Human health risk assessment of metal contamination through consumption of *Sesarma angolense* and *Macrobrachium macrombrachion* from Benin River, Nigeria

Enuneku, Alex Ajeh¹*, Ezemonye, Lawrence Ikechukwu², Ainerua Martins Oshioriamhe³

¹Department of Animal and Environmental Biology, Faculty of Life Sciences, University of Benin, PMB 1154, Nigeria.
Email: alex.enuneku@uniben.edu

²Ecotoxicology and Environmental Forensic Unit, National Centre for Energy and Environment, Energy Commission of Nigeria, University of Benin, Nigeria.
Email: ezemslaw@yahoo.com

³Department of Animal and Environmental Biology, Faculty of Life Sciences, University of Benin, PMB 1154, Nigeria.
Email: aineruamartins@yahoo.com

ABSTRACT

Human health risk assessment of heavy metal contamination through consumption of shrimps (*Macrobrachium macrombrachion*) and crabs (*Sesarma angolense*) from Benin River (Southern Nigeria) was studied. Assessment of heavy metal concentrations was conducted in surface water, sediment and whole tissues of fauna using Atomic Absorption Spectrophotometer. Mean heavy metal concentrations for Cu, Cd, V, Pb and Ni in surface water were 0.04, 0.01, 0.02, 0.02, 0.06 mg/L while in sediment, concentrations were 0.08, 0.02, 0.04, 0.06, 0.12 mg/kg. Mean bioaccumulation levels of heavy metals in shrimp were 3.43, 1.12, 1.79, 1.30, and 6.17 mg/kg respectively while in crab Cu, Cd, V, Pb and Ni had mean values of 2.26, 0.74, 1.92, 0.86 and 4.05 mg/kg. Target hazard quotients (THQs) for Cu, Cd, V, Pb and Ni in shrimp were 0.272, 0.3520, 0.5626, 0.1135, and 0.0970, and in crab, THQs were 0.0178, 0.2326, 0.6034, 0.0751, 0.0636. The total THQ (TTHQ) which measures the aggregated risk due to heavy metal uptake via the ingestion of *M. macrombrachion* and *S. angolense* were 1.1521 and 0.9925 respectively. TTHQ values in *M. macrombrachion* were greater than 1, indicating risk to human health from consumption of *M. macrombrachion*. TTHQ in *S. angolense* was less than unity, suggesting that the consumption of the crab is unlikely to cause any adverse health effects to consumers.

Keywords: Shrimp; Crab; Hazard; Aquatic; Bioaccumulation
1.0 INTRODUCTION
Heavy metal pollution is a worldwide environmental problem (Wang et al. (2010). Aquatic systems may be contaminated with heavy metals released from industrial and agricultural activities (Ezemonye and Enuneku 2012). Heavy metals are easily transported and accumulated in the environment. They arrive in aquatic ecosystem as dissolved and solid wastes from domestic, industrial and agricultural run offs. (Megateli (2009). Rivers are used as a source of drinking water for humans and considered as a sink for waste. Undoubtedly, a riverine aquatic environment suffers the consequences of domestic and industrial activities occurring in its watershed (Taweel et al., 2013). In Nigeria, environmental management practices are inefficient due to poor infrastructure and lack of environmental protection awareness (Ihedioha and Okoye 2012).

In the aquatic environment, heavy metals are easily taken up by aquatic organisms where they are strongly bound with sulfhydryl groups of proteins and accumulate in their tissues. The accumulation of heavy metals in the tissues of organisms can result in chronic illness and cause potential damage to the population (Amirah et al., 2013). Heavy metal intake by aquatic organisms in a polluted aquatic environment is dependent on ecological requirements, metabolism and other factors such as salinity, water pollution level, food and sediment. All heavy metals are potentially harmful to most organisms at some level of exposure and absorption (Yilmaz, 2003).

Human exposure to toxic metals has become a major health risk (Yabe et al. 2013). Seafood consumption has been reported as an important route of human exposure to a variety of chemical contaminants (Usero et al. 2003). Heavy metals deserve special attention as they represent a group of highly toxic substances accumulating in the tissues of aquatic organisms and being conveyed through the food chain to human. Several methods have been proposed for the assessment of the potential health risks from chemical exposure. Current non-cancer risk assessment methods are typically based on the use of target hazard quotient (THQ). THQ is a ratio between the estimated dose of a contaminant and the reference dose below which there will not be any appreciable risk (US EPA 2000). If the ratio is greater than 1, there may be concern for potential health. This method of risk estimation has been used by Wang et al., (2005) and Amirah et al., (2013) and has been shown to be valid and useful.

2.0 MATERIALS AND METHODS
2.1 Study site
The study area was selected due to rapid growth and development. It comprises residential, commercial, oil and gas industry, small and medium enterprises (SME) industry and logging.

The Benin River (figure 1) is located in the coastal belt of Southern Nigeria at the Western boundary of the upper Delta and the lowlands. This River drains the major rivers Ethiope, Ossiamo, Osse and Siluko into the Atlantic Ocean. It is approximately 93 km long with average width of 3.0 and 1.4 km in its downstream and upstream section, respectively. It is an important channel for small ships and other watercrafts like speed boat, yacht and canoe. Three distinct longitudinal zones can be recognized in this river; the upper freshwater zone, the middle transitional zone with salinity fluctuations and the lower coastal zone which is predominately saline. The predominant vegetations at the shed include Pandanus candelabrum; Elaeis guineensis; Nymphaea lotus; Salvinianymphellula; Echinochloapyramidalis; Pistiastratiotes; Azolla africana.

Samples of water for characterization of heavy metal concentrations were obtained from three stations designated along stretch of Benin River at Koko town, north central part of Delta State (Latitudes 05°59′43.6″ – 05°59′35.7″N; Longitude 005°28′06.7″- 005°25′56.2″E). Samples of M. macrobrachion were
collected within these designated stations. Along this stretch is located bitumen blending plant belonging to Total Nig. Ltd, facilities of Optima petroleum company and watercraft maintenance workshop.

2.2 Field sampling
The sampling period spanned from January, 2013 to June, 2013. Water samples for heavy metal determination were collected in acid washed polyethylene bottles at three different locations within the sampled stretch. The bottles were rinsed thoroughly with deionised water after washing with dilute nitric acid (HNO₃). In the field the bottles were rinsed several times with the river water and 1 litre sample was then collected at about 50 cm below the water surface. The water samples were acidified with concentrated nitric acid for preservation.

Samples of sediment for characterization of heavy metal concentrations were obtained by the aid of Eckmans grab.

Specimens of *M. macrobrachion* were collected at low tide regime using woven cylindrical traps with non-return valve. They were collected from a single fisherman in order to assure regularity in fishing methods. The samples were put in pre-cleaned polythene bags and preserved in ice chest at -4°C and transferred immediately to the laboratory for analysis.

2.3 Sample preparation and metal analysis
In the laboratory prior to drying in an oven at 105°C, weights of *M. macrobrachium* and *S. angolense* samples were measured with the aid of electronic balance. Two grams of dried homogenised sample of each tissue was digested in 15 ml hydrochloric acid, 5ml nitric acid, and 5ml perchloric acid (3:1:1) solution and heated in a digester until brown fumes were expelled, tissues dissolved completely and a colourless solution obtained. The flask and its contents were allowed to cool and thereafter the digested sample was made up to 50ml with distilled water (Raghuramulu et al. 2003). Surface water, sediment, crab and fish samples were analysed for Cu, Cd, V, Pb and Ni using Atomic Absorption Spectrometry PG 550.

2.4 Quality control analysis
The equipment (AAS) was first calibrated using certified reference standard (SRM 1570) of the National Institute of Standards and Technology for the respective heavy metals to obtain calibration curve with the equation $R^2=99.7$. Reagent blank was run at intervals of every five samples analysis to eliminate equipment drift. All samples were analyzed in duplicates for reproducibility accurate checks and precision.

2.5 Target Hazard Quotient
The method for the determination of THQ was provided in the United States EPA Region III Risk based concentration table (US EPA 1989). The dose calculations were carried out using standard assumptions from an integrated United States EPA risk analysis.

Assumptions for the health risk calculations are:

1. Ingested dose is equal to the absorbed pollutant dose (USEPA 1989).
2. Cooking has no effect on the pollutants (Cooper *et al.*, 1991).
3. The average body weight of a Nigerian is assumed to be 70 kg
4. Average lifetime of a Nigerian is 52 years.

THQ is determined by the following equation

$$THQ = \frac{Efr \times EDTot \times FIR \times C}{RFDo \times BWa \times ATn} \times 10^{-3}$$

Where EFr is exposure frequency (365 days/year); EDTot is the exposure duration 52 years, average lifetime); FIR is the food ingestion rate (g/day); C is the heavy metal concentration in crab/shrimp (µg/g);
RfDo is the oral reference dose (mg/kg/day). BWa is the average adult body weight (70 kg) and ATn is the averaging exposure time for non-carcinogens (365 days/year × number of exposure years assuming 52 years).

Since exposure to two or more pollutants may result in additive and/or interactive effects, total THQ in this study is treated as the arithmetic sum of the individual metal THQ values, derived by the method of Chien et al. (2002).

2.6 Statistical Analysis
Inter station comparisons were carried out to test for significant differences in the concentration of the heavy metals in the sediment samples using parametric analysis of variance (ANOVA). If significant value (P<0.05) were obtained in the ANOVA, Duncan multiple range test was performed to determine the location of significant differences.

3.0 RESULTS

Various heavy metals characterized in the surface water samples are summarized in table 1. With the exception of Cd and Pb, the concentrations of the heavy metals showed no significant difference (p>0.05) among the three designated stations water samples were collected. At average, the concentrations of heavy metal in the surface water samples were Cu: 0.04 mg/l; Cd: 0.01 mg/l; V: 0.02 mg/l; Pb: 0.02 mg/l and Ni: 0.06 mg/l. Furthermore the concentrations of these heavy metals followed the decreasing order of Ni > Cu > Pb = V > Cd (fig. 2).

Spatial variation in heavy metal concentrations of sediment samples is shown in table 2. Recorded concentrations of most analyzed elements were far below the lower limit of FEPA standards. Except for Cd and Ni, other heavy metal concentrations differed insignificantly (p>0.05) among the stations. Cadmium was the least accumulated heavy metal at stations 1 and 3 with average concentrations of 0.00 and 0.03 mg/kg respectively. Across the stations, Nickel was the most accumulated metal with an average concentration of 0.11, 0.11 and 0.14 mg/kg at stations 1, 2 and 3 respectively.

Mean heavy metal concentrations in the sediment samples obtained from the three designated stations of Benin River are shown in figure 3.

Table 3 shows the summary of the various heavy metals concentrations in the whole tissue of *M. macrobrachion*. From the table it can be observed that iron and cadmium respectively were the most and least accumulated of heavy metals in the whole tissue of *M. macrobrachion*.

The heavy metal concentrations in the whole tissue of crab obtained from sampled area is as summarized in table 4. The trend of the metals accumulation was Fe> Zn>Mn> Ni> Cr> Cu>Pb> Cd (Table 4).

The oral reference doses for the heavy metals and the target hazard quotients (THQs) of studied metals through the consumption of shrimps and crabs for residents are shown in table 5.

4.0 DISCUSSION
Various analysed heavy metals were bioaccumulated in the whole tissue of *M. macrobrachion*. The order of the magnitude of these heavy metals in the whole tissue of *M. macrobrachion* and *S. angolense* were Ni> Cu>V>Pb> Cd. Cd was the least accumulated heavy metal in both *M. macrobrachion* and *S. angolense*.

The range of concentrations of Cu (1.05-4.19 mg/kg) in crab and (2.18-4.91 mg/kg) in shrimp recorded in this study is lower than that (860-1620 mg/kg) reported by Anetekha et al. (2007) in a related species *M. vollenhovenii* in Ologe Lagoon, Lagos, Nigeria.

This difference might be due to greater metal load in Ologe Lagoon because of the presence of Agbara Industrial Estate, which discharges its waste into the lagoon (Kusemijuet et al., 2001).
Furthermore the ranges of concentrations of Cd (0.34-1.37) and Pb (0.40-1.59) for crab; and Cd (0.71-1.60 mg/kg) and Pb (0.82-1.86 mg/kg) for shrimp recorded in this study were high when compared to Cd (0.01 – 0.08 mg/kg) and Pb (0.03 - 0.06 mg/kg) documented by Omoigberale and Ikponmwosa-Eweka (2010). These differences are attributable to the prevailing anthropogenic activities going on at these aquatic ecosystems which differed spatially although within the same ecozone. These differences can also be attributed to the chemical composition of bedrock of these rivers. The high Lead concentration in the tissue of this shrimp as recorded in this study may have resulted from wastes generated by industries on its watershed and activities of motorized water craft which dominate the means of transportation therein. Edema and Egborge (1999) documented a similar result in the tissue of *Macrobrachium vollenhovenii* from Warri River (an aquatic ecosystem with similar anthropogenic activities as in Benin River).

Rantetampang and Mallongi (2013) reported that lead concentrations in water column, sediment, bivalve, pelagic and benthic fishes of Santani Lake, Papua, Indonesia ranged from 0.13 to 1.87 mg/l, 1.24 to 3.84 mg/kg dw, 0.43 to 2.76 mg/kg ww, 0.27 to 2.78 mg/kg ww and 1.39 to 3.55 mg/kg ww respectively. The relatively high levels of Cu in *M. macrobrachion* and *S. angolense* can be attributed partly to its function in the respiratory pigment haemocyanin (Van den Broek, 1979) and metalloenzymes (De Silva and Anderson, 1995). Aquatic organisms are known to be selective in metal accumulation due to toxicity effects. According to Hopkin (1989), Decapods regulate their net assimilation of metals, which require 0.07 mg/kg of Zn and 0.08 mg/kg of Cu to activate the enzymes and respiratory proteins.

Levels of heavy metals in aquatic biota are of particular interest because of the potential risk to humans who consume them. Concentrations of Pb and Cd are of health importance in this study. The concentration of these metals in the crab exceeded the FAO/WHO permissible limit for items to be consumed by man (Table 4).

The effects of heavy metals in the environment depend to a large extent on whether they occur in forms that can be taken up by plants or animals. Crabs are bottom feeders and are generally expected to concentrate more metals than surface feeders like prawn which is in agreement with earlier reports. The results obtained in this study showed that Sesarmid crab *S. angolense* accumulated in varied concentrations the various metals analyzed. Cd and Pb concentrations in the tissue of this crab species is of concern because *Sesarma angolense* is both a source of income and nutrition for populations within and outside this area. Consumption of food contaminated by these metals can serve as main source of heavy metal intake in people not occupationally exposed. *Sesarma angolense* from Benin River in Southern Nigeria is unsafe for consumption. This calls for an urgent action against any activity that brings about the release of Pb and Cd into this environment.

The THQ values for shrimp and crab were both in the order V>Cd>Pb>Ni>Cu. The highest THQ values were for Vanadium with the values 0.6034 and 0.5626 for crab and shrimp respectively. The least THQ values were for Cu with values 0.0270 and 0.0178 for shrimp and crab respectively. Vanadium was the major risk contributor while Cu was the least for both organisms studied. The THQ of each metal studied from this research is less than 1 which shows that people will not experience significant health risk from the consumption of individual metals through contaminated shrimp or crab from the river.

**CONCLUSION**

The shrimp (*M. macrobrachion*) and crab (*S. angolense*) bioaccumulated heavy metals. Ni had the highest mean bioaccumulation of 6.17 and 4.05 mg/kg in the shrimp and crab respectively for the stations studied. Cd was the least accumulated heavy metal in both *M. macrobrachion* and *S. angolense*.

THQ of each metal studied from this research is less than 1 which shows that people will not experience significant health risk from the consumption of individual metals through contaminated shrimp or crab from
the river. However, results from the study showed that TTHQ values in *M. macrobrachion* were greater than 1, indicating risk to human health from consumption of *M. macrobrachion*. TTHQ in *S. angolense* was less than unity, suggesting that the consumption of the crab by residents is unlikely to cause any adverse health effects to consumers.

REFERENCES


FIGURES AND TABLES

Figure 1: Map showing Sampled Stations
Table 1: Spatial variation in heavy metal concentrations of surface water samples.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Station 1</th>
<th>Station 2</th>
<th>Station 3</th>
<th>Average</th>
<th>FEPA Permissible Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.03±0.01</td>
<td>0.04±0.01</td>
<td>0.04±0.01</td>
<td>0.04±0.01</td>
<td>0.10</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.00±0.00*</td>
<td>0.02±0.00</td>
<td>0.01±0.01</td>
<td>0.01±0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.02±0.00</td>
<td>0.02±0.01</td>
<td>0.02±0.01</td>
<td>0.02±0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Lead</td>
<td>0.00±0.00*</td>
<td>0.03±0.01</td>
<td>0.03±0.01</td>
<td>0.02±0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.05±0.01</td>
<td>0.06±0.02</td>
<td>0.07±0.02</td>
<td>0.06±0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Heavy metal concentrations in the water were measured in mg/l; (*) - Significantly different (p<0.05).

Figure 2: Mean heavy metal concentrations in the surface water samples from the three designated stations in Benin River.

Table 2: Spatial variation in heavy metal concentrations of sediment samples.

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>STATION 1</th>
<th>STATION 2</th>
<th>STATION 3</th>
<th>p-Value</th>
<th>Average</th>
<th>FEPA Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.06±0.01</td>
<td>0.08±0.01</td>
<td>0.08±0.02</td>
<td>p&gt;0.05</td>
<td>0.08±0.02</td>
<td>36-190</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.00±0.00*</td>
<td>0.03±0.00</td>
<td>0.03±0.01</td>
<td>P&lt;0.01</td>
<td>0.02±0.02</td>
<td>0.8-12</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.04±0.01</td>
<td>0.04±0.00</td>
<td>0.04±0.01</td>
<td>p&gt;0.05</td>
<td>0.04±0.01</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>0.05±0.01</td>
<td>0.06±0.00</td>
<td>0.06±0.01</td>
<td>p&gt;0.05</td>
<td>0.06±0.01</td>
<td>85-530</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.11±0.01</td>
<td>0.11±0.01</td>
<td>0.14±0.03</td>
<td>p&lt;0.05</td>
<td>0.12±0.02</td>
<td>35-210</td>
</tr>
</tbody>
</table>
Figure 3: Mean heavy metal concentrations in sediment samples from the three designated stations in Benin River.

Table 3: Heavy metal concentrations in the whole tissue of *M. macrobrachion*.

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Bioaccumulation</th>
<th>WHO/FAO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{x}$±SD</td>
<td>Min- Max</td>
</tr>
<tr>
<td>Cu</td>
<td>3.43±1.07</td>
<td>2.18-4.91</td>
</tr>
<tr>
<td>Cd</td>
<td>1.12±0.35</td>
<td>0.71-1.60</td>
</tr>
<tr>
<td>V</td>
<td>1.79±0.56</td>
<td>1.13-2.55</td>
</tr>
<tr>
<td>Pb</td>
<td>1.30±0.41</td>
<td>0.82-1.86</td>
</tr>
<tr>
<td>Ni</td>
<td>6.17±1.92</td>
<td>3.91-8.81</td>
</tr>
</tbody>
</table>

Mean heavy metal concentrations in *M. macrobrachion* were measured in mg/kg.

Table 5: THQs of the studied heavy metals in shrimp and crab

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in shrimp</th>
<th>Concentration in crab</th>
<th>RfDo</th>
<th>THQ (Shrimp)</th>
<th>THQ (Crab)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3.43</td>
<td>2.26</td>
<td>0.04</td>
<td>0.0270</td>
<td>0.0178</td>
</tr>
<tr>
<td>Cd</td>
<td>1.12</td>
<td>0.74</td>
<td>0.001</td>
<td>0.3520</td>
<td>0.2326</td>
</tr>
<tr>
<td>V</td>
<td>1.79</td>
<td>1.92</td>
<td>0.001</td>
<td>0.5626</td>
<td>0.6034</td>
</tr>
<tr>
<td>Pb</td>
<td>1.30</td>
<td>0.86</td>
<td>0.0036</td>
<td>0.1135</td>
<td>0.0751</td>
</tr>
<tr>
<td>Ni</td>
<td>6.17</td>
<td>4.05</td>
<td>0.02</td>
<td>0.0970</td>
<td>0.0636</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TTHQ</th>
<th>1.1521</th>
<th>0.9925</th>
</tr>
</thead>
</table>
Table 4: Heavy metal concentrations in the whole tissue of *S. angolense*.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.26±1.15</td>
<td>1.05-4.19</td>
<td>30</td>
</tr>
<tr>
<td>Cd</td>
<td>0.74±0.38</td>
<td>0.34-1.37</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>1.92±0.98</td>
<td>0.89-3.56</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>0.86±0.44</td>
<td>0.40-1.59</td>
<td>0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>4.05±2.07</td>
<td>1.88-7.52</td>
<td>-</td>
</tr>
</tbody>
</table>

Mean heavy metal concentrations in *Sesarma angolense* were measured in mg/kg.