# ASSESSMENT OF HEAVY METALS AND CRUDE PROTEIN CONTENT OF MOLLUSCS AND CRUSTACEANS FROM TWO SELECTED CITIES IN NIGERIA

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## **ABSTRACT**

Crabs, shrimps, periwinkles and land snails form a source of aquatic food which is widely consumed in Nigeria. Therefore, there is need for comparison of nutritional information and heavy metals accumulation potentials of these organisms. The aim of this study was to quantify heavy metals (Cu, Zn, Pb and Cd) and crude protein content of these species that are sold in markets in Ibadan and Lagos, Nigeria. In addition, the influence of location, organism species, organism age, and processing on the levels of the analytes were also investigated. The results showed that mean Cu concentrations ranged from 4.88±0.54µg/g in edible land snail (Gabiella africana) to 34.1±3.0µg/g in raw guinea shrimp (Parapenaeopsis atlantica) and Zn concentrations from 21.4±1.6 in African giant snail (Archarcantina marginata) to 190±21µg/g in raw pink shrimp (Penaeus notialis). The concentration of Zn in all species was below the WHO maximum permissible limit of 100µg/g except in crabs and raw shrimps. Cu concentrations in all the samples except dry shrimps and snails were higher than the WHO permissible level of 10µg/g. Furthermore, highest Pb levels were found in crabs (Callinectes pallidus)  $(2.74\pm0.45\mu g/g)$  and the minimum mean level of  $0.66\pm0.07\mu g/g$  was observed in G. africana. All the samples except dried shrimps contained Pb above the EC limit of 0.5µg/g. The highest mean level (0.20±0.17µg/g) of Cd was detected in crab while the least (0.03±0.01µg/g) was found in periwinkle. However, these levels were lower than the EC limit of 0.5µg/g. The concentrations of Cu, Zn, Pb and Cd in the organisms differed a little between the two sampling locations. The concentration of heavy metals (HMs) varied with studied organisms. For instance, gladiator swim crab (Callinectes pallidus) and raw pink shrimp (P. notalis) bioconcentrated remarkably higher levels of Cu, Zn, Pb and Cd than the other organisms. The process of drying significantly decreased bioavailable HMs in shrimps. Matured snails contained highest concentrations of Cu and Pb while baby snails contained highest levels of Zn. About 63% Cu, 70% Pb, 87% Zn and 10% protein content appeared to be lost during the drying process in shrimps. Crude protein contents ranged from 35.7±2.5% in crabs (C. pallidus) to 79.5±2.0% in snails (G. africana), implying that shrimps, crabs, periwinkles and snails are good sources of animal protein if they are found in contamination free environment.

**Key words**: Heavy metals, protein, crustaceans, molluscs



#### INTRODUCTION

Shrimps, crabs, periwinkles and snails are organisms which are found mainly in water, in muddy and mouldy terrestrial environments. Shrimps and crabs are decaped crustaceans while periwinkle and snail are gastropod molluses. Shrimps live predominantly in either marine or fresh water environments, while crabs are adaptable to life both in water and on land [1]. The common characteristics of crustaceans include two pairs of jointed antennae, segmented body, a calcareous hard shell and paired jointed limbs. Molluses, unlike crustaceans are marine, freshwater or terrestrial soft-bodied animals without body segmentation. They are usually characterised by muscular foot, a shell and a mantle.

Periwinkles are marine gastropod molluscs known as edible sea snails [2]. Land snails are members of the class gastropod which live in trees, rocks, under decayed plants and in gardens [3].

Crustaceans and molluscs are common sources of foods. Their meats are cheap and rich in protein, omega 3 and low fat content. Furthermore, they can supply the recommended levels of essential nutrients such as Cu and Zn required for proper functioning of human body systems especially in developing countries where deficiency of these metals is common [4]. Zinc is an essential micronutrient required in the synthesis and degradation of carbohydrates, lipids, proteins and nucleic acids. It is also an essential element for gene expression and hormone receptor activities in the cell [5, 6]. Cu plays essential roles as metalloenzymes and as a cofactor of large number of enzymes and is also used for biological electron transport [5, 7]. A range of intake of 1.5–3mg/day for Cu and 12–15mg/day for Zn has been documented to be adequate for the body [7]. Beyond this range, toxic effects have been observed [7].

As nutritionally beneficial as crustaceans and molluscs are, they can be potential sources of health risks to man due to accumulation of toxic heavy metals (HMs) such as lead (Pb) and cadmium (Cd). At a certain trace amount, Pb and Cd are toxic to biological systems. Lead is capable of causing both acute and chronic toxicities. Acute toxicity occurs through accidental exposure to high concentrations of soluble Pb compounds. On the other hand, chronic toxicity can occur through consumption of lead-contaminated foods. Lead is known particularly to reduce intellectual development in children and causes cardiovascular diseases in adults and in extreme cases, death [6]. Chronic exposure to high levels of cadmium can cause kidney and liver damage in man [6].

Motivation to analyze shrimps, crabs, periwinkles and snails was due to the fact that they include sources of animal protein and are widely consumed in Nigeria. These organisms which are sold in the Nigerian markets are generally obtained from their natural environments (wild foods). Apart from snails, others are rarely reared. Since there is possibility of heavy metal contamination of their natural environment through anthropogenic activities, it is important to investigate the potential human health benefits and risks of consuming 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 snails, periwinkles, crabs and shrimps in a comparative study. Therefore, the goal of the present



study was to assess the levels of essential and non-essential components of crustaceans and molluscs using products from markets in Ibadan and Lagos, Nigeria. Influences of location, organism species, age, as well as processing on the levels of the components of interest were also investigated.

#### **MATERIALS AND METHODS**

#### Sample collection and pretreatment

Two species of about similar length and weight of shrimps, crabs, periwinkles and snails were purchased from local seafood vendors. They were sourced from six locations in Lagos and three locations in Ibadan which are known for the sale of seafoods. The locations in Lagos were Ketu, Mile 12, Agboyi-Ogudu lagoon side, Ibeshe-Ikorodu lagoon side, Odongunyan market and Abule-Ikorodu lagoon side markets. The Ibadan locations were Bodija, Eleyele-Okoro village and Ashejire river side markets. The geographical locations of the markets are as shown in Figures 1 and 2.



Figure 1: Sampling locations in Lagos



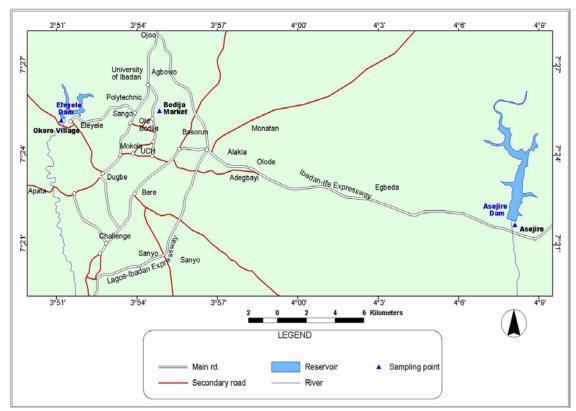


Figure 2: Sampling locations in Ibadan

Most of the markets are situated near a river, making it possible to get live and raw samples. Samples of dried shrimps were also purchased to assess the impact of traditional drying on heavy metals levels and protein contents in the organisms.

**Shrimps:** Raw and dried Pink shrimp (*Penaeus notialis*) and Guinea Shrimp (*Parapenaeopsis atlantica*) were purchased at two locations in Lagos (Ibeshe Ikorodu and Ogudu-Agboyi lagoon side market) and at three locations in Ibadan ( Ashejire, Eleyele (raw) and Ashejire and Okoro village (dried)). The samples were collected in polyethylene bags and transported to the laboratory.

**Crab:** Crab species (*Cardiosoma armatum*) were purchased from two locations in Lagos (Ibeshe-Ikorodu and Abule-Ikorodu lagoon side markets) and two locations in Ibadan (Eleyele and Ashejire River markets) while crab species (*Callinectes pallidus*) were purchased from the two locations in Lagos and Ashejire River market in Ibadan. The samples were collected in plastic buckets and transported to the laboratory.

**Periwinkle:** Periwinkle species (*Littorina littorea*) and (*Tympanotomus fuscatus*) were purchased from sea foods vendors in four locations in Lagos (Ketu market, Mile 12 market, Ogudu-Agboyi-Lagoon side market and Ikorodu-Odongunyan market) and two locations in Ibadan (Bodija and Eleyele-Okoro village markets). The samples were collected in polyethylene bags and transported to the laboratory.



**Snail:** Baby and matured African giant Snail (*Archarcantina marginata*) and Edible land snail (*Gabiella africana*) were purchased from two locations in Lagos (Ketu Mile 12 market and Ibeshe-Ikorodu lagoon side market) and in Ibadan (Ashejire River and Bodija markets).

The samples were collected in polyethylene bags and transported to the laboratory. All the samples were separated by species and identified in the Department of Zoology, University of Ibadan. The pictures of the species are as shown in Figure 3.



Guinea Shrimp (*Parapenaeopsis atlantica*)



Pink shrimps (*Penaeus notialis*))



Lagoon land crab (Cardiosoma armatum)

Gladiator swim Crab (Callinectes pallidus)



Periwinkle (Littorina littorea)



Periwinkle (Tympanotomus fuscatus)



African giant Snail (*Archarcantina marginata*)



Edible land snail (Gabiella africana)



## Preparation of composite samples

Except for shrimps, the edible parts of the samples were removed from their shells prior to analysis. They were thoroughly washed with distilled water and a composite sample was prepared for each species by pooling the samples together. Fifty samples of similar length and size of each of the two species of periwinkles were sorted, chopped and homogenised for each sampling location. Six samples of similar size and weight for each of the two species of crab were sorted, chopped and homogenized for each sampling location. Seven samples of Pink shrimps and 50 samples of Guinea Shrimp of similar length and size were sorted, chopped and homogenized for each sampling location. Four samples of similar size and weight of matured snails and ten samples of baby snails each of the two species were sorted, chopped and homogenized for each sampling location. The composite samples were dried in an oven at 70°C for 24 hours. The dried samples were ground into powder and kept in Ziploc polyethylene bags for analysis.

# Determination of heavy metals in the edible tissues of the organisms

To isolate the trace metals from the food samples, the organic matter content of the organisms was destroyed by wet digestion. One gram of each dried sample was digested with 20 mL of 3M HNO<sub>3</sub> for 3 hours while heating until a clear solution was obtained. Digested samples were filtered into 100mL volumetric flask, made up to mark with distilled water and then analyzed for Cu, Zn, Pb and Cd using atomic absorption spectrophotometry (Buck scientific model 210 VAP with an air-acetylene flame). The detection limits (µg/mL) for the element were: Zn 0.005, Cd 0.01, Cu 0.005, Pb 0.08.

## Quality assurance/quality control

For quality assurance/quality control, all samples were run in batches that included blind samples, method blanks and spiked samples. The results of the spiked samples showed good recovery. The percent recoveries ranged from 82.7-102% for Cu, from 92.3-107% for Zn and 101% for Pb. The coefficient of variation ranged between 1.3 and 10.2%.

## **Determination of percent Protein**

Protein nitrogen content in the samples was determined using Kjeldahl's method and then converted to crude protein by conversion factor of 6.25 [8]. In the method, the organic matter in 0.2 g of the dried organisms was oxidized by digesting the food sample with heated 10 mL conc. H<sub>2</sub>SO<sub>4</sub> in the presence of K<sub>2</sub>SO<sub>4</sub> (which raised the b.p) and selenium as catalyst. The nitrogen in the samples was converted to ammonium sulphate in a Kjedahl's apparatus. The solution was then distilled with an excess of conc. NaOH, followed by back titration using boric acid solution (0.1 M) and HCl (0.1 M). Bromocresol was used as indicator.

## Statistical analysis

Range, mean and standard deviations were calculated using Excel 2010.



#### **RESULTS**

#### Heavy metals concentrations and protein content in shrimps

The concentrations of heavy metals and protein contents in raw and dry species of shrimps from Lagos and Ibadan are presented in Table 1 and 2 respectively. Heavy metal concentrations in the organisms varied relatively between the two locations.

The non-essential metals, that is, Pb and Cd levels were lower in the organisms when compared with Cu and Zn levels. Lead concentrations in both species of raw shrimps from the locations in Ibadan are higher than the concentrations in shrimps from Lagos. As can be observed Cd was not detected in all the species. Highest levels of Cu and Zn were observed in raw shrimps from Ibeshe in Lagos and Ashejire in Ibadan. Copper, Zn and Pb concentrations in both raw shrimp species were higher than WHO permissible levels of  $10\mu g/g$  for Cu,  $100\mu g/g$  for Zn [9] and the EC permissible levels of  $0.5\mu g/g$  for Pb [10]. Raw pink shrimps accumulated higher levels of Zn than raw guinea shrimps. For example, the highest level of Zn in raw pink shrimp was  $220\mu g/g$  while that of raw guinea shrimp was  $195\mu g/g$ .

# Influence of drying on heavy metals contents of shrimps

The impact of drying on the HMs and crude protein contents of shrimps was demonstrated by comparing the parameters determined in both raw and dry shrimps. As indicated in Table 1 and 2, it is interesting to note that there was a major difference in the levels of the HMs of raw and dry shrimps. About 63% Cu, 70% Pb and 87% Zn might be possibly lost in both species of shrimps during local drying process. The process of drying brought the HMs concentrations in the species below the WHO permissible levels of  $10\mu g/g$  for Cu,  $100\mu g/g$  for Zn [9] and the EC permissible levels of  $0.5\mu g/g$  for Pb [10]. About 10% protein appeared to be lost to the process of drying.

## Heavy metals concentrations and protein content in crabs

The heavy metals concentrations and protein contents of Lagoon land crab (*C. armatum*) and Gladiator swim crab (*C. pallidus*) are shown in Table 3.

Based on locations, no consistent pattern in the heavy metal levels in the crabs was found. However, considerable differences in heavy metals accumulation by the two species of crabs were observed. *C.* contained higher levels of Cu, Zn, Pb and Cd than *C. armatum*. As shown in Table 3, the range of Cu, Zn, Pb and Cd levels in *C. armatum* and *C. pallidus* were 15.3-17.8 and 19.1-23.8μg/g; 140-170 and 170-190μg/g; 0.57-1.25 and 2.46-3.26μg/g; and 0.11-0.30 and 0.10 and 0.40μg/g respectively. However, the levels of Cd were lower than EC limit of 0.5μg/g set for crustaceans [10]. The concentrations of Cu in crabs in this study were consistent with the levels reported in previous studies. A range of mean Cu concentrations from 18.0 to 22.4μg/g for three species of crabs from French markets has been reported [11]. The highest Pb (3.26μg/g) and Cd (0.40μg/g) concentrations were found in *C. pallidus*. This may suggest natural Pb and Cd accumulation potential of this crab species. The ability of crab and periwinkle to accumulate Pb and Cd has been documented [2, 12, 13, 14]. Copper, Zn and Pb concentrations in the crab species were higher than the WHO permissible limits [9, 10].



## Heavy metals concentrations and protein content in periwinkles

The concentrations of heavy metals and protein contents in the two species (T. fuscatus and L.littorea) of periwinkles from Lagos and Ibadan are presented in Table 4. Heavy metal concentrations in the organisms varied comparatively between the two locations. The highest concentrations of Cu (17.2 $\mu$ g/g), Zn (37.6 $\mu$ g/g), Pb (1.77 $\mu$ g/g) and Cd (0.05 $\mu$ g/g) were found in the periwinkles collected from Lagos. But, no considerable differences in heavy metals accumulation between the two species were observed.

The concentrations of Cu and Zn in periwinkle in this study were comparable with the levels reported in previous studies. Highest Cu and Zn concentrations of 12.1 and  $35.5\mu g/g$  respectively were reported in periwinkle [15]. A mean Cu concentration of  $14.2\mu g/g$  was also reported for periwinkle [11]. Baseline concentrations levels of Cu, Zn, Cd and Pb which ranged from 25-264 (mean=99)  $\mu g/g$ , 51-186 (mean=77) $\mu g/g$ , 0.07-4.60 (mean=0.86) $\mu g/g$  and 0.05-6.49 (mean=0.78) $\mu g/g$  respectively were observed in Asian periwinkle[16]. Nevertheless, Cu and Pb concentrations in periwinkles in this study were higher than the WHO and EC permissible levels.

## Heavy metals concentrations and protein content in snails

Tables 5 and 6 show the HMs concentrations in the two species (*A. marginata* and *G. africana*) of matured and baby snails from Lagos and Ibadan respectively. Cadmium was not detected in the snails. Levels of Cu and Zn in the snails were much lower than what was observed with shrimps, crabs and periwinkle. This probably implies that snails have low accumulating power for these metals.

Relatively, heavy metal concentrations in the snails varied between the two locations. The snails from locations in Lagos have higher concentrations. As indicated, the two species of snails showed almost similar levels of HMs. However, influence of age on heavy metals levels was found between the matured and baby snails.

The species of matured snails exhibited a range of Cu and Pb concentrations that were higher than the same species of baby snails. For instance, Cu concentrations ranged from  $5.55-8.55\mu g/g$  and  $4.75-5.76\mu g/g$  for matured A. marginata and baby A. marginata respectively. It is interesting to note that the levels of Zn in baby snails were generally higher than the levels in matured snails. The concentrations of Cu and Zn in snail in this study were comparable with the levels of 3.80 and  $33.5\mu g/g$  respectively reported in previous study [15]. Copper and Zn were below the WHO permissible levels of  $10\mu g/g$  for Cu,  $100\mu g/g$  for Zn. In all the locations the levels of Pb were a little higher than EC limit of  $0.5\mu g/g$  set for crustaceans [10].

## **Crude protein content of the organisms**

The results of crude protein content in shrimps, crabs, periwinkles and snails are shown in Tables 1-6. There was not much variation in the protein content among the species of the same organism. Highest protein content was observed in both species of matured snails while the lowest were observed in both species of crab. Protein content ranged between 76.1-81.9% in matured African giant snails; 76.1-81.9% in matured edible land snail; between 65.1-81.2% in raw pink shrimps; 65.3-78.2 % in raw Guinea Shrimp; 71.2-76.2% in periwinkle (*L. littorea*); 71.2-75.7% in periwinkle (*T. fuscatus*); 33.2-



39.8% in Lagoon land crab and 33.3-38.2% in Gladiator swim crab. These results were within values of crude protein found previously in other studies both within and outside Nigeria [17, 18, 19]. Protein content of 74·84%, 65·29% and 60·93% were previously documented for crayfish, snail and periwinkle respectively [17]. These results were comparable to the protein content of the same organism in this study. Also crude protein contents which ranged from 72.92-85.35% in three species of shrimps were reported [20]. A range of 87-89 % crude protein in giant read shrimps caught from the Mediterranean Sea was documented [18]. These values were higher than the values in the Nigerian shrimps. Crude protein of 18.9% was reported in Chinese mitten crab [21]. Lower amounts of crude protein in the edible portion of crab were also reported by other authors [22, 23].

#### **DISCUSSION**

The concentrations of Cu and Zn in shrimps, crabs and periwinkles were higher than WHO permissible limits in crustacean while those of snails were within the limits. This may imply that the organisms have natural ability to bioconcentrate Cu and Zn or that the water bodies in Lagos and Ibadan where these organisms were caught were exposed to anthropogenic contamination from urban and industrial discharges. On many occasions, the highest values of Cu, Zn, Pb and Cd were observed in organisms purchased directly from the markets that are situated by the river side. The highest concentrations of Cu (37.5µg/g) in shrimp, Zn (220µg/g) in shrimp and Pb (3.26µg/g) in crab were observed in fresh organisms bought from a market by the side of Ashejire river in Ibadan while the highest Cd level (0.40µg/g) in crab was observed in crabs bought from Abule Ikorodu lagoon side market. These three marine organisms can serve as good indicators of Cu, Zn, Pb and Cd contamination of aquatic media. The contamination of the water bodies where the organisms live notwithstanding, it can be inferred from these results that shrimps, crabs and periwinkles are rich sources of essential trace metals, Cu and Zn. Other authors have also reported that these organisms are rich sources of Cu and Zn [22, 24]. Both snail species had Cu and Zn concentrations below the WHO permissible limit. Consequently, they can serve as a source of dietary intake of these trace elements in addition to their rich protein content.

Periwinkles and crabs are found in estuarine environments. They are particularly found at the lagoon edges in Lagos. The detectable levels of Pb and Cd in the two species of periwinkle and crabs may be attributed to the contamination of estuaries where they are usually located. Crabs burrow very close to river sediments and may also feed on sediment invertebrates with detectable levels of Pb and Cd. So also, periwinkles dwell at the bottom of rivers and oceans which acts as sink for heavy metal contaminants. The accumulation of Pb and Cd by crabs and periwinkles observed in this study is consistent with previous documentations [16, 25]. Lead concentrations ranging from 0.05- $9.02\mu g/g$  and Cd from 0.07- $2.85\mu g/g$  were observed in periwinkle that was employed as a biomonitor to assess metal pollution in Korean coastal water [16]. Heavy metal pollutants are introduced into the marine environment via industrial and agricultural inputs and runoff from land. These metals can be released and become available to estuarine living organisms [26]. Generally, all the marine organisms studied had higher levels of Cu, Zn, Cd and Pb than snail which lives and feeds on moist land. Therefore,



the safeguarding of the environment from contamination to keep these metals at the minimum required level for biological processes will be highly beneficial.

Copper and Zn are essential components of the human body and other lower organisms. Nevertheless, they are toxic when present beyond the concentrations required for biological processes. Copper is required by living organisms as an essential part of their oxygen-carrying pigment haemoglobin and several enzymes [26]. Zinc in the right concentrations is an essential component of many enzymes which catalyze biological metabolic processes. It has been found to be a vital part of nearly 300 enzymes of species of different phyla [27].

Lagos is a highly industrialized city with a lot of anthropogenic activities which can contribute to the contamination of aquatic environments while Ibadan is poorly industrialized. However, no substantial differences in heavy metals concentrations in the organisms were found in the two locations.

Different species of the organisms showed different HMs levels. Lead was highly accumulated in crab. For instance, Pb concentration in Gladiator swim crab was about 3 times higher than the level in lagoon land crab. This variation may be attributed on one hand, to their habitats and on the other hand to their inherent abilities to biomagnify the heavy metals. Lagoon land crab is a terrestrial organism that occasionally goes into water while Gladiator swim crab is mainly aquatic. These two species of crabs are important sources of animal protein for coastal and riverine communities in Nigeria. But, it is worth noting from this study that Gladiator swim crab bio-concentrates HMs above the permissible levels. Hence it should be consumed with caution. Pink shrimp demonstrated a much greater ability for accumulation of Zn and Pb than did guinea shrimp.

During wet seasons, Nigerian markets are always stocked with baby snails. This study also investigated variation in HMs concentrations and protein contents in the snail as a function of age. Baby snails of both species had higher concentrations of Zn in their tissues than the matured ones, signifying that age is an important consideration for Zn levels in the land snails. Higher concentrations of Zn in smaller snails have also been reported and are attributed to greater metabolic activities [16].

Shrimps in particular are indigenously consumed either in the fresh or dry form. Apart from being consumed locally, they are also exported. The drying process is utilized to prevent microbial spoilage during storage before sale locally or exportation. The commonly used traditional preservation methods include sun-drying and hot-smoking [28]. The sun-drying process involves open-air drying at ambient temperatures which would encourage metal loss through evaporation. Hot-smoking involves application of heat through fire wood to shrimps in a wire mesh supported by a semi-circular framework of a perforated drum to get rid of the water content of the organisms. During the process the dissolved metal contents might have also been lost fast through evaporation. Thus, the influence of drying on bioavailable HMs in shrimps was assessed. As indicated in Table 1 and Table 2, there was a considerable difference in the levels of the HMs and protein contents of raw and dry shrimps. The HMs concentrations and protein content in dried shrimp species were lower than those in the raw samples. Heavy metals were



reduced to below WHO and EC maximum permissible levels. Copper suffered about 63% reduction for both species while 87% of Zn appeared to be lost to evaporation. About 70% Pb was lost which appeared to be the other beneficial impacts of drying apart from prevention of spoilage. The loss in protein was not very significant. About 10% protein was lost. The decrease of HMs may probably be due to the amounts that were lost to evaporation and in protein due to denaturalization. The results demonstrated that drying process cause alterations of components of shrimps and consequently, the dietary intake. In view of the reduction in the HMs contents, it is advisable to eat dry shrimps instead of raw shrimps especially in contaminated environments.

Protein plays vital roles in human physiological processes. These include being catalysts for movements of long-chain fatty acids across the lipid bilayer in mammalian membranes, as antibodies defending the body from germs, and as catalysts that speed up chemical reactions in the human body [29]. The results demonstrate that shrimps, crabs, periwinkles and snails are good sources of animal protein. The snail species have the highest protein content, followed by raw pink shrimps and periwinkle species while crab species have the least. Apart from the high levels of protein, snails have been reported to contain low but highly polyunsaturated lipid content which prevents cardiovascular problems [30].

The protein contents in the species confirmed that shrimps, periwinkles, snail and crabs are excellent sources of protein if they are free of environmental contaminations.

#### **CONCLUSIONS**

The concentrations of Cu and Zn in shrimps, crabs and periwinkles were higher than WHO permissible limits in crustacean while those of snails were within the limits. It is therefore imperative to monitor heavy metals contamination of aquatic bodies in Lagos and Ibadan. Copper, Zn, Pb, and Cd content in land snails were much below the WHO and EC permissible limits. Consequently, human consumption of snail is safe from the point of being free from HMs contamination and their rich protein content. The values of essential and non-essential components of shrimps, crabs and periwinkle confirmed that they are excellent dietary sources of Cu, Zn and protein if uncontaminated by environmental pollutions. Gladiator swim crab (*C. pallidus*) bio-concentrates both essentials and non-essentials HMs above the permissible levels, hence, it should be consumed with caution. Shrimps, crabs and periwinkles are aquatic organisms and can be used to indicate the effects of anthropogenic activities on aquatic bodies in Nigeria. Drying reduced HMs in shrimps to levels below WHO and EC permissible limits. In view of this, it is advisable to eat dry shrimps instead of raw shrimps in areas of suspected environmental contamination.



Table 1: Heavy metals concentrations ( $\mu g/g$ , dry weight) and crude protein content (%) in raw shrimps

Locations	Sites	Raw Pink shrimp (P. notialis)					Raw Guinea Shrimp (P. atlantica)					
		Cu	Zn	Pb	Cd	Protein	Cu	Zn	Pb	Cd	Protein	
Lagos	Ibeshe	35.1	212	0.92	< 0.01	81.2	35.7	195	0.95	< 0.01	66.8	
	Ogudu	30.1	170	0.90	< 0.01	78.6	31.2	170	0.91	< 0.01	77.4	
Ibadan	Ashejire	36.2	220	1.35	< 0.01	65.1	37.5	150	1.12	< 0.01	65.3	
	Eleyele	31.2	175	1.10	< 0.01	77.6	32.1	174	1.12	< 0.01	78.2	



Table 2: Heavy metals concentrations ( $\mu g/g$ , dry weight) and crude protein content (%) in dry shrimps

Locations	Sites	Dry Pink shrimp (P. notialis)						Dry Guinea Shrimp (P. atlantica)					
		Cu	Zn	Pb	Cd	Protein	Cu	Zn	Pb	Cd	Protein		
Lagos	Ibeshe	12.8	18.3	0.33	< 0.01	64.3	11.3	17.6	0.35	< 0.01	64.3		
	Ketu	13.8	18.6	0.35	< 0.01	65.2	13.1	17.3	0.34	< 0.01	65.8		
Ibadan	Ashejire	11.9	45.6	0.25	< 0.01	71.8	12.2	39.8	0.31	< 0.01	71.2		
	Bodija	11.3	18.4	0.33	< 0.01	71.2	12.3	18.1	0.45	< 0.01	72.2		

Table 3: Heavy metals concentrations ( $\mu g/g$ , dry weight) and crude protein content (%) in crabs

Locations	Sites	Lagoon land crab (C. armatum)						Gladiator swim crab (C. pallidus)					
		Cu	Zn	Pb	Cd	Protein	Cu	Zn	Pb	Cd	Protein		
Lagos	Ibeshe	15.3	145	0.97	0.30	39.8	19.1	190	2.50	0.10	38.2		
	Abule	15.8	140	1.25	0.25	38.3	23.8	190	2.46	0.40	33.3		
Ibadan	Ashejire	17.8	170	0.63	0.15	33.7	21.6	170	3.26	0.10	35.7		
	Eleyele	17.2	165	0.57	0.11	33.2	n.a	n.a	n.a	n.a	n.a		



Table 4: Heavy metals concentrations ( $\mu$ g/g, dry weight) and crude protein content (%) in periwinkle

(70) III periwilkie											
Locations	Sites	Periwinkle		(T. fuscatus)			Periwinkle		(L. littorea)		
		Cu	Zn	Pb	Cd	Protein	Cu	Zn	Pb	Cd	Protein
Lagos	Ketu	17.2	36.3	1.75	0.03	75.7	16.3	35.9	1.77	0.03	76.2
	Ogudu	14.3	37.6	0.87	0.03	71.3	14.4	36.6	0.91	0.03	72.2
	Odoguyan	15.1	35.7	0.95	0.03	71.2	15.4	36.5	0.81	0.05	71.7
	Mile 12	15.2	32.1	1.10	0.05	72.4	15.4	32.8	0.96	0.03	73.1
Ibadan	Bodija	15.6	32.2	0.75	0.01	74.1	15.7	33.1	0.82	0.01	75.1
	Eleyele	15.1	32.6	0.75	0.03	70.2	15.6	32.2	0.76	0.03	71.2

Table 5: Heavy metals concentrations ( $\mu g/g$ , dry weight) and crude protein content (%) in matured snails

Locations	Sites		red Afr	_	ant snail	Matured Edible land snail (G. africana)						
		Cu	Zn	Pb	Cd	Protein	Cu	Zn	Pb	Cd	Protein	
Lagos	Ketu	7.15	22.8	0.75	< 0.01	81.4	6.55	22.1	0.72	< 0.01	81.9	
	Ibeshe	8.55	22.1	0.71	< 0.01	80.6	7.75	21.8	0.73	< 0.01	80.5	
Ibadan	Ashejire	5.65	19.2	0.56	< 0.01	78.9	5.15	20.2	0.55	< 0.01	79.3	
	Bodjia	5.55	21.4	0.65	< 0.01	76.2	6.12	22.2	0.62	< 0.01	76.1	



Table 6: Heavy metals concentrations ( $\mu g/g$ , dry weight) and crude protein content (%) in baby snails

Locations	Sites	Baby	Baby African giant snail					Baby Edible land snail					
		(A. marginata)					(G. africana)						
		Cu	Zn	Pb	Cd	Protein	Cu	Zn	Pb	Cd	Protein		
Lagos	Ketu	5.25	22.1	0.51	< 0.01	68.1	5.12	23.2	0.55	< 0.01	68.3		
	Ibeshe	4.75	24.2	0.57	< 0.01	67.2	4.26	23.8	0.55	< 0.01	68.2		
Ibadan	Ashejire	5.76	23.7	0.51	<0.01	65.2	5.25	24.10	0.61	<0.01	65.3		



#### **REFERENCES**

- 1. **Akin-Oriola G, Anetekhai M and K Olowonirejuaro** Morphometric and Meristic Studies in Two Crabs: *Cardisoma armatum* and *Callinectes pallidus*. Turk. J. Fish. Aquat. Sc. 2005; **5:** 85-89.
- 2. **Bebianno MJ and WJ Langston** Cadmium and metallothionein turnover in different tissues of the gastropod *Littorina littorea*. Talanta 1998; **46:** 301–313.
- 3. **Adeyeye EI and EO Afolabi** Amino acid composition of three different types of land snails consumed in Nigeria. Food Chem. 2004; **85:** 535–539.
- 4. **Bragigand V, Berthet B, Amiard JC and PS Rainbow** Estimates of trace metal bioavailability to humans ingesting contaminated oysters. Food Chem. Toxicol. 2004; **42 (11):** 1893-1902.
- 5. Barrento S, Marques A, Teixeira B, Vaz-Pires P, Carvalho M L and ML Nunes Essential elements and contaminants in edible tissues of European and American lobsters (shrimps). Food Chem. 2008; 111 (4): 862-867.
- 6. **WHO.** World Health Organization. Elemental speciation in human health risk assessment. Environmental Health Criteria 234. Geneva Switzerland: World Health Organization, 2006. Accessed from <a href="http://www.inchem.org/documents/ehc/ehc/ehc/234.pdf">http://www.inchem.org/documents/ehc/ehc/ehc/234.pdf</a> 08 March, 2013.
- 7. **Garcia-Rico L, Leyva-Perez J and ME Jara-Marini** Content and daily intake of copper, zinc, lead, cadmium, and mercury from dietary supplements in Mexico. Food Chem Toxicol. 2007; **45:** 1599–1605.
- 8. **Cox HE and D Pearson** The Chemical Analysis of Foods. Chemical Publishing Company, USA. 1962: 1-494.
- 9. **Liang LN, He B, Jiang GB, Chen DY and ZW Yao** Evaluation of molluscs as biomonitors to investigate heavy metal contaminations along the Chinese Bohai Sea. *Sci. Total Environ.* 2004; **324 (1–3):** 105-113.
- 10. **Commission Regulation (EC) No.** 420/2011 of 29 April 2011 amending Regulation (EC) No 1881/2006 setting maximum levels of certain contaminants in foodstuffs. Official journals of the European Union, 2011, L 111: 3-6.
- 11. **Guerin T, Chekri R, Vastel C, Sirot V, Volatier JL, Leblanc JC and L Noel** Determination of 20 trace elements in fish and other seafood from the French market. *Food Chem.* 2011; **127** (3): 934-942.
- 12. Marques A, Teixeira B, Barrento S, Anacleto P, Carvalho ML and ML Nunes Chemical composition of Atlantic spider crab *Maja brachydactyla*: Human health implications. *J. Food Compos. Anal.* 2010; **23** (3): 230-237.



- 13. **De Wolf H, Van den Broeck H, Qadah D, Backeljau T and R Blust** Temporal trends in soft tissue metal levels in the periwinkle *Littorina littorea* along the Scheldt estuary, The Netherlands. *Mar. Pollut. Bull.* 2005; **50:** 463–484.
- 14. **Van den Broeck H, De Wolf H, Backeljau T and R Blust** Effect of metal accumulation on metallothionein level and condition of the periwinkle Littorina littorea along the Scheldt estuary (the Netherlands). *Environ. Pollut.* 2010; **158:** 1791–1799.
- 15. **Onianwa PC, Adeyemo AO, Idowu OE and EE Ogabiela** Copper and zinc contents of Nigerian foods and estimates of the adult dietary intakes. *Food Chem.* 2001; **72:** 89-95.
- 16. **Kang SG, Wright D A and CH Koh** Baseline metal concentration in the Asian periwinkle Littorina brevicula employed as a biomonitor to assess metal pollution in Korean coastal water. *Sci. Total Environ.* 2000; **263** (1–3): 143-153.
- 17. **Umoh IB and O Bassir** Lesser known sources of protein in some Nigerian peasant diets. *Food Chem.* 1977; **2** (**4**): 315-321.
- 18. **Bono G, Gai F, Peiretti PG, Badalucco C, Brugiapaglia A, Siragusa G and GB Palmegiano** Chemical and nutritional characterisation of the Central Mediterranean Giant red shrimp (*Aristaeomorpha foliacea*): Influence of trophic and geographical factors on flesh quality. *Food Chem.* 2012; **130:** 104–110.
- 19. **Adeyeye EI, Adubiaro HO and OJ Awodola** Comparability of Chemical Composition and Functional Properties of Shell and Flesh of (*Penaeus notabilis*). *Pakistan J. Nut.* 2008; **7 (6):** 741-747.
- Liu L, Liu CC and JL Li Comparison of Biochemical Composition and Nutritional Value of Antarctic Krill (*Euphausia superb*) with Several Species of Shrimps. *Adv. Mat. Res.* 2011; 361 –363: 799-803.
- 21. **Chen D-W, Zhang M and S Shresth** Compositional characteristics and nutritional quality of Chinese mitten crab (*Eriocheir sinensis*). *Food Chem.* 2007; **103 (4):** 1343–1349.
- 22. Maulvault AL, Anacleto P, Lourenço HM, Carvalho ML, Nunes ML and A Marques Nutritional quality and safety of cooked edible crab (*Cancer pagurus*). *Food Chem.* 2012; **133:** 277–283.
- 23. **Benjakul S and N Sutthipan** Comparative study on chemical composition, thermal properties and microstructure between the muscle of hard shell and soft shell mud crabs. *Food Chem.* 2009; **112:** 627–633.
- 24. **Otitoloju AA and KN Don-Pedro** Integrated laboratory and field assessments of heavy metals accumulation in edible periwinkle, Tympanotonus fuscatus var radula (L.). *Ecotox. Environ. Safe* 2004; **57:** 354–362.



- 25. **De Wolf H, Backeljau T and R Blust** Heavy metal accumulation in the periwinkle *Littorina littorea*, along a pollution gradient in the Scheldt estuary. Sci. Total Environ. 2000; **262** (1–2): 111-121.
- 26. **Sivaperumal P, Sankar TV and PGV Nair** Heavy metal concentrations in fish, shellfish and fish products from internal markets of India vis-a-vis international standards. *Food Chem.* 2007; **102** (3): 612-620.
- 27. **Vallee BL and DS Auld** Zinc coordination, function, and structure of zinc enzymes and other proteins. *Biochemistry-US* 1990; **29** (**24**): 5647–5659.
- 28. **Akintola SL, Brown A, Bakare A, Osowo OD and BO Bello** Effects of Hot Smoking and Sun Drying Processes on Nutritional Composition of Giant Tiger Shrimp (*Penaeus monodon, Fabricius*, 1798). Pol. J. Food Nutr. Sci. 2013; **63(4)**: 227-237.
- 29. **Hamilton JA** New insights into the roles of proteins and lipids in membrane transport of fatty acids. *Prostag. Leukotr. Ess.* 2007; **77** (**5–6**): 355–361.
- 30. Milinsk MC, Padre RD, Hayashi C, Oliveira CC, Visentainera JV, Souza NE and M Matsushita Effects of feed protein and lipid contents on fatty acid profile of snail (*Helix aspersa maxima*) meat. J. Food Compos. Anal. 2006; 19: 212–216.

