HEAVY METAL LEVELS OF SOME EDIBLE SHELLFISH FROM KALARUGBANI CREEK IN RIVER STATE, NIGERIA

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ABSTRACT: Heavy metals present in high concentrations in the aquatic habitants are bioaccumulated within the tissue of intertidal organisms. The chemical analysis of animal tissues, river and sediment provides an indication of the bioavailability of heavy metals in the environment. Monitoring of the coastal pollution using organism is widely practiced all over the world. Chemical analysis of the tissue of oyster, periwinkle, sediments (mudflat) and river were used to monitor the environmental concentration of Copper, Zinc, Lead, Nickel, Chromium, Iron of Kalarugbani creek in River state for a period of seven months. Oyster had a higher accumulation of these metals (Pb, Cu, Ni and Zn) than periwinkle which had higher concentration of Fe and Cr. The concentration of Pb, Cu, Ni, Zn, Fe and Cr were higher in the sediments than the overlying water for the various month sampled. The results showed that oyster accumulated more of these heavy metals than periwinkle, while these shellfishes accumulated more heavy metal than the sediments and the river which had the least metal concentration. However, the observed heavy metals concentrations in these animals are below the recommended limits for human consumption. This study therefore advocates environmental surveillance of this creek in order to achieve good sediment quality and contaminant-free periwinkles and oyster for safe human health.

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1.0. INTRODUCTION

Heavy meals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Tam and Wong, 2000). Trace metals in natural waters and their corresponding sediments have become a significant topic of concern for scientists and engineers in various fields associated with water quality, as well as a concern of the general public. Direct toxicity to man and aquatic life and indirect toxicity through accumulations of metals in the aquatic food chain are the focus of this concern.

The presence of trace metals in aquatic systems originates from the natural interactions between the water, sediments and atmosphere with which the water is in contact. The concentrations fluctuate as a result of natural hydrodynamic chemical and biological forces. Man, through industrialisation and technology, has developed the capacity to alter these natural interactions to the extent that the very waters and the aquatic life therein have been threatened to a devastating point. The activity of trace metals in aquatic systems and their impact on aquatic life vary depending upon the metal species. Of major importance in this regard is the ability of metals to associate with other dissolved and suspended components. Most significant among these associations is the interaction between metals and organic compounds in water and sediment. These organic species, which may originate naturally from process such as vegetative decay or result from pollution through organic discharge from municipal and industrial sources, have a remarkable affinity and capacity to bind to metals. This phenomenon would naturally alter the reactivity of metals in the aquatic environment (Signer, 1974).

Many human activities (e.g.; mining, overuse of chemicals, industrial waste from ports and refineries) have a negative impact on several biological processes and there is no doubt that these will continue to affect the functioning of highly productive coastal ecosystems. Contamination caused by trace metals affects both ocean waters, those of the continental shelf and the coastal zone where, besides having a longer residence time, metal concentrations are higher due to input and transport by river runoff and the proximity to industrial and urban zones (various authors quoted in Guzman and Garcia, 2002). Many heavy metals occur naturally in the marine environments, some of them are described as pollutants when in sufficient amounts to produce deleterious effects on some features of the ecological system. Living organisms can be used as more efficient monitors of environmental contamination. Some of them such as bivalves' molluscs are well known for their biological features in their tissues. For example, oyster can accumulate cadmium in their tissues at levels up to 100,000 times higher than the observed in the water in which they live (Avelar et al., 2000).

High concentration of trace metals have been detected in several species of the marine bivalves in many parts of the world. Accumulation of metals by bivalves has been shown to be relatively rapid and to reflect ambient exposure level. Great variation in the metal concentrations in the bivalves has been reported from many parts of the world. Even in the relatively small areas such as a specific estuary, concentration of some metals can vary by a factor of 10 to 100 (Presley et al., 1990; Rainbow, 1995).

Bivalves like other organisms have complex interactions with the environment. Variations of bioaccumulated heavy metals within the body tissues of bivalves are a result of a complex combination of biotic and abiotic factors of the environment. Abiotic factors such as the physical and chemical properties of the environment and the chemical nature of the heavy metals influence on the heavy metal accumulation of bivalves (VanRoon, 1999). The chemical nature of the heavy metals in the aquatic environments plays an important role in the bioaccumulation in the bivalves. Heavy metals are mainly present in dissolved or suspended forms as free ions or as complex compounds in the aquatic habitats. It is free ions than the water soluble fraction which is bioavalable and ecologically more reactive (Kennish 1997).

In addition, heavy metal toxicity in the aquatic organism in the association with the long residence time within the food chains and the potential for human exposure makes it necessary to monitor heavy metal in the aquatic organisms. Marine organisms accumulate and concentrate heavy metals to a high level. Consequently they are used widely as biomonitors indicating the extent of metal pollution in the coastal waters (Szefer et al. 1998).

Metals are either necessary in low concentration to the human beings(trace metals) or extremely toxic for them in any concentration (heavy metals). High concentrations may cause many diseases and injuries to the human health. According to WRI (2006), humans are exposed to metals through the inhalation of air pollutants, consumption of contaminated soils or industrial wastes, food sources such as fish and shellfish may be contaminated by accumulating metals from surrounding soils and water.

The study looked at two molluscs *Typanotonus fuscatus* and *Crassosstrea spp* which are one of the most common shellfish in the Riverine area and are also highly appreciated for human consumption in the River state. The purpose of this study was to obtain quantitative information on the concentration of heavy metals in the these two mollusks, sediment and water from Kalarugbani Creek in Okrika, River State.

2.0. MATERIALS AND METHODS

2.1. Study Area

Samples were harvested from Kalarugbani Creek in Okrika L.G.A, River State.

2.2. Sampling Strategy

Samples of oyster were taken during the dry and wet seasons. Thirty of the same sizes were collected from the creek, Also samples of perwinkle of the same were taken during the dry and wet season. Thirty of the same sizes were collected from the creek. After collection, the shellfish were allowed to flush out undigested matter in the filtered seawater from the sampling sites for 24 hours. The soft tissues of these shellfish were carefully removed by shelling the oyster with stainless steel instrument (knife) which was inserted between the shell about 2 cm from the hinge area the knife was pushed into the shellfish and the meat removed from the shell. The perwinkle meat in the was cracked using a sterile hammer on the improvised sterile anvil then the meat is extracted individually from the broken shell using a sterile forceps (APHA 1970 as modified by Odu, 1989).

Five gram (5g) of these samples was digested with 20 ml of concentrated H_2SO_4 was added. The content was boiled again and small quantity of concentrated HNO_3 was added immediately the liquid began to blacken. The addition of concentrated HNO_3 was stopped when the liquid no longer blackened but the heating continued until a white fume begins to appear. The whole content was cooled and 10ml of saturated ammonium oxalate solution was added. The mixture was heated until copious white fumes were produced. The yellow solution then turned colourless. The digestate was stored in the polythene bottles. Blanks were prepared in the same way but omitting the samples (Ayenimo et al., 2005). The solution was analysed for Fe, Cu, Pb, Cr, Ni and Zn using the computerized scientific model 200a/20 atomic adsorption spectrophotometer (Davis et al., 2006; Adebowale et al., 2009)

2.3. Physiochemical Parameter Of The Overlying Water

The physiochemical parameter of the overlying water, salinity of the overlying water was determined using a refractometer (Antergo 28). A drop of the test water was placed on the lens of the instrument while the meter was held horizontally. The test water was allowed to remain for about five minutes and the salinity was then read off from the eyepiece and recorded in parts per thousand. Water temperature was measured in situ using mercury –in glass thermometer and the sampling site. The thermometer was immersed in water to about 6cm below the water surface and left to stabilize for about five minutes and the average values recorded in degree centigrade. Hydrogen- ion (pH) was taken immediately at the sampling site. A multiple meter, model U-10 micro from Horiba Limited Japan was used to determine the pH. The electrode was immersed into the beaker of water sample and the values recorded after 5 minutes to stabilize (Abowei, 2010).

3.0. RESULTS ANALYSIS

The concentration of heavy metal found in the edible portion of raw shucked oyster and raw extracted periwinkle as shown in Figure 1-6 indicates that RSO accumulated more heavy metal than REP. Oyster had a higher accumulation of these metals (Pb, Cu, Ni and Zn) than periwinkle which had higher concentration of Fe and Cr for the period sampled. The concentration of Pb, Cu, Ni, Zn, Fe and Cr were higher in the sediment than the overlying water for the various month sampled as shown in Figure 1-6**.**

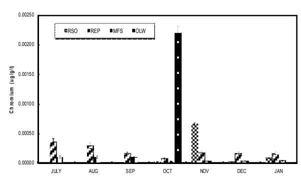

Figure 1 A bar chart showing the monthly variation in the in the incidence of chromium (ug/g/l) of the various samples.
Values represent the mean of determination two determinations. Bars indicate standard errors
REP = Raw extracted periwinkle; RSO = Raw Shucked oyster; OLW = Overlying water and MFS = Mud flat sample

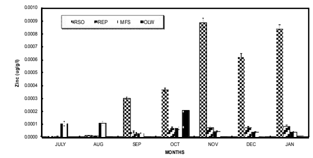

Figure2: A bar chart showing the monthly variation in the in the incident of Zinc (ug/g/l) of the various samples.
Values represent the mean of determination two determinations. Bars indicate standard errors
REP = Raw extracted periwinkle; RSO = Raw Shucked oyster; OLW = Overlying water and MFS = Mud flat sample

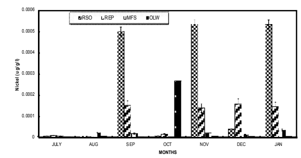

Figure 3: A bar chart showing the monthly variation in the in the incidence of Nickel (ug/g/l) of the various samples.
Values represent the mean of determination two determinations. Bars indicate standard errors
REP = Raw extracted periwinkle; RSO= Raw Shucked oyster; OLW = Overlying water and MFS = Mud flat sample

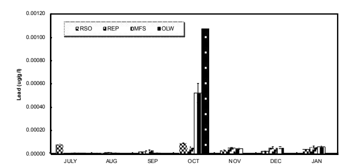

Figure 4; A bar chart showing the monthly variation in the in the incident of Lead (ug/g/l) of the various samples.
Values represent the mean of determination two determinations. Bars indicate standard errors
REP = Raw extracted periwinkle; RSO = Raw Shucked oyster; OLW = Overlying water and MFS = Mud flat sample

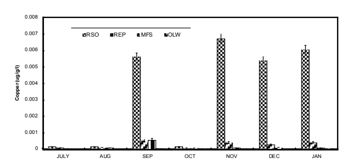

Figure 5: A bar chart showing the monthly variation in the in the incident of Copper (ug/g/l) of the various samples.
Values represent the mean of determination two determinations. Bars indicate standard errors
REP = Raw extracted periwinkle; RSO = Raw Shucked oyster; OLW = Overlying water and MFS = Mud flat sample

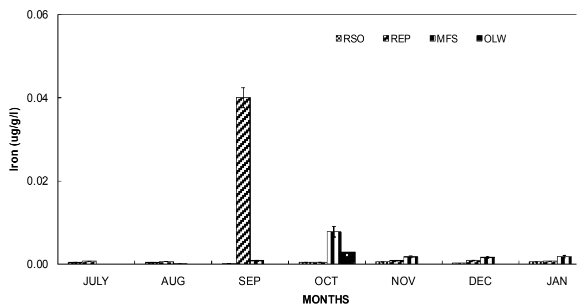

Figure 5: A bar chart showing the monthly variation in the in the incident of Iron (ug/g/l) of the various samples.
Values represent the mean of determination two determinations. Bars indicate standard errors
REP = Raw extracted periwinkle; RSO = Raw Shucked oyster; OLW = Overlying water and MFS = Mud flat sample

3.1. Metal concentration in the organism

The two molluscs have different amounts of metals in their tissues. The concentration of Ni, Zn, Cu and Pb was higher in oyster than periwinkle. Other the other hand Cr and Pb were higher in prewinkle than oyster. Some papers have already shown that different species of bivalves have different capacities for accumulating metals (Jeng *et al*., 2000). The most abundant elements in oyster were Zn and Cu. The Cu level in raw shucked oyster can be considered to be within the permissive level if compared with past works of bivalves' studies (FDA 2001; Baraj *et al*., 2003; Paulson *et al*., 2003). Also, the Zn concentration in raw shucked oyster was also within the permissive level if compared with past works of bivalves' studies (Cheggour *et al*., 2001; FDA, 2001; Shulkin et al., 2003).

It is common to find higher concentration of Zinc than Cu in bivalves' studies (Szefer *et al*., 1997; Wong *et al*., 2000). It has been well documented that the oyster, is capable of bioaccumulating heavy metals in its soft tissue to levels that are greater than in its corresponding environment. In this study, similar observations were made comparing the elemental concentrations in oyster tissue to those in the water column and surficial sediment. It is generally agreed that heavy metal uptake occurs mainly from water, food and sediment. However, effectiveness of metal uptake from these sources may differ in relation to ecological needs and metabolism of animals and concentrations of the heavy metals in water, food and sediment as well as some other factors such as salinity, temperature, interacting agents (Roesijiadi and Robinson, 1994).

Bivalves are sessile organisms which have various mechanisms to protect themselves from toxic effects of heavy metals. Some bivalves have the ability to neutralize the toxicity of metals and to store heavy metal at cellular level of the body tissue. However, a number of adverse effects of heavy metal on the health and productivity of bivalves have been reported in literature. Bivalves, like other organism have complex interactions with the environment. Variation of bioaccumulated heavy metals with in body tissues of bivalves are a result of a complex interaction combination of biotic and abiotic factors of the environment. Abiotic factors such as physical and chemical properties of the environment and the chemical nature of the heavy metals influence on the heavy metal accumulation of bivalves (Van Roon, 1999).

3.2. Metal concentration in sediments and water

The sediment accumulated more heavy metals than the water in this study as have been observed by Besada et al. (2001), Chindah and Braide (2003) and Eja et al. (2003). Sediment is the major depository of metals in some cases, holding more than 99 percent of total amount of a metal present in the aquatic system (Odiete 1999). Sediments are important storage compartment for the metal release into the surface waters. Further more because of their ability to accumulate heavy metal, sediments can reflect water quality and record the anthropogenic emissions. The occurrence of elevated levels of trace metals especially in sediments can be a good indication of man induced pollution and high levels of heavy metals can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering (Davies et al., 2006). Sediments, on the other hand, integrate contaminants over time and are in constant flux with the overlying water column.

The analysis of heavy metals in the sediments permits detection of pollutants that may be either absent or in low concentrations in the water column (Davies et al., 2006). Their distribution in coastal sediments provides a record of the spatial and temporal history of pollution in a particular region or ecosystem. Heavy metal concentrations in the water column may be relatively low, but concentrations in the sediment may be elevated. It has been estimated that about 90% of particulate matter carried by rivers settles in estuaries and coastal areas. Once heavy metals are discharged into estuarine and coastal waters, they rapidly become associated with particulates and are incorporated in bottom sediments. The effect of heavy metal contaminants in the sediments may be either acute or chronic (cumulative) on benthic organisms. The bioaccumulation of metals in various fish and shellfish organisms is well studied (Canli and Autili, 2003), whilst the bioavailability of trace metal concentrations is controlled by many chemical, physical and biological factors (Morse et al., 1993).

Many of these metals serve no known biological function in the marine environment, but can act synergistically with other chemical species to increase toxicity. Increased heavy metal concentrations and organic carbon will tend to be associated with finer-grained sediments because of their high surface to volume ratios and absorption abilities. The effect of metal pollutant on macrobiota and microbiota has been stressed by several workers; loss of species invisible extinction of species (Odiete, 1999); elimination of shellfish, molluscan, fish and crustaceans in coastal and estuarine zone. Other workers have explained that heavy metals constitute a significant threat to the aquatic environment: hindrance to fishing impairment of water quality and injury to living organisms' contamination of benthic fauna via bioaccumulation and biomagnification and changes in benthic communities (Odiete, 1999); indirect effect on man through consumption of sea foods (Odiete, 1999). Such changes have ecological and commercial importance on trophic levels.

These heavy metal are harmful to the human health, Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains. Nickel is not known to accumulate in plants or animals and as a result nickel has not been found to bio magnify up the food chain. For animals nickel is an essential foodstuff in small amounts. Excess iron in the body causes liver and kidney damage (haemochromatosis).

Some iron compounds are suspected carcinogens. Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. Zinc is a very common substance that occurs naturally Zinc may also increase the acidity of waters. Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish it is able to bio magnify up the food chain.

Figure 7 shows the pH values ranges from 6.51-6.78 in the wet season and 6.83-7.02 in the dry season. Seasonal variation of pH of the overlying water was observed in this study is in agreement with the results of previous studies conducted by(Dublin-Green, 1990) in Bonny River where the highest pH values were recorded in the dry season and lower value of pH in the wet season and other studies conducted (Abowei, 2010). This may be due to the influx and decay debris in the area as well as imbalance level of hydrogen ions inputs from surface runoff during the rainy season (Abowei, 2010).

Temperature and salinity are important physical factors that affect the bioaccumulation of bivalves. Relatively high temperature in seawater promotes copper adsorption in the bivalves (Abbe-Riedel et al., 2000). The rate of adsorption and accumulation of Lead by oyster has been favoured by low salinities than the accumulation rate in higher salinities (Denton and Burdon-Jones, 1981). However, Davis et al. (2006) observed decrease of net uptake of lead in bivalves at low salinities.

The salinity effect on lead uptake would cause an estimation of lead concentration in bivalves tissues in areas were salinities are lower than the normal values (Davis et al., 2006). However, adsorption and accumulation of Zinc in the tissues of bivalves are affected neither by temperature nor by the salinity of the seawater.

Figure 8 shows the temperature values ranges from 24.75- 26.05ºC for the wet season and 26.85-27.61ºC in the dry season. Seasonal variation in the ambient temperature was observed in Kalarugbani creek. Dry season was slightly higher than that of the wet season. Higher temperature values recorded in the dry season are expected since heat from the sunlight increases temperature of surface water, similarly the drop in the water temperature in the rainy season is attributed to heavy rainfall experienced during the period. This is similar to the observation of (Chindah *et al.*, 1998, 2003; Zabby, 2002; Ansa 2005; Kosa, 2007).

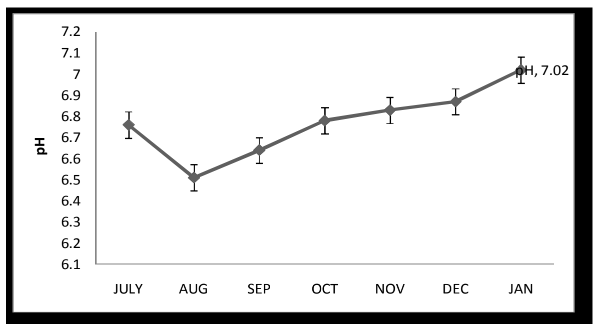

Figure 7: A graph showing the monthly variation in the pH of the overlying water. Values represent the mean of the determination two determinations. Bar indicates standard errors

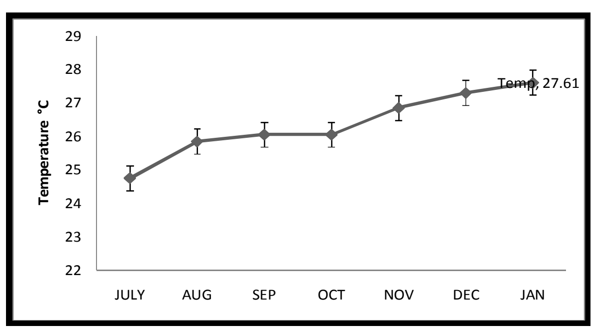

Figure 8: A graph showing the monthly variation in the Temp of the overlying water. Values

represent the mean of the determination two determinations. Bar indicates standard error

Figure 9 also shows the salinity values ranges from 1.094- 2.71% in the wet season and 2.89-3.79% in the dry season. Salinity has been viewed as one of the most important variables influencing the utilization of the organisms in estuaries (Marshall and Elliot, 1998). Seasonal variation was observed, high salinity values was recorded during the dry season than the wet season. This is because during the wet season high volumes of fresh water are discharged into coastal or estuarine water that lowers or dilute the water. Similarly, Mclusky (1989) reported that rain fall could cause dilution of estuaries and hence cause reduction in salinity, while heat generated by sun light in dry season months would cause evaporation of the surface water making it saltier and hence more saline.

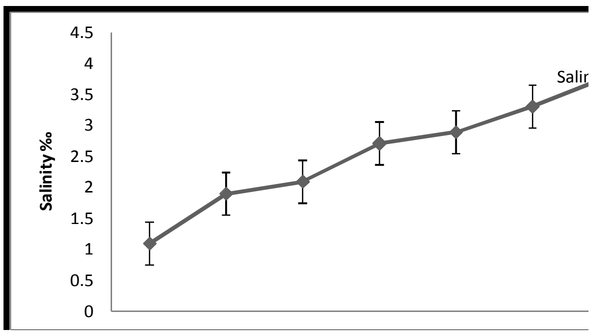

Figure 9: A graph showing the monthly variation in the Salinity of the overlying water. Values represent the mean of the determination two determinations. Bar indicates standard error

As bivalves live in the water sediment interphases, they have the potential to bioaccumulate heavy metals from contaminated sediments and water (Huanxin Lejun et al., 2000). The heavy metal concentration in bivalves' tissue gives a more reliable measurement of heavy metal concentration in sediment than water (Shulkin Presley et al., 2003). The concentration of heavy metal contaminants detected by the analysis of bivalves' tissue is not directly proportionate to the concentration of the heavy metals in the sediments, but is only related to extractable metal forms in the sediments (Shulkin Presley et al., 2003). This creek receives organic matter in amount exceeding its natural purification capacity due to high population and industrial growth. In the past natural purification and dilution were usually sufficient (Saad et al., 1994).

4.0. CONCLUSION

This study has shown that coastal areas have the potential to have anthropogenic inputs of pollutants which are great threat to the aquaculture industry. Hence heavy metal pollution could become a significant problem in the coastal environment especially areas with bivalves farming. Therefore heavy metal contamination of shellfishes is difficult to avoid. To avoid coastal pollution, control measures have to be exercised at the source of discharge. Industrial discharge of agricultural contaminants such as fertilizer and pesticides should be controlled as a remedy to minimize coastal pollution.

This study has also shown that the periwinkle and oyster, has a high potential to concentrate heavy metals though the observed concentrations are below WHO, FAO and FDA limits. However, indiscriminate effluents discharges should be stopped or effluent must be treated before being released into this creek. Also, there should be continuous environmental pollution monitoring to check heavy metals hazard.

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