



## **Heavy Metal Bioaccumulation in Periwinkle (*Tympanostomus* Spp) and Blue Crab (*Callinectes amnicola*) Harvested from a Perturbed Tropical Mangrove Forest in the Niger Delta, Nigeria**

Oluowo Elohor Freeman<sup>1\*</sup> and Olomukoro John Ovie<sup>1</sup>

<sup>1</sup>Department of Animal and Environmental Biology, Faculty of Life Sciences, University of Benin, Benin City, Nigeria.

### **Authors' contributions**

*This work was carried out in collaboration between both authors. Author OEF designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author OJO supervised the field work and helped in designing the field study. Both authors read and approved the final manuscript.*

### **Article Information**

DOI: 10.9734/JAERI/2017/31568

#### Editor(s):

(1) Ahmed Esmat Abdel Moneim, Department of Zoology, Helwan University, Egypt and Institute of Biomedical Research Center, University of Granada, Spain.

#### Reviewers:

(1) Sarah Abdul Wahab Al- Mahaqeri, Universiti Kebangsaan Malaysia, Malaysia.  
(2) Maria del Carmen Bermudez Almada, Centro de Investigacion en Alimentacion y Desarrollo, Mexico.  
Complete Peer review History: <http://www.sciencedomain.org/review-history/17968>

**Original Research Article**

**Received 14<sup>th</sup> January 2017**  
**Accepted 13<sup>th</sup> February 2017**  
**Published 25<sup>th</sup> February 2017**

### **ABSTRACT**

The last decade in Nigeria saw useful scientific contributions in biomonitoring different environmental matrices and understanding their health indices, however with scanty toxicological evidences, especially their oxidative stress response and oxygen affinity. The present study was designed to investigate the concentrations of heavy metals in edible food of periwinkle and crab harvested from a perturbed river in Niger Delta, Nigeria reported to constantly receive industrial effluent from two major oil and gas companies. Zn, Fe, Pb, Cu, Cr, Cd and Mn were assessed for two seasons from December 2009 to May 2010. Higher concentrations of heavy metals were obtained in the wet season than dry with crab bio-accumulating more metals than periwinkle. The bioavailability sequence of metals in periwinkle was Fe>Mn>Zn>Cu>Pb>Cr>Cd and crab, Fe>Mn>Pb>Zn>Cu>Cr>Cd. While Zn, Pb and Mn values in some of the stations in crab were

\*Corresponding author: E-mail: [hallabigfreeman@gmail.com](mailto:hallabigfreeman@gmail.com);

above FAO/FEPA regulatory limits and Fe in Periwinkle above FAO/WHO during the wet season. The study has not only provided some useful information on metal accumulation in the ichthyofauna of the river but call for more toxicological study and biomonitoring of anthropogenic sources to the river using crab and periwinkle.

**Aims:** The aim of the present study is to investigate the concentrations of heavy metals in periwinkle and crab by estimating their spatial and seasonal mean variation in the individual animals and compare.

**Study Design:** The design is comparative analytic study.

**Place and Duration of Study:** The study was conducted in Ekpan Creek, Warri, Delta State, Nigeria, from December 2009 to May, 2010.

**Methodology:** Five sampling stations were carefully selected for their proximity to anthropogenic activities from December 2009 to May 2010, to cover wet and dry seasons sampling. Samples of periwinkle and crab species were hand-picked monthly, between the hours of 7 am and 9:30 am on each sampling day, when human activities in the river were still very minimal along the sampling stations into a black polythene bag containing ice for storage in deep freezer. Samples were identified using appropriate keys and striking features, digested and analyzed for heavy metals.

**Results:** The study results showed the dominance of iron over other metals in both animals for both seasons, and have been observed in previous studies. Chromium and Cadmium levels were relatively stable temporally throughout the study, which is somewhat lower at station 5, expected to be higher, and was attributed to water velocity and other reported physiochemical parameters, such as increasing temperature. Crab bio-accumulated more metals than periwinkle with reports of higher concentrations.

**Conclusion:** Continues perturbation of the river from anthropogenic activities has remain a major concern to the water use, unregulated activities by Chevron, WRPC and other oil & gas related activities as well as human activities has placed the abundance and consumption of shell fishes (periwinkle and crab) as food delicious in the region at high risk, coupled with previous report of contamination of investigated periwinkle sold in market places, including the study area.

**Keywords:** Heavy metals; bioaccumulation; ichthyofauna; toxicity; bioavailability; Chevron; WRPC.

## 1. INTRODUCTION

While the occurrence of metals in both terrestrial and aquatic ecosystems in Nigeria has been reported extensively, their possible ecosystem and wildlife health risks are yet to be fully established. Metals are naturally present in trace amount in freshwaters from weathering of rocks and soil, but they become toxic when a certain threshold is exceeded [1,2,3,4]. Essential metals, such as manganese, zinc, copper and iron are present in trace concentrations and play important physiological functions of living tissues and regulates many biochemical processes [4,5]. These essential metals may become toxic to biological material, just as non-essential heavy metals when found in high concentrations [2,3,4,6].

The use of ichthyofauna of water bodies especially fish and shellfishes has received tremendous scientific attention in the last 15 years in Nigeria, representing useful contributions for monitoring anthropogenic pollution sources in different environmental matrices and toxicity through ingestion. However, there is still limited

toxicological evidence on some of these metals, especially their health risk indices and organ affinity from consumption in tropical countries.

Heavy metals, such as cadmium, lead, chromium, mercury and metalliod of arsenic have been implicated with high toxicity and in carcinogenicity [7]. Thus, these heavy metals are of severe environmental and public health significance. These metals connote systemic toxicants that are known to induce multiple organ damage, even in small quantity and at low temperature. The daily intake and exposure to these heavy metals has increased significantly due to increased occurrence of these metals in different aquatic ecosystems, through anthropogenic activities such as burning of fossil fuel, land run-off, oil spill, gas leaks, blow outs, canalization and discharge from oil and gas operations into surface water, or release from industrial operations such as mining, canning and electroplating [4,8,9,10,11,12].

Interestingly, the highest level of cadmium in edible food materials was reported in shellfish, liver and kidney meats [13,14,15] hence the

urgent call for in-depth studies of their toxicological effects.

Some notable studies with significant contribution to heavy metals bio-accumulation and bio-concentration in shellfishes were from, Ayenimo et al. [9] report of appreciable quantities of heavy metals such as iron, copper, barium, lead, cadmium and nickel in periwinkles purchased from public markets in Warri River, Nigeria including that of the study area; Falusi and Olanipekun [3] observed high bio-concentration of heavy metals in tropical crab (*Carcinus* sp) harvested from River Aponwe, Ado-Ekiti; Olalode et al. [6] reported high bio-concentration in tissues of investigated species of fish, crab and periwinkle, with elevated concentrations of manganese and zinc in crab, while cobalt, copper and iron in periwinkle; So also, Ikejimba and Sakpa [16] reported higher bio-accumulation of some heavy metals in similar Periwinkle species in Egboko River and Andem et al. [17] in Kwa Iboe River Basin, Akwa Ibom and, Isibor and Oluowo [18] observed high metals bio-accumulation in tissues of gariepinus fish harvested from Osse River, Delta State.

Elsewhere, Aina et al. [19] generously reported Phthalates ether group and observed accumulative organ differences in *Tilapia zillii* obtained from municipal water supply lakes in Ibadan, Nigeria and Arukwe et al. [20], assertion that solid waste deposits are significant sources of contaminants of emerging concern to the aquatic environment and recommended sustainable pollution management procedures.

The present study will contribute tremendously to the unavailable study of metal accumulation in ichthyofauna of the river. There is abundance of shellfishes (periwinkle and crab) in the studied area and they represent valuable food delicacies in the Nigeria Niger Delta area [9]. Further, quantifiable variables of climate change such as temperature, have been linked to heavy metals concentrations and was reported to increase metal bioaccumulation and bioconcentration in aquatic organisms [17,21].

Lead, for instance is a natural occurring bluish gray metal found in small amounts in the earth crust [9,22]. It gets into the aquatic system from coal burning, oil spillages, linkages from speed boats, inland run-off and direct dumping of waste from refinery or automobile exhaust [8,15]. Lead poisoning, according to Prasad [23] get to man through ingestion of lead contaminated food occurring between successive organisms in the

ecosystem, and once absorbed it is distributed to the liver and kidney and then stored in the bones, leading to anemic conditions and other hemopietic system (common effects) to organ (liver, kidney, heart and male gonad damages [2,23,24,25], and worse condition of edema which reduces intelligent quotient even in small amount.

Cadmium is reported to cause kidney diseases, long term effects of lung damages and fragile bone and abdominal pains [2,25,26]. Zinc, which is one of the most common metals in the natural environment is carcinogenic in nature and have been reported to cause throat dryness and bone weakness among others.

It has become imperative to study heavy metals contaminations in ichthyofauna of waters bodies in the Niger Delta, Nigeria especially shellfishes which are reliable source of protein requirement, food delicacies and abundant. And owing to the report of Oluowo and Isibor [4] that heavy metals concentrations has significantly increased from previously reported due to increase perturbation of the river known to receive effluent from Chevron Nigeria limited, Warri Refinery Petrochemical Company and other human activities. Consequently, the present study is aimed at assessing the concentrations of heavy metals in periwinkle and crab by estimating their seasonal mean variation in individual organisms and compare.

## 2. MATERIALS AND METHODS

### 2.1 Study Area

The study was conducted along the stretch of Ekpan Creek, Effurun, Delta State (Fig. 1), which is about 12 km long and one of the three major sinusoidal rivers which in conjunction form an astonishing tributary streams and creeks that drain the wetlands of the western Niger Delta. The river flows Westerly into the creek at NNPC jetty and empties into Warri River at Bennet Island [2,27].

The study area is within ( $5^{\circ} 3'5.11''N$   $5^{\circ} 40'44.11''E$ , altitude 13.5 – 17.5 m) the oil rich Niger Delta-Nigeria and as such, the major activities are characterize by oil & gas exploration activities from Chevron Nigeria Limited, petrochemical refining from the Warri Refinery and Petrochemical Company, a subsidiary of Nigerian National Petroleum Corporation (NNPC) and allied companies. The

economic activities of these companies has undoubtedly increased human population and thus, dumping of waste materials directly into the river, mainly from Delta Development Property Agency (DDPA). Others are aquaculture business along the river stretch, auto-mechanic workshops, wood-logging, cloth washing, bathing and swimming.

Five sampling stations were carefully selected for their proximity to facilities and human activities from December 2009 to May 2010, to cover wet and dry season's sampling. Station 1 was located at Olare quarters and downstream of the study with clusters of residential buildings, aquaculture, farming and bathing. Station 2 was just behind Delta Development Property Estate with fishing activities, laundry, and the use of water for construction, and was noted to be very turbid and murky. Station 3 was located at the Ekpan New Layout where logging activities was very high, aquaculture ponds and laundry. Station 4 was located under the Ekpan bridge, very close to NNPA house complex; the water surface was marked with oil films, murky and very turbid. This station was predominately noted for aquaculture and sparse agricultural farms. The Chevron-Texaco company bridge was station 5, it was dotted with oil films, highly restricted and upstream of the study. Detailing of the study area and station has been reported by Oluowo and Isibor [4].

The study area is characterized by high relative humidity (80-92%), annual average rainfall above 2800 mm and two distinct seasons (wet and dry).

As a result of the fresh salt water mixture, a brackish environment is created at the banks of the river. The vegetation was made up of mangrove plants of different species, dominated by *Rhizophora* species.

## 2.2 Sampling Technique and Analysis

### 2.2.1 Sample collection

Samples of periwinkle and crab species were collected once monthly from December 2009 to May, 2010 between the hours of 7 am and 9:30 am on each sampling day, when human activities in the river was still minimal. Samples of periwinkle and crab species were handpicked at the water shore along the sampling stations, and kept in black polythene bag containing ice for storage in deep freezer, and conveyed to the laboratory the following day for identification and digestion.

### 2.2.2 Species identification

Two species of periwinkle were identified using the appropriate keys and works of Penak [27,28,29]. The two species identified were, *Tympanostomus fucastus* with prominent rings and *Tympanostomus var radula* with blocks, without predominant rings and confirmed by Prof. Odieta of University of Lagos. While the *Callinectes amnicola* crab which is common in Nigeria mangrove was identified using the striking taxonomic features of their widened and arched carapace described by Prof. Cumberlidge of Northern Michigan University and used by Arimoro and Idoro [30].

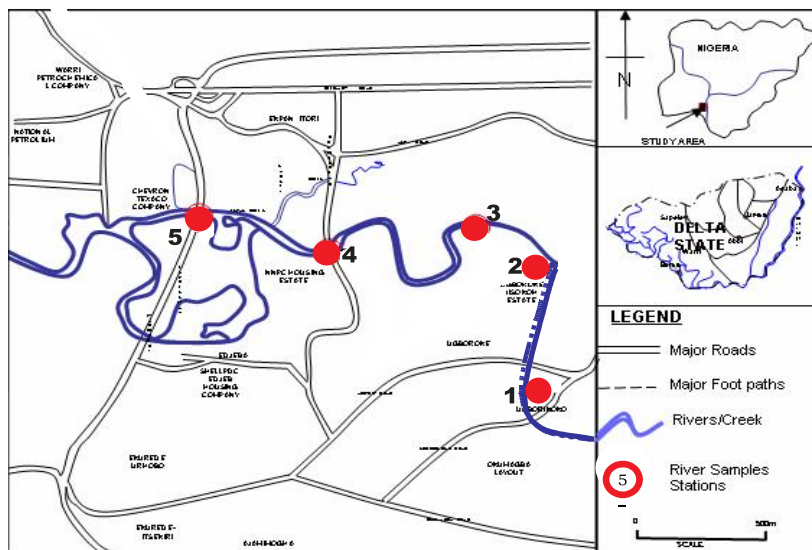


Fig. 1. Map of Warri showing the study area and sampled stations in red

The fully developed organisms were carefully selected using their matured stage taxonomic features and de-shelled, to retrieve their whole body mass for the purpose of the study. Equal weight of 0.5 g was weighed into a 25 ml beaker for digestion using the acid-mixed procedure.

### **2.2.3 Digestion**

The method used was the mixed acid procedure described by Fufeyin [8] and modified. 0.5 g each of periwinkle and crab contents were measured using the Ohaus Scout Pro SPU202 model into a 25 ml beaker. 5 ml of concentrated Nitric acid was added to each and was allowed to stand for 30 minutes. Thereafter 1 ml of Sulphuric acid was added to it and almost immediately 1 ml of 60% Perchloric acid was added. The mixture was swirled gently and was allowed to digest slowly over a period of time at moderate to high heat under a fume hood. It was further digested for 2 – 3 hours after the appearance of white fumes, it changed into a brown colouration and later into a black colouration.

The content was allowed to cool, the remaining solution was diluted to 5 ml and allowed to stand for a period of 6 hours and then diluted to 20 ml. The solution was filtered into sterile clean 25 ml beaker and later poured into 60 ml plastic containers. The final solution was directly aspirated for metal analysis in the laboratory. The blank was prepared following the same procedure as it was conducted for the five sampled station, except that the blank did not contain the periwinkle content.

### **2.3 Laboratory Analysis**

The digested organisms (periwinkle and crab) were taken to the laboratory for metal scanning and analyses using the Inductively Coupled Plasma-Mass Spectrometer (ICP) metal scanning and Atomic Absorption Spectrometer (AAS) respectively. The Inductively Coupled Plasma-Mass Spectrometer (ICPMS) was used to ascertain the presence of possible heavy metals in few of the samples. While the, ICP procedure was employed for simultaneous or sequential multielement determination of metals and trace elements in solution based on the measurement of atomic emission by an optical spectrometric technique [15,31].

For quality assurance purposes, AAS was calibrated for each metal by dissolving 1 gram analar grade metal salt in 1 litre of distilled water.

Standard and corresponding blanks were run with each set of experimental digest. The detection limits of zinc (0.5 µg/g), manganese (0.5 µg/g), copper (0.05 µg/g), nickel (0.02 µg/g), lead (0.03 µg/g), and cadmium (0.01 µg/g) were carefully observed. To ascertain quality control results of analysis were cross checked using standard reference materials for water and sediment; provided by FEPA [32].

The actual concentration of metal = RD x dilution factor [33].

RD connote: ASS reading of digest.

$$\text{Dilution factor} = \frac{\text{Volume of digested used}}{\text{Weight of samples digested}}$$

### **2.4 Statistical Analysis**

The study data were subjected to analysis of variance (ANOVA), regression, and correlation coefficients to show significant differences in the monthly metal concentrations in the organisms using the 2007 Excel and SPSS version 19 tool packages. Duncan Multiple Range test (DMR) was employed to ascertain the actual locations of the significant differences which occurred in the ANOVA.

## **3. RESULTS AND DISCUSSION**

The results of the investigated heavy metals along the stations for both seasons are presented in Figs. 2 and 3. Iron concentrations in crab range from 0.001 to 21.202 mg/kg; 0.002 to 1.917 mg/kg in copper; 0.001 to 2.072 mg/kg in zinc; <0.001 to 0.897 mg/kg in chromium; 0.10 to 3.28 mg/kg in lead; 0.001 to 3.074 mg/kg in manganese and 0.001 to 0.301 mg/kg in cadmium. While in periwinkle was, 0.014 to 0.378 mg/kg iron; 0.001 to 0.011 mg/kg copper; 0.007 to 0.069 mg/kg zinc; <0.001 to 0.003 mg/kg in chromium; 0.001 to 0.005 mg/kg lead; 0.001 to 0.202 mg/kg manganese and 0.001 to 0.003 mg/kg cadmium. As seen in Figs. 1 and 2, iron was the most bio-accumulated heavy metal throughout the study for both organisms with the highest values obtained in crab. The very high values obtained in crab in the study can be attributed to the vulnerability of the organism in aquatic system due to its large body mass and osmotic nature, which have been reported [34,35], and not surprising at station 5 in both seasons and organisms. This further implicate Chevron Nigeria Limited oil installation and stored pipes along the river bank at station 5, as

a major source of anthropogenic iron input to the river, and in line with both reports of Olomukoro and Azubuike [36] and Oluowo and Isibor [4] of very high concentrations of iron in the study area.

As expected, the test organisms accumulated more metals during the wet months in all the stations, except chromium (0.897 mg/kg) at station 5, lead (3.28 mg/kg) at station 1 in crab and cadmium (0.003 mg/kg) at station 2 in periwinkle. Strikingly in the study, the concentration of metals in periwinkle were very stable with higher metal bioaccumulation observed in the wet season months in all the stations studied, expect at station 2 with cadmium. This temporal homogenous concentrations of metals was also reported by Oluowo and Isibor [4] in the surface waters of the river, and they attributed it, to the somewhat stable ecological equilibrium of the aquatic environment, although with significant metal heterogeneity observed in crab in the present study (Fig. 2). It is also believed that, the river physiochemical characteristic, especially temperature known to influence dilution of substances in aquatic systems, increase metal uptake in fish and shell fishes, as well as water velocity must have played an undisputed role in the bioavailability of these metals in the river.

Especially in periwinkle, the concentrations of cadmium and chromium were relatively low throughout the study period, except station 5 (1.421 mg/kg) in crab. However, this does not downplay constant monitoring of these metals in the river, especially as higher values have been reported in the sediment of the river [4]. This is an important environmental considerations as

periwinkle and crab are burrowing animals, feed on sediment organisms with sediment widely reported as sink to heavy metals pollution in aquatic systems.

The bioavailability of metals obtained along the stations in decreasing order was Fe > Pb > Zn > Cu > Cr > Mn > Cd in crab, while periwinkle was Fe > Mn > Zn > Cu > Pb > Cr > Cd. The dominance of iron over other metals is now peculiar with the study area owing to previous study reports. Omoigberale and Ikponmwo – Eweka [37] reported similar sequence of Fe > Mn > Zn > Cu > Pb observed with periwinkle in the Palaemonid shrimps of Osse River, and a conformity of Fe followed by Mn reported by Olowoyo [21] somewhere in the study area. Both sequences (crab and periwinkle) disagree with Ololade et al. [6] on crab and periwinkle collected from rivers in Ondo region (Fe > Cu > Mn > Zn), except for iron.

The differences in metal values, thus their concentrations and sequence in different aquatic environment can be attributed to several factors, such as the affinity of organisms to metals, seasonality, temperature, age, size, body mass, water velocity and dilution and the anthropogenic source input to the water. In fact, Olalode et al. [6] attributed their concentrations to the metabolic rate of the organisms. Hogdson [2] further implicated the age, genetics, gender, diet, physiological condition or health status of the organism to play key roles in metal bio-availability, bio-concentration and thus, toxicological effect through consumption. However, there is still complexity in scientific assertions in toxicity as well as comparing metal concentrations in organisms.

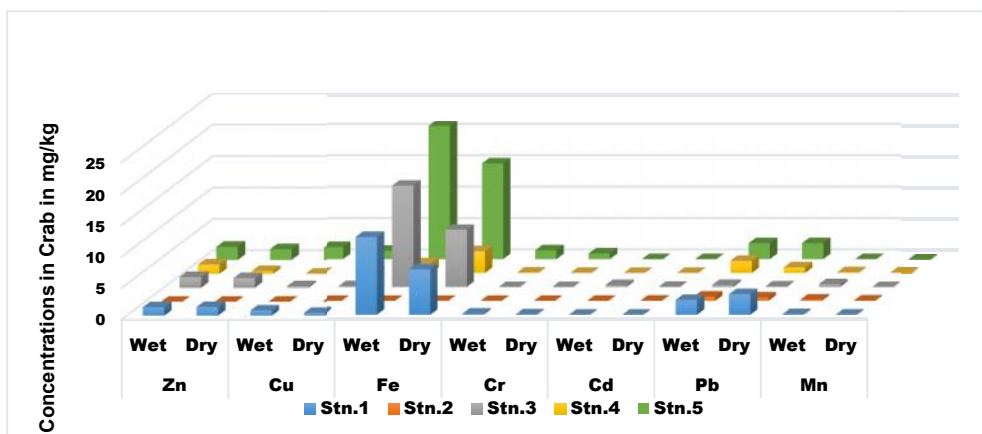


Fig. 2. Temporal spatial variation of heavy metals in Crab along the stations

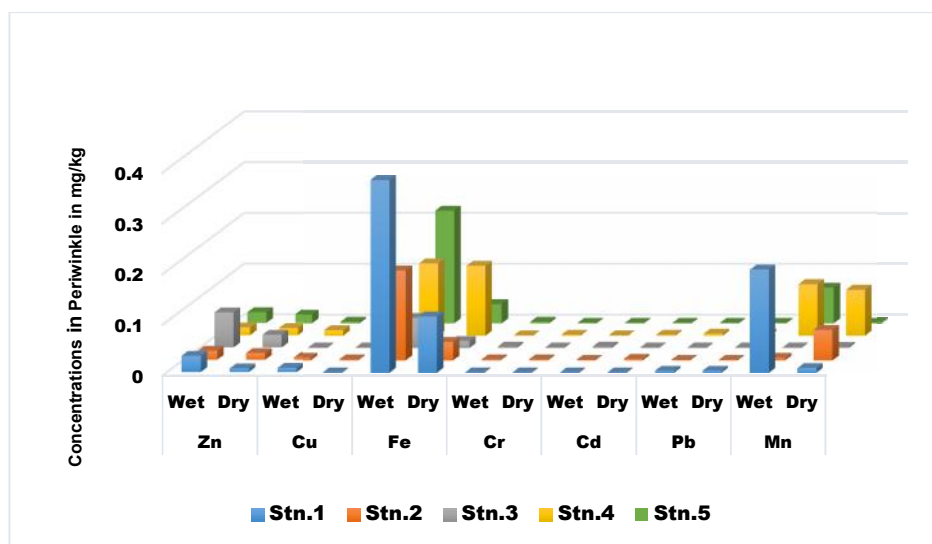


Fig. 3. Temporal spatial variation of heavy metals in Periwinkle along the stations

### 3.1 Mean Concentrations of Heavy Metals in Periwinkle and Crab

Table 1, Figs. 4 and 5 presented the mean concentrations of the investigated heavy metals in the shell fishes. Iron was the most bioaccumulated metals, while cadmium was the least in both crab and periwinkle, as observed along the studied stations. Periwinkle highest value of 0.195 mg/kg was obtained in iron, followed by manganese (0.168 mg/kg) were obtained in the wet season months. While the highest mean concentrations in the study of 10.251 mg/kg was observed in crab, followed by manganese (1.604 mg/kg) during the wet months.

The mean results, further validate the fact that, contaminants bioavailability increases with increasing water volume from their anthropogenic sources. Periwinkle and crab accumulated more of the available metals during the wet season, when the water volume was high. The anthropogenic inputs of some of these metals have been reported to result from industrial and domestic waste waters, such as burning of fossil fuel, land run-off, blow outs, oil spills, gas leaks and indiscriminate dumping of water materials which characterize the study area.

The operational activities of WRPC, Chevron and human activities may have significantly contributed to the levels in water and bio-

accumulation in organisms, especially as higher concentrations were obtained in the wet season than dry. This assertion align with both findings of Oluowo and Isibor [4] and Olomukoro and Azubuike [36].

The mean sequence in periwinkle was Fe > Mn > Zn > Cu > Pb > Cr > Cd. While crab was Fe > Mn > Pb > Zn > Cu > Cr > Cd. Although the concentration of Cr in the crab was observed to be higher during the dry season, all other metals show conformity of being higher during the wet season. This can be attributed to the unstable nature and varying oxidative states of the metal, from Cr<sup>+2</sup> to Cr<sup>+6</sup>, but only the trivalent (Cr<sup>+3</sup>) and hexavalent (Cr<sup>+6</sup>) forms, have been implicated of biological significance [2] and in carcinogenicity.

The studied metals showed very high significant metal differences (P < 0.05) throughout the study period (Table 1). The values of Zn, Pb and Mn in crab were found higher than FAO/FEPA regulatory limits for fish during the wet season, so also, Fe in all the stations above FAO/WHO (2011) limit for food. This call for urgent need to monitor sources of these organisms sold in public market places. Ayenimo et al. [9] reported heavy metal contamination in purchased periwinkle, including the public market of the study area. Elsewhere, Ololade et al. [6] reported metal contamination in crab and periwinkle, and worrisome levels of Cu, Fe, Pb in vegetables sold in public market in Minna, Nigeria [38].

**Table 1. Mean seasonal values of heavy metals bioavailability in periwinkle and crab**

Metals (Mg/kg)	Periwinkle							P-value
	Zn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	
<b>seasons</b>								
Dry	0.015 ± 0.006 (0.007-0.025)	0.0056 ± 0.05 (0.01-0.13)	0.002±0.00 (0.001-0.004)	0.001±0.00 (0.001-0.002)	0.001±0.00 (0.001-0.003)	0.032±0.04 (0.001-0.09)	0.001±0.00 (0.001-0.002)	P=0.001
Wet	0.031±0.022 (0.015-0.069)	0.195±0.11 (0.059-0.378)	0.002±0.001 (0.001-0.005)	0.002±0.001 (0.001-0.003)	0.001±0.00 (0.001-0.003)	0.168±0.16 (0.003-0.430)	0.005±0.003 (0.001-0.011)	P=0.0008
				<b>Crab</b>				
Dry	1.012±0.74 (0.002-1.71)	7.006±5.77 (0.002-15.214)	1.474±1.36 (0.1-3.28)	0.192± 0.39 (0.001-0.897)	0.018±0.01 (0.002-0.042)	0.978±0.92 (0.001-2.074)	0.385±0.55 (0.005-0.452)	P=0.0002
Wet	1.322±0.78 (0.001-2.072)	10.251±9.21 (0.001-21.202)	1.568±1.00 (0.69-2.531)	0.060±0.069 (0.001-0.171)	0.063±0.13 (0.001-0.301)	1.604±1.43 (0.001-3.074)	0.600±0.80 (0.01-1.917)	P=0.0009
FAO/ FEPA 2003 (mg/kg)	-	100	2.00	-	2.00	1.00	3.00	
FAO/WHO, 2011 (mg/kg)	0.3 - 1	0.8	0.3	-	2	-	0.5	

Note: Metals values in the control stations and in both seasons were 0.001 mg/kg and in some cases negative. The p-values for both periwinkle and crab for both seasons were very significant throughout the study with P < 0.05. FEPA [32] connote Federal Ministry of Environment; FAO [33]; Food and Agriculture Organization / WHO (World Health Organization [33])



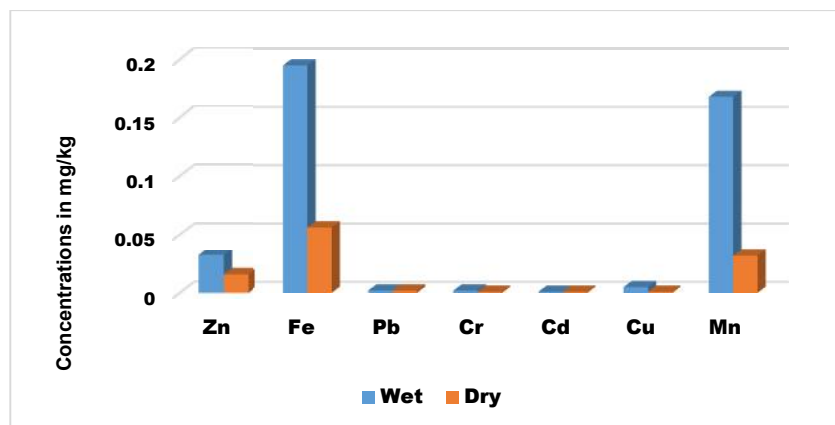


Fig. 4. Seasonal variation of heavy metals in periwinkle

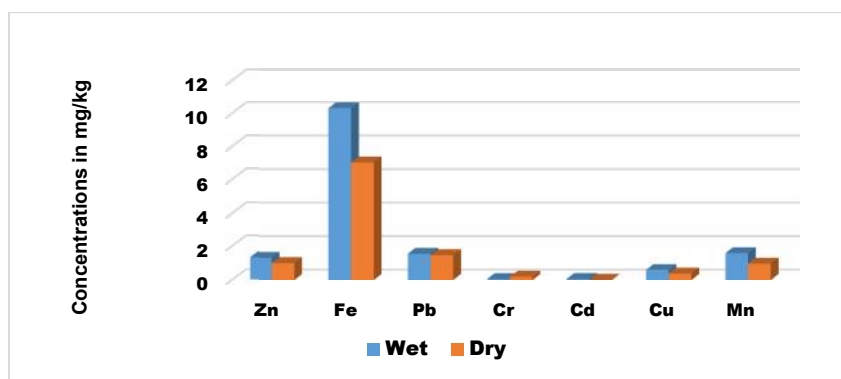


Fig. 5. Seasonal variation of heavy metals in Crab

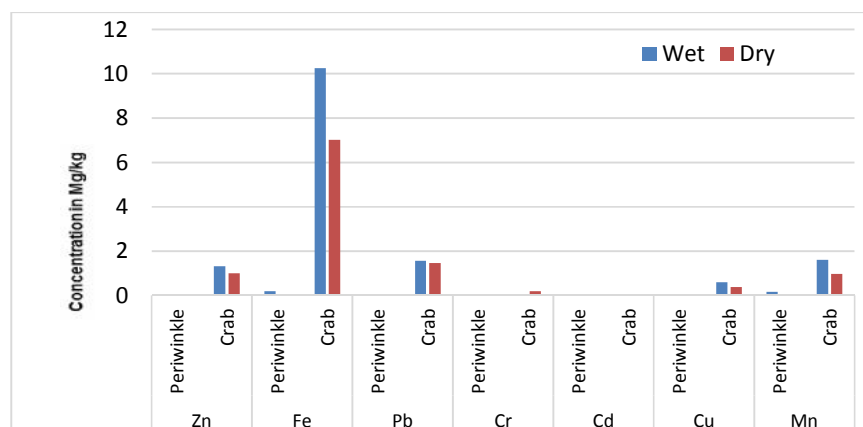
### 3.2 Mean Seasonal Variation of Heavy Metals in Periwinkle and Crab

Although, crab was noted to have bio-accumulated more heavy metals than periwinkle with higher values recorded. It was apparent and consistent in the study that, the concentrations of the investigated metals showed seasonal variation of being higher during the wet season than dry, except for chromium in crab and stability of Pb in periwinkle. This is not scientifically strange as water volume is known to increase from normal during the rainy season.

Fig. 6 further affirm the study result of seasonality and higher concentrations in crab. Several reasons have been attributed to organism bio-accumulation and bio-concentration of metals in aquatic lives to include feeding habit, body mass, sizes to their body cavity. It further buttress the dominance of iron over other metals throughout the study period. The weathering of this metal from anthropogenic source (s) is

evident, coupled with previous report in the river of being higher in the wet season months. Similarly, Falusi and Olanipekun [3] reported very high metal bioaccumulation of Cu, Cd and Zn in the tissues of tropical crab harvested from River Aponwe, Ado-Ekiti, Nigeria, in line with higher mean concentrations of Cd, Pb and Cr observed in crab than prawns above NAFDAC regulatory limits reported by Olowu et al. [12] in Ojo River, Lagos-Nigeria, however Zn and Cu were within safe limits.

The elevated levels of some of the investigated heavy metals in the sampled organisms were at variance with those obtained in the surface water of the study area, however was in conformity with the concentrations reported in the bottom sediment by Oluowo and Isibor [4]. The convergence relationship in heavy metals concentrations between the test organisms and sediment, further validate reports of steady anthropogenic pollution of Ekpan river; the feeding and habitat of periwinkle and crab as benthic organisms.



**Fig. 6. Seasonal comparison of heavy metals in periwinkle and crab**

The present study did not only affirm the reports of Oluowo and Isibor [4], of significant increases in heavy metals concentrations of Ekpan river, Ayenimo et al. [9] heavy metals contamination of periwinkle sold in public markets including that of the study area, but went further to alarm the potential health risk from consumption. An information vital to Nigeria government and importantly, regulatory agencies in monitoring anthropogenic sources of pollution to the river, and researchers alike for further investigation of ichthyofauna of the study area, as well as those sold in markets places for possible heavy metal contamination.

#### 4. CONCLUSION

Increase in perturbation from anthropogenic activities of the river has remain a major source of concern to the water. Heavy metals input has significantly increased due to unregulated activities, majorly from Chevron, WRPC and other oil & gas related activities as well as human activities, has placed the abundance and consumption of shell fishes (periwinkle and crab) as food delicious in the region at high risk, coupled with previous report of contamination of investigated periwinkle sold in market places. The present study recommend regular biomonitoring of the river to check source pollution and encourage government/institutional funding for in-depth research, especially on their oxidative stress responses, metallothioneins, oxygen affinity and thus, toxicological effects. This knowledge is useful for future biomonitoring of aquatic environment and regulating edible food sources to the markets. The present study has insightfully provided some background level information about edible food in the river,

especially with no available studies. The worrisome levels of some of the metals studied necessitate a call for more investigation and regulation of their anthropogenic sources.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

1. Marian E. Metals and their compounds in the environment: Occurrence, analysis and biological relevance. UCH, Weinheim-New York-Basel-Cambridge. Ed; 1991.
2. Hodgson E. A textbook of modern toxicology. 3<sup>rd</sup> Edition. John Wiley & Son, Inc., Hoboken, New Jersey. 2004;557.
3. Falusi BA, Olanipekun EO. Bioconcentration factors of heavy metals in tropical crab (*Carcinus* Spp) from River Aponwe, Ado-Ekiti, Nigeria. J. Appli. Sci. Env. Mgt. 2007;11(4):51–54.
4. Oluowo EF, Isibor PO. Assessment of heavy metals in surface water and bottom sediment of Ekpan Creek, Effurun, Delta State, Nigeria. Journal of Applied Sciences International. 2016;8(4):1-10. DOI: 10.9734/JALS/2016/29144
5. Sanders MJ. A field evaluation of freshwater river crab, *Potamonautes warren*, as a bioaccumulative indicator of metal pollution. M.Sc Thesis, Rand Africans University, South Africa; 1997.
6. Ololade AI, Lajide L, Amoo IA, Oladoja NA. Investigation of heavy metals contamination of edible marine seafood. African Journal of Pure and Applied Chemistry. 2008;2(12):121-131.

7. Paul BT, Clement GY, Anita KP, Dwayne JS. Heavy metals toxicity and the environment. NIH Public Access. 2014;101:133–164. DOI: 10.1007/978-3-7643-8340-4-6
8. Fufeyin PT. Heavy metal concentrations in the water, sediment and fishes of Ikpoba reservoir. Benin City. Nigeria. Ph.D (Thesis). 1994;167.
9. Ayenimo JG, Adeeyinwo CE, Amoo IA. Heavy metal pollutants in Warri River. Nigeria. Kragujevac J. Sci. 2005;27:43-50.
10. Ayenimo JG, Adeyinwo CA, Amoo IA, Odukudu FI. A preliminary investigation of heavy metals in periwinkles from Warri River, Nigeria. Journal of Applied Science. 2006;5(5):813-815.
11. Emoyan OO, Ogban F, Akarah E. Evaluation of heavy metal loading of River Ijana in Ekpan. Jour. Appli. Sci. Env. 2006;10(2):121–127.
12. Oluwa RA, Ayejuyo OO, Adejoro AI, Adewuji GI, et al. Determination of heavy metals in crab and prawn in Ojo Rivers Lagos, Nigeria. E. Journal of Chemistry. 2010;7(2):526-530.
13. James R, Sampath K, Alagurathinam S. Effects of lead on respiratory enzyme activity, glycogen and blood sugar levels of the teleost *Oreochromis mossambicus* (Peters) during accumulation and depuration. Asian Fishery Sci. 1996;9:87-100.
14. Occupational Safety Health Administration (OSHA). Screening and Surveillance; A guide to OSHA Standards, OSHA3162-12R. 2009;35.
15. United State Environmental Protection Agency (USEPA). List of contaminants and their maximum contamination limits. 2009;6.
16. Ikejimba CC, Sakpa S. Comparative study of some heavy metals' concentrations in water and *Tympanotonus fuscatus* var *radula* samples of Egbokodo River, Warri, Nigeria. International Journal of Modern Biological Research (Int. Mod. Biol. Res.). IJMBR. 2014;2:7–15.
17. Andern AB, Udofia UU, Okorafor KA, George UU. Bioaccumulation of some heavy metals and total hydrocarbon (THC) in the tissues of periwinkle (*Tympanotomus fuscatus* var *radula*) in the intertidal regions of Qua Iboe river basin, Ibeno, Akwa Ibom State, Nigeria. Greener Journal of Biological Sciences. 2013;3(7): 253–259.
18. Isibor PO, Oluowo EF. Evaluation of some heavy metals and total petroleum hydrocarbon in water and palaemonid shrimps (*Macrobrachium vollenhovenii*) of Egboko River, Warri, Delta State, Nigeria. Science Domain Journal of Applied Life Sciences International. 2016;6(4):1-12. DOI: 10.9734/JALSI/2016/27148
19. Aina OA, Azubuike VC, Chukwunonso PO, Augustine A. Concentration of polychlorinated biphenyl (PCB) congeners in the muscle of *Clarias gariepinus* and sediment from inland rivers of southwestern Nigeria and estimated potential human health consequences. Journal of Toxicology and Environmental Health, Part A Current Issues. 2016;16.
20. Arukwe A, Eggen T, Moder, M. Solid waste deposits as a significant source of contaminants of emerging concern to the aquatic and terrestrial environments — A developing country case study from Owerri, Nigeria. Science of the Total Environment. 2012;438:94–102.
21. Olowoyo DN. Heavy metal concentrations in Periwinkle (*Litorina littorea*) and tilapia (*Tilapia zilli*) from the coastal water of Warri, Nigeria. Am. J. Food. Nutr. 2011;1(3):102-108. DOI: 10.5251/ajfn.2011.1.3.102.108
22. Stevens AO, Nnabuk OE. Studies on the use of Oyster snail and periwinkle shells as adsorbents for the removal of Pb<sup>2+</sup> from aquatic solution. E. Journal of Chemistry. 2009;6(1):213-222.
23. Prasad VL. Subcutaneous injection of mercury: Warding off evil. Environmental Health Perspectives. 2004;111:1326–1328.
24. Center for Disease Control and Prevention (CDC). Food and drug administration office of inquiry and consumer information. Leaflet. 2009;800:300-3435.
25. Centers for Disease Control and Prevention (CDC). Adult blood lead epidemiology and surveillance. Morbidity and Mortality weekly Report. 2002;53:578–582.
26. Beers MH, Robert B. The merck manual of diagnosis and therapy, white house station. Psychiatric Emergies. 2004;15: 194.
27. Olomukoro JO, Osunde GA, Azubuike CN. Eichlornia crappies invasion and physiochemical characteristics of a creek flowing through an urban area in Southern Nigeria. African Scientist. 2009;10:1-14.

28. Pennak RW. Freshwater invertebrates of the United States, 2nd Ed. John Wiley & Sons, New York. 1978;803.
29. Olomukoro JO. Macro-benthic fauna of Warri River in Delta State. Ph.D Thesis, University of Benin, Benin City. 1996;245.
30. Arimoro FO, Idoro BO. Ecological studies and biology of *Callinectes amnicola* (Family: Portunidae) in the lower reaches of Warri River, Delta State, Nigeria. World Journal of Zoology. 2007;2(2):57-66.
31. American Public Health Association (A.P.H.A). Standard methods for the elimination water and wastewater. 19th American Public Health Association; 2007.
32. Federal Environmental Protection Agency (FEPA). Guidelines and standards for environmental pollution control in Nigeria. 2003;237-240.
33. FAO/WHO. Joint food standards programme codex committee on contaminants in food. 5<sup>th</sup> Edn. Working Document for Information and Use in Discussions Related to Contaminants and Toxins in the GSTFF. 2011;89.
34. Olaifa FE, Olaifa AK, Adelaja AA, Owolabi AG. Heavy metal contamination of *Clarias gariepinus* from lake and fish farm in Ibadan, Nigeria. Afr. J. Biomed. Res. 2004;7:145–148.
35. Jakinska A, Konieczka P, Skora K, Namiesnik J. Bioaccumulation of metals in tissues of marine animals. Part II: Metal concentrations in animal tissues. Pol. J. Environ. Stud. 2011;20(5):1127-1146.
36. Olomukoro JO, Azubuike NC. Heavy metals and macroinvertebrate communities in bottom sediment of Ekpan Creek. Jordan Journal of Biological Sciences. 2009;2:1-8.
37. Omoigberale MO, Ikponmwosa- Eweka O. Evaluation of heavy metals of the Palaemonid Shrimps (*Macrobrachium vollehovenii*) in Osse River, Nigeria. Bioscience Research Communication. 2010;22(5):247-254.
38. Jimoh TO, Ndamitso MM, Abdullahi SH, Bankole MT. Determination of copper, iron and lead levels in selected vegetables obtained from the three main markets, in Minna, North Central Nigeria. African Journal of Food Science. 2012;6(23):554-559.  
DOI: 10.5897/AJFS12.103

© 2017 Freeman and Ovie; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

The peer review history for this paper can be accessed here:  
<http://sciedomain.org/review-history/17968>