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ECOLOGICAL RISK ASSESSMENT OF TRACE METALS FROM INDUSTRIAL EFFLUENTS IN THE OKRIKA ESTUARY (NIGER-DELTA REGION) OF NIGERIA

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ABSTRACT: *Concentrations of heavy metals Aluminium (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Vanadium (V) and Zinc (Zn) were analyzed in the tissues of two estuarine fish species; Tilapia (Sarotherodon melanotheron) and silver catfish (Chrysichthys nigrodigitatus) from Okrika estuary in the Niger Delta area of Nigeria. The sampling was conveyed in two seasons, October/November, 2015 and January/February, 2016, representing the climax of both wet and dry seasons respectively. The levels of the metals in the fish species were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The sequence of the metal accumulations in Tilapia was; Fe > Al > Zn > Cu > Cr > V > Ni, in silver catfish; Fe > Al > Zn > Cu > Cr >Ni > V. Levels of the metals in the fish species were higher than the international permissible limits based on the criteria or application of relevant pollution indices. This indicates that the two fish species were not fit for human consumption. A two way analysis of variance (ANOVA) was used to test the difference in metal concentrations in the fish tissues. Mean differences were separated by the use of t-test. In comparison of the metal accumulations in the tissues of the fish species from oil impacted creeks (Ekerekana, Okari and Ogoloma) and non or less oil impacted counterpart (control site), higher levels (p<0.05) of the metals were observed in the impacted than the non-impacted creek. For most of the metals, Sarotherodon melanotheron had higher concentrations than the Chrysichthys nigrodigitatus. Seasonal variations reflected that there was higher accumulation of the metals in the two fish species in the rainy season than the dry season. Pearson Correlation Analysis and the use Vanadium/Nickel ratio were used to confirm the source of the metals in the fish from oil pollution. Therefore, it is mandatory and expedient to ensure regular monitoring of the trace element loadings in these creeks and to take appropriate measures to alleviate the incidence in order to safeguard the health of the public.*

KEYWORDS: heavy metals; tilapia; silver catfish; Okrika estuary; Niger-Delta

INTRODUCTION

Estuarine pollution has been regarded as the deliberate introduction by man of a diverse range of waste substances into an estuary, such as chemicals and waste products, which are hazardous or harmful to the estuarine ecosystem and even to man himself (McLusky, 1989)**.** The toxic substances that are commonly found in the estuaries include; heavy metals, thermal wastes, insecticides, herbicides, pesticides, agro-chemicals and petroleum products (Bryan and Langston, 1992; Keser *et al*., 2005). Estuaries are described as the most productive ecosystems of the world because they are vital links in the life histories of commercially important fin and shell-fishes, most of the near-shore and intertidal species, and all anadromous fishes, as they serve as migration routes, refuge, feeding and nursery areas (Day *et al*., 1987, McLusky and Elliott, 2004). Pollution of estuaries is among the greatest threats to our environmental health. This pollution is caused by and originated from both human and industrial activities such as

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refuse and sewage disposal, burning of fossil fuels, incineration of carbon containing substances, indiscriminate discharge of industrial or refinery effluents, mining, accidental spills, urban and agricultural run-off (Lipp *et al.*, 2001; Colombo *et al*., 2005; Ajani and Balogun, 2015) although, a relatively small amount occurs from natural sources such as volcanic eruption, land-slide, weathering of rocks, earthquake (Monroy *et al*., 2014). Rivers and creeks are the direct recipients of most of these natural, industrial, human and municipal wastes (Li *et al*., 2000; Unnikrishnan and Nair, 2004; Dhanakumar *et al*., 2015). The impacts of contaminants in the brackish environment depend largely on some factors such as; the type and amount of the pollutants and its biological role, period of exposure (resident time) and characteristics of the estuary itself, that is, how often it is flushed by the tides, type of organisms exposed to it and its regulatory mechanisms (Akan *et al.*, 2010; Jorgensen, 2011).

Recently, Nigeria was ranked as the largest oil producer in Africa and sixth in the world due to its massive oil deposit in the Niger-Delta (Gerner *et al.*, 2004; NNPC, 2014). Industrial growth in the Niger-Delta region has been rapid and escalating in the recent years (Akinrotimi *et al.,* 2015). There is no doubt that the Niger-Delta area plays a major role to the growth of Nigeria's economy because it is the base for many multi-national companies especially the oil industries (Akinrotimi *et al*., 2015, Uzoma and Mgbemena, 2015). **Exploration and extraction** (**drilling**) of petroleum by **oil-industries** has been on-going for over five decades in the Niger Delta (Uzoma and Mgbemena, 2015). The oil industry in the Niger Delta began commercial operation in 1958 when crude oil was first discovered at Oloibiri by Shell British Petroleum (now called Royal Dutch Shell) in 1956 (Robinson, 1996). This discovery led to the expansion and intensification of oil exploration located onshore and offshore (over 600 oil fields) in the region and about 2.5 million barrels of oil are drilled on a daily basis (Ndoms, 2005; Anejionu *et al.*, 2015). During drilling and extraction, crude oil is brought to the surface and a lot of wastes in form of liquid, solid and gas are generated, released and contaminated the environment (Rezende *et al*., 2002).

Pollution from **indiscriminate discharge of effluents and oil spillage** from industries has contributed immensely to the ecological damage of the region (Ajayi and Osibanjo, 1981; Oguzie, 2000; Okebukola, 2001; Ugochukwu and Ertel, 2008; Marcus *et al.*, 2013). The oil industries use a network of pipelines to transport and distribute petroleum products across the region (Anejionu *et al.*, 2015). Shell Petroleum Development Corporation (SPDC, 2014a) reported an increase to 3600 incidences of oil spills from 2001-2014. Brown (2009) reiterated that approximately 1.5 million tonnes of crude oil have spilled over five decades in the region. A number of factors combined together are responsible for oil spillage in the region, these include; ageing and corrosion of oil pipes, poor maintenance of infrastructure, indiscriminate effluent discharge during processing at refineries, human error during bunkering activities and sabotage (Obute and Osuji, 2002; Nwilo and Badejo, 2004).

Gas flaring and venting by oil companies is another prominent contributor to environmental degradation in the Niger-Delta since 1970 (NNPC, 1984; Anejionu *et al.*, 2015). It is described as the combustion of natural gas associated with crude oil/petroleum without making use of the energy generated and its simultaneous release into the atmosphere (Elvidge *et al*., 2009; Anejionu *et al*., 2015). UNDP (2006) reported that Nigeria flares 75% of the gas it produces far greater than any other country in the world. These gas flaring activities do not attain complete combustion with efficiency ranging from 60-80% (Abdulkareem, 2005a). Ibeawuchi (2016) reported that gas flares contains over 250 toxins which are released and detrimental to the environment. All aspects of the industrial activities have adverse effects on the ecosystems

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(Uzoma and Mgbemena, 2015). The impact of environmental damage in the region cannot be quantified (Baghebo *et al*., 2012). Baghebo *et al* (2012) reported that in 2002, waste disposal and pollution by the Warri Refining and Petrochemicals Company (WRPC) destroyed the fishing activities and reportedly caused a number of deaths among the Itsekiri indigenes through the consumption of contaminated seafood because a large section of people living in the Niger Delta rely on fishing for their sustainable livelihood- as their major occupation, income and food sources (Amnesty International, 2009). The poor environmental management practices by the oil and other industries coupled with negligence by the Nigerian government and failure of environmental laws and regulations have subjected and rendered the region seriously ecologically damaged with negative impacts on the environment, human health and socio-economic well-being (Holdway, 2002; Uzoma and Mgbemena, 2015). Among the most alarming types of pollutants generated and released to the receiving water-bodies in the area are the heavy metals (Rauf *et al*., 2009). Trace or heavy metals are metallic chemical elements with relatively high density greater than 6g/cm³ and toxic at low concentration (Duffus, 2001; Hoffman *et al.*, 2011) and have been regarded as one of the most common pollutants that are of ecological importance and deteriorate our aquatic ecosystems (Lawlor and Tipping, 2003; Ali *et al.*, 2013). Over 20 heavy metals are known among which are; arsenic, cadmium, nickel, mercury, cobalt, chromium, manganese, copper, zinc, antimony, platinum, vanadium (WHO, 1996; Carpenter, 2001). Heavy metals are accumulated by fish in the aquatic ecosystem based on their ecological requirements, physiology or metabolism and other factors such as salinity, extent or degree of pollution, food and sediment and can cause various kinds of ailments when ingested and in certain amounts (Amirah *et al*., 2013). For instance, recent studies indicated that although Zn is involved in bone formation, its elevated intake can cause gill, kidney and liver damage, growth retardation, mortality, muscular pain and intestinal haemorrhage (Sorensen, 1991; Honda *et al*., 1997; Jordao *et al*., 2002). High levels of iron have been reported in industrialized parts of the world (Rahman *et al*., 2012). High concentrations of Fe can cause convulsions, skin ulcer, kidney, liver and DNA damage and cancer (Payne *et al.*, 1998). Many authors have also reported that intensive exposure to Cr compounds can lead to lung cancer in man (Jordao *et al*., 2002).

Fish is a good indicator of pollution and has been used extensively for environmental monitoring because it can be obtained in large quantity, has potential to accumulate pollutants in its tissues and organs, long life-span, occupies different food chain levels, easily sampled and optimum size for analysis could be obtained (Rashed, 2001; Olaifa *et al*., 2004; Anim-Gyampo *et al.*, 2013). Most researches have only been focusing on the accumulation of pollutants, such as heavy metals, in the edible part (muscle) of the fish because it is the part that is often consumed by human (Keskin *et al.*, 2007). Muscle analysis alone cannot give the true situation of entire fish body contaminations, therefore it is expedient to analyse other body parts such as the gills and liver (Has-Schon *et al*., 2006). The presence of metal binding proteins, metallothioneins, in the liver gives it the tendency to accumulate higher concentration of heavy metals than the muscles (Ploetz *et al*., 2007; Uysal *et al.*, 2008a). Sediments have been identified and reported as the largest ecotoxicological component of the aquatic ecosystem because they act as a sink (repository) and source of pollutants, such as heavy metals, to the organisms and ultimately human consumers of those organisms (Gaillard *et al*., 1986; Burton, 1992; Calmano *et al.*, 1993; Davies and Abowei, 2009; Issa *et al*, 2010). Ayotunde *et al* (2012) and Kumar *et al* (2013) reported that when metals enter an aquatic ecosystem, a great portion settles and are absorbed by the bottom mud or sediment and can subsequently re-enter the overlying water and increase potential ecological risks and toxicity to aquatic fauna such as fish. Heavy metals can adsorb to sediment and their subsequent toxicity

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depends on the various forms and the amount of the metal bound to the sediment matrices (Yu *et al.*, 2000).

Statement of Problem and Justification of the Study

Before the discovery of crude oil in Oloibiri (located in the Niger-Delta) in 1956, agriculture was the mainstay of the Nigerian economy (Amnesty International, 2009; Anifowose, 2008). The crude oil bloom witnessed in the 1970s resulted in the rapid increase in the industrial activities of the region. Over the years, oil exploration, production and refinery operations in Nigeria have resulted in various ecological degradations (Adati, 2012). To aggravate the situation, the rise in human population coupled with improper disposal and inefficient management of municipal solid wastes and sewage contribute more problems to the environmental quality the region (Ogbonna *et al*, 2002).With abundant financial resources accrued from petroleum but no developmental policy, unguided urbanization and industrialization in place, the process technology of some of the oil-industries often resulted in unacceptable levels of toxic substances in the seafood and sediment (Amnesty International, 2009).

Port Harcourt Refining Company (PHRC) is the premier and largest of the three main refining companies owned and run by Nigerian government and its mandate is to process the crude oil into finished petroleum products like kerosene, diesel, automative gas oil, low pour fuel oil, high pour fuel oil, paraffin, etc. It began its operation fully in 1965 (Adati, 2012) and has processing capacity of 210,000 barrels per stream day (bpsd) and discharges waste-water into the nearby creeks.

Okrika estuary is well positioned and receives waste effluents directly and also gas flaring indiscriminately discharged from Port-Harcourt Refining Company (PHRC) in addition to other activities carried out along its course which include oil bunkering, domestic sewage, refuse and waste disposal, waste incineration, fishing, transportation, etc. Thick oil slums are seen floating all over the surface of the creek especially around the mangroves and other prop rooted plants. Fishermen and other people living in the area often complain of the tainted fish species they usually catch from the creek attributed to the oily effluents (Mbaneme *et al*., 2013). Therefore, it is important and useful to assess the status and quality of the fish species for human consumption because they are major source of food and economically important to the people living in the region and may pose serious health implications and likewise sediment quality and pollution status as well (Ogbuagu *et al*., 2011; Okoli *et al.*, 2011). However, there is little or no literature on the levels of heavy metals in fish and sediment samples from this estuary and hence necessitates this assessment which will provide baseline information for future use by the scientists, researchers and policy makers.

Aims and Objectives

Therefore, the aims and objectives of this study are:

(1) To evaluate the concentrations of specified heavy metals (Cu, Zn, Fe, Ni, Cr, V and Al, which are among the priority lists of Agency for Toxic Substances and Disease Registry (ATSDR, 2013), in two commercially important fish species caught from Okrika creeks and assess their quality and suitability for human consumption by comparing with permissible international standards [World Health Organization (WHO), European Commission (EC), Food and Agricultural Organization (FAO), Australian New Zealand Food

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Administration (ANZFA) and Food Standards Australia (FSA)] and pollution indices.

(2) To evaluate statistical differences in heavy metal accumulation in fish between oil impacted (Ekerekana, Okari and Ogoloma) and non or less oil impacted sites (Agbonchia-Okulu (Control Site)).

(3) To evaluate the possible source of the heavy metals (finger-printing).

Research Questions

- Do metals in the environmental matrix, fish samples, higher than the international standards and guidelines?
- Do heavy metal burdens in fish species from oil-impacted creek (experimental sites) significantly different from non or less oil impacted counterpart (control site)?
- Do investigated metals originate from crude-oil source?

MATERIALS AND METHODS

Description of the Study Area

The study area lies between latitudes 4° 44’ 00” to 4° 46’ 10” N and longitudes 7° 5’ 15” to 7° 6’ 15” with an area of 905.2sq.km. It is located in Okrika Local Government Area of Rivers State with a population of over 150,000 (NPC, 2006). **Okrika estuary** has an average length of 21km and lies in the north bank of the Bonny River with a distance of about 56km from the Bight of Benin in Eastern part of the Niger-Delta. It is a mangrove environment characterised by regular salt water inundation as a result of tidal action and flooding and extensive sandy bottom and mud-flat. The tidal amplitude ranges between 1.5-2m in normal tide. It originates from Marine Base and runs through **Okari** and crosses the Mainland to **Ekerekana** Ama and other creeks such as **Sandfilled/Mainland Bridge (Ogoloma**). It is characterized by tropical climate with alternating wet (March to October) and dry (November to February) seasons. Based on the Nigerian Meteorological (NIMET) data, the area is associated with warm temperature ranging from 26^0 to 34^0C, annual bimodal rainfall of 2300-4000 cubic metres and distinct relative humidity and evaporation. It is ecologically endowed with vast biodiversity; fish, mollusc, crustaceans, crabs, *Rhizophora mangle*, *Laguncularia racemosa*, *Avicennia africana*. Because it is located in the crude-oil reservoir region, this makes it a receiving and collecting basin for the effluents and gas flaring discharged by the Port-Harcourt Refining Company (PHRC) leading to its prone to ecological degradation and damage. Other major activities carried out along the creeks include; fishing, recreation, dredging, transportation by speed boat and discharge of domestic wastes (Marcus *et al.*, 2013).

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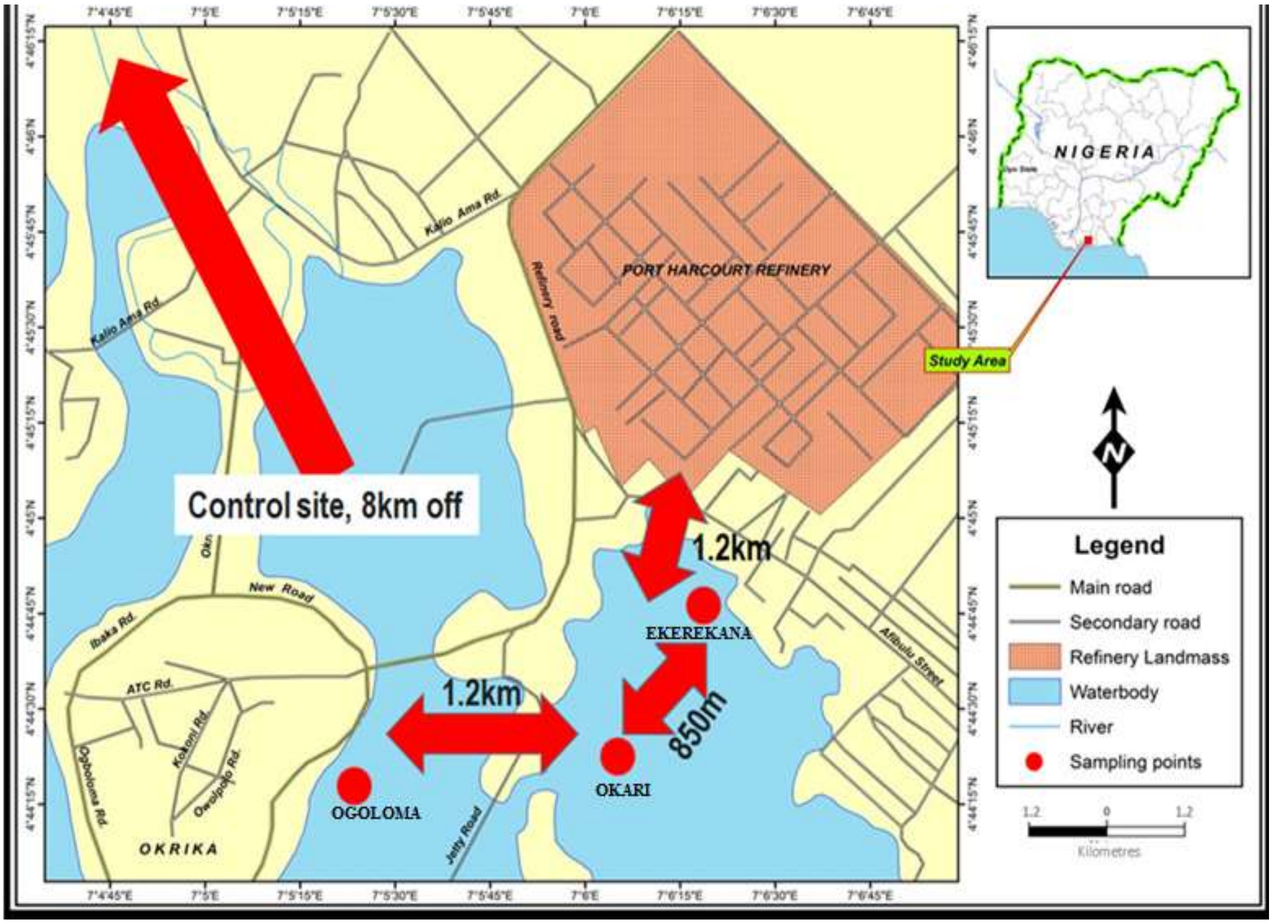

Figure 1: Map of Okrika estuary showing the sampling stations

Experimental Design

Three experimental sampling sites along the estuary course were utilized for data collection. Each site is about 1 - 2km from the other. The respective sampling sites were represented as **Ekerekana (EKR)**, **Okari (OKR)** and **Ogoloma (OGL).** These sites were chosen because of their proximity to the refinery discharge point and in addition to other activities such as domestic waste and sewage disposal, oil-bunkering, fishing and transportation carried out along its course. Sampling was done in October/November, 2015 and January/February, 2016 which represent the peak of both the wet and dry seasons respectively. **Control site** (**CST**) is located in Agbonchia-Okulu community about 8km away and was chosen because it was a non-oil or less polluted environment and it serves as a reference site (Bastami *et al*., 2014; Song *et al*., 2014; Fatoba *et al.*, 2016).

Fish = 4 Sites * 3 Replicates * 2 Species*2 Seasons **= 48 Samples**

Fish collection and preservation

The fish samples were collected directly from each sampling site by employing 2 fishermen who captured the fish species with beach-seine, cast net or gill-net. 2 species (5each); Silver catfish (*Chrysichthys nigrodigitatus*) and Tilapia (*Sarotherodon melanotheron*) were sampled from each sampling site based on their abundance, availability, economic importance, mostly

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eaten by the populace (market survey) and feeding habits. They were transported to the laboratory in ice cold chest to arrest microbial action. Their Standard Lengths, Total Lengths (using graduated plastic measuring board) and Body Weight (using sensitive balance) were measured. After taking their biometrics, they were dissected to remove the liver, gill and flesh (dorsal tissue) and weighed using a highly sensitive measuring balance (Kern 440-35A model). These organs (liver + gill + muscle) were selected because they are the major sites for metals accumulation or concentration, storage and mostly eaten by human (Javed, 2005; Rauf *et al*, 2009,Yilmaz *et al.,* 2010; Jayaprakash *et al,* 2015). The organs were thoroughly washed with distilled water, kept in 70% ethanol in scintillation vials and stored frozen at – 20^0C in a deep freezer) (Akpanyung *et al.,* 2014; Leung *et al.,* 2014; Bastami *et al*., 2015) until required for analysis. The scintillation vial bottles were pre-cleaned with 10% Nitric acid and well dried before use.

Fish preparations prior to analysis

All the frozen fish organs (muscle +liver +gill) samples were thawed at room temperature. Preservation ethanol was evaporated with a high speed revolution Refrigerated Vapour Trap (RVT-400, Thermo Scientific) and then freeze-dried at - 65°C for 3 days. These organs were selected because they are the primary sites of metal uptake and deposit/storage and integral parts of human diet especially when the fish is consumed whole (Rahman *et al*., 2012). Organ samples were ground with Cryomill to powder to ensure homogeneity. An aqua-regia acid digestion procedure similar to Iwegbue *et al* (2007) was employed. The composite homogenized fish tissue samples were accurately measured and weighed (0.5g) into the Teflon digestion tubes and pre-digested for 48hours with 5mL Nitric acid (69%) to minimise loss of volatile metals. Another 5mL of Nitric acid was added on the third day, thoroughly shaken and left for 1 hour. Then, 3.2ml of Hydrochloric acid (35%) was added and left for another 1 hour. Complete acid digestion was carried in the microwave (NARS Express 5, CEN, Germany) at 160°C for 35 minutes until a transparent solution was achieved. Acid fuming was done to separate the acid from the supernatant by transferring the digested samples into the Evapo-clean V-shaped tubes (AHF Analyse-technik, Germany). The product of the acid fuming was placed on the heating block for roughly 2 hours until almost dried extract was achieved. Samples extracts were collected separately from the two arms of the tubes described earlier and then cooled for 30minutes. The extract was diluted with 10ml de-ionized water, filtered with 8-10µm sieve (CFP40 from CEM GmbH, Kleve, Germany), centrifuged (Centrifuge 5430, Germany) at 13795rpm and 20,000 rcf for 10 minutes and finally transferred (4ml of supernatant) into auto-sampler vials for analysis.

Quality Assurance

For quality control, the suitability, precision, accuracy and reagent purity of the analytical procedures used was checked by analysing Certified Reference Materials; Dorm-4 (fish protein from National Research Council, Canada) and ERM-CE 278K (Mussel tissue from European Commission, Joint Research Centre, Belgium) and blanks (mixture of aqua-regia without the matrix prepared exactly as the respective regular samples), to ascertain the recoveries of the known concentrations of the metals under study and validate the analytical techniques used (Cantillo and Calder, 1990; Okafor and Opuene, 2007).

Determination of Trace Element Concentrations

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Inductively Coupled Plasma–Atomic Emission Spectroscopy- ICP-AES

The concentrations of the trace metal in the solutions of the environmental matrices were measured using Varian Vista-Pro CCD Simultaneous Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (radial plasma observation) under certain analytical conditions. This instrument was chosen because it was the only option available, could measure multiple elements, has high sample throughput, precision between 0.2-5% and sensitivity in µg/g. Limit of Detection (LOD) is defined as the concentration corresponding to thrice the standard deviation of the reagent blanks (Mendil *et al*., 2010). Calibration curve of each element was used to produce good correlation coefficient (r = 0.999).The samples were measured in triplicates and their final means were obtained. The detection limits (mg/L) for the trace elements are as follows; Al (0.05), Cr (0.01), Cu (0.01), Fe (0.05), V (0.01), Ni (0.01) and Zn (0.01).

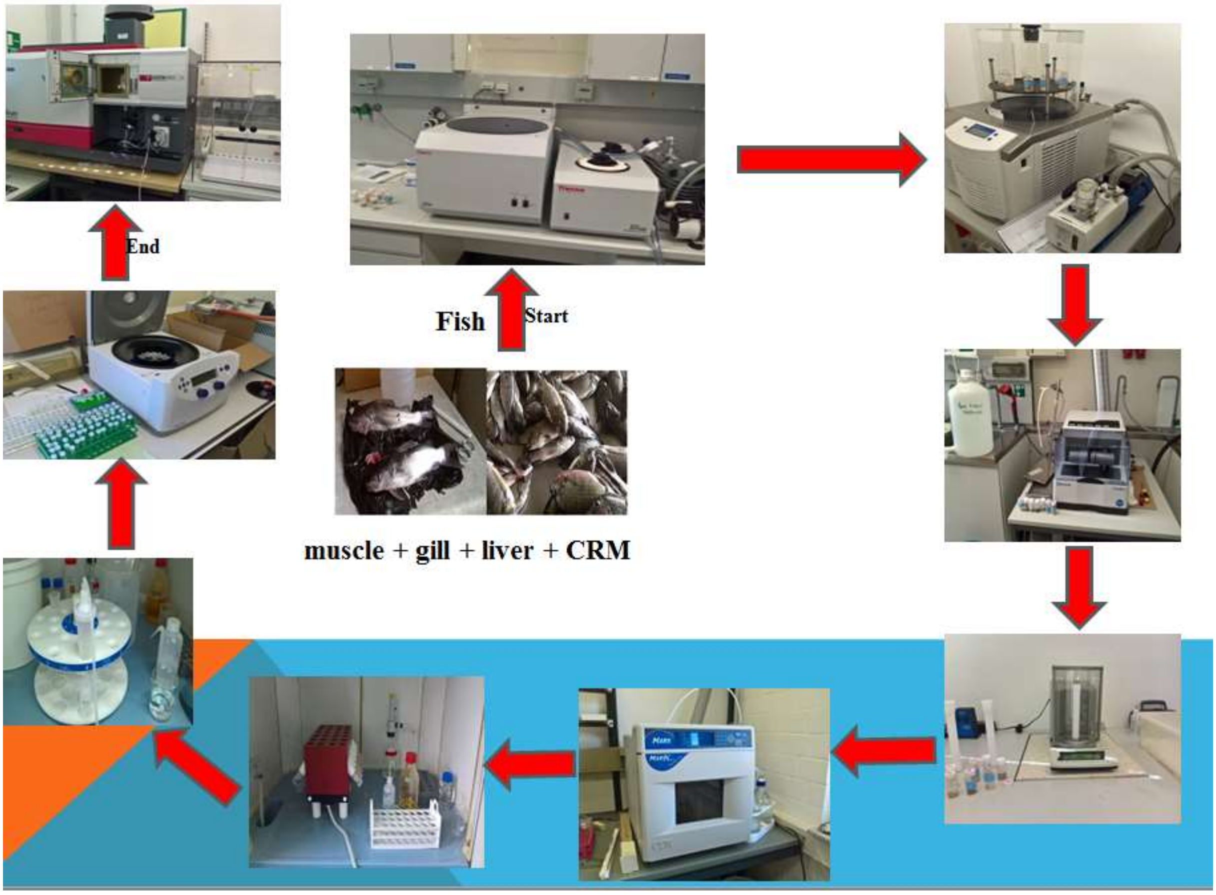

Figure 2: Steps for fish sample preparations and analysis

DATA ANALYSIS FOR RISK ASSESSMENTS

Estimation of Health Risk Assessment for Fish Consumption

Determination of Target Hazard Quotients (THQ)

The THQ describes the ratio between the exposure and reference doses of metals and is used to express the risk of non-carcinogenic effects of metals (Yi *et al*., 2011). It is a single metal assessment of contamination in aquatic biota like fish. If the ratio is less than 1, there will be no health risk and it means that the level of exposure is smaller than the reference dose but value above 1 will pose serious health risk (Yi *et al*., 2011). The values of the trace metals accumulation in the combined fish organs were used to calculate the target hazard quotients (THQ) to ascertain the human health risk from consuming the fish contaminated with trace elements from the oil-polluted site based on the Chien *et al* (2002) equation;

$$THQ = \frac{M_c \times IR \times EF \times ED}{RfD_{\circ} \times BWt \times ATn} \times 10^{-3}$$

where THQ is non carcinogenic risk and has no unit, **M_C** is Metal Concentration in fish (mg/kg); **IR** is the fish Ingestion Rate which is 20.8g/day in Nigeria (Bassey *et al.*, 2014); **EF** is the exposure frequency which is 365days/year; **ED** is the exposure duration which is 54.5years i.e average life span for Nigerians (WHO 2016); **RfD_o** is oral Reference dose (mg/kg/day) which are as follows; Cu (4 x 10^{-2}), Zn (3 x 10^{-1}), Fe (7 x 10^{-1}),Ni (2 x 10^{-2}), V (1 x 10^{-3}), Cr (1.5x10^{-3}), Al (1.0) (USEPA, 1989); **BW_t** is the average adult body weight for Nigerians (60kg) (Bassey *et al.*, 2014); **AT_n** is averaging exposure time for non-carcinogen (365 days × number of exposure years, assuming 54.5 years). Hallenbeck (1993) reported that exposure to two or more metals may have interactive or additive effects. Therefore, Total THQ was used to assess the overall potential health risk posed by more than one metal (Javed and Usmani, 2016). TTHQ is an integrated technique for more than one metal contamination. This method of risk estimation has been used by many researchers and has been shown to be valid and very useful (Chien *et al*., 2002; Wang *et al.*, 2005).Its basic assumptions are; cooking has no effect on the pollutant and that the ingested dose is equal to the absorbed pollutant dose (USEPA, 1989; Cooper *et al.*, 1991).

TTHQ= THQ (toxicant $_1$) + THQ (toxicant $_2$) + ……………. + THQ (toxicant $_n$).

Metal Pollution Index (MPI)

This index was used to assess the total loads of the trace metals in the studied organs of the fish based on the equation proposed by Usero *et al* (1997). It is also referred to as Pollution Load Index (PLI) and was proposed by Tomlinson *et al* (1980).

MPI= $(C_1 \times C_2 \times \ldots\ldots\ldots\ldots \times C_n)^{1/n}$

where C_n is the concentration of metal n (mg/kg) in the tissue of fish. MPI value < 1 indicates no pollution whereas value > 1 indicates polluted fish (Abdel-Ghani, 2015; Javed and Usmani, 2016). It is an integrated technique of evaluation of multiple metals contamination.

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Techniques for Identifying Heavy Metals Source

Analysis of Vanadium/Nickel ratio as a proxy tracer of Oil Pollution

The use of V/Ni ratio as fingerprinting technique for oil pollution has been widely embraced to identify the real or actual source and origin of heavy metals in environmental matrices (Yen, 1975; Oluwole *et al*., 1993). The value of V/Ni ratio of crude oil is fixed, stable and doesn't change and therefore is used to assess and fingerprint crude oil contamination. According to Barwise (1990), low V/Ni ratios, <0.5 is for crude oil derived from marine organic matter while high V/Ni ratio of 1-10 is for crude oil from lacustrine and terrestrial organic matter origin. Ogunlaja *et al* (2014) reported that V/Ni ratios; <0.5, 1.36 and 2.77 have been assigned for Nigeria's light, medium and heavy crude oil residues from the Niger-Delta.

Statistical Analysis

The data obtained from the experimental results were subjected to statistical analysis using R-Studio Version 0.98.1083 (2009-2014). Two way analysis of variance (ANOVA) was carried out to identify the significant difference ($p<0.05$) in metal concentrations in the fish tissues between the sampling stations grouped into two; oil-impacted creek (comprising of **Ekerekana, Okari and Ogoloma creek**s) and non or less oil impacted creek (**the control site** located some distance away (8km) which was a clean and less polluted creek). Generalised Linear Model (**GLM,** with family "Gamma" and function "inverse") was used except for Nickel and Vanadium (Linear Model). The metal concentrations were the dependent variables while the fish species, season and status (impacted vs non-impacted) were the independent variables. Any dependent variable (Ni and V) that did not meet the assumption of normality of error was either log or square-root transformed.

RESULTS AND DISCUSSIONS

Quality Assurance and Heavy metal concentrations in the combined fish organs

The results obtained for the certified reference materials (CRM), (DORM-4, ERM-CE 278K, PACS-2 and MESS-3, indicated a good agreement between the certified and observed values. The percentage recovery was between 65-106.8%.

Mean concentrations of the seven heavy metals, Al, Cr, Cu, Fe, Ni, V and Zn in the tissues of the two species during both wet and dry seasons are listed in **Table 1.** The results revealed that the heavy metals were in the following order; for Tilapia; Fe (299.64) > Al (222) > Zn (50.41) > Cu (16.32) > Cr (3.4) > V (2.00) > Ni (0.79) and for silver catfish; Fe (225.31) > Al (153) > Zn (35.14) > Cu (4.06) > Cr (3.43), Ni (0.59) and V (0.27) (mg/kg dry weight) respectively. Among the analysed metals, Fe was detected in the mean range of 183.47-324.42; Al 108.53-363.59; Zn 33.52-50.81; Cu 3.11-29.86; Cr 2.72-4.35; V 0.22-2.68 and Ni 0.53-0.87 for both fish species (mg/kg dry weight). Higher concentrations of the trace metals were found in the two fish species in the study area compared to the control site except for Cr and Ni.

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Table 1: Spatial and seasonal distribution (mean ± standard deviation) (mg/kg) of heavy metal concentrations in the combined organs of the selected fish species from the study area.

Metals	Fish species	Ekerekana	Okari	Ogoloma	Mean(mg/kg)	Control-Site
Al	TLP CHR	363±392.60 210.07±95.07	116.73±57.17 108.53±81.52	185.67±74.69 140.38±78.86	**222.00**±174.8 **153.00**±85.2	42.55±18.2 41.38±25.78
Cr	TLP CHR	4.35±2.57 3.8±2.20	2.72±0.73 3.67±2.0	3.14 ±2.15 2.81 ±0.84	**3.40**±1.8 **3.43**±1.7	4.06±2.30 3.47 ±1.89
Cu	TLP CHR	11.23±11.9 3.11±1.26	7.87±7.99 4.52±3.39	29.86±31.51 4.54±2.95	**16.32**±17.1 **4.06**±2.5	2.37±2.57 1.11±0.35
Fe	TLP CHR	324.42±150 269.13±72.44	242.84±80.17 183.47±42.09	331.65±96.9 223.32±100.35	**299.64**±109.0 **225.31**±71.6	225.86±130.24 148.58±52.28
V	TLP CHR	1.67±0.63 0.22±0.19	1.64 ±1.19 0.30±0.18	2.68±1.82 0.30±0.26	**2.00**±1.2 **0.27**±0.21	0.55±0.45 0.15±0.35
Ni	TLP CHR	0.87±0.33 0.56±0.08	0.80±0.31 0.69±0.14	0.70±0.29 0.53±0.17	**0.79**±0.31 **0.59**±0.13	1.57±0.35 0.47±0.24
Zn	TLP CHR	50.81±11.09 34.18±7.90	48.80±8.77 33.52±3.06	51.63±21.62 37.73±5.68	**50.41**±13.8 **35.14**±5.6	38.96±16.17 9.24±4.73

TLP=Tilapia (*Sarotherodon melanotheron*), CHR= *Chrysichthys nigrodigitatus*

Mean: Mean was calculated by finding the average for both wet and dry seasons

Comparison with International Food Standards

Mean concentrations of the metals in fish samples obtained were evaluated and compared with permissible limits set by World Health Organization (WHO), Food and Agricultural Organization (FAO), European Commission (EC), Australian-New Zealand Food Authority (ANZFA) and Food Standards Australia (FSA) (**Table 2**). All data were expressed in milligram per kilogram dry weight (mg/kg dw).

Chromium (Cr)

Chromium is an essential trace element in humans, although it does not normally accumulate in fish but in excess, it could have undesirable lethal effect on fish (Akan *et al.,* 2009; Rahman *et al.*, 2012). The results in this study showed a mean concentration range of 3.4-3.43 (mg/kg dw) for both fish species which was 7 to 23 times higher than the values stipulated by EC and WHO respectively indicating a higher level of contamination of fish in this area.

Zinc (Zn)

Zn is an essential element for human involving in various forms of biochemical reactions. Zn toxicity is rare in nature but high concentration up to 40mg/kg can result to muscular stiffness, dystrophy, nausea and Parkinson's disease with copper (Gorell *et al.*, 1997). The mean concentration range obtained for the fish species in the study was 35.14 - 50.41 (mg/kg dw). This amount is far higher than 30-40 (mg/kg) recommended by WHO, EC and FAO and 5.0 (mg/kg) by FSA.

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Copper (Cu)

Cu plays a major role in enzymatic reactions and synthesis of hemoglobin (Sivaperumal *et al*., 2007). High intake of copper is detrimental human health (Gorell *et al*., 1997). Its mean concentration range in this study was 4.06-16.32 mg/kg dw). This amount is still within the level (30mg/kg) stipulated by FAO, WHO but far higher than 0.5mg/kg of FSA.

Iron (Fe)

Fe is an essential element necessary for the production of hemoglobin, myoglobin, and certain enzymes. The mean concentrations of Fe in the fish samples ranged from 225.31 –299.64 (mg/kg.dw). This amount was 5 to 6 times higher than the permissible limit of 50mg/kg by WHO. Studies have shown that high intake of Fe is responsible for the deposition of iron oxides which has been reported in case of Parkinson's disease (Powers *et al.*, 2003).

Nickel (Ni)

Ni usually occurs at low levels in the environment but at high concentration can result to adverse effects on human (Forti *et al.*, 2011). The mean concentrations of Ni in the fish samples ranged from 0.59 to 0.79 (mg/kg dw). The permissible level of 0.5 (WHO) of Ni for fish in this study was exceeded. Thus, the concentrations of Ni in the fish samples were above the stipulated limit. Concentrations above the set limit can cause cancer of the pulmonary organs and nasal cavity (USFDA, 1993).

Vanadium (V)

Vanadium has no biological function in human body. The mean concentration obtained in fish of this study ranged between 0.27-2.00(mg/kg dw). This range was 4 times higher than the legal limit of 0.5 (mg/kg) set by WHO safe for human consumption. Its accumulation can result in breathing disorders, paralyses and negative effects on the liver and kidneys (USFDA, 1993).

Aluminium (Al)

Aluminium has no biological role and is a toxic non-essential metal (Olaniran *et al*., 2013). The mean range obtained for fish in this study was 153-222 (mg/kg dw). This range was far higher than the legal limit of 7.0 stipulated by WHO. Krewski *et al (*2009) reported that the greatest complications of aluminium toxicity are neurotoxicity effects such as neuronal atrophy in the locus ceruleus, substantia nigra and striatum.

Table 2: Comparison of the heavy metal contents in the combined fish organs of this study with permissible international standards.

METALS	THIS STUDY (mg/kg)		WHO (1985;1989)	EC (2001;2006)	FAO (2003;2012)	FSA/ANZFA (2001;2011)
	TLP	CHR				
Cr	**3.4**	**3.43**	0.15	0.5	-	5.5
Zn	**50.4**	**35.14**	30	30	40	5.0
Cu	**16.32**	**4.06**	30	-	30	0.5
Fe	**299.64**	**225.31**	50	-	-	-
Ni	**0.79**	**0.59**	0.5	-	-	-
V	**2.00**	**0.27**	0.5	-	-	-
Al	**222**	**153**	7.0	-	-	-

TLP=Tilapia(*S.melanotheron*);CHR=*C.nigrodigitatu*

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Comparison of heavy metal contents in the two fish species with studies from the same creeks and other regions

The utilization of fish as bio-indicator for monitoring aquatic pollution has received global attention because it forms a major component of human diet (Zhou *et al.*, 2008). The two fish species investigated for heavy metals in this study are commercially exploited species and occur frequently not only in Okrika creeks but also generally in Nigeria's coastal waters. Many studies have been conducted and published on the heavy metal contents of the two species from the Niger-Delta region (*C. nigrodigitatus* and *S. melanotheron*) (Ladigbolu *et al*., 2011).

The mean value of Fe (225.31±71.6mg/kg) in this study for *C. nigrodigitatus* was higher compared to values (42.63, 46.45 and 52.36mg/kg) reported for the same species in Ibeshe and Badagry Lagoons, Lagos and Cross River (Niger-Delta) (Unyimadu *et al*., 2008; Ladigbolu, 2011; Ladigbolu *et al*., 2011; Aderinola *et al.*, 2012), (1.18mg/kg) in Lekki Lagoon, Lagos (Akinsanya and Kuton, 2016) and was about 10 folds greater than (21.64 mg/kg) obtained in a creek in the Niger-Delta (Osibanjo *et al*., 1987). The mean concentration (222.00±174.8mg/kg) of **Al** in *S. melanotheron* from the study area was far higher than the value (70.76mg/kg) obtained for this species in Lake Taman Mutiria, Puchong, Malaysia (Ismail and Saleh, 2012). The mean concentration of **Zn** (35.14±5.6mg/kg) for *C. nigrodigitatus* obtained in this study far exceeded that (4.81mg/kg) reported for this species (Osibanjo *et al.*, 1987), 11.34 (mg/kg) in Badagry creek, Lagos (Ladigbolu, 2011) and (4.52mg/kg) in Lekki Lagoon, Lagos (Akinsanya and Kuton, 2016) but lower than the value for the species in Great Kwa River (Ada *et al.*, 2012) and similar pattern to what obtained for Zn in *C. nigrodigitatus* in Badagry creek reported (Ajani and Balogun ,2015). The mean value of 0.79±0.31 (mg/kg) for **Ni** in *S. melanotheron* in this study was slightly higher than that obtained (0.36 and 0.48 mg/kg) for the same species in Alaro River, Ibadan, Nigeria and Fosu lagoon, Ghana (Tyokumbur and Okorie, 2014; Akoto *et al*., 2014). The mean value (0.59±0.13) in *C. nigrodigitatus* of this study exceeded the value (0.012) obtained in Great Kwa River, Niger-Delta (Ada *et al.*, 2012). The mean level of 3.43±1.7 (mg/kg) of **Cr** in *C. nigrodigitatus* in this study was over 60 times greater than that obtained (0.054mg/kg) for this species in Ibaka and Ifiayong Rivers (Niger-Delta) (Akpanyung *et al.*, 2014). Chromium does not usually accumulate in fish hence low concentrations have been reported even in industrialized part of the world (Rahman *et al*., 2012). The results of this study contradict the opinion of Krishna *et al* (2014) that fish are resistant to excessive contamination of Chromium in their habitats. Asuquo *et al* (2004) reported mean concentration of (1.8mg/kg) for **Cu** in *C. nigrodigitatus* in Cross-River Estuary (Niger-Delta) which was far lower than the value (4.06±2.5mg/kg) obtained in this study.

Table 3: Summary of comparison of metal concentrations in the fish species of this study with literature from Okrika estuary and other parts of Niger-Delta.

Sampling area/Fish spp	**Fe (mg/kg)**	**Cu (mg/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**V (mg/kg)**	**Zn (mg/kg)**	**Al (mg/kg)**	**Distance (km)**	**References**
Okrika creeks *S. melanotheron* *C. nigrodigitatus*	 **299.64** **225.31**	 **16.32** **4.06**	 **3.4** **3.43**	 **0.79** **0.59**	 **2.0** **0.27**	 **50.41** **35.14**	 **222** **152.99**	-	**This study**
Cross River estuary (***C. nigrodigitatus***)	46.45	-	-	-	-	-	-	153	Unyimandu *et al.*, 2008
Seven creeks in the Niger-Delta (Warri, Ughelli,	-	0.73	-	-	-	-	-	varies	Osibanjo *et al.*, 1987

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Olumoro, Portharcourt, Oron, Ibeno and Calabar) **(*S. galileus*)**									
Ibaka and Ifiayong River (***C. nigrodigitatus***)	-	-	0.054	-	-	-	-		Akpanyung *et al.*, 2014
Great Kwa River (***C. nigrodigitatus***)	-	-	-	0.012	-	-	-	264	Ada *et al.*, 2012
Okrika estuary (**Tilapia**)	-	-	-	0.038-0.92	-	-	-	-	Marcus *et al.*, 2013
Seven creeks in the Niger-Delta (Warri, Ughelli, Olumoro, Portharcourt, Oron, Ibeno and Calabar) (***C. nigrodigitatus***)	-	-	-	-	-	1.91-7.45	-	varies	Osibanjo *et al.*, 1987
Okrika estuary (**Tilapia**)	-	-	-	-	Below Detection Limit	-	-	-	Marcus *et al.*, 2013

NB: Distance = Rough estimate of distance of this study site as compared to other regions in the Niger-Delta.

Statistical difference in trace metal concentrations in fish from oil impacted and non-oil impacted creeks

The results (**Table 4** and **Figures 3a and b**) showed that there was statistical difference in the metal concentrations in the fish species between the impacted (IMP) and non-impacted (NI) creeks.

The influence of season, site status (degree of pollution) and fish species from the Okrika creek on metal accumulation in the fish organs is shown in **Table 4 and Figures 3a and b**. The metal concentrations in the tissues of the fish species for two seasons were employed for ANOVA analysis. The data obtained showed that there was significant difference of the trace element concentrations in the two species between the oil-impacted and non-impacted sites which could be explained or influenced by season, status and fish species and one of their interactions. The observed significant metal concentrations differences ($p<0.001$) for **Al** was influenced by status only, **Cu, Fe, V** and **Zn** were influenced by individual factor of fish species and status ($p<0.05$, 0.01 and 0.001), **Ni** was explained by status and its interaction with season ($p<0.05$) and **Cr** was influenced by season and its interaction with both fish species and status ($p<0.05$ and 0.001) , these could be as a result of the following reasons; (1) **fish species** could explain these variations because it has been widely reported that the feeding habits, trophic level and diet of the fish coupled with their physiological conditions, self-regulatory metabolic activities and metal resistance could play a long role in metal accumulation and concentration in their tissues (Farkas *et al.*, 2000; Yilmaz , 2005; Mokhtar *et al.*, 2009; Bayode *et al.*, 2011; Aderinola *et al.*, 2012; Velusamy *et al.*, 2014; Atobatele and Olutona, 2015; Trevizani *et al.*, 2016). In this study, *S. melanotheron* had more metal levels in their tissues than *C. nigrodigitatus* because they are opportunistic feeders exploring both the pelagic and benthic regions of the creek. (2)

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status of site could also explain the observed differences which is attributed to the differences in the magnitude, level or amount of contaminants (industrial effluents or wastes) received by the two sites (Bentzen *et al.*, 1996; Akinrotimi *et al.*, 2015; Diop *et al.*, 2016; Trevizani *et al.*, 2016). Rejomon *et al* (2010) and Weber *et al* (2013) argued that characteristics of the sampling location and habitat play a crucial role in metal accumulation in fish. (3) **Interaction of status and season** could be as a result of more oil residues and remnants washed or flushed down to the creeks during the rainy season thereby escalating metal availability and accumulation (Don-Pedro *et al.*, 2004; Saha *et al*., 2016). (4) **Interaction (fish species:season:status)**, Köck *et al* (1996) reported that seasonal variation in the metabolic rate of the fish species and the extent of contaminants in their habitats play an important role in the variation of their tissue metal levels. This agrees with the reports by Mwashote (2003) and Olojo *et al* (2012) that the nature or status of the habitat, differences of fish species and season play a crucial role in metal bio-accumulation. As discussed earlier, higher concentrations of all the metals (**Figure 3b**) were found in *Sarotherodon melanotheron* than *Chrysichthys nigrodigitatus* probably because they occupy and explore different trophic levels of the estuary as they are both pelagic and detritus feeders (Oribhabor and Adisa-Bolanta, 2009). The adult diet consists mainly of detritus, algae, periphyton, benthic organisms, decomposing organic materials, material inhabiting or fouling submerged hard surfaces and ingestion of contaminated sediment with food items, therefore, a higher metal concentrations is expected (Diouf, 1996; Nakayama *et al*., 2010). **Although, less accumulation of the metals is expected for this species as it occupies lower trophic level but (Cui *et al.*, 2011) explained that contradictory results have been reported by many authors for certain metals.** In addition, higher concentrations of the metals in the fish tissues were found during the rainy season than the dry season (**Figure 3b**) as a result of flushing and more influx of oil residues and wastes from the refining company into creeks by the rainfall (Saha *et al.*, 2016). This same trend was observed in Ekerekana creeks for the selected sea-food investigated (Akinrotimi *et al*., 2015) as opposed to what was reported in Badagry creek (Ajani and Balogun, 2015).

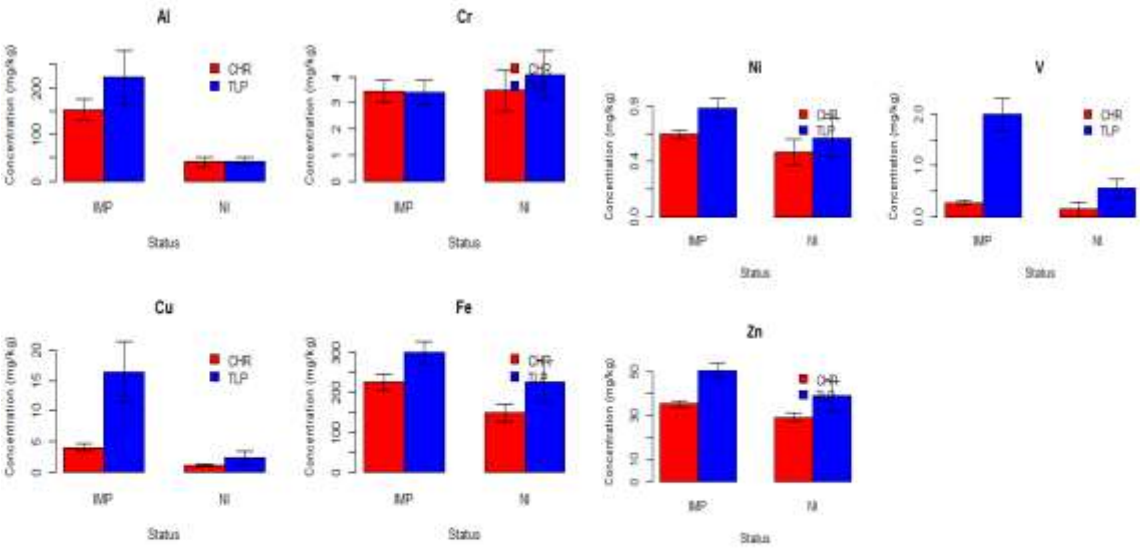

Figure 3a: Spatial metal concentrations/accumulations in the combined organs of the two species from impacted and non-impacted creeks. Aluminium, Chromium, Copper, Iron, Nickel, Vanadium, Zinc.

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NB: TLP= *Tilapia* (*S. melanotheron*), **CHR=** *C. nigrodigitatus*, **IMP=** Crude oil impacted creeks consisting of Ekerekana, Okari and Ogoloma, **NI**=Non-oil impacted creek (Control site in Agbonchia-Okulu)

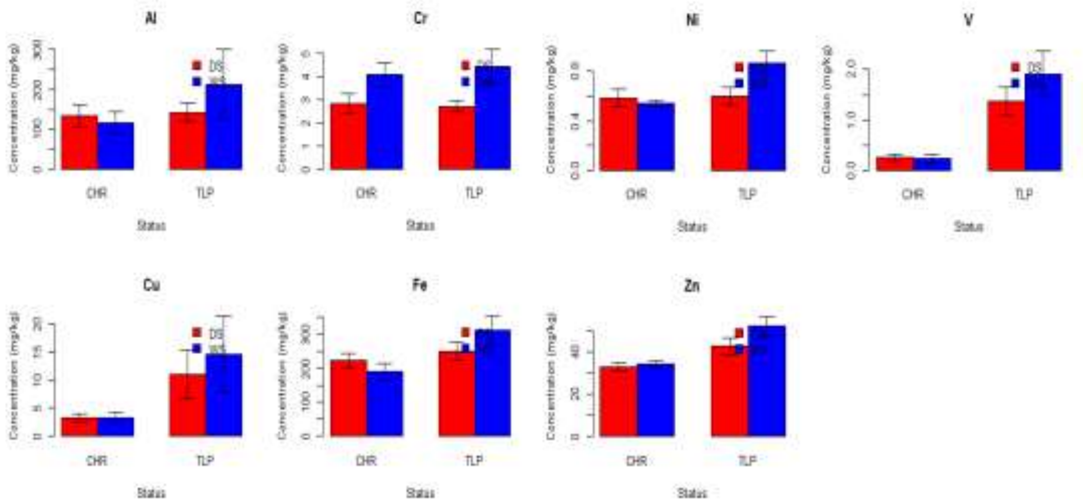

Figure 3b: Seasonal variations of heavy metal accumulations in the two fish species of the study area. Aluminium, Chromium, Copper, Iron, Nickel, Vanadium, Zinc, NB: TLP= ***Tilapia*** **(*S. melanotheron*, CHR=** ***C. nigrodigitatus***

Table 4: Two-way ANOVA of the effects of fish species, status and season on the variability of heavy metal concentrations in the combined fish organs of the study area.

	df	Al p value	Cr p value	Cu p value	Fe p value	Ni p value	V p value	Zn p value
FISH- SPP	1	0.1396	0.777	**$1.51X10^{-5}$ *****	**0.0072 ****	0.0859	**2.27×10^{-8} *****	**$4.55x10^{-6}$ *****
SEASON	1	0.4474	**0.0006*****	0.5306	0.6113	0.0958	0.5042	0.0848
STATUS	1	**$2.62X10^{-7}$ *****	0.5106	**$1.79x10^{-5}$ *****	**0.0142 ***	**0.0114***	**$3.8X10^{-4}$ *****	**0.0111 ***
FISH SPP:SEASON	1	0.3099	0.5541	0.8492	0.1078	0.0730	0.4125	0.3853
FISH SPP:STATUS	1	0.9024	0.5022	0.5079	0.5015	0.5306	0.0909	0.9514
SEASON:STATUS	1	0.9417	0.0779	0.1979	0.2461	**0.0496***	0.6686	0.4667
FISH SPP: SEASON: STATUS	1	0.5268	**0.0424***	0.5557	0.5863	0.8889	0.2222	0.2220
ERROR	40							
TOTAL	47							
ADJUSTED R-SQUARED		0.46	0.33	0.50	0.31	0.23	0.57	0.41

*Correlation is significant at $p < 0.05$
**Correlation is significant at $p < 0.01$
***Correlation is significant at $p < 0.001$

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Fish Pollution Indices

Total Target Hazard Quotient (TTHQ)

Based on the estimate of fish consumption in the coastal areas of Nigeria, Bassey *et al* (2014) indicated that an average Nigerian eats 20.8g of fish per day and recent report by World Health Organization (WHO, 2016) that the average life expectancy for Nigerians is 54.5 years. The results of **target hazard quotient** (**THQ**) of each metal due to fish consumption is generally less than 1 indicating that there would not be any health risk from the intake of individual metals through fish consumption. The estimated **TTHQ** values of both fish species from the study area ranged from 1.0 – 2.21 (**Table 5** and **Figure 4**) which depict that the population would experience very serious health hazard (additive or interactive effects) from the integrated or combined actions of individual metals (Bastami *et al*, 2015). The THQ values of Cr and V were higher than other metals for the inhabitants of the study area. This may be due to their lower oral reference doses. Although, in reality, a TTHQ > 1 may not reveal that the inhabitants are actually experiencing adverse health effects. This simply means that there is no evidence of unacceptable non cancer risk for the general population eating Okrika's estuarine fish. The value range of TTHQ (1.0 – 2.04) obtained in this study was far higher than the study on the fish species mostly consumed in Calabar (a Niger-Delta area) (Bassey *et al.*, 2014). Highest TTHQ (almost similar values) was observed in *S. melanotheron* from both Ekerekana and Ogoloma.

The THQ of each metal due to fish consumption is generally less than 1.The estimated **TTHQ** values of both fish species from the study area ranged from 1.0 – 2.21. The THQ values of Cr and V were higher than other metals for the inhabitants of the study area. This may be due to their lower oral reference doses.

Table 5: Estimated THQ and Total-THQ of the heavy metal contents in the fish samples from the study sites

SITES	Al	Cr	Cu	Fe	Ni	V	Zn	Total-THQ
EKR-TIL	0.126	1.005	0.097	0.16	0.015	0.578	0.058	**2.04**
EKR-CHR	0.07	0.88	0.027	0.1	0.01	0.076	0.03	**1.19**
OKR-TIL	0.04	0.63	0.07	0.12	0.014	0.57	0.056	**1.50**
OKR-CHR	0.037	0.84	0.04	0.091	0.012	0.10	0.04	**1.16**
OGL-TIL	0.06	0.73	0.26	0.16	0.012	0.93	0.06	**2.21**
OGL-CHR	0.05	0.65	0.04	0.11	0.01	0.10	0.04	**1.00**

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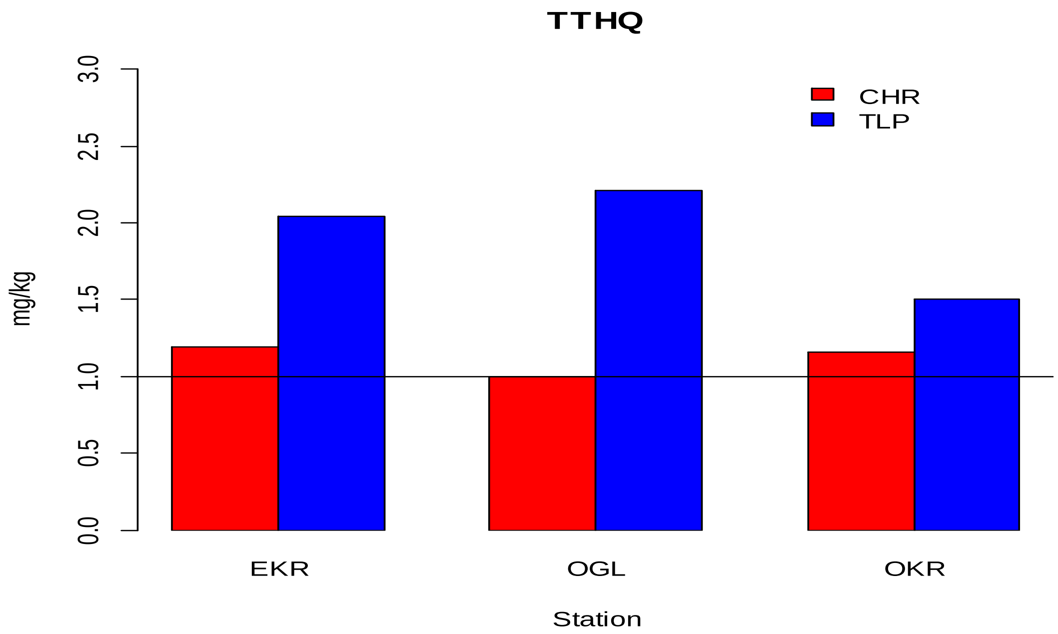

Figure 4: The pattern of total target hazard quotient of the multiple-metals in the fish species of the study area.

Metal Pollution Index (MPI)

Based on the results of **Metal Pollution Indices** (**MPI**) obtained for the two fish species (**Table 6** and **Figure 5**), the values ranged from (8.1-17.76) with the highest values in *S. melanotheron* from Ekerekana and Ogoloma due to their proximity to the effuents point source in addition to oil bunkering and transportation activities along the creeks. The values obtained far exceeded 1 therefore the fish are classified as polluted and unfit for consumption (Abdel-Ghani, 2015).

Table 6: Metal Pollution Index (MPI) of the fish from the study area

Stations/ Fish spp	Al	Cr	Cu	Fe	Ni	V	Zn	MPI-value	MPI value	Pollution status	References
EKR-TIL	363.59	4.35	11.2	324	0.87	1.67	50.81	**17.09**	MPI < 1	No pollution	Okafor and Opuene, 2007
EKR-CHR	210.07	3.8	3.11	269	0.56	0.22	34.18	**8.37**	MPI > 1	Polluted Fish	Essien *et al.*, 2009
OKR-TIL	116.73	2.72	7.87	242.84	0.80	1.64	48.8	**12.14**			Abdel-Ghani, 2015
OKR-CHR	108.53	3.67	4.52	183.5	0.69	0.30	33.52	**8.10**			
OGL-TIL	185.67	3.14	29.9	331.65	0.70	2.68	51.63	**17.76**			
OGL-CHR	140.38	2.81	4.54	223.32	0.53	0.30	37.73	**8.16**			

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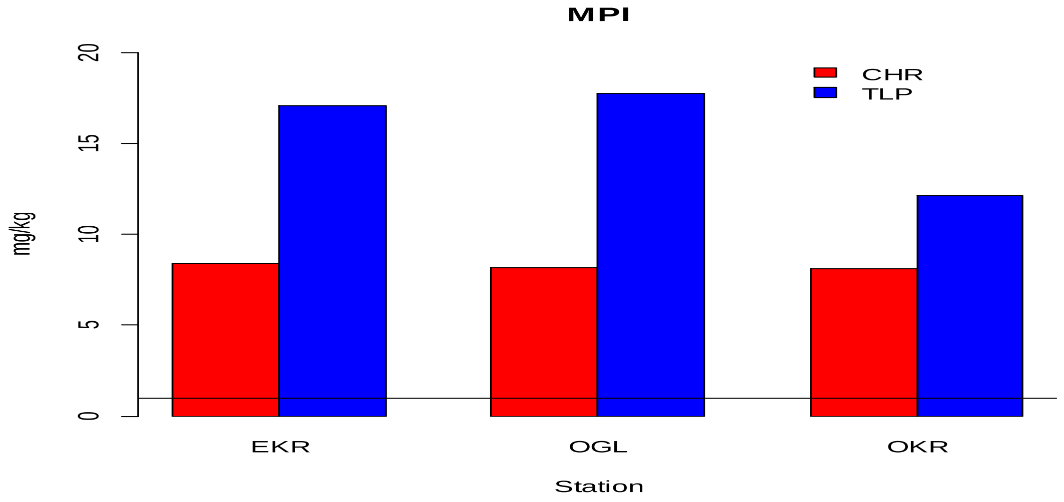

Figure 5: The pattern of Metal Pollution Index (MPI) of the multiple-metals in the fish species of the study area

EKR= EKEREKANA, OGL = OGOLOMA, OKR= OKARI, CHR=*Chrysicthys nigodigitatus*, TLP=Tilapia (*Sarotherodon melanotheron*)

Techniques for Identifying the Source of Heavy Metals

Pearson Correlation Matrix

Correlation matrix results for the trace metals in the two fish species are presented in **Table 7**. There were significant positive relationships or correlations ($p < 0.05$, 0.01 and 0.001) among the metal pairs for the two fish species as follows; **Cr-Al (r=0.36)**, Fe-Al (r=**0.66**), Ni-Al (r= **0.49**), Zn-Al (r =0.13), Fe-Cr (r=**0.46**), Ni-Cr (r =**0.38**), Zn-Cr (r=**0.43**), Fe-Cu (r=**0.37**), Ni-Cu (r=**0.33**), V-Cu (r=**0.80**), Zn-Cu (r=**0.67**),Ni-Fe (r=**0.55**), V-Fe (r=**0.40**), Zn-Fe (r=**0.57**), V-Ni (r=**0.39**), Zn-Ni (r=**0.51**) and Zn-V (r = **0.72**) .

These positive significant relationships (76%) between two metal pairs in the fish tissues indicate that their distributions were regulated by common local inputs, refinery effluents in this case, and similar dispersion process ((Li *et al.*, 2010; Rahman *et al.*, 2012; Jayaprakash *et al.*, 2015).

Table 7: Correlation matrix of heavy metals in the combined organs of both fish species

	Al	Cr	Cu	Fe	Ni	V	Zn
Al	1.00						
Cr	**0.36***	1.00					
Cu	-0.04	0.15	1.00				
Fe	**0.66****	**0.46****	**0.37***	1.00			

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Ni	**0.49****	**0.38***	**0.33***	**0.55*****	1.00		
V	0.07	0.16	**0.80*****	**0.40***	**0.39***	1.00	
Zn	0.13	**0.43****	**0.67*****	**0.57*****	**0.51****	**0.72*****	1.00

*Correlation is significant at $p < 0.05$
**Correlation is significant at $p < 0.01$
***Correlation is significant at $p < 0.001$

Vanadium/Nickel ratio as a proxy tracer of oil pollution

The determination of trace metal constituents in crude oils is important to predict crude-oil source. From the results obtained (**Table 8**) for the V/Ni ratio contents of the fish species and the sediment, the ratio was in the range of 0.4 – 3.83.These were exactly in line with the ratios for the Nigeria's light, medium and heavy crude oils and in strong agreement with Odeyemi and Ogunseitan (1985) that Nigeria's crude oil mainly consist of both light and heavy types which are usually processed by the refineries. The V/Ni values obtained for surface sediments in this study are in line with the value (1.31) for surface sediment impacted with oil and gas drilling operations off coast southern California (Steinhauer *et al.*, 1994). These results also tally with the V/Ni ratio values obtained for bivalve rock Oysters and sediment in Qeshm island coast and Bushehr Coasts (Persian Gulf) in Iran (Moradi *et al.*, 2011; Roozbeh *et al.*, 2013). Osibanjo *et al* (1983) and Nwachukwu *et al* (1995) reported that Nigerian crude oils contain relatively high concentrations of Fe, Zn, Cu, **V**, **Ni**, Mn, Cr, Hg, Pb, As, Cd, Co which cannot be completely removed during refining processes. Matthews-Amune and Kingsley (2013) reported that petroleum products are the major sources of heavy metals to the environmental matrices like sediment even in the absence of other major industry. Anoliefo and Vwioko (1995), Owamah (2013) and Akudo (2016) reported that the indiscriminate discharge of effluents into environment by the petroleum companies and oil spillage can degrade and escalate the levels of heavy metals in the aquatic ecosystems.

Table 8: V/Ni ratio values as proxy tracer of oil pollution from the study area.

FISH	EKEREKANA	OKARI	OGOLOMA
TLP	1.92	2.05	3.83
CHRY	0.40	0.44	0.57

Classification of Nigeria's Crude Oil based on V/Ni Ratios		References
< 0.5	1 - 10	
Light Crude Oil	Medium - Heavy Crude Oil	Barwise, 1990 Olajire and Oderinde, 1993 Odebunmi and Adeniyi, 2004 Ogunlaja *et al.*, 2014

TLP=Tilapia (*S. melanotheron*), CHR=*C. nigrodigitatus*

CONCLUSIONS

This study provided important information on the levels of trace metals in two fish species, *C. nigrodigitatus* and *S. melanotheron* from Okrika creeks in Niger-Delta area of Nigeria. Trace elements entering the fish have tendency to accumulate in different parts of its body and build up to a toxic level. It is globally reported that contamination of the environment by heavy metals can pose a great hazard to human and other organisms' health especially when they are in excess in the biological food chain (Martin *et al*., 1982). Furthermore, as a consequence of metal pollution of Okrika estuary, the growth, reproduction, survival and other metabolic activities of the aquatic organisms may be impaired, base shift or migration of the native species from highly polluted creeks to a suitable environment may be enhanced, seafood may be rejected affecting its marketability and low catch may be experienced by the fishermen who rely on the creeks for their livelihood (Kibria *et al*., 2016). Meanwhile, patients suffering from heavy metal poisoning are rarely diagnosed, this study has shown that the levels of all the trace metals in the fish tissues were outside the permissible international standards. It appears from the results presented in this study that Okrika creek is a highly contaminated ecosystem. The results of fish pollution indices of this study agree with few studies of many authors, who had previously reported serious pollution of water bodies in the Niger-Delta region of Nigeria. There was statistical significant difference ($p<0.05$) for most metal accumulations in fish between the oil-impacted (the study area) and the non-impacted (control site) creeks. The Ekerekana creek is highly polluted because it is the first receiving basin for refinery effluents indiscriminately discharged by Port-Harcourt Oil Refinery Company (PHRC) and from where it spreads the toxicants further to the neighbouring creeks and from where toxic effects are also observed (Guagliardi *et al.*, 2013). Similar patterns have been reported on adjoining water bodies to oil refinery companies (Adati, 2012; Ite *et al.*, 2013; Marcus *et al.*, 2013; Marcus and Ekpete, 2014). The outcomes of this study strongly tally with the opinions of Uwah *et al* (2013) and Ismail *et al* (2016) that petroleum production from oil industries serve as the main contributor to the increase and consequent negative impacts of trace metals in the environmental matrices. This study also agrees with Eaton (1997) who reported that oil refining companies in Nigeria are characterized by inefficient waste treatment facilities and anti-pollution devices. This statement does not agree with Odeyemi and Ogunseitan (1985) who reported that wastes from the refineries are efficiently treated before being disposed into the aquatic ecosystems.

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