HEAVY METALS AND HYDROCARBONS IN SEDIMENT AND CRAB (CARDISOMA ARMATUM) AND ECOLOGICAL RISK ASSESSMENT OF AMADI CREEK, PORT HARCOURT

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DOI: https://doi.org/10.56293/IJASR.2022.5513

IJASR 2023
VOLUME 6
ISSUE 2 MARCH – APRIL **ISSN: 2581-7876**

Abstract: Food security is hinged on quality and integrity of the surrounding environment. Food quality and security of coastline communities are tied to the constituents of benthic organisms in the area. This study assessed the heavy metals and hydrocarbons status of sediment and crab (*Cardisoma armatum*) in Amadi Creek in Port Harcourt. Sediment and crab samples were collected from five stations along a 10 km transect for four months. The heavy metals results for sediment showed the following: Zn (18.624 ± 1.254), Pb (0.791 ± 0.072), Cd (0.031 ± 0.012), Cr (3.323 ± 1.079), Ni (1.848 ± 1.329) and V (0.067 ± 0.102 mg/Kg). The heavy metals ranges in the crab were Zn (20.838 ± 7.803), Pb (0.000 ± 0.000) Cd (0.004 ± 0.014), Cr (0.500 ± 0.239), Ni (1.181 ± 0.562) and V (0.055 ± 0.112 mg/Kg). Hydrocarbon results for sediment were TPH (10.020 ± 11.255), PAH (1.377 ± 1.587 mg/Kg), while the crab had ranges of TPH (1.732 ± 2.235) and PAH (0.003 ± 0.007 mg/Kg). The results were within regulatory permissible limits of EGASPIN and WHO. ANOVA at $p>0.05$ indicated no significant spatial difference between the heavy metals and hydrocarbon concentrations in the sediments and crab at the various stations along the transect. Sediment heavy metal Ecological Risk Assessment revealed that contamination degree and pollution load index were < 1 (indicating no pollution); geo-accumulation index was grade 0 (unpolluted), individual potential risks and potential ecological risk index were < 40 and < 150 respectively (indicating low ecological risk). Sediment to biota transfer factor indicated that Zn was the only heavy metal biomagnified in the crab. Human health risk assessment of the heavy metals in the crab was less than 1 indicating no obvious health risk for cancer over a lifetime of exposure.

Keywords: Sediments, Heavy metals, Total Petroleum Hydrocarbons, ecological and human risk assessment

INTRODUCTION

Heavy metals are defined as electronegative metals that are chemically inert with densities above $5g/cm^3$ (Hawkes, 1997). Since they are inert, they are very difficult to degrade and thus tend to accumulate in the environment and bio-accumulate in aquatic organisms (Edet and Edet, 2014). This bioaccumulation varied depending on species-specific factors; others are feeding behavior, type of aquatic organisms, size, and age (Bawuro et al., 2018).

The concentrations of Polycyclic aromatic hydrocarbons (PAHs) in analyzed sediment and fish, crab and shrimp around Atlas Cove, Nigeria were higher than the maximum permissible limit of the United State Environmental Protection Agency (USEPA), (2000). Most of the detected PAHs were of petrogenic origin, which means that anthropogenic exercises were influencing PAH concentrations (Olayinka et al., 2019). Ediae *et al.*, (2020) investigated sediment sampled obtained from Bodo community in Ogoni Land, Niger Delta for physicochemical parameters, heavy metals, TPH, PAH, total heterotrophic bacteria (THBC), and fungi (THFC) using standards methodologies. The heavy metals profile revealed Fe > Cr > Zn > Ni > V in decreasing order while TPH and PAH concentrations were 30,797 and 52.12 mg/kg, thus exceeding the target and intervention values of 50 and 5,000 mg/kg, respectively of the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), (2002) which also adversely affected the microbial proliferation in the sediment.

Crab is among nutritious and cheap aquatic food in the coastal areas of the Niger Delta. Bio-accumulation study of heavy metals in crabs from four sampled stations at Bundu-Ama Community, Port Harcourt reported the mean concentration of the Cr (8.85mg/kg), Cu (196mg/kg), Ba (403mg/kg), Pb (< 1.00 mg/Kg), Ni (25.8mg/kg), As (0.83mg/kg), Cd (<2.00mg/kg), Hg (<1.00mg/kg), Se (< 0.50mg/kg) and V (11.3mg/kg). Revealing that Cr, Cu, Ba, Ni, As and V exceeded the standard limits of USEPA. WHO, (2012) and Nigerian Industrial Standard (NIS) for drinking water quality, thus concluded that anthropogenic activities in the study area have contributed to high heavy metal contamination? Thus the consumption of the crabs may be considered unsafe (Umunnakwe and Ogamba, 2013).

Pollution is a major threat to every living organism on earth as well as their metabolic activities (Abdel-Baki, et al., 2011). There are significant interactions that occur between benthic invertebrates (and other organisms) and sediment materials. These benthic organisms in sediment act as accumulators and conductors of contaminants by physical, chemical, and biological processes (Reynoldson, 1987). Bioconcentration and magnification has potential for high toxicity of metals in organisms, even when the exposure level is low. Apart from destabilizing the ecosystem, the accumulation of these toxic heavy metals in aquatic food web poses health risk when consumed and thus their potential long-term impact on ecosystem should be of concern (Ogoyi *et al*., 2011). It is in this regard that this study was carried out to determine the levels of heavy metals and hydrocarbon in sediment and crab **(***Cardisoma armatum***)** in Amadi Creek, Port Harcourt. The ecological and human risk assessment of the heavy metals in the sediment and in the crab was also assessed to determined the safety of consumers of the substance.

MATERIALS AND METHODS

Description of the study area

Amadi Creek is located in Port Harcourt, Rivers State. The river transect extends from Amadi village up to Abuloma town which is spatially situated at coordinates expending from N04°48'32.76" and E007°00'57.29" from the Nkpogu axis at Trans-Amadi leading to N04°46'16.33" and E007°03'34.57"at the open river in Abuloma leading to Bonny Island which is about 10 Kilometers long (Fig. 1). Vegetation in the area is predominantly mangrove that is the red mangrove (*Rhizophora racemoss*), white mangrove (*Avicenna racemosa*) and black mangrove (*Lagunculana racemoss*). Also, there are mangrove associates and a rich community of aquatic fauna. The climate of the area is basically equatorial tropical rainfall all months of the year except for the months of December, January, February and March which comprised the dry season. The annual mean meteorological parameters of the study area include precipitation is 2700mm, air temperature 29.60 - 33.3°C, and Wind speed 1.0 m/s. The surface seawater temperature values ranged between 25.9°C and 30.6°C with a salinity of the seawater between 8% and 20% (Gobo et al., 1988). The economic activities in the area are mainly fishing, sand dredging, transportation of human and commodities, oil company base-logistic offices and trading. The area is characterized by sedimentary rock formation, comprising of tertiary and quaternary (recent) marine or continental deposits, extensive petroleum deposits mask the underlying geological structure. The soil highly weathered and could be classified as coarse, loamy, with good drainage system, not water logged and is moderately acidic with low soluble salts contents.

Sample collection

The collection of 20 sediment and 20 crab samples from five geo-referenced sample locations with a distance of approximately 2 Km apart was done monthly from March 2020 to June 2020. The sediment was sampled using an Eckman grab or hand trowel from the shadow waters, samples for heavy metal analysis was collected in small Ziploc bags with the aid of a tea plastic spoon while the hydrocarbon samples was collected in a one hundred milliliter (100 ml) amber bottles, properly labeled and preserved in ice chest before delivery to the laboratory. Crab (Cardisoma armatum) samples was obtained from on-site local fishermen and preserved as in Ziploc bags in an ice chest prior to transfer to the laboratory

Sample analysis

American Public Health Association (APHA), (2017) 3110-B, C and D) standard analytical method was used for the heavy metal analysis. The total digestion procedure was employed by adding twenty milliliters (20 ml) of digestion solution (nitric acid, sulphuric acid, and perchloric acid in the ratio of 2:2:1) to 1 gram of samples (air-dried sediment and blended wet crab) into separately labeled two hundred and fifty milliliters (250 ml) conical flask. The samples were digested at three hundred-degree Celsius (300°C) for thirty (30) minutes to ensure complete dissolution of the heavy metals into the acidic solution. The digested solution was filtered using ash less Whatman filter and the filtrate made up to one hundred milliliters (100 ± 1.0 mL) before atomic absorption spectrophotometer (AAS) analysis.

Solid-liquid phase extraction procedure of blended wet samples of ten (10) gram was used, dichloromethane was the extracting solvent due to its ability to extract both aliphatic and aromatic hydrocarbon efficiently. The extract was concentrated to one milliliter (1 ± 0.5 mL) by rotary evaporator after silica gel clean up before gas chromatography analysis (Solid-Phase Extraction – EPA Method 3535A; silica gel cleanup - APHA 6410B; polynuclei aromatic hydrocarbons - EPA Method 8270D-GCMS and total petroleum hydrocarbons – EPA Method 8015D GC-FID.

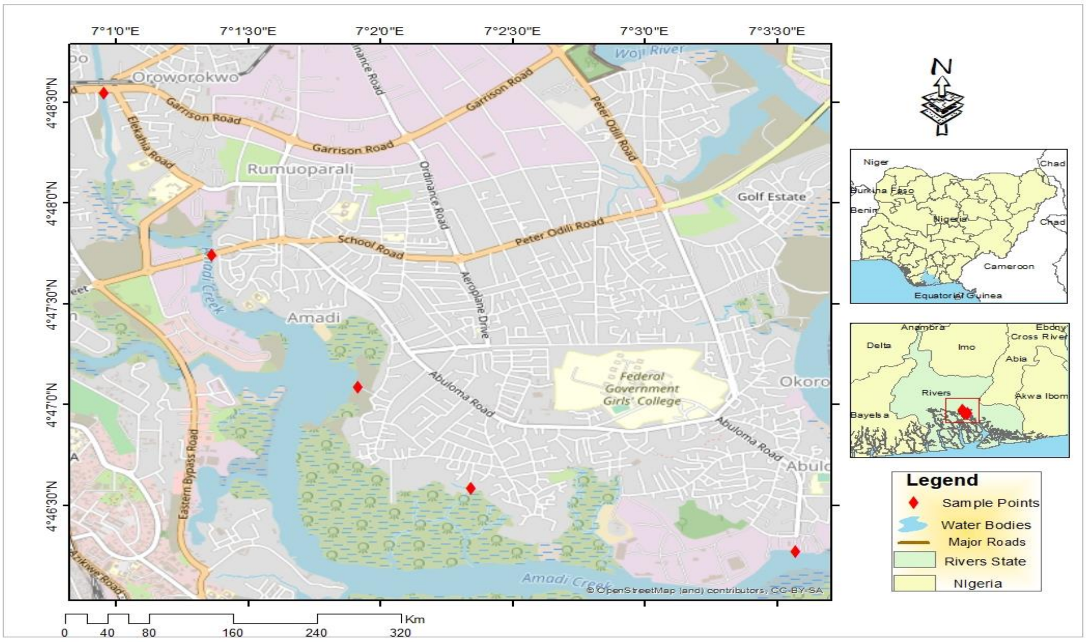

Fig. 1 Map showing study Area

Secondary data was obtained from AAS and GC FID/MS equipment used to analyze the extracts of the sediment and crab samples were statistical evaluated, assessment of ecological and human risk analysis, compared with DPR EGASPIN guidelines and WHO Seafood Safety Standards and descriptive statistical

Ecological Risk Assessment of Heavy Metals in Sediment

Pollution Load Index (PLI): This represents the number of times by which the metal content in the sediment exceeds the background concentration. It provides comprehensive information about the metal toxicity in a particular sample (Yang, *et al.*, 2011). The pollution load index (PLI) is defined as the nth root of the multiplications of the concentrations. The PLI value of > 1 indicates polluted, whereas < 1 indicates no pollution (Barakat *et al.*, 2012). PLI was calculated using the following formula proposed by (Tomlinson *et al.*, 1980).

$$PLI = (CF_1 \times CF_2 \times CF_3 \cdots \times CF_n)^{1/n}$$

Where:
n = number of metals (5 in the present study) and
CF = contamination factor.

The contamination factor was calculated from the following relation:

$$CF = \frac{\text{Metal concentration in sediment}}{\text{Background value of metal}}.$$

Consequently,

a. CF < 1 (low degree of contamination),
b. 1 < CF < 3 (moderate degree of contamination),
c. 3 < CF < 6 (considerable degree of contamination), and
d. CF > 6 (very high degree of contamination) (Hakanson, 1980).

Contamination Degree (CD): This refers to the summation of all contamination factors. It gives an indication of the degree of overall contamination in sediments from a sampling station. It is expressed as:

$$CD = \sum_{i=1}^{n} CF.$$

Håkanson (1980) proposed the classification

a. CD < 6 (low degree of contamination),
b. 6 ≤ CD < 12 (moderate degree of contamination),
c. 12 ≤ CD < 24 (considerable degree of contamination), and
d. CD ≥ 24 (very high degree of contamination).

Geoaccumulation Index (Igeo): Igeo is widely used to quantify the extent of heavy metal contamination in sediment by comparing current concentrations with pre-industrial levels (Muller, 1969). Igeo is mathematically expressed as:

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right]$$

Equation 4

Where:
Cn = concentration of element 'n' and
Bn = geochemical background value of each metal.

Background values of World surface rock average was used (Turekian and Wedepohl, 1961). The factor 1.5 in the Equation 4 is to account for possible variation in background data due to lithogenic effect (Wang et al., 2016). Muller (1969) classification of Igeo grouped it into seven grades:

a. Igeo ≤ 0 (grade 0), unpolluted;
b. 0 < ≤ 1 (grade 1), slightly polluted;
c. 1 <Igeo ≤ 2 (grade 2), moderately polluted;
d. 2 <Igeo ≤ 3 (grade 3), moderately severely polluted;
e. 3 <Igeo ≤ 4 (grade 4), severely polluted;
f. 4 <Igeo ≤ 5 (grade 5), severely to extremely polluted; and
g. 5 <Igeo> 5 (grade 6), extremely polluted.

Potential ecological risk index (RI): This is used to evaluate the ecological risk of heavy metals in sediments by considering the toxicity of the metal and a comparison between the concentration of the metal and the background value. RI was used in this study to quantify the potential ecological hazard of contaminated sediment to biota. Håkanson (1980) provided a formula to estimate RI. Firstly,

$$E_r^i = T_r^i \times CF,$$

Where:

Tir = toxic response factor for a given substance (
CF = contamination factor.

The toxic response factor assigned to the following heavy metals Cr, Cd, Zn, Pb, and Ni used in the calculation of potential ecological risk index (RI) are 2, 5, 30, 1, 5, and 5, respectively (Jiao *et al.*, 2015). The sum of the individual potential risks (Eir) is the potential ecological risk index (RI) for the water body. It is presented as:

$$RI = \sum_{i=1}^{n} T_r^i \times CF.$$

For the classification of individual potential risks (Eir) in sediments,

a. Eir ≤ 40 = low ecological risk,
b. 40 <Eir ≤ 80 = moderate ecological risk,
c. 80 <Eir ≤ 160 = considerable ecological risk,
d. 160 <Eir ≤ 320 = high ecological risk,
e. Eir> 320 = very high ecological risk.

Furthermore, classification of potential ecological risk index (RI) is as follows:

a. RI ≤ 150 = low ecological risk,
b. 150 < RI ≤ 300 = moderate ecological risk,
c. 300 < RI ≤ 600 = considerable ecological risk,
d. RI > 600 = very high ecological risk.

Sediment - To - Benthic Transfer Assessment: This was calculated as transfer factor (TF) as defined by the equation below. A transfer factor of 1 and above indicates that the metal is biomagnified.

$$TF = \frac{C_{fauna}}{C_{sediment}}$$

Where:

Cfauna = concentration of heavy metals in C. armatum
Csediment = concentration of heavy metals in sediment.

Human Health Risk Assessment of Heavy Metals in Sediment and Biota

i. Exposure Assessment: Exposure to toxic heavy metals is of immerse concern to people living close to contaminated aquatic ecosystems. There are three primary routes of exposure to heavy metals in sediments in regards to human health risk assessment. They are ingestion, dermal contact, and inhalation which can be calculated using equations below:

$$EXP\ (dermal) = \frac{C \times CF \times SA \times AF \times ABS \times EF \times ED}{BW \times AT},$$

$$EXP\ (ingestion) = \frac{C \times IRs \times ED \times EF}{BW \times AT},$$

$$EXP\ (inhalation) = \frac{C \times IR(inh) \times EF \times ED}{PEF \times BW \times AT},$$

Where:

C = concentration of heavy metals in the sediment;
IRs = ingestion rate (114 mg/day);
CF = unit conversion factor (10−6 kg/mg);
EF = exposure frequency (350 days/year);
ED = exposure duration (30 years);
BW = body weight (70 kg);
SA = exposed skin surface area (5700 cm2);
AF = adherence factor from sediment to skin (0.07 mg/cm2);

ABS = dermal absorption from sediment (0.001) (unitless);
SL = skin adherence factor (0.2 mg cm−2 h−1) for children and (0.2 mg cm−2 h−1) for adults;
PEF = particle emission factor (1.316 × 10−9 m3 kg−1);
AT = average time (for non-carcinogens, it is ED × 365 days. For carcinogens, it is 70 × 365 = 25,550 days).

Similarly, dietary intake of contaminated food has been implicated as a primary source of human exposure to toxic chemicals including heavy metals. The exposures through oral consumption of contaminated C. armatum was calculated using equation 8 as expressed below

$$\text{EXP(diet)} = \frac{C \times \text{IR(biota)} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT}},$$

Where:
C = concentration of the per mass of the medium (ppm),
IR = ingestion rate of the medium (0.114g/day),
ED = exposure duration (30 years),
EF = exposure frequency (350 days/year),
BW = body weight (70 kg) and
AT = averaging time (30 years x 365 days = 10,950).

ii. Risk Characterization

a. Non-Cancer Risk: The potential non-cancer risk of heavy metal concentrations in sediments and biota was calculated using a hazard quotient (HQ). Hazard quotient (HQ) assumes that there is a level of exposure known as the reference dose (RfD). It is estimated that a daily oral intake of the heavy metal at the reference dose will pose no reasonable risk even to sensitive populations over a 70-year lifetime (Afrifa *et al*., 2013). Hazard quotient (HQ) is defined as the ratio of the average daily intake or dose (ADD) (mg/(kg/day)) to reference dose (RfD, mg/(kg/day)). It was estimated using the formula:

$$\text{HQ} = \frac{\text{EXP}}{\text{RfD}}$$

Where:
HQ = hazard quotient (unitless),
ADD = average daily dose (mg/kg−day),
RfD = Reference dose (mg/kg−day).

For n number of heavy metals, the non-carcinogenic effect to the population is as a result of the summation of all the HQs due to individual heavy metals.

$$\text{HI} = \text{HQ}_1 + \text{HQ}_2 \cdots + \text{HQ}_n$$

If the HI is less than 1.0, it indicates that no significant additive or toxic interactions would occur, so no further evaluation is necessary. When the HI exceeds 1.0, potential non-cancer health effect may occur and calls for further evaluation.

b. Cancer Risk: The potential cancer risk of the heavy metals in the sediment and biota were estimated using the incremental or excess individual lifetime cancer risk using the following formula:

$$\text{Cancer Risk} = \sum_{k=1}^{n} \text{EXPk} \times \text{CSFk}$$

Where:
Risk = unitless probability of an individual developing cancer over a lifetime.
EXPk (mg/kg/day) = average daily intake while
CSFk = cancer slope factor (mg/kg/day) −1 for the kth heavy metal,

For n number of heavy metals. The slope factor converts estimated daily intakes averaged over a lifetime of exposure directly to the incremental risk of an individual developing cancer.

RESULTS AND DISCUSSION

Results of heavy metal and hydrocarbon from Amadi creek, Port Harcourt
The average results of heavy metals and hydrocarbon in sediments and crab of Amadi Creek with respect to the different locations investigated are presented in Tables 1, 2 and 3. Zn and Cr were highest while Cd is lowest of heavy metals in the sediments for all stations. Station 3 has the highest mean of heavy metals while station 2 is the lowest in a profile order of station 3 > 5 > 4 >1 > 2. The heavy metals in the crab showed station 5 has the highest metal concentrations and station 2 the lowest. Similarly, the profile order of TPH and PAH in the sediments were station 5 > 3 > 2 > 4 > 1 while that in the crab were station 5 > 3 > 2, hydrocarbon was not detected in stations 1 and 4.

Mean Variation in Heavy Metals in Sediments for All Study Areas

The mean variations of heavy metals in sediment and crab are depicted in Fig. 3, and 4, respectively. Zn showed the widest variation in concentration for sediment and crab in all the stations sampled, while Cd showed the least variation. The profile of concentrations of heavy metals in all sediment samples are Zn>Cr>Ni>Pb>V>Cd which is in accordance to Anani and Olomukoro (2017); Ipeaiyeda and Onianwa (2018) and not similar to Sayyad (2014).

Mean Variation of Heavy Metals in Crab (*C. Armatum*) For All Study Areas

The mean concentrations (mg/kg) of heavy metals in the whole tissue of *C. armatum* in Amadi Creek was presented Table 5 and Figure 4. The results showed that C. *armatum* had high mean concentrations of Zn in all investigated stations and Pb was not detected. The heavy metals were in the order of Zn>Ni>Cr>V>Cd>Pb, which is similar to Kpee and Edori, (2014) and not in accordance to Olowu *et al.*, (2010). It is evident from the analysis of Figure 6 that *C. armatum* accumulated heavy metals (Enuneku *et al.*, 2018).

Mean Variation Of Hydrocarbon Concentrations In Sediment And Crab For All Study Areas

The descriptive statistics of hydrocarbon analysis (TPH and PAH) in the sediment and crab from Amadi Creek was presented in Table 6, while the mean variation in Figure 5 and 6 respectively. TPH showed widest variation in concentrations for sediments and crab in all the stations sampled, while PAH showed the least variation which showed similarities with Ighariemu et al., (2019). The low hydrocarbon concentrations in the sediments are lower than the values gotten by Ediae *et al.,* (2020). *C. armatum* accumulated hydrocarbon in TPH as showed in Fig. 6 especially in station 3 and 5 as shown in Table 6. This is a result of high concentrations of TPH in these locations.

Table 1: Heavy metals concentrations in the sediment

Parameters	Zn	Pb	Cd	Cr	Ni	V
Station 1	16.996	0.763	0.027	3.661	2.143	0.105
Station 2	17.867	0.784	0.027	2.729	0.905	0.014
Station 3	18.892	0.731	0.032	4.602	3.172	0.056
Station 4	20.137	0.809	0.029	1.906	1.038	0.011
Station 5	19.228	0.871	0.040	3.718	1.981	0.151
Mean ± SD	18.624 ± 1.254	0.791 ± 0.072	0.031 ± 0.012	3.323 ± 1.079	1.848 ± 1.329	0.067 ± 0.102
Range (min - max)	16.058 - 20.941	0.705 - 0.926	0.011 - 0.059	1.591 - 5.491	0.168 - 4.197	0.000 - 0.413

Table 2: Heavy metals concentrations in the C. Armatum

Parameters	Zn	Pb	Cd	Cr	Ni	V
Station 1	15.242	0.000	0.000	0.399	1.570	0.003
Station 2	14.493	0.000	0.000	0.287	1.176	0.059
Station 3	15.153	0.000	0.016	0.516	1.743	0.103
Station 4	27.675	0.000	0.000	0.698	0.215	0.000
Station 5	31.629	0.000	0.003	0.601	1.202	0.110

Mean ± SD	20.838 ± 7.803	0.000 ± 0.000	0.004 ± 0.014	0.500 ± 0.239	1.181 ± 0.562	0.055 ± 0.112
Range (min - max)	14.079 - 35.962	0.000 - 0.000	0.000 - 0.063	0.138 - 0.979	0.164 - 1.931	0.000 - 0.413

Table 3: Hydrocarbon concentrations in the sediment and C. armatum

Parameters	Sediment		*C. armatum*	
	TPH	PAH	TPH	PAH
Station 1	0.015	0.004	0.000	0.000
Station 2	2.127	0.585	0.013	0.000
Station 3	22.639	3.384	3.824	0.000
Station 4	1.428	0.274	0.000	0.000
Station 5	23.982	2.636	4.823	0.016
Mean ± SD	10.020 ± 11.255	1.377 ± 1.587	1.732 ± 2.235	0.003 ± 0.007
Range (min - max)	0.011 - 29.381	0.000 - 4.975	0.00 - 5.148	0.000 - 0.019

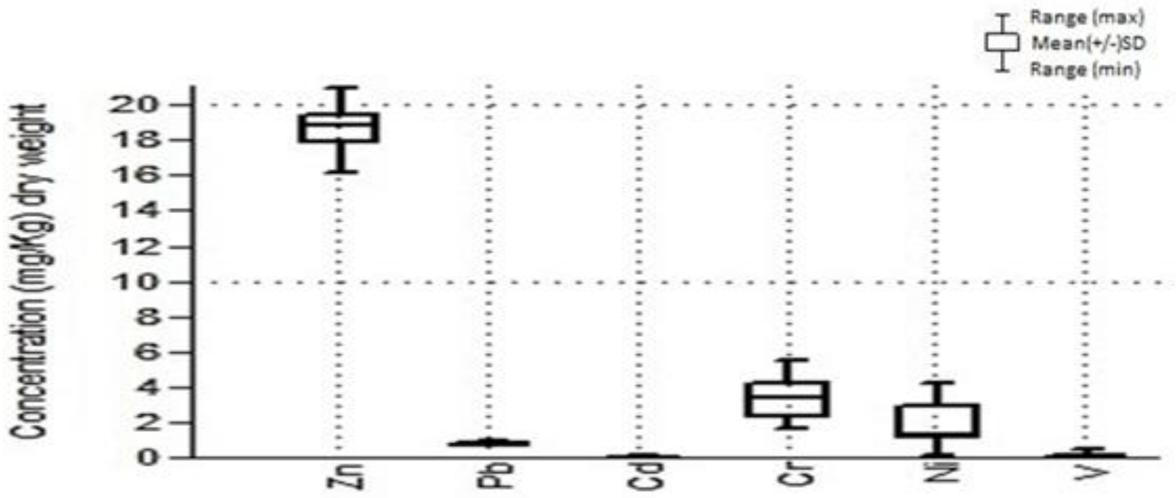

Figure 2: Box plot showing variation in heavy metals concentrations in sediment

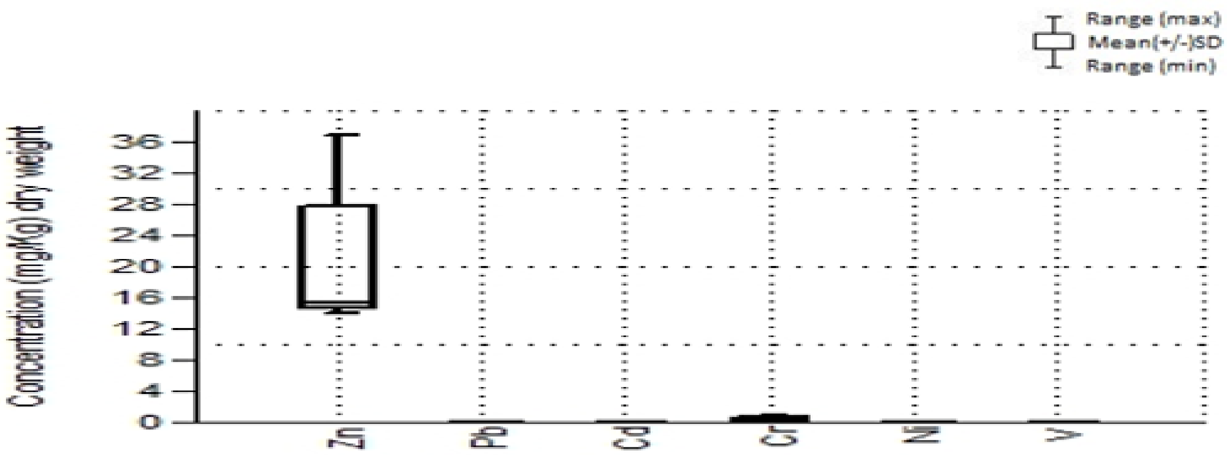

Figure 3: Box plot showing variation in heavy metals concentrations in C. armatum

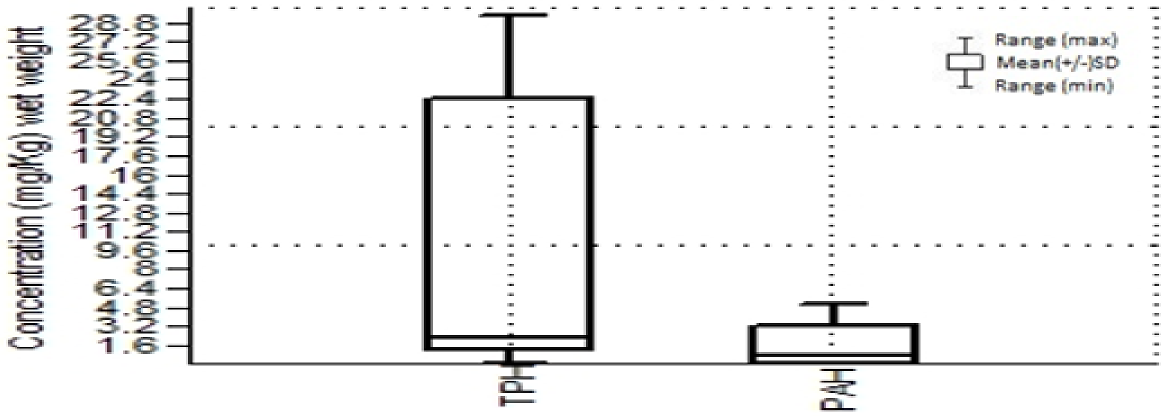

Figure 4: Box plot showing variation in hydrocarbon concentrations in sediment

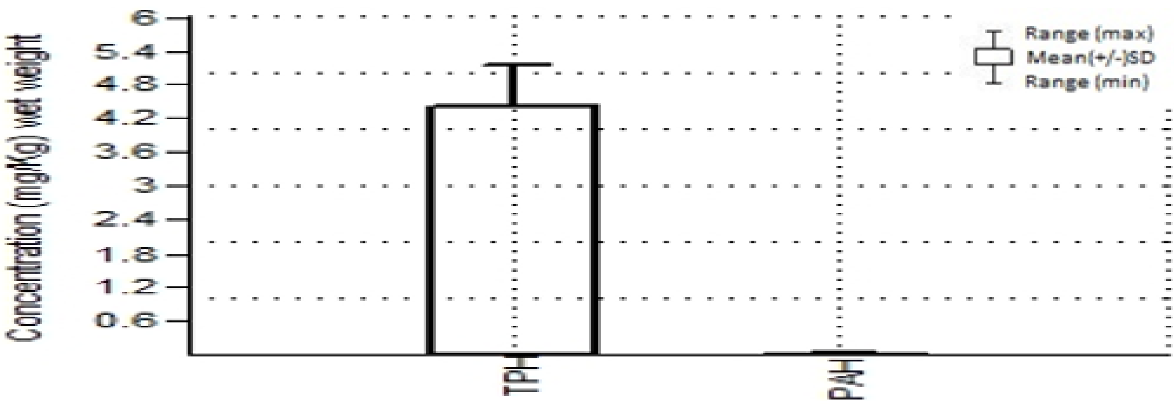

Figure 5: Box plot showing variation in hydrocarbon concentrations in C. armatum

Heavy Metal Concentrations in Sediments Compared with Permitted Values from EGASPIN 2018

The heavy metals concentrations in the sediments from all sampled locations were compared with the Environmental Guidelines and Standards for Petroleum Industry in Nigeria (DPR, 2018). It showed that the sediments were below the target and intervention values depicting compliances to the guidelines as showed in Table 4.

Mean Variation in Heavy Metal in Crab (*C. Armatum*) Compared With FAO/WHO Limits

Similarly, Table 4 shows the FAO/WHO limits and European Community maximum permitted concentrations (mg/Kg wet weight) for certain heavy metals in seafood, Pb was not detected in the crab while Cd with mean value of 0.016 mg/Kg was detected in station 3 which is lower than the permissible limits for consumption and it is found to be in compliance with WHO limit for seafood.

Analysis of Variance

Table 5 gives the summary of Analysis of Variance (ANOVA) showed that *F-calculated* is less than *F-critical*, which indicated that there is no significant difference at $p>0.05$ for:

i. Heavy metals and hydrocarbon concentrations in the sediments between the stations
ii. Heavy metals and hydrocarbon concentrations in the crab (*C. armatum*) sediments between the stations
iii. Values of the sediment and crab (*C. armatum*) in all the stations

Therefore, H_o is retained (accepted), H_A rejected.

Table 4: Heavy metals and hydrocarbon concentrations compared with EGASPIN guidelines

	Parameters	Sediment Samples	EGASPIN (2018) guidelines	
			Target value	Intervention value
Investigated heavy metals	Zinc, mg/kg	18.624	140.00	720.00
	Lead, mg/kg	0.791	85.00	530.00
	Cadmium, mg/kg	0.031	0.80	12.00
	Chromium, mg/kg	3.323	100.00	380.00
	Nickel, mg/kg	1.848	35.00	210.00
	Vanadium, mg/kg	0.067	NS	NS
Hydrocarbon	TPH, mg/kg	10.038	50.00	5000.00
	PAH, mg/kg	1.377	1.00	40.00

Table 5: Maximum permitted concentrations (m/Kg wet weight) for certain heavy metals in seafood

Organisation	Cd	Pb	Reference
FAO/WHO limits	0.50	0.50	FAO/WHO (1989)
FAO/WHO limits	-	0.30	JECFA (2011)
European Community	0.05	0.30	EC (2006)

Table 6: Analysis of variance (ANOVA)

Samples	Source of Variation	SS	Df	MS	F	P-value	F crit
Sediments	Between Groups (Station 1, 2, 3, 4 and 5)	400.669	4	100.167	2.04817	0.09032	2.43
	Within Groups	7580.38	155	48.9057			
	Total	7981.05	159				
Crab (*C. armatum*)	Between Groups (Station 1, 2, 3, 4 and 5)	172.022	4	43.0055	0.79481	0.53023	2.43
	Within Groups	8386.73	155	54.108			
	Total	8558.76	159				
Sediment and crab (*C. armatum*)	Between Groups (Sediment and crab)	8.681	1	8.681	0.182	0.676	4.600
	Within Groups	666.685	14	47.620			
	Total	675.366	15				

SS - Sum of squares, df - degreee of freedom, MS - Mean of squares, F - $F_{calculated}$, P-value - Probability value, F_{crit} - F critical

Ecological Risk Assessment

I. Contamination Degree (CD) And Pollution Load Index (PLI): Table 7 shows the calculated contamination factor (CF), average CD and PLI values for different heavy metals in the sediments collected from Amadi Creek. For all stations along the Amadi Creek, the CF value for Zn (0.212) in station 4 was highest although it was < 1, which follow the order of Zn>Cd>Pb>Cr>Ni>V all have CF values < 1. Therefore, on the basis of the mean values of CD in all the five sampled locations, which is < 6, low degree of contamination exists in Amadi Creek. Similarly, the mean PLI of <1 indicated no pollution (Barakat et al., 2012). The values obtained from the calculated CF, mean CD and PLI are different from evaluation of the potential health risks of heavy metal pollution in sediment and selected benthic fauna of Benin River, (Enuneku et al., 2018) where PLI > 1 was obtained in station 1.

II. Geoaccumulation Index (I_{geo}): The results of the calculated I_{geo} in Table 8 show that stations 1, 2, 3, 4 and 5 had values < 0 for Zn, Cd, Pb, Cr, Ni and V which fell into grade 0, unpolluted.

III. Ecological risk assessment: Table 9 summaries the individual potential risks (E^i_r) of the different heavy metals and their contributions to the potential ecological risk index (RI) of the sediments from the five investigated stations in the Amadi Creek. Zn had the highest E^i_r (although less than 40) while Cr had the lowest, both in station 4. The mean E^i_r for individual locations which is the RI followed the order of station 5 > 3 > 4 > 2 > 1. Hence, the E^i_r< 40 and RI < 150 indicating low ecological risk for both.

Table 1: Calculated Contamination factor, Contamination degree (CD) and Pollution load index (PLI) from sediment of Amadi creek

Heavy metals	Station 1	Station 2	Station 3	Station 4	Station 5	All Sample	Bn*
Zn	0.179	0.188	0.199	0.212	0.202	0.196	95.00
Pb	0.038	0.039	0.037	0.040	0.044	0.040	20.00
Cd	0.089	0.089	0.106	0.095	0.135	0.103	0.30
Cr	0.041	0.030	0.051	0.021	0.041	0.037	90.00
Ni	0.032	0.013	0.047	0.015	0.029	0.027	68.00
V	0.001	-	-	-	0.001	0.001	130.00
CD	0.379	0.360	0.439	0.384	0.452	0.403	
PLI	0.029	0.018	0.030	0.017	0.034	0.026	

Source: This study
*Bn - Background Sediment Shale values

Table 8: Geoaccumulation Index (I_{geo}) of the sediment

Heavy metals	Station 1	Station 2	Station 3	Station 4	Station 5	All Sample
Zn	-3.068	-2.996	-2.915	-2.823	-2.890	-2.938
Pb	-5.297	-5.258	-5.359	-5.214	-5.106	-5.247
Cd	-4.072	-4.072	-3.827	-3.979	-3.477	-3.886
Cr	-5.205	-5.628	-4.875	-6.146	-5.182	-5.407
Ni	-5.573	-6.816	-5.007	-6.619	-5.686	-5.940
V	-10.862	-13.740	-11.766	-14.147	-10.339	-12.171

Source: This study

Table 8: Individual potential risks (E^i_r) and potential ecological risk (RI)

Heavy metals	Station 1	Station 2	Station 3	Station 4	Station 5	All Sample
Zn	5.367	5.642	5.966	6.359	6.072	5.881
Pb	0.191	0.196	0.183	0.202	0.218	0.198
Cd	2.675	2.675	3.170	2.854	4.040	3.083
Cr	0.081	0.061	0.102	0.042	0.083	0.074
Ni	0.158	0.067	0.233	0.076	0.146	0.136
*V	-	-	-	-	-	-
IR	8.472	8.640	9.654	9.534	10.558	9.372

Source: This study
*No Toxic response factor for Vanadium

Human Health Risk Assessment

Transfer factor: Metal transfer factor from sediment to fauna is seen as a major route of human exposure to heavy metals via the food chain and can be used to assess the human health risk index. The calculated transfer factor values are presented in Table 9 which showed that investigated heavy metals were below 1 except Zn with a value of 1.119. Figure 7 points out the level for bio-magnification of these heavy metals a concentration that has occurred in *C. armatum*. A transfer factor of 1 (Ibhadon *et al.*, 2014) the threshold as seen in Figure 7 and above signifies that Zn is been biomagnified in *C. armatum*. Bioconcentration and magnification has potential for to high toxicity of metals in organisms, even when the exposure level is low (Ogoyi *et al.*, 2011).

Health risk assessment: The results of the average daily dose (ADD) and hazard quotient (HQ) for *C. armatum* of Amadi Creek are summarized in Table 10 with corresponding oral reference dose (RfD). The calculated HQ values for the selected heavy metals ranged from 0.000 to 0.2603. The human health risk assessment and HQ values for Zn, Pb, Cd, Cr, Ni and V were less than 1 indicating that there is no obvious health risk for cancer from these heavy metals over a lifetime of exposure. Hence no further evaluation is necessary carcinogenic effect to the population. The human health risk assessment of the present research work was evaluated with the one reported by Enuneku *et al.*, (2018). Results of HQ and HI were found to be lower than that of Enuneku *et al.,* (2018).

Table 2: Calculated transfer factor for heavy metals

Heavy metals	Sediment	*C. armatum*	Calculated transfer factor
Zn	18.624	20.838	1.119
Pb	0.791	0.000	0.000
Cd	0.031	0.004	0.123
Cr	3.323	0.500	0.150
Ni	1.848	1.181	0.639
V	0.067	0.055	0.816

Table10: ADD and HQ for *C. armatum*

Heavy metals	ADD	Rfd (mg/kg/day)	HQ
Zn	0.0325	0.3000	0.1085
Pb	0.0000	0.0035	0.0000
Cd	0.0000	0.0010	0.0059
Cr	0.0008	0.0030	0.2603
Ni	0.0018	0.020	0.0922
V	0.0001	-	-
HI			0.4669

ADD - average daily dose, Rfd - oral reference dose, HQ - hazard quotient, and HI - hazard index

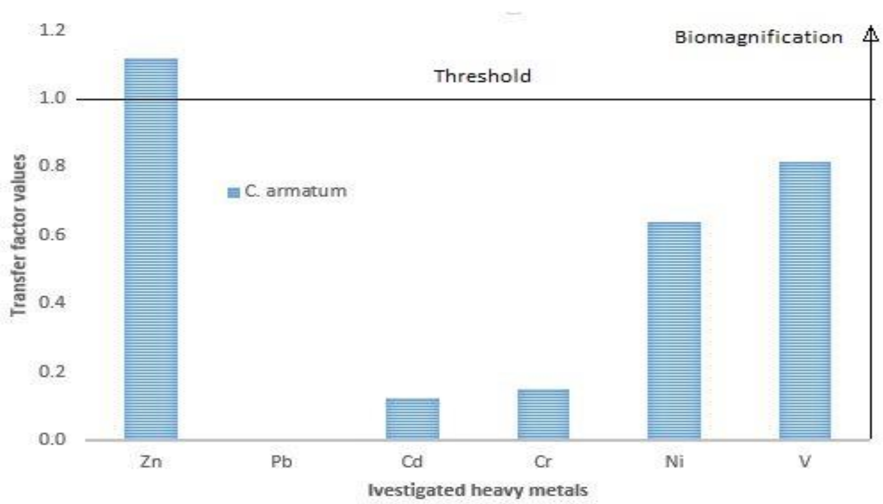

Figure 1: Transfer factor of heavy metals in C. armatum

CONCLUSION

This study investigated heavy metal and hydrocarbon concentrations in sediment and crab (*Cardisoma armatum*) of Amadi Creek and assessed the ecological and human health risk of contamination in sediment and *C. armatum*. The crab is a delicacy which provide relatively cheap source of animal protein to Amadi-Abuloma Community inhabitants. The study revealed the following levels of heavy metals in the sediments: Zn (18.624 ± 1.254 mg/Kg), Pb (0.791 ± 0.072 mg/kg), Cd (0.031 ± 0.012 mg/Kg), Cr (3.323 ± 1.079 mg/Kg), Ni (1.848 ± 1.329 mg/Kg) and V (0.067 ± 0.102 mg/Kg) while hydrocarbon status was: TPH (10.020 ± 11.255 mg/Kg) and PAH (1.377 ± 1.587 mg/Kg). The heavy metals concentrations obtained from *C. armatum* were Zn (20.838 ± 7.803 mg/Kg), Pb (0.000 ± 0.000 mg/Kg) Cd (0.004 ± 0.014 mg/Kg), Cr (0.500 ± 0.239 mg/Kg), Ni (1.181 ± 0.562 mg/Kg) and V (0.055 ± 0.112 mg/Kg). Hydrocarbon are TPH (1.732 ± 2.235 mg/Kg) and PAH (0.003 ± 0.007 mg/K). From the results gathered the mean data obtained were within regulatory permissible levels for seafood by EGASPIN (2018) and World Health Organization.

The results also showed that there was no significant difference ($p>0.05$) in the heavy metals and hydrocarbon concentrations in the sediments and *C. armatum* along the stations. Ecological risk parameters of the heavy metals in the sediment revealed that contamination degree and pollution load index were < 1 indicating no pollution; geoaccumulation index fell into grade 0 unpolluted and, individual potential risks and potential ecological risk index were < 40 and < 150 respectively indicating low ecological risk for both the sediment and crab. Sediment to fauna transfer factor suggested that Zn is the only heavy metal that was bio-magnified in *C. armatum*. Human health risk assessment of the heavy metals in the *C. armatum* were < 1 indicating that there was no obvious health risk for cancer from these heavy metals over a lifetime of exposure.

From the above, it is safe to state that the sediment from Amadi creek pose no ecological risk and the consumption of the crab from the creek by the people pose minimal health risk due to its bio-magnification of Zn.

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