IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 15, Issue 5 Ser. II (May 2021), PP 01-06
www.iosrjournals.org

Comparative Assessment of Heavy Metals in Periwinkles (*Tympanotonus fuscatus*) sourced from three different Markets in Rivers State.

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Abstract

Background: *Rapid industrial development, large quantities of industrial waste are discharged continuously into the water without proper treatment causing contamination of the marine biota. Most aquatic animals accumulate large quantities of xenobiotic matter and the accumulation of these depends on the intake and elimination of these from their system. One of such animals is the periwinkle which is a common source of protein and iodine for the people. Heavy metals accumulation has been reported in some seafoods hence the need for this study.*

Materials and Methods:*The levels of Pb, Hg, As, Cd, Ni, Cr and Zn were determined in the periwinkles (Tympanotonusfuscatus) obtained from composite sampling collection from three different markets in Rivers State in the Niger Delta region. The samples were prepared using an oxi-acidic mixture of* concentrated trioxonitrate (v) acid and perchloric acid (4:1 v/v) *and analysed using AAS.*

Results*: The AAS analysis showed that Bonny market samples had the highest concentrations of Pb, Cr, Ni and Cd. The samples from Ogu market has the highest concentrations of Zn compared to those from Bonny and Bori markets. However, the Zn concentrations were within acceptable limits. The levels of Cd were higher in Bori market samples than Ogu market samples. Concentrations of Pb, Ni, Cr and Cd in these samples were higher compared to WHO safe levels of 0.10mg/kg. Arsenic (As) and mercury (Hg) were found to be in minute quantities of <0.001 – 0.002 mg/kg. The true metal intake (TMI) values for Pb, Cd, Cr and Ni from Bonny and Ogu markets were within acceptable limits.*

Conclusion: *The values for daily TMI are lowest for Bori market samples followed by Ogu market samples then Bonny market samples. However, the consumption of these periwinkles over time can pose potential health risks.*

Key Words: *Periwinkles, Heavy Metals, Bioaccumulation, Bioindicator, Health risks, Carcinogenicity, True metal intake (TMI).*

Date of Submission: 06-05-2021 Date of Acceptance: 20-05-2021

I. Introduction

Environmental pollution is a major hazard facing the world today and there is an increasing awareness of the alarming rate of human diseases caused by anthropogenic activities of industrial projects[1]. Their adverse impacts result in industrial pollution due to the indiscriminate discharge of effluents into the marine environment. Other reported[2] sources include geogenic, industrial, agricultural, pharmaceutical and domestic effluents. Industrial sources include refineries, mining, electroplating, tanning, metallurgical operations and energy production. Downwash from intensive agriculture and sludge dumping have led to the release of persistence toxic metals into the marine environment such as Co, Cu, Zn, Hg, Pb, As, Sb and Bi[3]. Other sources of environmental contamination are corrosion, atmospheric deposition, soil erosion of metal ions, leading to heavy metals, sediments[4] re-suspension and metal evaporation from water resources to soil and ground water.[5] indicated that the concentrations of these metals in aquatic sediments reflect the occurrence and abundance of certain rocks or mineralized deposits in drainage area. Heavy metals are known to be insidious toxic pollutants and their presence in the environment, especially aquatic environment is of great concern[6]. These metals may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organism, human health, agricultural development and the ecosystems are all at risk unless water and land systems are effectively managed[7]. Naturally, these heavy metals cannot be degraded or destroyed and to some extent they enter human bodies in small amounts via food, drinking water and air exposures. Heavy metals are well known for causing many diseases, birth defects and cancer. Many human diseases can be traced to the exposure of environmental and occupational chemicals for which evidence of carcinogenic and bio-magnification exists. Chromium is considered an essential biochemical element when it is chromium III, but chromium VI is highly toxic to man. Mercury is a liquid volatile metal, a trace component of many mineral, which can be bio-translocated and bio-transformed by metabolic processes into a toxic and resist degradable methyl mercury. Due to their high degree of toxicity arsenic, cadmium, chromium, lead and mercury rank among the priority metals that are of public health significance to induce multiple organ damage at lower levels of exposure[8] . Over 80% of all marine pollution originates from land-based source's which are primarily industrial, agricultural and urban[9]. Aquatic animals accumulate large quantities of xenobiotic matter and the accumulation of these depends on the intake and elimination of same from their body[10]. The rapid industrialization, urbanization and several oil bunkering activities at the Ogu creek, Onne-Ikpokiri Federal Ocean Terminals and Bonny Terminal are evidence of environmental source. The industrial heavy metals wastes enter the water by dissolution. Heavy metals are dangerous because they tend to bio-accumulate in tissues of living organisms. However, at higher concentrations they can lead to poisoning. Due to rapid industrial development, large quantities of industrial waste are discharged continuously into the water without proper treatment. This causes contamination of the marine biota of fishes, shrimps, oysters, mussels and crabs[11]. These seafoods accumulate large quantities of heavy metals due to their habitat and feeding nature. High toxic levels of exposure may result in biochemical effects on human which in turn cause problems in the synthesis of haemoglobin, kidneys, gastrointestinal tracts, joints, reproduction system function as well as damaging the nervous system[12]. Bioaccumulation of heavy metals are used for environmental monitoring largely because aquatic organisms are in direct contact with contaminated water, thus, bioaccumulation and biomagnification of heavy metal via food chain are finally assimilated by human consumers resulting to health risk of the consumer[13]. Most metals, including the heavy metals are naturally occurring elements and are present to some extent in the environment. They enter the aquatic ecosystem where they pose a lot of threat because of their toxicity, long time persistence and bioaccumulation in the seafood chain[14]. Many metals (Co, Cu, Mn, Fe and Zn) are essential trace elements for aquatic organisms and are involved in biochemical processes such as enzyme activation. Above certain levels, they become toxic. Other metals such as Cd, Pb, As and Hg have no known benefits or biological functions and are therefore detrimental to essential life processes[15].

Periwinkle (*Tympanotonus fascatus*) are phyla molluscs with un-segmented soft body externally covered by hard calcareous V-shaped spiral shell for protection. They are found in the mangrove soil within the intertidal zone. Periwinkle is a relatively cheap source of animal protein, vitamins and minerals. The organism is also very medicinal for cases like endemic goitre due to its iodine content anddue to its calcium, phosphate and iron content. They are recommended for pregnant women[16]. They are also a common source of protein and iodine for the people. The employment of molluscs, sea phanerogams, oysters and seaweeds are often recommended as bioindicators for heavy metal contamination because of their remarkable bioconcentration capacity. This is possible when the presence of a direct correlation between internal and environmental levels of the various metals has been verified. They are the organisms of choice in most of the programmes of biological monitoring of coastal marine waters.

The aim of this study is to assess and compare the concentrations of some heavy metals (Pb, Cd, As, Hg, Cr, Ni and Zn) in periwinkles from three different markets in three zones within a geographical distribution in Rivers State. Results obtained will enable us propose the possible use of these aquatic molluscs as bioindicator for environmental monitoring of the bioaccumulation of these heavy metals.

Study Area

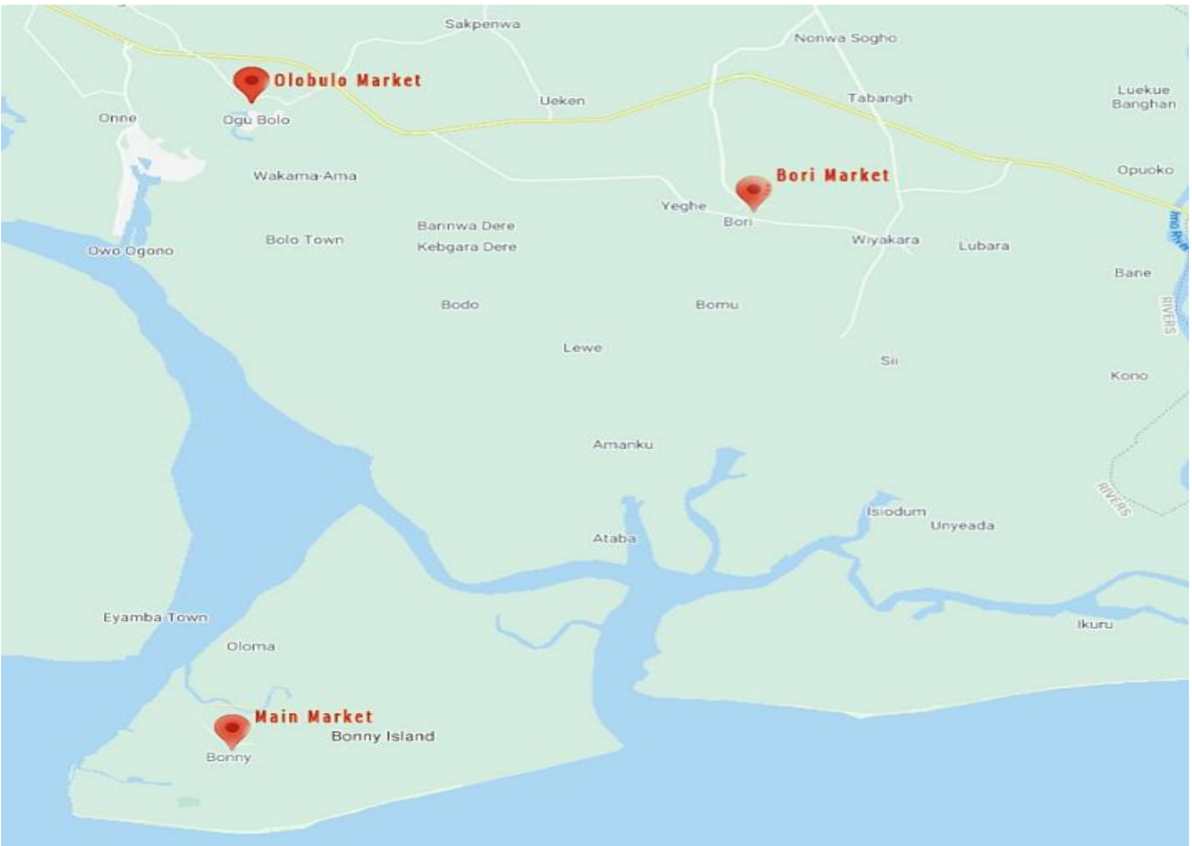

Fig. 1 Map of Bonny, Ogu and Bori Markets Location

II. Materials and Methods

Sample collection: The periwinkles were obtained by composite sampling technique at three different selected markets in Rivers State, and these are Bonny, Ogu and Bori. They are identified as follows: Bonny market at Latitude 4.40166, Longitude 7.15721; Borimarket at Latitude4.66170, Longitude 7.28740 andOgu (Olobulo) market at Latitude 4.80679, Longitude 7.32739.The sampling markets were carefully selected from coastal communities. Samples of periwinkles were purchased randomly from the markets every week for 4 months. They were packaged in different polyethylene bags that were properly labelled and then preserved in an ice - cooled box. These were later transported to the laboratory and stored in the freezer at -4^{0}C prior to wet digestion and AAS analysis.

Sample Preparation: The shells of the fresh periwinkle (*Tympanotonous fuscastus*) sample from each market were cracked and separated to obtain the edible part which were put in clean acid washed petri dishes and then dried at 50^{0}C for 48 hours. The dried samples were ground into powder using porcelain mortar and pestle ready for digestion.

Digestion process: The samples were prepared using wet digestion method. 2g of each composite sample was weighed and poured into a beaker. 20ml of the oxi-acidic mixture of concentrated trioxonitrate (v) acid and perchloric acid (4:1 v/v) which was prepared according to [17] was added to the samples in various beakers, stirred and heated for 2 hrs. When digestion was completed, they were allowed to cool. The resulting solution was filtered with Whatman filter paper, then transferred into 50ml volumetric flasks and made up to mark with deionized water.

Heavy Metals Analysis: After digestion, the samples were analysed for lead (Pb), cadmium (Cd), arsenic (As), mercury (Hg), chromium (Cr), nickel (Ni) and zinc (Zn) using atomic absorption spectrophotometer (AAS-model 210VGP Buck scientific).

Statistical Analysis: True metal intake (TMI) calculation was carried out using an adopted equation for dietary intake rate (DIR)[17]

$$= \frac{C_{metal} \text{ x } D_{food\ intake}}{B_{average\ weight}}$$

Where = C_{metal} is heavy metal concentration

$D_{food\ intake}$ is daily food intake

$B_{average\ weight}$ is the adult body weight

True Metal Intake (TMI) in a year

$$= \frac{C_{metal} \times D_{sea\ food\ intake}}{B_{average\ weight}}$$

Where = C_{metal} is heavy metal concentration
$D_{food\ intake}$ is daily intake of periwinkle (<5kg per year)
$B_{average\ weight}$ is the adult body weight

$$\frac{C_{metal}(mg/kg) \times 5\ kg/year}{60.7\ kg}$$

The average body weight is 60.7 kg for Africa[18].

:. Daily TMI values = $\frac{\text{TMI (in a year)}}{365\ \text{days}}$ = value (mg/kg/day)

III. Results

Table 1. Results of heavy metals concentrations (mg/kg) in composite samples of periwinkles from Bonny Market.

S/N	Metals	1mth	2mth	3mth	4mth	Ave/Std	Min.	Max.	WHO / FAO mg/kg
1.	Pb	1.14	1.50	1.96	1.78	1.60±0.31	1.14	1.96	0.50
2.	Cd	3.42	3.36	4.50	4.59	3.97±0.47	3.36	4.50	0.02
3.	As	0.002	0.004	0.011	0.007	0.006±0.004	0.002	0.011	0.014
4.	Hg	<0.001	<0.001	<0.001	<0.001	0	0	0	0.005
5.	Cr	3.23	3.56	4.69	4.35	3.96±0.56	3.23	4.60	0.01
6.	Ni	1.48	1.51	1.56	1.60	1.55±0.034	1.51	1.60	-
7.	Zn	34.08	36.01	39.21	41.06	37.59±2.72	34.08	41.06	1.50

Table 2. Results of heavy metals concentrations (mg/kg) in composite samples of periwinkles from Ogu Market

S/N	Metals	1mth	2mth	3mth	4mth	Ave/Std	Min.	Max.	WHO/FAO mg/kg
1.	Pb	0.122	0.120	0.200	0.280	0.18±0.066	0.12	0.28	0.5
2.	Cd	0.24	0.26	0.26	0.29	0.26±0.018	0.24	0.29	0.02
3.	As	<0.001	<0.001	0.002	0.002	0.002±0.001	0.001	0.002	0.014
4.	Hg	<0.001	<0.001	<0.001	<0.001	0	0	0	0.05
5.	Cr	2.349	2.386	2.408	2.72	2.46±0.181	2.23	2.72	0.01
6.	Ni	1.50	1.48	1.53	1.54	1.52±0.023	1.48	1.54	-
7.	Zn	54.9	56.9	56.1	57.5	56.35±0.973	54.9	57.5	1.50

Table 3. Results of heavy metals concentrations (mg/kg) in composite samples of periwinkles from Bori Market.

S/N	Metals	1mth	2mth	3mth	4mth	Ave/Std	Min.	Max.	WHO/FAO mg/kg
1.	Pb	0.12	0.16	0.16	0.18	0.155±0.022	0.12	0.18	0.5
2.	Cd	0.34	0.35	0.38	0.42	0.373±0.031	0.34	0.42	0.02
3.	As	<0.001	0.001	0.002	0.002	0.002±0.001	0.001	0.002	0.014
4.	Hg	0.002	0.001	0.002	0.002	0.002±0.001	0.001	0.002	0.05
5.	Cr	0.143	0.160	0.199	0.209	0.177±0.028	0.143	0.209	0.01
6.	Ni	0.19	0.38	0.48	0.52	0.393±0.128	0.19	0.52	-
7.	Zn	44.1	44.8	45.4	46.1	45.10±0.738	44.1	46.1	1.50

Table 4. True Metal Intake rate (TMI) (a) mg/person/year (b) mg/person/day.

		Bonny Mkt.		Ogu Mkt.		Bori Mkt.	
S/No.	Metals	mg/kg/ year	mg/kg/ day	mg/kg/ year	mg/kg/ day	mg/kg/ year	mg/kg/ day
1.	Pb	1.32E-01	3.61E-04	0.014868	4.07E-05	1.28E-02	3.50E-05
2.	Cd	3.27E-01	8.95E-04	0.021623	5.92E-05	3.07E-02	8.41E-05
3.	As	4.94E-04	1.35E-06	0.000124	3.39E-07	1.24E-04	3.39E-07
4.	Hg	-	-	-	-	1.44E-04	3.39E-07
5.	Cr	3.36E-01	8.93E-04	0.0203068	5.56E-04	1.46E-02	4.01E-05
6.	Ni	1.27E-01	3.47E-04	0.124691	3.42E-04	3.23E-02	8.86E-05

7.	Zn	3.09617	8.48E-03	4.63818	1.27E-02	3.711903	1.02E-02

IV. Discussion

The levels of Pb in the periwinkles from Bonny market were high, while the lowest levels were obtained from the Bori market samples. These high values can be attributed to the activities in the Bonny sea shores. From the TMI calculations, exposure to Pb poisoning for persons eating the periwinkles on a daily basis is minimal in Bori samples (3.50 E-05 mg/kg/day) when compared to those from Bonny (3.61E-05 mg/kg/day). The bioaccumulation of Pb may be the reason for the higher values from Bonny market samples. The periwinkles feed on sea organisms that may have taken some quantity of Pb that had found its way into the water bodies as a result of the anthropogenic activities in the immediate environment. Pb has been reported to be associated with crude oil exploration and pipeline transportation. High levels of Cd were also recorded for Bonny samples (8.95E-04 mg/kg/day). This may also be as a result of pollutants from industrial activities in the area as well as crude oil exploration. Samples from Ogu market and Bori had values of 5.92E-05 mg/kg/day and 8.41E-05 mg/kg/day respectively. Very low concentrations were recorded for Arsenic (As) from all three sampling locations. The TMI values were 1.35E-06 mg/kg/day,3.39E-07 mg/kg/day and 3.39E-07 mg/kg/day for Bonny, Ogu and Bori market samples. Mercury (Hg) levels were below detection (<0.001 mg/kg) for Bonny and Ogu market samples. This is in accordance with the results obtained by Jamabo[19] in their study. However, TMI values for Bori samples was 3.95E-07 mg/kg/day. This value is similar to that obtained for arsenic. Chromium concentration values of 8.93E-04 mg/kg/day, 5.56E-04 mg/kg/day and 4.01E-05 mg/kg/day for Bonny, Ogu and Bori respectively. TMI values of Ni were 3.47E-04 mg/kg/day, 3.42E-04 mg/kg/day and 8.86E-05 mg/kg/day for the three markets respectively. The levels of these two metals were found to be within maximal range when compared to WHO[20] acceptable limits and therefore should be monitored closely. The values recorded for Zn from the three markets (8.84E-03 mg/kg/day, 1.27 E-02 mg/kg/day and 1.02 E-02 mg/kg/day) are within acceptable limits in Bonny, Ogu and Bori markets respectively.

V. Conclusion

The levels of Pb, Cd, As and Hg varied from month to month. However, these metals may pose serious health risks to consumers who consume these periwinkles on a daily basis. True Metal Intake (TMI) is an indication of the quantities of these metals that have been ingested over a certain period of time. Their toxicity may result in biochemical changes in humans and may also lead to organ dysfunction. The order of heavy metals accumulation in periwinkles is as follows: Bonny market is Zn > Cr > Cd > Pb > Ni > As > Hg; Ogu market is Zn > Cr > Ni > Cd > Pb > As > Hg and Bori market is Zn > Ni > Cd > Cr > Pb> As = Hg.

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Akien-Alli Job, et. al. "Comparative Assessment of Heavy Metals in Periwinkles (Tympanotonus fuscatus) sourced from three different Markets in Rivers State.." *IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)*, 14(5), (2021): pp 01-06.