophobic and may be absorbed to organic matter, thereby being trapped and immobilized in sediments. In spite of low R^2 value indicated by some carcinogenic PAHs, fish may be used as a good accumulator and bio-indicator of PAHs pollution from effluents and oil field waste occasioned by oil production and exploitation activities in Imo River.

The assessment of the concentration of polycyclic hydrocarbon bioaccumulation in fish was determined using multiple linear regression models. In this study, the concentration of PAHs in fish is regarded as the dependent variables, while the concentration of PAHs in water and sediment are regarded as the predictor variables (independent variables) and result was computed as shown in Tables 4.70 and 4.71. In Imo River, the R for Chrysene, Fluorantene, B(b)F, B(K)F, B(a)A, Ind(1,2,3-cd)P and DB(a,h)A were found to be 0.741, 0.708, 0.591, 0.160, 0.287, 0.600 and 0.587 respectively. Their corresponding R^2 values were respectively 0.558, 0.502, 0.348, 0.000, 0.026, 0.367 and 0.345. The results for R in LMW-PAHs ranged from Ace(0.150) to Phen(0.947) while that of HMW PAHs ranged from B(k)F(0.018) to Chry(0.749). According to USEPA, PAHs value of R greater than 0.7 can pose health risk to individual.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

Physicochemical parameters were investigated in the three sampling locations. The following parameters: conductivity, turbidity, phosphate, exceeded WHO, NIS, NESREA, USEPA standard for water and sediment while other parameters fall within the permissible limit stipulated by WHO. The level of pollution was higher during the dry season than wet season. Physiochemical characteristics of sediment varied according to season, according to site and did not adhere to any specific trend. The high level of salinity observed in some locations within the study area indicated possible mixing of fresh water tributaries and shore of Atlantic Ocean while some salinity is related to chloride content. The physico-chemical parameters of Imo River were within the allowable limits for fresh water apart from Asa Owaza which was below standard. The sediment is relatively polluted with organic pollutants from anthropogenic sources such as the surrounding communities and water front dwellers releasing raw human excreta, detergents, and waste water and cleaning agents from the communities. The present experimental data indicates increasing high level of pollution along the Imo River. The results obtained in the study in particle size determination suggested that Imo River is weathering products of sandstone.

The section of the Imo River studied is moderately polluted as indicated by the water quality index (values < 26), which falls between the numerical ranges of the classification of moderate (10 – 26). The study also showed that nutrient levels may trigger eutrophication while dissolved oxygen is at a level where changes in aquatic community structure may lead to fish kill incidents and create undue environmental stress on the fish is plausible. The data glaring show that areas outside the influence of Urban activities (Onuimo) have most of its water quality parameters falling within permissible limits while areas affected by inputs from urban activities (Owerri-nta) is polluted. All heavy metals studied are continuously found in sedi-

ment and water, corroborating that heavy metals are naturally occurring. Cd and Cu were above WHO limits for heavy metals which makes the water unsafe without treatment. Most heavy metals were within the recommended limits, hence these metals have no immediate health threat on the users (people/community) but will likely have adverse effects in the prolonged use of water and consumption of the fish species since heavy metals accumulate. The highest heavy metals concentration was observed in fish followed by sediment and the lowest in water. The seasonal variation, distribution pattern, enrichments and contamination of heavy metals in water, sediments and fishes in Imo River showed elevated concentrations during the dry season than in wet season. The increased values of heavy metals in fish muscle from the Imo River may be mainly derived from industrial effluents, waste water, domestic sewage, agricultural pesticides, insecticides and run-offs. In this study, it is obvious that Iron (Fe) has the highest concentration while vanadium (V) has the lowest in the 2 kinds of fish species. This order might be attributed to the different uptake, metabolism and detoxification of metals in fishes. The results obtained from the study indicated that Imo River is contaminated with carcinogenic PAHs.

5.2 Conclusion

The results of the physicochemical parameters of Imo River in this study showed distinct, temporal and spatial variations throughout the study period. These findings gave valuable information in heavy metals and PAHs concentrations in water, sediment and selected two kinds of fish from Imo River. Heavy metal concentration at Imo River was investigated in this study using models and the data was subjected to correlation and factor analysis which yielded three factors representing three possible sources of pollution anthropogenic activities, vehicular emission and discharge of untreated industrial effluent and laundry waste. Although, the levels of heavy metals were found to be within permissible limits, bioaccumulation and magnification is capable of leading to toxic level of these metals in fish even when exposure is high. Results obtained from ecological risk factor showed that all sampling

points had low ecological risk in terms of heavy metals except for Cd and Pb. Sixteen (16) priority polycyclic aromatic hydrocarbons (PAHs) were detected in various locations of Imo River in this study but they existed at very low concentration in both seasons. However, Benzo (a) pyrene and indeno (1,2,3-cd) pyrene concentrations considered most carcinogenic to human were above safe margins stipulated by WHO. Thus the continuous daily intake of fish is a potential health concern as long term exposure to low activity concentrations is likely to activate bio-toxicity. Exposure to PAHs through oral ingestion of water samples was most significant than dermal contact. It was observed that children were the most vulnerable group (2.026×10^{-6} to $0.08-53$). The PAHs diagnostic ratio analysis indicated that the sample had a petrogenic and pyrogenic origin. This might be due to combustion of coal, wood, grass and petroleum combustion. From the results obtained from the work, although there was no cholera outbreak in the past these communities that depend on the river for consumption, people should always purify and sterilize the water from studied river before usage in order to free it from contaminants. Thus Imo River can be classified as moderately polluted from the findings of this study.

5.3 Recommendation

It is recommended that:

1. Careless disposal of industrial wastes in Imo River without pre-treatment should be discouraged.
2. There is need that each industry should treat their effluents in accordance with the legal requirements. "Polluter pays" principle should be implemented in Nigeria.
3. Imo State/Abia State government should exist on edict probably anybody from dumping waste into rivers.
4. Periodic monitoring of heavy metal in Imo River should be done since the water serves as a source of drinking water, fish and for all year round irrigational farming.

5. Federal government of Nigerian should a mater of urgency develop an ecological land use planning which will control and regulate all costal development.
6. Methodology for sampling, analysis and emission estimationneed to be harmonized in order to properly asses the effect of future control measures.
7. The public and communities along Imo River should be educated and be aware of the need to safeguard the quality of their water resource.
8. Deposition of toxic chemicals used in agriculture and industry in Imo –Abia states should also be monitored.
9. Climate change adaptation measures should be such that will minimize surface run-off into the river system to reduce pollution of the river body.
10. The biological impact in terms of total PAHs intakes into the body via respiratory, dermal and gastro intestinal routes should be monitored precisely.
11. Public awareness and education about sources and health effects of PAHs should be improved.
12. Authorities concerned in water resources management in Nigeria should not leave any stone unturned to ensure that both underground and surface water remain unpolluted.
13. Filtration of individual emission/effluents should be carried out strictly particularly in developing countries like Nigeria. The use of local water filters is recommended for those who drink and use the Imo water for domestic purpose.

5.4 Contribution to Knowledge

This study has provided reference data on quality, levels of toxic metals and PAHs for water and fish (Tilapia and cat fish) in Imo River. Human exposure to carcinogenic and non-carcinogenic stressors is mainly due to Pb, Cd and Ni as well as the high-molecular weight PAHs.

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APPENDIX 1

Physicochemical Analysis Result for Water samples in January 2016.

PARAMETER	ASA OWAZA	- ONUIMO	OWERRI-NTA
Colour (Pt/co)	5.20	5.10	5.70
Temperature	28.90	28.80	28.70
Ph	7.00	6.90	7.00
Conductivity (us/cm)	130.00	130.00	150.00
Total Dissolved solid (mg/l)	28.90	28.80	28.90
Total suspended solid (Mg/l)	16.20	15.28	16.20
Turbidity	8.50	9.00	8.00
Nitrate mg/l	8.20	7.84	7.94
Phosphate mg/l	0.50	0.40	0.60
Sulphate mg/l	10.00	8.20	8.90
Dissolved Oxygen mg/l	8.90	10.00	8.80
Biochemical Oxygen Demand mg/l	3.80	3.40	3.60
Chemical oxygen Demand mg/l	28.00	27.20	28.20
Total Hardness mg/l	58.40	50.40	49.20
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total colifom Bacteria ctu/100ml	ND	ND	ND
Salinity	0.74	0.72	0.74
Acidity	13.20	15.10	17.00
Alkalinity	70.30	78.20	80.80

Appendix 2

Physicochemical Analysis Result for Water samples in February 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	5.30	5.70	5.90
Temperature	27.80	28.60	28.00
Ph	7.10	6.90	7.20
Conductivity (us/cm)	150.00	140.00	170.00
Total Dissolved solid (mg/l)	28.70	28.60	30.00
Total suspended solid (mg/l)	15.90	15.30	16.40
Turbidity (NTU)	8.30	9.10	8.50
Nitrate mg/l	8.00	7.91	7.95
Phosphate mg/l	0.50	0.42	0.64
Sulphate mg/l	9.00	7.20	8.70
Dissolved Oxygen mg/l	8.60	11.0	8.70
Biochemical Oxygen Demand mg/l	3.40	3.20	3.50
Chemical oxygen Demand mg/l	30.20	29.20	28.60
Total Hardness mg/l	70.20	69.20	58.60
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.80	0.79	0.79
Acidity	15.80	17.20	18.60
Alkalinity	60.40	68.30	78.20

Appendix 3

Physicochemical Analysis Result for Water samples March 2016.

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	4.90	5.20	5.80
Temperature	27.60	27.90	27.80
Ph	6.90	6.80	7.00
Conductivity (us/cm)	120.00	116.00	140.00
Total Dissolved solid (mg/l)	26.00	27.00	28.10
Total suspended solid (mg/l)	20.70	19.50	20.40
Turbidity (NTU)	9.50	10.00	12.20
Nitrate mg/l	6.20	7.20	6.40
Phosphate mg/l	0.50	0.42	0.58
Sulphate mg/l	12.00	11.40	11.20
Dissolved Oxygen mg/l	10.20	14.00	9.90
Biochemical Oxygen Demand mg/l	3.60	3.80	3.40
Chemical oxygen Demand mg/l	26.00	25.10	26.50
Total Hardness Mg/l	46.40	48.20	47.20
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.62	0.66	0.72
Acidity	20.00	18.60	24.60
Alkalinity	52.60	56.30	66.40

Appendix 4

Physicochemical Analysis Result for Water samples in April 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	4.80	5.00	5.70
Temperature	26.80	26.90	27.00
Ph	6.80	6.85	6.94
Conductivity (us/cm)	105.00	108.00	120.00
Total Dissolved solid (mg/l)	25.80	26.90	28.00
Total suspended solid (mg/l)	28.70	24.80	25.40
Turbidity (NTU)	10.80	11.20	13.00
Nitrate mg/l	8.20	8.00	7.80
Phosphate mg/l	0.58	0.52	0.60
Sulphate mg/l	18.60	19.00	18.80
Dissolved Oxygen mg/l	19.50	20.70	10.20
Biochemical Oxygen Demand mg/l	5.70	5.80	15.00
Chemical oxygen Demand mg/l	28.00	26.20	26.40
Total Hardness mg/l	38.80	40.10	46.20
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.40	0.40	0.40
Acidity	20.80	19.70	42.60
Alkalinity	50.20	60.30	70.00

Appendix 5

Physicochemical Analysis Result for Water samples in May 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	4.70	4.90	5.60
Temperature	26.70	26.8	26.80
pH	6.80	6.84	6.86
Conductivity (us/cm)	102.00	104.00	116.00
Total Dissolved solid (mg/l)	25.60	26.40	26.80
Total suspended solid (mg/l)	30.60	26.80	28.60
Turbidity (NTU)	12.40	11.80	15.00
Nitrate mg/l	8.20	8.10	7.90
Phosphate mg/l	0.48	0.45	0.56
Sulphate mg/l	20.20	21.30	18.80
Dissolved Oxygen mg/l	20.60	22.90	12.50
Biochemical Oxygen Demand mg/l	5.60	5.70	5.20
Chemical oxygen Demand mg/l	30.00	27.30	26.80
Total Hardness mg/l	30.60	38.00	42.40
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.20	0.30	0.28
Acidity	30.40	26.80	28.40
Alkalinity	30.40	26.30	28.90

Appendix 6

Physicochemical Analysis Result for Water samples in June 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour Pt/Co)	4.60	4.82	5.54
Temperature	26.60	26.60	26.70
pH	6.70	6.82	6.85
Conductivity (us/cm)	101.00	103.00	115.00
Total Dissolved solid (mg/l)	25.50	26.20	26.70
Total suspended solid (mg/l)	38.70	32.40	37.40
Turbidity (NTU)	15.40	15.80	15.20
Nitrate mg/l	8.20	8.30	7.92
Phosphate mg/l	0.50	0.52	0.70
Sulphate mg/l	30.60	32.50	38.40
Dissolved Oxygen mg/l	30.20	34.80	28.20
Biochemical Oxygen Demand mg/l	5.70	5.60	5.30
Chemical oxygen Demand mg/l	28.60	29.40	27.80
Total Hardness mg/l	20.40	28.20	35.40
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.18	0.22	0.26
Acidity	38.40	30.60	36.20
Alkalinity	20.40	17.20	20.80

Appendix 7

Physicochemical Analysis Result for Water samples in July 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	4.40	4.60	5.00
Temperature	26.60	26.50	26.60
pH	6.50	6.60	6.60
Conductivity (us/cm)	38.00	36.00	50.00
Total Dissolved solid (mg/l)	20.20	24.20	23.60
Total suspended solid (mg/l)	50.70	48.20	49.60
Turbidity (NTU)	30.20	33.40	32.50
Nitrate mg/l	10.20	8.70	9.60
Phosphate mg/l	0.80	0.40	0.60
Sulphate mg/l	30.80	38.40	40.20
Dissolved Oxygen mg/l	60.40	80.20	74.60
Biochemical Oxygen Demand mg/l	5.80	5.70	5.60
Chemical oxygen Demand mg/l	34.60	32.70	31.20
Total Hardness mg/l	10.20	12.30	15.40
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.10	0.15	0.18
Acidity	50.40	48.20	46.80
Alkalinity	10.20	9.30	9.60

Appendix 8

Physicochemical Analysis Result for Water samples in August 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	4.60	4.80	5.40
Temperature	26.70	26.70	26.60
pH	6.80	6.80	6.90
Conductivity (us/cm)	92.00	101.00	108.00
Total Dissolved solid (mg/l)	23.40	25.80	26.00
Total suspended solid (mg/l)	32.60	30.10	38.6
Turbidity (NTU)	14.60	11.92	25.40
Nitrate mg/l	8.80	9.20	10.10
Phosphate mg/l	0.40	0.41	0.50
Sulphate mg/l	22.10	23.60	20.20
Dissolved Oxygen mg/l	50.20	47.30	47.70
Biochemical Oxygen Demand mg/l	8.00	8.10	6.30
Chemical oxygen Demand mg/l	38.00	21.80	15.90
Total Hardness Mg/l	22.60	28.70	30.80
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.10	0.25	0.22
Acidity	50.20	48.60	44.70
Alkalinity	21.60	15.95	18.60

Appendix 9

Physicochemical Analysis Result for Water samples in September 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	4.60	4.70	5.30
Temperature	26.60	26.50	26.60
pH	6.70	6.80	6.80
Conductivity (us/cm)	68.00	82.00	84.00
Total Dissolved solid (mg/l)	20.20	21.60	20.80
Total suspended solid (mg/l)	50.20	48.60	70.20
Turbidity (NTU)	20.80	15.90	30.80
Nitrate mg/l	10.80	12.40	17.20
Phosphate mg/l	0.50	0.70	0.90
Sulphate Mg/l	32.80	47.20	50.20
Dissolved Oxygen mg/l	70.20	82.70	68.70
Biochemical Oxygen Demand mg/l	10.20	11.20	12.50
Chemical oxygen Demand mg/l	18.40	17.60	15.40
Total Hardness mg/l	ND	ND	ND
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	24.80	20.60	28.60
Salinity	0.10	0.20	0.18
Acidity	59.60	51.20	60.40
Alkalinity	18.40	15.20	16.80

Appendix 10

Physicochemical Analysis Result for Water samples in October 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	4.80	4.90	5.20
Temperature	26.70	26.60	26.80
pH	6.60	6.70	6.80
Conductivity (us/cm)	6.90	10.20	9.80
Total Dissolved solid (mg/l)	22.60	24.70	21.80
Total suspended solid (mg/l)	50.10	46.70	69.60
Turbidity (NTU)	20.90	16.70	32.80
Nitrate mg/l	11.20	15.20	20.40
Phosphate mg/l	0.30	0.60	0.80
Sulphate mg/l	35.70	50.20	58.10
Dissolved Oxygen mg/l	69.20	72.50	60.20
Biochemical Oxygen Demand mg/l	10.40	11.00	11.80
Chemical oxygen Demand mg/l	16.40	11.20	13.60
Total Hardness mg/l	25.60	21.20	25.40
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.16	0.20	0.18
Acidity	48.9	50.2	42.6
Alkalinity	22.30	14.06	20.20

Appendix 11

Physicochemical Analysis Result for Water samples in November 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	5.00	5.20	5.00
Temperature	26.90	27.40	26.90
pH	6.90	6.80	6.90
Conductivity (us/cm)	13.00	13.60	15.00
Total Dissolved solid (mg/l)	27.40	26.80	29.60
Total suspended solid (mg/l)	20.60	22.80	28.60
Turbidity(NTU)	10.20	12.50	11.60
Nitrate mg/l	8.00	7.90	8.10
Phosphate mg/l	0.60	0.50	0.72
Sulphate mg/l	10.20	9.60	9.80
Dissolved Oxygen mg/l	19.80	25.80	20.20
Biochemical Oxygen Demand mg/l	8.20	7.00	7.80
Chemical oxygen Demand mg/l	16.40	17.20	13.60
Total Hardness mg/l	30.80	30.70	40.80
Total viable bacteria (ctu/100ml)	ND	ND	ND
Total coliform Bacteria ctu/100ml	ND	ND	ND
Salinity	0.10	0.20	0.40
Acidity	50.00	42.80	62.60
Alkalinity	10.80	9.80	12.60

Appendix 12

Physicochemical Analysis Result for Water samples in December 2016.

PARAMETER	ASA-OWAZA	ONUIMO	OWERRI-NTA
Colour (Pt/Co)	5.20	5.10	5.30
Temperature	27.90	27.80	28.40
pH	6.90	6.90	7.00
Conductivity (us/cm)	14.00	13.80	16.00
Total Dissolved solid (mg/l)	28.00	27.60	28.70
Total suspended solid (mg/l)	16.00	14.00	15.00
Turbidity(NTU)	8.00	8.80	9.00
Nitrate mg/l	6.20	7.50	8.20
Phosphate Mg/l	0.50	0.40	0.60
Sulphate mg/l	10.00	9.40	9.60
Dissolved Oxygen mg/l	10.20	20.20	19.60
Biochemical Oxygen Demand mg/l	8.00	6.90	7.40
Chemical oxygen Demand mg/l	13.40	16.20	14.60
Total Hardness mg/l	40.80	50.0	59.10
Total viable bacteria (Ctu/100ml)	ND	ND	ND
Total coliform Bacteria (Ctu/100ml)	ND	ND	ND
Salinity	0.14	0.22	0.41
Acidity	18.80	19.6	20.40
Alkalinity	28.90	30.20	40.10

Appendix 13

Physiochemical analysis result of sediment sample from Imo River (IMR) in January 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
pH	6.9	6.85	6.9
Temperature	26.8	26.9	26.8
Conductivity $\mu\text{s}/\text{cm}$	100	80	150
Total organic carbon	0.33	0.39	0.38
Total nitrogen	0.03	0.03	0.02
Sand %	43.67	45.86	48.88
Silt %	39.11	41.61	41.02
Clay %	17.22	12.53	10.1

Appendix 14

Physiochemical analysis result of sediment sample from Imo River (IMR) in February 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
pH	6.80	6.80	6.75
Temperature	26.70	27.10	26.80
Conductivity $\mu\text{s}/\text{cm}$	80.00	78.00	120.00
Total organic carbon	0.96	0.89	0.93
Total nitrogen	0.02	0.04	0.05
Sand %	53.26	56.11	70.25
Silt %	23.41	33.60	20.70
Clay %	23.33	10.29	9.05

Appendix 15

Physiochemical analysis result of sediment sample from Imo River (IMR) in March 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
pH	6.8	6.7	6.7
Temperature	26.7	26.8	26.9
Conductivity $\mu\text{s}/\text{cm}$	78	64	10
Total organic carbon	0.28	0.30	0.26
Total nitrogen	0.03	0.047	0.034
Sand %	46.03	52.78	62.18
Silt %	26.04	24.08	20.82
Clay %	27.93	23.14	17.00

Appendix 16

Physiochemical analysis result of sediment sample from Imo River (IMR) in April 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
pH	6.8	6.8	6.7
Temperature	26.7	26.8	26.6
Conductivity $\mu\text{s}/\text{cm}$	60	70	85
Total organic carbon	0.42	0.35	0.33
Total nitrogen	0.029	0.025	0.049
Sand %	46.08	37.66	64.44
Silt %	32.05	35.26	28.11
Clay %	21.87	7.08	7.45

Appendix 17

Physiochemical analysis result of sediment sample from Imo River (IMR) in May 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.7	6.6	6.7
Temperature	26.7	26.6	26.04
Conductivity $\mu\text{s}/\text{cm}$	50.00	68.00	70.00
Total organic carbon	0.33	0.96	0.93
Total nitrogen	0.049	0.038	0.034
Sand %	71.06	66.20	77.84
Silt %	20.14	22.09	20.13
Clay %	8.80	11.71	2.03

Appendix 18

Physiochemical analysis result of sediment sample from Imo River (IMR) in June 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.7	6.6	6.7
Temperature	26.7	26.6	26.4
Conductivity $\mu\text{s}/\text{cm}$	40	64	69
Total organic carbon	0.93	0.96	0.94
Total nitrogen	0.034	0.049	68.78
Sand %	71.06	72.84	73.31
Silt %	20.14	20.13	22.60
Clay %	8.80	7.03	4.09

Appendix 19

Physiochemical analysis result of sediment sample from Imo River (IMR) in July 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.6	6.5	6.6
Temperature	26.5	26.8	26.4
Conductivity $\mu\text{s}/\text{cm}$	40	60	68
Total organic carbon	0.89	0.96	0.93
Total nitrogen	0.044	0.047	0.042
Sand %	73.84	70.10	73.0
Silt %	20.13	25.25	22.4
Clay %	6.03	4.65	4.6

Appendix 20

Physiochemical analysis result of sediment sample from Imo River (IMR) in August 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.7	6.6	6.7
Temperature	26.2	26.7	26.1
Conductivity $\mu\text{s}/\text{cm}$	50.00	70.00	75.00
Total organic carbon	0.82	0.92	0.79
Total nitrogen	0.012	0.008	0.009
Sand %	68.20	68.14	66.60
Silt %	25.14	28.24	25.20
Clay %	6.05	3.62	8.20

Appendix 21

Physiochemical analysis result of sediment sample from Imo River (IMR) in September 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.70	6.60	6.60
Temperature	26.40	26.70	26.50
Conductivity $\mu\text{s}/\text{cm}$	60.00	80.00	78.00
Total organic carbon	0.80	0.70	0.62
Total nitrogen	0.014	0.009	0.008
Sand %	64.40	66.23	68.17
Silt %	28.15	22.06	20.24
Clay %	7.45	11.71	11.63

Appendix 22

Physiochemical analysis result of sediment sample from Imo River (IMR) in October 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.9	6.8	6.8
Temperature	26.3	26.2	26.4
Conductivity $\mu\text{s}/\text{cm}$	65	74	80
Total organic carbon	0.59	0.51	0.855
Total nitrogen	0.038	0.029	0.035
Sand %	64.40	66.25	57.66
Silt %	28.10	22.04	20.16
Clay %	7.50	11.71	22.18

Appendix 23

Physiochemical analysis result of sediment sample from Imo River (IMR) in November 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.8	6.8	6.9
Temperature	26.8	26.7	26.9
Conductivity $\mu\text{s}/\text{Cm}$	70	75	82
Total organic carbon	0.5	0.52	0.54
Total nitrogen	0.012	0.040	0.013
Sand %	57.66	57.75	53.07
Silt %	20.16	36.01	25.61
Clay %	22.81	6.24	21.32

Appendix 24

Physiochemical analysis result of sediment sample from Imo River (IMR) in December 2016

PARAMETER	ASA	ONUIMO	OWERRI-NTA
Ph	6.90	6.80	6.80
Temperature	26.80	26.70	26.70
Conductivity $\mu\text{s}/\text{Cm}$	85.00	82.00	100.00
Total organic carbon	0.42	0.38	0.50
Total nitrogen	0.038	0.039	0.032
Sand %	53.07	50.77	57.66
Silt %	22.01	31.01	20.16
Clay %	24.92	18.22	22.18

Appendix 25

Concentration of Physico Chemical Parameters in Water During Both Season

Physicochemical parameter	Dry	Wet
Colour	5.34	4.946
Temperature	28.23	26.79
Ph	6.94	6.76
Conductivity	140	90.546
TDS mg/L	28.22	24.416
TSS mg/L	18.13	40.886
Turbidity WTU	9.6	19.356
Nitrate mg/L	7.57	10.523
Phosphate Mg/L	0.526	0.563
Sulphate Mg/L	9.66	30.226
DO mg/L	13.71	41.54
BOD mg/L	5.12	7.976
COD mg/L	22.7	24.06
Total mg/L Hardnes	47.99	27.436
TVB	0	0
TCB	0	0
Salinity mg/L	0.537	0.223
Acidity mg/L	24.98	41.7
Alkalinity mg/L	49.606	24.893

Appendix 26

Seasonal Variation of Sediments in Both Seasons (Wet & Dry)

Heavy Metal	Dry season	Wet season
Ph	6.81	6.69
Temperature 0°C	26.58	26.49
Conductivity ps/cm	89.8	65.05
Total organic carbon	5	0.77
Total Nitrogen	0.049	0.23
Sand %	53.94	66.17
Silt %	28.36	24.19
Clay %	17.72	8.77

Appendix 27

Mean Concentration of Heavymetals in water from IMR in both seasons in mg/L

Heavy Metal	Dry season	Wet season
Iron (Fe)	0.181	0.021
Cadmium (Cd)	0.163	0.0013
Lead (Pb)	0.032	0.056
Nickel (Ni)	0.028	0.027
Zinc (Zn)	0.093	0.09
Copper (Cu)	0.023	0.017
Vanadium (V)	0.02	0.014

Appendix 28

Mean concentration of Heavy Metals in sediments In IMR During Both Seasons in mg/kg

Heavy metals	Dry season	Wet season
Iron (Fe)	1.56	0.453
Cadmium (Cd)	0.0028	0.03
Lead (Pb)	0.053	0.045
Nickel (Ni)	0.037	0.033
Zinc (Zn)	3.36	3.01
Copper (Cu)	0.77	0.99
Vanadium (V)	0.55	0.036

Appendix 29

Mean Concentration of Heavy Metals in Tilapia Zilli in Imo River During Both Seasons

Heavy metals	Dry season	Wet season
Iron (Fe)	4.64	3.01
Cadmium (Cd)	0.00053	0.0003
Lead (Pb)	0.045	0.037
Nickel (Ni)	0.039	0.031
Zinc (Zn)	0.413	0.31
Copper (Cu)	0.025	0.085
Vanadium (V)	ND	ND

ND= Not Detected

Appendix 30

Seasonal Variation of Heavy Metals in Cat Fish From Imr In Both Season

Heavy metals	Dry season	Wet season
Iron (Fe)	7.68	4.17
Cadmium (Cd)	0.0014	0.1012
Lead (Pb)	0.051	0.05
Nickel (Ni)	0.033	0.032
Zinc (Zn)	0.72	0.65
Copper (Cu)	0.11	0.11
Vanadium (V)	ND	ND

ND= Not Detected

Appendix 31

Mean Concentration of PAHSin Water In Imo River During both Season

PAHs Conc	Dry	Wet
Nap	0.363	0.057
Methyl	0.095	0.034
Ace	0.303	0.193
Acy	0.38	0.47
Flu	0.077	0.227
Phen	0.067	0.03
Ant	0.204	0.204
Pyr	0.043	0.0403
Chr	0.017	0.001
FL	0.084	0.0039
B (a) A	0.031	0.057
B (b) FL	0.024	0.021
B (K) FL	0.013	0
B (a) P	0.021	0.00397
Ind (1,2,3 c.d) P	0.017	0.012
DB (a, h) A	0.57	0.004

Appendix 32

Mean Concentration of PAHs in Sediment in Both Seasons in mg/kg

PAHs Conc	Dry	Wet
Nap	0.17	0.0016
Methyl	0.014	0.821
Ace	0.028	0.033
Acy	0.022	0.006
FL	0.027	0.0156
Phen	0.09	0.0128
Ant	0.17	0.0017
Pyr	0.15	0.19
Chy	0.33	0.023
Flt	0.09	0.01
B (a) A	0.294	0.153
B (b) F	0.38	0.52
B (k) F	0.00	0.00
Bap	0.0015	0.09
Ind (1,2,3-Cd) P	0.115	0.046
DB (a, h) A	0.001	0.000

APPENDIX 33

Concentration of PAHs IN FISHES (*Tilapia*) in Dry and Wet Season

PAHs	DRY SEASON	WET SEASON
Nap	0.027	0.015
Methyl	0.004	0.005
Ace	0.007	0.004
Acy	0.0001	0.000
Flt	0.019	0.09
Phen	0.001	0.000
Anth	0.037	0.012
Pyr	0.007	0.013
Chy	0.002	0.001
Fl	0.003	0.040
BaA	0.004	0.002
B(a)F	0.0033	0.001
B(k)F	0.003	0.00
B(a)P	0.002	0.018
Ind(1,2,3,c,d)P	0.013	0.003
Diben20(a,h)A	0.001	0.000

Appendix 34

WHO/NOAA STANDARD FOR PHYSICOCHEMICAL PARAMETERS OF WATER

	WHO Limit/Standard	(NOAA) Standard
Temp	25°C	250
Conductivity	80	250
Turbidity	6.5 – 85 600mg/l	NTU 6.5 – 8.5
pH Hardness	5	>5
DO	6	>5
BOD	10	<5
COD	50	0.002
THC	50	-
Mg	250	-
Na	250	-
K/ Zn	250	0.12
Acidity	-	-
Sulphale	250	-
Nitrate	4.5	50
Nitrite	5	-
Cl ⁻	250	
NH ₄ ⁺	<1.0	<0.1
Phosphate	0.1	-
Salinity	-	> 20

WHO (World Health Organization)

NOAA (National Oceanic and Atmospheric Administration)

Appendix 35

NATIONAL SANITATION FOUNDATION WATER QUALITY INDEX (NSFWQI)

Water Quality Index (WQI)	Rating of Water
91-100	Excellent water quality
71-90	Good water quality
51-70	Mediun water quality
26-50	Bad water quality
0-25	Very bad water quality

Source: WHO Geneva (2000)

Appendix 36

PAHs AND THEIR TOTAL EQUIVALENT FACTOR

PAHs	TEF (Total equivalent factor)
Naphthalene	0.001 ^b
Anthracene	0.01 ^b
Fluorene	0.001 ^b
Phenanthrene	0.001 ^b
Acenaphthene	0.001 ^b
Acenaphythere	0.001 ^b
Pyrene	0.001 ^b
Fluoranthene	0.08 ^a
Benzo (b) fluoranthene	0.8 ^a
Benzo (a)pyrene	1 ^a

a = USEPA, b= Nekhavhambeet *al.*, (2014)

Appendix 37

DIAGNOSTIC RATIO

Diagnostic Ratio	Petrogenic	Pyrogenic
Ant/Ant+Phen	< 0.1	> 0.1
Flu/Flu+Py	< 0.4	> 0.4
LMW/HMW	> 1	< 1

Source: Edokpayi et al., (2016).

Appendix 38

SLOPE FACTOR FOR PAHs

Priority PAHs	Relative potency factors (slope factor)
Anthracene	0.4
Benz (a) Anthracene	0.2
Benzo (b) pyrene	1
Benmo (b) fluoranthene	0.8
Bemo (b) fluorine	20
Benzo (g, h,i) pyrene	0.009
Bemzo (j) fluoranthene	0.3
Bemzo (k) fluoranthene	0.03
Chrysene	0.1
Cyclopenta (c,d) or	0.4
Dibenz (a,h) pyrene	0.9
Dibenzo (a,i) pyrene	0.6
Dibenzo (a) pyrene	30
Fluoranthene	0.08
Indeno (1,2,3 – (cd))pyrene	0.07
5 methy chrysere	1
6 Nitro chrysene	1

Culled (guidance for evaluating the cancer potency of PAHs Feb 8 (2016 Pdf)

Appendix 39

TOXICITY STANDARDS FOR PAHs

S/N	Sample	Level (mg/l)	PAHs
1	Water	0.0001	benzo(a) anthracene
2	Water	0.0002	benzo (a) pyrene benzo (b) fluoranthene benzo (k) fluoranthene chrysene
3.	Water	0.003	dibenzo(a,h) anthracene

Source: USEPA Guideline (2016)

APPENDIX 40

CONTAMINATION FACTOR

Class	Mcd	Contamination degree
0	<1.5	Unpolluted
1	$1.5 \leq Cd < 2$	Slightly polluted
2	$2 \leq Cd < 4$	Moderately polluted
3	$4 \leq Cd < 8$	Moderately heavily polluted
4	$8 \leq Cd < 10$	Denselyly polluted
5	$16 \leq Cd < 32$	Severelly polluted
6	≥ 32	Extremely polluted

Source: *CT Vu et al., (2013)*

APPENDIX 41

PLI (Pollution Load Index)		
1	PLI = 0	background concentration
2	0<PLI<1	Unpolluted
3	1<PLI≤2	Moderately polluted to unpolluted
4	2<PLI≤3	Moderately polluted
5	3<PLI≤4	Moderately to highly polluted
6	4<PLI<5	Densely polluted
7	PLI>5	Extremely polluted

Source: *Sahard Jorfi et al., (2012)*

APPENDIX 42

GEOCHEMICAL INDICES

Class	Sediment Igeo Value	Sediment quality
6	>> 5	Very highly polluted
5	>>4-5	Highly polluted
4	>>3-4	Moderately to highly polluted
3	>>2-3	Moderately polluted
2	>>1-2	Moderately polluted to unpolluted
1	>>0-1	Unpolluted
0	<<0	Practically none

Source: *Shale Taylor (2003).*

APPENDIX 42

STANDARD PERMISSIBLE LEVEL FOR PAHs BY USEPA (µg/l)

Physicochemical parameter	USEPA
Nap	140
Ace	3400
Ph	2300
Ant	1700
Flu	2300
Py	1700
BaA	0.15
Chr	15
Bbf	0.15
Bkf	1.5
ap	0.015
DahA	0.015

Source: *Km Erick (2016)*

Appendix 43

SAMPLE QUESTIONNAIRE ON POLLUTION STATUS OF IMO RIVER

Name of Investigator: Chikwe, Oluchukwu Benedicta.

Start time: January 2016 - **End Time:** December 2016

My name is Chikwe Oluchukwu Benedicta. I am a Ph.D. student of Nnamdi Azikiwe University Awka and a research student trying to assess the pollution status of Imo River from Onuimo to Asa-Owaza. Every personal information about you shall be kept confidential and used strictly for the purpose of this research.

Section 1: Demographic Questions

1. What is your name? -----
2. Gender of respondent Male ☐ Female ☐
3. Age -----
4. Address -----
5. Type of Family Nuclear ☐ Extended ☐
6. What is the main source of drinking water for members of your household?
Tick where ☒ applicable
River water ☐ Dug well ☐ Bottled water ☐ Surface water ☐
7. Tap ☐ Others Specify -----
8. How long does it take to go there, get water and come back (in minutes) ?-----
9. Who usually goes to the source to the fetch water for your household?
Adult woman ☐ Adult Man ☐ Female child under 15yrs. ☐
Male child under 15 yrs. ☐

Tick the code that best describes the person:
10. DO you treat your water in any way to make it safe for drinking?
Yes ☐ No ☐
11. If yes, what do you do to make the water safer for drinking? Tick ☒
Boil ☐ Filter ☐ Left to stand and settle ☐ Add bleach/Chlorine ☐

Others specify-----
12. What is the frequency of water supply?
13. Is this frequency sufficient for your needs? Yes ☐ No ☐
14. Is water available through out the year? ☐ Yes No ☐
15. Which month do you have/face scarcity?

16. Does the water has smell taste colour
17. Has there been any outbreak of disease in this community? Yes No
18. How often does it happen?
19. How often does it last?
20. If there has been an outbreak of disease (water-borne disease), what are the measures used in circulating/controlling it?
- Circulating: -----
- Controlling: -----
21. To what extent is the pollution control agent and disposal authority effective in your community or Local Government Area?
- Highly Effective Effective Ineffective

Thank You.

Appendix 43

Regression NAPHTHALENE

Regression

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00003, VAR00002 ^b	.	Enter

a. Dependent Variable: VAR00001

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.625 ^a	.391	-.015	.09660

a. Predictors: (Constant), VAR00003, VAR00002

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.018	2	.009	.964	.475 ^b
	Residual	.028	3	.009		
	Total	.046	5			

a. Dependent Variable: VAR00001

b. Predictors: (Constant), VAR00003, VAR00002

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	T	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.150	.058		2.584	.082	-.035	.335
	VAR00002	-.001	.153	-.005	-.009	.994	-.489	.487
	VAR00003	-2.867	2.500	-.623	-1.147	.335	-10.825	5.090

a. Dependent Variable: VAR00001

Appendix 44

Regression METHYL NAPHTHALENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00006, VAR00005 ^b	.	Enter

a. Dependent Variable: VAR00004

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.341 ^a	.117	-.472	.03095

a. Predictors: (Constant), VAR00006, VAR00005

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.198	.830 ^b
	Residual	.003	3	.001		
	Total	.003	5			

a. Dependent Variable: VAR00004

b. Predictors: (Constant), VAR00006, VAR00005

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.043	.020		2.145	.121	-.021	.107
	VAR00005	-.113	.187	-.357	-.606	.587	-.707	.481
	VAR00006	.000	.002	-.046	-.079	.942	-.006	.005

a. Dependent Variable: VAR00004

Appendix 45

Regression ACENAPHTHYLENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00012, VAR00011 ^b	.	Enter

a. Dependent Variable: VAR00010

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.263 ^a	.069	-.551	.32730

a. Predictors: (Constant), VAR00012, VAR00011

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.024	2	.012	.111	.898 ^b
	Residual	.321	3	.107		
	Total	.345	5			

a. Dependent Variable: VAR00010

b. Predictors: (Constant), VAR00012, VAR00011

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.097	.301		.321	.769	-.861	1.055
	VAR00011	.186	.598	.174	.312	.775	-1.715	2.088
	VAR00012	-.2268	6.438	-.196	-.352	.748	-22.756	18.220

a. Dependent Variable: VAR00010

Appendix 46

Regression ACENAPHTHLENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00009, VAR00008 ^b	.	Enter

a. Dependent Variable: VAR00007

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.150 ^a	.023	-.629	.03827

a. Predictors: (Constant), VAR00009, VAR00008

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.035	.966 ^b
	Residual	.004	3	.001		
	Total	.004	5			

a. Dependent Variable: VAR00007

b. Predictors: (Constant), VAR00009, VAR00008

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.026	.029		.887	.441	-.066	.117
	VAR00008	-.005	.078	-.038	-.067	.951	-.253	.243
	VAR00009	.110	.446	.142	.247	.821	-1.310	1.530

a. Dependent Variable: VAR00007

Appendix 47

Regression FLUORENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00003, VAR00002 ^b	.	Enter

a. Dependent Variable: VAR00001

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.375 ^a	.140	-.433	.43673

a. Predictors: (Constant), VAR00003, VAR00002

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.094	2	.047	.245	.797 ^b
	Residual	.572	3	.191		
	Total	.666	5			

a. Dependent Variable: VAR00001

b. Predictors: (Constant), VAR00003, VAR00002

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error				Lower Bound	Upper Bound
1	(Constant)	.347	.316		1.099	.352	-.658	1.353
	VAR00002	-.645	1.200	-.295	-.537	.628	-4.465	3.176
	VAR00003	-2.252	4.050	-.305	-.556	.617	-15.140	10.635

a. Dependent Variable: VAR00001

Appendix 48

Regression ANTHRACENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00009, VAR00008 ^b	.	Enter

a. Dependent Variable: VAR00007

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.519 ^a	.270	-.217	.00045

a. Predictors: (Constant), VAR00009, VAR00008

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.554	.624 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00007

b. Predictors: (Constant), VAR00009, VAR00008

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	T	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.000	.000		1.389	.259	-.001	.001
	VAR00008	-.001	.001	-.421	-.824	.470	-.004	.003
	VAR00009	-.002	.002	-.432	-.845	.460	-.008	.005

a. Dependent Variable: VAR00007

Appendix 49

Regression PYRENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00012, VAR00011 ^b	.	Enter

a. Dependent Variable: VAR00010

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.741 ^a	.549	.249	.00173

a. Predictors: (Constant), VAR00012, VAR00011

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	1.828	.303 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00010

b. Predictors: (Constant), VAR00012, VAR00011

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	T	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.005	.001		4.113	.026	.001	.009
	VAR00011	-.046	.024	-.759	-1.873	.158	-.124	.032
	VAR00012	.004	.004	.369	.912	.429	-.009	.017

a. Dependent Variable: VAR00010

Appendix 50

Regression PHENANTHRENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00006, VAR00005 ^b	.	Enter

a. Dependent Variable: VAR00004

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.942 ^a	.888	.813	.00379

a. Predictors: (Constant), VAR00006, VAR00005

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	11.900	.037 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00004

b. Predictors: (Constant), VAR00006, VAR00005

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.005	.004		1.433	.247	-.006	.017
	VAR00005	.328	.070	.927	4.700	.018	.106	.550
	VAR00006	.008	.023	.066	.334	.760	-.067	.082

a. Dependent Variable: VAR00004

Appendix 51

Regression CHRYSENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00003, VAR00002 ^b	.	Enter

a. Dependent Variable: VAR00001

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.747 ^a	.558	.263	.00082

a. Predictors: (Constant), VAR00003, VAR00002

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	1.893	.294 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00001

b. Predictors: (Constant), VAR00003, VAR00002

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	T	Sig.	95.0% Confidence Interval for B	
		B	Std. Error				Lower Bound	Upper Bound
1	(Constant)	.001	.001		2.681	.075	.000	.003
	VAR00002	-.410	.296	-.698	-1.387	.260	-1.352	.531
	VAR00003	.004	.002	.975	1.938	.148	-.002	.010

a. Dependent Variable: VAR00001

Appendix 52

REGRESSION FLUORANTHENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00006, VAR00005 ^b	.	Enter

a. Dependent Variable: VAR00004

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.708 ^a	.502	.170	.00372

a. Predictors: (Constant), VAR00006, VAR00005

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	1.510	.352 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00004

b. Predictors: (Constant), VAR00006, VAR00005

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.007	.002		3.837	.031	.001	.013
	VAR00005	-.023	.017	-.560	-1.342	.272	-.076	.031
	VAR00006	-.023	.017	-.571	-1.367	.265	-.075	.030

a. Dependent Variable: VAR00004

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.708 ^a	.502	.170	.00372

a. Predictors: (Constant), VAR00006, VAR00005

Appendix 53

Regression BENZO(a)ANTHRACENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00009, VAR00008 ^b	.	Enter

a. Dependent Variable: VAR00007

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.287 ^a	.082	-.530	.00300

a. Predictors: (Constant), VAR00009, VAR00008

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.134	.879 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00007

b. Predictors: (Constant), VAR00009, VAR00008

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.005	.004		1.404	.255	-.007	.018
	VAR00008	-.002	.049	-.026	-.037	.973	-.158	.155
	VAR00009	-.004	.009	-.302	-.433	.694	-.032	.024

a. Dependent Variable: VAR00007

Appendix 54

Regression BENZO(b)FLUORANTHENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00012, VAR00011 ^b	.	Enter

a. Dependent Variable: VAR00010

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.591 ^a	.349	-.085	.00340

a. Predictors: (Constant), VAR00012, VAR00011

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.804	.525 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00010

b. Predictors: (Constant), VAR00012, VAR00011

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.005	.002		2.096	.127	-.003	.013
	VAR00011	-.069	.060	-.703	-1.164	.329	-.260	.121
	VAR00012	.003	.009	.214	.353	.747	-.025	.032

a. Dependent Variable: VAR00010

Appendix 55

Regression BENZO(k)FLUORANTHENE

Warnings

For models with dependent variable VAR00001, the following variables are constants or have missing correlations: VAR00003. They will be deleted from the analysis.

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00002 ^b	.	Enter

a. Dependent Variable: VAR00001

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.018 ^a	.000	-.250	.00509

a. Predictors: (Constant), VAR00002

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	1	.000	.001	.973 ^b
	Residual	.000	4	.000		
	Total	.000	5			

a. Dependent Variable: VAR00001

b. Predictors: (Constant), VAR00002

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.003	.003		1.021	.365	-.005	.011
	VAR00002	.010	.279	.018	.036	.973	-.765	.785

a. Dependent Variable: VAR00001

Appendix 56

Regression BENZO(a)PYRENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00006, VAR00005 ^b	.	Enter

a. Dependent Variable: VAR00004

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.160 ^a	.026	-.624	.00193

a. Predictors: (Constant), VAR00006, VAR00005

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.039	.962 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00004

b. Predictors: (Constant), VAR00006, VAR00005

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error				Lower Bound	Upper Bound
1	(Constant)	.005	.001		4.453	.021	.001	.008
	VAR00005	.000	.038	-.003	-.005	.996	-.121	.120
	VAR00006	-.002	.008	-.161	-.273	.802	-.028	.024

a. Dependent Variable: VAR00004

Appendix 57

Regression INDENOL(1,2,3,cd)PYRENE

Regression

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00009, VAR00008 ^b	.	Enter

a. Dependent Variable: VAR00007

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.606 ^a	.367	-.054	.00830

a. Predictors: (Constant), VAR00009, VAR00008

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.871	.503 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00007

b. Predictors: (Constant), VAR00009, VAR00008

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.012	.005		2.493	.088	-.003	.026
	VAR00008	-.284	.218	-.687	-1.302	.284	-.979	.411
	VAR00009	.041	.049	.437	.829	.468	-.116	.198

a. Dependent Variable: VAR00007

Appendix 58

REGRESSION DIBENZO {A,H} ANTHRACENE

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	VAR00012, VAR00011 ^b	.	Enter

a. Dependent Variable: VAR00010

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.587 ^a	.345	-.092	.00122

a. Predictors: (Constant), VAR00012, VAR00011

ANOVA^a

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.000	2	.000	.790	.530 ^b
	Residual	.000	3	.000		
	Total	.000	5			

a. Dependent Variable: VAR00010

b. Predictors: (Constant), VAR00012, VAR00011

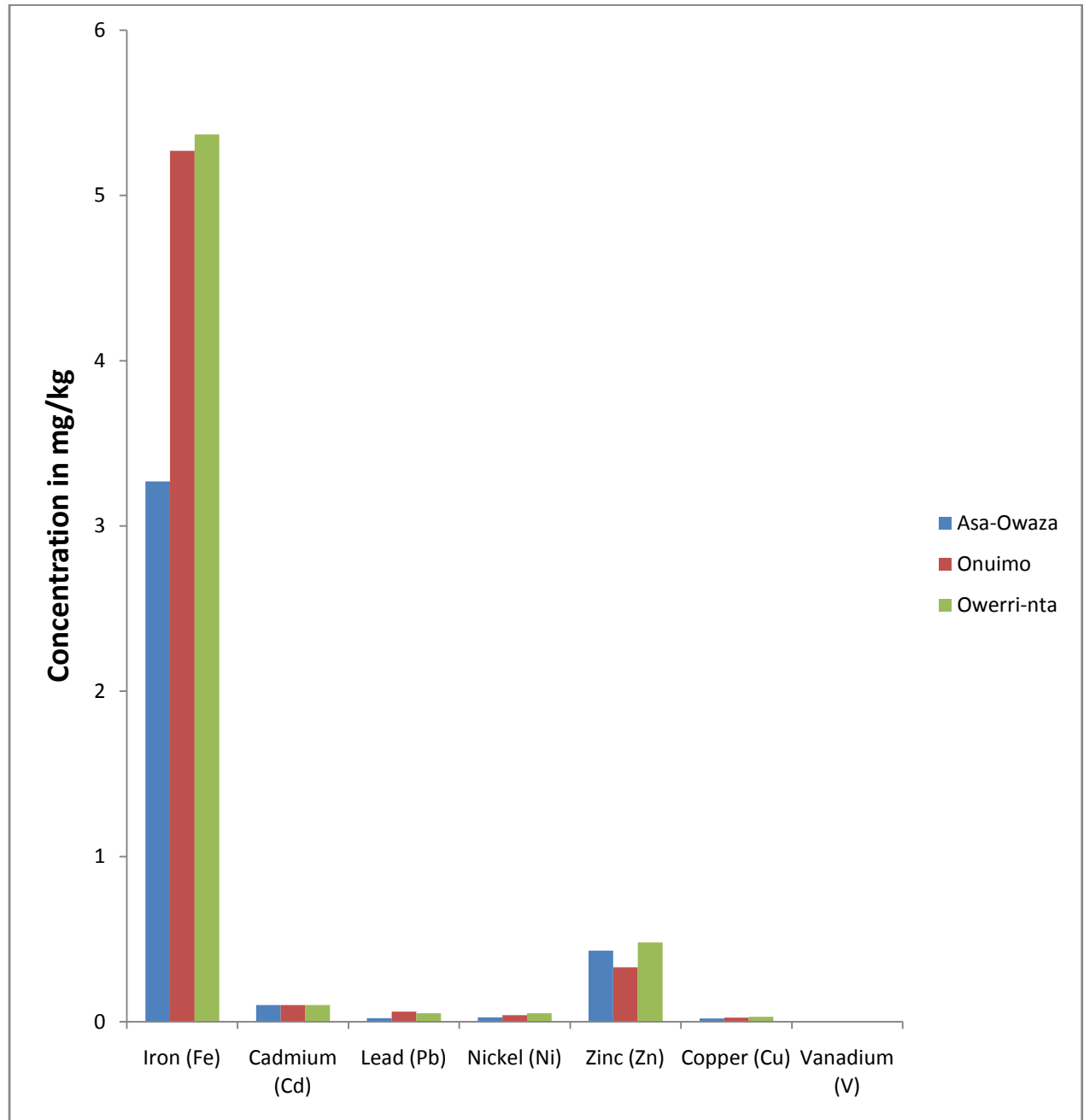
Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	.001	.001		.783	.491	-.002	.004
	VAR00011	.002	.001	.592	1.254	.299	-.002	.006
	VAR00012	-.191	.733	-.123	-.260	.812	-2.524	2.143

a. Dependent Variable: VAR00010

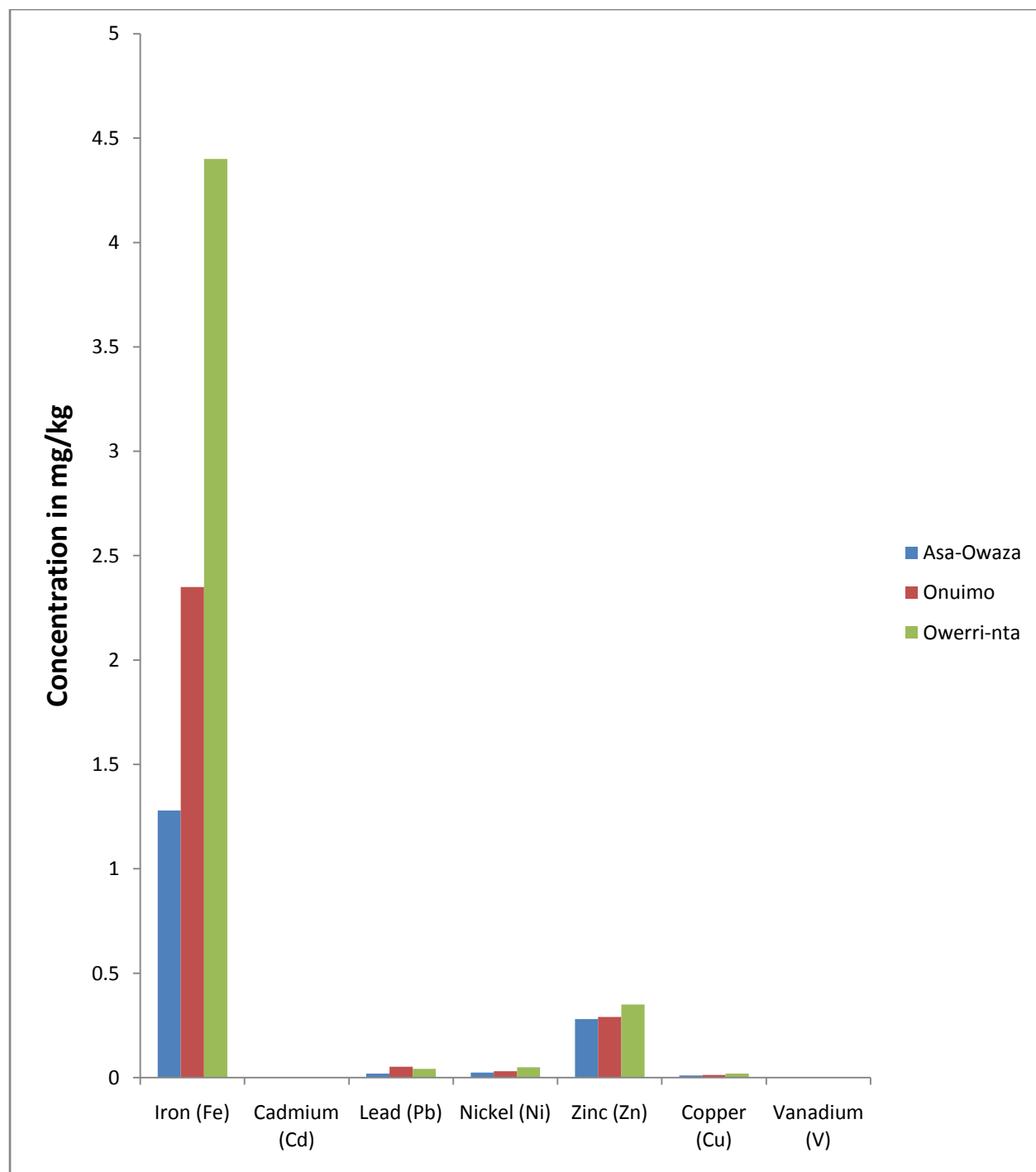
Appendix 59

Mean Heavy Metal Concentration in *Tilapia Zilli* from Imo River during Dry Season.



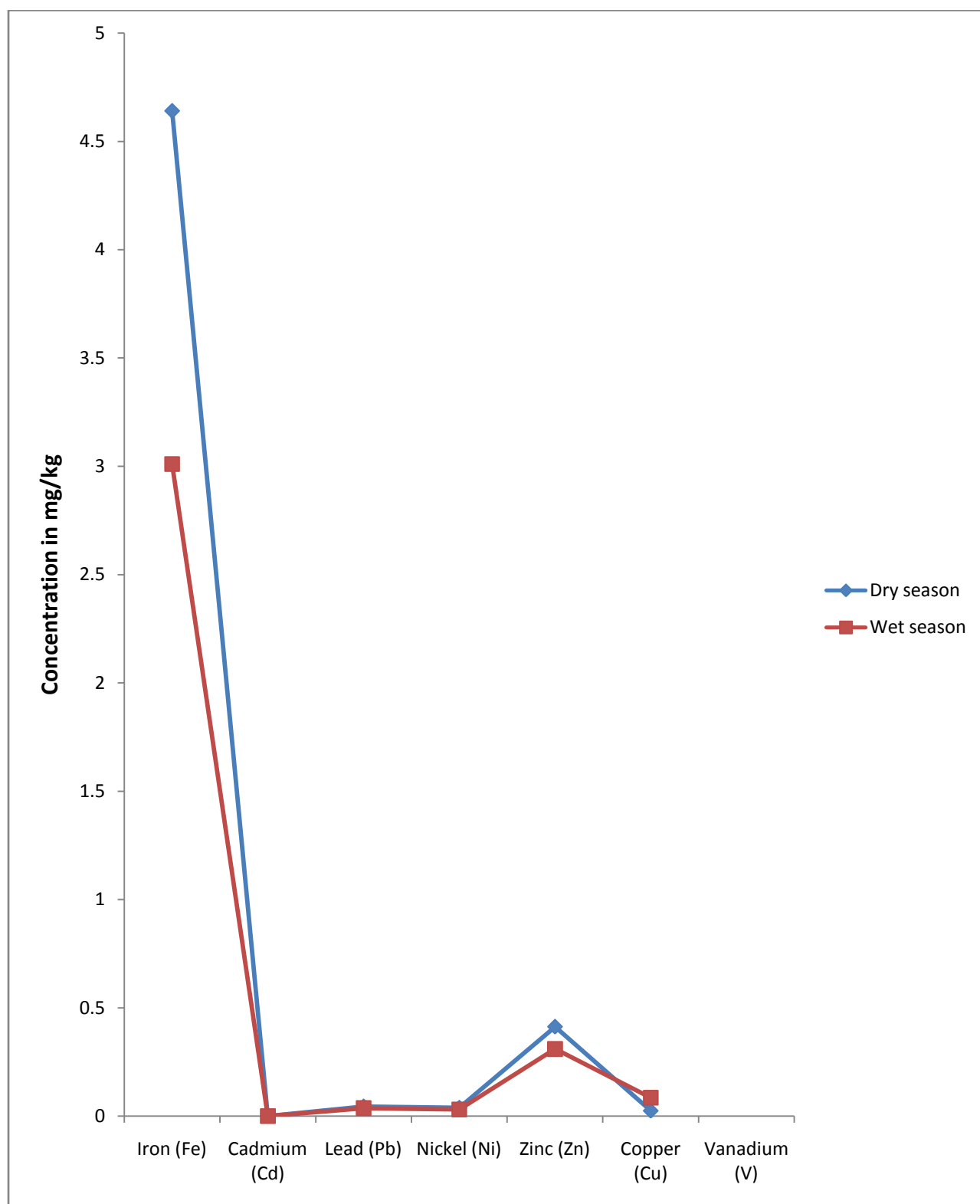
Appendix 60

Mean Heavy Metal Concentration in *Tilapia Zilli* from Imo River during Wet Season.



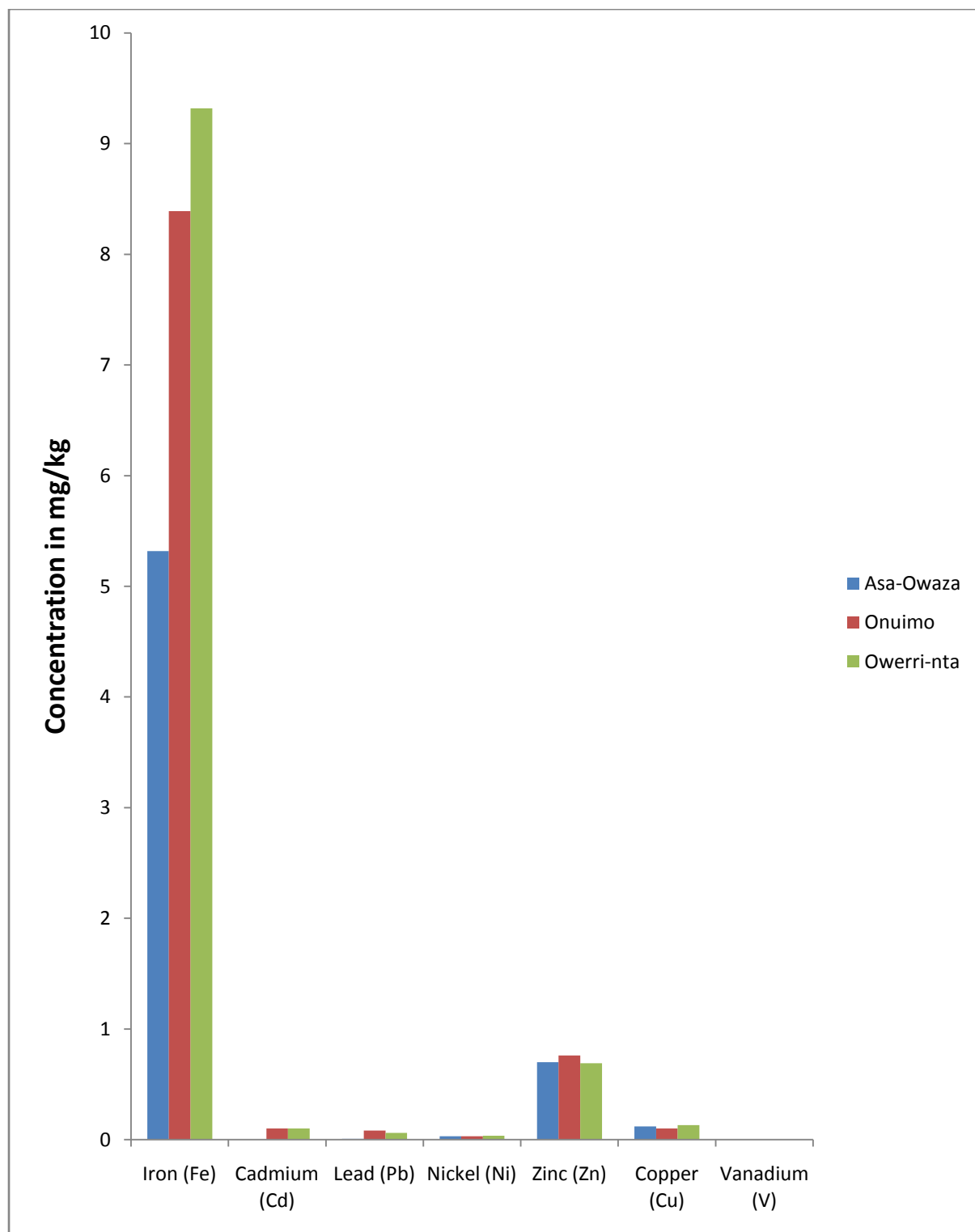
APPENDIX 61

Fig. 4.13: Seasonal Variation of Mean Concentration of Heavy Metals in *Tilapia zilli* from Imo River in both Season.



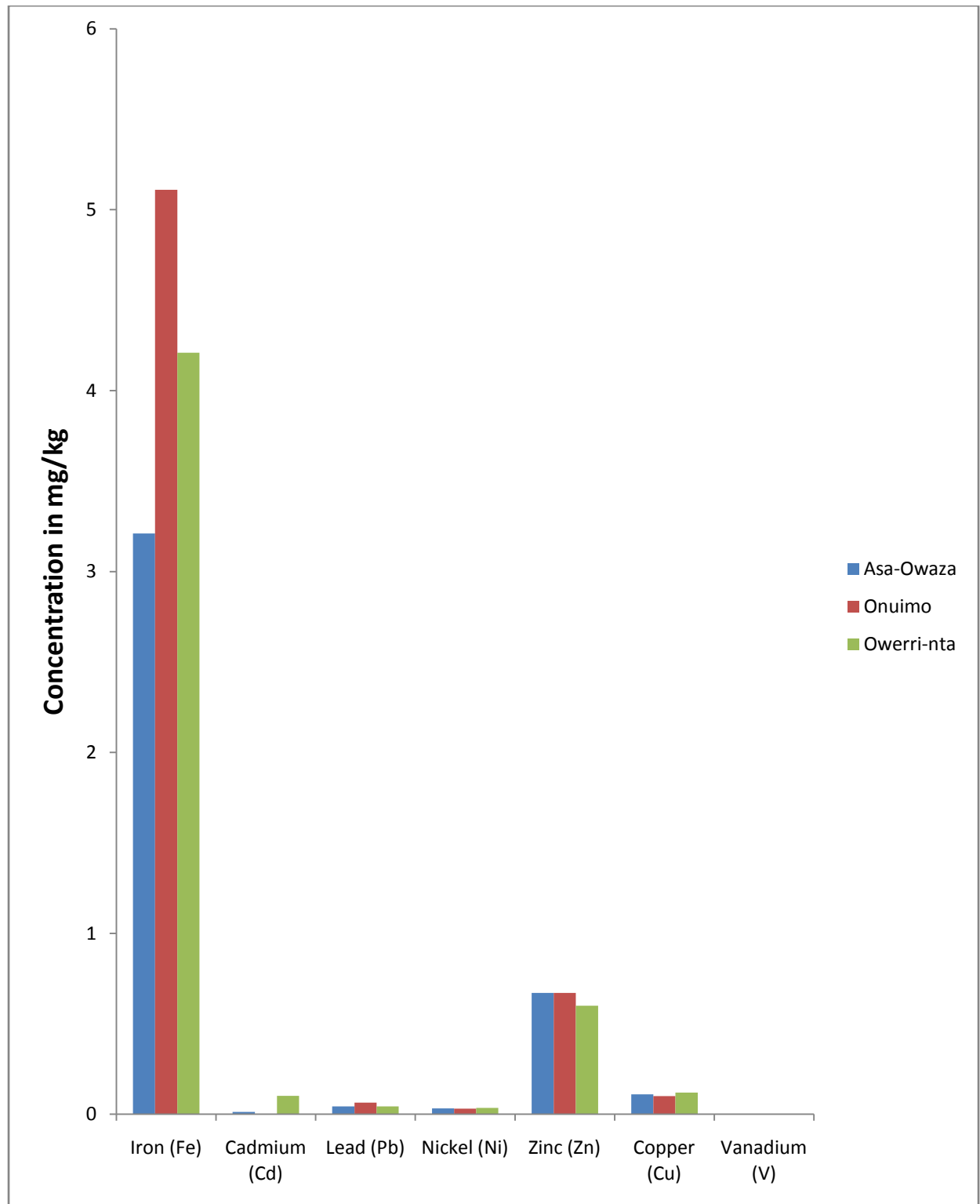
Appendix 62

Mean concentration in cat fish from Imo River during dry season.



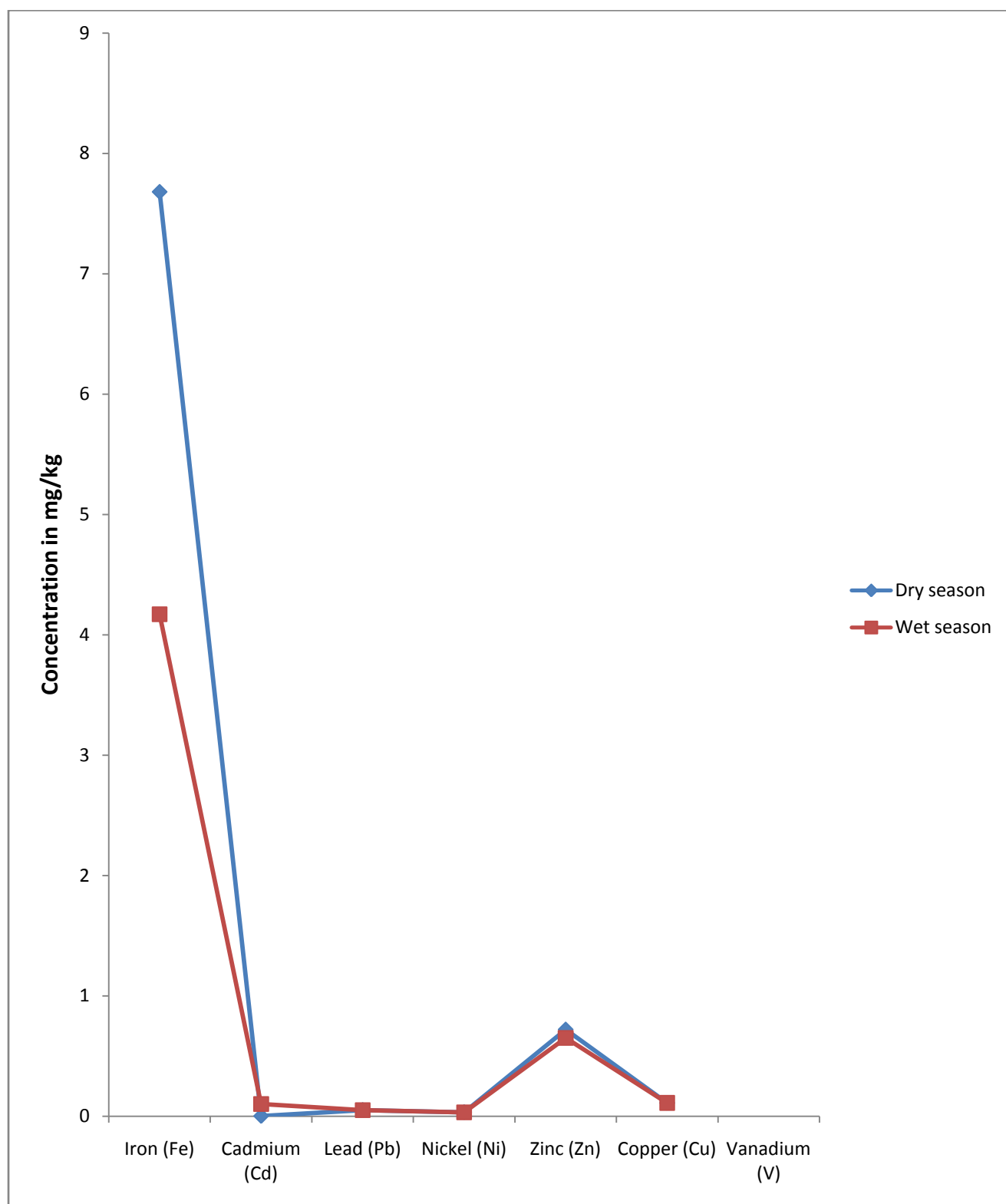
Appendix 63

Mean concentration in cat fish from Imo River during wet season.



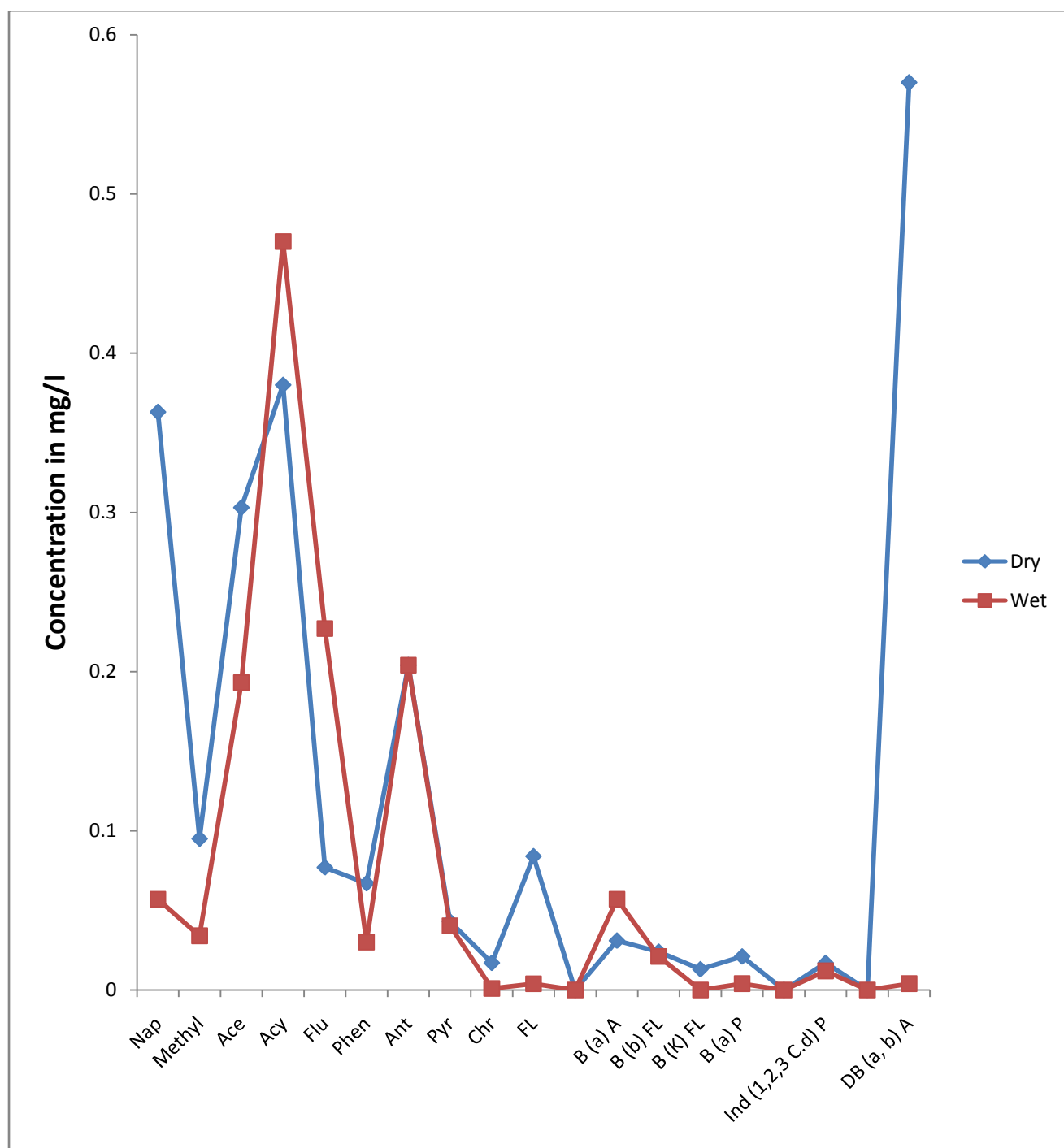
Appendix 64

Seasonal variation of mean concentration of heavy metals of Cat fish from Imo River in both seasons in mg/Kg.



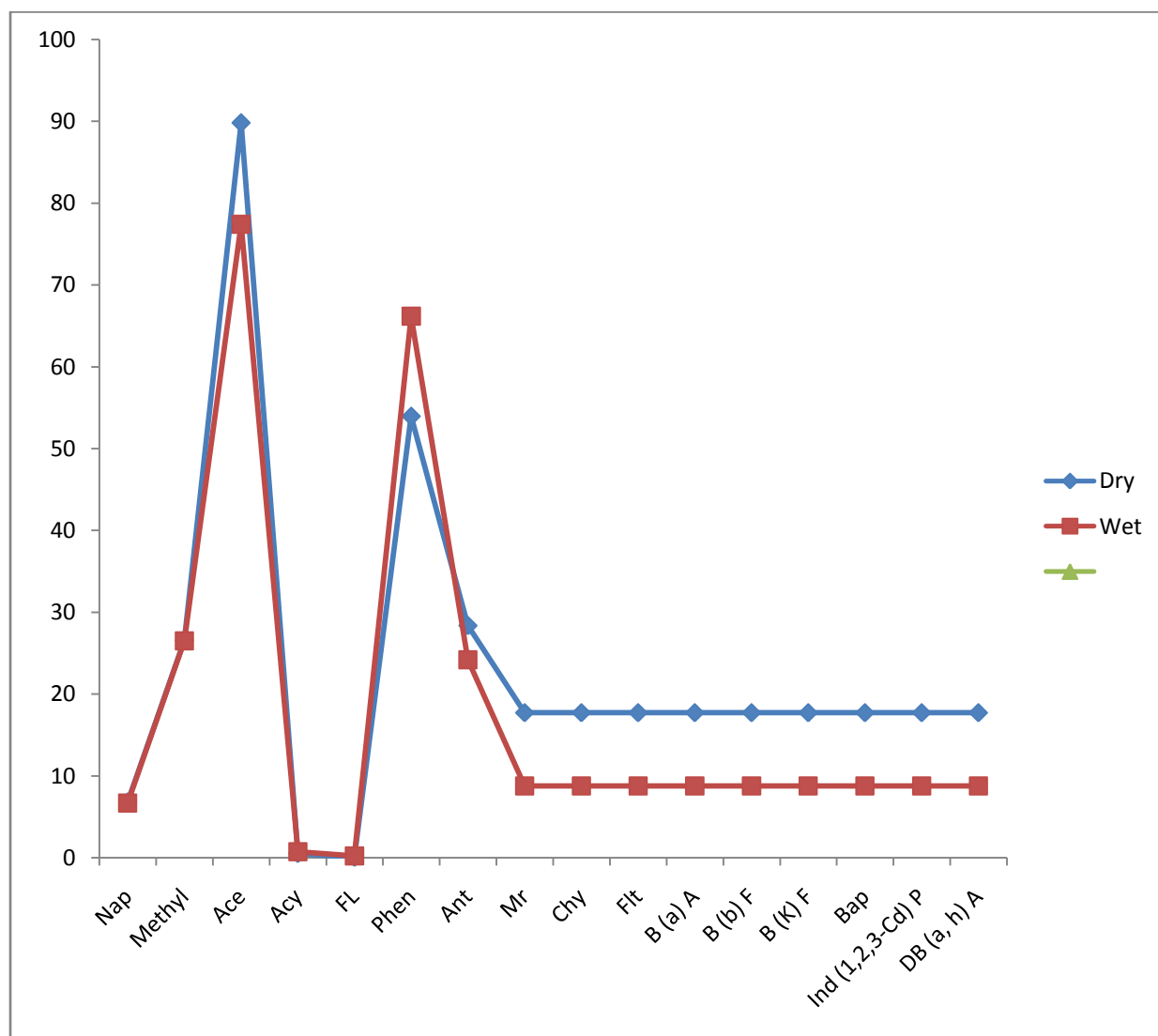
Appendix 65

Seasonal variation of PAHs in water from Imo River for both Season (wet and dry).



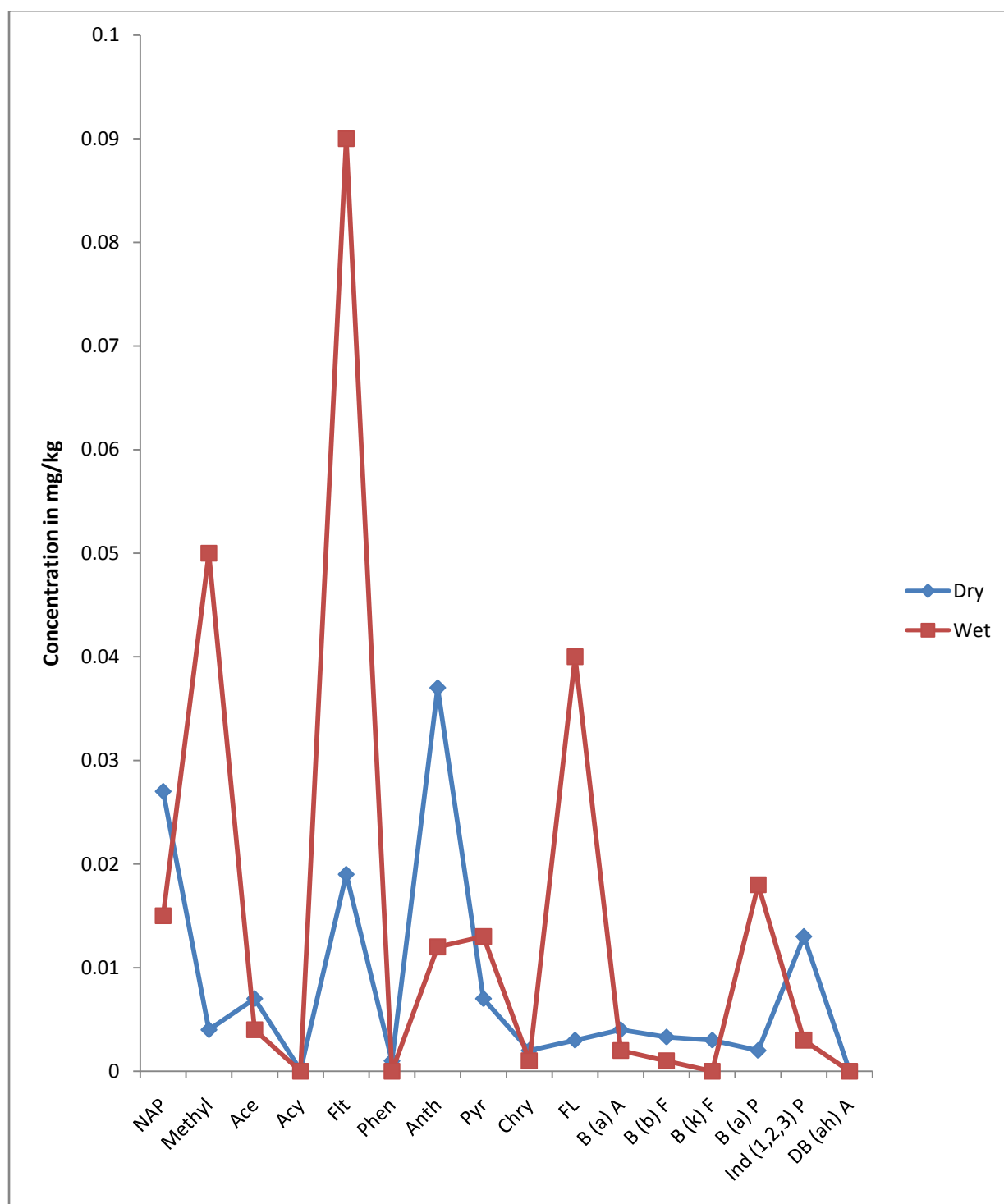
Appendix 66

Seasonal variation of PAHs in sediments from Imo River for both seasons (wet and dry).



Appendix 67

Seasonal variation of PAHs on *Tilapia* fish from Imo River in both Seasons.



Appendix 68



Refuse Dump Site near Imo River

Appendix 69



Gas Flaring at Asa-Owaza