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Assessment of Bioaccumulation Tendency of Heavy Metals in Crab and Prawn from Esierebom Beach, Calabar South Local Government Area, Cross River State Nigeria.

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Abstract
The present study is focused on the assessment of the level of bioaccumulation tendency of heavy metals in Crab (Brachyura) and Prawn (Panaeus monodon) from Esierebom Beach in Calabar South Local Government Area, Cross River State. The physico-chemical parameters of water were found to be as follows: pH (6.34); Dissolve oxygen (1.92); Conductivity (0.1µs/cm) and Temperature (26.85^{o}c). The moisture content of Prawn and Crab were found to be 38.00% and 56.00% respectively. Atomic Absorption Spectrophotometer was used to analyse the level of bioaccumulation of selected heavy metals. The result showed that the concentration of heavy metals varies thus; Zn > Cu > Fe > Pb > Co > Cr > Mn > Hg > As > Cd in Crab; Prawn; Fe > Cu > Zn > Cr > Co > Pb > Mn > Hg > As > Cd and in water; Zn > Fe > Pb > Cu > Mn > Cr > Co > As > Hg > Cd respectively. No significant difference was found between the concentration of As and Hg but Pb was found to be significantly higher than the WHO acceptable limit of intake. This study revealed that Crab shows a higher bioaccumulation tendency compared to prawn. The presence of higher Pb concentration can pose serious hazard to the organism and the environment. This is attributed to the high anthropogenic activities in the area under study.

Keywords: Assessment, Bioaccumulation, Crab, Esierebom Beach, Heavy metals, Prawn

INTRODUCTION
Heavy metals naturally occur in aquatic environment in very low concentration, but their concentration can increase due to incursion of anthropogenic pollutants over time (Kargin *et al.,* 2001). Industrial, agricultural, and mining activities create a potential source of heavy metals pollution in aquatic environment. Pollution of aquatic ecosystems by heavy metals is of utmost concern to the environment as it constitutes most dangerous toxicants that can bioaccumulate (Benson *et al.* 2007). Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage also posing a threat to human health due to biomagnifications over time (Yilmaz and Yilmaz, 2007). Aquatic organisms have been reported to accumulate heavy metals in their tissues several times above ambient levels (Canli and Atli, 2003). In Nigeria, over 80% of the industries discharge their waste containing toxic metals such as Cd, Cu, Zn, Hg, and Cr into the environment

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without any prior treatment (Sobvha *et al.*, 2007). While just only 18% of industries undertake rudimentary recycling prior to disposal. These pollutants including agricultural wastes find their way into the water bodies through runoff (Cempel and Nekel, 2006). The problem is further amplified when rivers carry their pollutant to estuaries and finally to oceans, while during the transition from the terrestrial to the ocean harmful substances enter into the food chain and subsequently become bioaccumulated in marine organisms (Schmitt *et al.*, 2006).

This research work was designed to assess the bioaccumulation tendency of heavy metals in two main marine organisms; Crab and Prawn from Esierbom Beach of Calabar South Local Government Area with the view of ascertaining the bioaccumulation tendency of the two organisms.

Study Area

The study area was Esierebom Beach (Esuk Nsidung) located in Calabar South Local Government Area of Cross River State, Nigeria which is between longitude 8^0, 20′ 30.124′′E, and latitude 4^0, 58′ to 32.578′′N and has a surface area of about 264km. Esuk Nsidung is where large quantity of assorted fishes and bags of crayfish are sold in wholesale to retailers. These goods are brought from the Bakassi Peninsula and other fishing settlements along the shores of Atlantic Ocean. The prevalent activities within the area include timber logging, fishing, and sand mining. Surrounding this beach also is a jetty, the Export Processing Zone (EPZ) and other industrial activities like the sales of petroleum products.

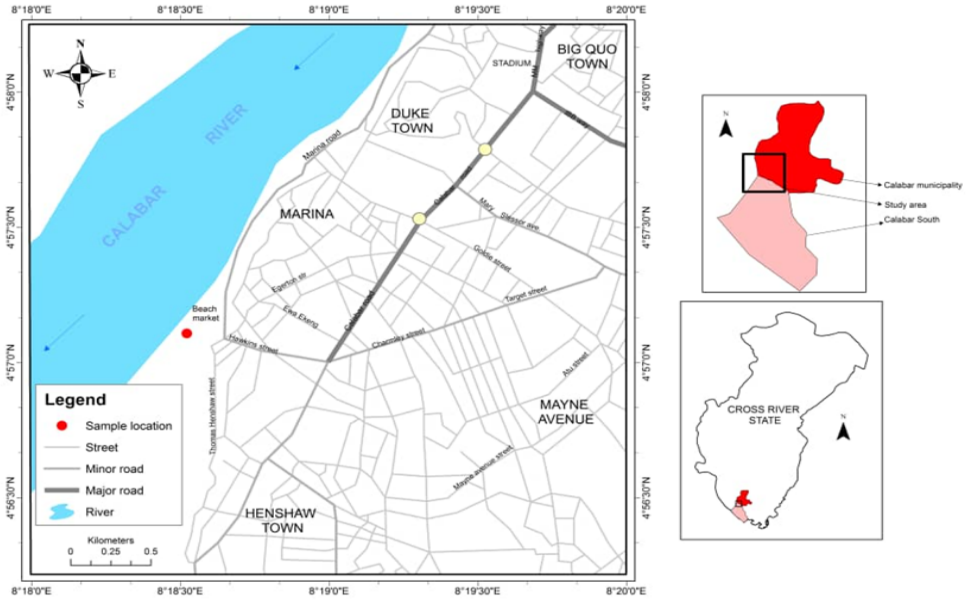

Fig 1: Map showing Esierebom Beach (Esuk Nsidung) Calabar.

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MATERIALS AND METHOD

Sample Collection and Preparation:

Prawn (*Panaeus monodon*) and crab (*Brachyura*) were collected from Esierebom Beach, stored in a container with ice. Water from which the crab and prawn were collected was also sampled and brought to the laboratory. The crab and prawn were weighted using electronic weighing balance (model 6354). The samples were oven dried and preserved in sample bottles for analysis.

Determination of some physicochemical properties of water

- Temperature and pH: Temperature and pH of water sample were determined *insitu* using Temperature and pH meter. The pH meter was calibrated with a buffer at pH = 6.9, the probs was then rinsed with distilled water before use to determine the pH and temperature of water sample.
- Dissolve oxygen (DO): Dissolved oxygen meter (model OX 197) was used to determine dissolve oxygen and salinity present in the water sample. The probe was rinsed with distilled water and immersed into the sample and the dissolved oxygen meter was pressed which automatically read the dissolved oxygen concentration in the water sample.
- Conductivity: Conductivity meter (Blank H, 8733) was used to determine the amount of dissolved salt present in the water sample.

Digestion of Sample

1g of the powdered sample (prawn and crab) were taken in different conical flask, 5ml of HNO_3 was added to each sample and the mixture was kept overnight at ambient temperature. Then 5.0ml of perchloric acid ($HCLO_4$) was added to the mixture and was heated in a digester with gradual increase in temperature starting from 50^oC-250^OC. Appearance of white fumes indicated complete digestion. The mixture was cooled, filtered and the contents of the tubes were transferred to 100ml volumetric flasks and made up to the mark with de-ionize water. The wet digested solution was transferred to bottles and stored for analysis.

Analysis of digested sample

Analysis of samples was carried out using Atomic Absorption Spectrophometer (GC system 7890A, MS Agilent 5974C Series) to detect the presence of Zn, Cu, Fe, Mn, Cr, Cd, Co, Pb, As and Hg. All determinations were carried out in triplicate.

RESULTS

Table 1: Physiochemical analysis of water and moisture content of prawn and Crab

	pH	DO	Conductivity (μS/cm)	Temperature (^{0}C)	Moisture content
Water sample	6.34	1.91	0.11	26.85	
Prawn					30.00%
Crab					56.00%

Table 2: Concentration of heavy metals in crab, prawn and water

S/N	Element	Crab (mg/kg)	Prawn (mg/kg)	Water (mg/L)	WHO standard Limit (mg/L)
1.	Zn	4.0452±0.0049	0.8442±0.0959	0.442±0.100	3.0
2.	Cu	1.4083±0.0585	1.0332±0.0158	0.033±0.001	2.0
3.	Fe	1.0318±0.0099	1.9811±0.0585	0.381±0.054	3.0
4.	Mn	0.0359±0.0095	0.0201±0.0101	0.020±0.003	0.4
5.	Cr	0.1366±0.0095	0.1121±0.0049	0.012±0.005	0.05
6.	Cd	0.0013±0.0002	0.0009±0.0001	0.00017±0.00055	0.003
7.	Co	0.2409±0.0057	0.1017±0.0004	0.003±0.001	NA
8.	Pb	0.811±0.0493	0.0711±0.0052	0.038±0.009	0.001
9.	As	0.0030±0.0005	0.0028±0.0005	0.00072±0.00005	0.001
10	Hg	0.0031±0.0005	0.0076±0.0009	0.00019±0.00052	0.001

Data are: Mean ± Standard Deviation of triplicate determination

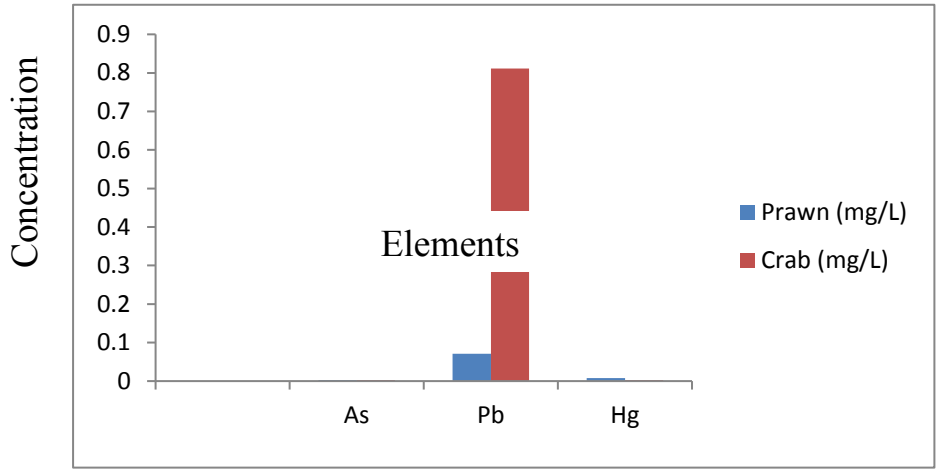

Figure 2: Bar chart showing concentration of toxic heavy metals

Discussions

From result shown in table 2, heavy metal concentration in water, Prawn and Crab decreasing in the following order: Zn > Fe > Pb > Cu > Mn > Cr > Co > As > Hg>Cd; Fe > Cu > Zn > Cr > Co > Pb > Mn > Hg > As > Cd and Zn > Cu > Fe > Pb > Co > Cr > Mn > Hg > As > Cd, respectively. In this study, Zn in crab (*Brachyura*) has concentration which is higher than that of prawn (*Penaeus monodon*), indicating that Zn in crab has higher bioaccumulation tendency compared to prawn. The concentration of Zn in water sample lower compared to that of both prawn and crab due to the bioaccumulation tendency of both crab and prawn. However, the concentration of Zn in crab is greater than the permissible limit of WHO 2001. Uwa *et al.* (2018), in their studies reported that Zn has 1.01mg/L in crab which is lower compare to its concentration in the present study.

The concentration of Cu in Crab and Prawn was greater than that of water showing that crab and prawn has bioaccumulation tendency in them. However, the concentrations of Cu in crab, prawn and water samples are less than the standard limit of WHO (< 2.0mg/kg). Wei Peng Lee *et al.* (2014) reported that Cu in prawn head, flesh and shell are 28.884mg/kg, showing greater concentration than that of the present study. The level of Fe in prawn was found to be of higher concentration than that of crab. Both prawn and crab has lower concentration of Fe which are below WHO permissible limit of intake (3.0mg/kg).

The permissible limit of Manganese (Mn) 0.05mg/kg is higher than the concentration in crab and prawn samples. Mn concentration in crab was higher than that of prawn. This depicts the fact that crab bioaccumulates Mn more than prawn. Chromium (Cr) has higher concentration in crab and prawn compared to its concentration in water sample indicating that both organisms have almost equal bioaccumulation tendency of Cr. The WHO permissible limit of intake for Manganese (Mn) was higher than its concentration in the present study.

Cadmium (Cd), Cobalt (Co) and Lead (Pb) concentrations in crab were higher than the concentration in prawn, indicating that crab has greater bioaccumulation tendency than prawn in the present study. Uwa *et al.* (2018) reported that there is no significance difference between the concentration of iron (Fe) and lead (Pb), while in the present study, there is significant difference between Fe and Pb concentrations in the same study location. The concentration of Cd was below the WHO permissible limit of intake. The high concentration

of Pb in the present study is similar to the result (1,1616mg/g) reported for the mean concentration of this heavy metal in sediment samples in the Calabar River (Edodi et al, 2019). This is higher than the WHO permissible limit of intake. Arsenic (As) concentration in crab was higher than that of Prawn. While mercury (Hg) concentration in crab shows lower concentration than in prawn showing a higher bioaccumulation tendency of As in crab and Hg in prawn. The concentration of As and Hg is lower than the WHO permissible limit of intake.

Conflict of interest

There is no conflict of interest.

CONCLUSION

The concentration of the metals with high toxicity such as Pb, As and Hg showed results higher than the accepted limited by WHO which depicts a high health risk in these organisms related to the environment under analysis. We therefore recommend that companies around the EPZ, Harbour and the petroleum jetty must treat their waste before disposal into the environment.

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