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BIOACCUMULATION OF HEAVY METALS IN *THAIS SPP* OBTAINED FROM THE NIGER DELTA REGION OF NIGERIA AND ASSOCIATED HEALTH RISKS DUE TO CONSUMPTION

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ABSTRACT

Heavy metal concentrations were assessed in *Thais* spp obtained from four stations in Bakana (RVS1 and 2) and Ikang (CRS1 and 2) of the Niger Delta. Fifty samples were collected from each station for six months from October 2018 to March 2019. The Atomic Absorption Spectrophotometric method was used for analysis of heavy metals. Mean metal concentrations in *Thais spp* at Ikang and Bakana were as follows: **Cr**:CRS1=4.03, CRS2=3.82, RVS1=4.21, RVS2=4.038,**Cd**:CRS1=0.78,CRS2=0.57, RVS1=0.86, RVS2=0.73, **Pb**:CRS1=4.64,CRS2=3.62,RVS1=5.88,RVS2=4.83,**Zn**:CRS1=26.46, CRS2=21.34, RVS1:38.77, RVS2=37.43,**Cu**:CRS1=14.96,CRS2=18.39,RVS1=31.45,RVS2=31.86,**Fe**:CRS1:103.86,CRS2=100. 18,RVS1=132.42,RVS2=129.24. Health risk assessment was also carried out to evaluate the estimated daily intake, hazard quotient (carcinogenic and non-carcinogenic) and hazard index. The concentrations of five heavy metals were also compared with WHO permissible limit and were all higher except Zn. Estimated Daily Intake values were lower than the reference oral doses of the respective metals indicating low risk. THQ, HQ and Hazard index (carcinogenic and non-carcinogenic) for all stations were < 1 indicating minimal health risk to consumers of *Thais spp* contaminated with heavy metals in the study area . This study thereby concluded that *Thais spp obtained* from Ikang and Bakana areas of the Niger Delta is safe for consumption.

INTRODUCTION

The rapid development of industries and agriculture has resulted in increasing pollution by heavy metals, which are a significant environmental hazard for invertebrates, fish, and humans (Uluturhan and Kucuksezgin, 2007). Pollution is the altering of the environment by activities of man, by addition of substances partially or wholly which will result in an imbalance and hence have deleterious effect on the living organisms including man (Sunder,1988). The sea and other water bodies are receptacles for the wastes being generated by industries and humans that live near rivers, sea animals are always part of the organisms endangered and have the potential to accumulate these poisonous wastes like heavy metals (Paul and James, 2011). Used oil and other petroleum products are also deposited in drainages and washed down the sea and rivers as runoffs (Johnson,2008). The Niger Delta is located in the southern part of Nigeria and plays host to several oil exploring companies and manufacturing industries. It also accommodates Petrochemical, refining and fertilizer industries (Akpila , 2006) which implies that the region is prone to pollution.

Heavy metal pollution is one of the challenges of coastal waters as a result of human activities such as oil exploration and exploitation, construction and fabrication of marine boats, disposal of industrial and domestic wastes and sailing (Moslen and Miebaka, 2016). Pollution of aquatic ecosystems by heavy metals is an important environmental problem, as they constitute some of the most dangerous toxicants that can be bioaccumulated in living tissues (Guo, *et al*., 1997; Omoregie *et al*., 2002). Otitoju and Otitoju, (2013) stated that heavy metal pollution of terrestrial and aquatic environments in Niger Delta region of Nigeria is on the increase due to increased urbanization and crude oil exploration. Inhabitants of areas where the source of sea fish is highly polluted by heavy metals are at risk in terms of consumption (Ombretta, *et al*., 2017). Calderon, *et al*., (2003) and Powers, *et al*., (2003) had also stated that dietary intake of toxic elements is the main route of exposure for most people, so when these pollutants find their way into the water bodies, sea organisms or aquatic organisms ingest them either in the cause of feeding or respiration and these toxicants remain within the body until man harvests them for consumption and end up ingesting these metals and the health implications associated with the consumption of these metals is deleterious. Copat, *et al*., (2012) also found out that fish raised in contaminated waters take up heavy metals in large quantities enough to cause potential health risks to the consumers. Heavy metals have been reported to exert negative effect on biological processes in general and may influence the nutritional and biological status of sea foods (Udosen, *et al*., 2001). Regularly discharged pollutants have imminent detrimental effect on the flora and fauna of coastal ecosystems especially mangrove ecosystems and tropical mudflats (Ansari, *et al*., 2014). Many aquatic organisms for example *Thais spp* have the ability to accumulate and biomagnify contaminants like heavy metals in the environment (Davies *et al.*, 2006) therefore monitoring programs and investigations on the existence of heavy metals in marine water environments have increased significantly due to alarms over the accumulation of contaminants and toxic effects in marine organisms and to humans over the food chain (Otchere, 2003). *Thais spp* (Lamarch, 1816) commonly known as Rock Shell is a mollusc and class of gastropods with a humped or spined, thick-walled shell, mostly with short whorls with the shell closed by a honey operculum. They are up to 5cm in length and are dirty grey to brown in colour. The aperture is red and the lip toothed (Avil and Ross, 1999). They are salt water molluscs, found on rocks and mussel banks and exhibit both restricted geographical and local distribution (Davis and Fitzgerald, 2004). *Thais spp* locally called Nkonko in efik is an important source of cheap protein for the coastal people of southeast Nigeria, its fisheries supports a thriving, but subsistent economic activity. After consuming their soft-flesh, the empty shells are constantly thrown away as waste (Malu *et al*., 2009). They are deposit feeders and bioindicators of heavy metal and hydrocarbon pollution in the aquatic environment. Deposit feeding has to do with sediment and benthic dwellers, this implies that the organism has the ability to bioaccumulate heavy metals in its tissues in the process of deposit-feeding and so integrate the environmental conditions of the water and sediment over time (Moslen and Miebaka 2017).

The ultimate discharge of effluents by industries and other anthropogenic activities in and around creeks and rivers constitute a major environmental problem particularly in developing areas such as the Niger Delta in Nigeria (Moslen and Daka, 2016). Therefore, this study intended to evaluate concentrations of heavy metals in *Thais spp and attendant health implication associated with consumption* within some areas of the Niger Delta.

MATERIALS AND METHODS

Study site description

The study sites for this work were Bakana and Ikang in the Niger Delta region of Nigeria (Figure 1). Bakana area is characterized by mangrove swamp forest with mangrove species like *Rhizophora spp*, *Avicennia species*, Nipa palm. Anthropogenic activities within the area includes artisanal fishing, lumbering, hunting and sometimes bunkering. Ikang is on the eastern flank of the Niger Delta and also characterized by mangrove swamp forest with activities such as building of local boats, occasional transport of illegally refined petroleum products and fishing

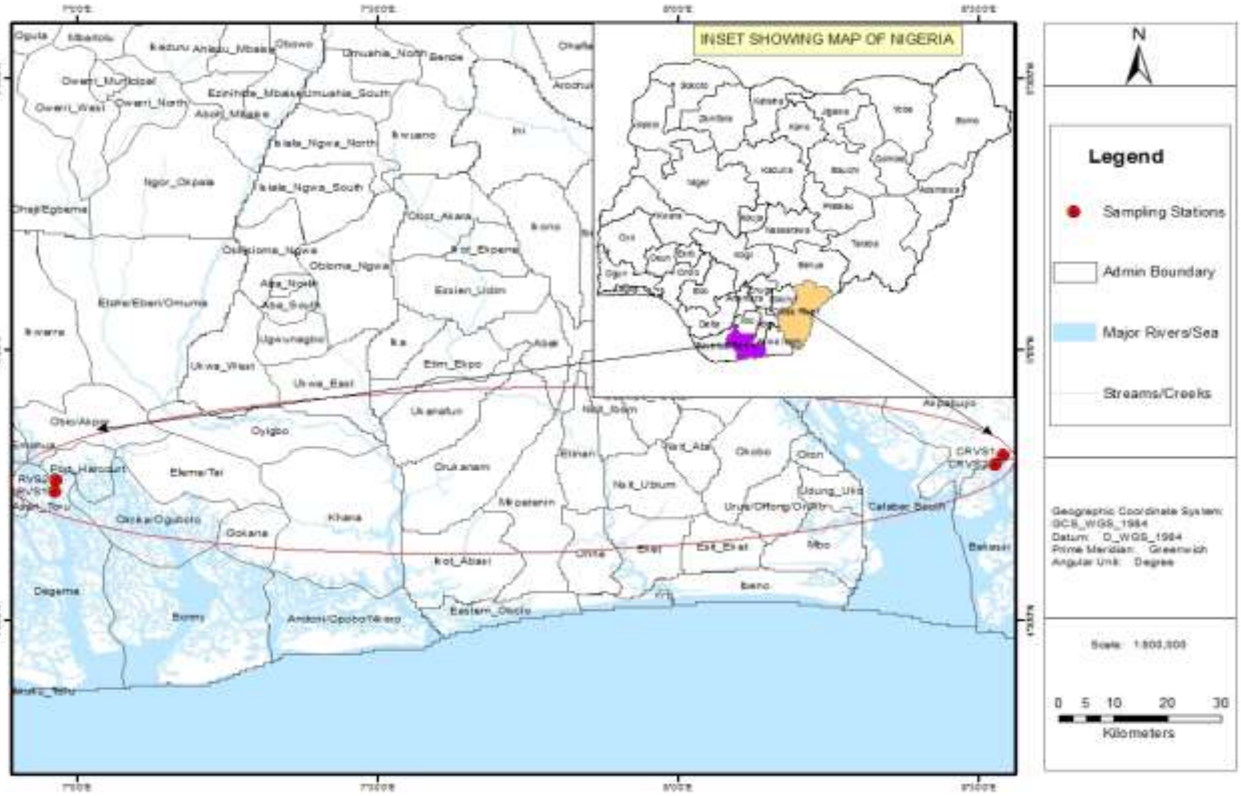

Figure1: study site with sampled points

SAMPLE COLLECTION

Samples were collected from two different stations in each site. Fifty samples of *Thais spp* were randomly collected from each station, washed and put in well labeled plastic containers. The samples were collected by handpicking at the intertidal mudflats. All samples were preserved in ice-packed coolers while in transit before laboratory analysis.

SAMPLE ANALYSIS

Sample preparation for heavy metals

Samples were removed from their shell with a clean acid washed stainless steel needle and dried in the oven to constant weight at 80°C for two days in a clean acid washed petridish., After drying, grinding of the samples to fine powders with a porcelain mortar and pestle was done. Platinum dish was cleaned, dried, ignited and covered at 500°C for 30minutes in the furnace, dish was allowed to cool and covered in a desiccator and weighed until a constant weight was obtained. Four grams of the sample was weighed, samples were ashed in the furnace to a build up of 500°C, the cover was slightly opened for escape of gases, it was checked periodically for complete ashing and later brought down to cool (Moslen and Miebaka, 2017).

Digestion for heavy metals

5ml/10% HCL and 5ml/10% nitric acid were added to the sample, it was then poured into a beaker and placed on a hot plate and digested to near dryness, then it was brought out to cool off. It was transferred quantitatively using a stirring rod and through a funnel and filter paper into a clean dry 20ml standard volumetric flask with 20ml of deionized water, the filtrates were collected with clean acid-washed and appropriately labeled 30ml plastic containers for aspiration on presentation to the Atomic Absorption

Spectrophotometer (AAS-Model 210VGP BUCK SCIENTIFIC,USA) (MMAF,2005). Then the concentration of Cr, Cd, Fe, Zn, Pb, Cu were determined as it displayed on the computer connected to the AAS.

STATISTICS

Analysis of variance was done using the General linear model in order to detect significant differences in the concentration of heavy metals in the tissues of whelk between the stations examined. The software package Minitab 16 was used for the analysis.

Health Risk Analysis

Health risk assessment was done and the following were calculated: Estimated daily intake (EDI), Target Hazard Quotient (THQ) (non-carcinogenic), Hazard Quotient (HQ) (carcinogenic) and Hazard Index (HI),

$$EDI = \frac{E_F \times E_D \times F_{IR} \times C_F \times C_M \times 10^{-3}}{W_{AB} \times T_A}$$

as used by Moslen and Miebaka, (2017)

Where E_F: exposure frequency, (365days)

E_D: exposure duration, (65years)

F_{IR}: fresh food Ingestion rate(48g/person/day)(Ali and Hau, 2001)

C_F : conversion factor =0.208

C_M: heavy metal concentration in food stuffs (mg/kg dry weight

W_{AB} : average body weight (60kg)

T_A: (E_F X E_D) is the average exposure of time for non- carcinogens (Wang *et al.*, 2005).

Estimated Daily Intake (EDI) was used to determine the carcinogenic (THQ) and non-carcinogenic risk (HQ).

- $THQ = \frac{EDI}{RFDO}$
- $HQ = EDI \times SF$

Where RFDO is the Reference oral dose and SF is slope factor (Moslen and Miebaka, 2017)

- $HI = \sum HQ$

Hazard Index estimates the total risk from multiple contaminant pathways, it was determined by summing the HQs of the contaminant pathway (Moslen and Miebaka, 2017).

RESULTS

The summary results for heavy metals and WHO maximum limit is presented in **Table 1.** The mean concentration was highest in RVS1 and lowest in CRVS 2 for Fe, Cr, Cd, Pb and Zn with mean values (mg/kg) ranging from 100.18-132.42, 3.82-4.21, 0.57-0.86, 3.62-5.88 and 21.34-38.77 respectively. The mean concentration for Cu was highest at RVS2 (31.86mg/kg) and lowest in CRVS1(14.96 mg/kg). Analysis of variance showed significant difference ($p<0.05$) between periods and no significant difference ($p>0.05$) between stations sampled. The concentration of all heavy metals were higher than WHO maximum limit except Zn (Table 1). The estimated daily intake for Pb, Cd, Cr, Zn, Cu, Fe, is presented in Table 2 while Target Hazard Quotient (non-carcinogenic) is presented in Table 3 and Hazard Quotient (carcinogenic) is given in Table 4. The hazard index for carcinogenic and non-carcinogenic risk is shown in Table 5 with the following observations. HI for carcinogenic risks CR1=0.00034, CR2=0.00035, RVS1=0.00049, RVS2=0.00038, with values below 1. Hazard index for non-carcinogenic risk gave: CR1=0.667, CR2=0.59, RVS1-=0.84 and RVS2=0.76.

Table 1: Mean Concentration of Heavy Metals with WHO Permissible Limit (mg/kg).

	CR1	CR2	RVS1	RVS2	WHO 1993	WHO 2011
CR	4.031	3.82	4.21	4.038	0.05	-
Cd	0.78	0.57	0.86	0.73	0.10	-
Pb	4.64	3.62	5.88	4.83	0.30	-
Zn	26.48	21.34	38.77	37.43	50	-
Cu	14.96	18.39	31.45	31.86	10	-
Fe	103.86	100.18	132.42	129.24	-	43

Table 2: Estimated daily intake of heavy metals (mg/kg)

Metals	CR1	CR2	RV1	RV2
Cd	0.000129	0.000094	0.000143	0.00012
Pb	0.00077	0.00060	0.000978	0.000825
Cr	0.00067	0.000635	0.00070	0.00067
Cu	0.0024	0.00306	0.0052	0.0053
Zn	0.0044	0.0035	0.0064	0.0062
Fe	0.017	0.0166	0.02	0.02

Table 3: Target Hazard Quotient of Heavy Metals

Metals	CR1	CR2	RV1	RV2
Cd	0.129	0.094	0.143	0.12
Pb	0.22	0.17	0.279	0.235
Cr	0.22	0.21	0.23	0.22
Cu	0.064	0.080	0.140	0.14
Zn	0.014	0.011	0.02	0.02
Fe	0.02	0.02	0.028	0.028

Table 4: Hazard Quotient of Heavy Metals

Metals	CR1	CR2	RV1	RV2
Cd	0.000049	0.000036	0.000054	0.000046
Pb	0.0000065	0.0000051	0.0000083	0.0000070
Cr	0.00335	0.00031	0.00035	0.00033
Cu	NA	NA	NA	NA

Zn	NA	NA	NA	NA
Fe	NA	NA	NA	NA

NA= not available

Table 5 : Hazard Index of heavy metals at study stations

	CRVS1	CRVS2	RVS1	RVS2
nNon-carcinogenic risk	**0.667**	**0.59**	**0.84**	**0.76**
Carcinogenic risk	**0.0034**	**0.00035**	**0.00049**	**0.00038**

Discussion

Thais spp is a relevant source of protein and the rate at which it is gradually becoming scarce in the Niger Delta region is very alarming hence there is need for regular monitoring. In this study there was significant variation in the concentration of heavy metals between months (P<0.05) but no significant difference between stations, which implies that there is a change in concentration with time, and the anthropogenic activities that result in the concentration of these contaminants within Bakana and Ikang occur at different rates with time. The levels of concentration of heavy metals in this study followed this trend Fe>Zn>Cu>Pb>Cr>Cd for CR1 with Fe having the highest concentration of 132.42mg/kg, this agrees with the work of Moslen and Miebaka in (2017) on heavy metals bioaccumulation in a named gastropod in the Niger Delta, where Fe had the highest concentration. The mean concentration of metals in the tissues of *Thais spp* were higher in this study (Fe=103.86mg/kg, Pb=4.64mg/kg, Cd=0.78mg/kg, Cu=14.96mg/kg,Cr=4.03mg/kg and Zn=26.48mg/kg) when compared to concentrations of Fe, Pb,Cd,Cu,Cr and Zn in a study done by Eze and Ogbuehi (2015). The concentration of Cr had its mean value above the WHO maximum level of 0.05mg/kg across all four stations which is in line with a study done by Piotr, *et al.* (2014) where mean value for Cr was 0.69 mg/kg above WHO maximum level suggesting exposure risk. Exposure to chromium may result in severe respiratory, cardiovascular, gastrointestinal, haematological, hepatic, renal, and neurological effects leading to death (ATSDR, 2008).

Cd concentration also has its mean value above WHO maximum level of 0.10 mg/kg across all four stations, this agrees with the study conducted by Kouakou, et al. (2016) where the least Cd concentration level (4.59) was higher than WHO permissible limit. This indicates potential risk to consumers of *Thais spp* within the vicinity. Nwadinigwe , *et al.* (2014) opined that Cd is a non-essential metal and when it enters the body it is capable of remaining there and cause severe damage to the system. Pb concentration also had its mean value higher than the WHO maximum limit of 0.30 mg/kg for all four stations, Kamaruddin *et al.* (2018) reported Pb having the following values in *C. obtusa*:3.802mg/kg, 4.909mg/kg, 2.355mg/kg which are higher than the WHO maximum limit. Akinrotimi *et al.* (2019) also reported Pb in *Thais coronata* with these value (0.33mg/kg) still higher than the WHO maximum limit of 0.30 mg/kg. This implies that residents in this region who consume *Thais spp* may be predisposed to health risk due to Pb. Monisha, *et al.* (2014) had said that Pb is a very toxic metal and that its widespread use has resulted to environmental degradation and health implications. For Cu the mean concentrations in all four stations were higher than the WHO permissible limit of 10 mg/kg. The concentrations in this study were higher than concentrations reported by Ajiboye, *et al.* (2011) for *Upeneus vittatus*, *Anchovilla commersonii*, *Pomadasys maculates*, *Lutjanus adetii*, *Ambassis commersoni* with values of 0.009mg/kg, 0.014mg/kg, 0.008 mg/kg, 0.008 mg/kg, 0.006 mg/kg respectively. The mean concentration of Fe was also above the WHO permissible limit of 43 mg/kg which is in tandem with the work of Tiimub and Mercy (2013) where concentration of Fe (49mg/kg) was higher than WHO maximum limit. Excess amount of Fe causesrapid increase in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness (Davies *et al*.,2006). ANOVA and Turkey Test showed that there was significant difference between periods (months) (P<0.05) and no significant difference between stations in the concentration of heavy metals. This variation with time, is an indication of influence of anthropogenic activities that occur at different rate in different times. This variation agrees with the study of Nsikak *et al.* (2007) where monthly variations were significantly different in the concentrations. The estimated daily intake of heavy metals were seen to be lower than the reference oral dose indicating low risk. THQ for all stations were <1, indicating low risk of heavy metals of non-carcinogenic origin. The THQ in this study agrees with the findings of Moslen and Miebaka (2017). THQ of heavy metals in this study also agrees with the findings of Tao *et al.*, (2012) and Taweel *et al.* (2013) but disagrees with the findings of Krishna *et al*. (2014) who reported THQ (non-carcinogenic) for Pb and Cr to be >1 in fish from the coast of India. The hazard quotient for Cd, Cr, Pb in this study were < 1, indicating minimal carcinogenic risk upon human exposure to Cd, Cr and Pb in the study region. Generally, HQ < 1 indicates no carcinogenic health risk to humans exposed to Cr, Cd and Pb. Hazard Index for Carcinogenic risk across all stations were < 1, indicating minimal carcinogenic risk of exposure through consumption of *Thais* spp in the study region. Hazard Index for non-carcinogenic risk value for all stations were < 1 indicating minimal health risk of non-carcinogenic origin. ,Guerra, *et al.* (2012) said that non-carcinogenic impacts may occur in the residents when HI >1, while the exposed person is unexpected to experience evident harmful health effects when HI < 1. Oyibo *et al.* (2018) opined that exposed populations are prone to experience health risk if the THQ value is equal to or greater than 1. HI in this study agrees with Ali, et al.(2019) in a study of carcinogenic and non-carcinogenic health risk assessment of some contaminants in Khorramabad, Iran, where HI values where < 1, this findings agree with Moslen and Miebaka (2017) were HI were less than 1(0.64), it also agrees with the work of Patrick, et al. (2018) in Delta State, Nigeria and Malakotian *et al*. (2016)

were HI values were less than 1 which poses no serious health concern within that area .

CONCLUSION

The concentration of Heavy metals in *Thais spp* in the study areas varied significantly across months and it means that the sources of these contaminants increase or decrease at different times. Heavy metals concentration were generally above WHO recommended limit but health risk assessment indicated values safe for consumption of the sea food (Thais spp) in the study region.

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