

## INTEGRATED RISK ASSESSMENT USING *CHRYSICHTHYS NIGRODIGITATUS*: A CASE STUDY OF NEW CALABAR RIVER BASIN

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**ABSTRACT:** *The aim of this study was to assess human and ecological risk posed by water and sediment quality of New Calabar New (NCR) using *Chrysiichthys nigrodigitatus*. For this study, chemical- and bio-monitoring assessments were carried out in three sampling stations (Choba, Ogbogoro and Iwofe) of NCR. A Fish Consumption Survey (FCS) was also implemented to assess the risk of exposure of subsistence fishers from host communities of the sampling stations of NCR. Using data from FCS, mathematical models were used to characterize risk due to the consumption of fish. Chemical monitoring involved the assessment of physico-chemical variables of water with an evaluation of Environmental Water Quality Index (EWQI) and sediment quality. Biomonitoring involved the assessment of the edible part of fish tissue (skin and muscle) for chemicals of potential concern (COPC). Physico-chemical water analysis and set against SON benchmarks, results showed that temperature, pH, conductivity and dissolved oxygen values were abnormal, while heavy metals and PAH were normal. The evaluated EWQI was marginal for NCR. Sediment quality showed slightly elevated PAH level at Ogbogoro station while heavy metals remain normal. Fish edibility study set against RfD benchmarks of USEPA, indicated a slightly elevated PAH, hence fish from NCR was unsafe for consumption. The FCS showed that an average of 1.2kg/day/ of *C. nigrodigitatus* was consumed by respondent from NCR basin, with an age group range of 18-34 forming the highest consumers.  $HQ < 1$  for COPC, meaning their levels in the edible part of tissue are not acutely hazardous on consumption, but PAH, a carcinogenic chemical forming part of the assessed COPC, showed a carcinogenic risk characterization of  $1.4E-04$ ,  $1.3E-04$  and  $1.3E-04$  respectively for subsistent fishers from Choba, Ogbogoro and Iwofe.*

**KEYWORDS:** Biomonitoring, Integrated Risk Assessment, Water Quality Index, Fish Consumption Survey,

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### INTRODUCTION

Humans are the most social and mentally advanced organism that has walked the earth. The protection of human life has become ubiquitous, not just for the sustenance of human life, but for the protection of the life of other organisms; which forms an intricate balance of human ecosystem. The balance between biotic and abiotic components of human ecosystem maintains the environmental conditions upon which human life is sustained or disturbed; a disruption of this intricate balance have mostly been implicated in the cause of human diseases, climate change and/or threatened biodiversity.

The protection of human health is necessitated by the drive to sustain life for progeny: the ability to reproduce and transfer healthy genes to the next generation. With the knowledge of the intricate relationship of the environment, human disease and physical disturbance, human science has thus advances in the areas of safety, hygiene and food and nutrition. Over the years, hygiene, which is the science and practice of maintaining health (Merriam Webster, 2000), has been subjectively viewed and analysed from the perspective of human health, forgetting that the epidemiology of disease transmission almost always involves: a medium or primary habitat like air, water and soil; a vector or intermediate habitat and; a secondary habitat like human. The environmental component of hygiene (i.e environmental hygiene) is even more important in order to break the vicious cycle of disease transmission. Humans would have lived healthy, if not for pathogens or chemicals that are foreign to the human body, all of which form the natural or anthropogenic components of our environment. Thus medical and environmental scientist must take a holistic and integrated approach in disease control and management strategy by applying scientific assessments that would incorporate both human health and ecological health analytical tools in environmental monitoring and risk assessment programmes.

Historically, human health and environmental risk assessment methodologies have generally developed independently. Regulatory agencies often use a chemical-by-chemical approach, focusing on a single media, a single source, and a single toxic endpoint. Many international and national organizations have expressed a need for an integrated, holistic approach to risk assessment that addresses real life situations of multichemical, multimedia, multiroute, and multispecies exposures (Damstra et al., 2003).

The need for an integrated assessment of human and ecological systems on an international scale has also been emphasized by some internationally recognized organisation and global environmental partners like the WHO, USA Environmental Protection Agency (EPA), the European Union through its Environmental Protection Agency and the numerous Environmental Directives, and the OECD (Organization for Economic Co-operation and Development, Paris) which deals with global issues of chemical safety and chemical industry. The aim has been to improve quality of environmental measurements, which include important biomarkers, improve risk assessment and management and formulate policy implementation (Munns et al., 2003; Smolders et al., 2008; Hagger et al., 2008).

Water, which is the major component of the aquatic ecosystem, is one of the most essential and precious natural resources on earth. It plays a major role in sustaining life and has numerous benefits to mankind, which includes fisheries, wild life, agriculture, urban, industrial and social developments (Allan and Flecker, 1993). Over the last few years, there has been growing concern internationally over contamination of aquatic ecosystems with a wide range of pollutants (Ali and Soltan, 1996; Canli and Kalay, 1998; Van der Oost et al., 2003; Yang and Rose, 2003; Dutta and Dalal, 2008).

Water quality, defined as the suitability of water to sustain different uses or process (Meybeck et al., 1996; Codd, 2000), is influenced by a large variety of natural factors (hydrological, biological, geological, meteorological and topographical). These factors all interact and may vary seasonally

according to the variation in weather condition, run-off volumes, and water levels. Another wide ranging influence on water quality is human (anthropogenic) activity, and may be due to hydrological influence through, for example, flow diversion, water abstraction, and wetland drainage or dam construction. Human activities in river basins produce pollution residues in the water, compromising multiple uses (Lloyd, 1992; Tucker and Burton, 1999; Tundisi, 2001). More obvious influence of human activities on water quality are the discharge of sewage, agricultural, industrial and urban wastewater, and the diffuse run-off of agricultural fertilizers and pest-control chemicals into water bodies (Kennish, 1992; Codd, 2000; Schlacher et al., 2007).

The degradation of aquatic ecosystem restricts its uses and can render a whole water body useless. The consequence is not only on aquatic life, but also on water resource base itself. Pollution may intensify water scarcity and inflict a huge cost on other uses. Water quality deterioration has a serious economic impact because the value of the resources is grossly affected and frequently needs significant restoring and management input to bring it back to a useable state (Meybeck et al., 1996, Codd, 2000, Schlacher et al., 2007). Thus protection of natural environments and water resources is vital.

Heavy metal pollution is ubiquitous in our environment (Don-Pedro et al., 2004) and result from diverse activities such as industrialeffluent, foundry waste, wearing of metals parts and equipment, paints, auto-mobiles, mining, and rock weathering. These are subsequently deposited on soil surface and may be leached through municipal drainages to near by ponds, streams, and rivers or directly discharged into these waterbodies. The major concern of heavy metals lie with their acute toxicity and ability to bioaccumulate in biological systems (Otitolaju and Don-Pedro, 2002), resulting in a number of deleterious effects such as immunosuppression (Carey and Bryant, 1995). According to Vuuren et al. (1999) metal pollutants are currently considered to be some of the most toxic contaminants present world-wide.

PAHs consist of hydrogen and carbon arranged in the form of two or more fused benzene rings (Barnett, 1976; Lo and Sandi, 1978; Neff, 1979). There are thousands of PAH compounds, each differing in the number and position of aromatic rings, and in the position of substituents on the basic ring system (Neff, 1985; EPA, 1980; Futoma et al., 1981). PAHs of environmental concern are those that range in molecular weight from 128.16 (naphthalene, 2-ring structure) to 300.36 (coronene, 7-ring structure). Unsubstituted lower molecular weight PAH compounds, containing 2 or 3 rings, exhibit significant acute toxicity and other adverse effects to some organisms, but are noncarcinogenic; the higher molecular weight PAHs, containing 4 to 7 rings, are significantly less toxic, but many of the 4- to 7-ring compounds are demonstrably carcinogenic, mutagenic, or teratogenic to a wide variety of organisms, including fish and other aquatic life, amphibians, birds, and mammals. There are two basic sources of PAH in the environment; natural and anthropogenic. Both sources produce PAH through the processes of pyrolysis of organic matter (pyrogenic PAH) and or in naturally occurring fossil fuel or Petroleum exploration and processing activities, which includes leakages and spilages (petrogenic PAH). In water, PAHs may either evaporate, disperse into the water column, become incorporated into bottom sediments, concentrate in aquatic biota, or experience chemical oxidation and biodegradation (Suess 1976). The most important degradative processes for PAHs in aquatic systems are photooxidation, chemical oxidation, and biological transformation by bacteria and animals (Neff 1979). Most PAHs in aquatic

environments are associated with particulate materials; only about 33% are present in dissolved form (Lee and Grant 1981). PAHs dissolved in the water column will probably degrade rapidly through photooxidation (EPA 1980), and degrade most rapidly at higher concentrations, at elevated temperatures, at elevated oxygen levels, and at higher incidences of solar radiation (McGinnes and Snoeyink 1974; Suess 1976; Bauer and Capone 1985). In sediment, the ultimate fate of PAHs accumulation is believed to be biotransformation and biodegradation by benthic organisms (EPA 1980). PAHs in aquatic sediments, however, degrade very slowly in the absence of penetrating radiation and oxygen (Suess 1976), and may persist indefinitely in oxygen poor basins or in anoxic sediments (Neff 1979). In animals and microorganisms PAH can metabolize into other products that may ultimately experience complete degradation. In mammals, PAHs can be taken into the mammalian body by inhalation, skin contact, or ingestion, although they are poorly absorbed from the gastrointestinal tract. The main routes of elimination of PAHs and their metabolites include the hepatobiliary system and the gastrointestinal tract (Sims and Overcash 1983). Most authorities agree that metabolic activation by mixed-function oxidase enzyme system is a necessary prerequisite for PAH-induced carcinogenesis and mutagenesis (Neff 1979). This enzyme system is known to be present in rodent tissues, and human liver, skin, placenta, fetal liver, macrophages, lymphocytes, and monocytes (Lo and Sandi 1978). Fish and most crustaceans tested to date possess the enzymes necessary for activation (Statham et al. 1976; Varanasi et al. 1980; Fabacher and Baumann 1985), but some molluscs and other invertebrates are unable to efficiently metabolize PAHs (Jackim and Lake 1978; Varanasi et al. 1985). Several polycyclic aromatic hydrocarbons (PAHs) are among the most potent carcinogens known to exist, producing tumors in some organisms through single exposures to microgram quantities. PAHs act at both the site of application and at organs distant to the site of absorption; their effects have been demonstrated in nearly every tissue and species tested, regardless of the route of administration (Lee and Grant 1981). The evidence implicating PAHs as an inducer of cancerous and precancerous lesions is becoming overwhelming, and this class of substances is probably a major contributor to the recent increase in cancer rates reported for industrialized nations (Cooke and Dennis 1984).

Crude oil is the major revenue earner for Nigeria. Crude Oil exploration and exploitation is a major source of PAHs contamination in the basin of the oil rich Niger Delta states of Nigeria. But, like most industrial activities, it produces environmental hazards that are "slow poisons," in that they often take months and years to cause disease and death (WHO, 2002). Oil spill is a common fallout of oil exploration and exploitation in the Niger delta region (UNDP, 2011). There are no consistent figures of the quantity of crude oil spilled in the Niger delta, but it is widely believed that an estimated 13 million barrels (1.5 million tons) of crude oil have been spilled since 1958 from over 7000 oil spill incidents; a yearly average of about 240,000 barrels (UNDP, 2011). The oil spills often resulted in contamination of surface water with hydrocarbons and trace metals (Ordinioha et al., 2009). Oil pollution, one of the environmental consequences of crude oil exploration and exploitation activities, produces aqua-toxicological effects, which are deleterious to aquatic life (Kori-Siakpere, 2000; Agbogidi et al., 2005).

Aquatic organisms can acquire trace elements from food, suspended particles or directly from the water (Carvalho and Fowler, 1993). Many of these pollutants are non-biodegradable compounds and dangerous due to their innate ability to constantly remain within the ecosystem (Hernandez-Hernandez et al., 1990). Fish are often highly exposed to these aquatic contaminants especially in

areas where the dilution rate of wastewater is low. This has adverse effects particularly when contaminants: are not or only slightly decomposable; exhibit a high biological effectiveness; pose a high potential for accumulation; and influence each other in an additive way, in case of multiple contaminants.

Fish are mentioned in the literature as good bio-accumulative indicators of metal pollution because they are known to readily accumulate metals from their environment. This can be detrimental to the health of both the organism itself, as well as to consumers, be they animals or humans. The investigation of metal bio-accumulation in fish is important because it supports the monitoring of the chemical and physical quality of water and sediment in aquatic ecosystems (Van Vuren et al., 1999).

One of the core missions of IRA is to combine human and ecological risk assessment in a single analytical approach. It incorporates toxicological and ecological methods in the assessment of risk to environmental and human health. Integration may provide early signs of previously unidentified risks, with both human and wildlife species in the role of sentinel organisms. Integration of studies can enhance quality of measurements, cost-effectiveness and predictive capability. (Hagger et al., 2006; Beliaeff and Burgeot, 2000; Galloway, 2006; Sarkar et al., 2006).

The focus of this study was to assess human and ecological health risk posed by the water and sediment quality of New Calabar New (NCR) using the edibility study of *Chrysichthys nigrodigitatus* as a biomarker. Incorporated in this study was a physico-chemical analysis, which includes EWQI, sediment quality assessment, edibility study - bioaccumulation assessment and an Integrated Risk Assessment (IRA), which includes Fish Consumption Survey (FCS). These results were compared with existing international guidelines (Agency for Toxic Substances and Disease Regulations (ATSDR). 2002, 2003; United State Environmental Protection Agency (US EPA), 1986, 1987, 1992, 1998; World Health Organization (WHO), 2003; and National Oceanic Atmospheric Administration (NOAA) 2006) to determine whether the harvested fish were living under healthy environmental condition, whether fishes were safe for human consumption and whether they pose some risk on subsistent fisher through fish consumption.

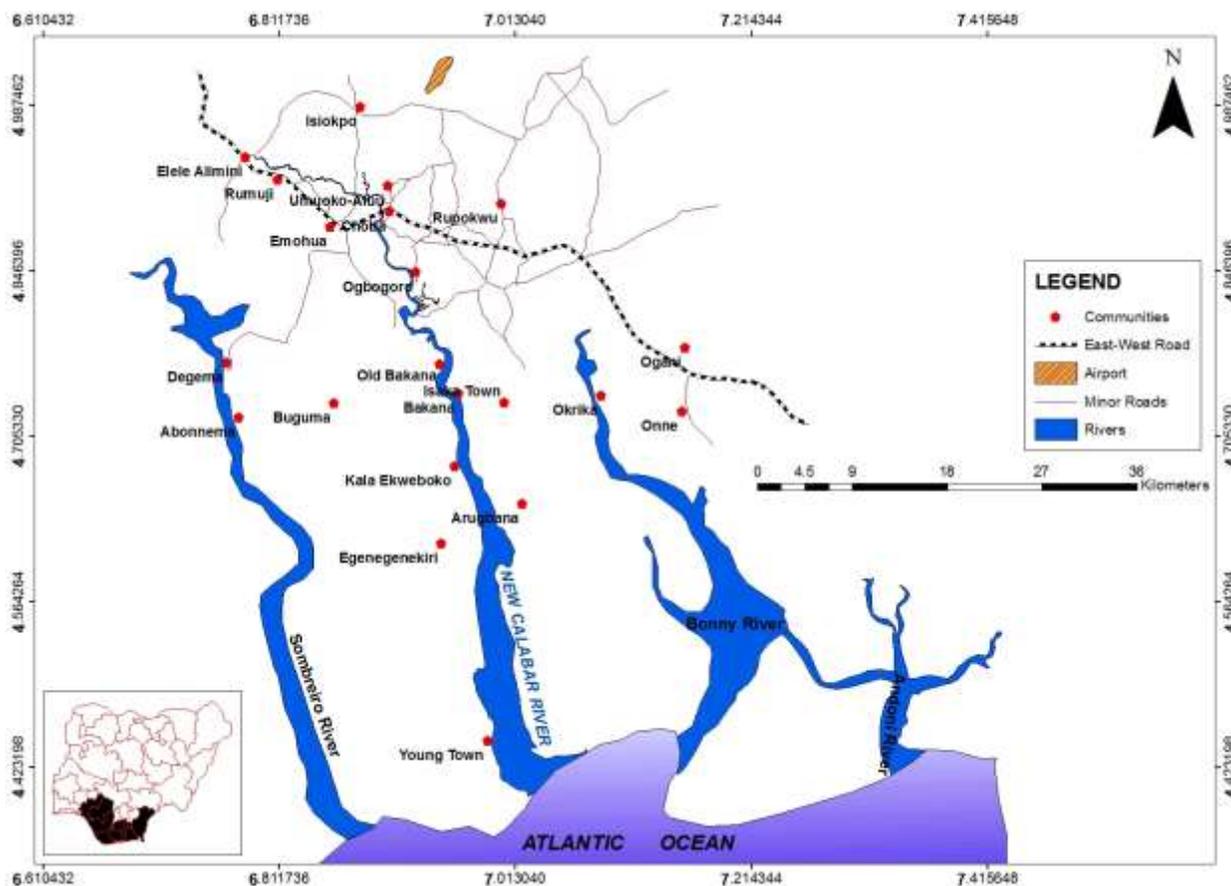


Figure 1. Map of lower Niger Delta, adopted from Francis and Elewuo (2012), showing the New Calabar River drainage system and study area with the sampling stations (Choba, Ogbogoro and Iwofe). Inset is map of Nigeria showing position of the lower Niger Delta.

## MATERIALS AND METHOD

### Study Area

The study was carried out in New Calabar River (NCR). Sampling for water, sediment and fish were done in three different stations (Choba, Ogbogoro and Iwofe) of NCR. NCR and its tributaries are located in Rivers States, one of the oil bearing states, in the Niger Delta Region of Nigeria. It is a low lying deltaic river which rises at approximately latitude  $5^{\circ}10'N$  and longitudes  $6^{\circ}50'E$  near Elele-Alimini and flows Southward for roughly 150km before its discharge into the Atlantic Ocean at about latitude  $4^{\circ}20'N$  and longitudes  $7^{\circ}00'E$ . It occupies a low relief region, ranging from 0-50m above sea level at the low zone, to 50-100 above sea level at its source. The soil of the river basin consists of clays, silt and sand, with high organic matter, classed as either 'lithosols' (mangrove soil type) or 'hydromorphic' soil type (alluvial deposits). The bedrock of the basin consists of post-cretaceous, recent sedentary formation. The river is unidirectional in the upper reach and tidal in the lower reach. Its upstream reach is fresh water with tropical lowlands rain (dense) forest through secondary forest/farmland vegetation. The downstream reach is however brackish and consists of Mangrove swamp forest. The climate of the area is characterized

by wet and dry seasons. The wet season period stretches from April to October each year with monthly average rainfall of 254mm (Department of Meteorological Services Report, Rivers State, 2000), and however with occasional precipitation in the dry season month of November-March. NCR river basin is sub-urban in structure with about 40% of the rural populace predominantly artisanal fishermen. However, the life style of the indigenes has been greatly influenced by the presence of the University of Port Harcourt and the several industries along its river bank. Population growth results in conversion of open land into non-permeable surfaces which increase the rate of run-off and can negatively impact water quality (Jiang et al., 2001). Human activities including defecation, washing, recreation (swimming/bathing and fishing) and waste disposal are prevalent especially where human settlements exist along the river banks. Similarly, several industries are located along the river banks. The social and health impacts are numerous since most communities living on the river banks use the shores as dumpsites for their wastes, which are washed into the ecosystems during rains.

### **Selection of Target Analytes**

Target Analytes for this study was done base on: 1. Published evidence of environmental systems or sources of contaminants & contamination of NCR (Chinda, 1998; Woke and Aleleye 2007; Wegwu and Akaninwor 2006; Akaninwor and Egwin 2006; Sikoki et al., 2013). 2. Analytes recommended for WQI: Acceptable & Health parameters (CCME, 2001). 3. Target analytes prioritized based on water and sediment sampling results, land use within the watershed, geographic characteristics and analytical costs. (USEPA, 2000)

### **Sampling**

Water and sediment sampling were carried out in all three delineated study stations (Choba, Ogbogoro and Iwofe) of NCR. ARAC was chosen as the reference site for fish samples based on the consideration that the centre has a highly controlled fish culture tanks that can hardly be contaminated. Four different water and sediment samples were collected, at one month interval, spanning the dry and rainy season (between February and September). Water sampling was done in accordance with USEPA (2013) and sediment sampling was done in accordance with USEPA (2001). Fish sampling was carried out in Choba station only, and sampling was done during the rainy season, between August and September 2014. During this period the river receives them organic and industrial loads carried out by runoff. Gill nets were used at site to attain the required sample size of twenty fish for the species (Marchand, 2009; DWA, 2012).

### **Physico-chemical and Environmental Water Quality Index (EWQI)**

The physico-chemical water quality variables were recorded at three sites in the NCR. Site 1: upstream - Inflow to NCR (Choba); Site 2: midstream (Ogbogoro); Site 3: downstream - most southern part of the NCR (Iwofe). Water temperature (°C), pH, Dissolved oxygen (DO) and conductivity (µS) were analysed in situ with a HORIBA, U-50 series Multi-parameter water quality checker. Water samples for heavy metal analysis were taken from the river using polypropylene bottles; 2ml of sulphuric acid was added and frozen for further analysis. Atomic absorption Spectrophotometry (Buck Scientific Model 210) using element specific hollow cathode lamps in default condition by flame absorption mode was used to approximate the Nigerian metal concentration within samples. The empirical screening values obtained from the physico-chemical EWQ parameters were further analysed mathematically to give a baseline EWQ screening score for

NCR. Essentially, the EWQI model consists of three measures of variance from selected water quality objectives (Scope; Frequency; Amplitude). The “Scope (F1)” represents the extent of water quality guideline non-compliance over the time period of interest. The “Frequency (F2)” represents the percentage of individual tests that do not meet objectives. The “Amplitude (F3)” represents the amount by which failed tests do not meet their objectives. These three factors combine to produce a value between 0 and 100 that represents the overall water quality (CCME 2001).

### **Sediment Quality Analysis**

An aliquot of the sediment sample was filtered and made up to 50ml with distilled water. The filtrate was stored in plastic bottles for heavy metals and PAH analysis. Samples were analysed using GBC Avanta atomic absorption spectrophotometer (AAS).

### **Fish Edibility Study: Bioaccumulation**

The fishes harvested from NCR were sacrificed and then 5 grams of muscle and skin tissues were excised from each fish and placed in different plastic containers containing ice cubes and covered. The ten sample plastic containers were subsequently placed in a deep freezer for preservation prior to their transfer for bioaccumulation tests. During Extraction and Analysis of Extract, Fish sample was allowed to thaw and then oven-dried, 2 grams of dry fish samples were put in an amber-coloured bottle. 20mls of an organic solvent (chloroform) was added to the fish sample. The whole was then stirred with a stirring rod and a funnel was placed over a beaker, and the mixture of fish extract, the filtrate (fish extract) was then taken to the Gas Spectrometer (HP 5890 series GC) and GBS AVANTA AAS for analyses to detect possible heavy metals and PAH.

### **Integrated Risk Assessment (IRA)**

This risk assessment follows the methodology recommended by the U.S. Environmental Protection Agency (USEPA) for the assessment of cancer and noncarcinogenic toxicity (USEPA 1997a). This methodology generally includes the following four steps:

#### **Hazard identification**

It is the identification of the chemicals of potential concern (COPC) to be included in the risk assessment and characterization of the toxicological hazards posed by these chemicals in human. COPCs for this study were identified in the bioaccumulation analysis of fish muscle and skin results and their characterization was made based on the literature review on their weight of evidence of toxicity.

#### **Dose-response assessment:**

It is the quantitative characterization of the relationship between the dose of a toxicant and the incidence of adverse health effects in humans. For this study default benchmark Oral reference dose (RfD) values (US EPA, 2000b) were used as substitute values for Dose-response assessment.

#### **Exposure assessment:**

It is the characterization of the magnitude, frequency, and duration of exposure to COPCs in fish. This assessment addresses how often individuals eat fish, how much and what portions of the fish

are consumed, and for how long fish have been consumed from the study area by target populations. A FCS of target population (subsistent fishers) were carried out in communities of the study area in accordance with US EPA (1998) Guidance for Exposure Assessment.

### **Risk characterization:**

It is the estimation of the potential for adverse health effects by integrating the information from the dose-response assessment with the exposure assessment in a mathematical model to analyse hazardous quotient (HQ) for non-carcinogenic compounds and carcinogenic risk characterization. Risk Characterization. Noncarcinogenic and carcinogenic risk estimates are calculated separately because of fundamental differences in their critical toxicity values. Equations used to derive risk estimates for both types of health effects are presented below.

### **Noncarcinogenic Health Effects: Hazardous Quotient (HQ)**

The potential for noncarcinogenic health effects is evaluated by calculating the ratio of the chemical exposure over a specified time period to an RfD that is derived for a similar time period. This ratio of exposure to toxicity for an individual chemical is called the hazard quotient (HQ):

$$HQ = CDI/RfD$$

Where:

HQ = Chemical-specific hazard quotient (unitless)

CDI = Chemical-specific chronic daily intake (mg/kg-day)

RfD = Route- and chemical-specific reference dose (mg/kg-day)

The noncarcinogenic HQ assumes that there is a threshold level of exposure, the RfD, below which it is unlikely that even sensitive populations will experience adverse health effects (USEPA 1989). If the exposure exceeds this threshold ( $HQ > 1$ ), there may be concern for potential noncarcinogenic health effects. Generally, the greater the magnitude of the HQ above a value of 1, the greater the level of concern for noncarcinogenic health effects. It should be noted, however, that exposures above the RfD do not represent the same increase in risk for all chemicals as RfDs do not have equal accuracy or precision and are not based on the same severity of toxic effects (USEPA 1989; Hayes 1994). Furthermore, the level of concern does not increase linearly as the RfD is approached.

The HQ values presented in this risk assessment evaluate chronic exposure durations, which in humans are defined as ranging in duration from seven years to a lifetime (USEPA 1989). Subchronic exposures of two weeks to seven years or shorter-term exposures are not evaluated in this risk assessment.

### **Carcinogenic Risk**

Risk for carcinogens is estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen (USEPA 1989). Under current risk assessment guidelines, USEPA assumes that a threshold dose does not exist for carcinogens and that any dose can contribute to health risks (USEPA 1997a). In other words, the risk of cancer is proportional to dose exposure and there is never a zero probability of cancer risk when exposed to carcinogenic chemicals. Carcinogenic risk probabilities were calculated by multiplying the estimated exposure level by the SF for each chemical. This product represents the excess cancer

risk, or the additional risk that an individual has of developing cancer in their lifetime due to exposure to a particular toxic substance.

$$\text{Risk} = \text{CDI} \times \text{SF}$$

where:

Risk = Estimated chemical-specific individual excess lifetime cancer risk (unitless)

CDI = Chemical-specific chronic daily intake (mg/kg-day)

SF = Route- and chemical-specific cancer slope factor (kg-day/mg)

For this risk assessment, an individual lifetime excess cancer risk of 1.0E-04 (EVS2000a) was adopted as the Acceptable Risk Level (ARL) to assess the potential for adverse health effects due to ingestion of fish containing carcinogenic chemicals. To assess the risk posed by simultaneous exposure to multiple carcinogenic chemicals in fish tissue, the excess cancer risk for all carcinogenic chemicals was summed to calculate a total cancer risk.

## RESULT

### Physico-Chemical Result

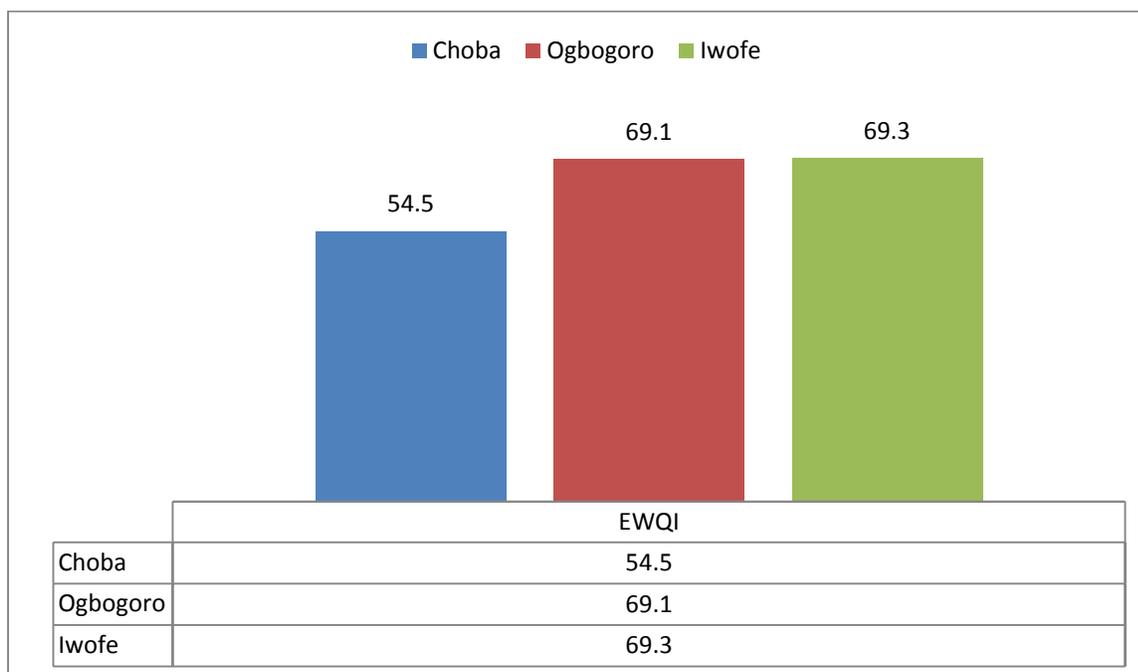
All recorded physical water variables, such as temperature, pH, Conductivity, and dissolved oxygen (DO), and water chemical variables, such as Cd, Cr, Cu, Pb and Zn are represented in Table 1. Temperature and pH levels were within benchmark ranges, but DO was lower than the allowable level while conductivity at all stations were higher than benchmark values. Heavy metal variables were normal, that is, they are within allowable screening values for fresh water aquatic ecosystems.

**Table 1.: Physico-Chemical water variable analysis result**

PARAMETERS	CHObA	OGBOGORO	IWOFE	GUIDELINES (SON)
Temperature (oC)	24.3	22.2	24.3	Ambient
pH	5.1	6.7	6.7	5.5-9.0
DO (mg/L)	3.7	4.2	4.5	>5 mg/L
Conductivity	1152.5	1343.5	1186.0	1000 (uS/cm)
Cd (mg/L)	<0.001	<0.001	<0.001	0.003 mg/L
Cr (mg/L)	<0.001	<0.001	<0.001	0.05 mg/L
Cu (mg/L)	<0.001	<0.001	<0.001	1 mg/L
Pb (mg/L)	<0.001	<0.001	<0.001	0.01 mg/L
Zn (mg/L)	<0.001	<0.001	<0.001	3 mg/L

### Environmental Water Quality Index (EWQI)

The Physico-Chemical screening values for the different stations of NCR were used to evaluate the EWQI using CCME (2001) mathematical model approach for determination of water quality index. The EWQ index values for each station (fig.1) shows that Choba was marginal while Ogbogoro and Iwofe were fair.

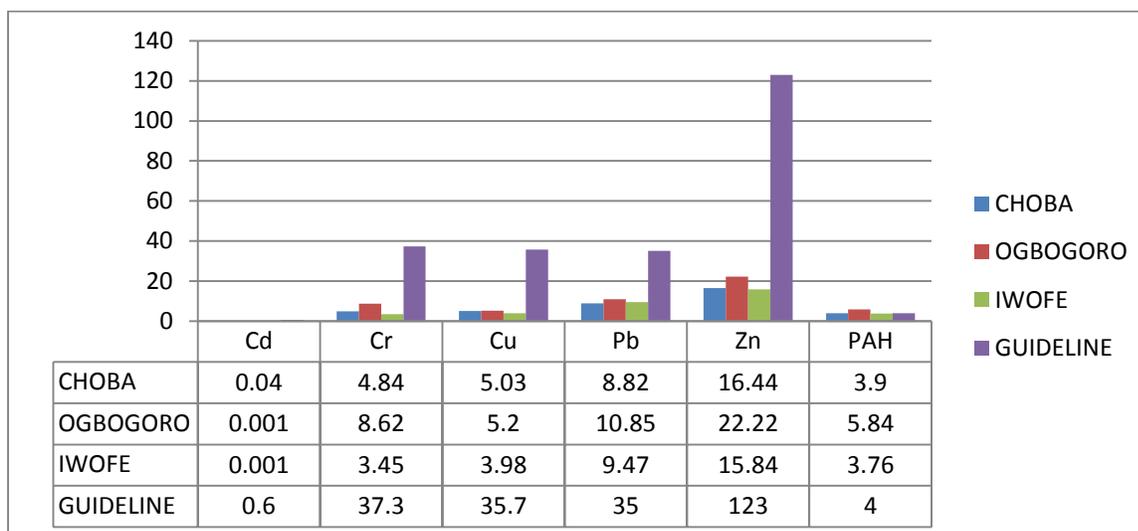


Canadian water quality (CCME, 2001) guidelines for the protection of aquatic life = 0-44 (poor), 45-64 (marginal), 65-79 (fair), 80-88, (good) and 89-94 (very good)

**Fig. 1.:** Graph showing the comparison of EWQ Indexes between stations (Choba, Ogbogoro and Iwofe) using CCME (2001) as a guidelines.

### Sediment Quality Analysis

The result of heavy metals present in the sediment from the three stations are represented in fig.2. Heavy metals were within the allowable benchmark values for fresh water aquatic ecosystems, but the PAH level for Ogbogoro station was higher than the benchmark value.



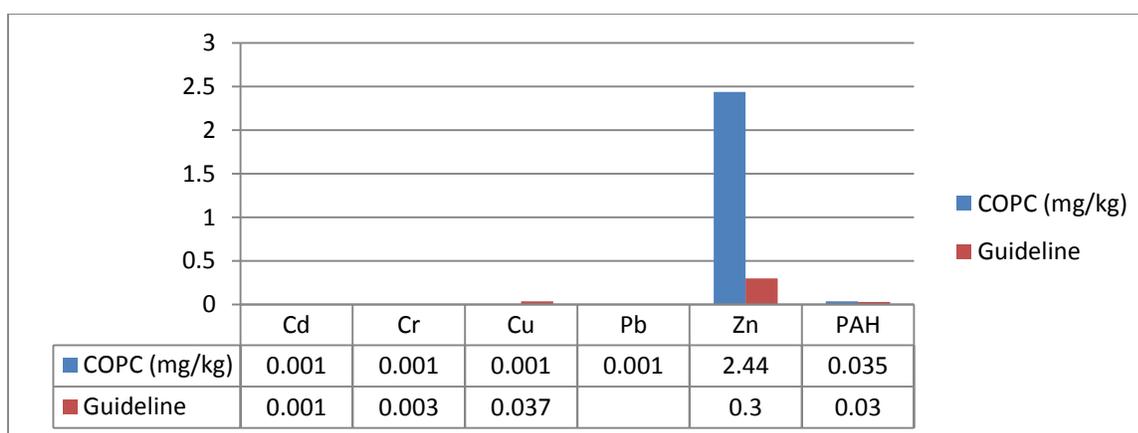
*Cd, Cr, Cu, Pb & Zn Guideline* = (NOAA, 2009)

*PAH Guideline* = effects range low based on British Columbia Water Quality Guidelines (2006)

**Fig. 2:** Graph showing the comparison of COPC in sediment samples from Choba, Ogbogoro and Iwofe stations.

### The edibility of fish

Mean Concentration of heavy Metals and PAH in edible part (muscle and Skin tissue) of the fish from NCR was compared with standard Oral reference dose (RfD) values/benchmarks of US EPA (2009) for fish consumption in human. All heavy metals values were within normal values, but PAH was slightly above the normal or allowable RfD values.



**Fig. 3:** Graph showing the average concentrations of COPC measured in muscle samples from the NCR.

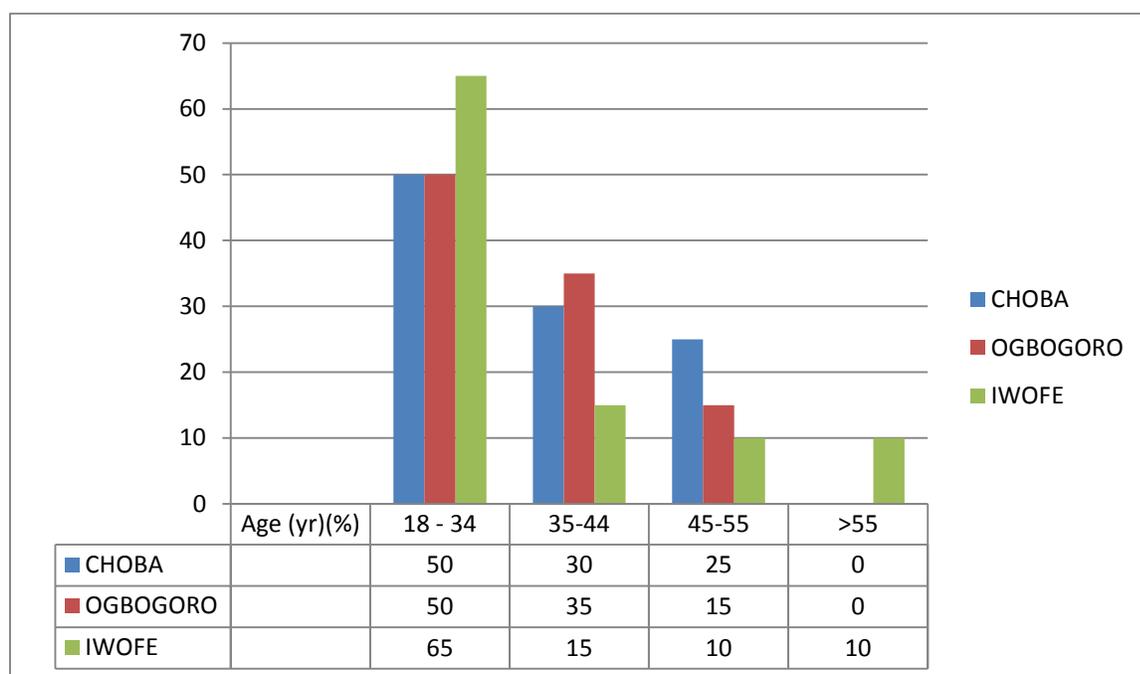
## Integrated Risk Assessment (IRA)

### Exposure Assessment: Fish Consumption Survey (FCS)

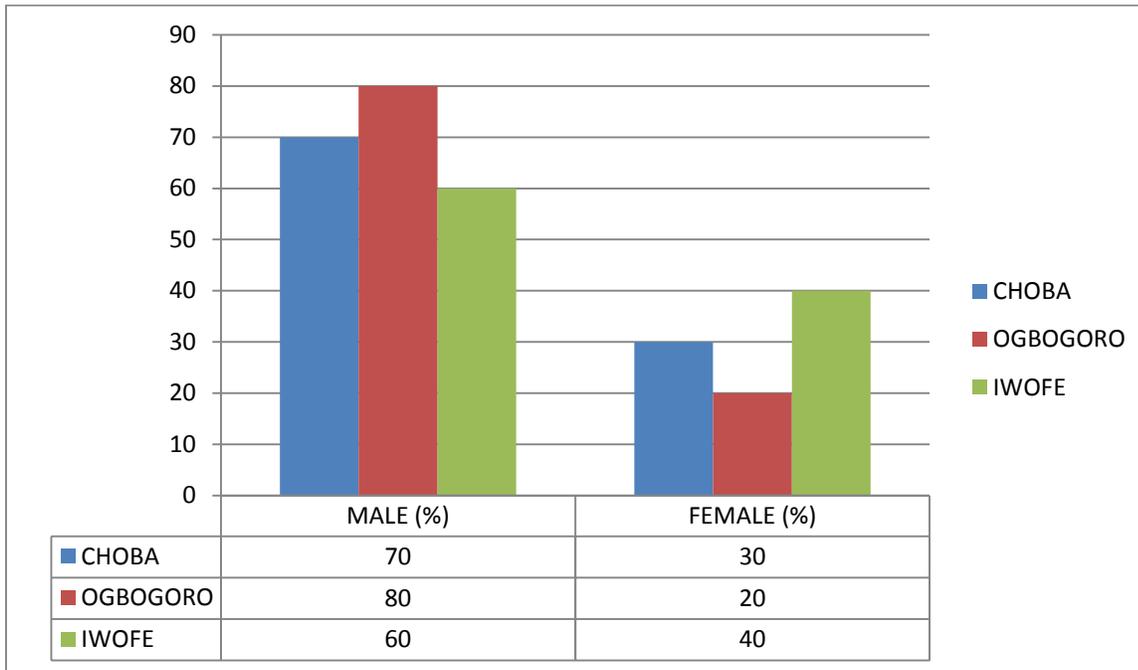
A FCS questionnaire was used to assess exposure pathway and quantification of exposure of subsistent fisher populations from Choba, Ogbogoro and Iwofe communities in NCR basin for potential exposure to contaminants through the consumption of *C. Nigrodigitatus* from NCR. A total of Sixty (60) subsistent fishers were questioned; twenty (20) per community.

### Identification of Exposed Pathway and Population Biodata

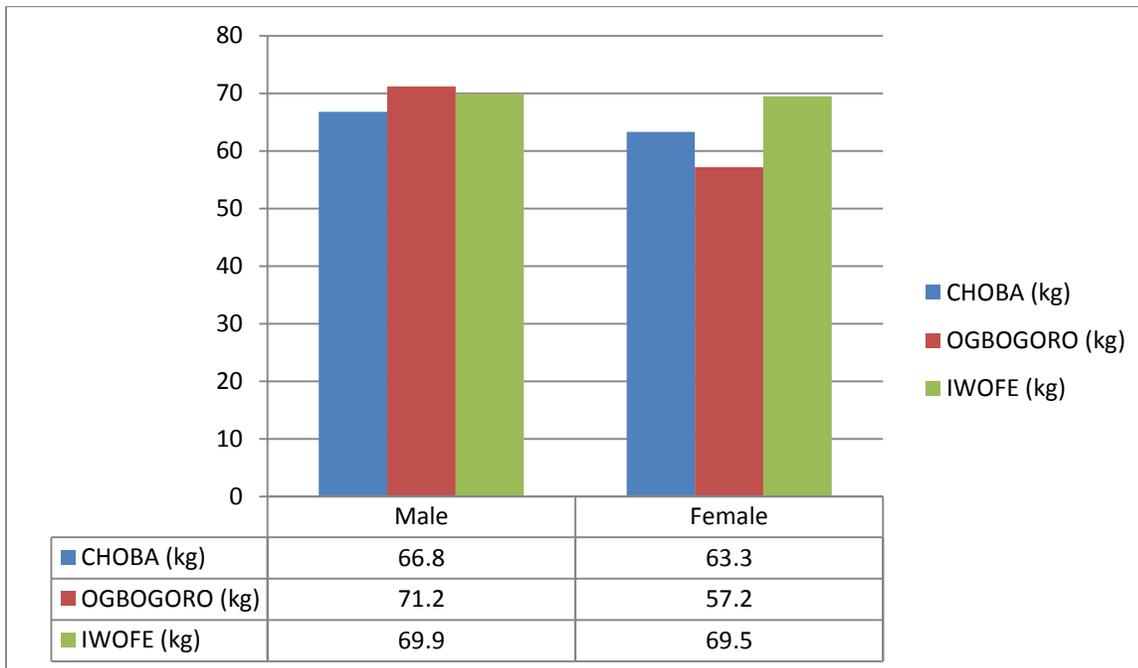
The pathway of exposure is through fish (*C. Nigrodigitatus*) consumption and target population are subsistence fishers, these are stratified in a random sampling technique. Below are the some demographic results of target population biodata of respondents from Choba, Ogbogoro and Iwofe obtained from the FCS.



**Fig. 4: A Graph showing age distribution among respondent**



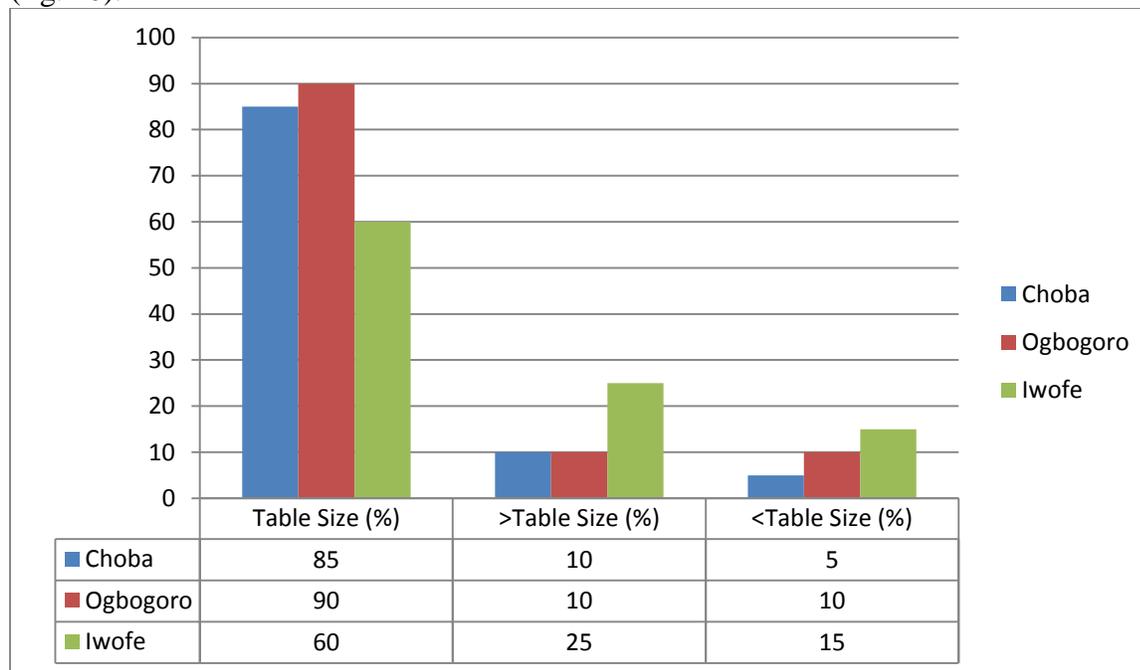
**Fig. 5: A graph showing gender distribution among respondent**



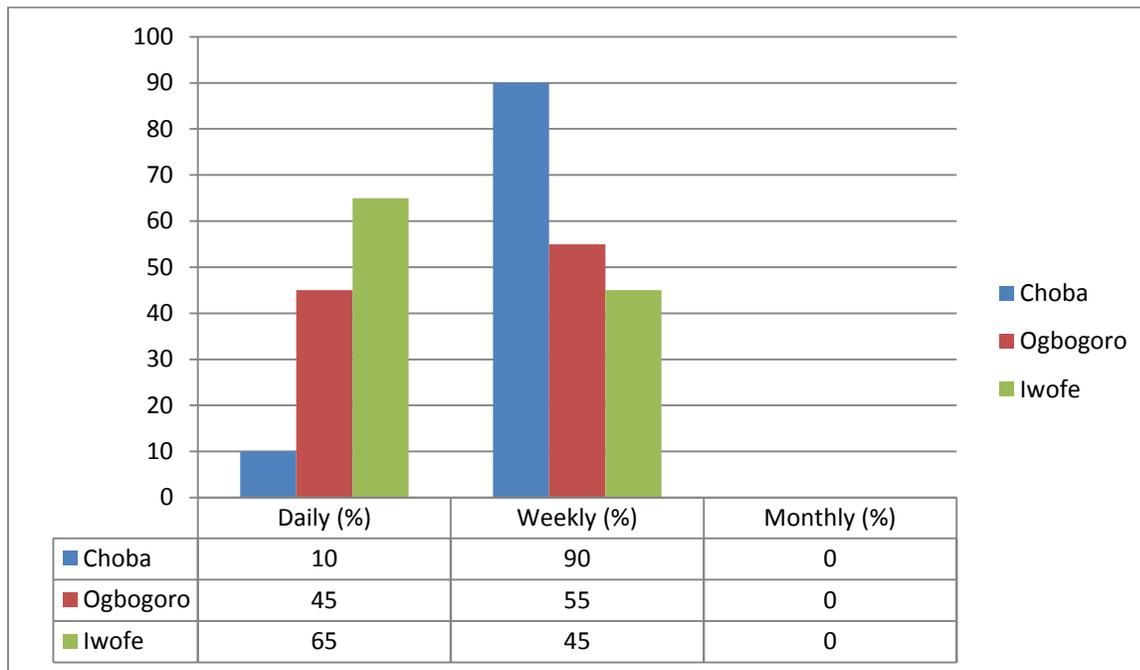
**Fig. 6: A graph showing weight distribution in different gender of respondent**

**3.5.1.2. Quantification of Exposure.**

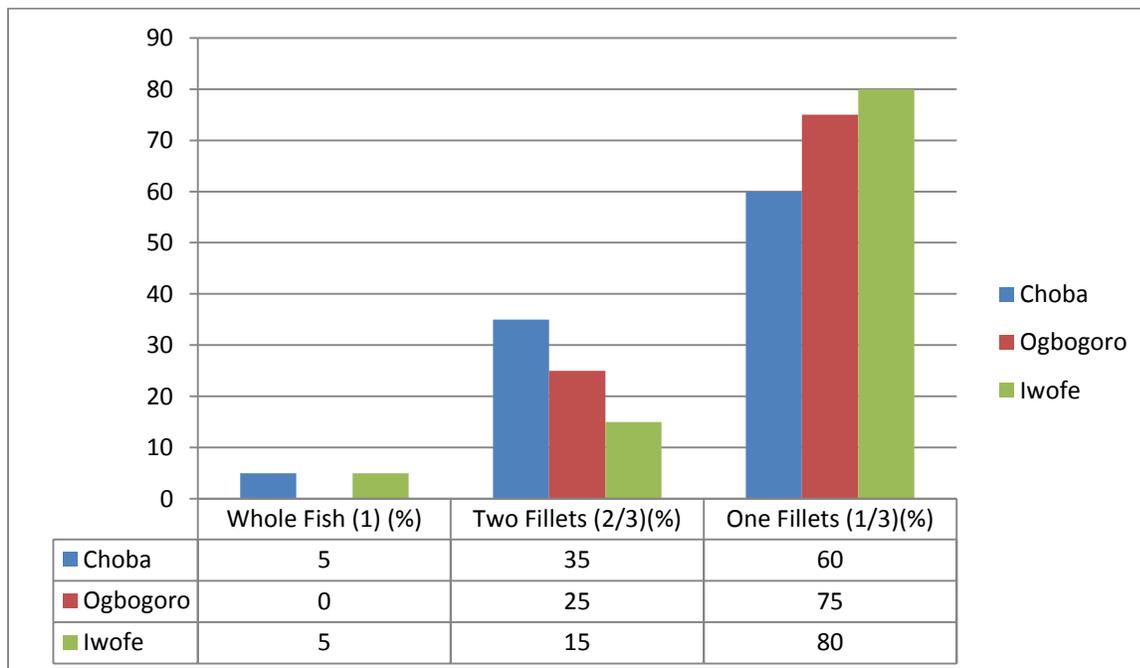
This involves the magnitude, frequency, and duration of exposure of subsistent fishers from Choba, Ogbogoro and Iwofe communities to COPC from the consumption of *C. Nigrodigitatus*. The fish size per meal, Frequency of fish consumption and amount of fish consumed per meal were estimated from the FCS questionnaire, while consumption rate (CR) and chronic daily intake (CDI) were mathematically deduced from the FCS questionnaire and default recommended values. Below are graphs showing results of average size of fish consumed per meal (fig.7), mean fish frequency consumed (fig. 8), amount of fish consumed per meal (fig. 9) and CR by target population (fig. 10).



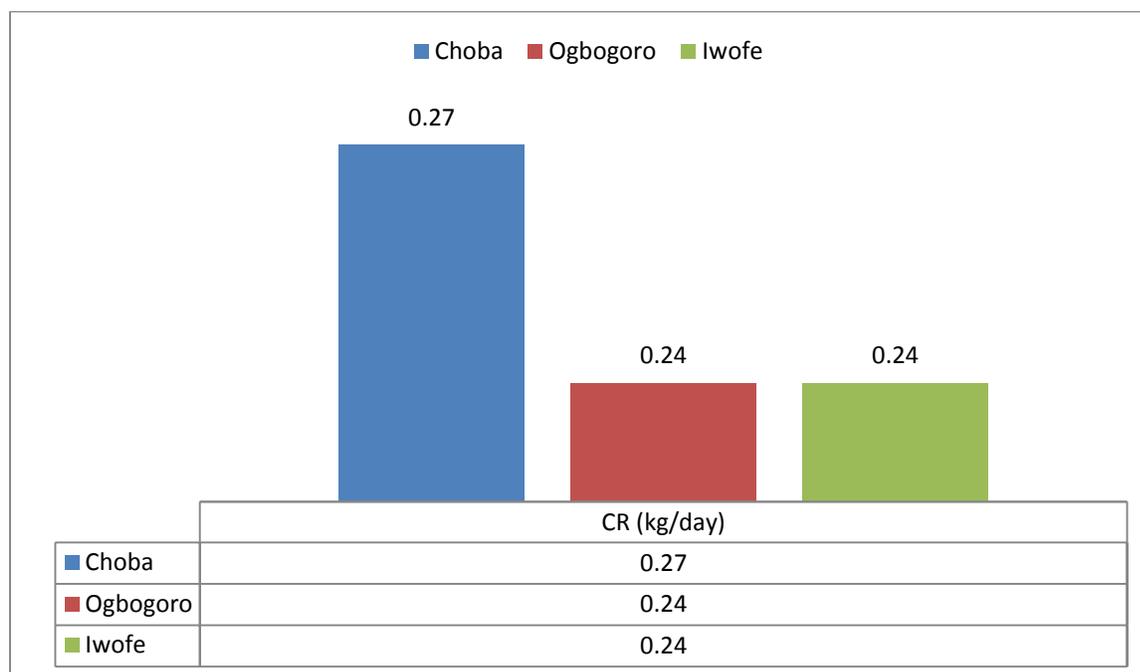
**Fig.7: A graph showing the result of Average size of fish consumed per meal**



**Fig. 8:** A graph showing the result of mean frequency of Fish consumption



**Fig. 9:** A graph showing the result of the amount of fish consumed per meal



**Fig. 10: A graph showing the result of consumption rate (CR) by target population**

### 3.5.1.3. Chronic Daily Intake (CDI)

When the average rate of COPC consumption is expressed as a function of body weight of fish ingested, the resulting exposure rate is referred to as the chronic daily intake (CDI). The CDI of chemicals present in fish tissue was calculated using the following equation:  $CDI = C \times CR \times EF \times ED / BW \times AT$ . Table 2. Shows parameters, both experimental and default values, used in evaluating CDI. Table 3 shows the CDI of target populations.

**Table 2: Shows values used for exposure parameters to calculate chronic daily intake for target populations.**

Parameter	ChobaOgbogoroIwofe	Source
<b>Tissues Conc. (C)</b> a)heavy metals (Cd, Cr, Cu, Pb& Zn) b) PAH	average/station (see table) average/station (see table)	PS* PS*
<b>Consumption rate (CR)</b>	0.27    0.24kg    0.24kg	PS**
<b>Exposure Frequency (days/year) (EF)</b>	365 for all stations	DV
<b>Exposure Duration (years) (ED)</b>	adult average see (70)	DV*
<b>Body Weight (kg) (BW)</b>	67.3	PS
<b>Averaging Time (days) (AT)</b> a) Carcinogens b) Noncarcinogens	25,550    25,550    25,550 (ED x EF) (ED x EF) (ED x EF)	

PS = present study.

DV\* (Default value) = Average life expectancy of the general public (USEPA 1989)

**Table 3: Showing average CDI of respondents from target population in this study**

CDI	Choba (Kg/mg/day)	Ogbogoro (Kg/mg/day)	Iwofe (Kg/mg/day)
<b>Cd</b>	$0.41 \times 10^{-5}$	$0.37 \times 10^{-5}$	$0.37 \times 10^{-5}$
<b>Cr</b>	$0.41 \times 10^{-5}$	$0.37 \times 10^{-5}$	$0.37 \times 10^{-5}$
<b>Cu</b>	$0.41 \times 10^{-5}$	$0.37 \times 10^{-5}$	$0.37 \times 10^{-5}$
<b>Pb</b>	$0.41 \times 10^{-5}$	$0.37 \times 10^{-5}$	$0.37 \times 10^{-5}$
<b>Zn</b>	$1.0 \times 10^{-2}$	$0.9 \times 10^{-2}$	$0.9 \times 10^{-2}$
<b>PAH</b>	$1.4 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.3 \times 10^{-4}$

#### Risk Characterization

Noncarcinogenic and carcinogenic risk estimates are calculated separately because of fundamental differences in their critical toxicity values.

### 3.5.2.1. Noncarcinogenic Health Effects

Hazard Quotient was calculated for each COPC for the different target populations. Hazardous quotient which is the ratio of exposure to toxicity for an individual chemical.  $HQ = CDI / RfD$  Where: HQ = Chemical-specific hazard quotient (unitless), CDI = Chemical-specific chronic daily intake (mg/kg-day, RfD = Route- and chemical-specific reference dose (mg/kg-day. All results were less than the critical exposure threshold ( $HQ > 1$ ) (US EPA 1989).

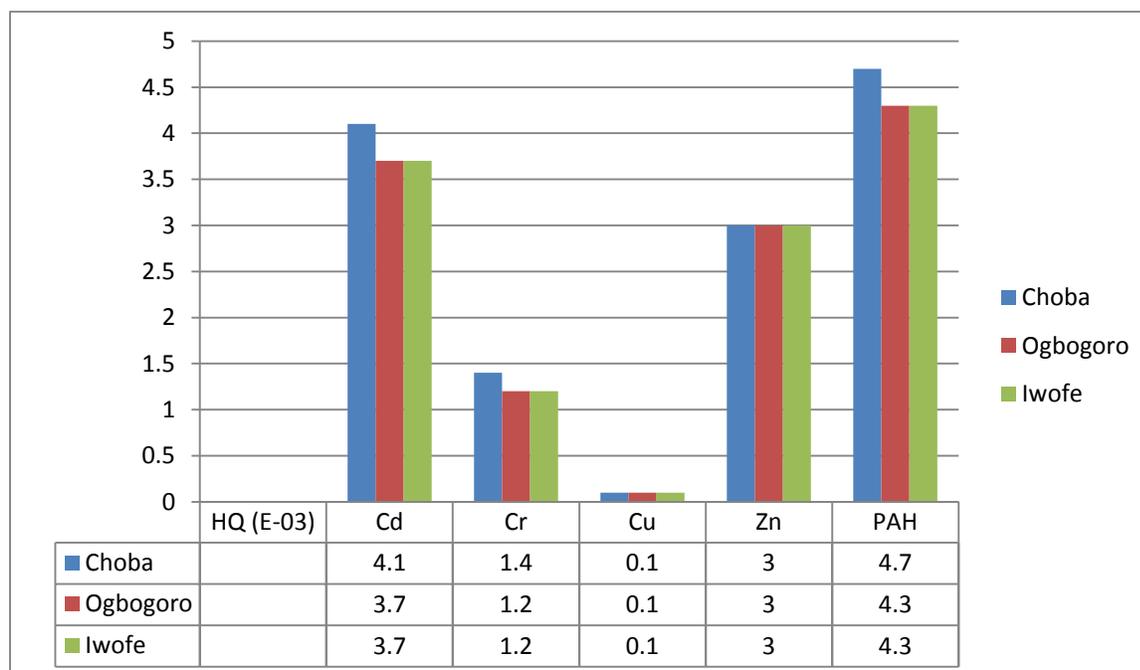


Fig. 11: A graph showing the result of HQ of target populations

### 3.5.2.2. Carcinogenic Risk

Due to IRIS weight-of-evidence for carcinogenicity of the COPC, PAH was the only compound estimated as a known human carcinogen. Human exposure to PAH is typically to a mixture of PAH chemical, not to individual PAH chemicals. The relative potency factor approach assumes that individual PAH potencies relative to an index compound (i.e. Benzo(a)pyrene, [BaP]) are added together to yield a cancer risk for the whole mixture (USEPA,2010). The oral carcinogen toxicity value of Benzo(a)pyrene with Slope Factor (SF) of  $7.3E+00$  and weighted evidence of B2, with a resultant effect of Forestomach, squamous cell papillomas and carcinomas (USEPA 2000b) was the resultant slope Factor used for PAH in this study.

Table 4: Showing the carcinogenic risk effect of PAH on the target population.

Choba	Ogbogoro	Iwofe

<b>PAH</b>	1.4E-04	1.3E-04	1.3E-04
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The excess cancer risk estimates in this report are shown in scientific notation format. For example, the PAH risk value for Choba population,  $1.4 \times 10^{-6}$ , should be interpreted as an increased risk of 1.4 in Ten thousand (10,000).

## DISCUSSION

### Physico-Chemical analysis and EWQI

The EWQI values for the Choba, Ogbogoro and Iwofe were 54.5, 69.1 and 69.3 respectively. The values showed that the water can be ranked as marginal at Choba station, and fair at the Ogbogoro and Iwofe stations. The EWQI result shows that the water quality gets better as the river flows downstream in the direction of Choba, Ogbogoro and Iwofe. This order of increase in EWQI between station might be due to dilution and flow factors because of the downstream tidal pattern (i.e. the upper reaches of NCR are non-tidal while the lower reaches are tidal) and proximity to the estuary which is a short distance to the Atlantic ocean. This order is also a reflection of the cosmopolitan pattern of the host communities of the station: Choba is more remote to the estuary and more populated with more built up areas (including the University of Port Harcourt Campus) and a relatively higher socio-economic (a popular Choba market and) and industrial (Ndomie food factory) along its riverbank, while Ogbogoro and Iwofe follow in the same order with lesser population and industrial activities, but more important is their closeness to the estuary leading up to the ocean. The overall EWQI of NCR is an indication of the various anthropogenic activities at those stations. Contaminants such as discharge of untreated or partially treated effluent by various industries at the bank of river, domestic sewage, abattoir waste, runoff water from agricultural lands near the bank of the river may be responsible for the marginal state of water quality.

### Sediment quality analysis

Sediment's heavy metals (Cd, Cr, Cu, Pb and Zn) concentration profile values for the three sampling stations of Choba, Ogbogoro and Iwofe, were within the normal NOAA (2009) screening guideline range for the protection of freshwater aquatic life. Nevertheless, Ogbogoro station recorded the highest values in Cr, Cu, Pb and Zn, while Cd value was highest in Choba. Iwofe recorded the lowest values in Cd, Cr, Cu and Zn, while the lowest values of Pb was recorded in Choba. Of all three stations, Ogbogoro recorded a relatively marginal outcome in heavy metal concentration profile, which calls for concern. PAH concentration was highest in Ogbogoro (5.84 mg/kg), which was higher than NOAA (2009) sediment screening guideline for freshwater river (4.0 mg/kg). The rest of stations recorded PAH values within the NOAA guideline range as follows: Iwofe (3.76 mg/kg) and Choba (3.76).

On the average, Ogbogoro had the highest levels in most of the heavy metals of potential concern and in PAH. This is a reflection of the high level of oil servicing companies activities in the Ogbogoro station compared to the other stations of the NCR. Although the results of the chemical sediment analysis did not show any alarming concentrations of substances tested for, except for PAH, nevertheless, this exposure of fish to mixt

ure of known pollutants. Fishes are known to bioaccumulate chemicals, especially heavy metals and PAH, to a considerably higher concentration than the levels found in the water or sediment. This is mainly due to the lipid solubility and resistance of these compounds to several degenerative processes in animal tissue (Miranda et al., 2008; Vaclavik et al., 2006). It has also been reported that accumulation of toxic metals can hence (and in particular cases, even directly cause) pathology in fish (Moiseenko et al., 2008) and also interfere with molecular and cellular events, inducing some negative or harmful effects in the energy reserves, resulting in reduced growth and/or reproduction (Moiseenko et al., 2008). The ultimate fate of those PAHs that accumulate in sediments is believed to be biotransformation and biodegradation by benthic organisms (EPA 1980). PAHs in aquatic sediments, however, degrade very slowly in the absence of penetrating radiation and oxygen (Suess 1976), and may persist indefinitely in oxygen-poor basins or in anoxic sediments (Neff 1979). Some investigators have shown that aquatic invertebrates, fish, and amphibians collected from areas of high sediment PAH content show elevated frequencies of hyperplasia and neoplasia (Rose 1977; Mix 1982; Black 1983; Malin et al. 1984, 1985a, 1985b; Black et al. 1985; Baumann et al., in press), and, recently, that the hepatic carcinoma has been induced in rainbow trout (*Salmo gairdneri*) by PAH (benzo(a)pyrene) through dietary and intraperitoneal injection routes (Hendrick et al. 1985).

### **Fish Edibility: Bioaccumulation Analysis**

When doing human health risk assessments, the main focus is on the edible parts of the fish. These may vary according to the individual consumers; some prefer other parts of the fish to others but in general, the edible part excludes the head, external viscera (e.g. skin) internal viscera (e.g. muscle and bones). For this study, the focus was placed on the skin and muscle tissue. The heavy metals detected were within the normal screening NOAA available guideline level acceptable for fish protection and consumption, while PAH (0.035 mg/kg) was slightly above the NOAA acceptable level (0.03 mg/kg).

A growing literature exists on uptake, retention, and translocation of heavy metals and PAHs by aquatic plants and animals. Authorities generally agree that: most species of aquatic organisms studied to date rapidly accumulate (i.e., bioconcentrate) heavy metals and PAHs from low concentrations in the ambient medium; uptake of heavy metals and PAHs are highly species specific. Based on the level of PAHs on skin and muscle tissues of harvested fishes from NCR and with a known and documented effect of PAH on human, consumption of fish from the NCR would portend some health consequence on human. This would depend on the consumption rate and the concentration of PAH in the edible part of fish tissue at that particular time.

### **Integrated Risk Assessment (IRA)**

#### **Exposure Assessment: Fish Consumption Survey**

Currently, most states do not have sufficient data available to calculate local consumption rates or to identify special populations at risk. As a result, a variety of methods are used for estimating consumption rates without calculating risk associated with the consumption of chemically contaminated fish tissue (U.S. EPA, 19

89). As states increase their focus on the type of risk assessment, the need for site-specific fish—and now wildlife—consumption surveys has become more apparent (U.S. EPA, 1998).

In this study, the demography and fish consumption status of subsistent fishers show that most respondents were between the ages of 18-34 years and >55 was the least age frequency recorded for the three survey sites of Choba, Ogbogoro and Iwofe. Males were noted as the most frequent respondent with a highest value of 80% noted in Ogbogoro. The average body weight of respondents ranged between 65.1-69.7 kg, with Iwofe registering the highest average weight of 69.7 kg. The average body weight of respondents is vital because it is a factor in estimation of the fish Consumption rate (CR) and chronic daily intake (CDI). Table size of fish (15-30 cm: FAO, 1978b) was noted as the most consumed size of *C. Nigrodigitatus* from NCR. This followed by fishes < table size. The reason for this is that most subsistence fisher traditionally sell large sizes of fish caught to the open market while smaller sizes of harvest are kept for household consumption. All respondents surveyed reported eating fish on at least one occasion per week, closely followed by those recorded as having daily consumption of the fish (i.e. over 50% of the respondents from Ogbogoro and Iwofe village claimed to eat fish on a daily basis). Most respondents frequently ate one fillet (1/3 of a whole table size fish), followed by those who ate two filets. The FCS data and default values were used to mathematically evaluate the fish CR and CDI. The estimated CR was highest in Ogbogoro with a record of 2.74 kg/day. Zn and PAH recorded the highest CDI.

### Non-carcinogenic Health Effects

The noncarcinogenic HQ assumes that there is a threshold level of exposure, the RfD, below which it is unlikely that even sensitive populations will experience adverse health effects (USEPA 1989). If the exposure exceeds this threshold ( $HQ > 1$ ), there may be concern for potential noncarcinogenic health effects. Generally, the greater the magnitude of the HQ above a value of 1, the greater the level of concern for noncarcinogenic health effects. It should be noted, however, that exposures above the RfD do not represent the same increase in risk for all chemicals as RfDs do not have equal accuracy or precision and are not based on the same severity of toxic effects (USEPA 1989; Hayes 1994). Furthermore, the level of concern does not increase linearly as the RfD is approached. In this study all COPC values were less than 1. Nevertheless, the values of Zn and PAH are of potential concern, because of the marginal accumulative level compared to their RfD levels. Further accumulation of these chemicals by *C. Nigrodigitatus* would increase their risk quotient, thus their ability to cause deleterious effect on human.

### Carcinogenic risk.

The excess cancer risk estimates in this report are shown in scientific notation format. These values, for example 1.0E

06, should be interpreted as an increased risk of 1.0 in 1 million of developing cancer over a lifetime. The interpretation of cancer risk estimates requires that an individual, organization or state determine what increased risk is acceptable. This threshold is referred to as the acceptable risk level (ARL)

(USEPA 1997a). Eleven states in the United States of America currently use  $1.0E-04$  (1 in 10,000), fourteen states use  $1.0E-05$  (1 in 100,000), and eight states use  $1.0E-06$  (1 in 1,000,000) as the ARL for issuing state fish consumption advisories (EVS 2000a). The Oregon Health Division has used an ARL of  $1.0E-06$  for some carcinogensto issue fish advisories within the state (EVS 2000a). For this study, an individual lifetime excess cancer risk of  $1.0E-04$  was used as the ARL to assess the potential for adverse health effects due to consumption of fish from NCR containing carcinogenic chemicals. From the current study result therefore, PAH (the only COPC with weighted evidence to cause cancer in human) was above the ARL in all stations Choba, Ogbogoro and Iwofew with values of  $1.4E-04$ ,  $1.3E-04$  and  $1.3E-04$  respectively.

Numerous PAH compounds are distinct in their ability to produce tumors in skin and in most epithelial tissues of practically all animals species tested; malignancies were often induced by acute exposure to microgram quantities. In some cases, the latency period can be as short as 4 to 8 weeks, with the tumors resembling human carcinomas (EPA 1980). Target organs for PAH toxic action are diverse, due partly to extensive distribution in the body and also to selective attack by these chemicals on proliferating cells (EPA 1980). Damage to the hematopoietic and lymphoid system in experimental animals is a particularly common observation (EPA 1980). In general, PAH carcinogens transform cells through genetic injury involving metabolism of the parent compound to a reactive diol epoxide. This, in turn, can then form adducts with cellular molecules, such as DNA, RNA, and proteins, resulting in cell transformation (Dipple 1985; Ward et al. 1985)

## Conclusion

The EWQI has shown that NCR is of a marginal quality. The PAH concentration in sediment in Ogbogoro station is above the recommended guideline of  $4.0\text{mg/kg}$ . The PAH found in muscle of some of the fish from NCR were just above the recommended guideline of  $0.03\text{mg/kg}$  in the edible portion of the fish. This should therefore render the fish unsafe for human consumption. However the edible part of the fish was considered safe to eat concerning the heavy metals levels according to the guidelines set by the FDA and EPA. The fish consumption survey has shown a fish consumption pattern by subsistence fishers. They consume an average of  $1.2\text{kg/day}$  of *C. Nigrodigitatus*. The highest fish consumers are of the age range of 18-34 years. In conclusion according to the risk assessment, if the fish is consumed over a long term basis, adverse health effects are expected. These results contribute to supporting evidence that poor water quality has impacted on the health and edibility status of *C. Nigrodigitatus* found in NCR. However if consumption of fish is lower than that considered to be a reasonable exposure, these risks are considerably reduced. The Integrated Risk Assessment is a first tier or screening exercise and indicates that more information is needed to make an informed decision.

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