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Research Article

Determination of Pb, Hg, Cd, Cu, Ni and V in Periwinkle *(Tympanotonus fuscatus)*, Crab *(Callinectes pali)* and Fish *(Rhodeus amarus)* from Bodo River

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ABSTRACT

This study was carried out to determine the concentration of Lead (Pb), Mercury (Hg), Cadmium (Cd), Vanadium, (V), copper (Cu) and Nickel (Ni) in periwinkle (Tympanotonus fuscatus), crab (collinect pali)) and fish (Rhodeus amarus) harvested from Bodo River. The samples were de-shelled and then oven dried at 80^{0}C, thereafter homogenized into powder. Two grams (2g) each of the samples were digested with 10% hydrochloric acid (HCl) and analyzed using Atomic Absorption Spectrophotometer, Model SU 71906. The result showed that the concentration of Ni in Crab, periwinkle, fish-muscle and fish-liver were 4.203±0.004ppm, 3.919±0.077ppm, 3.240±0.007ppm and 3.218±0.022ppm respectively followed by Cu in which its concentration in periwinkle, Crab, Fish-liver and Fish-muscle were 4.476±0.006ppm, 3.428±0.003ppm, 2.063±0.050ppm, and 1.56± 0.023ppm respectively. This was followed by Pb in which it concentration in crab, periwinkle, fish-liver and fish-muscle were 3.859±0.053ppm, 2.427±0.006ppm, 1.189±0.015ppm, and 0.895±0.019ppm respectively. This was followed by Cd in which it concentration in periwinkle, Crab, fish-liver and fish muscle were 0.0261±0.001ppm, 0.0176±0.001ppm, 0.017±0.000ppm, and 0.00995±0.003ppm respectively. Followed by V in which it concentration in Crab, Periwinkle, Fish-liver and Fish-liver were 0.0065±0.001ppm, 0.0049±0.002ppm, 0.0051±0.000ppm, and 0.0016±0.000ppm respectively. This was followed by Hg in which it concentration in Crab, Fish-liver, Fish-muscle and periwinkle were 0.00395±0.000ppm, 0.00295±0.000ppm, 0.0021± 0.002ppm and <0.001±0.000ppm respectively. The concentrations of the elements were more in the shellfish and the fish-liver and the lowest values were observed in fish-muscle. In all, Ni, Cu and Pb concentrations were higher than the permissible limit set by WHO, FAO, FEPA, NAFDAC, and UNEP respectively, while the values for Cd, Hg and V were found to be lower than the permissible limit set by WHO and UNEP. From this research, it therefore shows that Bodo River is polluted with heavy metals. Therefore care should be taken in the consumption of fishes from Bodo River to avoid too much exposure of these elements. And also more research should be carried out on bio-remediation of heavy metals in aquatic environment.

Key words: *Pollution, Heavy metals; bioaccumulation; Aquatic environment, Human being, Toxicity.*

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INTRODUCTION

Environmental pollution is among the serious challenges that attracted the attention of scientists as some of these pollutants such as heavy metals contributed greatly to aquatic pollution due to their non-biodegradable nature[9]. Metals are divided into two major categories namely; essential elements and non-essential elements and the example of essential elements include Copper (Cu), Iron (Fe), Zinc (Zn), etc. These are called essentials elements because they play vital roles in biochemical processes such as enzyme activation for aquatic organisms, human being, and other living organisms. However, over certain level of concentration these elements can still become toxic to living organisms[1]. While the non-essential elements such as Cadmium (Cd), Mercury (Hg), Lead (Pb), etc. possess no known biological function and are seriously detrimental to essential life process[10]. Lead (Pb) replaces bivalent Cations such as Calcium (Ca), Magnesium (Mg), and Iron (Fe) and mono valent Cations such as Sodium (Na) which inturn lead to numerous biochemical process obstruction in human, Mercury (Hg) is very toxic and exceedingly bio-accumulative and it present in the marine environment always pose stress to aquatic organisms and the microorganism within aquatic media picks up the Mercury and transformed it into methyl Mercury and the routine exposure of this poisonous form of Mercury to human is through consumption of contaminated aquatic organisms and the brain remain the target organ for Mercury and Mercury vapour can cause bronchitis problem. Cadmium (Cd) is the seventh most toxic heavy metal that when absorbed by human remain in human system throughout life[6].

Heavy metals entered into aquatic environment through natural process and human activities and the various source are; soil erosion, natural weathering of the earth' crust, mining, industrial effluents, urban run-off, sewage discharge, insects or diseases agent applied to crops and many more others[8]. The industrial effluents that is discharge into the environment if it contained heavy metals, it accumulated in the soil and water bodies were the lower aquatic organisms absorbed and transferred them through the food chain into higher trophic levels including fish, fish provide nutrients such as protein, vitamins and minerals to human body, however, consumption of fishes polluted with heavy metals over prolong period of time can lead to the accumulation of heavy metals in the organs such as kidney, liver of human system and then resulted to numerous biochemical process obstruction[5].

Aquatic organisms that accumulated larger quantity of this xenobiotic depends upon the intake and elimination from their body and among the different aquatic organisms oyster, periwinkle, crab etc. accumulated larger quantities of heavy metals due to their habit and feeding nature and hence are good bio-indicator in the assessment of the level of pollutants within the aquatic system[4].

Research had revealed that Cd, Pb, Zn, Mn, Fe and Cr were present in the fishes harvested from Bodo River in Gokana, B-Dere and Kaa in Khana Local Government Area of Rivers States and their concentration exceeded that of the permissible limit set by WHO[8]. Research has also revealed that fishes in general provide essential nutrients needed for the normal body function of human and it contained some micronutrients that are very important for physiological and biochemical process through which the human body take's in and utilizes food to live healthy and micronutrients play an important role in human body such as Iron needed for red blood cell production, Zinc for healthy skin, reproductive system and Calcium for strong bones and teeth, the human body cannot provide all these micronutrients and hence must be supply through different food consumed[2].

Fishes are good bio-indicator of heavy metals and they also play important role in human nutrition hence adequate screening of fishes become necessary to ensure that unnecessary high level of some toxic trace metals are not being transfer to man through food chain[3]. Therefore, this research is aimed

at the determining the concentrations of Pb, Hg, Cd, Cu, Ni, and V present in Periwinkles *(Tympanostonus fuscatus)*, Crab *(Collinectes pali)* and fish *(Rhodeus amarus)* from Bodo River.

MATERIAL AND METHODS

STUDY AREA:

The research work was carried out in Bodo River located in Ogoni Land in Gokana Local Government Area of Rivers State, Nigeria; (See figure 1.0).

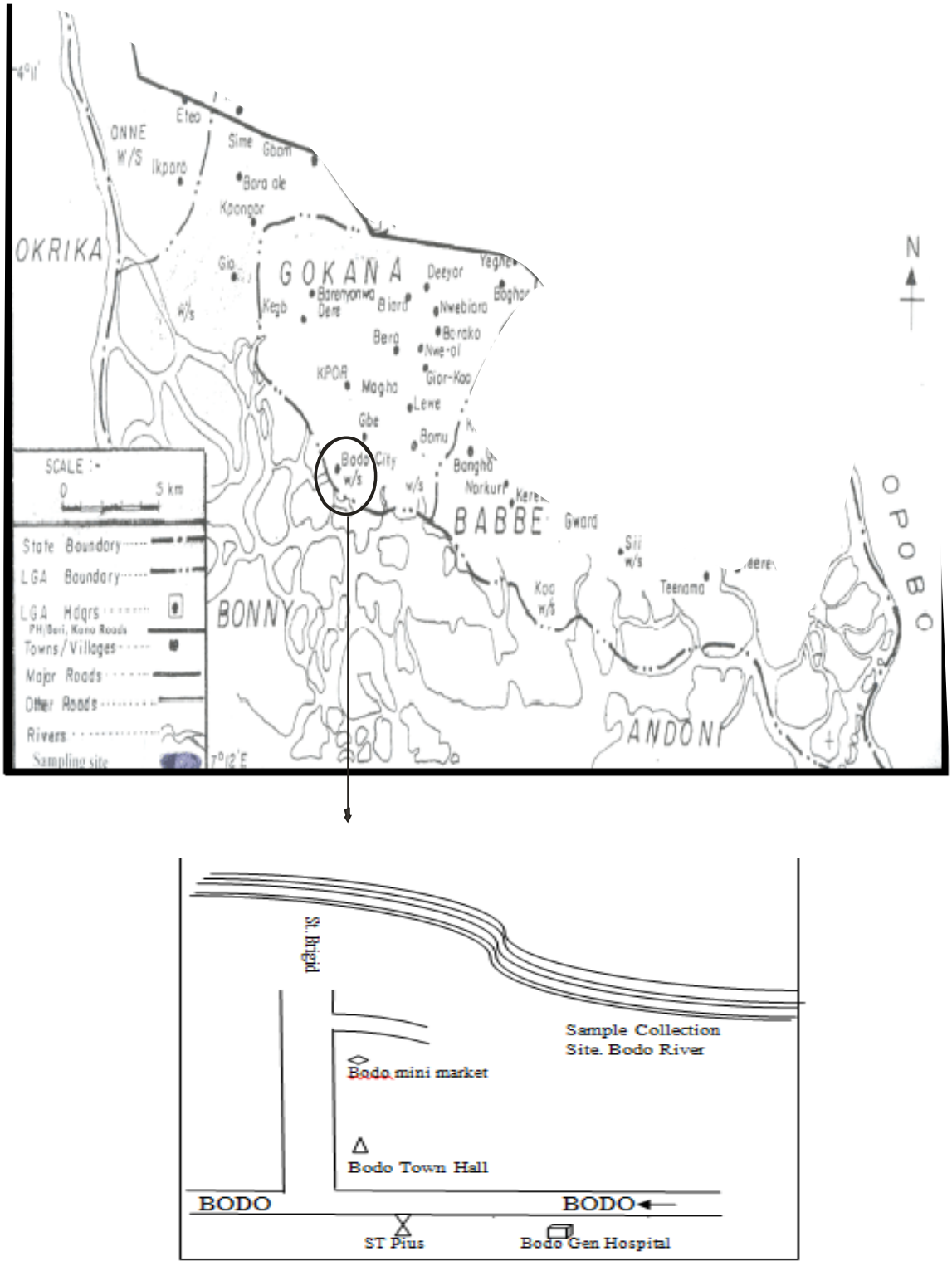

Figure 1.0: **Map showing samples collection site from Bodo River in Gokana L.G.A**

POPULATION SIZE

Gokana is among the 23 Local Government Area in Rivers State of Nigeria. The Local Government comprises of 35 villages in which Bodo community is one of them with an estimated population of 49,000 people. Bodo is located around oil industrial area and the activities of these industries had led to heavy pollution of the environment which had drastically harmed the agricultural activities in this area.

COLLECTION OF TEST SAMPLES

Fresh samples of shellfish; periwinkle *(Tympanotonus fuscatus),* crab *(Callinect spp)* and fish (*Rhodeus amarus*) bought from sellers at the bank of Bodo River in Gokana Local Government Area of Rivers State of Nigeria. The identity of aquatic organisms were confirmed by the supervisor, each specie was collected and clean and wrapped in a separate clean compartment and ice packed before transporting to the laboratory for analysis.

SAMPLE PREPARATION

The samples were separated according to their species and thereafter washed with distilled water to remove all loose and dirty parts and then drained. The edible part of the periwinkle was detached from the shell and weighed, also the crab was properly rinsed with distilled water and weighed and the fish was dissected to obtain the liver and muscle and as well weighed using weighing balance. Thereafter, all samples were transferred into aluminum foils and label accordingly and then oven dried at 80^0C for eight (6) hours and later cut into pieces and then oven dried to a constant weight. It was allowed to cool in a desiccators and thereafter, each of the sample was homogenized to powder form using porcelain mortar and pestle and then sieved through a fine sieve before it was transferred into various sample bottles and labeled accordingly.

SAMPLE DIGESTION

The samples were digested by taking a dried beaker and transferring into it two grams (2g) of each sample and then added 10% hydrochloric acid (HCL). The mixture was placed on a hot plate and heated, not allowing it to boil, until the organic matter was broken down as evident in volume reduction. On cooling, the content was transferred into a 100ml volumetric flask fitted with a filter paper and filtered. The filtrate was made up to the mark with distilled water and transferred into sample bottles and labeled for analysis.

SAMPLE ANALYSIS

The samples were analyzed using Atomic Absorption Spectrophotometer (AAS). A Stock solution consisting of standard solutions of the elements of interest was obtained followed by serial dilutions of the stock solution, the AAS was turned ON and warm up to 15 minutes after which the air and the acetylene gas was adjusted according to the flow rate of the maximum sensitivity of the element of interest and then ignite and the flame was allowed to stabilized, the serial diluted solutions were aspirated after adjusting the instrument scale reading to zero, the maximum absorbance of the serial diluted solution was again aspirated and the instrument was adjusted to it full scale sensitivity. The blank (distilled water) was aspirated for each trace metal in each sample of analysis in order to zero the absorbance after calibration before running the sample. The aspirated samples, their values were subtracted from the blank readings and various cathode lamps according to the element of interest were used and their cumulated results were recorded accordingly.

DATA ANALYSIS

The data was analyzed using one-way analysis of variance (ANOVA). All analysis was performed in duplicate. The results were expressed in mean $\pm$ SD, statistical significance was established and the means were separated using Tukey's procedure.

RESULTS AND DISCUSSION

Table 1.0, shows the average heavy metals concentration in Part Per Million (ppm) and expressed in mean ± S.D obtained by analysis of two shellfish; periwinkle *(tympanotonus fuscatus),* and crab *(callinects spp)* and fish *(Rhodeus amarus);* fish-liver, and fish-muscle harvested from Bodo river. A Total of six metals namely; Lead (Pb), Mercury (Hg), Cadmium (Cd), Copper (Cu), Nickel (Ni), and Vanadium (V) were analyzed in duplicate. All the samples shows detectable amounts of the afore-mentioned elements at varying concentrations. The crab and the periwinkle show higher concentration of these elements followed by the fish-liver and the fish muscle. Nickel tended to be higher among other element with values ranges from (4.203±0.004ppm) in crab, (3.919±0.077ppm) in periwinkle, (3.240±0.001ppm) in fish-muscle and (3.218±0.022ppm) in fish-liver. This is followed by Copper (Cu) in which the values ranges from (4.476±0.0064ppm) in periwinkle, (3.428±0.003ppm) in Crab, (2.063±0.050ppm) in fish-liver and (1.56±0.023ppm) in fish-muscle respectively. The concentrations of Lead (Pb); (3.859±0.053ppm) in crab, (2.427± 0.006ppm) in periwinkle, (1.189±0.15ppm) in fish-liver, and (0.895±0.019ppm) in fish-muscle. Other elements of study such as; Mercury (Hg), Cadmium (Cd), and Vanadium (V). Mercury (Hg) ranging from (0.00395±0.000ppm) in Crab, (0.00295±0.000ppm) in fish-liver, (0.0021±0.002ppm) for fish-muscle and (<0.001±0.000ppm) in periwinkle. For Cadmium (Cd) the values ranges from (0.0261±0.001ppm) in periwinkle, (0.0176±0.001ppm) in crab, (0.017±0.000ppm) in fish-liver, (0.00995±0.003ppm) in fish-muscle. For Vanadium (V) the values ranges from (0.0065±0.001ppm) in crab, (0.0051±0.000ppm) in fish-liver, (0.0049±0.000ppm) in periwinkle, and (0.0016±0.000ppm) in fish-muscle.

Table 1.0; selected heavy metals concentration in the samples (mean± S.D, ppm) from Bodo River.

S/N	Elements	Periwinkle	Crab	Fish-liver	Fish-muscle
1.	Pb	2.427± 0.055ppm^{b}	3.859± 0.053ppm^{b}	1.189.± 0.015ppm^{c}	0.895± 0.019ppm^{c}
2.	Hg	<0.001± 0.000ppm^{a}	0.00395± 0.000ppm^{a}	0.00295± 0.000ppm^{c}	0.0021± 0.002ppm^{d}
3.	Cd	0.0261± 0.001ppm^{a}	0.0176± 0.001ppm^{c}	0.017± 0.000ppm^{d}	0.00995± 0.003ppm^{e}
4.	V	0.0049± 0.000ppm^{a}	0.0065± 0.001ppm^{a}	0.0051± 0.000ppm^{c}	0.0016± 0.000ppm^{d}
5.	Cu	4.476± 0.006ppm^{c}	3.428± 0.003ppm^{a}	2.063± 0.050ppm^{b}	1.56 ± 0.023ppm^{f}
6.	Ni	3.919 ± 0.077ppm^{ab}	4.203± 0.004ppm^{a}	3.218 ± 0.022ppm^{a}	3.240± 0.001ppm^{b}

Values are in means ± SD of duplicate analysis, means on the same column with different superscript (a,b,c...e) differ significantly ($P \leq 0.05$)

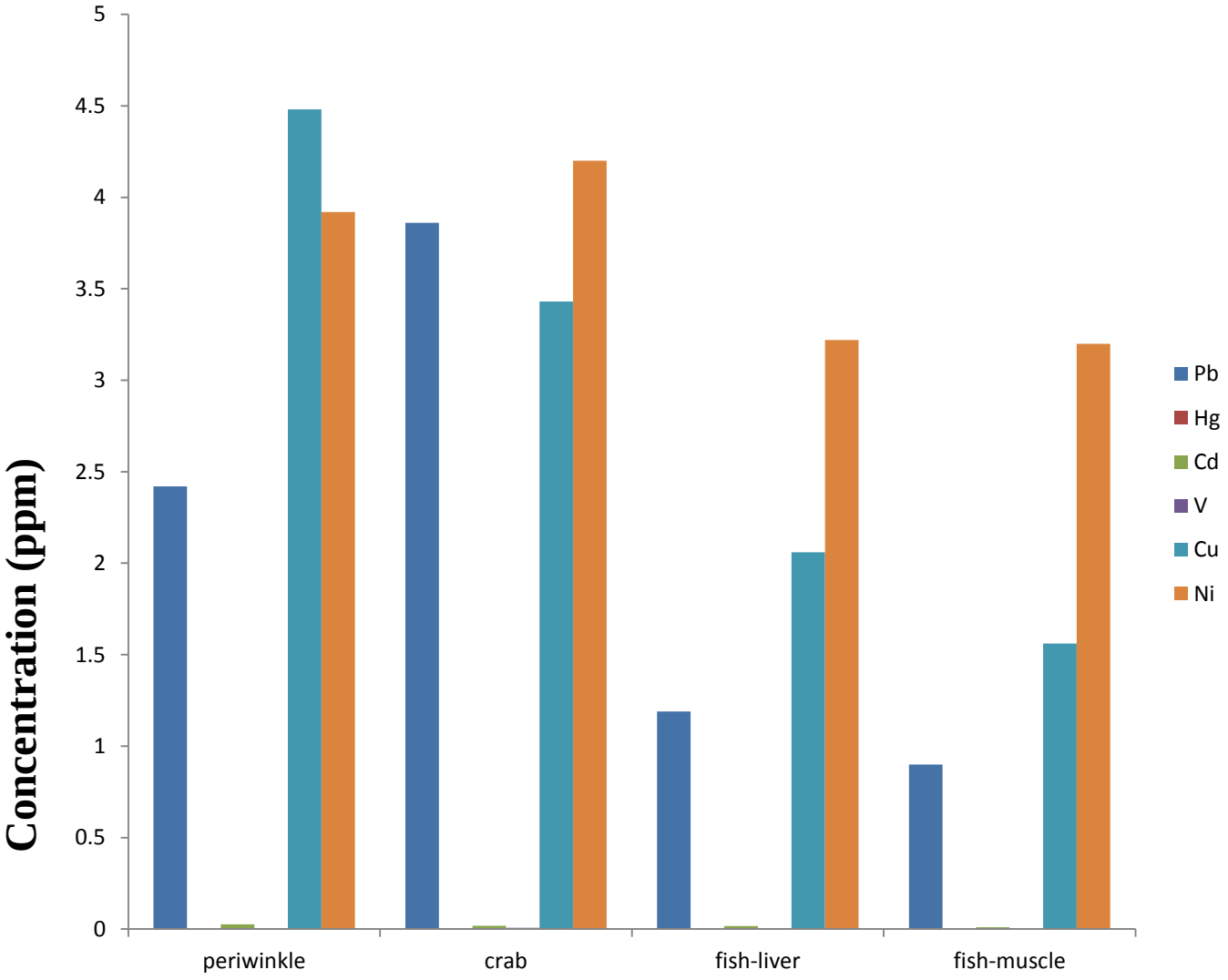

Figure 2.0; The Bar-chart showing the average level of heavy metals in shellfish and fish

DISCUSSION

From the table 1.0 and figure 2.0 indicated that all the aquatic organisms collected from Bodo River contained detectable amounts of the elements studied (Pb, Hg, Cd, Cu, Ni and V). These elements were present in all the fish and the shellfish samples at varying concentrations and the concentrations in all the samples were more in the shellfish than the fish. Thus, this research is in agreement with the research conducted by[4] which stated that among the different aquatic organism's shellfish (Oysters, Periwinkles, and Crabs) accumulated larger quantities of heavy metals due to their habit and feeding nature, hence they are good bio-indicators in the assessment of the level of pollutant within the aquatic system. Nickel tended to be the highest concentration in all the analyzed samples, varying from 4.203±0.004ppm in Crab, 3.919±0.077 ppm in periwinkle, 3.240±0.007ppm in fish-muscle and 3.218±0.022ppm in fish-liver. The concentrations of Nickel in all the analyzed samples were above the permissible limit set by World Health Organization (WHO) which is 0.02ppm. It has been reported that higher exposure to Nickel can lead to numerous health problems such as Cardio vascular disease, kidney disease and respiratory diseases (Duba-Chodak and Blazy, (2008). The concentration of copper (Cu) was also indicated to be high in the samples analyzed with values ranging from 4.476±0.006ppm in periwinkle, 3.428± 0.003ppm in Crab, 2.063±0.050ppm in fish-liver and 1.56± 0.023ppm in fish-muscle. The concentration of Copper (Cu) was observed to be higher than the permissible limit set by WHO and UNEP

which is 0.5ppm. Although Copper is said to be among the essential trace elements according to (MahurPawer,2015) and plays an important role in metabolic functions in human being as well as other living organisms, its deficiency in humans can lead to anaemia, low white blood cells count, osteoporosis, defects in connective tissue leading to skeletal problems. Also higher concentration of copper (Cu) can damage the blood cells and cause kidney and liver diseases etc. The result obtained for Lead (Pb) ranged from 3.859±0.053ppm as recorded in Crab, 2.427±0.006ppm recorded in periwinkle, 1.189±0.015ppm recorded in fish-liver and 0.895± 0.019ppm in fish-muscle. These results were higher than the permissible limit of FAO, FEPA and WHO which is 0.5ppm and NAFDAC 0.001ppm. This is a clear evidence that the Bodo River is polluted with Lead an observation that is in agreement to the finding by Nkpaa *et al.*[8] and the concentration was more in crab followed by periwinkle. This observation is also in agreement with the report of Moghdain *et al.*, which stated that shellfish accumulated larger quantity of heavy metals than other fishes. Based on the research conducted by Ijeoma *et al.*[5], Lead (Pb) is said to be among the non-essential elements which had no known biological function and are very detrimental to human because it damages vital organs such as kidney, liver and causes obstruction to numerous biochemical processes. More so, Lead (Pb) can also replace other bivalent cations like Ca, Mg, and Fe and monovalent Cations such as Na. This exchange affects the biological metabolism of the cell as well as cause defects of bones and teeth[6]. The evidence from this research showed that the activities of the oil company in Bodo community had impacted negatively on the aquatic environment causing the presence of heavy metals in the river. The results obtained for Mercury showed values ranging from 0.00395±0.000ppm in Crab, 0.00295±0.000ppm in fish-liver, 0.0021±0.002ppm for fish-muscle and <0.001±0.000ppm in periwinkle. For Cadmium (Cd), the values ranged from 0.0261±0.001ppm in periwinkle, 0.0176±0.001ppm in crab, 0.017±0.000ppm in fish-liver, 0.00995±0.003ppm in fish-muscle. For Vanadium (V), the values ranged from 0.0049±0.000ppm in periwinkle, to 0.0065±0.001ppm in crab, 0.0051±0.000ppm in fish-liver, and 0.0016±0.000ppm in fish-muscle. These results were below the permissible limits set by WHO, UNEP, FAO, FEPA and NAFDAC and the order of the decrease in concentration in the four Samples were as follows; Hg<V<Cd. Research have also shown that heavy metals because of their non-biodegradable nature can bio-accumulate in the environment, in which chronic exposure to them even at low concentrations can still pose risk to living organisms.

CONCLUSION

The results from this study has established the facts that heavy metals were presents in the aquatic organisms study from Bodo River. These organisms are periwinkle *(tympanotonus fuscatus),* Crab *(callinects spp),* fish *(Rhodeus amarus)* harvested from Bodo River. The concentration of these elements were found to be more in the shellfishes (periwinkle and crab) than in the fish. Nickel (Ni) was found to be higher in concentration followed by Copper (Cu) and Lead (Pb) in the order (Ni>Cu>Pb). Their concentrations in both the fish and the shellfish were found to be higher than the permissible limit set by the national and international regulatory bodies such as WHO NAFDAC, FAO, FEPA and UNEP. The other elements studied (Hg, Cd and V) were found to occur at lower concentrations, lower than the permissible limit set by the above regulatory agencies. Based on the results obtained from this study, it is therefore concluded that fish and shellfish from Bodo river were contaminated with heavy metals and so care should be taken in their consumption to avoid much exposure to these elements, since they can bio-accumulate and causes damages to different vital organs in the body of the humans such as kidney, liver and brain.

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