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Concentrations of Heavy Metals in *Macrobrachium vollenhovenii* (Herklots, 1857) from Epe Lagoon, Lagos, Nigeria

A.A. Jimoh, E.O. Clarke, P.E. Ndimele, C.A. Kumolu-Johnson and F.A. Adebayo
Department of Fisheries, Faculty of Science, Lagos State University,
Ojo, Lagos State, Nigeria

Abstract: The levels of five metals, Fe, Cu, Zn, Cr and Pb in *Macrobrachium vollenhovenii* from Epe Lagoon were investigated from March, 2008 to December, 2008. The monthly concentrations of the metals varied significantly ($p<0.05$) but seasonal dynamics (dry and rainy) had no effect on the concentrations of these metals except Zn. The values of these metals recorded in this study are below the values reported in previous studies carried out in industrialised parts of Nigeria. They are also lower than the recommended limits set by Food and Agriculture Organisation and World Health Organisation. This study suggests that the *Macrobrachium vollenhovenii* from Epe Lagoon contains the heavy metals studied but their levels in this shell fish is still within acceptable limits.

Key words: Bio-indicator, Epe Lagoon, heavy metals, *Macrobrachium vollenhovenii*, physico-chemistry

INTRODUCTION

Lagos state is situated within the low-lying coastal zone of Nigeria. This coastal terrain is dominated by a maze of estuaries, lagoons, creeks and rivers. Out of the total land area covered by Lagos state, one-quarter is liquid surface: lagoons, creeks and coastal river estuaries (Ndimele, 2003). These water bodies act as sinks for the disposal of wastes from about 2000 medium and large scale industries located in the Lagos metropolis (Anetekhai *et al*., 2007). This situation has arisen as a result of increasing urbanization and industrialization, and laxity in enforcing environmental regulations in developing countries (Biney *et al*., 1994). In addition, the occurrence of metals in the environment through processes such as weathering and volcanism (Moore and Ramamoorthy, 1984) and the high absorption capacity of detritus for trace metals (Zhang *et al*., 1990) can significantly increase the metal burden in aquatic ecosystems.

Epe Lagoon (Fig. 1) is one of the four major lagoons in Lagos state, Nigeria (Kumolu-Johnson *et al*., 2010). The other three lagoons are Ologe Lagoon, Lekki Lagoon and Lagos Lagoon. Lekki Lagoon is situated to the east, Lagos Lagoon in the central and Ologe Lagoon is situated to the west. Epe Lagoon lies between latitudes 6º29′N and 6º38′N; and longitudes 3º30′E and 4º05′E (Agboola and Anetekhai, 2008).

Copper, an essential micronutrient for fish and aquatic life, is also widely used as an effective algaecide and molluscicide (Abou-Zaid *et al*., 1988). Since copper from anthropogenic sources eventually contaminates water bodies, toxicity of this metal to aquatic organisms has been intensely studied over the past two decades (Getachew, 1988). Zinc is an essential trace element in living organisms, being involved in nucleic acid synthesis and occurs in many enzymes. Background values of zinc in natural inland surface waters may vary from 0.001 to 0.2 mg/L or even higher (Oyewo, 1998). Zinc and its compounds are extensively used in commerce and in medicine. The common sources of it are galvanized ironwork, zinc chloride used in plumbing and paints containing zinc. It is soluble in water and illness may be caused by drinking water containing zinc (Clarke *et al*., 1981). Zinc wastes can have a direct toxicity to aquatic life, and fisheries can be affected by either zinc alone or more often together with copper and other metals (Ali and Fishar, 2005).

Organic lead compounds (Tetraethyl lead and tetramethyl lead) are extensively used as an additive in petrol and this releases Pb, which is not easily biodegradable, into the aquatic environment through drainage and surface run-offs. Lead is still the single most important chemical toxin for children and is probably the best known example of a neurotoxin to which children are particularly vulnerable (Dietrich *et al*., 1993). Lead pollution is a subject that demands urgent and consistent attention in Africa because Africa's contribution to global lead Pollution have increased from just 5% in 1980's to 20% in 1996 (Anonymous, 1996). In Nigeria, the level of Pb in petrol is estimated at 0.7 g/L (Sridhar *et al*., 2000). This is close to 0.84 g/L recorded in Malaysian petrol,

Corresponding Author: P.E. Ndimele, Department of Fisheries, Faculty of Science, Lagos State University, Ojo, Lagos State, Nigeria. Tel: +234803-820-5109

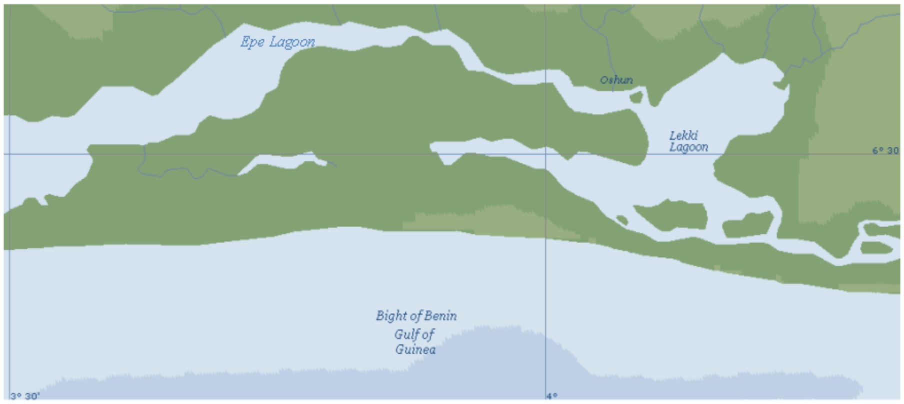

Fig. 1: Map of Epe Lagoon

which is one of the highest in the world (Osibanjo and Ajayi, 1989). Chromium is used in metal alloys and pigment for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney damage, and damage to circulatory and nervous tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium.

Shell-fishes have been widely used as bio-indicators to monitor heavy metal concentrations in the environment due to their wide range of distribution and their importance in food chain (Asuquo and Udoh, 2002). Prawns and shrimps are known to consume sand and mud along with detritus during feeding (Koli *et al*., 1978; Jimoh and Anetekhai, 2004). This sediment act as sink for the heavy metals in aquatic ecosystems and since these metals are non-biodegradable and can persist in the environment for a very long period (Kumolu-Johnson *et al*., 2010), they can be taken up by shell-fishes during feeding. Another factor that makes shell-fishes ideal for aquatic bio-monitoring is because of their slow mobility. Unlike the fin fishes that will quickly swim away from polluted environment, shell-fishes may remain in the polluted environment and this makes them a better bio-monitor than fin fishes (Kumolu-Johnson *et al*., 2010).

Macrobrachium vollenhovenii is one of the species of *Macrobrachium* found in fresh and brackish waters of West Africa (Marioghae, 1982). It large size also makes it a suitable choice for aquaculture in Nigeria (Anetekhai *et al*., 2007). Post-larvae and broodstock are usually sourced from the wild due to difficulty of procuring hatchery-raised prawns. It becomes important to ascertain the safety of these post-larvae and broodstock before they are raised and subsequently consumed by man. The specific objective of this study is to determine the heavy metal (Fe, Cu, Zn, Cr and Pb) content of *Macrobrachium vollenhovenii* from Epe Lagoon, and compare them with national and international standards and this will help to ascertain their safety for human consumption.

MATERIALS AND METHODS

Physico-chemical parameters: Water samples were collected directly from each sampling station in 2 L plastic containers washed with nitric acid to remove contaminants. Samples were stored immediately in a cooler, in order to ensure that the physical properties of the water samples were maintained, and transported to the laboratory for analysis. Temperature and pH were determined *in situ* while dissolved oxygen, salinity, total alkalinity and total hardness were determined by titration (Boyd, 1981). Temperature was determined using a mercury-in-glass thermometer; pH was measured using a Metrohm Herisau E520 pH meter and turbidity was measured using nephelometer.

Dissolved oxygen: Water samples were collected in a 250 mL dissolved oxygen bottle below the surface of the water. 2 mL of Manganous sulphate solution followed by 2 mL Potassium iodide (KI) solution were added to water samples in order to fix the oxygen. The bottle was carefully closed with a stopper to exclude air bubbles and mixed thoroughly by shaking the bottle. The formed precipitate was immediately taken to the laboratory for analysis.

In the laboratory, 2 mL of H_2SO_4 was added and the bottle shook thoroughly to dissolve the precipitate. 10 mL of this solution was placed into conical flask and titrated against 0.0250 N $Na_2S_2O_3.5H_2O$ (Sodium thiosulphate solution) using 2 drops of starch solution as indicator. Dissolved oxygen (mg/L) was calculated as follows:

$$\text{DO (mg/L)} = \frac{\text{Vol. of } Na_2S_2O_3.5H_2O \text{ (mL)} \times 0.0250\text{N} \times 8 \times 1000}{\text{Vol. of water sample (mL)}}$$

Salinity: 10 mL of water samples were measured into conical flasks and 15 mL of potassium chromate were added to each sample. The above were titrated with silver nitrate until the initial yellow colour turned into a brick-red precipitate.

$$\text{Salinity} = \text{Ml of silver nitrate} \times 1.8065$$

Total alkalinity: Total alkalinity was determined by adding 4 drops of methyl orange indicator to 100 mL of the water sample. The sample turned yellow. This was then titrated with standard sulphuric acid (0.02N H_2SO_4) until the yellow colour of the sample changed to faint orange.

$$\text{Total alkalinity (mg/L)} = \frac{\text{mL of standard } H_2SO_4 \times 0.02\text{N} \times 50 \times 1000}{\text{Vol. of water sample (mL)}}$$

Total hardness: Total hardness was determined by titrating disodium Ethylenediamine Tetra Acetic Acid (EDTA) with the water sample using Eriochrome B-T (EBT) as indicator. 100 mL of the water samples were measured into conical flasks using measuring cylinder. 2 mL of buffer solution were added to the samples with the aid of pipette. The samples were thoroughly mixed. Using dropping pipette, 8 drops of EBT indicator were added to the 100 mL of water samples in the conical flasks and the samples turned wine-red. The samples were then titrated with 0.010 M standard EDTA solution until the sample changes from wine-red to pure blue.

$$\text{Total hardness (mg/L)} = \frac{\text{mL of EDTA} \times 0.010\text{M} \times 100.1 \times 1000}{\text{Vol. of water sample (mL)}}$$

Metal analyses:

Sample collection, storage and preservation: 150 Specimens of *Macrobrachium vollenhovenii* were obtained from Epe Lagoon (Fig. 1) by fishermen using barrier trap (with non-return valve) between March, 2008 and December, 2008, which includes three months of dry season (March, November and December) and seven months of rainy season (April - October). The prawns were washed in flowing water to remove adhering dirt and stored in deep freezer (-10ºC).

Sample treatment: All frozen samples were allowed to thaw at room temperature (i.e., ~27ºC). The prawn samples were homogenised after drying in an oven at 105ºC. The head regions of the specimens were separated from the abdomen/tail and digested according to APHA (1985) and FAO/SIDA (1986). The flesh for metal analyses was taken from the left dorso-ventral muscle of the samples. Composite samples were also prepared from prawns whose muscles were not enough to give 10 g sub-sample. 10 g of each sample was digested using 1:5:1 mixture of 70% perchloric acid, concentrated nitric acid and concentrated sulphuric acid at 80±5ºC in a fume chamber until a colourless liquid was obtained. Each digested prawn sample was analyzed for metal concentration using an Atomic Absorption Spectrophotometer Unican 969, 1996 model. The analytical procedure was checked using reference material (DORM 1, Institute of Environmental Chemistry, NRC Canada). Levels of metals (Fe, Cu, Zn, Cr and Pb) were expressed in mg/g dry weight.

Table 1: Physico-chemical parameters of Epe Lagoon

Properties	Values (Mean±SE)
Temperature (ºC)	30.35±0.17
pH	7.56±0.05
Salinity (ppt)	0.24±0.19
Turbidity (NTU)	25.48±2.01
Dissolved Oxygen (mg/L)	4.58±0.29
Total Alkalinity (mg/L)	91.05±15.13
Total Hardness (mg/L)	110.75±10.43

Statistical analysis: Monthly variations in metal content in *M. vollenhovenii* were tested by a one-way Analysis of variance (ANOVA) while seasonal (dry and wet) variations were tested by t-test. The Chi-square test was used to compare heavy metal levels in *M. vollenhovenii* to the standards set by Food and Agricultural Organisation/World Health Organisation (FAO/WHO, 1992) and WHO (2008). In all cases, the level of significance was set at $\alpha = 0.05$.

RESULTS AND DISCUSSION

The mean value of temperature (30.35±0.71ºC), pH (7.56±0.05), salinity (0.24±0.19 ppt), and dissolved oxygen (4.58±0.29 mg/L) (Table 1) recorded in Epe Lagoon were within the range (temperature <40ºC, pH 6.5-9.5, salinity <0.5 ppt for fresh water, and dissolved oxygen, 3.0-5.0 mg/L) recommended by the Federal Environmental Protection Agency (FEPA, 2003). However, the concentrations of total alkalinity (91.05±15.13 mg/L) and total hardness (110.75±10.43 mg/L) were above the values (total alkalinity 3.05-5.3 mg/L; and total hardness 0-75 mg/L) recommended by FEPA (2003).

The monthly concentrations of metals in *Macrobrachium vollenhovenii* at Epe Lagoon are presented in Table 2 while Table 3 shows the seasonal variation of the metals in the fish. The highest concentration (3.88±0.04 μg/g) of Fe was recorded in December (dry season) while the lowest (1.67±0.20 μg/g) was observed in March (onset of rainy season). Cu and Zn recorded their highest concentrations (Cu = 13.56±0.02 μg/g; Zn = 14.67±0.03 μg/g) in September (rainy season) while lowest concentrations (Cu = 9.63±0.01 μg/g; Zn = 9.33±0.05 μg/g) were observed in May (rainy season) and March (onset of rainy season), respectively. The highest

Table 2: Heavy metal concentrations (μg/g) in *Macrobrachium vollenhovenii* from Epe Lagoon

Month	Fe	Cu	Zn	Cr	Pb
March	1.67±0.20[af]	10.52±0.01[a]	9.33±0.05[a]	0.56±0.03[a]	0.56±0.06[ae]
April	2.58±0.19[bd]	11.68±0.03[b]	9.56±0.03[a]	1.33±0.02[b]	0.88±0.06[bc]
May	2.88±0.25[bc]	9.63±0.01[c]	12.78±0.02[b]	0.96±0.01[cd]	0.96±0.08[c]
June	3.10±0.26[bc]	10.58±0.01[a]	11.69±0.03[c]	0.86±0.01[d]	1.34±0.07[d]
July	3.33±0.17[ce]	11.56±0.02[b]	10.58±0.03[d]	1.20±0.03[bc]	0.93±0.03[bc]
Aug	2.85±0.13[bc]	10.25±0.02[a]	12.78±0.03[b]	1.21±0.02[be]	0.45±0.06[a]
Sept	2.95±0.03[bc]	13.56±0.02[d]	14.67±0.03[e]	0.98±0.01[cde]	0.75±0.05[be]
Oct	2.13±0.13[df]	13.33±0.02[d]	12.89±0.01[b]	0.87±0.11[d]	0.45±0.03[a]
Nov	3.78±0.28[e]	12.20±0.03[e]	11.54±0.02[c]	0.97±0.12[cde]	1.20±0.06[d]
Dec	3.88±0.04[e]	11.25±0.03[b]	12.33±0.03[b]	1.33±0.20[b]	1.56±0.13[f]

Figures in the same column and with the same superscript letters are not significantly ($p>0.05$) different; All values are expressed as Mean±SE

Table 3: Seasonal variation in heavy metal concentrations (μg/g) in *Macrobrachium vollenhovenii* from Epe Lagoon

Season	Fe	Cu	Zn	Cr	Pb
Dry	2.98±0.29[a]	11.41±0.19[a]	10.69±0.39[a]	1.05±0.11[a]	1.05±0.12[a]
Rainy	2.87±0.11[a]	11.48±0.36[a]	12.57±0.30[b]	1.01±0.04[a]	0.81±0.08[a]

Figures in the same column and with the same superscript letters are not significantly ($p>0.05$) different; All values are expressed as Mean±SE

concentrations for Cr (1.33±0.20 μg/g) and Pb (1.56±0.13 μg/g) were recorded in December (dry season) while their lowest values (Cr = 0.56±0.03 μg/g; Pb = 0.45±0.03 μg/g) were recorded in March (onset of rainy season) and October (end of rainy season), respectively.

The concentration of the metals in *M. vollenhovenii* varied significantly ($p<0.05$) among the months (Table 2) but seasonality did not have significant ($p>0.05$) effect on the metal concentrations in *M. vollenhovenii* from Epe Lagoon except for Zn (Table 3). However, the values obtained are lower than the maximum allowable limits in food fish set by the World Health Organisation (Fe = 100 μg/g; Cu = 30 μg/g; Zn = 10-75 μg/g; Cr = 50 μg/g; Pb = 2 μg/g) WHO (2008) and Federal Environmental Protection Agency (Cu = 1-3 μg/g; Fe = 100 μg/g; Zn = 75 μg/g) FEPA (2003). Though, the values of Pb, are just slightly below the standards. The implication of this finding is that the consumption of *M. vollenhovenii* from Epe Lagoon is still safe but regular monitoring (annual) should be undertaken to promptly detect sudden increases in these metals, especially for Pb, which causes mental retardation in children (Fergusson, 1990).

The range of concentrations of Cu (9.63±0.01 - 13.56±0.02 μg/g) and Zn (9.33±0.05-14.67±0.03 μg/g) recorded in this study is lower than the range of values (Cu = 860-1620 μg/g; Zn = 6910 - 10400 μg/g) reported by Anetekhai *et al*. (2007) in *M. vollenhovenii* in Ologe Lagoon, Lagos, Nigeria. This might be due to greater metal load in Ologe Lagoon because of the presence of Agbara Industrial Estate, which discharges its waste into the lagoon (Kusemiju *et al*., 2001).

The range of values of Fe (1.67±0.20 - 3.88±0.04 μg/g), Cu (9.63±0.01 - 13.56±0.02 μg/g), Zn (9.33±0.05 - 14.67±0.03 μg/g), Cr (0.56±0.03 - 1.33±0.02 μg/g) and Pb (0.45±0.06 - 1.56±0.13 μg/g) in *M. vollenhovenii* recorded in this study is higher than the values of these metals reported in fin fishes in previous studies; Kumolu-Johnson *et al*. (2010) reported range of Cu concentration of 1.19±0.23 - 1.57±0.26 μg/g in *Cynothrissa mento* from Ologe Lagoon, Lagos, Nigeria, Adefemi *et al*. (2008) reported Zn concentration of 0.62-2.33 μg/g in *Tilapia mossambicus* from Ureje Dam in Southwest, Nigeria, Oguzie (2009) reported Cr concentrations of 0.10±0.002 - 1.80±0.05 μg/g in muscle, gut and gill of *Parachanna obscura, Clarias gariepinus* and *Chromidotilapia guentheri* from Ikpoba River, Benin City, Edo state, Nigeria and Ndimele *et al*. (2009) reported Pb values of 0.19±0.08 - 0.30±0.25 μg/g in *Chrysichthys nigrodigitatus* from Ologe Lagoon, Lagos, Nigeria. The reason for the high values of heavy metals recorded in *M. vollenhovenii* in this study than previous studies where the biota used are fin fishes might be due to the presence of exoskeleton in *M. vollenhovenii*, which is able to accumulate heavy metals. It could also be due to the feeding habit of *M. vollenhovenii*. Prawns are benthic feeders (Anetekhai *et al*., 2007) and this exposes them to alot of metal load in detritus and sediments, which act as sink for the non-biodegradable heavy metals (Kumolu-Johnson *et al*., 2010; Ndimele *et al*., 2009). These heavy metals are usually accumulated and transferred along the food chain (New and Singholka, 1982). Another reason for the higher metal load in *M. vollenhovenii* than fin fishes might be due to limited mobility of *M. vollenhovenii* compared to the fin fishes. This makes them accumulate more metals than fish, which makes them a better aquatic bio-monitor than the fin-fish, which swims away as quickly as possible from polluted environment.

The range of values of Cu (9.63±0.01 - 13.56±0.02 μg/g), Zn (9.33±0.05 - 14.67±0.03 μg/g), and Pb (0.45±0.06 - 1.56±0.13 μg/g) in *M. vollenhovenii* recorded in this study is lower than the values of these metals reported in *M. vollenhovenii* in previous studies: Abulude *et al*. (2006) reported 2400, 1600 and 1300 μg/g for Cu, Zn and Pb, respectively in *M. vollenhovenii* from coastal waters of Ondo state, Nigeria; Banjo *et al*. (2010) reported Cu (150 μg/g), Zn (560 μg/g) and Pb (50 μg/g) in *M. vollenhovenii* from different markets in south-west, Nigeria while Kakulu *et al*. (1987) reported

Cu (8500 µg/g), Zn (14100 µg/g) and Pb (2470 µg/g) in *M. vollenhovenii* from Niger Delta, Nigeria. These low concentrations of metals in Epe Lagoon might be due to less agro-chemical usage by farmers around Epe Lagoon and less industrial activities around Epe town as a whole, which are the major sources of heavy metal contaminants in aquatic environment (Banjo *et al*., 2010).

CONCLUSION

This study showed that *Macrobrachium vollenhovenii* from Epe Lagoon in Lagos, Nigeria contains metals in measurable quantities, although, the levels in this shell fish are still within safe limits for human consumption. However, periodic metal monitoring of Epe Lagoon is recommended in view of the nutritional and socio-economic importance of the Lagoon to the inhabitants of the area.

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