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BIOACCUMULATION OF HEAVY METALS IN SHELLFISH FROM SELECTED RIVERS OF RIVERS STATE, NIGERIA

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Abstract

The accumulation of three heavy metals; chromium (Cr), cadmium (Cd) and lead (Pb) in; *Goniopsis cruentata* (crab), *Palaemon hastatus* (crayfish), *Crassostrea gasar* (oyster), *Tympanotonus fuscatus* (periwinkle) and *Penacus indicus* (prawn) was studied. The water, sediment and shellfish samples were processed and analyzed for heavy metals with Atomic absorption spectrometer (AAS Model FS 240 Varian). 5gram of the collected sample (shellfish) was digested in 250ml conical flask by adding 30ml of aqua regia and heated on a hot plate until volume remained about 7-12ml. The digest was filtered using What-man filter paper and the volume made up to the mark in a 100 ml volumetric flask, and was then stored in a plastic container analysis. The results shows that the heavy metal content of sampled shellfish was in the order: *Tympanotonus fuscatus* > *Palaemon hastatus)* > *Goniopsis cruentata* > *Crassostrea gasar* > *Penacus indicus* in Andoni and *Tympanotonus fuscatus* > *Palaemon hastatus* > *Goniopsis cruentata* in Kono river. In Sama river, the cadmium, chromium and lead content of periwinkle were (0.89±0.01), (1.06±0.01) and (1.05±0.00) respectively while Choba crab content (7.35±0.07), (2.25±0.07) and (31.85±0.07) respectively. In Andoni, periwinkle had the highest bio concentration factor (BCF) of 49.17 for cadmium while prawn (0.17) had the least value. *Penacus indicus* (13.5) had the highest lead content while periwinkle had the least lead value. In Kono and Sama rivers, periwinkle also had the highest cadmium content of 48.3mg/l and 8.3mg/l respectively. All the sampled shellfish were found not to be bioaccumulative in all the sampled stations with their BCF < 1000. The sampled shell-fish in Andoni all rated as micro and macroconcentrator with (BSAF>1>2) except prawn which rated as a deconcentrators(BAF<1) with a value of 0.5. The sampled shell fishes in Kono all rated as micro and macroconcentrator with (BSAF>1>2) except Crayfish which rated as a deconcentrators(BAF<1) with a value of 0.21, the sampled shellfish in Sama and Choba were rated as macroconcentrator with (BSAF>2). However, the observed heavy metals concentrations of oyster, prawn and crab were below the recommended limits for human consumption. Consumption of shellfishes with high level of heavy metal contamination can be a serious health hazard. Therefore, this study suggests a regular environmental surveillance of this water bodies in order to achieve contaminant-free shellfish for safe human health.

Key word: Bioaccumulation, Heavy Metals, Water, Sediment, Shellfish

1.0 INTRODUCTION

There are various sources of heavy metals in the surface water ecosystem such as draining of sewage, dumping of domestic wastes, industrial activities and recreational activities. Surface water pollution may also occur in small amounts naturally through the leaching of rocks, airborne dust, forest fires and vegetation (Özmen , Külahçı , Çukurovalı , Doğru 2004)

Fish is considered as one of the most significant indicators of metal pollution in aquatic environment (Rashed,2001). Fish may absorb dissolved elements and heavy metals from surrounding water and sediment. When fish are exposed to heavy metals, they tend to take these metals up which may accumulate in the tissues eliciting toxicological effects. Some edible fish species such as shellfish have been widely investigated for these hazardous effects of heavy metals on human health. Shellfish refers to exoskeleton-bearing aquatic invertebrates used as food sources by humans. it is considered as one of the major indicators of metal pollution in aquatic environment**.**

Heavy metals could be found in water at the trace levels; nonetheless, these constituents are very toxic and tend to accumulate over a long period of time.

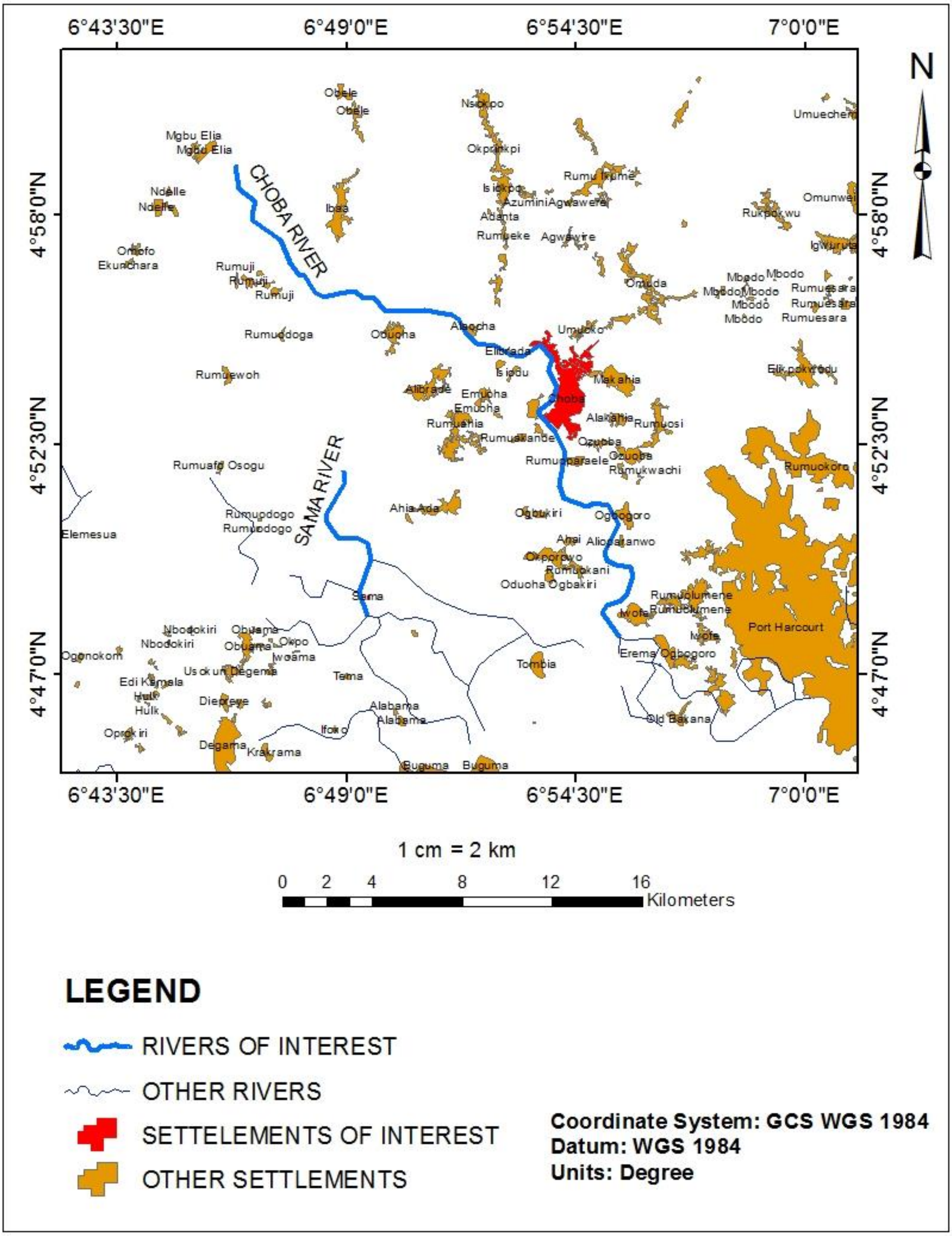
Heavy metals are non-biodegradable and once discharged into water bodies, they can either be adsorbed on sediment particles or accumulated in aquatic organisms. Heavy metals such as Pb, Cd and Cr are micro-pollutants and of special interest as they have both health and environmental significance due to their persistence, high toxic and bio-accumulation characteristics in water (WHO 2008). Heavy metals in human body can affect his health, hence the need to know the concentration of heavy metals in water, sediment and selected fishes in selected rivers in Rivers state, because of its daily usage by man.

MATERIALS AND METHODS

Study Area

This study was carried out in four rivers of : Andoni River in Andoni LGA, Kono River in Khana LGA, Sama River in Asaritoru LGA and Choba water side in Obiakpor LGA all in Rivers State, Nigeria. Rivers State lies between latitudes N 4^o 51’29 and longitudes E 6^o 55’15. It is one of the 36 states of Nigeria. According to census data released in 2006, the state has a population of 5,198,716, making it the sixth most populous state in the country. Its capital and largest city, Port Harcourt is economically significant as the centre of Nigeria’s oil industry. Rivers State is bounded on the South by the Atlantic Ocean, to the North by Imo, Abia and Anambra State, to the East by Akwa Ibom State and to the West by Bayelsa and Delta States. It is a home of many ethnic groups: Ikwere, Ijaw, Obolo and other ethnic groups.

GPS COODINATES OF SAMPLING POINTS			
	Latitude	**Longitude**	**Elevation**
Andoni River, Andoni LGA, Rivers State	N4^o 34 167	E7^o 22 04	-13.0m
Kono River, khana LGA, Rivers State	N4^o 35 733	E7^o 30 912	8.0m
Sama River, Asaritoru LGA, Rivers State	N4^o 49 513	E6^o 49 918	1.0m
Choba waterside, Obiakpor LGA, Rivers State	N4^o 53 314	E6^o 53 891	6.0m



Sample Collection

A reconnaissance survey was performed to have first-hand information about the study area and to establish the sampling points. A Global Positioning System was used to establish

Coordinates and elevation of sampling points. Water, sediment and shellfish samples crab (*Goniopsis cruentata)*, crayfish (*Palaemon hastatus)*, oyster (*Crassostrea gasar)*, perinwinkle (*Tympanotonus fuscatus)* and prawn (*Penacus indicus*) were collected from four different rivers of Andoni, Sama, Kono and Choba rivers respectively. Water and sediment samples were collected at 0.5m below the surface. Precleaned sterile 10L glass bottles were used to collect water samples. Sediments were collected using a grab. While shellfish were obtained with the help of fishermen. Samples were preserved in an ice pack during transportation to laboratory. The water samples were filtered through a 47mm glass fiber filters (Whatman GF/F, 0.7 um pore sizes) precombusted at 450^{0}C for 4 h beforehand. Then, the GF/F filters were stored at −20^{0}C until analysis.

Shellfish Digestion for Heavy Metal Analysis (Wet Digestion Method)

5grams of sample was digested in 250ml conical flask by adding 30ml of aqua regia and heated on a hot plate until volume remained about 7-12ml. The digest was filtered using What-man filter paper and the volume made up to the mark in a 100 ml volumetric flask, and was then stored in a plastic container for analysis.

Sediment Digestion for Heavy Metal Analysis (Wet Digestion Method)

2.0 gram of sample was digested in 250 ml conical flask by adding 30 ml of aqua regia and heated on a hot plate until volume remains about 7-12ml. The digest was filtered using What-man filter paper and the volume made up to the mark in a 100ml volumetric flask, and was then stored in a plastic container for AAS analysis

Water Digestion for Heavy Metal Analysis

50 ml of water sample was digested in 250 ml conical flask by adding 10 ml of aqua regia (conc. HNO_3, HCl, HF in ratio 3:2:1), and heated on a hot plate until volume remains about 7-12 ml. The digest was filtered using What-man filter paper into a 50 ml volumetric flask and the volume made up to the mark using distilled de-ionized water, and was then stored in a plastic container for AAS analysis

Data analysis

SPSS software version 20 was used to carry out the statistical analysis. A one-way analysis of variance was carried out at $P<0.05$, and Duncan multiple range test statistics was used to determine the source of the observed difference.

Calculation of bioconcentration factor:

Bioconcentration is the result of the direct uptake of a chemical by an organism only from water and the result of such a process is measured by the Bioconcentration Factor (BCF), which represents the ratio of steady state concentration of the respective chemical in the biota (CB) (mass of chemical per kg of organism/dry weight) and the corresponding freely dissolved chemical concentration in the surrounding water (CW) (mass of chemical/l) (Geyer *et al*., 2000):

BCF = CB/CW……………………….Equation 1

Nevertheless, heavy metals do accumulate in marine biota from the sediments also, and this is expressed by the Biota-Sediment Bioaccumulation Factor (BSAF). BSAF is a parameter

describing bioaccumulation of sediment-associated organic compounds or metals into tissues of ecological receptors (Kleinov *et al*., 2008).
The Biota-Sediment Bioaccumulation Factor (BSAF) is calculated using the following equation:

BSAF = CB/CS……………………. Equation 2

Where:

CB is the chemical concentration in the biota (mass of chemical per kg of biota/dry weight),

CS is the concentration in the related sediment (mass of chemical per kg of sediment/dry weight) (Nenciu *et al*., 2014).

RESULTS AND DISSCUSION

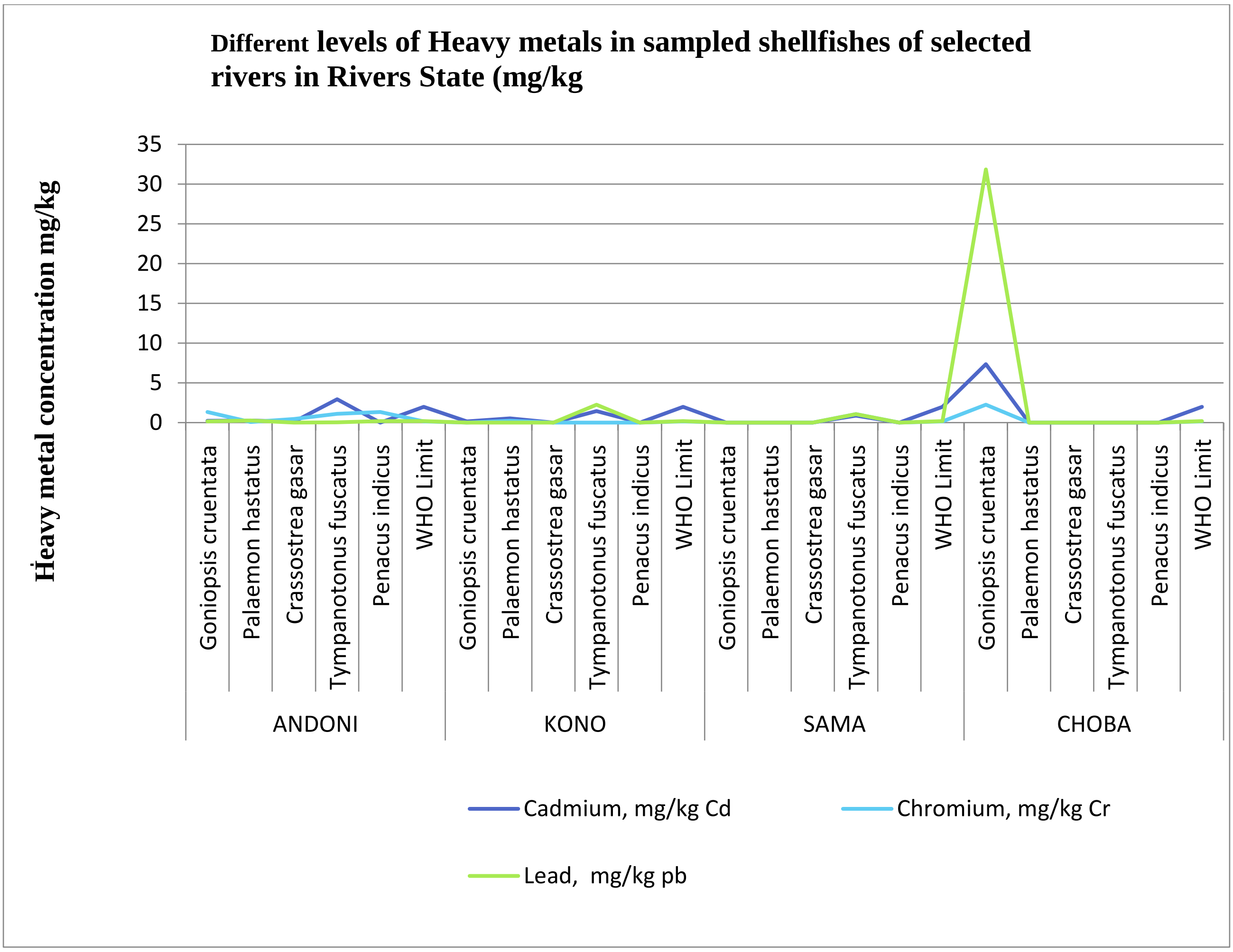


Fig 1 Different levels of Heavy metals in sampled shellfishes of selected rivers in Rivers State

Concentration of heavy metal in shellfish samples

Figure 1 shows the different levels of heavy metals in the sampled shellfish in four different rivers, there was significant variation in the heavy metal content of the sampled organisms. The shellfish under consideration were not uniformly present in all sampled sites as shown in the chart. In Andoni river cadmium, chromium and lead were detected in all the shell-fish (Crab, Crayfish, Oyster, Periwinkle and Prawn) sampled except in the oyster sample.

In Kono river, cadmium (0.13±0.00) was the only heavy metal detected in crab amongst the three heavy metal examined. the cadmium and chromium content of crayfish ranged between (0.21±0.01 to 0.54±0.01) while the cadmium and lead content of periwinkle ranged between (1.45±0.07 and 2.25±0.07) were detected in periwinkle.

Crab, oyster, crayfish and prawn were not sampled in Sama river, the chromium (1.06±0.01) content of periwinkle was highest when compared with other metals analyzed. In Choba river, periwinkle, crayfish, prawn and oyster were not sampled. The analyzed heavy metals were detected in crab with lead being the highest heavy metal accumulated by the crab.

Table 2: Concentration of Heavy Metals in Sediment Samples.

	Cadmium, mg/kg Cd	**Chromium, mg/kg Cr**	**Lead, mg/kg Pb**
Sema	0.05±0.00[b]	0.28±0.00[d]	0.03±0.00[b]
Kono	0.07±0.00[c]	0.00±0.00[a]	0.00±0.00[a]
Andoni	0.02±0.00[a]	0.04±0.00[b]	0.00±0.00[a]
Chuba	0.12±0.01[d]	0.12±0.00[c]	0.09±0.00[c]

Concentration of heavy metals in sediment samples

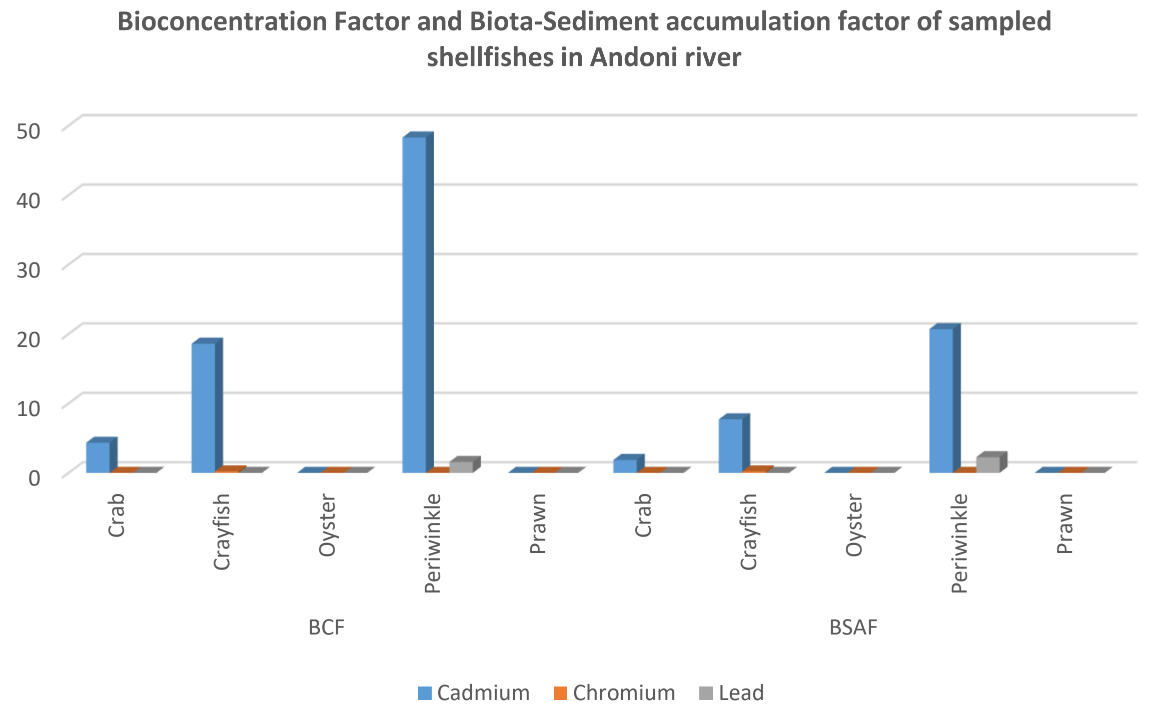
Table 2 above shows the total extractable concentration of heavy metals from sediments in the study area. Cadmium was detected in the four locations, while Cr and Pb were significantly ($p>0.05$) higher in location D (chuba) than in other locations. The chromium content of location A was significantly higher than other locations. The results obtained showed that the sediment samples were lower in heavy metals concentration.

Table 3: Concentration of Heavy Metals in Water Samples.

	Cadmium, mg/l Cd	**Chromium, mg/l Cr**	**Lead, mg/l Pb**
Sema	0.10±0.00[c]	0.01±0.00[c]	1.84±2.12[a]
Kono	0.03±0.00[a]	0.00±0.00[a]	1.44±0.00[a]
Andoni	0.06±0.00[b]	0.00±0.00[b]	0.02±0.00[a]
Chuba	0.24±0.00[d]	0.03±0.00[d]	6.54±0.01[b]
W H O (Mg/l)	2.00	0.05 -0.15	0.1-0.2

Concentration of heavy metals in water samples

Heavy Metal concentrations in water samples from four different locations in Rivers state is presented in Table 3. Lead (Pb) and Cadmium were detected in all the locations, although cadmium was present in trace levels (0.01 -0.24). chromium was also present in trace levels (0.01 -0.03) in two locations out of the four sampled locations. The heavy metal load in water was far below toxicity threshold level in comparison with W.H.O allowable limits in water (W.H.O 2008).

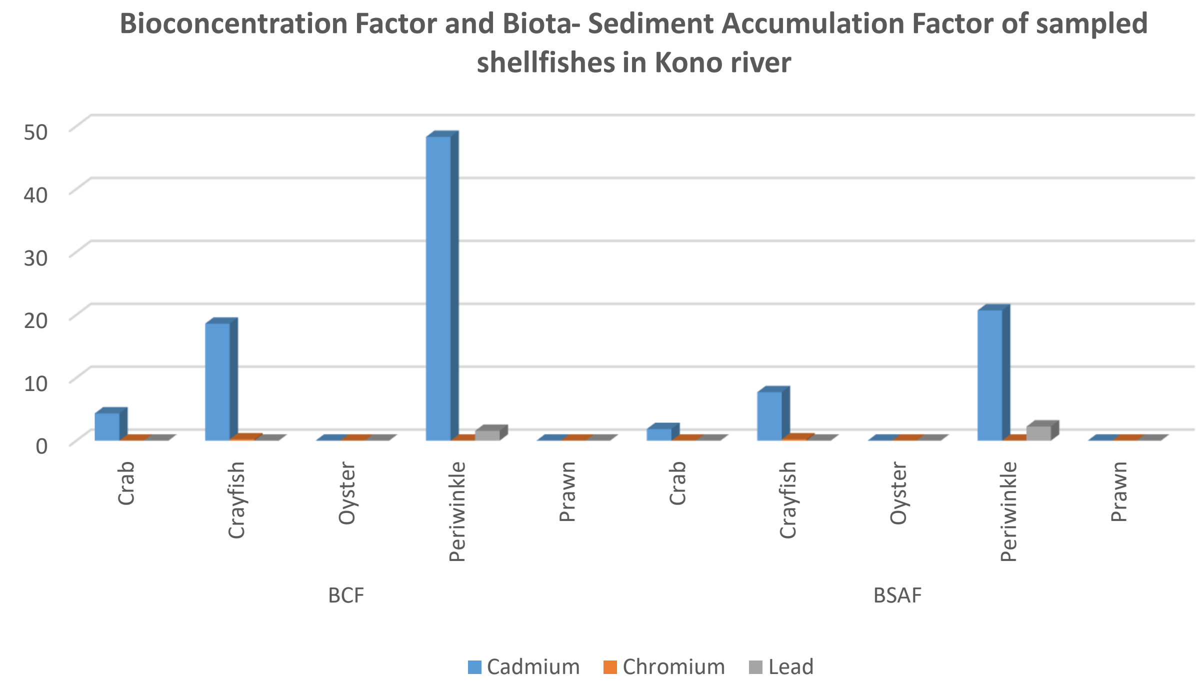


Crab (*Goniopsis cruentata*), Crayfish (*Palaemon hastatus*), Oyster (*Crassostrea gasar*), Perinwinkle (*Tympanotonus fuscatus*) and Prawn (*Penacus indicus*)

Figure 2: BCF and BSAF of sampled shellfishes in Andoni river.

BCF ≥ 1000 (bioaccumulative) (REACH); BCF ≥ 2000 (bioaccumulative) (TSCA); BCF ≥ 5000 (very bioaccumulative) (REACH & TSCA); ND: Below detection limit

BSAF>1 (microconcentrator); BSAF>2 (macroconcentrator); BSAF< (deconcentrator)
ND: Below detection limit



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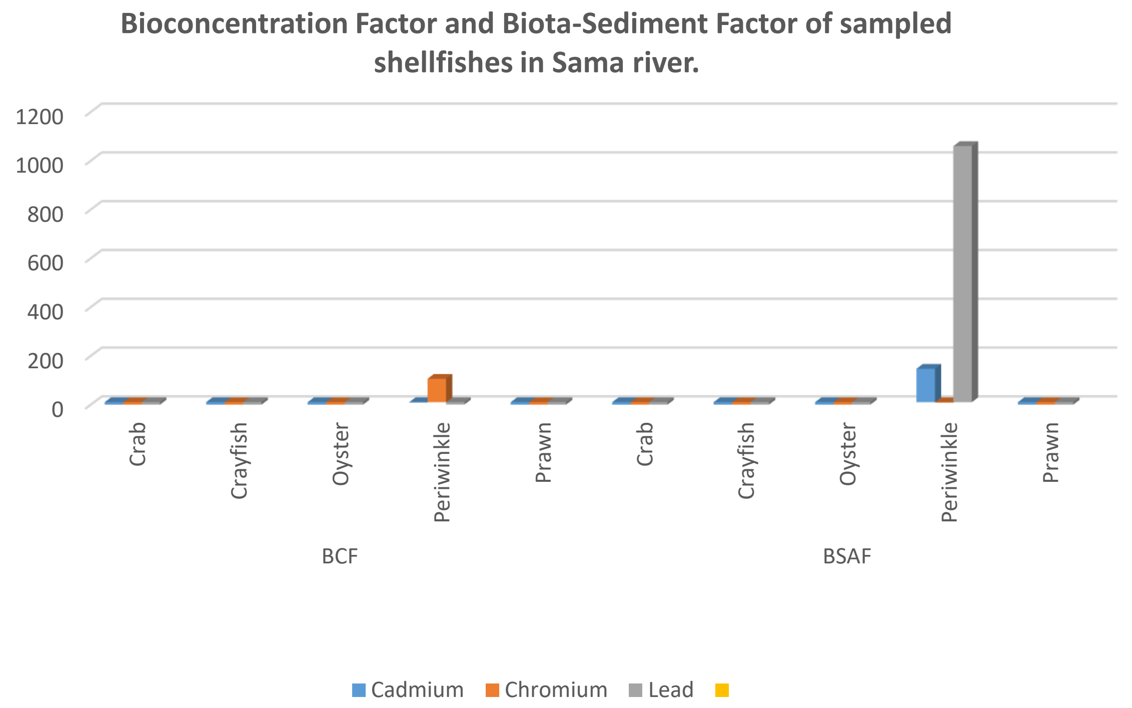
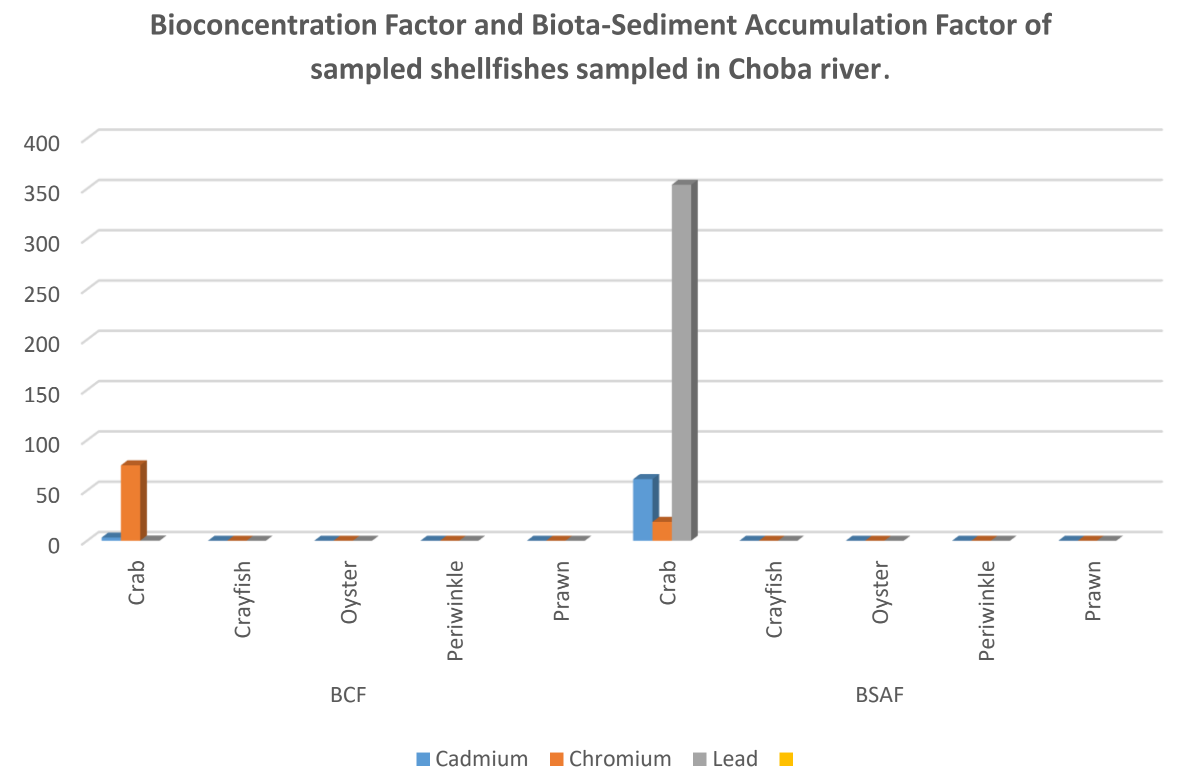


Crab (*Goniopsis cruentata),* Crayfish (*Palaemon hastatus),* Oyster (*Crassostrea gasar),* Perinwinkle (*Tympanotonus fuscatus)* and Prawn (*Penacus indicus*)

Figure 4: BCF and BSAF of sampled shellfishes in Sama river.

BCF ≥ 1000 (bioaccumulative) (REACH); BCF ≥ 2000 (bioaccumulative) (TSCA); BCF ≥ 5000 (very bioaccumulative) (REACH & TSCA); ND: Below detection limit

BSAF>1 (microconcentrator); BSAF>2 (macroconcentrator); BSAF< (deconcentrator);



Crab (*Goniopsis cruentata*), Crayfish (*Palaemon hastatus*), Oyster (*Crassostrea gasar*), Perinwinkle (*Tympanotonus fuscatus*) and Prawn (*Penacus indicus*)

Figure 5: BCF and BSAF of sampled shellfishes in Andoni river.

BCF ≥ 1000 (bioaccumulative) (REACH); BCF ≥ 2000 (bioaccumulative) (TSCA); BCF ≥ 5000 (very bioaccumulative) (REACH & TSCA); ND: Below detection limit

BSAF>1 (microconcentrator); BSAF>2 (macroconcentrator); BSAF< (deconcentrator); ND: Below detection limit

Bio-concentrations and Biota- accumulation Factor of heavy metals in sampled shellfishes

Figures 2 to 5 shows the concentration values of the investigated heavy metals in the shell-fish. In Andoni, periwinkle had the highest bio concentration factor of 49.17 for cadmium while prawn (0.17) had the least value. Crayfish (13.5) had the highest lead content while periwinkle had the least lead value. In kono and sama, periwinkle also had the highest cadmium content of 48.3 and 8.3 respectively. The chromium content of the examined fishes was relatively low. In all the sampled shellfishes, they were found not to be bio accumulative in all the sampled stations with their BCF < 1000.

The biota sediment accumulation factor of the analyzed heavy metals in shell fishes were relatively high, In Sama, periwinkle had 1060 lead and 147 cadmium content. Crab had 353.9 lead content, 61.25 cadmium and 18.75 chromium content in Choba. In andoni prawn had 5.67 lead content, 33 chromium content and 0.5 chromium content. The sampled shell fishes in Andoni all rated as micro and macroconcentrator with (BSAF>1>2) except prawn which rated as a deconcentrators(BAF<1) with a value of 0.5 the sampled shell-fish in Kono all rated as micro and macroconcentrator with (BSAF>1>2) except Crayfish which rated as a deconcentrators(BAF<1) with a value of 0.21 the sampled shellfish in Sama and Choba were rated as macroconcentrator with (BSAF>2).

Discussion

The heavy metal concentration of the water samples was higher than that of the sediment, this could be due to the nature of the river and the point of collection of water samples. The observed low concentrations of Cr and Cd in this present work are consistent with the findings of Obire *et al*. (2003) while the high concentration of Pb in the water body was also observed by Chindah and Braide (2003) who observed higher values of Cd and Pb in similar aquatic body.

The present study revealed that the concentration of heavy metals such as cadmium and lead in surface water were relatively high and this could be due to the anthropogenic activities going on around the place, as also noted by Adeniyi *et al* 2008. The observed differences in metal concentrations in the four species of shellfish examined indicated difference in metal accumulation as reported by Oguzie (2003). Metal uptake and accumulation has a direct link with the feeding habit of shellfish and where shellfish resides in water. (Shrivastava , Saxena , Swarup 2001).

The study shows that the concentration of cadmium, chromium, and lead metal concentrations are found higher in the periwinkle than the other shellfish sampled which could be due to the fact that *T. fuscatus*, has a high potential to concentrate heavy metals in its shell.The Bioconcentration Factor (BCF) recorded low values (<1000) for all metals in the shellfish samples but the Biota-Sediment Bioaccumulation Factor (BSAF) values was rated as micro and macroconcentrator with (BSAF>1>2) for cadmium and lead.

Conclusion

This study examined the concentrations of cadmium (Cd), chromium (Cr) and lead (Pb) content of different shellfish samples from different rivers in Rivers state and compared the results with the World Health Organization (W.H.O) allowable limits in food. Also, the same metals were analyzed in water and sediment. The observed differences in metal concentrations in the four species of shellfish examined indicated difference in metal uptake, the ability of different shellfishes to accumulate metals could be due to its feeding habit or its habitat Consumption of shellfishes with high level of heavy metal contamination can be a serious health hazard (Salamat *et al.,* 2015). Cd can be seriously injurious to health, causing kidney damage, respiratory dysfunction, renal and hepatic system damage, bone disease, hypertension, poor reproductive capacity, tumors etc. due to its long term uptake by the human body (Satarug *et al.*, 2017; Lee *et al.*, 2016).

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