ANALYSIS AND ESTIMATED DAILY INTAKE OF TOXIC METALS IN CARDISOMA ARMATUM AND ITS HEALTH RISK INDEX IN LAGOS, SOUTHWEST NIGERIA.

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ABSTRACTS

Background: Cardisoma Armatum has been one of the popular sources of protein among many people for this reason, we are motivated to identify and quantify the levels of Pb, Cr, Mn, Cd, Zn, Cu, As, and Ni from the edible tissues of Cardisoma Armatum. **Objectives:** This study aimed to quantify the level of metals in Cardisoma Armatum, estimate the daily intake of these metals then use that to determine the health risk index of the samples. Methodology: Samples were collected from a fresh water coastal area and the edible tissues were separated from the other parts; this was then digested for Atomic Absorption Spectrophotometer (AAS) for the analysis of the samples. Results: Mean concentration of lead (Pb) range is 0.013±0.01 - 0.0015±0.10 mg/kg with mean of 4.73E-03 mg/kg. Chromium (Cr) range is 0.01±0.50 – BDL with mean of 5.54E-03 mg/kg Zinc (Zn) the value range is 5.13±0.10 - 0.73±0.40 and its mean is 3.94E+00 mg/kg; Cadmium (Cd) has its value range of 0.0065±0.05 - 0.0005±0.25 and the mean of 1.43E-03 mg/kg. Copper (Cu) has the range of 0.31±0.10 - 0.028±0.04 and a mean of 1.82E-01 mg/kg; Nickel (Ni) has the range of 3.25±0.06 – BDL with a mean of 1.59E+00; Manganese (Mn) has the range of 1.54±0.03 - 0.12±0.01 an mean of 9.55E-01 mg/kg the Arsenic (As) has the concentration of 0.0018±0.76 – BDL and a mean of 9.06E-04 mg/kg. These values were used to compute the Estimation of Daily Intake (EDI) per metals per sample. The Mean EDI for each metal is in the range of: (Pb) 8.99E-06 - 1.08E-06; (Cr) 0.00 - 1.80E-06; (Zn) 3.95E-03 - 1.47E-03; (Cd) 4.77E-06 - 3.59E-07; (Cu) 2.19E-04 - 1.97E-05; (Ni) 0.00 - 3.24E-05; (Mn) 9.82E-04 – 8.63E-05; (As)0.00 – 1.79E-07. Conclusion: Health risk index (HRI) was obtained; the metal levels in edible tissues of Cardisoma Armatum did not exceed the standard guideline values. Thus, the estimated hazard index (HI) suggests that these metals in the edible tissues of the Cardisoma Armatum were not toxic for consumers, where the HIs of all the considered metals were below the value of 1.

Keywords: Cardisoma Armatum, Heavy metals, Hazard quotient, Health risk index, Cancer, Non-carcinogens.

INTRODUCTION

Nearly every part of our environment has been contaminated by heavy metals and this has compromised the ability of our environment to foster life and offer its intrinsic values, so human and animal's health has become threatened. Contaminations from heavy metals are an important factor due to its hazardous effects on ecosystem. From an ecological. evolutionary, nutritional, and environmental perspective, metal toxicity arising from different sources may be a problem if the concentration increases significantly (Jaishankar et al., 2014; Nagajyoti et al., 2010). However, at relatively

low levels, most of the metals are tolerable, but at certain concentration they become toxic in aquatic life even to those that consumed them. Heavy metals like, Lead, cadmium, mercury, and arsenic are widely dispersed in the environment, but they have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Draghici et al., 2010; Vieira et al., 2011). Toxic metals can impair important biochemical systems, constituting an important threat for the health of plants and animals. Heavy metal contamination of aquatic life and coastal ecosystem is associated with a wide range of sources such as dumping industrial and

domestic waste. Most of the aquatic animals such as crabs, fish etc., may not escape the harmful effects of heavy metals. Thus, the extent of accumulation in biota is dependent on the chemical effects of the metal, its tendency to bind to materials. Recently, there are concerns about the worldwide pollution by heavy metals (long biological half-lives) in relation to their bioaccumulation over time period in food chain and aquatic life, that may be causing serious health risks in human's consumers of these animals (Liu et al., 2003; Lie et al., 1990; Aghamirlou et al., 2015). Immoderate accumulation of heavy metals in human bodies may generate problems such as: cardiovascular kidney, nervous and bone diseases (Steeland et al., 2000). Thus, this study aims to quantify the quantity of intake of the identified toxic metals in Cardisoma Armatum and make recommendations based on the outcome of the results.

MATERIAL & METHODS

Sampling Location

University of Lagos lies on longitude 3^0 23' 45" E and latitude 6^0 27' 11" N and is bounded to the south by Lagos lagoon (figure 1) which link to the Atlantic Ocean. This huge body of water provides the breeding ground for the crabs of various types at the shore. There is lagoon is a busy place for the local fishermen and the marketers of these aquatic life that are harvested from both the lagoon and the Atlantic Ocean.



Figure (1): Map of University of Lagos and Lagos Lagoon (Sowunmi Map) Sample collection

Cardisoma Armatum generally called crabs used in this work were collected based on their availability at University of Lagos waterfront and their popularity in local diets. Five healthy medium size adult Cardisoma Armatum (figure 2), per collection points were harvested from University of Lagos waterfront the designated sampling points. The crabs were collected for a period two years.



Figure (2): Cardisoma Armatum commonly found along University of Lagos waterfront.

Sample preparation and Concentration measurements

Cardisoma Armatum collected was clean in fresh water for few hours. Muscle was dissected out from these crabs and taken into petri-dishes and was placed in a hot air oven at a constant temperature of 60° C for 48 -72 hours. Digestion of samples was in beaker on a hot plate, 0. 5 gm. of the muscle was weighed out in an open beaker then followed by the addition nitric acid (HNO₃) with per chloric acid (HClO₄) in (4:1) ratio for digestion to take place. This was kept on hot plate with the temperature gradually allowed to rise to 60° C continues adding both acids in (4:1) ratio to obtained colorless sample. This was allowed to cool and transferred to 25 ml volumetric flasks and made up to mark with de-ionized water. The heavy metals concentration was analyzed from the muscle. The digests were stored in plastic bottles afterwards the heavy metal concentration was determined using Atomic Absorption spectrophotometer (AAS) model 306, manufactured by Perkin-Elmer

RESULTS

The mean concentrations of heavy metal were recorded from the samples of Cardisoma Armatum collected from each of the sampling location is as shown in Table 1.

Table (1): Mean \pm SD of the neavy metal concentration in Crabs (mg/kg)									
Sample site	Pb	Cr	Zn	Cd	Cu	Ni	Mn	As	
1	0.013±0.	DDI	5.13±0.	1.25E-	0.27±0.0	2.50±0.	1.37±0.	0.25E-	
	01	BDL	01	03±0.01	1	13	13	03±0.31	
2	0.010±0.	DDI	4.83±0.	0.05E-	0.073±0.	DDI	0.36±0.	0.75E-	
	00	BDL	13	02 ± 0.00	22	BDL	00	03±0.04	
3	0.003±0.	DDI	5.50±0.	0.01E-	0.11±0.0	DDI	1.07±0.	0.01E-	
	01	BDL	33	01±0.02	4	BDL	31	01±0.15	
4	0.005±0.	0.01.0.25	4.65±0.	0.15E-	0.14±0.1	0.75±0.	0.94±0.		
	02	0.01 ± 0.25	02	02±0.14	6	01	13	BDL	
5	0.003±0.	BDL	2.70±0.	0.75E-	0.15±0.1	0.25±0.	0.79±0.	1.75E-	
	50		13	03±0.03	5	01	02	03±0.76	
6	0.002±0.	0.01±0.50	0.73±0.	0.01E-	0.24±0.0	0.75±0.	0.83±0.	0.75E-	
	10		40	01±0.13	2	21	04	03±0.00	
7	0.003±0.	0.003 ± 0.1	4.80±0.	0.05E-	0.29±0.0	0.05±0.	1.20±0.	0.05E-	
/	24	0	25	02 ± 0.02	5	04	02	02 ± 0.08	
8	0.005±0.	0.005 ± 0.3	2.05±0.	0.75E-	0.31±0.1	וחם	0.12±0.	1.25E-	
	51	1	01	03±0.01	0	DDL	01	03±0.25	
9	0.005±0.	BDL	3.90±0.	0.05E-	0.23±0.0	3.25±0.	1.54±0.	0.01E-	
	15		03	02 ± 0.25	5	06	03	01±0.12	
10	$0.002\pm0.$	0.0002±0.	5.13±0.	0.65E-	0.03 ± 0.0	וחק	1.35±0.	BDL	
	51	01	10	02 ± 0.05	4	DDL	05		
Mean	4 73E 03	5.54E-03	3.94E+0	1 43F-03	1.82E-01	1.59E+0	9.55E-	9.06E-04	
	ч. <i>тэ</i> ц-05		0	0		0	01		

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n = 5; BDL - Below the Detectable Level

Table 1 shows that the mean concentrations of lead (Pb) range is 0.013±0.01 - 0.002±0.10 mg/kg with mean of 4.73 x 10⁻⁰³ mg/kg. Chromium (Cr) range is 0.01 ± 0.50 – BDL with mean of 5.54 x 10^{-03} mg/kg, Zinc (Zn) the value range is 5.13±0.10 - 0.73±0.40 and its mean is 3.94 mg/kg; Cadmium (Cd) has its value range of 0.65 x $10^{-02} \pm 0.05 - 0.05 \times 10^{-02} \pm 0.25$ and the mean of 1.43E-03 mg/kg. Copper (Cu) has the range of 0.31±0.10 - 0.03±0.04 and a mean of 1.82E-01 mg/kg; Nickel (Ni) has the range of 3.25 ± 0.06 – BDL with a mean of 1.59; Manganese (Mn) has the range of 1.54±0.03 - 0.12±0.01 an mean of 9.55 x 10^{-01} mg/kg the Arsenic (As) has the concentration of $1.75 \times 10^{-03} \pm 0.76$ – BDL and a mean of 9.06 x 10⁻⁰⁴ mg/kg. In general, the values obtained for these heavy metals, are very low, the bioaccumulations effects of these metals, for a long period of consumption time of this crabs be very significant, the degree of severe toxic effects on most organisms by other metals varied (Fergusson 1990).

DISCUSSIONS

Risk Assessment of metals in Cardisoma Armatum

Estimated daily intake of metals (EDI) were computed to assess the risk of metals intake through ingestion using the Hazard Quotient (HQ) and the Health Risk index as described in the research articles (Khan et al 2008).

Estimation of Daily Intake (EDI) of the identified metals

Estimated daily intake (mg\kgbw\day) of metals of heavy metals identified through ingestion by consumption of Cardisoma Armatum as the medium (pathway) to human can be estimated (Song et al., 2009).

Estimated daily intake was determined by using the average concentration obtained for each heavy metal in Cardisoma Armatum samples and these relationships.

$$EDI = \frac{MC \times CIR}{ABW}$$

MC the mean concentration of heavy metals in the samples collected (mg/kg wet weight); CIR the average rate ingestion of Cardisoma Armatum per person taken as 49.5 x 10^{-3} kg/day ABW the average body weight of the consumers 68.8kg (Little et al., 2002; Speedy, 2003).

Target Hazard Quotient (THQ)

For non-carcinogenic, THQ estimated the risk level due to pollutant exposure. The human health risk can be estimated using the metal contaminated Cardisoma Armatum consumed, Using THQ calculations obtained from USEPA (United States Environmental Protection Agency, 2008), the needed equation used for the estimation of THQ is given below.

$$THQ = \frac{FE \times BD \times CIR \times Cf \times MC}{ABW \times ATn \times RfD} \times 10^{-3}$$

FE the exposure time (365 days/year); BD the period of exposure (30 years for non-cancer risk);

CIR Cardisoma Armatum ingestion rate (49.5 g/person/day); Cf is conversion factor (0.208) to convert fresh weight (FW) to dry weight

(DW) given that 79% in moisture content of Cardisoma Armatum; MC is concentration of heavy metal in Cardisoma Armatum (mg/kg ww), ABW is average body weight taken to be 68.8 kg; ATn is average exposure time for non-carcinogens (FE×BD) (365 days/year for 30 years, hence ATn = 10,950 days, this is used characterizing no cancer risk (United States Environmental Protection Agency 2010). RfD (mg kg⁻¹ day⁻¹) the oral reference dose for specific metal; this is estimate of the daily exposure that human population may be continuously exposed to over a lifetime without an appreciable risk of deleterious effects (United States Environmental **Protection Agency 2016**).

Table (2): THQ estimated the health risk level due to pollutant exposure for non-carcinogenic

Pb	Cr	Zn	Cd	Cu	Ni	Mn	As
3.53E-04	0	0.15	3.53E-05	7.62E-03	7.06E-02	3.85E-02	7.06E-06
2.68E-04	0	0.14	1.41E-05	2.05E-03	0	1.00E-02	2.12E-05
7.06E-05	0	0.16	2.82E-05	2.97E-03	0	3.01E-02	2.82E-05
1.41E-04	2.82E-04	0.13	4.24E-05	3.95E-03	2.12E-02	2.64E-02	0
7.06E-05	0	0.08	2.12E-05	4.24E-03	7.06E-03	2.23E-04	4.94E-05
4.23E-05	2.82E-04	0.02	2.82E-05	6.71E-03	2.12E-02	2.34E-02	2.12E-05
7.06E-05	7.06E-05	0.14	1.41E-05	8.12E-03	1.27E-03	3.39E-02	1.41E-05
1.41E-04	1.41E-04	0.06	2.12E-05	8.61E-03	0	3.39E-03	3.53E-05
1.27E-04	0	0.11	1.41E-05	6.35E-03	9.17E-02	4.35E-02	2.82E-05
4.94E-05	5.65E-06	0.15	1.84E-04	7.76E-04	0	3.82E-02	0

Health Risk Index (HRI)

HRI = THQ(Pb) + THQ(Mn) + THQ(Cr) + THQ(Cd) + THQ(Zn) + THQ(Cu) + THQ(As)THQ (Pb) is the Targeted Quotient.

HRI obtained from the sum of THQs of individual elements (Warren, 1981).

For HRI less than unity is safe; then for HRI greater than unity is hazardous

Target Cancer Risk (TCR)

TCR has been used to indicate carcinogenic risks. This is provided by USEPA 2011 chat.

$$TCR = \frac{EF \times EDI \times CIR \times MC \times CPSo}{WAB \times ATc} \times 10^{-3}$$

MC the metal concentration (mg/kg), in Cardisoma Armatum; CIR the ingestion rate (g/day) in Cardisoma Armatum; CPSo the carcinogenic potency slope for oral route (mg/kg bw/day)⁻¹ (Pb = 0.0085; As = 1.5); ATc the time average of carcinogens (365 days/year for 70 years), as used by USEPA (United States Environmental Protection Agency 2008).





points.

From all the samples collected from various points the EDI was obtained for each element detected from the samples. Comparison of EDI for each of the samples per element is as illustrated in figure 3a - 3j above. In sample 1, figure 3a, shows the EDI obtained with Zn has the highest of 0.369×10^{-02} , Ni is 0.180x 10⁻⁰², Cu is 0.019 x 10⁻⁰², Mn is 0.098 x 10⁻⁰², Pb is 8.994 x 10⁻⁰⁶ and As is 1.798x 10⁻ ⁰⁷. Figure 3b shows the EDI for sample 2, this indicates that the elements detected from this sample have EDI for Zn to be 0.347x 10⁻⁰², Cu is 0.052x 10⁻⁰², Mn is 0.026 x 10⁻⁰², Pb is 6.835x 10⁻⁰⁶ and As is 5.396x 10⁻⁰⁷. Figure 3c shows the EDI comparison from sample 3, for

Zn to be 0.395x 10⁻⁰², Cu is 0.076x 10⁻⁰², Mn is $0.077 \ x \ 10^{-02}$, Pb is $1.789x \ 10^{-06}$ and As is 7.194x 10⁻⁰⁷. Figure 3d shows the EDI comparison for sample 4, with Zn to be 0.335x10⁻⁰², Cu is 0.010x 10⁻⁰², Mn is 0.067 x 10⁻⁰², Pb is 3.597x 10⁻⁰⁶ and As is 0, Cd is 0.011x 10⁻⁰³, Cr is 0.072x 10⁻⁰², Ni is 0.054x 10⁻⁰², Figure 3e shows the EDI comparison for sample 5, with Zn to be 0.194x 10⁻⁰²,Cu is 0.011x 10⁻⁰²,Mn is $0.057 \ x \ 10^{-02}$, Pb is $1.779x \ 10^{-06}$ and As is 1.259x10⁻⁰⁶, Cd is 0.054x 10⁻⁰⁴, is 0.072x 10⁻⁰² ,Ni is 0.018x 10⁻⁰², Figure 3f shows the EDI comparison for sample 6, with Zn to be 0.052x10⁻⁰²,Cu is 0.017x 10⁻⁰²,Mn is 0.060 x 10⁻⁰²,Pb is 1.079x 10⁻⁰⁶ and As is 5.396x10⁻⁰⁷, Cd is 0.072x 10⁻⁰⁵, Cr is 0.072x 10⁻⁰², Ni is 0.054x 10⁻⁰², Figure 3g shows the EDI comparison for sample 7, with Zn to be 0.345x 10⁻⁰², Cu is 0.021x 10⁻⁰², Mn is 0.086 x 10⁻⁰², Pb is 1.798x 10⁻⁰⁶ and As is 3.597 x10⁻⁰⁷, Cd is 0.036 x10⁻⁰⁵, Cr is 0.018x 10⁻⁰⁵, Ni is 0.032x 10⁻⁰³, Figure 3h shows the EDI comparison for sample 8, with Zn to be 0.345×10^{-02} , Cu is 0.021×10^{-02} , Mn is 0.086 x 10⁻⁰², Pb is 1.798x 10⁻⁰⁶ and As is 3.597x10⁻⁰⁷, Cd is 0.036x 10⁻⁰⁵, Cr is 0.018x 10⁻⁰², Ni is 0.032x 10⁻⁰², Figure 3i shows the EDI comparison for sample 9, with Zn to be 0.147x 10⁻⁰², Cu is 0.022x 10⁻⁰², Mn is 0.086 x 10⁻⁰³, Pb is 3.597x 10⁻⁰⁶ and As is 8.993x10⁻⁰⁷, Cd is 0.054x 10⁻⁰⁵, Cr is 0.036x 10⁻⁰⁴, Ni is 0., Figure 3j shows the EDI comparison for sample 10, with Zn to be 0.369x 10⁻⁰², Cu is 0.002x 10⁻⁰², Mn is 0.097 x 10⁻⁰², Pb is 1.259x 10⁻⁰⁶ and As is 0, Cd is 0.047x 10⁻⁰⁴, Cr is 0.014x 10⁻⁰⁵, Ni is 0.,

In the estimation of the HRI using the THQ, we took into considerations the non-carcinogenic pollutants and the carcinogenic

Pollutants as identified in the samples. Hence, human health risks have been estimated from consuming metal contaminated Cardisoma Armatum in each of the samples. Fig 4 indicates the average levels of HRI in each of the samples. Samples 1 and 2 have the value of HRI of about 0.26 and 0.25respectively and the other samples have less than these values. However, for high health risk Cardisoma Armatum the value of HRI must be greater than unity (HRI > 1), but from all the samples the value of HRI is less than unity (HRI < 1) as illustrated in fig 4.

According to USEPA report 2011, TCR have been used to indicate carcinogenic risks and in this report risk-based concentrations have been provided, hence carcinogenic potency slope (CPSo) for oral route in both Pb and As was. obtained.



Figure (4): Health Risk Index (HRI) per sample collected.

These values are for Pb = 0.0085; and for As = 1.5. Fig 5 shows the target cancer risk (TCR) level from Pb in each of the samples. Samples 1 and 2 have the highest values of 3.71×10^{-08} and 2.82×10^{-08} , while samples 4, 8 and 9 values are 1.48×10^{-08} , 1.48×10^{-08} and 1.34×10^{-08} respectively.

Samples 3, 5 and 7 TCR values are 7.42 $x10^{-09}$, 7.42 $x10^{-09}$, and 7.42 $x10^{-09}$ respectively. Then samples 6 and 10 had TCR values of 4.45 $x10^{-09}$ and 5.19 $x10^{-09}$. These values though are small but can be significant over a period. In Fig 6 the TCR in As have been illustrated. Sample 5 had a TCR value of 9.16 $x10^{-07}$ this the highest for the exposure to As.





While samples 8 TCR value for As is 6.54×10^{-07} , samples 3 and 9 have the same TCR values of 5.24×10^{-07} for As each respectively.



Figure (6): Target Cancer Risk (TCR) indicator due to As.

In samples 4 and 10, As was not detected therefore the TCR exposure level is zero. But samples 2 and 6 have the TCR value of 3.93×10^{-07} each respectively. In samples 1 and 7 the level of TCR is 1.31×10^{-07} and 2.62×10^{-07} in As respectively.

CONCLUSION

In this study Pb, Cr, Mn, Cd, Zn, Cu, As, and Ni have been quantified in Cardisoma Armatum and the mean EDI of each metals in each of the samples have been estimated this is as shown in figures 3 a - 3j. Though the values of EDI of the metals were less, it is evident that Cardisoma Armatum consumers may be unsafe as heavy metals bioaccumulation may post health risk over a long time of consumption. Sample 8 shows a significant values of EDI when compared metals by metals in the samples (Fig. 3h) with Zn EDI of $0.345x \ 10^{-02}$, Cu EDI of $0.021x \ 10^{-02}$,Mn EDI of $0.086 x \ 10^{-02}$,Pb

EDI of 1.798x 10-06 and As is of EDI of 3.597x10⁻⁰⁷, Cd is of EDI of 0.036x 10⁻⁰⁵, Cr is of EDI of 0.018x 10⁻⁰², Ni EDI of 0.032x 10⁻⁰². The average Health risk index (HRI) was also estimated in the study and the values obtained are generally less than unity. HRI < 1 implies less risk in the consumptions of Cardisoma Armatum indicating that our samples of Cardisoma Armatum are free from any risk; however, HRI > 1 indicates the level is hazardous this was not obtained in this study, however more work may show significant change over a long period of time. For the target cancer risk due to exposure in Pb and As the values obtained from this study was small and therefore we can concluded that it safe to take Cardisoma Armatum collected from the coastline area of Lagos Southwest Nigeria.

RECOMMENDATIONS

It is recommended that the consumptions of Cardisoma Armatum from the University of Lagos waterfront and the immediate coastline area are safe. However, more study is required on seasonal collections of Cardisoma Armatum in the area for more investigation on the toxic metals. The data collected can also use as a baseline data for the area of study.

It is also recommended that other aquatic life around the area be studied for toxic metals because there are huge wastes begin deposited in the coastline area.

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