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CONCENTRATION OF HEAVY METALS IN THREE AFRICAN PRAWNS (CRUSTACEA: PALAEMONIDAE) FROM OVIA RIVER IN EDO STATE, NIGERIA

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ABSTRACT

Heavy metals concentrations in three African prawns sampled at three sites along Ovia river bank in Edo State were investigated by means of an atomic absorption spectrophotometer. The combined mean values of Pb, Ni, Fe, Cr, Mn and V in the prawn samples are presented in the following ranges: *Macrobrachium macrobrachion*- Pb (0.00-0.250 mg/kg), Ni (0.00-0.250mg/kg), Fe (0.560-0.631mg/kg) Cr(0.00-0.210mg/kg, Mn (0.850-2.250mg/kg) and V (0.00-0.033mg/kg). *M. felicinium*- Pb (0.00-1.50mg/kg), Ni (0.00-0.145mg/kg), Fe (0.105-1.510mg/kg), Cr (0.00-0.350mg/kg), Mn (0.156-1.320mg/kg), and V(0.00-0.10mg/kg). *M. vollenhovenii*- Pb (0.105-1.360mg/kg), Ni (0.103-0.210mg/kg), Fe (0.535-2.450mg/kg), Cr (0.013-0.230mg/kg), Mn (0.652-0.835mg/kg) and V (0.00-1.050mg/kg). No significant differences (P>0.05) were recorded between the concentrations of Fe and Mn in the prawn samples caught at the three study sites. The marginal high concentrations of Ni, Fe and Mn in the prawn samples are higher than recommended values in fish and fishery products by the Food and Agricultural Organization (FAO) and the World Health Organisation, (WHO). An evaluation of the possible risks associated with prawns contaminated with these metals could be deduced from this study. Findings from this study necessitate the need for caution in the discharge of pollutants into the Ovia river.

Keywords: Heavy metals, African prawns, Ovia River, Edo State, Nigeria.

INTRODUCTION

Fresh water organisms including prawns accumulate contaminants from the environment and have been used extensively in pollution monitoring programmes UNEP (1993). Industrial, agricultural and domestic activities in many countries including Nigeria have led to the increased discharge of chemical effluents into many inland water bodies (Ayodele *et al*., 1991). This situation has led to the deterioration of water bodies which serve useful purposes (domestic, recreational, transportation and drinking) to humans and other organisms (Ndiokwere and Ezihe, 1990). Heavy metals which are prominent contaminants in the discharged effluents when not properly managed before discharge, destroy freshwater species diversity and ecosystems by way of their accumulative behavior and toxicity (Matta *et al.,* 1999). Some freshwater bodies serve as spawning and nursery grounds for diverse species of commercially valuable prawns and fish. These organisms are directly affected by the discharge of metal contaminants into aquatic habitats (Gibson, 1994). The accu-

mulation patterns of metal contaminants in aquatic organisms including prawns depend on their uptake and elimination rates (Guven *et al.,* 1999). The pathways of metals uptake are through absorption of metal ions through the gills, adsorption onto food and particulates and ingestion with water (Connell and Miller, 1984). Though metal concentrations are relatively low in natural waters, their concentrations become higher when they become concentrated along the food chain. The result is that the components of the food chain including prawns concentrate the metals a thousand times higher than levels in the water column (Deb and Santra 1997).

Thus, the consequence of metals acquired through the food chain as a result of pollution could be potential chemical hazards threatening prawn consumers. It therefore, becomes mandatory to check chemical contaminants in prawns from the aquatic environment in order to understand their hazard levels.

In Nigeria, most studies on prawns had centered on their culture potentials and population ecology (Anetekhai, 1986; Marioghae, 1987; Bello-Olusoji, 1997; Edema and Egborge, 1999; Bello Olusoji *et al.,* 2005). Scanty information exist on the concentration levels of metal contaminants in prawns. The purpose of this study was to report the concentration levels of selected heavy metals in prawns of Ovia River in Edo State.

MATERIALS AND METHODS

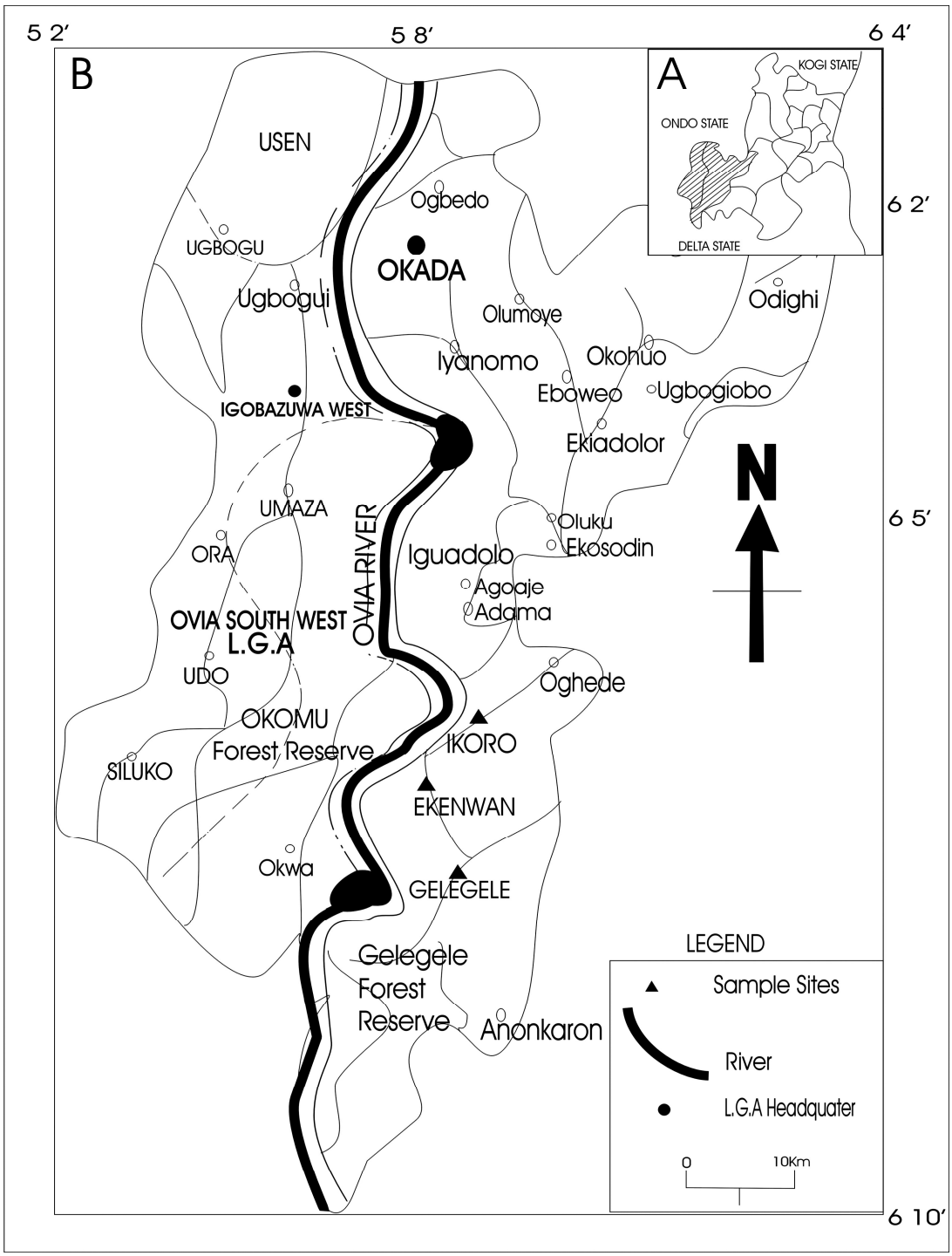
The study area

Ovia River in Edo State had previously been described (Oghenekaro and Oguzie, 2008) and is presented in Fig. 1. The area comprises a stretch of Ovia river which covers a distance of about 50 kilometers and is located in Ovia North-East of Edo State. The river lies approximately around Latitude 6.5^{0}N and Longitude 5.8^{0}E and flows in a South West direction through several villages. The sampled sites along the river are located in villages (Gelegele, Ekenwan and Ikoro) which were chosen based on their effluent characteristics. Site 1 (Gelegele) is characterized by petroleum industrial effluents and domestic wastes. Site 2 (Ekenwan) which is located about 10km from Gelegele is characterized by mixed effluent sources (agricultural, domestic and petroleum). Site 3 (Ikoro) acted as a control site because it is located at the upper reaches of the river and was assumed to be contaminant free based on its location compared to other sites.

Collection of samples

A total of 30 palaemonid prawn samples comprising 10 species each of *Macrobrachium macrobrachion, Macrobrachium felicinium* and *Macrobrachium vollenhovenii* were selected randomly from catches made by fisher-folks who used fish cages and woven cylindrical non-return valve traps for prawn capture between July and September, 2007. The gears were set overnight using coconut and cassava as baits and prawns were harvested at the three sites the following morning. Duplicate water samples (2L) were collected randomly at the same sites at 30cm depth into polythene bottles previously soaked overnight in dilute nitric acid and rinsed with distilled water. The water samples were acidified to pH 1.5 with nitric acid after collection (APHA, 1998) and stored frozen at- 5^{0}C. Prawns along with water samples were transported to the laboratory in ice packs to Faculty of Agriculture laboratory in the University of Benin.

In the laboratory, the prawns were identified by means of identification guides by Powell



A: Map of Edo State showing the study area (Ovia River)
B: Map of Ovia River showing sampling sites

(1982, 1983). They were further separated on the basis of species and processed whole. Routine body measurements (total prawn length and weight) were determined with a plastic meter rule, a venier caliper and a top loader (Mettler, P.E. 230) and recorded to the nearest 0.1cm and 0.1g respectively. 10 prawn samples representing each species were oven dried at 80^0C for 72 hours to constant weight and milled separately to powder by means of a porcelain mortar and pestle. They were subsequently stored in labelled plastic packs, sealed and stored at -10^0C prior to digestion and analysis.

Digestion and Analysis

Pulverised dry prawn samples (lg) from the various sites were placed in a 100ml decomposing beaker. Concentrated nitric acid (20ml) and perchloric acid (10ml) were added to contents of the beakers. These were evaporated to near dryness on a hot plate at a temperature of between 200-250^0C under a hood (Van Loon, 1980). The resulting residues were dissolved and washed into 50ml volumetric flasks with 0.1M HNO_3 and made up to mark with distilled de-ionised water. The flasks and their contents were stored for 2 to 3 weeks until metal concentrations could be determined. The metals (Pb, Ni, Cr, Mn and V) except Fe, were analysed using an atomic absorption spectrophotometer (UNICAM 929) according to APHA (1998). The concentration of Iron (Fe) was determined by the Orthophenantroline method (Allen, 1989) with some modifications as described by Oguzie and Izevbigie (2009). Water samples were not given further treatment but were in each case vigorously shaken and aspirated into the flames of the atomic absorption spectrophotometer (AAS). Digested samples were analysed thrice. The AAS was calibrated for each metal. The standard solution for instrument calibration was prepared by dissolving 1000mg analar grade metal salt using 1litre of distilled water. Standard and corresponding blanks were run with each sets of experimental digests. The limits of detection of the various metals were as follows: Pb, 0.05μg/g., Ni, 0.02μg/g., Cr, 0.05μg/g., Mn, 0.5μg/g and V, 0.02μg/g. One way analysis of variance (ANOVA) was used in all cases for mean metals level comparison at 5% level of significance. Means were separated using the Duncan Multiple Range Test.

The actual concentration of each metal was calculated using the formula:

Actual concentration of metal = PPMR x Dilution factor (Olaifa *et al.,* 2004).

where PPMR = AAS reading of digest

$$\text{Dilution factor} = \frac{\text{Volume of digest used}}{\text{Wt. of sample digested}}$$

RESULTS AND DISCUSSION

The concentrations of heavy metals in the water and three prawn species (*M. macrobrachion, M. felicinium* and *M. vollenhovenii)* sampled at the three sites (Site 1, Gelegele, Site 2, Ekenwan and Site 3, Ikoro) are presented in Tables 1 and 2. At the three study sites lead (Pb) in the prawns showed concentration range of 0.00-1.50mg/kg dry weight of sample. The lowest mean concentration of Pb (0.105mg/kg) was recorded in *M. vollenhovenii* caught at site 2, while the highest mean Pb value (1.50mg/kg) was recorded in *M.* caught at site 1. The rank profile of Pb content of the three prawn species in descending order was *M. felicinium* > *M. vollenhovenii* > *M. macrobrachion.* One-way analysis of variance (ANOVA) conducted on metals data, showed significant differences ($P< 0.05$) between the concentration of Pb in the prawns caught at sites 1 and 2. However, no signifi-

cant differences (P> 0.05) were recorded between Pb concentrations in prawns caught at sites 2 and 3 (Table 2).

Lead was detected in 77.7% of total prawn samples. In the present study the total mean Pb value (1.615mg/kg) recorded in the dominant *M. vollenhovenii* at the three study sites is lower than Pb value (2.47mg/kg) reported by Kolade (1999) in *M. vollehovenii* caught in Ogba river in Benin City but higher than Pb value (0.029mg/kg) reported by Edema and Egborge (1999) for the same prawn species in Warri river. The total mean levels of lead recorded in *M. macrobrachion* (0.406mg/kg), *M. felicinium* (1.672mg/kg) and the dominant *M. vollenhovenii* (1.615mg/kg) are lower than Pb value (2mg/kg) recommended in fish and fishery products by the Food and Agricultural Organization (FAO, 1983).

Table 1: Mean concentration values (mg/l) of heavy metals in the water samples from the three sites on the Ovia River, Edo State, Nigeria.

Site	Metal concentrations (mg/l) in water					
	Pb	Ni	Fe	Cr	Mn	V
1(Gelegele)	0.010± 0.001	0.012 ± 0.003	1.250± 0.02	0.020± 0.001	0.035± 0.003	0.015± 0.001
2(Ekenwan)	0.013± 0.002	0.006± 0.002	0.825± 0.03	0.018± 0.001	0.048± 0.002	0.012± 0.003
3(Ikoro)	0.005± 0.002	0.003± 0.002	0.653± 0.03	0.013± 0.002	0.030± 0.001	0.010± 0.002
WHO (1996)	0.01	-	0.3	-	0.05	-
DPR (1991)	-	1.0	-	-	-	0.01

Values are presented as means of three replicate samples ± SD

Table 2: Mean length, weight and concentrations (mg/kg) of heavy metals in prawn samples caught at three sites on Ovia River, Edo State, Nigeria. (Ranges for lengths and weights are shown in parenthesis)

Site	Prawn Species	No. of Samples	Mean length	Mean weight	Heavy metals					
			(cm)	(g)	Pb	Ni	Fe	Cr	Mn	V
Site 1 (Gelegele)	*M. macrobrachion*	10	108.50 ±10.14 (82.40 – 120.20)	14.32 ± 2.15 (10.60 – 20.12)	0.00	0.250^{ab} ± 0.01	0.560^{ab} ± 0.02	0.00	2.250^{a} ± 0.01	0.033^{ab} ± 0.01
	M. felicinium	10	96.75 ± 16.12 (75.60 – 112.40)	17.20 ± 1.60 (16.30 – 24.52)	1.50^{a} ± 0.01	0.00	1.510^{a} ± 0.01	0.530^{ab} ± 0.01	1.320^{a} ± 0.01	0.101^{ab} ± 0.02
	M. vollenhovenii	10	140.10 ± 8.80 (110.35 – 161.42)	22.20 ± 3.45 (18.50 – 28.12)	0.150^{ab} ± 0.02	0.160^{ab} ± 0.01	2.450^{a} ± 0.03	0.230^{ab} ± 0.01	0.835^{ab} ± 0.02	1.050^{a} ± 0.02
Site 2 (Ekenwan)	*M. macrobrachion*	10	100.42 ± 9.65 (65.10 – 120.35)	18.15 ± 4.92 (13.60 – 24.28)	0.250^{c} ± 0.01	0.00	$0.60^{ab}5$ ± 0.01	0.035^{c} ± 0.01	1.653^{ab} ± 0.02	0.00
	M. felicinium	10	120.00 ± 15.28 (92.30 – 132.65)	13.20 ± 4.00 (9.60 – 17.14)	0.00	0.145^{ab} ± 0.01	0.516^{ab} ±0.01	0.00	0.525^{ab} ± 0.01	0.00
	M. vollenhovenii	10	152.42 ± 18.50 (115.63 – 170.44)	23.96 ± 3.10 (19.20 – 40.25)	0.105^{c} ± 0.02	0.210^{ab} ± 0.03	1.875^{a} ± 0.03	0.230^{c} ± 0.01	0.765^{ab} ± 0.02	0.035^{ab} ± 0.01
Site 3 (Ikoro)	*M. macrobrachion*	10	119.30 ± 10.65 (88.10 – 130.75)	16.63 ± 3.45 (12.35 – 22.15)	0.156^{c} ± 0.02	0.124^{c} ± 0.02	0.631^{ab} ± 0.01	0.210^{c} ±0.01	0.850^{ab} ± 0.02	0.012c ± 0.02
	M. felicinium	10	121.10 ± 10.36 (80.70 – 148.72)	10.20 ± 3.90 (6.50 – 14.15)	0.172^{c} ± 0.03	0.00	0.105^{c} ± 0.03	0.018^{c} ± 0.01	0.156^{c} ± 0.01	0.025^{c} ± 0.01
	M. vollenhovenii	10	125.25 ± 16.30 (108.15 – 135.60)	12.36 ± 5.05 (8.00 – 16.50)	1.360^{ab} ± 0.01	0.103^{c} ± 0.01	0.535^{ab} ± 0.01	0.013^{c} ± 0.02	0.652^{ab} ± 0.01	0.00
FAO (1983)	Food fish limit				2.0	-	-	-	-	-
FAO/ WHO (1992)	Food fish limit				-	0.5 – 0.6	1.00 – 3.00	2.00	0.1 – 0.5	-

Data are presented as means ± SE of two determinations. Means in the same vertical row having the same superscript are no significantly different at the 5% probability level. N = 9

Nickel levels in the prawns showed concentration range of 0.00-2.50mg/kg of dry weight. The lowest mean Ni value (0.103mg/kg) was recorded in *M. vollenhovenii* caught at site 3 (Ikoro) while the highest mean Ni value (0.250mg/kg) was recorded in *M. macrobrachion* caught at site 1 (Gelegele). The rank profile of Ni in the prawns in descending order was *M. vollenhovenii* > *M. macrobrachion* > *M. felicinium*. No significant differences (P > 0.05) were recorded between the concentrations of Ni in the prawn samples caught at sites 1 and 3 (Table 2). Nickel was detected in 66.6% of total prawns samples. The total mean Ni value (0.473mg/kg) recorded in *M. vollenhovenii* caught at the three study sites is higher than Ni value (0.047mg/kg) reported by Kolade (1999) in *M. vollenhovenii* caught in Ogba river but lower than Ni value (52.23mg/kg) reported in *Caridina africana* procured from Erin-Ijesha water falls (Bello -Olusoji, *et al*, 2006. Ni values recorded in *M. felicinium* (0.145mg/kg) and *M. vollenhovenii* (0.473mg/kg) are lower than Ni value (0.50-0.60mg/kg) recommended in fish and fishery products by FAO/WHO, (1992). Table 2. The concentration of Fe in the prawns showed a range of 0.105mg/kg – 2.450mg/kg. dry weight of sample. The lowest mean Fe value (0.105mg/kg) was recorded in *M. felicinium* caught at site 2 while the highest mean Fe value (2.450mg/kg) was recorded in *M. vollenhovenii* caught at site 3 (Ikoro). The rank profile of Fe in the prawns in descending order was *M. vollenhovenii* > *M. felicinium* > *M. macrobrachion*. No significant differences (P > 0.05) were recorded between the concentrations of Fe in the prawn samples caught at the three study sites (Table 2). Iron was detected in 100% of all prawn samples caught and used in this study. The total mean Fe value (4.860mg/kg) recorded in *M. vollenhovenii* caught at the three study sites is higher than Fe value (0.874mg/kg) reported by Edema and Egborge (1999) in *M. vollenhovenii* caught in Warri river but lower than Fe value (160.70mg/kg) reported in *M. vollenhovenii* caught at the Lagos lagoon by Adeyeye (2000). The total mean concentration of Iron recorded in *M. vollenhovenii* (4.860mg/kg), is higher than Fe value (1.00 – 3.00mg/kg) recommended in fish and fishery products by FAO/WHO, (1992).

Chromium levels in the prawns showed concentration range of 0.00-0.530mg/kg dry weight. The lowest mean Cr value (0.013mg/kg) was recorded in *M. vollenhovenii* caught at site 3 while the highest mean value (0.530mg/kg) was recorded in *M. felicinium* caught at site 1. The rank profile of Cr in the prawn species in descending order was *M. felicinium* > *M. vollenhovenii* > *M. macrobrachion.* One-way analysis of variance (ANOVA) conducted on Cr data showed significant differences (P <0.05) between the concentrations of Cr in the sampled prawns caught at sites 1 and 3 (Table 2). Chromium was detected in 77.7% of all prawn samples. The total mean Cr value (0.473mg/kg) recorded in *M. vollenhovenii* caught at the three study sites is higher than Cr value (0.067mg/kg) reported by Kolade (1999) in *M. vollenhovenii* caught at Ogba river but lower than Cr value (4.85mg/kg) reported in *Caridina africana* caught at Erin-Ijesha water falls by Bello-Olusoji, *et al*, 2006. The total mean values of chromium recorded in *M. macrobrachion (0.245mg/kg), M. felicinium* (0.548mg/kg) and *M. vollenhovenii* (0.473mg/kg) are lower than Cr value (2mg/kg) recommended in fish and fishery products by FAO/WHO, (1992).

Manganese levels in the prawns showed concentration range of 0.156mg/kg – 2.250mg/kg. *M. felicinium* caught at site 3

recorded the lowest concentration (0.156mg/kg) of Mn while the highest mean Mn value (2.250mg/kg) was recoded in *M. macrobrachion* caught at site 1 (Gelegele) Manganese concentration in the prawns showed the following rank profile in descending order, *M. macrobrachion* > *M. vollenhovenii* > *M. felicinium*. No significant differences (P>0.05) were recorded between the concentrations of Mn in the prawn species caught at the three study sites. *Manganese* was detected in 100% of total prawn samples caught and used in the study. The total mean Mn value (2.252mg/kg) recorded in *M. vollenhovenii* caught at the three study sites is higher than Mn values (2.015mg/kg) reported by Edema and Egborge (1999) in *M. vollenhovenii* caught at Warri river but was lower than (95.96mg/kg) reported in *Caridina africana* caught at Erin Ijesha water falls by Bello-Olusoji, *et al* 2006). The total mean concentrations of manganese recorded in *M. macrobrachion* (4.753mg/kg), *M. felicinium* (2.001mg/kg) and *M. vollenhovenii* (2.252mg/kg) are higher than Mn value (0.10 – 0.50mg/kg) recommended in fish and fishery products by FAO/WHO, (1992).

Vanadium levels in the prawns showed concentration range of 0.00-1.050mg/kg. *M. macrobrachion* caught at site 3 recorded the lowest concentration (0.012mg/kg) of V while the highest mean value (1.050mg/kg) was recorded in *M. felicinium* caught at site 1 (Gelegele).

The rank profile of V in the prawn species in descending order was *M. vollenhovenii* > *M. felicinium* > *M. macrobrachion.* One-way analysis of variance (ANOVA) conducted on metals data showed significant differences (P<0.05) between the concentrations of V in the sampled prawns at sites 1 and 3 (Table 2). Vanadium was detected in 66.6% of total prawn sample. The total mean V value (1.085mg/kg) recorded in *M. vollenhovenii* caught at the three study sites is lower than V value (3.29mg/kg) reported in *M. vollenhovenii* caught at the River Niger by Kakula *et al.* (1987) but higher than V value (0.720mg/kg) reported for the same prawn species obtained from Ogba river by Kolade (1999). Stendaih and Sprague (1982) had reported that the U.S.S.R set a limit of 0.1mg per litre of vanadium in surface water supply and confirmed that inadequate information exist about vanadium as a water pollutant because many nations water quality organizations did not consider the metal as a pollutant.

Based on the rank profiles of the heavy metals, the prawn with the highest concentration of heavy metals was *M. vollenhovenii*

CONCLUSION

The concentrations of heavy metals recorded in Ovia River were generally lower than FAO/WHO recommended standards in water and food. This might suggest that the water and prawns are safe for human consumption. However, the marginally higher concentrations of Ni, Fe and Mn in the prawn samples in Ovia River need to be monitored closely because findings from this study have valuable information about heavy metals content in Ovia River.

An evaluation of the possible risks associated with prawn consumption could be deduced from this study.

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