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Heavy Metal Contamination Profile of Four Selected Seafoods Harvested on Itu River in the Niger Delta Region of Nigeria

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ABSTRACT: The Niger Delta region is notorious for oil and remains the most exploited region. As a result, pollution from anthropogenic sources is on the increase. Heavy metals mercury (Hg), lead(Pb), cadmium(Cd), iron(Fe), copper(Cu) and zinc(Zn) were studied in four species namely *Austropotamobius pallipes*, *Penaeus notialis, Tympanotonus fuscatus* and *Archachatina maginata* at two different periods of three months interval. The samples were analysed using atomic absorption spectrophotometer and triplicate results obtained were analysed using ANOVA. Hg and Pb were not detected (<0.0001ppm) in both study periods and species examined. Zn, Fe, Cu and Cd were detected in all species but were all below maximum allowable limits of international guidelines. Thus, all four seafoods studied are safe for consumption. However, there is need to monitor seafoods coming out from the region from to time.

KEYWORDS: Heavy Metal, Contamination Profile, Seafoods Harvested, Itu River, Niger Delta, Nigeria.

1 INTRODUCTION

Heavy metals are defined as electronegative metals that are chemically inert with densities 5g/cm^3 and above. These metals are toxic to not just human but to other organisms. Physiologically, they form bonds with sulphur atom in the body and also have the ability to attack the free amino and carboxylic acid groups of proteins. Other mechanisms exist that they use to disrupt basic and important physiological functions in the body [1], [2]. Since they are inert or stable, they are very difficult to degrade and thus tend to accumulate in soils, water, atmosphere and also bioaccumulate in aquatic organisms [1], [3], [4]. The metals are introduced into the environment via natural cycles but also worrisomely through a number of anthropogenic activities [1], [2], [3], [4]. At low concentration, these metals do not cause any health or environmental issues but do so at high concentrations [3], [5].

The Niger Delta region which is the economic hub of the country is not spared by the resultant exploitation of its abundant oil and mineral resources. The effect is seen by the incessant crude oil spillages such as that recently revealed by the UNEP report on Ogoniland spillage where it was concluded that this little part of the Niger Delta is heavily contaminated by crude oil and its numerous fractions and that clean efforts could take between 20-30 years costing some $100million. [4], [6]. Given the coastal nature of the region, it is therefore not surprising that fishing is a major employer of labour and as a result, seafood both shelled and fleshy form a major part of the diet of the people of the region. A number of studies abound on the effect of crude oil and heavy metals on both land and aquatic floras and funas in the region. Studies have shown that heavy metals can accumulate in seafood in this region and beyond [4], [5], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17]. The study by Nkpaa *et al* have shown that fish and crustacean harvested from the polluted region of the Ogoni land are contaminated with heavy metals and in concentrations above permissible levels [4]. Another study by Gbaruko *et al* raised alarm about high levels of metals such as mercury and lead in plants and seafood [5]. While Otitoju *et al* did not detect any heavy metal above allowable limits [9].

Unlike water pollution which may be visible to the naked eye even without further analytical studies, heavy metal contamination of floras and funas are more difficult to see physically. However, given the toxic nature of these heavy metals on floras and funas, increasing urbanisation and the possibility of bioaccumulation in economically important aquatic organisms, we decided to study the accumulation of cadmium (Cd) , copper (Cu) , iron (Fe), mercury (Hg), lead (Pb), and zinc (Zn) on two crustaceans (crayfish and shrimps) ,and also two molluscs (perewinkle, snails) harvested on Itu River and sold on the Itu River Head Bridge, which divides two oil rich states of Akwa Ibom and Cross River.

2 MATERIALS AND METHODS

Study Site

Samples for this study were obtained directly from merchants at the Itu head Bridge in Itu Local Government Area of Akwa Ibom State of Nigeria. The seafoods sold on both sides of the bridge were harvested by local fishermen and they did so using nets or baits. The geographical coordinates of the study area is 5^{o} 39’ North and 8^{o} 0’ East. This river is an important one in the region because it demarcates both states of Akwa Ibom and Cross River State and also employs the locals. The area also houses Calabar-Itu Express road which connects Cross River State with the rest of the country and is quiet a busy route. There are no heavy industries in the area and the main source of income still remains fishing, farming and petty trading. The map of the study area is as given below.

Figure 1 (Source: Google Map). The river is the long blue line and the bridge is located is located where the river meets the road A342 in the south eastern part of the map (position of the arrow)

Sampling and Collection of Samples

The four different species used in this study were purchased at random from the traders without size or quality preference. Once the right species was identified, they were bought from the vendors. As informed by the vendors, harmless species were handpicked and the rest caught with traps or nets. None was harvested with chemicals. The molluscs and crustaceans picked were *Austropotamobius pallipes* (crayfish), *Penaeus notialis* (shrimps), *Archachatina maginata* (giant Snail) and *Tympanotonus fuscatus* (perewinkle). Samples were washed thoroughly and rinsed with distilled water. They were then transported to the laboratory in ice. The samples were collected twice over a period of three months.

Treatment and Analysis of Samples

In the laboratory, the samples were oven dried at about $90^{o}C$ and then made into powder using a clean and dry mortar and pestle. The grinded samples were then sieved using a 2mm sieve and stored in clean and air tight desiccators. They were further oven dried to obtain fine powder or ash and allowed to cool down. From each of the four samples, about 5grams was weighed out and made was moist with a few drops of distilled water and 10ml of HCl added to the samples. The resulting samples were then filtered into a cylinder and made into a 20ml solution with distilled water. The samples were then analysed for heavy metals using Scientific Atomic Absorption Spectrophotometer 200A Model. The instruction of the manufacturer was followed completely during the chemical analysis. The carrier gas was air acetylene gas and was used with the right cathode lamps.

Analysis of Data

The resulting data were then analysed with ANOVA using Graphpad Prism version 6.0. The average concentration for each metal studied is presented as mean ± S.E.M (ppm). Significance was also tested at 0.05 probability level and results of analysis are presented in tables 1 and 2.

3 Results And Discussion

Mercury (Hg), Lead (Pb) and Cadmium (Cd)

In the last decade, a number of heavy metals have been studied extensively and they include tin, manganese, titanium, iron, vanadium, cobalt, nickel, copper, zinc, mercury, lead, and cadmium. Mercury, lead and cadmium top the list because they are more damaging to organisms and the environment [4], [10], [18]. Mercury occurs naturally in nature but can be released into the environment via industrial activities. As a metal it can accumulate in soils, sediments and surface water. It is present in seafood as methylmercury, where it has the potential to bioaccumulate in the food chain and cause damage to the kidney and central nervous system. The developing brain of foetus is even more sensitive [2], [3], [5]. The permissible tolerable weekly intake of mercury has been set at 5µg/kg body weight, equalling 300µg mercury/week for a 60kg person [19]. For crustacean, fish and shellfish, the maximum level of contamination is set at 0.5mg/kg. However, in all samples collected and analysed, this latent neurotoxin was not detected (below 0.0001ppm) in all seafood studied during the two study periods.

Lead has the potential to accumulate in the body and also affect the nervous system, kidneys and reproductive system [3]. It is also been linked to reduced cognitive development in children [10]. In our study, it was also not detected in all samples collected during both study periods. However, the European Commission sets the limit at 0.2ppm in canned fish [20]. Cadmium was not detected in all samples analysed during the first study period. In the second period, it was detected in all species except *Austropotamobius pallipes*. The mean concentration did not vary much in *Penaeus notialis, Tympanotonus fuscatus* and *Archachatina maginata.* The allowable limit in shellfish is set at 2mg/kg and this is well below our maximum mean value of 0.011ppm. All mean concentrations of Hg, Cd and Pb were less than those obtained by Zodpa *et al* in 2011 in India. In another study, Hg was not detected in tissues, soil and water samples from Itu and Abuloma Rivers but was 64.2mg/kg in Oron River sediment [10]. In nearby Warri, Hg and Cd were not detected in a similar study in *Tympanotonus fuscatus* [18]. The below detectable levels of Hg and Pb could be explained by the absence of industries close by as opposed to other parts of the Niger Delta region.

Table 1. Mean concentration (ppm) of the heavy metals during study period 1

Seafoods	Copper	Iron	Zinc
Austropotamobius pallipes	0.062 ± 0.001	0.120 ± 0.001	0.123* ± 0.002
Penaeus notialis	0.006 ± 0.001	0.121 ± 0.001	0.112 ± 0.002
Tympanotonus fuscatus	0.063 ± 0.001	0.117 ± 0.001	0.007 ± 0.001
Archachatina maginata	0.005 ± 0.001	0.130 ± 0.001	0.063 ± 0.000

**Values are expressed as Mean±SEM (ppm). Cadmium, Mercury and Lead were not detected during the first sample period. The differences across the rows are all significant (P<0.05).*

Table 2. Mean concentration (ppm) of the heavy metals during study period 2.

Seafoods	Cadmium	Copper	Iron	Zinc
Austropotamobius pallipes	-	0.034 ± 0.001	0.060 ± 0.000	0.096* ± 0.002
Penaeus notialis	0.010 ± 0.001	0.035 ± 0.002	0.050 ± 0.001	0.082 ± 0.002
Tympanotonus fuscatus	0.010 ± 0.000	0.034 ± 0.001	0.050 ± 0.001	0.082 ± 0.001
Archachatina maginata	0.011 ± 0.000	0.031 ± 0.003	0.079 ± 0.001	0.081 ± 0.002

**Values are expressed as Mean±SEM (ppm). Mercury and Lead were again not detected. Across the rows, the differences are all significant (P<0.05).*

Copper (Cu), Zinc (Zn) and Iron (Fe)

Copper, Zinc and Iron are important cellular components of organisms but have been found to be toxic under certain condition and at high concentrations. Their major inputs include natural and anthropogenic sources [1], [2], [21]. Unlike, mercury and lead which were not detected during both sampling periods, Zn, Fe and Cu were all detected in all species and in varying concentrations. More of iron and zinc were seen in the species compared to copper in both study periods. More iron was detected in study period 1 than 2. It was observed in this sequence: *A. Maginata* > *P. notialis* > *A. pallipes* > *T. Fuscatus,* for period 1. In the second period, the highest of iron was seen in *A. Maginata* and the least seen in *A. pallipes.* When compared to the 100µg/g World Health Organization maximum allowable limit in food, the concentrations recorded were far lower. It is also lower than the concentrations previously reported [4], [10], [22]. Copper another important cellular constituent [21] was detected in all species studies during both study periods. The highest and lowest concentration of copper was recorded in first study period. During this period, the pattern of accumulation was *T. fuscatus> A. pallipes > P. notialis > A. maginata.* During period two, the concentrations were fairly same across all species studied. Again, these concentrations were much lower than previously recorded and also that of WHO maximum limit of 30µg/g. [4], [10], [22]. Zinc was also detected in all samples studied and during both study periods. Just like Fe, Zn was the second most abundant heavy metal in this study and was more consistent in period 2 than 1. The highest concentration of Zn was observed in *A. pallipes* in both periods and the least seen in *T. Fuscatus.* When compared with the previously reported studies, the concentration of Zn was lower than of Nkpaa *et al* but was in range to that of Chukwujindu *et al* [4], [15] in the Niger Delta. In other regions of the world it was lower than those previously reported [13], [14].

4 CONCLUSION

The present study reveals the presence of heavy metals zinc, iron, copper and cadmium, but not mercury and lead in *T. Fuscatus, A. pallipes, P. notialis,* and *A. maginata.* All metals detected were well lower than acceptable maximum limits set by WHO and FAO. This therefore indicates that the studied Seafoods within study 1 and 2 harvested and a sold along Itu Bridge are very safe for consumption. However, there is need for continuous monitoring of the seafoods for heavy metals and other pollutants. There is also need to monitor already operational industries so that they treat their effluents before discharging them into the environment, and to extend the study to include species of fishes commercially available on the bridge head as well.

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