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Metal concentrations in some commercially important shell in port-harcourt, Rivers State, Nigeria

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Abstract
Heavy metals concentration in some shell fishes (*Crassostreagasar, Senilia senilis, Tympanotonos fuscatus and Thais coronata*) sold in Port Harcourt, Rivers State, Nigeria, was investigated. Samples were procured from Creek road marketat three consecutive times and categorized into three class sizes: small (<25mm), medium (25-50mm), and large (>50mm). Samples were analysed for chromium (Cr), nickel (Ni),cadmium (Cd), lead (Pd) and zinc (Zn).The results showed that the metals (Cr, Ni, Cd, Pd and Zn) concentration (mean ± SD, µg/g, n= 10) in the soft tissues of all shell fishes sampled apart from Cr and Ni concentrations in *T. fuscatus*were within the permissible limit by the World health organisation (WHO).Chromium concentration inthe soft tissue of *T. fuscatus* ranged from 3.36 to 5.55 µg/g. There were no overall statistical significant difference (p>0.05) in metals concentration in the soft tissues in all three sizes (small, medium and big) sampled for *T. coronate*, *S. senilis*, and *C. gasar*apart from *T. fuscatus*. There was significant (p<0.05) increase with size in Cd concentration in the soft tissue of *T. fuscatus*.

Keywords: Shell fish, Creek road, market, Heavy metals, Pollution, Aquatic environment

1. Introduction
Heavy metal can be described as naturally occurring metallic element with high atomic weight and density at least 5 times greater than that of water (Fergusson, 2011, Tochunwou *et al*.,2012) [11, 26]. Heavy metals occurs naturally in the earth and become concentrated in the aquatic environment as a result of. human related activities. Activities such as mining, wastes disposal and effluents discharge from homes and industries have been reported to enhance the influx of heavy metals into aquatic environment through runoffs. They cause threats to the environment and bio-organism (Akinrotimi *et al*., 2015) [4]. Moreover, uncontrolled use of heavy metal containing fertilizer and pesticides in farms ultimately end up in the aquatic environment (Makinde *et al*., 2015) [19].
Aquatic environment pollution as a result of heavy metals has been a critical issue all over the world, this is because they are indestructible and most of them have toxic effects on organisms (Macfarlane and Burchett, 2011) [18]. Heavy metals enter rivers and lakes from a variety of sources which include the rocks and soil directly exposed to surface water in addition to the discharge of various treated and untreated liquid wastes to the water bodies (APHA, 2005; Alaa and Osman, 2010) [8, 5]. Over the last few years, there has been a growing interest in determining the level of heavy metal in shell fishes from brackish water environment. This has led to attention being drawn to the measurement of their contamination level in water (Kalay *et al*., 2014) [16]. Heavy metal concentrations in aquatic ecosystems are usually monitored by accessing their concentrations in sediments, biota and water (Moronkola *et al*., 2011) [21]. They generally exist in low quantities in water but subsequently attain considerable levels of concentrations in sediments and biota. Many of these heavy metals are toxic to organisms at low concentration (Murtala *et al*., 2012) [22].
Shell fishes have been considered as one of the most significant indicators in water systems for the estimation of metal pollution level (Abiogba and Henadou, 2006, Nigro *et al*., 2006) [1, 23]. Examples of shell fish include shrimp, crab, lobsters, oysters, shrimps and periwinkles among others. Different types of shell fish have been widely investigated for heavy metals (Sokolowski *et al*., 2007; Ferreira *et al*., 2004; Censi *et al*., 2006) [25, 12, 9]. The transfer factor of heavy metals in shell fish organs such as gills, liver, muscles and exoskeleton in respect to water and sediments, has been studied to give information on how these metals are transferred

to fish from aquatic ecosystem (Udo and Arazu, 2012) [28]. Sediments are important sinks for various pollutants such as pesticides and heavy metals and play a significant role in the remobilization of contaminants in aquatic systems under favourable conditions (Fowler *et al*., 2008) [13].
Motivation to analyze some shellfishes sold in the market is due to the fact that they include sources of animal protein and are widely consumed by the populace. These organisms which are sold in the Nigerian markets are generally obtained from their natural environments (wild foods). Since there is possibility of heavy metal contamination of their natural environment through anthropogenic activities, it is important to investigate the potential human health risks associated with consumption of these aquatic foods. In Nigeria, much has been done in the case of fish but little information is available on the essentials and toxic components of oyster, periwinkle, bloody cockle and whelk in a comparative study. The aim of the study is to assess the levels of heavy metals in some shell fishes sold in Creek road market, Port Harcourt.

2. Materials and Methods
2.1 Study Area
The study was carried out at Creek Road Market (also called town market), Port Harcourt. The market is located along Creek road and is one of the oldest markets in Port Harcourt, Rivers State. It has variety of sea foods and assorted dried and fresh fishes.

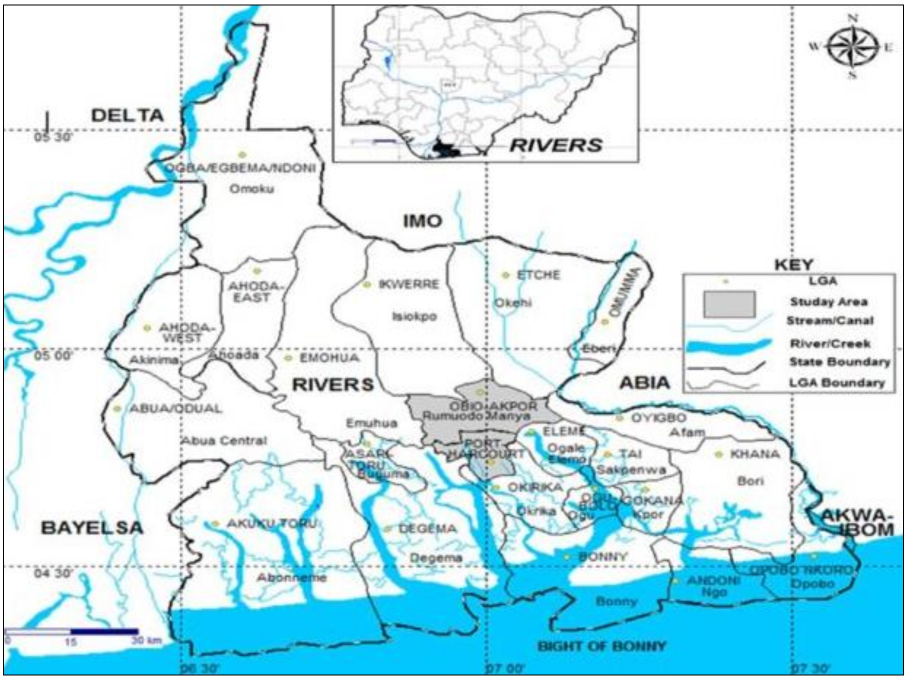

Fig 1: Map showing Rivers state showing creek road market

2.2 Sample Collection and heavy metal analysis
Shellfishes including whelk, *Thais coronate* (Lamarck, 1816); bloody cockle, *Senilia senilis* (Linnaeus, 1758); periwinkle, T*ympanotonus fuscatus* (Linnaeus, 1758) and oyster, *Crassostrea gasar* (Deshayes 1830) were purchased from creek road market. Dead and damaged specimens were eliminated. Samples were taken in a cold box to the Fisheries laboratory, Rivers State University, Port Harcourt. Sample were grouped into three shell sizes: small (<25mm), medium (25-50mm) and large (>50mm) according to (FAO, 2002) [10]. The flesh was separated from shell with kitchen knife and the flesh stored in labelled clean sample container. Thereafter, samples were oven dried at to a constant weight. Each sample was grinded into fine powder and two (2g) each of grinded samples placed into individual digestion flask. Thereafter, 10ml of aqua regia (HCl: HNO3 v/v =3:1) was added to the sample of the individual digestion flask. The contents of the flasks were digested on a hot plate for about 30minutes until the contents got to near dryness. It was then allowed to cool. 10ml of de-ionized/ distilled water was added to each and stirred gently with glass rod. The digest was filtered with Whatman No 1 filter paper into a 50ml volumetric flask, and was made up to the mark with de-ionised/ distilled water. The content of each flask was preserved in sample bottles and kept in refrigerator pending analysis. The levels of heavy metals in samples of shell fishes were carried out using atomic absorption Spectrophotometry Buck Scientific model 200A equipped with air- acetylene flame.

2.3 Statistical Analysis
Data were analysed with SPSS version 17.0 for windows. The data were analysed using two way analysis of variance (ANOVA) to test if there were significance differences in the concentrations of heavy metals between different sampling sizes and species.

3. Results
3.1 Heavy metals concentration in Shellfishes Sold in Creek Road Market, Port Harcourt
The results of the heavy metals concentration(mean ± SD) in the soft tissues of the three sizes of *T. coronate*, *S. senilis*,*C. gasar*and *T. Fuscatus* bought from Creek road market, Port Harcourt are shown (Tables 1 to 4). The metals concentration (mean ± SD) in the soft tissues of all shell fishes sampled were below the permissible limit by WHO (2003), apart from Cr and Ni concentrations in *T. fuscatus*(Table 1-4).Heavy metal concentration (µg/g)in the soft tissue of *T. fuscatus* ranged from 3.36 to 5.55 for Cr and 2.88 to 3.08 for Ni.Also, there were no overall statistical significant difference in metals concentration in the soft tissues in all three sizes

(small, medium and big) sampled for *T. coronate*, *S. senilis*, and*C. Gasar* apart from *T. fuscatus*. *T. fuscatus* showed significant (p<0.05) increase with size in Cd concentration in the soft tissue (Table 4).

3.2 Comparative Heavy Metals in Three Sizes of Shell Fishes Sold in Creek Road Market, Port Harcourt

Comparative values of Cr in some shell fishes sold in creek road market are presented in Figure 2. The highest values of Cr were observed in bigger sizes of *T.fuscatus*, while the lowest was observed in small sizes of *C.gasar*. However, the specie *T.fuscatus* had the highest values in all sizes. Comparatively, highest values of Ni were obtained in *T.fuscatus*, while lowest values were recorded in the specie *S.senilis*.(Figure 3). Comparative values of Cd in some shell fishes sold in creek road market are presented in Figure 4. The specie *T.fuscatus*, recorded the highest values in all sizes. While lower values were observed in other species. Comparative values of Pb in some shell fishes sold in creek road market as shown in Figure 5 revealed that *T.fuscatus* and *T.coronata* had higher values of Pb, when compared to *C.gasar* and *S.senilis*. Comparatively, higher values of Ni were obtained in *T.fuscatus and T.coronata*, while lower values were recorded in *C.gasar* and *S.senilis*. (Figure 6).

Table 1: Heavy Metals in Mangrove Oyster (*Crassotrea gasar*) Sold in Creek Road Market, Port Harcourt (Mean ± SD)

Heavy Metals (µg/g)	Sizes of *C.gasar* Small Medium Big			FEPA / WHO Limits (2003)
Cr	1.83 ± 0.06[a]	2.63 ± 0.06[b]	2.95 ± 0.06[b]	3.0
Ni	1.43 ± 0.28[a]	2.43 ± 0.10[b]	2.77 ± 0.12[b]	3.0
Cd	0.04 ± 0.00[a]	0.05 ± 0.00[a]	0.05 ± 0.00[a]	1.0
Pb	0.26 ± 0.07[a]	0.30 ± 0.03[a]	0.34 ± 0.02[a]	2.0
Zn	5.73 ± 1.06[a]	5.80 ± 1.08[a]	7.77 ± 0.28[b]	30

Means within the same roll with different superscripts are significantly different (P<0.05)

Table 2: Heavy Metals in Bloody Cockle (*Senilia senilis*) Sold in Creek Road Market (Mean ± SD)

Heavy Metals (µg/g)	Sizes of *S. senilis* Small Medium		Big	FEPA / WHO Limits (2003)
Cr	2.15 ± 0.05[a]	2.44 ± 0.01[a]	2.84 ± 0.06[a]	3.0
Ni	1.04 ± 0.07[a]	1.17 ± 0.05[a]	1.21 ± 0.02[a]	3.0
Cd	0.04 ± 0.01[a]	0.06 ± 0.01[a]	0.08 ± 0.01[a]	1.0
Pb	0.21 ± 0.10[a]	0.29 ± 0.06[a]	0.33 ± 0.02[a]	2.0
Zn	4.58 ± 0.67[a]	5.57 ± 0.61[b]	6.15 ± 0.20[c]	30

Means within the same roll with different superscripts are significantly different (P<0.05)

Table 3: Heavy Metals in Whelk (*Thais coronata*) Sold in Creek Road Market (Mean ± SD)

Heavy Metals (µg/g)	Sizes of *T.coronata* Small Medium		Big	FEPA / WHO Limits (2003
Cr	2.15 ± 0.05[a]	2.44 ± 0.01[b]	2.84 ± 0.06[b]	3.0
Ni	1.04 ± 0.07[a]	1.17 ± 0.05[a]	1.21 ± 0.02[a]	3.0
Cd	0.05 ± 0.01[a]	0.06 ± 0.01[a]	0.07 ± 0.01[a]	1.0
Pb	0.20 ± 0.10[a]	0.29 ± 0.06[b]	0.33 ± 0.02[b]	2.0
Zn	4.58 ± 0.67[a]	5.57 ± 0.61[b]	6.15 ± 0.20[c]	30

Means within the same roll with different superscripts are significantly different (P<0.05)

Table 4: Heavy Metals in Periwinkle (*Tympanotonus fuscatus*) Sold in Creek Road Market (Mean ± SD)

Heavy Metals (µg/g)	Sizes of *T. fuscatus* Small Medium		Big	FEPA / WHO Limits (2003
Cr	3.36 ± 0.94[a]	4.74 ± 0.35[b]	5.55 ± 0.35[c]	3.0
Ni	2.88 ± 0.13[a]	3.08 ± 0.01[b]	3.08 ± 0.01[b]	3.0
Cd	0.65± 0.00[a]	0.88 ± 0.00[b]	0.98 ± 0.00[b]	1.0
Pb	1.04 ± 0.05[a]	1.05 ± 0.02[a]	1.07 ± 0.02[a]	2.0
Zn	6.95 ± 1.00[a]	8.50 ± 0.42[b]	8.54 ± 0.51[b]	30

Means within the same roll with different superscripts are significantly different (P<0.05)

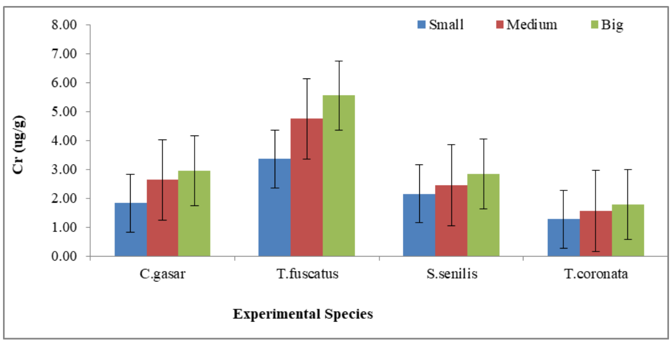

Fig 2: Comparative values of Cr in Some Shell Fishe Sold in Creek Road Market, Port Harcourt

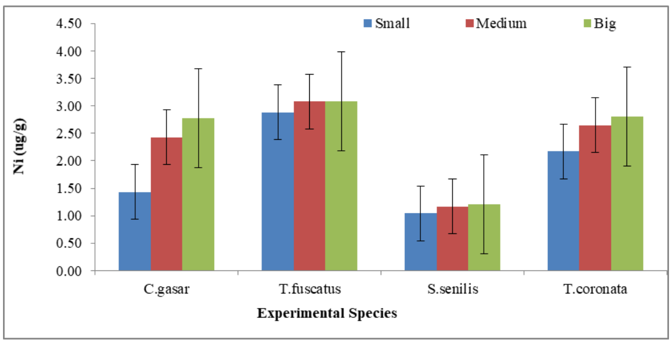

Fig 3: Comparative values of Nickel (Ni) in Some Shell Fishes Sold in Creek Road Market Port Harcourt

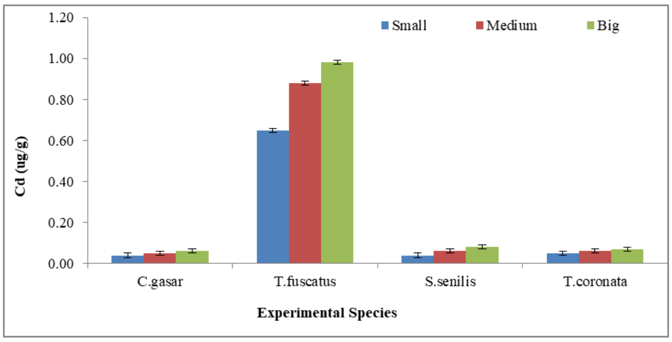

Fig 4: Comparative values of Cadmium (Cd) in Some Shell Fishes Sold in Creek Road Market

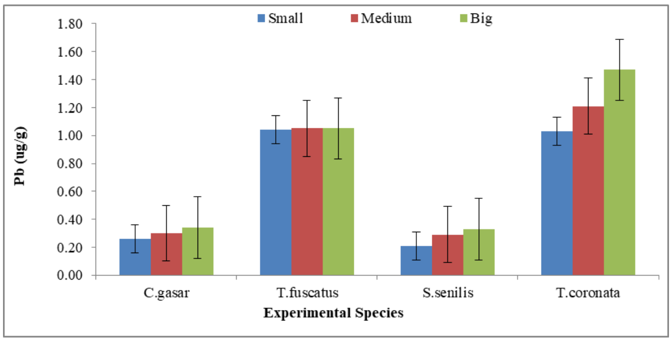

Fig 5: Comparative values of Lead (Pb) in some shell fishes sold in Creek Road Port Harcourt

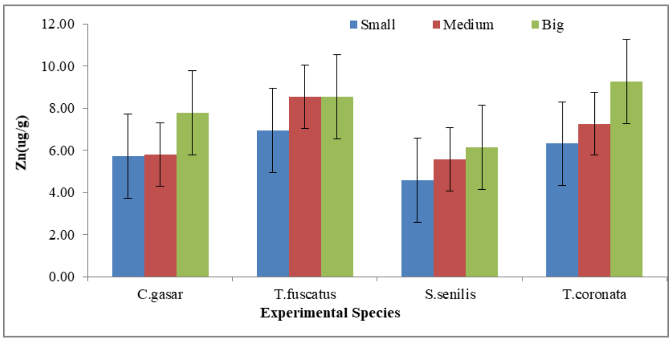

Fig 6: Comparative values of zinc (Zn) in some shell in sold in creek road market port Harcourt

4. Discussion

Heavy metals concentration in Shell fishes Sold in Creek Road Market, Port Harcourt

Heavy metals recorded in this study varied from species to species and in different sizes. The species *T.fuscatus* and *T.coronata* were found to have higher values than other species. This assertion corroborated with findings of Koh *et al*. (2011) [17], who compared heavy metals *Anadara granosa* and periwinkle in Malaysia. They attributed higher heavy metals in periwinkle to its shape and life history. Accumulations of metals were generally found to be species specific and may be related to their feeding habits and the bio-concentration capacity of each species (Tuzen, 2003) [27]. Heavy metals concentrations in fish may depend upon factors like duration of exposure to contaminants, feeding habits, concentrations of contaminants in their habitat, water chemistry, any contamination of fish during handling and processing, sex, weight, season of sampling etc (Ross, 2014) [24].

Lead concentrations reported in different species of in faunal of bivalve (*Macomabalthica*, *Macomanasuta*, *Chione subrugosa*, *Cerastoder maedule*) around the world are normally between 1 and 4 µg/g dw, reaching values of 8 µg/g in some moderately polluted sites (Jung *et al*., 2006) [15]. Mean values of lead recorded in this study were very low, when compared to the values obtained in some shell fishes from lagoon systems in the Southern Gulf of Mexico which was several orders of magnitude higher than the range of values of lead obtained in some shell fishes considered in the present study (Mohammad *et al*., 2011) [20]. The Lead content observed in the studied shell fishes may be attributed to a higher state of contamination from the use of leaded gasoline (Allen *et al*., 2003) [6] in operation in and around the water. Lead can displace calcium in bone, fish or from animal – derived food (Abowei and Sikoki, 2005) [2]. It binds with the sulfhydryl bonds and inactivates the cysteine – containing enzymes, thus allowing more internal toxicity from free radicals, chemicals, and other heavy metals (Adite *et al*., 2013) [3]. Cadmium levels in observed in these shell fishes were comparable to those of (Woke *et al*., 2016) [29], in some shell fishes from Andoni flats. Cadmium levels obtained in this work were within acceptable limits for human consumption of 0.5 – 1.0 mg/kg as reported by (FAO, 2002) [10].

In a study conducted to investigate the effects of size on heavy metal accumulation in soft tissues of some shell fishes from the Andoni flats in Niger Delta, (Woke *et al*. 2016) [29], reported mean Zn values in large-sized clams that were nearly twice values obtained in small-sized clams during the sampling period. Even at very low concentrations, there is considerable variation in heavy metal content of small-sized and large-sized clams. However, the relative significance of these variations in heavy metal content across class size are generally metal and specie specific as observed in this study.

Variations in Ni, Cr and Zn contents of the shell fishes across the across class size were pronounced in big sized organisms. Horward *et al*. (2009) [14] reported the same in fresh water clams in Niger Delta, Nigeria. Large-sized clams, therefore, have the potential to accumulate higher concentrations of heavy metals in their tissues compared to small-sized and medium-sized individuals. Amisah *et al*., (2009) [7] also observed relatively higher Zn concentrations in large-sized individuals of the clam, *Galatea paradoxa* compared to small-sized individuals. Overall the abundance of all studied metals in *T.fuscatus* as obtained in this work is indicative of its ability to accumulate metals in its tissues. According to Howard *et al*. (2009) [14], *T. fuscatus* are known to accumulate contaminants and form biological indicators of pollution.

5. Conclusion and Recommendations

The heavy metal content, in soft tissues of *C. gasar*, *S.senilis*, *T,fuscatus*and *T. corona* were higher in the large-sized compared to the small-sized and medium-sized oysters. The size of the shell fishes therefore, plays a key role in determining the uptake of heavy metals. In general, the heavy metal was found to be related to size. On a size-specific basis, the uptake of heavy metals will probably occur more in large-sized, compared to small-sized and medium-sized oysters. However, the levels of heavy metals recorded in soft tissues of *C. gasar and S.senilis*in this study were generally very low when compared with*T.fuscatus* and *T. coronata*. The findings from this study, suggests that size is a factor in heavy accumulation in these shell fishes, hence size should be reckon when reporting heavy metals accumulation in these species.

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