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Full Length Research Paper

Spatiotemporal assessment of metal concentration in fish and periwinkles in selected locations of Lagos Lagoon, Nigeria

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Fish and periwinkles, from nine locations in the Lagos Lagoon, were processed and analysed for the presence of heavy metals (chromium Cr, manganese Mn, iron Fe, nickel Ni, copper Cu, zinc Zn, cadmium Cd and lead Pb) during the dry and wet seasons. Results showed that significant differences existed in the levels of metals in periwinkle and fish caught from the different locations while the influence of the period of sample collection on elemental levels indicated no significant difference in the levels of metals accumulated between the periods. Generally, the level sequence of the elements studied was, in most cases, similar in both locations and the period of sample collection for both periwinkle and fish. The sequence was different for periwinkle and fish: for periwinkle the sequence was Fe > Mn > Zn > Cd > Ni > Cu > Cr > Pb and for fish the sequence was Fe > Zn > Cd > Cu > Mn > Ni >Pb > Cr. The observed heavy metals concentrations in these organisms were below the recommended limits for human consumption.

Key words: Fish, periwinkle, heavy metals, cluster analysis, Lagos Lagoon.

INTRODUCTION

Many pollutants, including heavy metals, which are toxic to aquatic organisms and cause their lethal or sublethal deterioration, may find their way to aquatic ecosystems through various sources located at the catchment area or at distant places. Lagoons are directly exposed to different contaminants from various sources and the Lagos Lagoon is not an exception. It is a shallow expanse of water with restricted circulation in a micro tidal environment. This aquatic resource of multiple usages receives inputs of domestic sewage, industrial waste waters, sawdust and particulate wood wastes, petroleum hydrocarbons, cooling water from a thermal power station and emissions from automobile exhaust. Moreover, the chemical quality of the marine organisms, their contents of pollutant heavy metals, will become of major importance to resources managers and public health officials (Barbour et al., 1999). It is well documented that heavy metals have a great ecological significance due to their toxicity and accumulative behaviour. They accumulate in the tissues of aquatic animals and may become toxic when accumulation reaches substantially high levels. Accumulation levels vary considerably among metals and species (Heath, 1987). The presence of some heavy metals in aquatic environments and their accumulations in fish and periwinkles has been investigated during recent years (Hornung and Kress, 1991; Kalay et al., 1999; Canli and Atli, 2003; Ayenimo et al., 2005; Dural et al., 2006; Davies et al., 2006; Yalçın et al., 2008; Burger and Gochfeld, 2005; Chindah et al., 2009). Human beings may be contaminated by organic and inorganic pollutants associated with aquatic systems and inorganic pollutants

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associated with aquatic systems by consumption of contaminated fish and other aquatic foods from this environment (Mackay and Clarck, 1991). This fact is due to the capacity of some aquatic organisms to concentrate heavy metals up to 105 times the concentration present in the water (Singh and Narwal, 1984; Aderinola et al., 2009). Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain. Bioaccumulation and magnification is capable of leading to toxic level of these metals in fish, even when the exposure is low. The presence of metal pollutant in fresh water is known to disturb the delicate balance of the aquatic ecosystem. Fishes are notorious for their ability to concentrate heavy metals in their muscles and since they play important role in human nutrition, they need to be carefully screened to ensure that high levels of some toxic trace metals are not being transferred to man through fish consumption (Olowu et al., 2010).

Metals, such as iron, copper, zinc and manganese, are essential metals since they play important roles in biological systems, whereas mercury, lead and cadmium are toxic, even in trace amounts. The essential metals can also produce toxic effects at high concentrations. Only a few metals with proven hazardous nature are to be completely excluded in foods for human consumptions (Yalçın et al., 2008). Due to the deleterious effects of metals on aquatic ecosystems, it is necessary to monitor their bioaccumulation in key species, because this will give an indication of the temporal and spatial extent of the process, as well as an assessment of the potential impact on the health of organisms. In order to elucidate the evidence of the pollution effects on the aquatic fauna of the Lagos Lagoon, determination of these metals in periwinkle and fish from nine locations of the lagoon was performed during the dry and rainy seasons. Furthermore, considering the nutritional values of fish and the large quantities consumed in Nigeria, the results are briefly discussed in the light of some guidelines for human consumption. The comparison of the study areas in term of elemental impregnation in fish and periwinkle was performed using multivariate statistical analysis.

MATERIALS AND METHODS

Sampling and sample preparation

The choice of the benthic organism – *Tympanotonus fuscatus* (Periwinkle) is based on the fact that they have poor mobility and are typically in direct contact with sediments, they have the greatest exposure to pollutants. On the other hand, the choice of the pelagic organism - *Tilapia guineensis* (Fish) is due to their availability round the year, which makes them useful in field monitoring of pollution. These organisms occupy different community in Lagos Lagoon. And since the levels of certain elements were dependent on the size of the fish, wet weights were used to compare their levels found in each location. Data obtained from nine sampling stations in the study area (Figure 1) during the periods of investigation were processed.

The fish species *Tilapia guineensis* was caught at each station by employing cast nets and set (gill) nets which are usually left overnight in each station in the lagoon. The fish selected for use weighed between 120 – 150 g. *Tympanotonus fuscatus* (Periwinkle) weighing between 9 – 12 g were collected at each sampling point where the water is shallow because the animal apparently had a preference for shallow waters. Five fish samples and 10 periwinkle samples were collected from each sampling location. The samples were frozen in different polythene bags and deposited at Biological Sciences Department of University of Lagos, Akoka for identification. The samples were washed thoroughly with double distilled water and air dried for about 6 h after which they were transferred to a well-ventilated oven set at 60°C for 24 h. When the samples were confirmed dry, they were pulverised whole to fine powder and stored in air tight crew-capped plastic containers.

Dry tissue samples weighing 0.5 g were digested with 6 ml of concentrated nitric acid and 1 ml of 30% hydrogen peroxide. The digestion was carried out in a microwave digester using the microwave digestion. The completely digested samples were filtered and diluted to 25 ml in volumetric flasks with distilled water. The resulting solutions were analysed for metals using Flame Atomic Absorption Spectrophotometer (Perkin Elmer AA Winlab equipped with MS Windows application software).

Statistical analysis

Statistical analysis was performed using the Graph Prism statistical package version 5.0. All statistical samples submitted to tests were first checked for normality and homogeneity of the variances by means of Shapiroe Wilk. In all cases there was departure from normality therefore non-parametric tests were used in the subsequent analysis. The significance of differences of trace element levels among the fish caught at different locations was tested by Friedman (F) tests and the influence of the period of sample collection on elemental levels was tested by means of Kruskal Wallis (KW) tests followed by Wilcoxon test for paired samples.

RESULTS AND DISCUSSION

The levels of metals in the periwinkle and fish caught during the sampling periods at the different locations of the lagoon are given in Tables 1 to 4. The concentration of Cr in the periwinkle varied between 0.01 and 0.14 µg/g during the J07 period and 0.01 and 0.13 µg/g during the F08 sampling period. The mean values for all the locations during these periods were 0.06 and 0.04 µg/g respectively. Accumulation of Cr by periwinkle was found to be higher than that accumulated by the fish which was 0.002 – 0.06 µg/g and 0.001 – 0.08 µg/g in the J07 and F08 periods respectively. The variation in concentration of Cr in fish and periwinkle caught in all the locations was significant during the sampling periods ($p > 0.005$ at 95% Confidence level).

Manganese was the second highest in the level of metals' concentrations in periwinkle from all locations. The values recorded ranged between 43 to 95 µg/g in the J07 samples and 48 to 99 µg/g in F08 samples and mean

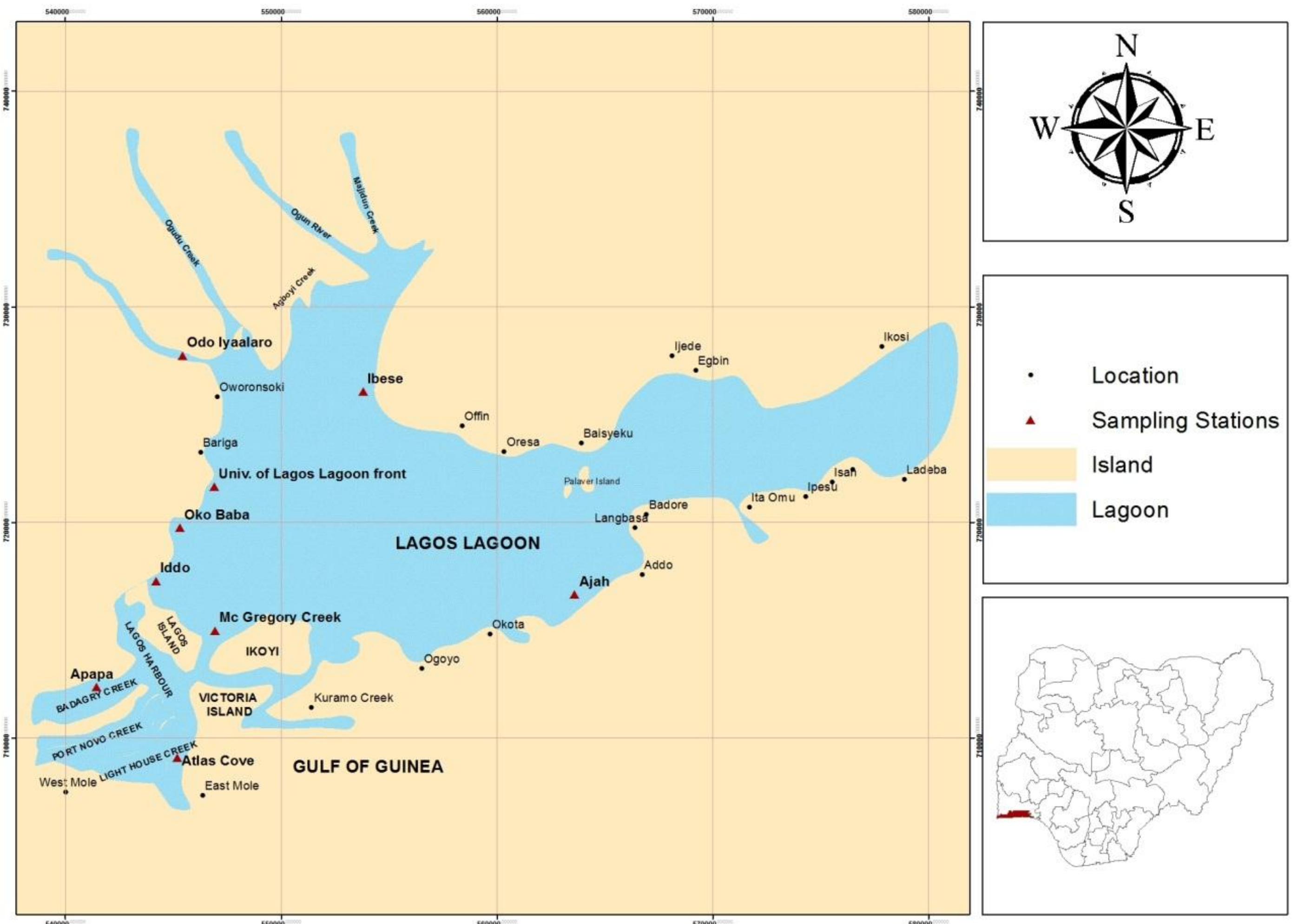

Figure 1. Map of the Lagos Lagoon showing sampling areas.

Table 1. Levels of heavy metal (µg/g) in homogenates of periwinkle *Tympanotonus fuscatus* collected from different locations of the Lagos Lagoon in the July 2007 sampling period.

Location	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
L1	0.01	59	4000	1.6	0.75	2.2	2.2	0
L2	0.01	53	3920	1.3	0.62	2	2.1	0
L3	0.02	47	3625	1.82	0.52	3.1	2.8	0
L4	0.03	43	1650	1.65	0.62	1.1	2.7	0
L5	0.01	62	1420	2.5	0.75	3.2	4.6	0.04
L6	0.1	64	640	2.7	0.8	2.8	3.5	0.05
L7	0.14	81	372	3.9	0.77	5.2	3.6	0.06
L8	0.12	95	3245	3.2	1.9	6.7	4.2	0.07
L9	0.14	85	2960	2.9	1.6	2.6	5.1	0.09

values of 65.44 and 70.11 µg/g respectively. The variations of Mn during these periods were not significant for all the locations ($p < 0.005$) during the periods samples were collected. The concentrations of Mn recorded in the fish caught from all the locations were relatively much lower than the levels found in the

Table 2. Levels of heavy metal (µg/g) in homogenates of periwinkle *Tympanotonus fuscatus* collected from different locations of the Lagos Lagoon in the February 2008 sampling period.

Location	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
L1	0.01	63	4200	1.8	0.78	2.5	2.1	0.00
L2	0.02	54	4100	1.6	0.65	2.2	2.2	0.00
L3	0.03	51	3780	2.1	0.68	4.0	3.2	0.00
L4	0.04	48	1480	1.9	0.85	2.0	3.1	0.04
L5	0.01	72	1340	2.2	0.95	5.0	5.1	0.06
L6	0.13	68	462	2.4	1.1	2.0	4.2	0.06
L7	0.01	85	301	3.8	1.2	6.0	3.8	0.07
L8	0.01	91	3568.5	3.7	1.6	9.0	4.8	0.08
L9	0.11	99	3014	3.4	1.8	2.3	5.6	0.11

Table 3. Levels of heavy metal (µg/g) in homogenates of the fish *Tilapia guineensis* collected from different locations of the Lagos Lagoon in the July 2007 sampling period.

Location	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
L1	0.00	1.6	72.1	0.02	2.1	6.2	2.1	0.01
L2	0.00	1.6	72	0.01	2.0	6.1	2.9	0.01
L3	0.00	2.4	60	0.03	1.8	8.5	3.9	0.02
L4	0.01	1.1	52	0.04	1.9	8.8	4.2	0.04
L5	0.01	1.0	46	0.06	2.4	14	3.8	0.04
L6	0.02	0.8	47	0.09	2.7	13	3.6	0.03
L7	0.03	0.9	46	0.08	2.5	12	3.4	0.02
L8	0.01	1.6	62	0.05	2.9	12.5	4.1	0.03
L9	0.06	3.1	57	0.06	2.7	15	4.6	0.80

Table 4. Levels of heavy metal (µg/g) in homogenates of *Tilapia guineensis* collected from different locations of the Lagos Lagoon in the February 2008 sampling period.

Location	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
L1	0.01	2.5	78.2	0.04	2.2	8.0	2.7	0.01
L2	0.01	2.6	76	0.04	2.2	8.0	2.8	0.02
L3	0.01	3.2	65	0.06	2.4	11	3.7	0.03
L4	0.01	2.9	57	0.06	2.6	10	3.8	0.05
L5	0.01	1.5	51	0.08	3.2	13	4.3	0.07
L6	0.00	1.2	49.5	0.07	3.5	12	4.1	0.06
L7	0.01	1.6	52.6	0.06	3.2	13	4.2	0.03
L8	0.01	2.8	70.6	0.06	2.8	15	4.4	0.05
L9	0.08	4.3	67	0.08	3.1	18	5.4	1.10

periwinkle. The values varied from 0.80 to 3.1 µg/g and 1.2 to 4.3 µg/g in J07 and 08 samples, respectively. The mean values for the locations during these periods are 1.57 and 2.51 µg/g for J07 and F08 samples respectively and the concentrations of Mn in the fish samples did not show any significant variation ($p < 0.005$ at 95% confidence level).

Fe is found in natural fresh waters and has no health-based guideline value, although high concentrations in water give rise to consumer complaints (WHO, 2004). The concentration of the metals when analysed in periwinkle and fish indicated that Fe showed the highest concentrations and mean levels relative to the other metals analysed in all locations. Comparatively, periwinkles had relatively higher mean Fe concentrations than the fish, suggestive of differences due to physiology and feeding habits and the fact that periwinkles are exposed to more Fe from sedimentary sources (Tay et al., 2005). The high concentrations of iron in the periwinkles could further be associated with the fact that this metal is naturally abundant in Nigerian soils and because the source of metal depositories are the aquatic system (Olowu et al., 2010). The concentrations found in the periwinkles sometimes exceeding the concentrations found in sediments. The concentrations of Fe found ranged from 372 to 4000 µg/g in J07 samples and 301 to 4200 µg/g in F08 samples. The mean values for all the locations were 2425.78 and 2471.72 µg/g for J07 and F08 samples respectively. The variations in the concentration of Fe in the periwinkle during these periods were not significant (p < 0.005). The levels of Fe recorded in the periwinkles were in most cases about five times higher than the concentrations recorded for the fish samples. The concentration of Fe was the highest of all the metals in the fish and it ranged from 46 to 72.1 µg/g and 49.5 to 78.2 µg/g in samples collected during the J07 and F08 periods respectively. This finding agreed with that reported by Olowu et al. (2010) who worked on fish caught from the Epe and Badagry sections of the Lagos Lagoon. They reported further that more of the metal concentrated in the intestine of both fishes (*Tilapia zilli* and cat fish, C*hryscichthys nigrodigitatus*) they investigated from the aquatic environment and attributed this to the function of intestine, which serves as the ultimate depository of all substance coming into the fish alimentary canal. The mean concentrations of Fe from all the locations were 57.12 and 62.99 µg/g for J07 and F08 samples, respectively. The concentration of Fe in the fish samples caught from the different locations also did not show any significant variation (p < 0.005).

The concentrations of Ni found in the periwinkle were higher than the values found in fish. The concentration found in periwinkle ranged from 1.3 to 3.9 µg/g and 1.6 to 3.8 µg/g for J07 and F08 samples respectively. The mean values of Ni for all the locations during the J07 and F08 sampling periods were 2.40 and 2.54 µg/g respectively and variation in the concentration for samples caught at the different locations did not vary significantly during the period of investigation (p < 0.005). The concentration of Ni recorded in the fish samples were much lower than those recorded for periwinkle. The concentrations in fish ranged from 0.01 to 0.09 µg/g during the J07 period and 0.04 to 0.07 µg/g during the F08 period. The mean for all the locations during the J07 period was 0.05 and 0.06 µg/g respectively; the variation in the concentration of Ni from all the locations was significant (p < 0.005). The concentration range of Ni reported by Olowu et al. (2010) for fish had a maximum higher than range recorded for fish samples in this work. The level of Ni concentration reported ranged from BDL – 4.0 µg/g and from BDL – 2.30 µg/g in Epe and Badagry sections of the lagoon respectively.

Copper is one of the metals classified as essential to life due to its involvement in certain physiological processes and metabolic activities in organisms, however, elevated levels of Cu have been found to be toxic. The periwinkle in many cases concentrated less Cu compared to the fish. The concentrations recorded ranged from 0.52 to 1.90 µg/g in J07 samples and 0.78 to 1.80 µg/g in F08 samples. The concentrations of Cu in periwinkles caught from all the locations did not vary significantly and the mean values for all the locations are 0.92 and 1.07 µg/g for J07 and F08 samples. The range found in fish was 1.8 to 2.9 and 2.2 to 3.5 µg/g for J07 and F08 samples respectively. The mean values for all the locations were 2.33 and 2.80 µg/g respectively for J07 and F08; the variation of Cu in fish caught from the different locations was not significant (p < 0.005).

Studies have shown that, Zn could be toxic to some aquatic organisms such as fish (Alabaster and Lloyd, 1980). Although Zn has been found to have low toxicity to man, prolonged consumption of large doses could result in some health complications such as fatigue, dizziness and neutropenia (Tay et al., 2005). Fish accumulated more Zn than periwinkle in all the locations studied. The concentration of Zn in fish ranged between 6.1 and 14 µg/g in the J07 samples and 8.0 and 18.0 µg/g in the F08 samples. The mean concentrations for all the locations are 10.68 and 12.0 µg/g for J07 and F08 samples respectively; the concentration of Zn in fish samples caught in the different locations did not vary significantly (p < 0.005). The concentration found in the work was higher than the concentrations (0.16 - 1.95 µg/g and 0.20 - 1.32 µg/g) reported by Olowu et al. (2010) for fish caught in Epe and Badagry sections of the lagoon respectively. The level of Zn in periwinkle ranged from 1.10 to 6.70 µg/g in the J07 samples and 2.0 to 9.0 µg/g in F08 samples. The mean concentrations obtained for all the locations were 3.21 and 3.89 mg/kg for J07 and F08 samples respectively. The level of Zn like in the fish did not vary significantly from one location to another during this investigation (p < 0.005).

Cadmium is a highly toxic metal and its uptake from water by aquatic organisms is extremely variable and depends on the species and various environmental conditions, such as water hardness (notably the calcium ion and zinc concentration), salinity, temperature, pH, and organic matter content (Rosenberg and Costlow, 1976). Cadmium is one of the most toxic elements with reported carcinogenic effects in humans (Goering et al., 1994). High concentrations of Cd have been found to lead to chronic kidney dysfunction. Cd may bio-accumulate at all levels of aquatic and terrestrial food chains. Intestinal absorption of Cd is low and biomagnification through the food chain may not be significant (Sprague, 1986). The periwinkle and fish accumulated Cd to about the same extent. The high concentration of Cd in the periwinkle could be due to the bottom-dwelling and bottom-feeding habits which are likely to ingest and contact considerable Cd-laden sediment. However, some of the fish and periwinkle caught in some locations had Cd content higher than the WHO guideline value of 2 µg/g (Kakulu et al., 1987) while they all exceeded the European Commission recommended value of 0.1 µg/g. The concentration recorded in periwinkle ranged from 2.1 to 5.1 µg/g and 2.1 to 5.6 µg/g for J07 and F08 samples respectively. The mean concentrations for all the locations were 3.42 and 3.79 µg/g for J07 and F08 samples respectively. The level of Cd in the periwinkle caught from the different locations did not vary significantly from one location to another during this investigation ($p < 0.005$). The concentration of Cd in fish ranged between 2.1 and 4.6 µg/g in the J07 samples and 2.7 and 5.4 in the F08 samples. The mean concentrations for all the locations are 3.62 and 3.93 µg/g for J07 and F08 samples respectively; the concentration of Cd in fish samples caught in the different locations did not vary significantly ($p < 0.005$). Cd contamination in inland and coastal environments could be attributed to discharge of contaminants containing Cd. Activities which may introduce Cd into these environments include electroplating and plastic manufacturing. Cd is a constituent of some pigments and significant quantities are released during the smelting of raw sulphide ores. Atmospheric depositions from non-ferrous metal mines and refineries, coal combustion and refuse incineration are other probable sources of Cd. The levels of Cd contamination in fish and periwinkle in this study have both been observed to be relatively higher than those (0.27 µg/g for fish and 0.56 µg/g for periwinkle) reported by Aderinola et al. (2009) suggesting increased industrial and domestic activities during the period these samples were taken.

The United States Environmental Protection Agency has classified Pb as being potentially hazardous and toxic to most forms of life (USEPA, 1986). This metal has been found to be responsible for quite a number of ailments such as chronic neurological disorders especially in foetuses and children (Tay et al., 2005). The mean concentration of Pb in fish was relatively higher than the concentration found in periwinkle. This could be due to the source of lead and its mode of availability to the organisms; while most trace metals originate from land-based particulate sources, Pb is mainly of anthropogenic origin as a result of emissions from automobile exhaust fumes. Such sources of Pb could be more available to fishes (caught from coastal waters, at the bank of which, there are vast trunks of roads, on which there are heavy vehicular traffics) than to periwinkles, to which only sedimentary sources are available. The relatively higher Pb content of the fish could also be due to the presence of small bones embedded within the muscle tissue of the fish; these bones may serve as repositories for Pb (Nord et al., 2004). The concentration in the periwinkle ranged between 0.001 to 0.09 µg/g in the J07 and F08 samples respectively. The mean concentrations obtained for periwinkle caught in all locations were 0.04 and 0.05 µg/g for J07 and F08 samples respectively. The concentrations of Pb varied significantly from one location to the other during the period of this study ($p > 0.005$). The concentration of Pb in fish ranged from 0.01 to 0.80 µg/g in J07 samples and 0.01 to 1.10 µg/g for F08 samples. The mean concentrations obtained for Fish samples caught from all locations during the sampling periods were 0.11 and 0.16 µg/g for J07 and F08 samples respectively. The variation in the concentration of Pb in fish from different locations was very significant ($p > 0.005$). In many locations, the levels of Pb in fish exceeded the guideline value (0.4 µg/g) adopted by the European Commission.

Generally, there were significant variations in trace metal levels between fish and periwinkle. This may be due to the differences in physiology and feeding habits (Tay et al., 2005). Freidman statistical test showed that significant differences existed in the levels of metals in periwinkle and fish caught from the different locations while the influence of the period of sample collection on elemental levels tested by means of Kruskal Wallis (KW) test indicated no significant difference in the level of metals accumulated between the periods. Generally, the level sequence of the elements studied was, in most cases, similar in both locations and the periods of sample collection for both periwinkle and fish (Tables 1 to 4). The sequence was different for periwinkle and fish: for periwinkle the sequence was Fe > Mn > Zn > Cd > Ni > Cu > Cr > Pb > Hg (Cd and Zn exchanged places in F08 samples), for fish the sequence was Fe > Zn > Cd > Cu > Mn > Ni >Pb > Cr > Hg. Furthermore, the sequence of non-essential metals in both periwinkle and fish is worthy of note; it was as follows: Cd > Pb > Hg. Non-essential metals do not present any function for fish and periwinkle metabolism and are by consequent not regulated by the metabolism. The concentrations of Cd, Hg and Pb in fish and periwinkle may be used as an indication of the level of metal pollution of the water and sediment respectively from which they are caught (Kojadinovic et al., 2007). However, the observed heavy metals concentrations in these animals are below the recommended limits for human consumption (Davies et al., 2006; Olowu et al., 2010). The heavy metal concentration in the fish caught at the three locations could be attributed to anthropogenic metal sources affecting their environment. The public health implication of the research seems to show no possibility of acute toxicity of the heavy metals of edible

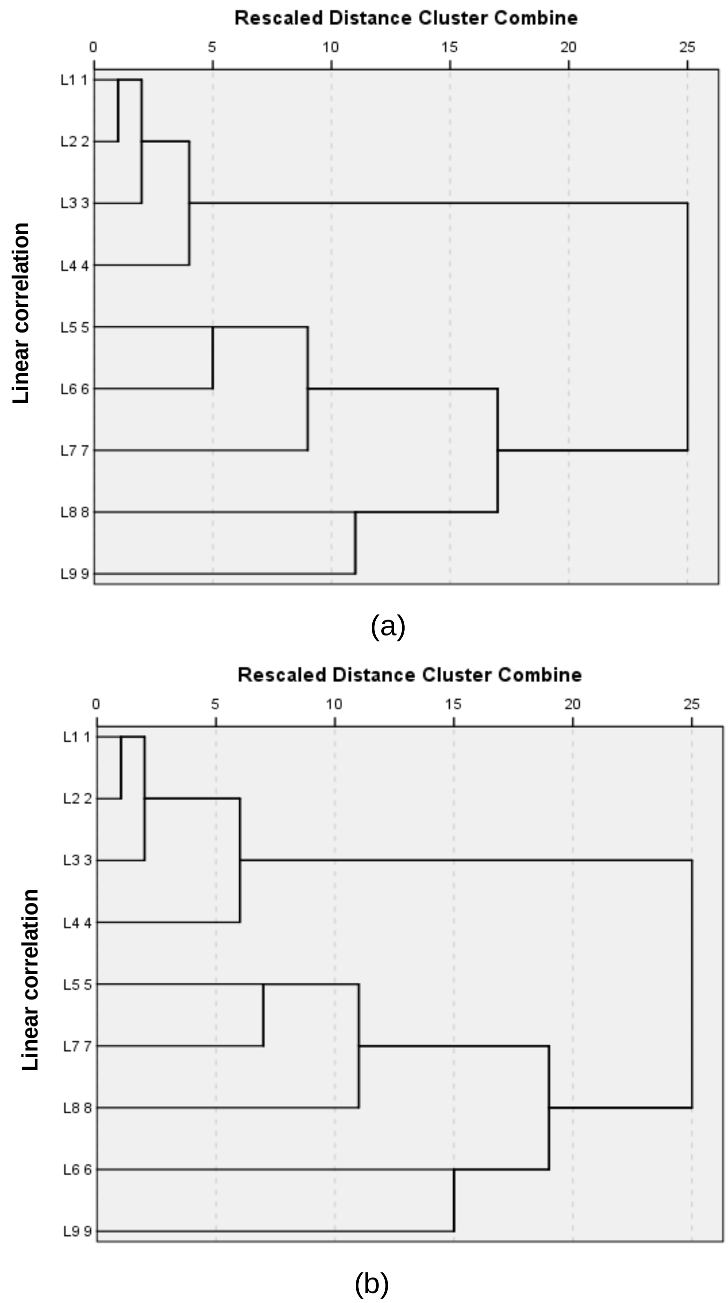

Figure 2. Dendrograms illustrating linear correlation between the heavy metals in periwinkles caught during the (a) dry season and (b) wet season.

fishes consumed (Oshisanya and Oshinsanya, 2009). Although levels of Cd, Cr and Pb, were within the normal minimum range allowable in diet of man, however, continual consumption could lead to accumulation with adverse health implications, while Cd has been linked to renal diseases and cancer (Kjellstroem, 1986) thus making periodic monitoring very imperative.

Pattern recognition and similarity in periwinkle and fish caught from the different locations during the periods of sample collection were determined by hierarchical cluster analysis based on the metals determined and presented in form of dendrograms (Figures 2). The periwinkles and fish from the different locations contained different levels of metals, however, some similarities existed between

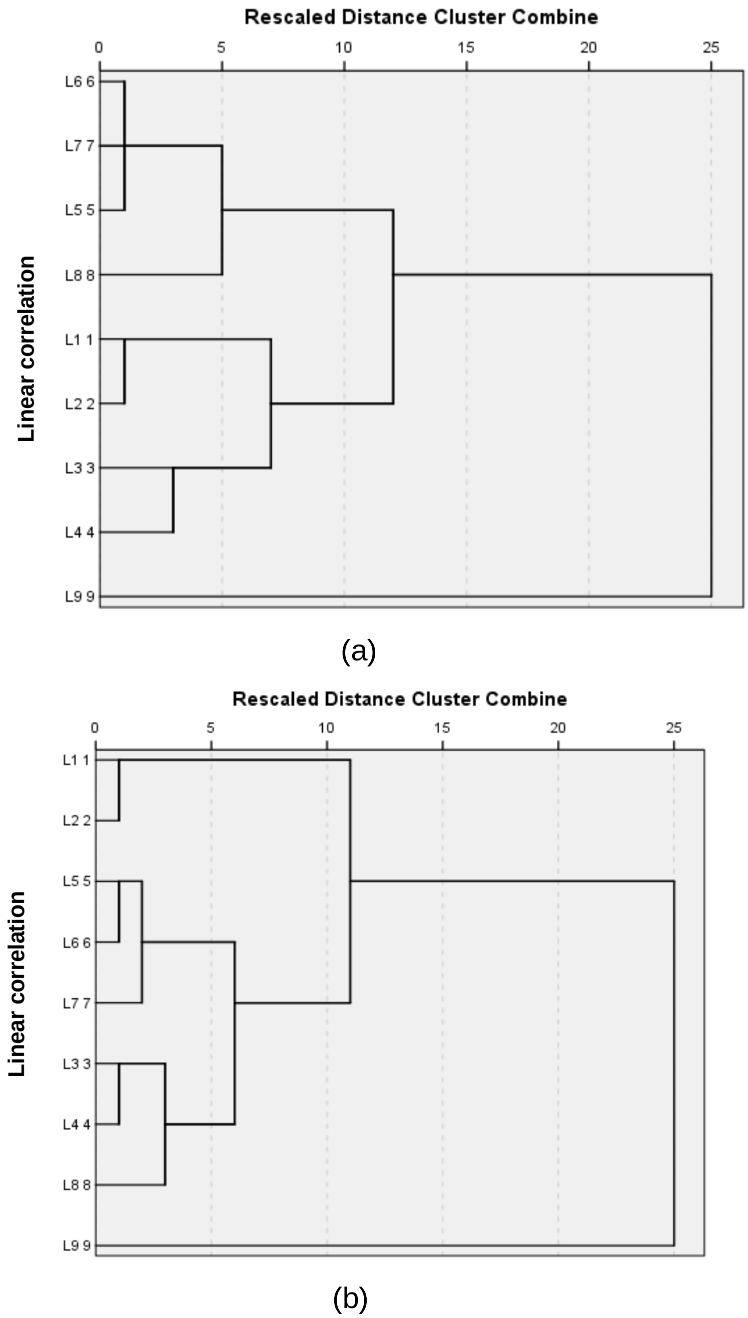

Figure 3. Dendrograms illustrating linear correlation between the heavy metals in fish caught during the (a) dry season and (b) wet season.

them. Dendrograms illustrating linear correlation between the heavy metals in periwinkles caught during the dry season and wet season (Figure 2) are made up of two clusters with greater similarities during the dry season. Cluster I consisting of periwinkles with relatively high levels of Fe and low in the other metals, while cluster II with relatively low levels of Fe and high in the other metals. Dendrograms illustrating linear correlation between the heavy metals in fish caught during the dry season and wet season consist of three main clusters (Figure 3).

The pattern was different for the different periods samples were collected; only fish from location L9 seem to be consistently different from the remaining locations. The dendrograms obtained was difficult to interpret probably due to the pelagic nature of fish.

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