

BIO-CONCENTRATION OF MACRO AND TRACE MINERALS IN FOUR PRAWNS LIVING IN LAGOS LAGOON

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Mineral levels of trace (Cd, Zn, Ni, Fe, Cu and Co) and macro (Ca, Mg, Na, K and P) were determined in four prawns: *Macrobrachium vollenhovenii*, *Palaemon* species A, *Penaeus notialis* and *Penaeus kerathurus* in the Lagos lagoon water in Epe area of Lagos State, Nigeria. The levels of Cd, Zn, Ni, Fe, Cu, Na, and P were higher in prawn samples than in water while Mg was more concentrated in water but Co was not detected in water. There was evidence of mineral bioconcentration in all the samples. Individual prawn mineral concentration followed the following patterns: *M vollenhovenii* > *P notialis* > *P species A* > *P kerathurus* (for trace minerals) and *P kerathurus* > *P notialis* > *P species A* > *M vollenhovenii* for macrominerals suggesting that mineral concentration may be a factor of size and species.

Key words: Prawns, Mineral bioconcentration, Metal pollutant.

Introduction

In natural aquatic ecosystems, metals occur in low concentrations, normally at the nanogram to microgram per litre level. In recent times, however, the occurrence of metal contaminants especially the heavy metals in excess of natural loads, has become a problem of increasing concern. This situation has arisen as a result of the rapid growth of population, increased urbanisation, expansion of natural resources, extension of irrigation and other modern agricultural practices as well as the lack of environmental regulations (Calamari and Naeve 1994).

The proven toxicity of high concentrations of heavy metals in water to fishery and wild life (Cain *et al* 1980; Babich and Stoczky 1985) poses the problem of an ultimate disequilibrium in the natural ecological balance. Under such conditions, the toxicity of a moderately toxic metal could be enhanced by synergisms (Pickering 1980) and fishery populations may decline (Laws 1981).

The Lagos lagoon forms an economically important fishery resource for the mostly fishing communities living around it. No data on the trace and macro minerals in water and prawns have so far been published.

Fisheries interest in shrimps in Nigeria has been centred on the marine penaeid species harvested offshore by commercial trawlers (Powell 1983). The importance of this group-mainly just one species, *Penaeus notialis* - is well known (Powell 1983). Shrimp fishery in Nigeria is mainly export oriented (Balogun and Akegbejo - Samsons 1992), although the annual production estimate of shrimps in Nigeria is not available (Rosenberry 1992).

The species under study are the African river prawn, *Macrobrachium vollenhovenii* (Herklots); Blackegg prawn,

Palaemon species A (Powell); Southern pink shrimp, *Penaeus* (Farfante) *penaeus* *notialis* (Perez-Farfante) and Caramote prawn, *Penaeus* (Melicertus) *kerathurus* (Forskal) (Powell 1983). All the species under study are "true" shrimps (Crustacea Decapoda Natantia) (Powell 1983; Yoloye 1988).

The immediate purpose of this paper is two fold: one is to document data on the prawn mineral composition (hence, trace and macro mineral determination) which would add information to the food composition and nutrition tables and to assess the level of pollution in the lagoon water since the prawns may present a clearer indication of metal inputs and accumulation in aquatic environments better than the lagoon water (Okoye 1991a, b; Adeyeye 1993, 1996).

Materials and Methods

1. *Sampling.* Samples of shrimps were collected from Epe (along the Lagos lagoon). The shrimps were briefly washed with distilled de-ionised water to remove any adhering contamination and then drained under folds of filter paper. They were then identified, kept in crushed ice in insulated containers and sent to the laboratory for preservation prior to analysis.

Water samples were taken just below the water surface at two different locations where the shrimp samples were caught using 1-l acid-leached polyethylene bottles. The water samples were pooled together making a total of two litres per site of collection.

2. *Preservation of samples.* Washed shrimp samples were wrapped separately in aluminium foil and kept frozen at -4°C for 2 to 5 days before analysis was carried out. The water samples were also stored at the same temperature.

3. *Samples treatment.* Five ml of concentrated hydrochloric acid was added to 250 ml of water sample at the time of analysis and evaporated to 25 ml. The concentrate was transferred to a 50 ml standard flask and diluted to the mark with distilled de-ionised water (Parker 1972).

After defrosting, whole shrimps were separated according to species and then weighed. The various samples (the two biggest of each species) were dried at 105°C, blended and weights ranging from 0.7728g to 0.9789g were accurately weighed prior to digestion.

Two ml of concentrated nitric acid was added to each sample in a beaker and covered with a wash glass and allowed to stand overnight in a fume cupboard. The beakers were heated gently on a plate until frothing stopped and no visible solid material was observed. Heating continued at a temperature of between 75°C to near dryness. Two ml of 5% lanthanum chloride solution was added and the beakers were heated for a second time until near dryness. Each of the final solution was washed into a 25 ml standard flask with 0.1 M HNO₃ and made up to the mark with distilled de-ionised water (Varian 1975; Harper *et al* 1989).

4. *Analysis of the samples.* The minerals were analysed from solutions obtained above and in the water samples. Sodium and potassium were determined using a flame photometer (Corning UK Model 405) (AOAC 1990). Phosphorus was determined colorimetrically using Spectronic 20 (Gallenkamp UK) as described by Pearson (1976). All other metals in this report were determined by means of atomic absorption spectrophotometer.

Earlier, the detection limits of the metals had been determined using the methods of Varian (1975) with the following values ($\mu\text{g g}^{-1}$): Mg (0.002), Ca (0.04), Zn (0.005), Cu (0.005), Fe (0.02) Na (0.001), K (0.005), Cd (0.001), Co (0.002) and Ni

(0.02). The optimum analytical range was 0.5 - 10 absorbance units with a coefficient of variation of 0.05% to 0.40%.

5. *Statistical evaluation.* Statistical evaluation of the results obtained was carried out (Chase 1976). The statistical evaluations reported included the range and average weights of prawn samples (wet weight), coefficient of variation percent (C.V.%), chi-square (X^2C), correlation coefficient (C.C.), regression coefficient (R.C.), coefficient of alienation (C.A.) and index of forecasting efficiency (I.F.E.) per cent. Bioconcentration factors (B.F.) of the minerals were also calculated in the various prawn samples (Varshney 1991). The level of significance was set at $\alpha = 0.05$

Results and Discussion

The weight distribution (Table 1) showed that weight differences occurred among the prawn samples. On the average the weight ratio of *M vollenhovenii* to *Palaemon* species A is 8:1 and *M vollenhovenii* to *Penaeus notialis* is 5:1. High and significant correlation coefficient (0.99) ($\alpha = 0.05$) existed among them with low coefficient of alienation (0.14 or 14% and high index of forecasting efficiency (which reduces the error of prediction of relationship by 85.89%). No weight value was recorded for *Penaeus kerathurus* because only one fresh specimen of its group was in the catch. However dried sample of the similar specimen was analysed with the catch.

Table 2 shows that the trace minerals were mostly concentrated in *M vollenhovenii* and *P notialis*. Cd and Co were low in concentration in all the samples. Ni, Zn, Fe and Cu were better highly concentrated in the prawn samples. Significant relationship occurred ($\alpha = 0.05$) among the samples.

Some micronutrients and heavy metals such as Zn, Fe, Cu, Co and Ni are essential for the growth and well-being of living organisms including man (Buss and Robertson 1976; Mertz

Table 1
The live weight values (g) of prawn samples available for study

Sample	Range (four samples)	Average	C.C.*	C.A.	I.F.E.	R.C.
<i>Macrobrachium</i>						
<i>vollenhovenii</i>	24.48 - 26.55	25.52				
<i>Palaemon</i> species A	2.57 - 3.74	3.15				
<i>Penaeus notialis</i>	4.77 - 5.44	5.11	0.99	0.14	85.89	0.94
Overall mean	10.61 - 15.24	11.26				
Overall standard deviation	12.06 - 18.47	12.39				
Coefficient of variation (%)	113.37 - 121.19	110.04				

C.C. = Correlation coefficient; C.A. = Coefficient of alienation; I.F.E. = Index of forecasting efficiency per cent; R.C. = Regression coefficient; *Significant at $\alpha = 0.05$

1981; Oshodi and Ipinmoroti 1990; Fagbemi and Oshodi 1991). Iron's major role is in the formation of haemoglobin, cobalt (II) is a component of vitamin B₁₂ (cyanocobalamin) which is essential for the prevention of anaemia, copper and zinc are essential metals and play an important role in enzyme activity (Carter and Fernando 1979). Cadmium is toxic even at very low concentration and has no known function in biochemical processes. Environmental sources of cadmium result largely from industrial exploitation and include the air, especially near busy roads (WHO 1963), water plants and sewage sludge (OECD 1975). Cadmium when ingested accumulates in the kidney.

The current report is compared to literature standard values. In New Zealand, the maxima value reported for fish and fishery products are 1.0 µg g⁻¹ (Cd), 40.0 µg g⁻¹ (Zn), 30.0 µg g⁻¹ (Cu), and 50.0 µg g⁻¹ (Zn) in the United Kingdom, all on wet

weight basis (Nauen 1983). The value of Cd reported for fish muscle in Epe (Lagos lagoon) ranged from 0.18-0.303 µg g⁻¹ wet weight (Odukoya and Ajayi 1987a) while the value of Cu ranged between 0.05 - 0.21 µg g⁻¹ and Zn ranged between 1.5 - 4.6 µg g⁻¹ wet weight (Odukoya and Ajayi 1987b). The World Health Organisation (WHO) limits in marine fish (µg g⁻¹ fresh weight) are Cd (2.0); Cu (30.0) and Zn (1000.0) (Kakulu *et al* 1987). The prawn samples under discussion may be regarded as being free from pollution since they were determined on dry weight basis.

The comparisons between the trace mineral concentration in prawns and water is shown in Tables 3. The minerals were generally more concentrated in the prawns than in water on pairwise comparison (Okoye 1991a,b; Adeyeye 1994, 1996; Adeyeye *et al* 1996). The minerals were more widely distributed in the prawns than in the water as indicated by the various

Table 2
Trace mineral composition of four different prawns in lagoon water

Sample	Trace mineral concentration (µg g ⁻¹) ^a					
	Cd	Zn	Ni	Fe	Cu	Co
<i>Macrobrachium</i>						
<i>vollenhovenii</i>	7.60±0.2	137.90±0.1	209.60±0.3	160.70±0.1	163.50±0.3	10.30±0.4
<i>Palaemon</i> species A	4.20±0.1	75.70±0.1	91.00±0.1	58.50±0.1	17.30±0.2	3.80±0.2
<i>Penaeus notialis</i>	5.30±0.3	112.50±0.0	94.70±0.2	150.00±0.2	28.70±0.2	9.00±0.2
<i>Penaeus kerathurus</i>	3.80±0.2	38.60±0.2	122.30±0.4	10.60±0.3	37.40±0.1	5.60±0.1
Chi-square calculated (X ² C)			26.59			
Chi-square table (X ² T)			25.00			
Remark			*			

*Significant at $\alpha = 0.05$; ^aDeterminations were in triplicate on dry weight basis. Representative sample of each specimen was analysed.

Table 3
Intercorrelation between the trace mineral concentration in four prawns and lagoon water (µg g⁻¹)^{*}

Trace mineral	Lagoon water	<i>M. vollenhovenii</i>	<i>Palaemon</i> species A	<i>Penaeus notialis</i>	<i>Penaeus kerathurus</i>
Cd	0.002±0.0	7.60±0.2	4.20±0.1	5.30±0.3	3.80
Zn	0.04±0.0	137.90±0.1	75.70±0.1	112.50±0.0	38.60
Ni	0.07±0.0	209.60±0.3	91.00±0.1	94.70±0.2	122.30
Fe	2.78±0.2	160.70±0.1	58.50±0.2	150.00±0.2	10.60
Cu	1.71±0.1	163.50±0.3	17.30±0.2	28.70±0.2	37.40
Co	N.D.	10.30±0.4	3.80±0.2	9.00±0.2	5.60
Overall mean	1.60	114.93	42.72	66.70	36.38
Overall standard deviation	2.01	85.34	38.19	60.60	44.86
C.C.		-0.42	-0.52	-0.27	-0.54
C. A.		0.91	0.85	0.96	0.84
I.F.E.		9.23	14.58	3.71	15.83
R. C.		-0.01	-0.03	-0.01	-0.02

*Determinations were in triplicate; N.D. = not detected.

overall standards of deviation (Tables 3). Negative none significant correlation values ($\alpha = 0.05$) were recorded in all the tables. The correlation coefficient values were negative in *M vollenhovenii* / water (-0.42), *Palaemon* species A/water (-0.52), *Penaeus kerathurus*/water (-0.54) and in *Penaeus notialis*/water (-0.27). The regression coefficients were also low with values between -0.01 to -0.03 meaning that for every unit increase in the trace mineral composition of the prawns there is corresponding decrease of -0.01 to -0.03 in the trace mineral composition of water. The prediction in the relationship between the trace mineral concentration in the prawns and water is difficult because the reduction in the error of prediction (index of forecasting efficiency) was low with values ranging between 3.71% - 15.83%. The values of some of the trace minerals in Lagos lagoon as reported in literature are (ng ml^{-1}): Cd (2.0), Cu (3.0), Zn (15.0) and Fe (86.0) (Okoye 1991a). The range and average values of the trace minerals in literature as reported by Okoye (1991a) for Lagos lagoon are higher than the current report; also the values reported by Kakulu (1985) for Niger Delta are higher than the EPA (1976) maxima but

slightly higher than the water quality criteria for warm water fisheries (Gulp *et al* 1980). The low levels of metals determined could be ascribed to dilution, continuous water exchange and sedimentation (Okoye 1991b) as well as the collaborative work of scientists who now monitor environmental pollutants, postulate on the probable or potential impacts of such pollutants on the environment and on life, and advise government accordingly (Ekundayo 1981). The lagoon water under study cannot be said to be polluted.

The bioconcentration factors (BF) for the trace minerals are shown in Table 4. The bioconcentration factor values provides the basis from which inferences are drawn as to probable biologic indicators for various metals in the organisms as follows: *Mvollenhovenii*- Cd, Zn, Ni, Fe and Cu. hence *M vollenhovenii* is significant among all the four species studied here. The prawns under study are better pollution indicators as they recorded higher BF values than *Tilapia quinensis* also found in Lagos lagoon (Okoye 1991b). The metal concentrations observed here are consistent with the biological magnification hypothesis (Montague and Montague 1971). The fact that co-

Table 4
Bioconcentration factors^a of the trace minerals in the prawn samples*

Mineral	<i>M vollenhovenii</i>	<i>Palaemon species A</i>	<i>Penaeus notialis</i>	<i>Panaeus kerathurus</i>
Cd	3800.00	2100.00	2650.00	1900.00
Zn	3447.50	1892.50	2812.50	965.00
Ni	2994.29	1300.00	1352.86	1747.14
Fe	57.81	21.04	53.96	3.81
Cu	95.61	10.12	16.78	21.87
Co	-	-	-	-
X ² C		22.04		
X ² T		21.03		
Remark		*		

^aRatio concentration in prawn ($\mu\text{g g}^{-1}$) to concentration in water (ppm); *For prawn and water concentration, see Tables 2-3

Table 5
Macro mineral composition of four different prawns in lagoon water

Sample	Major mineral concentration ($\mu\text{g g}^{-1}$) ^a				
	Ca	Mg	Na	K	P
<i>Macrobrachium vollenhovenii</i>	7300.00±20.0	400.00±15.6	585.06±25.0	881.49±21.5	13440.00±21.2
<i>Palaemon species A</i>	5040.00±25.0	760.00±20.0	5177.80±29.1	924.61±23.0	16050.00±10.5
<i>Penaeus notialis</i>	4690.00±18.0	940.00±22.1	2203.10±20.0	1193.40±30.0	19920.00±12.1
<i>Penaeus kerathurus</i>	31500.00±22.0	2800.00±19.2	6255.50±30.0	11468.50±32.0	6600.00±14.0
X ² C	24.32				
X ² T	21.03				
Remark	*				

^aDeterminations were in triplicate on dry weight basis; Representative sample of each specimen was analysed.

balt was detected in the prawn samples and not in the water shows that the prawns will be better to study water pollution rather than using the water sample alone. The fact that the minerals are more concentrated in the prawns than in the water environment is consistent with literature reports (Adeyeye 1994; Adeyeye *et al* 1996).

The macro mineral composition of the prawns is shown in Table 5. They were all good sources of the essential macro minerals determined. The determination of macro minerals particularly Ca, Mg, Na and K during pollution study is unusual. This is because these minerals are not known to cause water pollution. Literature reports are scarce, those available are mostly from fish ponds (Adeyeye *et al* 1996; Adeyeye 1996; Ipinmoroti and Oshodi 1993; Adeyeye 1997) and in aquatic plant (*Pistia stratiotes*) (Sridhar 1988). The determination of phosphorus is also necessary because of the use of fertilizers for crop growth which may be washed to the lagoon.

Comparison of Tables 2 and 5 will show that the macro miner-

als were far more concentrated in the prawns than the trace minerals. A few metals such as mercury have been shown to undergo biomagnification through the food chain (Biney *et al* 1994). The relatively high values of Na, K, Ca, Mg and P in the prawns suggested that they are capable of concentrating these minerals in their body from the aquatic environment. The comparisons between the macro mineral concentration in prawns and water are shown in Table 6 where it was shown that magnesium was consistently higher in water than in any prawn sample with the exception of *P. kerathurus*. Magnesium is one of the earth's most common elements with many soluble salts (Grass and Encleson 1987), this and other discharges might be responsible for this observation. The high values of phosphorus could be due to fertilizer discharge to the lagoon. Sodium and potassium are also relatively high in the lagoon water. Sodium and potassium are the 6th and 7th most abundant elements in the earth's crust (Lee 1977), the high aqueous solubility of Na and K salts might have contributed to their relatively high concentration in the lagoon water sample. More-

Table 6
Intercorrelation between the macro mineral concentration in four prawns and lagoon water ($\mu\text{g g}^{-1}$)

Major mineral	Lagoon water	<i>Mvollenhovenii</i>	<i>Palaemon species A</i>	<i>Penaeus notialis</i>	<i>Penaeus kerathurus</i>
Ca	29.34±2.4	7300.00±20.0	5040.00±25.0	4690.00±18.0	31500.00±22.0
Mg	1500.16±10.5	400.00±15.6	760.00±20.0	940.00±22.1	2800.00±19.2
Na	194.00±5.3	585.06±25.0	5177.80±29.1	2203.10±20.0	6255.50±30.0
K	155.10±3.5	881.49±21.5	924.61±23.0	1193.40±30.0	11468.50±32.0
P	510.00±4.5	13440.00±21.2	16050.00±10.5	19920.00±12.1	6600.00±14.0
Overall mean	477.72	4621.31	5590.48	5789.30	11724.80
Overall standard deviation	598.34	5766.10	6224.52	8037.16	10265.99
C.C.		-0.21	-0.18	-0.08	-0.60
C.A.		0.98	0.98	0.78	0.80
I.F.E.		2.23	1.63	0.32	20.00
R.C.		-0.02	-0.02	-0.01	-0.03

Table 7
Bioconcentration factors^a of the macro minerals in the prawn samples^{**}

Mineral	<i>Mvollenhovenii</i>	<i>Palaemon species A</i>	<i>Penaeus notialis</i>	<i>P. kerathurus</i>
Ca	248.81±10.5	171.78±6.2	159.85±5.1	1073.62±10.1
Mg	0.27±0.1	0.51±0.1	0.63±0.1	1.87±0.1
Na	3.02±0.2	26.69±2.0	11.36±1.1	32.24±6.2
K	5.68±0.5	5.96±0.6	7.69±0.4	73.94±5.6
P	26.35±2.5	31.47±1.1	39.06±2.1	12.94±0.3
X ² C		22.04		
X ² T		21.03		
Remark		*		

^aRatio of concentration in prawn ($\mu\text{g g}^{-1}$) to concentration in water (ppm), ^{**}For prawn and water concentration, see Tables 5-6.

over, K being a well known constituent of plant (Liprot 1974), its level in the soil would be enhanced by dead plant residues and this would enrich the associated water. The tables showed that the concentration of most of the minerals in the prawns were several orders of magnitude greater than their corresponding values in water. The correlation coefficients are negatively low with values ranging between -0.08 to -0.60, the regression coefficient also ranged between -0.01 to -0.03. Reductions in error of forecasting efficiency between the prawns mineral concentration and water range between 0.32% -20.00% showing that the values were low due to the low mineral concentration in the lagoon water sample.

Table 7 depicts the bioconcentration factors (BF) of the macro minerals in the prawn samples. A comparison between Tables 4 and 7 will show that the trace minerals were more bioconcentrated than the macro minerals. While *M. vollenhovenii* showed the highest bioaccumulation factors of the trace minerals, *P. kerathurus* showed the highest bioaccumulation factors of the macro minerals. The low values of BF in the prawns particularly for Mg, Na, K and P were due to high values of those minerals in the lagoon water (Adeyeye 1996; Adeyeye *et al* 1996) while the BF for Ca were relatively higher because Ca recorded the lowest concentration among the major minerals in water. The pattern of BF in the prawns samples were *P. kerathurus* - Ca, K and Na; *P. notialis*- Ca and P. Significant differences ($\alpha = 0.05$) occurred in the BF of the prawns in the macro minerals. The results above showed that prawns particularly *Machrobrachium vollenhovenii* and *Penaeus kerathurus* will be good indicator species to monitor pollution. All the prawn species were good sources of the beneficial minerals. The lagoon water environment was not found to be polluted. It is however hoped that this report will contribute to the base-line information for the use of prawns in monitoring pollution with the setting of the appropriate standards (like in the fishes) since they tend to be detritivores (general scavengers) with a preference for animal food (Powell 1983).

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