ASSESSMENT OF HEAVY METAL CONTAMINATION AND HYDROCARBON CONTENT IN SELECTED AQUATIC RESOURCES IN GREAT QUA RIVER CALABAR, NIGERIA

BY

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CERTIFICATION

This is to certify that this work **"ASSESSMENT OF HEAVY METAL CONTAMINATION AND TOTAL HYDROCARBON CONTENT IN SELECTED AQUATIC RESOURCES IN GREAT QUA RIVER CALABAR, NIGERIA. ,"** was carried out by **ETINOSA-OKANKAN OSARENAYE PETER (Reg. No. 20134872018)** in partial fulfillment for the Award of Masters Degree (M.Sc.) in the Department of Environmental Technology, Federal University of Technology, Owerri.

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DEDICATION

This piece of work is dedicated to my lovely wife Mrs. Regina O. Etinosa-okankan

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The joy am experiencing this moment wouldn't have been if not for the support of those who in one way or the other assisted me in making sure I completed the program successfully. This is a piece put together to really show my heartfelt gratitude.

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ABSTRACT

Assessment of heavy metal contamination and hydrocarbon content in selected aquatic organism in the Great Qua River was studied. The Great Qua River receives effluents from industries, human settlement, nearby farms and runoff from towns. Water, sediment and aquatic biota (*Typanotonous fuscatus, Macrobrachium macrobrachion* and *Notropis atherinoides*) obtain from the Great Qua River was analyzed for heavy metals and total hydrocarbon content (THC). The mean heavy metal concentration values in water across stations were in the range: (Cd), 0.012±0.06 – 0.087±0.06 mg/l; (Cr), 0.017±0.06 – 0.316±0.06 mg/l; (Mn), 0.067±0.02 – 0.071±0.06 mg/l; (Ni), 0.013±0.06 – 0.083±0.01 mg/l; (Cu), 0.092±0.06 – 0.113±0.06 mg/l; (Pb), 0.064±0.12 – 0.081±0.06 mg/l; (Zn), 0.022±0.06 – 0.098±0.06 mg/l; (Fe) 0.048±0.029 – 0.082±0.06 mg/l. The mean heavy metal concentration in sediment were in the range: (Cr), 0.053±0.06 - 0.193±0.06 mg/kg; (Cd), 0.152±0.06 – 0.188±0.06 mg/kg; (Mn), 0.096±0.06 - 0.185±0.06 mg/kg; (Ni), 0.112±0.06 – 0.782±0.06 mg/kg; (Cu) 0.145±0.06 – 0.167±0.06 mg/kg; (Pb), 0.075±0.06 – 0.098±0.06 mg/kg; (Zn), 0.164±0.06 – 0.179±0.06 mg/kg; (Fe), 0.150±0.06 – 0.377±0.06 mg/kg. The mean heavy metal concentration in *Macrobrachium macrobrachion* were in the range: (Cr), 0.012±0.06 – 0.019±0.06 mg/kg; (Cd) 0.043±0.06 – 0.681±0.06 mg/kg; (Mn), 0.015±0.06 – 0.314±0.06 mg/kg; (Ni), 0.044±0.06 – 0.073±0.06 mg/kg; (Cu), 0.113±0.06 – 0.275±0.06 mg/kg; (Pb), 0.042±0.06 – 0.108±0.06 mg/kg; (Zn), 0.201±0.06 – 0.369±0.06 mg/kg. The mean heavy metal concentration in *Typanotonus fuscatus* were in the range: (Cr), 0.057±0.06 – 0.120±0.06 mg/kg; (Cd), 0.049±0.06 – 0.169±0.06 mg/kg; (Mn) 0.163±0.01 – 0.241±0.06 mg/kg; (Ni), 0.183±0.06 – 0.215±0.06 mg/kg; (Cu) 0.155±0.06 – 0.179±0.06 mg/kg; (Pb), 0.144±0.06 – 0.147±0.06 mg/kg; (Zn), 0.106±0.06 – 0.217±0.06 mg/kg; (Fe), 0.163±0.06 – 0.247±0.06 mg/kg. The mean heavy metal concentration in *Notropis atherinoides* were in the range: (Cr), 0.011±0.06 – 0.137±0.06 mg/kg; (Cd), 0.133±0.06 – 0.86±0.06 mg/kg; (Mn), 0.082±0.06 – 0.195±0.06 mg/kg; (Ni), 0.029±0.06 – 0.267±0.06 mg/kg; (Cu), 0.106±0.06 – 0.129±0.06 mg/kg; (Pb), 0.138±0.06 – 0.203±0.06 mg/kg; (Zn), 0.123±0.06 – 0.207±0.06 mg/kg; (Fe), 0.111±0.06 – 0.337±0.06 mg/kg. The results showed that the mean heavy metal concentration statistically differ significantly across stations in all samples analysed when compared to control ($P<0.05$) except in the case of cadmium (Cd) in water and Iron (Fe) in sediment and T. fuscatus where there was no statistical significance when compared to control ($P>0.05$). The profile of heavy metal bioaccumulated was in the order *Typanotonous fuscatus*>*Macrobrachium macrobrachion*>sediment>*Notropis atherinoide*s>water. The mean THC value in water were in the range: 0.215±0.06 – 0.395±0.06 mg/l; sediment, 0.379±0.06 - 0.481±0.06 mg/kg; *Macrobrachium macrobrachion*, 0.106±0.06 – 0.167±0.06 mg/kg; *Notropis atherinoides*, 0.0063±0.06 – 0.288±0.06 mg/kg and *Typanotonus fuscatus*, 0.142±0.06 – 0.157±0.06 mg/kg.The total hydrocarbon content statistically differ significantly in all samples analysed across stations ($P<0.05$) and the order of THC bioaccumulation was in the order sediment>water>*N. atherinoides*>*T.fuscatus*>*M. macrobrachion*. The result from the correlation analysis between heavy metals, THC and physicochemical properties revealed that there was a perfect relationship between the uptake of these heavy metals / hydrocarbons by these aquatic organisms and the physicochemical properties of the water. Apart from Mn, Zn and Fe that were below the WHO acceptable limit, all other metals analysed were slightly above the WHO acceptable limit. The THC values in all samples analysed were above the WHO acceptable limit. These suggest that the river has been polluted by anthropogenic activities around its environs. Close monitoring of pollution stress, public enlightenment and appropriate laws should be put in place to avert possible metal and hydrocarbon compound induced health hazards from the consumption of the aquatic biota from the river.

Keyword: Heavy metal, hydrocarbon, Aquatic resources, Great Qua River

CHAPTER ONE

1.0 INTRODUCTION

Many of the sediments and sea organisms in our rivers, lakes, and oceans have been contaminated by pollutants. Human activities play a major role in the introduction of various anthropogenic pollutants in surface waters (Okorafor, et al., 2015).

Among the pollutants are heavy metals and hydrocarbons. Heavy metals which were at the beginning considered as natural elements, essential to the development of living organisms at small concentration, was later discovered that high concentration of these elements are toxic. The discharge of heavy metals into river or any aquatic environment can change both aquatic species diversity and ecosystem due to their toxicity and accumulative behaviour (Health, 1987;Allen, 1995). These anthropogenic pollutants in surface waters results in high concentration of heavy metals which lower water quality and at the same time accumulate in the sediment and benthos like mollusc, arthropods and other species in the benthic Communities (Abida,et al., 2009).

Contaminated sediments can threaten the lives of benthic organisms exposing worms, crustaceans and insects to hazardous concentrations of toxic chemicals. Some kinds of toxic sediments kill benthic organisms, reducing the food available to larger animals such as fish. Some contaminants in the sediment are taken up by benthic organisms in a process called bioaccumulation. When larger animals feed on these contaminated organisms, the toxins are taken into their bodies, moving up the food chain in increasing concentrations in a process known as bio-magnification (Abida et al, 2009).

Contaminated sediments do not always remain at the bottom of a water body. Anything that stirs up the water, such as dredging, flooding can re-suspend sediments. Re-suspension may mean that all of the animals in the water, and not just the bottom-dwelling organisms, will be directly exposed to toxic contaminants.

Aquatic organisms such as fish and shell fish accumulate metals to concentrations many times higher than present in water or sediment (Olaifa *et al*; 2004, Gumgum *et al*; 1994). They can take up metals concentrated at different levels in their different body organs (Khaled, 2004). Certain environmental conditions such as salinity, pH, water accumulates in the living organisms up to toxic concentrations and cause ecological damage (Guven *et al*., 1999). Different aquatic organisms often respond to external contamination in different ways, where the quantity and form of the element in water, sediment, or food will determine the degree of accumulation (Abida et al, 2008: Abida et al, 2009).The region of accumulation of heavy metals within fish varies with route of uptake, heavy metals, and species of fish concerned. Thus heavy metals acquired through the food chain as a result of pollution are potential chemical hazards, threatening consumers. At low levels, some heavy metals such as copper, cobalt, zinc, iron and manganese are essential for enzymatic activity and many biological processes. Other metals, such as cadmium, mercury and lead have no essential role in living organisms and are toxic even at low concentrations. The essential metals also become toxic at high concentrations (Bryan, 1976). Studies carried out on fish have shown that heavy metals may have toxic effects, altering physiological activities and biochemical parameters both in tissues and in blood of fish (Larsson et al, 1985).

The consequence of heavy metals pollution can be hazardous to man through food chain contamination. Heavy metals accumulation adversely affects various biological processes like reproduction, feeding, growth, maturity and so on. Therefore, it is important to always determine the bioaccumulation capacity for heavy metals by organisms, especially edible ones like prawns, periwinkle and other aquatic organisms in order to assess and ascertain potential risks to human health. Prawns are an important food source for larger animals from fish to whales. As with other sea food, prawns are high in calcium, iodine and protein but low in food energy. Consumption of prawns from rivers and streams polluted by heavy metals by humans is thought to lead to disorders or diseases like: Liver dysfunction, Parkinson's disease, heart failure, decreased fertility, still

births, some types of cancers, poisoning etc.(Okorafor et al.,2015) These metals don't readily breakdown in the environment (Adedeji and Okocha, 2011) and as such they bioaccumulate in the environment and become toxic to living organism.

Metals can cause serious health effects with varied symptoms depending on the nature and quantity of metal ingested (Adepoju-Bello and Alabi, 2005). The most common metals that humans are exposed to are: aluminum, arsenic, cadmium, lead and mercury. Aluminum has been associated with Alzheimer's and Parkinson's disease, senility and pre-senile dementia. Arsenic exposure can cause among other illnesses or symptoms, cancer, abdominal pain and skin lesions. Cadmium exposure produces kidney damage and hypertension. Lead is a cumulative poison and a possible human carcinogen (Bakare-odunola, 2005) while for mercury, toxicity results in mental disturbance and impairment of speech, hearing, vision and movement (Hammer and Hammer, 2004). In addition, lead and mercury may cause the development of autoimmunity in which a person's immune system attacks its own cells. This can lead to joint diseases and ailment of the kidneys and circulatory system and neurons. At high concentrations, lead and mercury can cause irreversible brain damage.

Heavy metals found in natural water bodies occur at varying concentrations and are usually monitored by measuring their concentrations in water, sediment and biota. Aquatic organisms can acquire these heavy metals from food, suspended particles or directly from the water. Many aquatic organisms have been used as sensitive indicators of heavy metal pollution (Osibanjo and Ajayi, 1980: Foulkes, 1990). Biota that inhibit contaminated sites are generally exposed to very high concentrations of the pollutants (Woo, et al., 1993).

The petroleum industry according to (Abowei, 1996) contributes greatly to aquatic environmental degradation and pollution. Oil from the petroleum industry enters the aquatic environment through several sources such as, fall outs from gas flaring, disposal of used lubrication oils, washings from oil tanks, leakages from marine vessels and out board engines,

sabotage, erosion and run off from crude oil polluted lands, seepage, refinery effluents, rupture of ill maintained flow lines/installations, maintenance and engineering errors. Even after use by burning for fuel, the resultant gases contain un-burnt hydrocarbons discharged into air from which they can be washed by the rain and back to land and also into the sea.

A greater majority of these spilt oil get into the rivers, ocean, streams etc. directly or indirectly where a reasonable fraction either mixes with water or sink into the sediment, (Partin, 1999) causing severe damage to benthic organisms. According to (Dambo, 1992) hydrocarbon pollution impairs the growth and development of marine organisms, causes fish, crustaceans and mollusks to acquire objectionable odour or flavor which reduces their market value and acceptability, ultimately it leads to death of both flora and fauna which is common in the Niger Delta (Nwankwo et al., 1981).

1.1 AIM OF THE RESEARCH

The aim of this work is to determine the levels of heavy metal contaminants and total hydrocarbon content in water, sediments and selected sea organisms obtained from the Great Qua River in Cross River State, Nigeria.

1.2 OBJECTIVES OF THE RESEARCH

- To determine the levels of Cr, Cd, Mn, Ni, Cu, Pb, Zn, and Fe in water, sediments and selected aquatic species.
- To determine the Total Hydrocarbon Content, in water, sediments and selected aquatic species.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 POLLUTION

The term pollution is a derivation of the word pollutes which means to make something dirty or no longer pure, especially by adding harmful of unpleasant substance to it.

In another development; the committee on pollution of the United States National Research Council (1965) defined pollution as; an undesirable change in physical, chemical or biological characteristics of our air, land and water that may or will harmfully affect human life or that of other desirable species, our industrial processes, living conditions cultural assets that may or will waste or deteriorate our raw material resources.

Pollution according to the above definition is a disorder within an environment and is a by-product of energy conversion and the use of resources.

Ekuri and Eze (1999) defined pollution as "a contamination, a defilement, mischief, perturbation and reduction in the value of an object or thing".

2.2 HEAVY METAL

The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004).

Heavy metals" is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 , or 5 times or more, greater than water (Huton and Symon, 1986; Battarbee et al., 1988; Nriagu and Pacyna 1988; Nriagu, 1989; Garbarino et al., 1995,Hawkes, 1997). However, being a heavy metal has little to do with density but concerns chemical properties. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn),mercury (Hg), arsenic (As), silver (Ag) chromium (Cr),copper (Cu) iron (Fe), and the platinum group elements.

2.2.1 OCCURRENCE AND RECOVERY OF HEAVY METALS

Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. To a small extent, they enter the body system through food, air, and water and bio-accumulate over a period of time. (Lenntech,2004; UNEP/GPA, 2004). In rocks, they exist as their ores in different chemical forms, from which they are recovered as minerals. Heavy metal ores include sulphides, such as iron,

arsenic, lead, lead-zinc, cobalt, gold silver and nickel sulphides; oxides such as aluminum, manganese, gold, selenium and antimony. Some exist and can be recovered as both sulphide and oxide ores such as iron, copper and cobalt. Ore minerals tend to occur in families whereby metals that exist naturally as sulphides would mostly occur together, likewise for oxides. Therefore, sulphides of lead, cadmium, arsenic and mercury would naturally be found occurring together with sulphides of iron (pyrite, FeS_2) and copper (chalcopyrite, $CuFeS_2$) as minors, which are obtained as by-products of various hydrometallurgical processes or as part of exhaust fumes in pyrometallurgical and other processes that follow after mining to recover them. During mining processes, some metals are left behind as tailings scattered in open and partially covered pits; some are transported through wind and flood, creating various environmental problems (Habashi,1992). Heavy metals are basically recovered from their ores by mineral processing operations (Peplow, 1999; Lenntech, 2004; UNEP/GPA, 2004; United States Department of Labor (USDOL), 2004).

2.2.2 HEAVY METAL EMISSION

Heavy metals can be emitted into the environment by both natural and anthropogenic causes. The major causes of emission are the anthropogenic sources specifically mining operations (Hutton and Symon, 1986; Battarbee et al., 1988; Nriagu, 1989). In some cases, even long after mining activities have ceased, the emitted metals continue to persist in the environment. Peplow (1999) reported that hard rock mines operate from 5-15 years until the minerals are depleted, but metal contamination that occurs as a consequence of hard rock mining persist for hundreds of years after the mining operations discontinued.

Apart from mining operations, mercury is introduced into the environment through cosmetic products as well as manufacturing processes like making of sodium hydroxide. Heavy metals are emitted both in elemental and compound (organic and inorganic) forms. Anthropogenic sources of emission are the various industrial point sources including former and present mining sites, foundries and smelters, combustion by-products and traffics (UNEP /GPA, 2004). Cadmium is

released as a by- product of zinc (and occasionally lead) refining; lead is emitted during its mining and smelting activities, from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl lead antiknock) and from old lead paints; mercury is emitted by the degassing of the earth's crust. Generally, metals are emitted during their mining and processing activities (Lenntech, 2004).Environmental pollution by heavy metals is very prominent in areas of mining and old mine sites and pollution reduces with increasing distance away from mining sites (Peplow, 1999).These metals are leached out and in sloppy areas, are carried by acid water downstream or run-off to the sea. Through mining activities, water bodies are most emphatically polluted (Garbarino et al., 1995;INECAR, 2000). The potential for contamination is increased when mining exposes metal-bearing ores rather than natural exposure of ore bodies through erosion (Garbarino et al., 1995), and when mined ores are dumped on the earth surfaces in manual dressing processes. Through rivers and streams, the metals are transported as either dissolved species in water or as an integral part of suspended sediments, (dissolved species in water have the greatest potential of causing the most deleterious effects). They may then be stored in river bed sediments or seep into the underground water thereby contaminating water from underground sources, particularly wells; and the extent of contamination will depend on the nearness of the well to the mining site. Wells located near mining sites have been reported to contain heavy metals at levels that exceed drinking water criteria (Garbarino et al., 1995; Peplow, 1999).

2.2.3 CHEMISTRY OF HEAVY METAL POLLUTION

Mining activities and other geochemical processes often result in the generation of acid mine drainage (AMD), a phenomenon commonly associated with mining activities. It is generated when pyrite (FeS_2) and other sulphide minerals in the aquifer and present and former mining sites are exposed to air and water in the presence of oxidizing bacteria, such as *Thiobacillus ferrooxidans*, and oxidised to produce metal ions, sulphate and acidity (Ogwuegbu and Muhanga, 2005).

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$

$2FeSO_4 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + SO_2 + 2H_2O$

$Fe_2(SO_4)_3 + 2FeAsS + {}^{9/}2O_2 + 3H_2O \rightarrow 2H_3AsO_4 + 4FeSO_4 + S$

Literature survey shows that heavy metals (M) at mining sites are leached and carried by acidic water downstream. They can be acted upon by bacterial and methyllated to yield organic forms, such as monomethylmercury and dimethylcadmium. This conversion is effected by bacteria in water, in the presence of organic matter, according to the following simplified equation.

M + organic matter $H_2O\rightarrow$ bacteria CH_3 M + $(CH)_2$ M

In the non-biological conversions, the following reactions have been identified for mercury:

Hg^{2+} $\underline{H_2S}$ HgS $\rightarrow$ Hg_2So_4 $\rightarrow$ CH_3Hg^+

(eutrophic condition) less soluble aeration more soluble methylmercury

These organic forms have been reported to be very toxic and adversely affect water qualities by seepage to pollute underground water sources. Low pH values do not need to be established for metals to be released from mine wastes at adverse concentrations because, near neutral pH (pH 6-7) have been established for some metals, such as Zn, Cd, and As (INECAR, 2000; Lenntech, 2004). Factors such as downstream distances from the mining sites, colloid loads, pH perturbations, and dilution ultimately control the quality of water sources.

2.3 ROUTE OF HEAVY METAL EXPOSURE

2.3.1 HUMAN EXPOSURE THROUGH FOOD, AIR AND WATER

Heavy metal pollution of surface and underground water sources results in considerable soil pollution and pollution increases when mined ores are dumped on the ground surface for manual dressing (Garbarino et al., 1995; INECAR, 2000). Surface dumping exposes the metals to air and rain thereby generating much AMD. When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissues (Trueby, 2003).Animals that graze on such contaminated plants and drink from polluted waters, as well as marine lives that breed in

heavy metal polluted waters also accumulate such metals in their tissues, and milk, if lactating (Habashi, 1992; Garbarino et al., 1995; Horsfall and Spiff, 1999; Peplow, 1999). Humans are in turn exposed to heavy metals by consuming contaminated plants and animals, and this has been known to result in various biochemical disorders. In summary, all living organisms within a given ecosystem are variously contaminated along their cycles of food chain.

2.3.2 HUMAN EXPOSURE THROUGH INDUSTRIAL PRODUCTS

Industrial products that are used in homes, and which have been produced with heavy metals are sources of human exposure to such heavy metals. Mercury exposure is through disinfectants (like mercurochrome), antifungal agents, toiletries, creams and organo-metallics (McCluggage, 1991); cadmium exposure is through nickel/cadmium batteries and artist paints; lead exposure is through wine bottle wraps, mirror coatings, batteries, old paints and tiles and linolein amongst others. Infants are more susceptible to the endangering effects of exposure to heavy metals.

2.3.3 OCCUPATIONAL EXPOSURE

Heavy metal exposure occurs significantly by occupational exposure. Workers of the mining and production of cadmium, chromium, lead, mercury, gold and silver have been reported to be thus exposed; also inhabitants around industrial sites of heavy metal mining and processing, are exposed through air by suspended particulate matters (SPM) (Heyer, 1985; USDOL, 2004; Ogwuegbu and Muhanga, 2005).

2.4 TOXICOLOGICAL EFFECT OF HEAVY METAL

The toxicological effects of heavy metals refer to the harmful effects of heavy metals to the body when consumed above the bio-recommended limits. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with

cadmium, lead, arsenic, mercury, zinc, copper and aluminum poisoning: gastrointestinal (GI) disorders, diarrhea, stomatitis, tremor, hemoglobinuria causing a rust–red colour to stool, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia when volatile vapours and fumes are inhaled (McCluggage, 1991). The nature of effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic. Cadmium is toxic at extremely low levels. In humans, long term exposure results in renal dysfunction, characterized by tubular proteinuria. High exposure can lead to obstructive lung disease, cadmium pneumonitis, resulting from inhaled dusts and fumes. It is characterized by chest pain, cough with foamy and bloody sputum, and death of the lining of the lung tissues because of excessive accumulation of watery fluids. Cadmium is also associated with bone defects, viz; osteomalacia, osteoporosis and spontaneous fractures, increased blood pressure and myocardia dysfunctions. Depending on the severity of exposure, the symptoms of effects include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. Severe exposure may result in pulmonary odema and death. Pulmonary effects (emphysema, bronchiolitis and alveolitis) and renal effects may occur following subchronic inhalation exposure to cadmium and its compounds (McCluggage, 1991; INECAR, 2000; European Union, 2002; Young, 2005). Lead is the most significant toxin of the heavy metals, and the inorganic forms are absorbed through ingestion by food and water, and inhalation (Ferner, 2001). A notably serious effect of lead toxicity is its teratogenic effect. Lead poisoning also causes inhibition of the synthesis of haemoglobin; dysfunctions in the kidneys, joints and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system (CNS) and peripheral nervous system (PNS) (Ogwuebgu and Muhanga, 2005). Other effects include damage to the gastrointestinal tract (GIT) and urinary tract resulting in bloody urine, neurological disorder and can cause severe and permanent brain damage. While inorganic forms of lead, typically affect the CNS, PNS, GIT and other biosystems, organic forms predominantly affect the CNS (McCluggage, 1991; INECAR, 2000; Ferner, 2001; Lenntech, 2004). Lead affects children

by leading to the poor development of the grey matter of the brain, thereby resulting in poor intelligence quotient (IQ) (Udedi, 2003).

Its absorption in the body is enhanced by Ca and Zn deficiencies. Acute and chronic effects of lead result in psychosis. Zinc has been reported to cause the same signs of illness as does lead, and can easily be mistakenly diagnosed as lead poisoning (McCluggage, 1991). Zinc is considered to be relatively non-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that result in impairment of growth and reproduction (INECAR, 2000; Nolan, 2003). The clinical signs of zinc toxicosis have been reported as vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, kidney failure and anemia (Fosmire, 1990). Mercury is toxic and has no known function in human biochemistry and physiology. Inorganic forms of mercury cause spontaneous abortion, congenital malformation and GI disorders (like corrosive esophagitis and hematochezia). Poisoning by its organic forms, which include monomethyl and dimenthylmecury presents with erethism (an abnormal irritation or sensitivity of an organ or body part to stimulation), acrodynia (Pink disease, which is characterized by rash and desquamation of the hands and feet), gingivitis, stomatitis, neurological disorders, total damage to the brain and CNS and are also associated with congenital malformation (Ferner, 2001; Lennetech, 2004). As with lead and mercury, arsenic toxicity symptoms depend on the chemical form ingested (Holum, 1983;Ferner, 2001). Arsenic acts to coagulate protein, forms complexes with coenzymes and inhibits the production of adenosine triphosphate (ATP) during respiration (INECAR,2000). It is possibly carcinogenic in com-pounds of all its oxidation states and high-level exposure can cause death (Ogwuegbu and Ijioma, 2003; USDOL, 2004). Arsenic toxicity also presents a disorder, which is similar to, and often confused with Guillain-Barre syndrome, an anti-immune disorder that occurs when the body's immune system mistakenly attacks part of the PNS, resulting in nerve inflammation that causes muscle weakness (Kantor, 2006; NINDS, 2007).

2.5 BIOLOGICAL IMPORTANCE OF HEAVY METALS

Some heavy metals (like Fe, Zn, Ca and Mg) have been reported to be of bio-importance to man and their daily medicinal and dietary allowances had been recommended and is presented in Table 2. Their tolerance limits in drinking and potable waters have also been reported, and are indicated in Table 3. However, some others (like As, Cd, Pb, and methylated forms of Hg) have been reported to have no known bio-importance in human biochemistry and physiology and consumption even at very low concentrations can be toxic (Holum, 1983; Fosmire, 1990; McCluggage, 1991; Ferner, 2001; European Union, 2002; Nolan, 2003; Young, 2005). Even for those that have bio-importance, dietary intakes have to be maintained at regulatory limits, as excesses will result in poisoning or toxicity, which is evident by certain reported medical symptoms that are clinically diagnosable (Fosmire, 1990; Nolan, 2003; Young, 2005). Zinc is a 'masculine' element that balances copper in the body, and is essential for male reproductive activity (Nolan, 2003). It serves as a co-factor for dehydrogenating enzymes and in carbonic anhydrase (Holum, 1983). Zinc deficiency causes anaemia and retardation of growth and development (McCluggage, 1991). Calcium is a very vital element in human metabolism. It is the chief element in the production of very strong bones and teeth in mammals. Its tolerance limit is high relative to other biologically useful metals, that is, at 50 mg/l of drinking water as shown in Table 3. The daily dietary requirement of calcium soars at the highest across both sexes and all ages of humans as shown in Table 2, and it can be accommodated at higher doses in the body because its concentration in the blood is well regulated by thyrocalcitonin and parathormone hormones (Holum, 1983). Magnesium is an important electrolytic constituent of the blood, present in the blood plasma and body fluids,viz; interstitial and cell fluids. Its daily dietary requirement increases from infants to adults and from males to females, with the highest daily requirements for pregnant and lactating women (Holum, 1983). Arsenic has been reported to be a trace element of nutritional importance to humans but its functions in the biological system is not clear (Holum, 1983). Any level of concentration of silver in drinking water has been disallowed, both by the

World Health Organization (WHO) and National Agency for Food and Drugs Administration and Control (NAFDAC), Nigeria. Lead, cadmium and mercury have been reported not to have any known function in human biochemistry or physiology, and do not occur naturally in living organisms (Lenntech, 2004). Hence dietary intakes of these metals, even at very low concentrations can be very harmful because they bioaccumulate.

2.6 HYDROCARBONS

Hydrocarbons are organic compounds containing carbon and hydrogen and found in crude oil and natural gas. Hydrocarbons are formed from the remains of marine animals and plants that lived in shallow inland seas, died, and drifted to the bottom. The term petroleum is used as a common detonation for crude oil (mineral oil) and natural gas, i.e., the hydrocarbons from which various oil and gas products are made. Petroleum is a collective term for hydrocarbons, whether solid, liquid or gas.

Total petroleum hydrocarbon is a term used to describe a broad family of several hundred chemical compounds that originally come from crude oil. In this sense TPH is really a mixture of chemicals. They are called hydrocarbons because almost all of them are made entirely from carbon and hydrogen. Crude oil can vary in how much of each chemical they contain, and so can the petroleum products that are made from crude oils. Most of the product that contain TPH will burn. Some are clear or light-colored liquids that evaporate easily, and others are thick, dark liquids or semi-solids that do not evaporate. Many of these products have characteristic gasoline, kerosene, or oily odors. Because modern society uses so many petroleum based products (for example, gasoline, kerosene, fuel oil, mineral oil and asphalt), contamination of the environment by them is potentially widespread. Contamination caused by petroleum products will contain a variety of these hydrocarbons. Because there are so many, it is not usually practical to measure each one individually. However, it is useful to measure the total amount of all hydrocarbons found together in a particular sample of water, air and soil.

The amount of Total Hydrocarbons found in a sample is useful as a general indicator of petroleum contamination at that site.

2.6.1 HYDROCARBON PATHWAYS IN THE ENVIRONMENT

TPH is released to the environment through accidents, as releases from industries, or as byproducts from commercial or private uses. When TPH is released directly to water through spills or leaks, certain TPH fractions will float in water and form thin surface films. Other heavier fractions will accumulate in the sediment at the bottom of the water, which may affect bottom-feeding fish and organisms. Some organisms found in the water, primarily bacteria and fungi, may break down some of the TPH fractions. TPH released to the soil may move through the soil to the groundwater. Individual compounds may then separate from the original mixture, depending on the chemical properties of the compound. Some of these compounds will evaporate into the air and others will dissolve into the groundwater and move away from the release area. Other compounds will attach to particles in the soil and may stay in the soil for a long period of time, while others will be broken down by organisms found in the soil.

2.6.2 ROUTE OF HYDROCARBON EXPOSURE

Everyone is exposed to TPH from many sources, including gasoline fumes at the pump, spilled crankcase oil on pavement, chemicals used at home or work, or certain pesticides that contain TPH components as solvents. A small amount of lighter TPH components are found in the general air you breathe. Many occupations involve extracting and refining crude oil, manufacturing petroleum and other hydrocarbon products, or using these products. If you work with petroleum products, you may be exposed to higher levels of TPH through skin contact or by breathing contaminated air. If TPH has leaked from underground storage tanks and entered the groundwater, you may drink water from a well contaminated with TPH. You may breathe in some of the TPH compounds

evaporating from a spill or leak if you are in the area where an accidental release has occurred. Children may be exposed by playing in soil contaminated with TPH.

2.6.3 PATHWAYS IN THE BODY

TPH can enter and leave your body when you breathe it in air; swallow it in water, food, or soil; or touch it. Most components of TPH will enter your bloodstream rapidly when you breathe them as a vapor or mist or when you swallow them. Some TPH compounds are widely distributed by the blood throughout your body and quickly break down into less harmful chemicals. Others may break down into more harmful chemicals. Other TPH compounds are slowly distributed by the blood to other parts of the body and do not readily break down. When you touch TPH compounds, they are absorbed more slowly and to a lesser extent than when you breathe or swallow them. Most TPH compounds leave your body through urine or when you exhale air containing the compounds.

2.6.4 HEALTH EFFECTS

Health effects from exposure to TPH depend on many factors. These include the types of chemical compounds in the TPH, how long the exposure lasts, and the amount of the chemicals contacted. Very little is known about the toxicity of many TPH compounds. Until more information is available, information about health effects of TPH must be based on specific compounds or petroleum products that have been studied.

The compounds in different TPH fractions affect the body in different ways. Some of the TPH compounds, particularly the smaller compounds such as benzene, toluene, and xylene (which are present in gasoline), can affect the human central nervous system. If exposures are high enough, death can occur. Breathing toluene at concentrations greater than 100 parts per million (100 ppm)

for more than several hours can cause fatigue, headache, nausea, and drowsiness. When exposure is stopped, the symptoms will go away. However, if someone is exposed for a long time, permanent damage to the central nervous system can occur. One TPH compound (n-hexane) can affect the central nervous system in a different way, causing a nerve disorder called peripheral neuropathy characterized by numbness in the feet and legs and, in severe cases, paralysis. This has occurred in workers exposed to 500–2,500 ppm of n-hexane in the air. Swallowing some petroleum products such as; gasoline and kerosene causes irritation of the throat and stomach, central nervous system depression, difficulty breathing, and pneumonia from breathing liquid into the lungs. The compounds in some TPH fractions can also affect the blood, immune system, liver, spleen, kidneys, developing fetus, and lungs. Certain TPH compounds can be irritating to the skin and eyes. Other TPH compounds, such as some mineral oils, are not very toxic and are used in foods.

To protect the public from the harmful effects of toxic chemicals and to find ways to treat people who have been harmed, scientists use many tests.

One way to see if a chemical will hurt people is to learn how the chemical is absorbed, used, and released by the body; for some chemicals, animal testing may be necessary. Animal testing may also be used to identify health effects such as cancer or birth defects. Without laboratory animals, scientists would lose a basic method to get information needed to make wise decisions to protect public health. Scientists have the responsibility to treat research animals with care and compassion. Laws today protect the welfare of research animals, and scientists must comply with strict animal care guidelines. Animal studies have shown effects on the lungs, central nervous system, liver, kidney, developing fetus, and reproductive system from exposure to TPH compounds, generally after breathing or swallowing the compounds.

One TPH compound (benzene) has been shown to cause cancer (leukemia) in people. The International Agency for Research on Cancer (IARC) has determined that benzene is carcinogenic to humans (Group 1 classification). Some other TPH compounds or petroleum products, such as benzo(a)pyrene and gasoline, are considered to be probably and possibly carcinogenic to humans (IARC Groups 2A and 2B, respectively) based on cancer studies in people and animals. Most of the other TPH compounds and products are considered not classifiable (Group 3) by IARC.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 DESCRIPTION OF STUDY AREA

The Great Qua River flows through Cross River State, Nigeria, draining the east side of the city of Calabar. It is located between latitude 80 15'E and 80 30'E and longitude 40 45'N and 50 15'N. It has an estimated length of 56km and is about 2.8km wide. The river originates in the Oban Hill, in the Cross River National Park, and flows southwards to the Cross River estuary (Fig 1.0).Two climatic seasons (wet and dry) prevail in the study area. The wet season is characterized by high rainfall while the dry season experiences occasional downpours. The shorelines are lined

and rich in macro-invertebrates, fish fauna and debris. The banks are also surrounded by Lush evergreen forest vegetation with different species of trees, shrubs and grasses.

The river ecology is under threat from human activities. Human activities such as farming on the adjoining lands, aquaculture and artisanal fisheries have created some ecological impacts in the river. However, Calabar is growing, due in part to the Calabar Free Trade Zone, that has resulted in the reclamation of the mangroves swamps of Great Qua river, for construction of housing estates and factories.(Okorafor et al.,2015)

The Great Qua River runs through farmlands, industrial, commercial and recreational areas such as Obufa Esuk, Esuk Atu, Calabar Free Trade Zone, Teaching Hospital, University of Calabar, Satellite Town and Peri-urban areas before it finally enters Calabar Estuary (Fig 1.0). Calabar Municipality has no waste treatment facilities, and heavy rains wash human and industrial wastes into the river.

3.2 SOURCE AND SAMPLING LOCATIONS

Station 1: This station is located at Esuk Ekpo Eyo Community. It situates between longitude $E8^0$ 23’ 23.6 and latitude $N4^0$ 56’ 53.5. The water in this station is highly turbid. There are grasses along the bank of the river at this station. The major human activities in this station include, boat building and sand mining.

Station 2: This station is located at Esuk Atu. It situates between longitude $E8^0$ 21’ 50.6 and latitude $N4^0$ 57’ 19.9. The bed of the River at this station is covered by smooth sand and mud. The water at this station is turbid. The vegetation here includes palm trees, fan palm and elephant grasses. Human activities here are mainly fishing and small scale farming.

Station 3: This station is located behind Cross River University of Technology (CRUTECH). It situates between longitude $E8^0$ 32' 83.1 and latitude $N4^0$ 95' 46.3. The river bed at this station is covered by mud and the water is highly turbid. Vegetation here includes fan palm and grasses. The major human activity here is small scale farming.

The distance between station one and station two is about 3.8km and about 3.3km from station two to station three. Therefore a total distance of about 7.1km was covered along the length of the Great Qua River. The distance between station three and the control site is about 6km.

Control samples: Control sample a pond at Aqua Vista Farms and Resort located at No 1 Mesembe Close, Anantigha Village, Calabar, Cross River State, Nigeria.

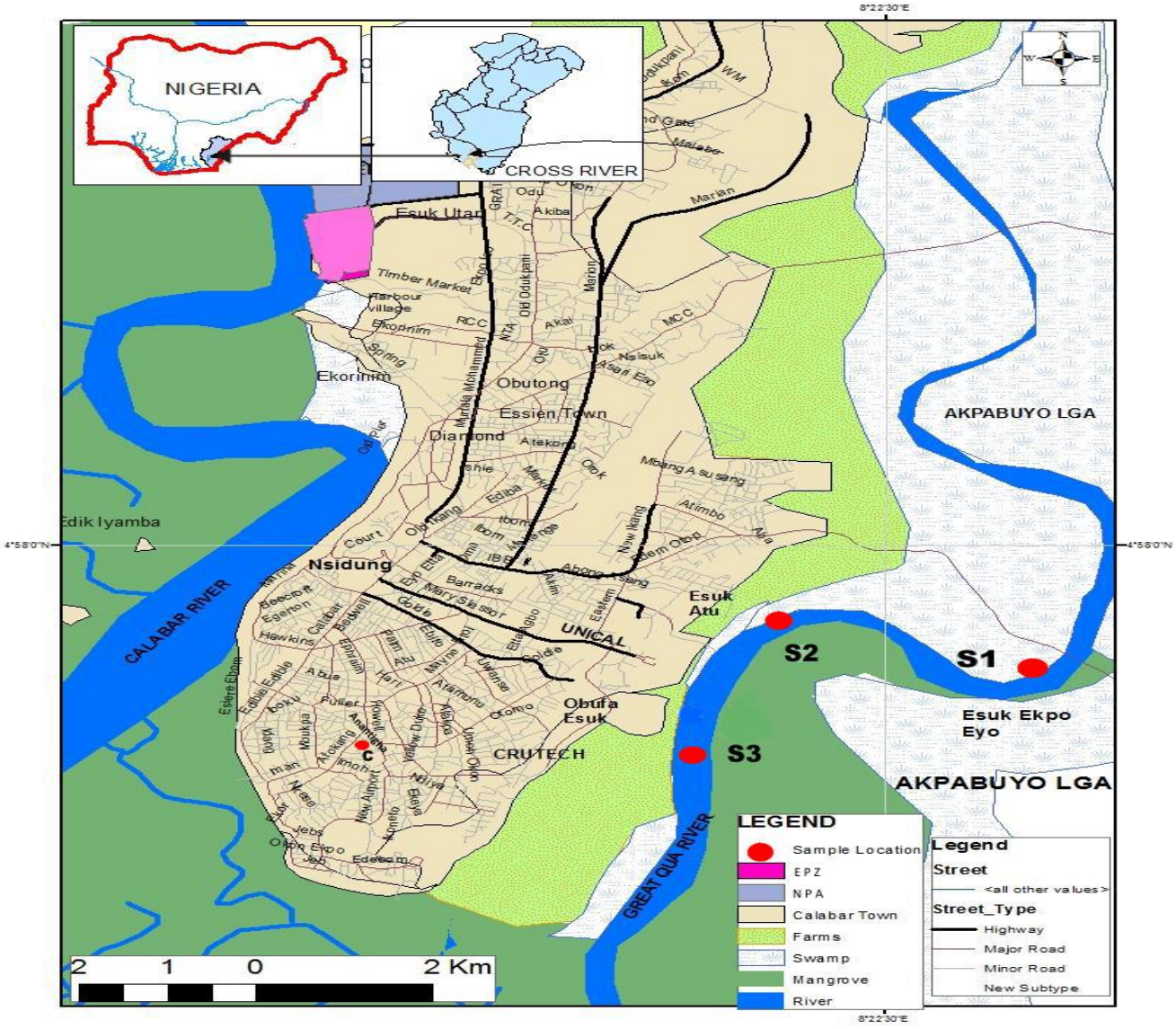

Figure 1.0: The map above shows the study area and the sampling location.

3.3 SAMPLES COLLECTION

Water, sediment and aquatic species (fish, prawn and periwinkle) were collected from three designated stations of the Great Qua River between the months of September to November.

The water samples for heavy metal analysis were collected in sterile one liter plastic bottles with screw-capped covers while that for THC analysis were collected in a clean glass bottle. The sample bottle was plunged neck downward 15cm below the water surface and about 12 feet from the bank of the river. When full, the bottle was brought rapidly above the water surface and immediately covered. Triplicate samples were collected from each site.

The sediment sample was collected from each of locations at the river bottom carefully into a polyethene bag. Aquatic species samples i.e prawn (*Macrobrachium macrobrachion*), periwinkle (*Typanotonus fuscatus*) and emerald shiner fish (*Notropis atherinoides*) were bought from local fishermen working at each of the sampling locations of the river. The aquatic species samples were rinsed with the water from the river to remove debris before it was bagged.

All samples collected were labeled accordingly and placed in a cooler containing ice block and was transported to the laboratory for analysis.

3.4 PROCEDURE FOR SAMPLE ANALYSIS

3.4.1 PRINCIPLE OF HEAVY METAL ANALYSIS USING ATOMIC ABSORPTION SPECTROPHOTOMETER (AAS)

Metals in water, sediment and biological samples are usually determined using Atomic Absorption Spectrophotometer. The sample is first aspirated into the flame or electro thermal device where it is vaporized and atomized, ration of the proper wavelength is then passed through

the ground state atoms of the metals where absorption occurs. The magnitude of the AAS signal is directly proportional to the concentration of the analyte metal in the sample solution.

3.4.2 PREPARATION OF SAMPLES FOR HEAVY METAL DETERMINATION

The water samples, obtained from the river were filtered through a 0.45µm micropore membrane filter and kept at 4^0 C until analysis. The water samples were analyzed directly.

The periwinkles were first de-shelled. All aquatic species were dried in an oven at a temperature of 80^{0C} for 4 hours. The dried samples were then ground in an acid proof ceramic mortar and pistil to very fine particles. The sediment sample was air dried for 7 days before it was powdered using the acid proof mortar and pistil into fine particles and was later passed through 160µm sieve. The samples were packed in polyethylene bags and stored at -20^0C to preserve the analyte prior to analysis.

To a round bottom flask containing 1g of each samples, 20ml of nitric acid and 10ml of perchloric acid were added and then placed in a heating mantle inside a fume cupboard until the samples were broken down which was observed through the reduced volume and clarity of the solution. After cooling the digested samples were transferred to a 100ml standard volumetric flask and were filled up to the mark with distilled water. A blank was also prepared along the digested samples. The blank contains 20ml of nitric acid and 10ml of perchloric acid. This was also heated along the samples been digested. At the end of the digestion process, the volume was made up to 100ml mark in a volumetric flask. The digested samples were transferred to sample bottles and were labeled accordingly. Procedural blank was aspirated along with the analytical samples in other to correct for background absorption. The total metal (Cr, Cd, Mn, Ni, Cu, Pb, Zn, and Fe) concentration of the samples were determined using the desired hallow cathode lamp in Bulk Scientific Atomic Absorption Spectrophotometer model 200A.

3.4.3 PREPARATION OF STANDARD SOLUTIONS FOR HEAVY METAL DETERMINATION

3.4.3.1 DETERMINATION OF COPPER

A stock solution containing 100mg/ml of Cu^{2+} ions was prepared by dissolving 2.682g of $CuCl_2.2H_2O$ in de-ionized water and finally diluted to 100ml. Standard solutions of concentration 0.0, 0.5, 1.0, and 2.0ppm were prepared from this stock solution.

3.4.3.2 DETERMINATION OF ZINC

A stock containing 100mg/l of zinc ion was prepared by dissolving 1.0g of zinc ribbon in 10ml of concentrated HCL. The solution was evaporated almost to dryness and the salt was redissolved in 100ml of de-ionized water, standard solution of concentration 0.0, 0.5, 1.0, and 1.5ppm were prepared from this stock solution.

3.4.3.3 DETERMINATION OF IRON

A stock solution containing 100mg/ml of Fe^{3+} ions was prepared from 1.0g of pure iron wire. The wire was dissolved in10ml conc.HNO_3 boiled in a water bath and diluted to 100ml with distilled water. From this stock solution, standard solutions of concentration 0.0, 0.5, 1.0, 2.0 and 4.0ppm were prepared.

3.4.3.4 DETERMINATION OF NICKEL

A stock solution containing 100mg/ml of nickel ions was prepared by dissolving 1.0g of nickel metal in 10 ml of HNO_3 (conc.) and was diluted to 1L with distilled water. From this stock solution, standard solution of concentration 0.0, 0.5, 1.0, 1.5 and 2.0ppm were prepared.

3.4.3.5 DETERMINATION OF MANGANESE

A stock solution of 100mg/ml of manganese ion was prepared by dissolving 1.0g of manganese metal in 10 ml of redistilled HNO_3 (conc.) and diluted to 1L with distilled water. From this stock solution, standard solution of concentration 0.0, 0.5, 1.0, 1.5 and 2.0ppm were prepared.

3.4.3.6 DETERMINATION OF LEAD

A stock solution of 100mg/ml of Pb^{2+} ion was prepared by dissolving lead nitrate, $Pb(NO_3)_2$, in distilled water. It was then acidified with 10 ml of redistilled HNO_3 and dilute to 1L with distilled water. From this stock solution, standard solution of concentration 0.0, 0.5, 1.0, 1.5, and 2.0ppm were prepared.

3.4.3.7 DETERMINATION OF CHROMIUM

A stock solution of 100mg/ml of Cr^{2+} was prepared by dissolving 1.923g of chromium trioxide, CrO_3, in distilled water and was acidified to pH 2 with redistilled HNO_3 (conc.), and was diluted to 1L with distilled water. From this stock solution, a standard concentration of 0.0, 0.5, 1.0, 1.5 and 2.0ppm were prepared.

3.4.3.8 DETERMINATION OF CADMIUM

A stock solution of 100mg/ml was prepared by dissolving 1.0g of cadmium metal in 20ml of 1:1HNO_3 and was diluted to 1L with distilled water. From this stock solution, standard solution of concentration 0.0, 0.5, 1.0, 1.5, and 2.0 were prepared.

Calibration curve were prepared for each element using standard solution. The appropriate lamps and correct wavelength for each element used for the analysis is tabulated below.

WAVELENGTHS OF HEAVY METALS ANALYSED

ELEMENT	WAVELENGTH (nm)
COPPER	324.7
ZINC	213.9
1RON	248.3
LEAD	283.3
CADMIUM	228.8
CHROMIUM	357.9
MANGANESE	279.5
NICKEL	232.0

3.4.4 DETERMINATION OF TOTAL HYDROCARBON CONTENT (THC) BY UV-VIS SPECTROPHOTOMETRIC INSTRUMENTAL METHOD

3.4.4.1 PRINCIPLE OF ANALYSIS

Determination of THC is frequently necessary as a measure of oil carry-over in a sample. The sample is extracted with the appropriate organic solvent and the transmittance of the organic solvent extract is measured with a photometer. The photometer reading is converted to concentration (ppm or mg/l) by reference to a calibrated curve, which is prepared using crude oil.

3.4.4.2 DETERMINATION OF TOTAL HYDROCARBON CONTENT IN SEDIMENT, FISH, PRAWN AND PERINWINKLE

5g of the grounded samples was weighed into a 100ml beaker. 25ml of n-Hexane was added to the sediment contained in the 100ml beaker. This was transferred to an orbital shaker

were it was shake for 10minutes. At the expiration of 10 minutes, it was left to stand covered. It was then filtered and the filtrate was read at a wavelength of 460nm.

The standard stock 1000ppm was prepared from Forcados Blend Crude Oil. 1.18ml of Forcados Blend Crude Oil was pipette into a volumetric flask and was made up to 1000ml with n-Hexane. From the standard stock, 0, 10, 20, 40, 60, 80, and 100ppm working standards was prepared.

The formula below was employed in calculating the concentration of THC in the sediment sample.

$$\text{THC (ppm)} = \frac{\text{Absorbance} \times \text{Slope Reciprocal} \times 25}{5\text{g}}$$

3.4.3 DETERMINATION OF TOTAL HYDROCARBON CONTENT IN WATER

50ml of the water sample was measured into a 250ml separating funnel using a measuring cylinder. This was followed by adding 10ml of Hexane and was shaken for 2 minutes manually. The stopper was removed after shaking and was allowed to settle for 20 minutes. At the expiration of 20 minutes, two layers were observed the water layer and hexane layer.

The water layer was drained off while the hexane layer was collected and was read at a wavelength of 460nm.

The standard stock 1000ppm was prepared from Forcados Blend Crude Oil. 1.18ml of Forcados Blend Crude Oil was pipette into a volumetric flask and was made up to 1000ml with n-Hexane. From the standard stock, 0, 10, 20, 40, 60, 80, and 100ppm working standards was prepared.

The formula below was employed in calculating the concentration of THC in the sediment sample.

$$\text{THC (mg/l)} = \text{Absorbance} \times \text{Slope Reciprocal} \times 25 \times 20$$

Note: Hexane was use as the blank.

3.4.5 DETERMINATION OF ELECTRICAL CONDUCTIVITY

The conductivity meter cell was rinsed with 25ml the water sample. This was followed by adjusting the temperature to 25^0C. The sample conductivity was measured and the temperature was noted.

3.4.6 DETERMINATION OF DISSOLVE OXYGEN

The water sample was first, transferred to a BOD bottle. 2ml of $MnSO_4$ reagent was added to the sample using a dropper. Also, 2ml of sodium Azide solution was added followed by the addition of 2ml of KI. In each case the tip of the pipette was 2-5cm below the neck of the bottle so that the 2ml quantities are discharged directly into the bulk of the contents. The stopper was placed in the bottle while I ensured that no air was trapped in it. This was followed by inverting the bottle to distribute the precipitate uniformly. When the precipitate was settled for about 3cm below the stopper, 1ml of conc. H_2SO_4 was introduced on the surface until the precipitate dissolves. This was followed by measuring exactly 200ml of the acidified sample into a 500ml conical flask. It was then titrated with 0.025N $Na_2S_2O_3.5H_2O$ until the iodine colour becomes faint. Then 5ml of starch indicator was introduced and the titration was completed.

3.4.7 DETERMINATION OF PH

The PH meter was first standardize using buffer PH 4 and 7. The PH determination was made immediately after opening the sample by immersing the electrode in the sample and the PH read.

3.4.8 DETERMINATION OF TEMPERATURE

The thermometer was dipped into the water sample for five minutes. The temperature was then read on the scale in centigrade.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 RESULTS

TABLE 4.1.1: Mean Heavy Metal Concentration in Water Sample

SITE	Cr (mg/l)	Cd (mg/l)	Mn (mg/l)	Ni (mg/l)	Cu (mg/l)	Pb (mg/l)	Zn (mg/l)	Fe (mg/l)

S1	0.012±0.06^{bc}	0.033±0.06^{a}	0.071±0.06^{a}	0.083±0.01^{a}	0.092±0.06^{b}	0.054±0.06^{c}	0.041±0.06^{b}	0.048±0.029^{c}
S2	0.024±0.12^{b}	0.017±0.06^{a}	0.069±0.06^{ab}	0.013±0.06^{b}	0.086±0.06^{b}	0.081±0.06^{a}	0.022±0.06^{c}	0.082±0.06^{a}
S3	0.087±0.06^{a}	0.316±0.41^{a}	0.067±0.02^{b}	0.016±0.06^{b}	0.113±0.06^{a}	0.064±0.12^{b}	0.098±0.06^{a}	0.062±0.06^{b}
S4	0.007±0.15^{c}	0.001±0.01^{a}	0.006±0.01^{c}	0.002±0.02^{c}	0.0008±0.03^{c}	0.0001±0.01^{d}	0.003±0.02^{d}	0.001±0.0^{d}

Values represent Mean±StDev on the same column with different letters differ significantly.

Where:

SI = Station located at Esuk Ekpo Eyo Community.

S2 = Station located at Esuk Atu.

S3 = Station located behind Crutech,

S4 = Control

Table 4.1.1 shows the heavy metal concentrations of the water sample obtain from the Great Qua River.

Chromium metal (Cr) in the water sample had the highest concentration in station three (0.087 ± 0.06 mg/l) and the lowest concentration was recorded at station one (0.012 ± 0.06 mg/l). There was a significant difference in value between concentration value recorded from the different station and control. ($P<0.05$)

The highest concentration of cadmium (Cd) in water sample was recorded at station three (0.316 ± 0.41 mg/l) and the lowest concentration was recorded in station two (0.017 ± 0.00 mg/l). There was no significant difference in value between values recorded at the different sampling station and control. ($P>0.05$)

The concentration of manganese (Mn) in water sample had the highest concentration in station one (0.071 ± 0.06 mg/l) with the lowest concentration recorded at station three (0.067 ± 0.02 mg/l). There was a significant difference in value between values recorded at the different sampling station when compared with control. ($P<0.05$)

Nickel (Ni) had the highest concentration value at station one (0.083 ± 0.01 mg/l) with the lowest concentration value recorded at station two (0.013 ± 0.06 mg/l). There was no difference ($P>0.05$) in value between station two and three but there was a significant difference between values recorded at the different sampling station when compared with control.

Copper (Cu) had the highest concentration value at station three (0.113 ± 0.06 mg/l) and the lowest concentration recorded at station two (0.086 ± 0.06 mg/l). There was a significant difference between the concentration values recorded at different sampling station and control. ($P<0.05$)

Lead (Pb) had the highest concentration at station two (0.081 ± 0.06 mg/l) with the lowest concentration value recorded at station one (0.054 ± 0.06mg/l). there was a significant difference between the concentration values recorded and at the different sampling station and control. ($P<0.05$)

The concentration of Zinc (Zn) in the water sample had the highest concentration at station three (0.098 ± 0.06 mg/l) with the lowest concentration value recorded at station two (0.022 ± 0.06 mg/l). There was a significant difference in value between the concentration value recorded at the different sampling station and control. ($P<0.05$)

The concentration of iron (Fe) in the water sample had the highest concentration value at station two (0.082 ± 0.06 mg/l) with the lowest value recorded at station one (0.048 ± 0.03 mg/l). There was a significant difference in value between the concentration values recorded at the different sampling station and control. ($P<0.05$)

TABLE 4.1.2: Mean Heavy Metal Concentration in Sediment

SITE	Cr (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
S1	0.127±0.06[b]	0.152±0.06[c]	0.096±0.06[c]	0.512±0.06[b]	0.513±0.06[b]	0.093±0.06[a]	0.179±0.06[a]	0.150±0.06[a]
S2	0.053±0.06[c]	0.174±0.06[b]	0.121±0.06[b]	0.112±0.06[c]	0.167±0.06[a]	0.087±0.01[b]	0.121±0.06[c]	0.377±0.35[a]
S3	0.193±0.06[a]	0.188±0.06[a]	0.185±0.06[a]	0.782±0.06[a]	0.145±0.06[c]	0.075±0.06[c]	0.164±0.06[b]	0.201±0.06[a]
S4	0.002±0.03[d]	0.004±0.02[d]	0.009±0.06[d]	0.005±0.0[d]	0.003±0.04[d]	0.000±0.00[d]	0.001±0.02[d]	0.006±0.06[a]

Values represent Mean±StDev on the same column with different letters differ significantly.

Where:

SI = Station located at Esuk Ekpo Eyo Community.

S2 = Station located at Esuk Atu.

S3 = Station located behind Crutech

S4 = Control

Table 4.1.2 shows the concentrations of heavy metals in sediment obtained from the Great Qua River.

The concentration of chromium (Cr) in sediment had the highest concentration value at station three (0.193 ± 0.06 mg/kg) with the lowest value recorded at station two (0.053 ± 0.01 mg/kg). There was a significant difference in value between the concentration values recorded at the different sampling stations and control. ($P<0.05$)

The cadmium (Cd) concentration in sediment had the highest value at station three (0.188 ± 0.06 mg/kg with the lowest value recorded at station one (0.152 ± 0.06 mg/kg).There was a significant difference in value at the different sampling stations and control. ($P<0.05$)

The manganese (Mn) in the sediment had the highest concentration value at station three (0.188 ± 0.06 mg/kg) with the lowest concentration value recorded at station one (0.096 ± 0.06 mg/kg). There was a significant difference in value between the concentration value recorded at the different sampling stations and control. ($P<0.05$)

The highest concentration of nickel (Ni) in sediment was at station three (0.782 ± 0.06 mg/kg) with the lowest concentration recorded at station two (0.112 ± 0.06 mg/l). The value of nickel significantly differed with that of control. ($P<0.05$)

The highest concentration of copper (Cu) in sediment was at station two (0.167 ± 0.06 mg/kg) with the lowest concentration recorded at station three (0.145 ± 0.06 mg/kg). The value of copper differed significantly with that of control. ($P<0.05$)

Lead (Pb) in the sediment had the highest concentration at station one (0.093 ± 0.06 mg/kg) with the lowest value at station three (0.075 ± 0.06 mg/kg). The value of lead differed significantly with that of control. ($P<0.05$)

The highest concentration of zinc was recorded at station one (0.179 ± 0.06 mg/kg) with the lowest concentration at station two (0.121 ± 0.06 mg/kg). The value of zinc differed significantly with that of control. ($P<0.05$)

The highest concentration of iron (Fe) in the sediment was at station two (0.377 ± 0.35 mg/kg) with the lowest concentration recorded at station one (0.150 ± 0.06 mg/kg). There was a significant difference in value at the different sampling stations and control. ($P<0.05$)

4.1.3 HEAVY METAL CONCENTRATION IN PRAWN (*Macrobrachium macrobrachion*)

TABLE 4.1.3

SITE	Cr (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
S1	0.013 ± 0.02^{a}	0.043 ± 0.06^{c}	0.015 ± 0.03^{c}	0.015 ± 0.06^{b}	0.113 ± 0.06^{c}	0.108 ± 0.06^{a}	0.201 ± 0.06^{c}	0.142 ± 0.06^{b}
S2	0.012 ± 0.06^{a}	0.562 ± 0.06^{b}	0.221 ± 0.06^{b}	0.014 ± 0.06^{c}	0.275 ± 0.06^{a}	0.042 ± 0.06^{c}	0.321 ± 0.06^{b}	0.127 ± 0.06^{c}
S3	0.019 ± 0.06^{a}	0.681 ± 0.06^{a}	0.314 ± 0.06^{a}	0.073 ± 0.06^{a}	0.262 ± 0.06^{b}	0.068 ± 0.06^{b}	0.369 ± 0.06^{a}	0.166 ± 0.06^{a}
S4	0.0007 ± 0.01^{a}	0.0007 ± 0.06^{d}	0.0007 ± 0.01^{d}	0.001 ± 0.01^{d}	0.0007 ± 0.06^{d}	0.0003 ± 0.06^{d}	0.001 ± 0.06^{d}	0.002 ± 0.06^{d}

Values represent Mean±StDev on the same column with different letters differ significantly.

Where:

SI = Station located at Esuk Ekpo Eyo Community.

S2 = Station located at Esuk Atu.

S3 = Station located behind Crutech

S4 = Control

Table 4.1.3 shows the concentrations of heavy metals in prawn (*macrobrachium macrobrachion)* obtained from the Great Qua River.

The highest concentration of chromium (Cr) in the prawn sample obtained from the river was recorded at station three (0.019 ± 0.06 mg/kg) with the lowest value at station two (0.012 ± 0.06 mg/kg). There was no significant difference in value at the different sampling station and control. ($P<0.05$)

The highest concentration of cadmium (Cd) in the prawn sample obtained from the river was recorded at station three (0.681 ± 0.06 mg/kg) with the lowest concentration value recorded at station one (0.043 ± 0.06 mg/kg). There was a significant difference in value when values from different sampling station were compared with control. ($P<0.05$)

The highest concentration of manganese (Mn) in the prawn sample was recorded at station three (0.314 ± 0.06 mg/kg) with the lowest value recorded at station one (0.015 ± 0.03 mg/kg). There was a significant difference in value between count recorded at the different sampling station and control. ($P<0.05$)

The highest concentration of manganese (Ni) was recorded at station three (0.073 ± 0.06 mg/kg) with the lowest value recorded at station two (0.014 ± 0.06 mg/kg). There was a significant difference in value between concentration value recorded at different sampling station and control. ($P<0.05$)

The highest concentration of copper (Cu) in prawn was recorded at station two (0.275 ± 0.06 mg/kg) with the lowest concentration recorded at station one (0.113 ± 0.06 mg/kg). There was a significant difference in value between concentration value recorded at different sampling station and control. ($P<0.05$)

The highest concentration of lead (Pb) in prawn was recorded at station one (0.108 ± 0.06 mg/kg) with the lowest concentration value recorded at station two (0.042 ± 0.06 mg/kg). There was a significant difference in value at the different sampling stations and control. ($P<0.05$)

The highest concentration of zinc (zn) in prawn was recorded at station three (0.368 ± 0.06 mg/kg) with the lowest concentration value recorded at station one (0.201 ± 0.06 mg/kg) There was a significant difference in value at the different sampling stations when compared to control. ($P<0.05$)

The highest concentration of iron (Fe) in prawn was recorded at station three (0.166 ± 0.06 mg/kg) with the lowest concentration value recorded at station two (0.127 ± 0.06 mg/kg). There was a significant difference in value at the different sampling stations when compared with control. ($P<0.05$)

TABLE 4.1.4: Mean Heavy Metal Concentration in Periwinkle (*Typanotonus fuscatus*)

SITE	Cr (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
S1	0.057 ± 0.06^{C}	0.049 ± 0.06^{bC}	0.177 ± 0.06^{b}	0.183 ± 0.6^{C}	0.155 ± 0.06^{b}	0.145 ± 0.06^{b}	0.217 ± 0.06^{a}	0.163 ± 0.12^{a}
S2	0.092 ± 0.06^{b}	0.103 ± 0.06^{ab}	0.241 ± 0.06^{a}	0.194 ± 0.06^{b}	0.179 ± 0.06^{a}	0.144 ± 0.06^{b}	0.106 ± 0.06^{c}	0.195 ± 0.06^{a}
S3	0.120 ± 0.06^{a}	0.169 ± 0.06^{a}	0.163 ± 0.01^{c}	0.215 ± 0.06^{a}	0.146 ± 0.06^{c}	0.147 ± 0.06^{a}	0.124 ± 0.06^{b}	0.247 ± 0.06^{a}
S4	0.001 ± 0.00^{d}	0.0007 ± 0.06^{c}	0.0003 ± 0.06^{d}	0.0002 ± 0.06^{d}	0.0003 ± 0.06^{d}	0.0003 ± 0.06^{c}	0.0003 ± 0.06^{d}	1.34 ± 2.31^{a}

Values represent Mean±StDev on the same column with different letters differ significantly.

Where:

SI = Station located at Esuk Ekpo Eyo Community.

S2 = Station located at Esuk Atu.

S3 = Station located behind Crutech

S4 = Control

Table 4.1.4 shows the mean heavy metal concentrations in periwinkle (*Typanotonus fuscatus*) obtain from the Great Qua River.

The highest concentration of chromium (Cr) in periwinkle was recorded at station three (0.120 ± 0.06 mg/kg) with the lowest concentration recorded at station one (0.057 ± 0.06 mg/kg) there was a significant difference in value between the different sampling stations and control. ($P<0.05$)

The highest concentration of cadmium (Cd) was recorded at station three (0.169 ± 0.06 mg/kg) with the lowest value recorded at station one (0.049 ± 0.06). There was a significant difference in value between the values obtain at the different sampling stations and control. ($P<0.05$)

The highest concentration of manganese (Mn) was recorded at station two (0.241 ± 0.06 mg/kg) with the lowest value recorded at station three (0.163 ± 0.01 mg/kg). There was a significant difference between the values obtain at the different sampling stations and control ($P<0.05$)

The highest concentration of nickel (Ni) was recorded at station three (0.215 ± 0.06 mg/kg) with the lowest value recorded at station one (0.183 ± 0.006 mg/kg). There was a significant difference between the values obtained at different sampling stations and control. ($P<0.05$)

The highest concentration of copper (Cu) was recorded at station two (0.179 ± 0.06 mg/kg) with the lowest value recorded at station three (0.146 ± 0.06 mg/kg). There was significant difference in value between the values recorded at the different sampling stations and control. ($P<0.05$)

The highest concentration of lead (Pb) was recorded at station three (0.147 ± 0.06 mg/kg) with the lowest concentration value recorded at station one and two (0.145 ± 0.06 mg/kg) (0.144 ± 0.06 mg/kg) respectively. There was a significant difference in value between the values recorded at the different sampling stations and control. ($P<0.05$)

The highest concentration of zinc (Zn) was recorded at station one (0.217 ± 0.06 mg/kg) with the lowest concentration value recorded at station two (0.106 ± 0.06 mg/kg). There was a significant difference in value between the values recorded at different sampling stations and control. ($P<0.05$)

The highest concentration of iron (Fe) was recorded at station three (0.247 ± 0.06 mg/kg) with the lowest concentration recorded at station one (0.163 ± 0.121 mg/kg). There was no significant difference in value between the values recorded at different sampling stations and control. (P>0.05)

TABLE 4.1.5: Mean Heavy Metal Concentration in Emerald Shiner Fish *(Notropis atherinoides)*

SITE	Cr (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
S1	0.098±0.06^{b}	0.133±0.06^{C}	0.094±0.06^{b}	0.062±0.06^{b}	0.129±0.06^{a}	0.138±0.06^{b}	0.207±0.06^{a}	0.337±0.06^{a}
S2	0.011±0.06^{c}	0.442±0.06^{b}	0.195±0.06^{a}	0.029±0.06^{c}	0.122±0.06^{b}	0.141±0.06^{b}	0.123±0.06^{c}	0.111±0.06^{c}
S3	0.137±0.06^{a}	0.86±0.06^{a}	0.082±0.06^{c}	0.267±0.06^{a}	0.106±0.06^{c}	0.203±0.06^{a}	0.185±0.06^{b}	0.129±0.06^{b}
S4	0.01±0.06^{d}	0.0003±0.06^{d}	0.003±0.06^{d}	0.000±0.06^{d}	0.0007±0.06^{d}	0.0003±0.06^{c}	0.0007±0.06^{d}	0.001±0.01^{d}

Values represent Mean±StDev on the same column with different letters differ significantly.

Where:

SI = Station located at Esuk Ekpo Eyo Community.

S2 = Station located at Esuk Atu.

S3 = Station located behind Crutech

S4 = Control

Table 4.1.5 shows the mean heavy metal concentration in *Notropis atherinoides* obtained from the Great Qua River.

The highest concentration of chromium (Cr) in the emerald shiner fish was recorded at station three (0.137 ± 0.06 mg/kg) with the lowest value recorded at station two (0.011 ± 0.06 mg/kg).

There was a significant difference in value between the concentration values recorded at different sampling station and control. ($P<0.05$)

Station three had the highest concentration of cadmium (Cd) in *N. atherinoides* (0.86 ± 0.06 mg/kg) with the lowest value recorded at station one (0.133 ± 0.0006 mg/kg). There was a significant difference in value between values obtain from the different sampling stations and control. ($P<0.05$)

Station two had the highest concentration of manganese (Mn) in *N. atherinoides* (0.195 ± 0.06 mg/kg) with the lowest value recorded at station three (0.082 ± 0.06 mg/kg). There was a significant difference in value between the concentration value recorded from the different sampling stations and control. ($P<0.05$)

The highest concentration of nickel (Ni) in *N. atherinoides* was recorded at station three (0.267 ± 0.06 mg/kg) with the lowest concentration recorded at station two (0.029 ± 0.06 mg/kg). There was a significant diference in value between values recorded at the different sampling stations and control. ($P<0.05$)

The highest concentration of copper (Cu) in *N. atherinoides* was recorded at station one (0.129 ± 0.06 mg/kg) with the lowest concentration value recorded at station three (0.106 ± 0.06 mg/kg). There was a significant difference in value between values recorded at the different sampling stations and control. ($P<0.05$)

The highest concentration of lead (Pb) in *N. atherinoides* was recorded at station three (0.203 ± 0.06 mg/kg) with the lowest concentration value recorded at station two and one (0.141 ± 0.06 mg/kg) (0.138 ± 0.06 mg/kg).there was no difference in value between station one and two but there was a significant difference in value between values from different sampling stations and control, ($P<0.05$)

The highest concentration of zinc (Zn) in *N. atherinoides* was recorded at station one (0.207 ± 0.06 mg/kg) with the lowest value recorded at station two (0.123 ± 0.06 mg/kg). There was a significant difference in value between the concentration values recorded at the different sampling stations and control. (P<0.05)

The highest concentration of iron (Fe) in *N. atherinoides* was recorded at station one (0.337 ± 0.06 mg/kg) with the lowest concentration recorded at station two (0.111 ± 0.06 mg/kg). There was a significant difference in value between the concentration value recorded at different sampling stations and control. (P<0.05)

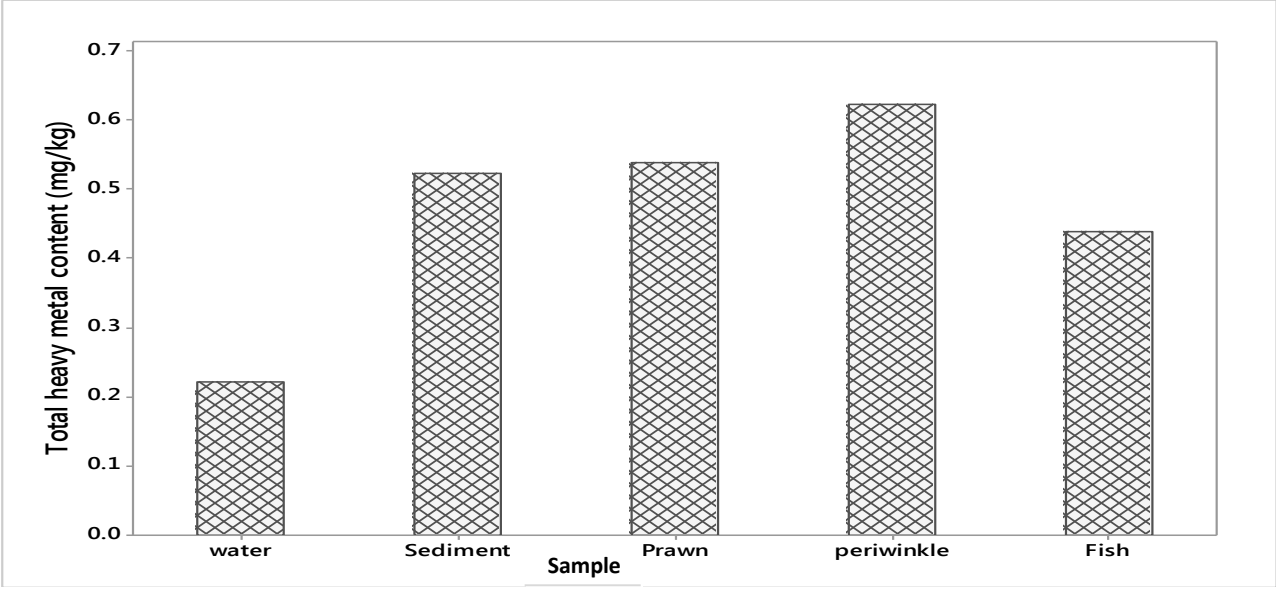

Figure2: shows the total heavy metal concentration in water, sediment, prawn, periwinkle and emerald shiner fish.

From the graph it can be deduce that periwinkle had the highest concentration of heavy metals followed by prawn, sediment, fish and water respectively.

TABLE 4.1.6: Mean Total Hydrocabon Concentartion in Water, Sediment, Emerald Shiner Fish, Prawn and Periwinkle

SITE	WATER (mg/l)	SEDIMENT (mg/kg)	PRAWN (mg/kg)	FISH (mg/kg)	PERIWINKLE (mg/kg)
S1	0.245±0.06[b]	0.466±0.06[b]	0.118±0.06[b]	0.273±0.06[b]	0.134±0.06[b]
S2	0.215±0.06[C]	0.379±0.06[C]	0.106±0.06[C]	0.271±0.06[b]	0.142±0.06[c]
S3	0.395±0.06[a]	0.481±0.06[a]	0.167±0.06[a]	0.288±0.06[a]	0.157±0.06[a]
S4	0.001±0.06[d]	0.007±0.06[a]	0.004±0.06[d]	0.0063±0.06[c]	0.002±0.06[a]
TOTAL MEAN	0.856±0.02	1.333±0.02	0.395±0.02	0.838±0.02	0.435±0.02

Values represent Mean±StDev on the same column with different letters differ significantly.

Where:

SI = Station located at Esuk Ekpo Eyo Community.

S2 = Station located at Esuk Atu.

S3 = Station located behind Crutech

S4 = Control

Table 4.1.6 shows the Total hydrocarbon content in water, sediment and aquatic biota obtained from the Great Qua River.

The highest concentration in of total hydrocarbon in water was recorded in station three (0.395 ± 0.0006 mg/l) with the lowest value recorded at station two (0.215 ± 0.0006 mg/l). There was a significant difference in values between values from the different sampling station and control. ($P<0.05$)

The highest concentration of THC in sediment was recorded at station three (0.481 ± 0.06 mg/kg) with the lowest concentration recorded at station two (0.379 ± 0.06 mg/kg). There was a significant difference in value between concentration recorded at the different sampling stations and control. ($P<0.05$)

The highest concentration of THC in *M.macrobrachion* was recorded at station three (0.167 ± 0.06 mg/kg) with the lowest value recorded at station two (0.106 ± 0.06 mg/kg). There was a significant difference in value between values from the different sampling stations and control. ($P<0.05$)

The highest concentration of THC in *N. atherinoides* had the highest concentration in station three (0.288 ± 0.06 mg/kg) with the lowest concentration recorded in station one and two (0.273 ± 0.06 mg/kg) (0.271 ± 0.06 mg/kg) respectively. There was a significant difference in value between the values obtained from the various sampling stations and control. ($P<0.05$)

The highest concentration of THC in *T. fuscatus* was recorded at station three (0.157 ± 0.06 mg/kg) with the lowest concentration value at station two (0.142 ± 0.06 mg/kg). There was a significant difference in value between the different sampling stations and control. ($P<0.05$)

Table 4.1.7: Correlation Matrix of Heavy Metals and Hydrocarbon Uptake By *Macrobrachium macrobrachion* (Prawn) and Physicochemical Properties of The Great Qua River

	Cr	**Cd**	**Mn**	**Ni**	**Cu**	**Pb**	**Zn**	**Fe**	**THC**
PH	-0.771	-0.535	-0.567	-0.978^{s}	-0.660	-0.860	-0.813	-0.957^{s}	-0.970^{s}
EC(µs/cm)	0.682	0.626	0.601	0.898	0.843	0.775	0.910	0.967^{s}	0.914
DO (mg/l)	-0.359	-0.900	-0.883	-0.884	-0.986^{s}	-0.482	-0.998^{s}	-0.897	-0.902
TEMP (^{o}C)	0.561	0.778	0.777	0.959^{s}	0.900	0.677	0.968^{s}	0.970^{s}	0.971^{s}

Where:

EC= Electrical conductivity, DO= Dissolve oxygen, TEMP= Temperature

Table 4.1.7 shows the correlation matrix of heavy metal and hydrocarbon uptake by *Macrobrachium macrobrachion* (prawn) and physicochemical properties of the Great Qua River. From the table there was a strong negative relationship between the uptake of Cr, Cu, Pb, and Zn metal by *M. macrobrachion* and the PH value of the water, r(95) = - 0.771, - 0.660, - 0.860 and – 0.813 respectively $P<0.05$. There was a moderate negative relationship between the uptake of Cd and Mn metal by *M. macrobrahion* and PH values in water, r (95) = -0.535 and – 0.567 respectively $P<0.05$. There was a perfect negative relationship between the uptake of total hydrocarbon and Fe by *M. macrobrachion* and PH value of the water, r (95) = -0.970 and – 0.957 respectively $P<0.05$.

A strong positive relationship was observed in the uptake of Cr, Cd, Mn, Ni, Cu, Pb, Zn and Total hydrocarbon by *M. macrobrachion* and the electrical conductivity of the water r (95) = 0.682,0.626,0.601, 0.898, 0.843,0.775,0.910 and 0.914 respectively $P<0.05$. Fe uptake by M. macrobrachion shows a perfect relationship with electrical conductivity r (95) = 0.967 $P<0.05$. the correlation between temperature and heavy metal/ THC shows that a perfect relationship exist between the uptake of Ni, Zn, Fe and THC by *M. macrobrachion* and temperature of the water r (95) = 0.959, 0.968, 0.970, 0.971 respectively $P<0.05$. That is to say, an increase in temperature leads to an increased uptake of Ni, Zn, Fe, and THC by *M.macrobrachion*. A strong relationship was observed for the uptake of Cr, Cd, Mn, Cu, and Pb by *M. macrobrachion* and temperature of the water r (95) = 0.561, 0.778, 0.900, and 0.677 respectively $P<0.05$.

Table 4.1.8: Correlation Matrix of Heavy Metals and Hydrocarbon Uptake By *Typanotonus fusctus* (Periwinkle) and Physicochemical Properties of The Great Qua River

	Cr	**Cd**	**Mn**	**Ni**	**Cu**	**Pb**	**Zn**	**Fe**	**THC**

PH	-0.822	-0.981[s]	-0.668	-0.902	-0.786	-0.885	-0.819	-0.955[s]	-0.970[s]
EC(µs/cm)	0.874	0.910	0.955[s]	0.989[s]	0.992[s]	0.998[s]	0.820	0.971[s]	0.914
DO (mg/l)	-0.989[s]	-0.881	-0.877	-0.936	-0.892	-0.894	-0.514	-0.866	-0.902
TEMP(ºC)	0.962[s]	0.962[s]	00.855	0.976[s]	0.909	0.946	0.686	0.952[s]	0.971[s]

Where :

EC= Electrical conductivity, DO= Dissolve oxygen, TEMP= Temperature

Table 4.1.8 shows the correlation matrix of heavy metal and hydrocarbon uptake by *Typanotonus fuscatus* (periwinkle) and physicochemical properties of the Great Qua River. From the table, a strong negative relationship exist between the uptake of Cr, Mn, Ni, Cu, Pb and Zn by *Typanotonus fuscatus* r (95) = - 0.822, - 0.668, -0.902, -0.786, - 0.885 and – 0.819 respectively $P<0.05$ and the PH of the water. Changes in PH lead to a decrease uptake of the heavy metals. The uptake of Mn, Ni, Cu, and Pb by *Typanotonus fuscatus* shows perfect relationship with electrical conductivity r (95) = 0.955, 0.989, 0.992, 0.998 and 0.971 respectively $P<0.05$. this means that an increase in Electrical conductivity had an influence on the increased uptake of the heavy metals. A strong relationship also exist between the uptake of Cr, Cd, Zn and THC r (95) = 0.874, 0.910, 0.820, and 0.914 respectively $P<0.05$ and the electrical conductivity of the water. A perfect negative relationship exists between the uptake of Cr, by *Typanotonus fuscatus* and dissolve oxygen (DO) r (95) = -0.989. This means that an increase in dissolve oxygen of the water, lead to a decrease uptake of Cr. A strong negative relationship was observed between the uptake of Cd, Mn, Ni, Cu, Pb, Fe, and THC by *Typanotonus fuscatus* and dissolve oxygen (DO). A moderate relationship was observed for Zn.

Cr, Cd, Ni, Fe, and THC uptake by *Typanotonus fuscatus* shows a perfect relationship with temperature r (95) =0.962, 0.962, 0.976, 0.952 and 0.971 respectively P<0.05. Mn, Cu, Pb and Zn uptake shows strong relationship with temperature of the water r (95) =0.855, 0.909, 0.946, 0.686 respectively P<0.05

Table 4.1.9: Correlation Matrix of Heavy Metals and Hydrocarbon Uptake By *Notropis atherinoides* (Emerald Shiner Fish) and Physicochemical Properties of The Great Qua River

	Cr	**Cd**	**Mn**	**Ni**	**Cu**	**Pb**	**Zn**	**Fe**	**THC**
PH	-0.892	-0.706	-0.385	-0.780	-0.825	-0.946	-0.964[s]	-0.654	-0.970[s]
EC(µs/cm)	0.678	0.627	0.800	0.467	0.988[s]	0.925	0.904	0.622	0.914
DO (mg/l)	-0.639	-0.869	-0.778	-0.629	-0.827	-0.936	-0.721	-0.241	-0.902
TEMP(ºC)	0.747	0.821	0.677	0.691	0.887	0.986[s]	0.864	0.451	0.971[s]

Where :

EC= Electrical conductivity, DO= Dissolve oxygen, TEMP= Temperature

From the table above there was a perfect negative correlation between Zn and THC uptake by *Notropis atherinoides* and the water PH r (95) = -0.964 and -0.970 respectively P<0.05. this means that a decrease uptake of Zn and total hydrocarbon is heavily dependent on increase change in PH.

All other heavy metals except Mn (which shows weak relationship) shows strong relationship with PH. Cu uptake by *Notropis atherinoides* shows strong relationship with electrical conductivity r (95) = 0.988. All other heavy metals analyzed had strong relationship with electrical conductivity. There was a strong relationship between *Notropis atherinoides* and dissolve oxygen. A perfect relationship exist between Pb, THC uptake by *Notropis atherinoides* and temperature r (95) = 0.986 and 0.971 respectively $P<0.05$. All other metal analysed showed strong relationship between uptake by *Notropis atherinoides* and temperature.

4.2 DISCUSSION

Aquatic ecosystems globally are polluted through anthropogenic activities with chemical pollutants from agricultural, domestic and industrial waste which finally finds its way into aquatic plants and animal through absorption. According to Omoregie et al., (2002), heavy metal pollution in aquatic ecosystem is an important environmental problem, since heavy metals are among some of the most dangerous toxicants that bioaccumulate in aquatic plant and animal tissue.

Chromium metal in water was detected in all stations sampled with the highest concentration recorded at station three. This could be attributed to the discharge of effluent from cement industry, municipal runoff containing chromium which finds its way into the water body. One of the activities around the stations sampled is antisanal farming, the presence of chromium in water could be attributed to leached chemicals from fertilizers and pesticides used by farmers who farms nearby the river. The presence of chromium in water could also be attributed to re-suspension of the chromium metal from sediment. It has been observed that anything that disturb the sea bed re-

suspend its content in water. Re-suspension of heavy metals can affect all aquatic animals both those in water and bottom dwelling animals exposed to toxic content.

Cadmium metal in water sample was detected in all stations. The presence of cadmium in water was insignificant when compared to control. Their presence could be attributed to other factor rather than anthropogenic. These factors could be natural factors such as rain fall and other precipitation. The values recorded, was slightly above the world health organization (WHO) acceptable limit for water bodies.

Manganese metal in water was also detected in all stations sampled. Their presence could be attributed to anthropogenic activities around the river such as the discharge of domestic waste water into the river. The presence of manganese could also be from sewage sludge disposal in that Calabar do not have a special waste treatment plant and as such, all waste effluent are directly discharge into the river.

Nickel was detected in all stations sampled with the highest concentration at station one. There was a significant difference across stations sampled. Nickel concentration at station one and two were below the WHO allowable limit. The presence of nickel in water could be attributed to runoff from nearby agricultural farms that uses fertilizers to support the growth of their agricultural produce. High values of Ni in station one was at variance to the work carried out by Akinyeye et al., (2011) in Alaro River in Ibadan, were levels of Ni reported was lower as compared to that obtained from this work. The differences in values could be attributed to differences in activities that take place in the river and the types of effluents it receives.

Copper metal was detected in all the stations sampled with the highest concentration recorded at station three. The value obtained in station one and two were slightly below the WHO acceptable limit of 0.1mg/l except in station three where values obtained was above the acceptable limit of

WHO. The high concentration value could be attributed to runoff from agricultural farms, municipal runoff containing copper and electrical waste etc.

The concentration of copper reported in this work was quite higher than that reported by Erahbor et al.,(2011) where the mean concentration of copper recorded in Ibiekuma stream was lower.

Lead metal was also detected in all sampling station. Station two had the highest concentration of lead. The presence of lead could be attributed to re-suspension of lead from sediment during fishing activities. It can also come from municipal runoff containing waste from mining and chemicals from paint industries. The lead concentration recorded in this study, was slightly above the WHO acceptable limit of 0.05mg/l. Results obtained here was above that recorded at Ibiekuma Stream where concentration of Pb ranges from 0.005-0.007mg/l (Erahbor et al.,2011)

Zinc metal was detected at all station sampled. There was variance in the concentration of the zinc metal in all the stations with the highest concentration recorded at station three. The presence of zinc metal in the water could be attributed to leached chemical from agricultural farms. These chemicals could come from pesticides and fungicides. Also the presence of zinc in the water could also arise from municipal runoff containing motor oil from zinc tanks which releases zinc compound on the road, wear car tire etc. the concentration of zinc was below the WHO acceptable limit of 3.0mg/l for water. Concentrations of zinc obtained here was below that recorded for Ibiekuma Stream where values recorded ranges from 0.93-1.11mg/l.

Iron metal was detected at all the stations sampled. Values obtained from the stations varied with the highest concentration recorded at station two. Though iron exist naturally in rivers, lakes and underground water, High levels of iron at this station could be attributed to anthropogenic sources such as discharge of effluents from industries (smelting industries) and corrosion of materials containing iron. The concentration of iron recorded in water was below the WHO acceptable limit

for water. The values obtained in this study, agrees with the study conducted by Ewa et al,(2013) where the concentrations of iron metal analysed was below WHO acceptable limit.

Generally, from the analysis, station three had the highest concentration of heavy metal contaminants in the water sample except Mn, Ni, Pb and Fe. The heavy metal concentration profile was in the order: Cd>Cu>Mn>Pb>Fe>Zn>Cr>Ni respectively.

The highest concentration of chromium in sediment was observed in station three. There was variance in the concentration amongst the station sampled. The presence of Cr in sediment could be attributed to the discharge of untreated effluents from cement industry, municipal runoff, leached chemicals from agricultural farms as a result of pesticide and fertilizer application. The concentration of Cr detected in this study, was at variance to that obtain from Elenchi Creek (Davis et al., 2006) where concentration of Cr (0.01) was far less than that obtained in this study. This could be attributed to different anthropogenic activities that take place in the river, geographical location and types of industries around. The Cr in the sediments exceeded the values obtained in water as observed by (Bower, 1979).

Cadmium concentration in sediment was in variance to values recorded in all the stations unlike in the water sample where there was no variation in values. The highest concentration of cadmium was recorded at station three. The high concentration of cadmium could be attributed to anthropogenic activities that take place in this location. The values recorded exceeded the WHO acceptable limit of 0.01mg/kg. The result obtained was in variance to the study conducted by Davis et al., (2006) in Elenchi Creek Niger Delta. Higher concentration which agrees with this study was reported in some streams and rivers around Akpabuyo LGA in Calabar (Barth et al., 2015)

Manganese concentration varies along stations sampled with the highest concentration recorded at station three. The presence of manganese could be attributed to the discharge of domestic and

industrial waste into the river. Activities at this station could also play a significant role. The concentration of Mn was below the WHO acceptable limit. The value obtained agrees with that conducted by Okorafor et al.,(2015).

Nickel metal varies across stations sampled. The highest value for Ni was at station three. Nickel presence could come from agricultural farms through chemical leaching, municipal runoff and discharge of Ni from industries that deals with nickel. High concentration values were recorded at all stations which exceeds the WHO acceptable limit of 0.02mg/kg. High concentration of Ni was also reported by okorafor et al., (2015).

Copper metal values vary across all the station sampled. The concentration of copper was high in all stations. The highest value recorded was at station two. The high concentration at this stations could be due to municipal runoff containing electrical waste, chemical leach from agricultural farms around the river etc. the values obtained, shows that the levels of copper metal was higher than the WHO acceptable limit.

The concentration of lead in sediment varies amongst all stations sampled. Highest lead concentration was recorded at station one. This could be attributed to the discharge of waste containing lead into the river, municipal runoff etc. the values obtained in station two and three exceeded the acceptable limit of WHO.

The concentration of zinc had the highest concentration in station three. The concentration varies amongst all station. The presence could be attributed to the discharge of zinc containing materials into the river. All concentrations within the stations were below WHO acceptable limit.

Iron concentration in all the three stations varied. All the stations except station two were below the WHO acceptable limit. The highest concentration of iron recorded at station two was slightly above the WHO acceptable limit. Their presence in sediment could arise from corrosion from

metal, municipal runoff, industrial effluents and through natural mean. The value obtained were far below the values obtained in River Annaba, Algeria where the average mean value were about 2400.80 mg/kg (Achour et al.2012).The total heavy metal concentration profile was in the order: Ni > Fe > Cd >Cu > Zn >Mn > Cr > Pb. This order of heavy metal profile in water varies from the order of heavy metal profile observed in water. From this study it was revealed that station three was more heavily polluted with heavy metal than other stations.

Heavy metals were detected in all aquatic biota (*Macrobrachium macrobrachion, typanotonus fuscatus and Notropis atherinoides*) used for this study. Chromium concentration in *M. macrobrachion* was not significant when compared to control samples. This indicates that the presence of Cr in *M. macrobrachion* could be attributed to the fact that *M.macrobrachion* must have develop an adaptive mechanism in avoiding the absorption of Cr from sediment.

Apart from Cr which shows insignificant difference in *M. macrobrachion*, all other heavy metals in the aquatic biota used for the study shows significant difference when compared to control. All heavy metals except Zn, Mn and Fe analysed in the aquatic biota slightly exceeded the WHO acceptable limit for food.

The presence of these heavy metals in the aquatic biota studied could be attributed to their feeding habit. While *T. fuscatus* and *M. macrobrachion* are deposit feeders, that is; they obtain their food from sediment; *N. atherinoides* obtain their food directly from water and even feed on smaller aquatic animals (Okorafor et al., 2015). This aquatic animal can with time bioaccumulate in the aquatic animals and becomes toxic to human who depends on them for food.

The heavy metal concentration profiles for the aquatic biota studied are as follows:

M. macrobrachion is in the order: Cd > Zn > Cu > Fe > Mn > Pb > Ni > Cr.,

T.fuscatus is in the order: Fe > Ni > Mn > Cu > Zn > Pb > Cd > Cr.,

N. atherinoides is in the order: Cd > Fe > Zn > Pb > Mn > Ni > Cu > Cr.

From the order of heavy metal profile in the aquatic biota above it was observed that Cr metal was the least heavy metal bioaccumulated by them.

The total heavy metal content in water, sediment, *M. macrobrachion, T.fuscatus* and *N. atherinoides* was in the order: *T.fuscatus* > *M. macrobrachion* > Sediment > *N. atherinoides* > water. This order shows that *T.fuscatus* had the highest concentration of heavy metal bioaccumulation in the river, followed by *M. macrobrachion*, Sediment, *N. atherinoides* and water respectively. This order of heavy metal bioaccumulation, agrees with the study conducted by Onwuli et al., (2014), where heavy metals present in *T. fuscatus* obtained from Eagle Island River was higher than that present in sediment. This order also agrees with the work conducted by Chindah et al., (2009) where the concentration of heavy metals and THC in *T. fuscatus* was higher than that present in sediment. It has also been reported by Olaifa et al., (2004) that aquatic organisms accumulate metals to concentration many times higher than present in water or sediment. The higher concentration of heavy metals in sediment and aquatic biota was confirmed by Namminga et al.,(1976). He observed that heavy metals generally exist in low levels in water and attain considerable levels in sediment and biota.

Total Hydrocarbon was detected in water, sediment and the three aquatic animals obtained from all the stations. Station three had the highest level of THC concentration in all sample which could be attributed to the presence of industries that utilizes organic solvent for its production (paint industry). The concentration of THC in all sample analysed where significant when compared to control values. The values obtained was above WHO acceptable limit of 0.0001mg/kg suggesting that both sediment, water and aquatic biota obtained from this river are polluted by hydrocarbon compounds. The contamination of the aquatic ecosystem could be linked to the discharge of hydrocarbon containing compounds in to the river through municipal runoff from

roads, mechanic village, filling stations etc. From the results obtained, THC values in sediment were found to have the highest mean values than in water, and aquatic biota. This observation tallies with the work conducted by Clinton et al., (2009) which reported higher levels of THC in sediment than in water, *T. fuscatus* and *Periophthalmus papilla* (Mudskipper). Also, Clinton et al., (2008) reported higher levels of THC in sediment than in water and aquatic biota. The high levels of THC in sediment could be attributed to hydrocarbon compound hydrophobic properties which tend to settle out of water and accumulate in the bottom sediment.

The result from the correlation analysis between heavy metals, THC and physicochemical properties revealed that there was a strong and perfect relationship between the uptake of these heavy metals / hydrocarbons by the three selected aquatic animals and the physicochemical properties of the water.

From the studies carried out, it can be discovered that the Great Qua River is slightly polluted with hydrocarbon compounds and heavy metals. Their presence in aquatic ecosystem pose great treat to aquatic biota and man that depends on them for food. Otitoju et al., (2013), reported that the consumption of food such as fish with high levels of heavy metals such as Pb can induce convulsion, abdominal pains, drowsiness, vomiting, kidney and reproductive system malfunction in humans.

The contamination of metals in biota and sediment is of major concern especially in many industrialized countries because of their toxicity, persistence and bioaccumulation nature (Ikem et al., 2013).

CHAPTER FIVE

5.0 SUMMARY CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY

This study measured the levels of THC and some heavy metals in water, sediment and aquatic biota in the Great Qua River. Data obtained has provided information on the impact of anthropogenic activities on the Great Qua River. From results obtained for heavy metals, Mn, Zn, and Fe were below WHO acceptable limit while all other metals in the samples analysed were slightly above the WHO acceptable limit. Apart from cadmium which was statistically insignificant in water and iron which was also statistically insignificant in sediment and *T. fuscatus,* all other heavy metals analysed in the various samples, were statistically significant when compared to control. Higher levels of THC were observed in aquatic biota and the values obtained were significant in all samples analysed when compared to control samples. This shows that the pollution of the Great Qua River arises from anthropogenic sources.

5.2 CONCLUSION

From the analysis carried out on water, sediment and the three aquatic organisms obtained from the Great Qua River, it is discovered that the river is polluted with heavy metals and hydrocarbon compounds. The presence of these pollutants in our river poses a threat not only to aquatic life but also to man who depends on these aquatic animals for food. Researches by eminent scholars in the field of environmental toxicology have implicated many of these pollutants as a major cause to

some deadly ailment such as cancers, neurological disorders, organ failures etc. Hence there is the need to protect our water bodies and in doing so we are also protecting our lives too from these dreaded ailments.

5.3 RECOMMENDATIONS

Anthropogenic activities which lead to the input of heavy metals and hydrocarbon compounds in the Great Qua River should be discouraged in other to avoid possible health effect after a long period of time.

Industries with waste effluents emanating from their production plant should endeavour to make appropriate treatment of effluents following the WHO and other relevant agencies standards in other to maximize the load of heavy metals and hydrocarbon contaminants.

Constant monitoring of heavy metals and THC concentrations in this river is recommended to evaluate the levels accumulated overtime. Activities around the river should be monitored by responsible agencies to reduce the influx of heavy metals and hydrocarbon compounds into the water body.

Relevant laws as pertaining the safety of the aquatic environment and the aquatic life therein, should be promulgated in other to serve as a guide to environmental and public health workers to adequately monitor the acceptable concentration of waste effluent discharge into water bodies.

Public enlightenment should be vigorously entrenched as a way of educating farmers and industries on the need to consider the possible health implication of the use of pesticides, herbicides and fertilizers containing heavy metals and discharge of heavy metals and hydrocarbon contaminants in water bodies. Consumers also should also be enlightened on the implication of consuming sea foods from contaminated sources. Hence making them enquire the sources of their sea food before purchase and final consumption.

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APPENDIX

Correlations: tempt, Cr, Cd, Mn, Ni, Cu, Pb, Zn, Fe, THC, pH, EC, DO (Prawn)

	tempt	Cr	Cd	Mn	Ni	Cu	Pb	Zn	Fe
Cr	0.561								
	0.058								
Cd	0.778	-0.039							
	0.003	0.904							
Mn	0.777	-0.026	0.994						
	0.003	0.935	0.000						
Ni	0.959	0.656	0.696	0.718					
	0.000	0.021	0.012	0.009					
Cu	0.900	0.220	0.936	0.909	0.798				
	0.000	0.493	0.000	0.000	0.002				
Pb	0.677	0.967	0.090	0.104	0.762	0.343			
	0.016	0.000	0.781	0.749	0.004	0.275			
Zn	0.968	0.400	0.889	0.878	0.914	0.974	0.523		
	0.000	0.198	0.000	0.000	0.000	0.000	0.081		
Fe	0.970	0.715	0.650	0.652	0.979	0.816	0.814	0.920	
	0.000	0.009	0.022	0.021	0.000	0.001	0.001	0.000	
THC	0.971	0.648	0.712	0.729	0.999	0.821	0.755	0.929	0.985
	0.000	0.023	0.009	0.007	0.000	0.001	0.005	0.000	0.000
pH	-0.902	-0.771	-0.535	-0.567	-0.978	-0.660	-0.860	-0.813	-0.957
	0.000	0.003	0.073	0.055	0.000	0.019	0.000	0.001	0.000
EC	0.942	0.682	0.626	0.601	0.898	0.843	0.775	0.910	0.967
	0.000	0.014	0.030	0.039	0.000	0.001	0.003	0.000	0.000
DO	-0.954	-0.359	-0.900	-0.883	-0.884	-0.986	-0.482	-0.998	-0.897
	0.000	0.252	0.000	0.000	0.000	0.000	0.113	0.000	0.000

	THC	pH	EC
pH	-0.970		
	0.000		
EC	0.914	-0.857	
	0.000	0.000	
DO	-0.902	0.773	-0.903
	0.000	0.003	0.000

Cell Contents: Pearson correlation
P-Value

Correlations: rep, Cr, Cd, Mn, Ni, Cu, Pb, Zn, Fe, pH, EC, DO, THC, tempt (periwinkle)

	rep	Cr	Cd	Mn	Ni	Cu	Pb	Zn	Fe
Cr	-0.364								
	0.244								
Cd	-0.551	0.915							
	0.063	0.000							
Mn	-0.765	0.808	0.759						
	0.004	0.001	0.004						
Ni	-0.683	0.926	0.955	0.917					
	0.014	0.000	0.000	0.000					
Cu	-0.790	0.845	0.852	0.984	0.967				
	0.002	0.001	0.000	0.000	0.000				
Pb	-0.771	0.872	0.928	0.937	0.991	0.983			
	0.003	0.000	0.000	0.000	0.000	0.000			
Zn	-0.919	0.504	0.760	0.701	0.781	0.790	0.840		
	0.000	0.095	0.004	0.011	0.003	0.002	0.001		
Fe	-0.723	0.872	0.973	0.856	0.982	0.933	0.983	0.862	
	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
pH	0.577	-0.822	-0.981	-0.668	-0.902	-0.786	-0.885	-0.819	-0.955
	0.049	0.001	0.000	0.018	0.000	0.002	0.000	0.001	0.000
EC	-0.771	0.874	0.910	0.955	0.989	0.992	0.998	0.820	0.971
	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
DO	0.431	-0.989	-0.881	-0.877	-0.936	-0.892	-0.894	-0.514	-0.866
	0.162	0.000	0.000	0.000	0.000	0.000	0.000	0.088	0.000
THC	-0.534	0.934	0.999	0.773	0.960	0.860	0.930	0.736	0.970
	0.074	0.000	0.000	0.003	0.000	0.000	0.000	0.006	0.000
tempt	-0.547	0.962	0.962	0.855	0.976	0.909	0.946	0.686	0.952
	0.066	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.000

	pH	EC	DO	THC
EC	-0.857			
	0.000			
DO	0.773	-0.903		
	0.003	0.000		
THC	-0.970	0.914	-0.902	
	0.000	0.000	0.000	
tempt	-0.902	0.942	-0.954	0.971
	0.000	0.000	0.000	0.000

Cell Contents: Pearson correlation
P-Value

EMERALD SHINER FISH (Notropis atherinoides)

Correlations: rep, Cr, Cd, Mn, Ni, Cu, Pb, Zn, Fe, pH, EC, DO, THC, tempt (Shiner fish)

	rep	Cr	Cd	Mn	Ni	Cu	Pb	Zn	Fe
Cr	-0.383								
	0.219								
Cd	0.006	0.670							
	0.986	0.017							
Mn	-0.636	0.194	0.398						
	0.026	0.545	0.200						
Ni	0.061	0.796	0.878	0.001					
	0.851	0.002	0.000	0.997					
Cu	-0.861	0.635	0.499	0.797	0.356				
	0.000	0.026	0.099	0.002	0.256				
Pb	-0.519	0.822	0.844	0.595	0.766	0.865			
	0.084	0.001	0.001	0.041	0.004	0.000			
Zn	-0.771	0.823	0.533	0.481	0.587	0.910	0.893		
	0.003	0.001	0.075	0.113	0.045	0.000	0.000		
Fe	-0.899	0.517	-0.059	0.268	0.101	0.717	0.470	0.810	
	0.000	0.085	0.856	0.400	0.754	0.009	0.124	0.001	
pH	0.577	-0.892	-0.706	-0.385	-0.780	-0.825	-0.946	-0.964	-0.654
	0.049	0.000	0.010	0.217	0.003	0.001	0.000	0.000	0.021
EC	-0.771	0.678	0.627	0.800	0.467	0.988	0.925	0.904	0.622
	0.003	0.015	0.029	0.002	0.126	0.000	0.000	0.000	0.031
DO	0.431	-0.639	-0.869	-0.778	-0.629	-0.827	-0.936	-0.721	-0.241
	0.162	0.025	0.000	0.003	0.028	0.001	0.000	0.008	0.450
THC	-0.534	0.851	0.819	0.541	0.782	0.860	0.996	0.920	0.520
	0.074	0.000	0.001	0.069	0.003	0.000	0.000	0.000	0.083
tempt	-0.547	0.747	0.821	0.677	0.691	0.887	0.986	0.864	0.451
	0.066	0.005	0.001	0.016	0.013	0.000	0.000	0.000	0.141

	pH	EC	DO	THC
EC	-0.857			
	0.000			
DO	0.773	-0.903		
	0.003	0.000		
THC	-0.970	0.914	-0.902	
	0.000	0.000	0.000	
tempt	-0.902	0.942	-0.954	0.971
	0.000	0.000	0.000	0.000

Cell Contents: Pearson correlation
P-Value