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Determination of Heavy Metal Content in Warri River Using Crab as Bio-Indicator

R. Hector*, V.I.E Ajiwe* and S.I Okonkwo**

*Dept of Pure and Industrial chemistry, Nnamdi Azikiwe University, Awka, Nigeria
**Dept of Pure and Industrial chemistry, Anambra state University Uli, Nigeria
hectorrobi@yahoo.com,

ABSTRACT

Heavy metal concentrations of Warri river were carried out. Water and crab samples were collected and analyzed for heavy metals concentration using Atomic Absorption spectrometer (AAS). The results obtained indicated that lead ranged from 0.01 – 9.89mg/l with percentage coefficient of variation (CV%) of 109.94% in rainy season and 0.00 – 9.58 with CV% of 153% in dry season in water samples. Lead ranged from 0.06 to 1.32mg/g with CV% of 61.19% in rainy season and 0.00 – 8.25mg/g with CV% of 122.85% in dry season in crab samples. Mercury ranged from 0.00 – 9.82 mg/l with CV% of 169.19% in rainy season and 0.03 – 2.41mg/l with CV% of 128.81 in dry season in water samples. Equally mercury ranged from 0.00 – 2.11mg/g with CV% of 98.30% in rainy season and 0.08 – 2.88 mg/g with CV% of 105.05 in dry season in crab samples. Cadmium ranged from 0.00 – 2.00 mg/l with CV% of 87.50% in rainy season and 0.22 – 1.75mg/l with CV% of 69.87% in dry season in water samples. Also cadmium ranged from 0.03 – 0.90 mg/g with CV% of 75.67% in rainy season and 0.02 – 1.60mg/g with CV% of 83.60% in dry season in crab samples. The concentrations of Zn and Ca were far below WHO recommended limit in the crab and water samples while the concentrations of Cd, Cr, Co, Hg, As, Fe, and Pb in all the samples studied were in excess of the WHO recommended limit for safe water and aquatic foods. These results confirmed that Warri river was highly polluted. For sustainability of development, reduction of the sources of heavy metal pollution should be encouraged so as to reduce health risk to man and aquatic animals

Key words: Heavy metals, river water, crab, marine pollution

Corresponding Author: R. Hector

INTRODUCTION

Heavy metals are one of the severe pollutants in natural environment due to their toxicity, persistence and bioaccumulation problems [1, 2]. Most of the heavy metals are present in seawater in trace concentrations, whereas excessive concentration can affect marine biota and pose risk to consumers of sea food [3].

The impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to urban areas [4]. Pollution of the natural environment by heavy metals is a worldwide problem because these metals are persistent and most of them have toxic effects on living organisms when they exceed a certain concentration [5].

In coastal environments and estuaries, which are often characterized by large industrial settlements and urban areas, the impact of effluent discharges leads to the accumulation of heavy metals [6]. Discharge of greater quantity of pollutants into the aquatic environment may result into deterioration of ecological imbalance, changes the physical and chemical nature of the water and aquatic bi-ota [7].

Dumping wastes into rivers contribute to the larger problem of river pollution, which can seriously damage the marine environment and causes health hazard to people in some areas. Danger to public health from polluted water comes not only from direct use of the water, but also from consuming food; for example fish that have lived in polluted river. Many poisonous substances are absorbed by fish, often in a concentrated form. Hence eating of fish from polluted water may be even more hazardous than drinking the water [8].

For example the danger of the presence of mercury in seafood were demonstrated by the appearance in the 1950s and 1960s of a cripping neurological disorder among the inhabitants of a town in southern Japan. The victims were poisoned by eating fish and shellfish that had concentrated mercury discharge at sea by a chemical plant [9].

Metal pollution of the sea is less visible and direct than any other type of marine pollution but its effect on marine ecosystem and human are very extensive. The base of the marine food chain consists of planktonic life abundant in the upper 3mm of ocean water. The young of certain fish and shellfish also reside in the upper few millimeters of water in the early stage of their life [10]. Unfortunately, the upper few millimeters of the ocean also tend to concentrate pollutants, such as toxic chemicals and heavy metals. One study reported that the concentration of heavy metals including zinc, lead and copper in the upper 3mm (or microlayer) are from 10 to 1000 times higher than in the deeper waters.

Fish accumulate substantial concentrations of mercury in their tissue and thus can represent a major dietary source of this element for humans. Fish are the single largest sources of mercury and arsenic for man. Mercury is a known human toxicant and the first source of mercury contamination in man is fishes. Biotransformation of mercury and methyl mercury formation constitutes a dangerous problem for human health [10, 12].

MATERIALS AND METHOD

Water Sample

Four different water samples were each collected with two litre plastic container with a screw cap from four designated sampling points at about 2km apart along Warri river. The containers were initially washed with detergent and rinsed with distilled water; they were finally rinsed with an acid before sampling, and at the point of collection; the containers were rinsed three times with the sample. At each sample point three water samples were drawn from the lower, middle and upper part of the river; which were then pooled to form a representative sample. This was carried out by dipping the bottle below the water surface to minimize contamination by surface film.

The samples were collected for six months of the year 2011which comprised three months of rainy season (May to July) and three months of dry season (November to January). The samples were stored in the refrigerator from where they were taken for digestion on daily basis.

Aquatic samples

Crab samples were harvested from the four designated sampling points. The crabs used in this work were selected based on their abundance in the river and their popularity in local diets. Crab sample were dried using advantex fs-60s electric drying oven at a temperature of 105^{o}C for about six to eight hours. Any sample that was not fully dried after these interval was given some extra time in the oven until the required amount of dryness was achieved.

SAMPLE DIGESTION

Procedure: The dried crab samples were reduced to powder form in a mortar. 10g of powdered sample was weighed into a conical flask and then 10ml of H_2SO_4 was added to dissolve the sample followed by heating for about 10 minutes. Then, 10ml of concentrated HNO_3 was also added to the solution and the solution was heated for another 10minutes, thereafter, 5ml of ammonium oxalate was then added to the solution followed by heating to completely digest the sample.

The completely digested sample was allowed to cool to room temperature; and then washed with distill water into a 100ml volumetric flask which was then made up to the mark by adding distill water. The solution above was then filtered through a glass funnel containing Whattman No.1 filter paper into a 120ml sample bottle for storage and analysis. 100ml of each water sample was measured and filter into 120ml sample bottle and 5ml of concentrated HCl was added. Metal concentrations of the samples were read against appropriate blank and standard solutions using a Perkin-Elmer model 306 Atomic Absorption spectrophotometer (AAS) with an oxy-acetylene flame. The data generated was subjected to statistical analysis using Mean, Coefficient of Variation, Correlation analysis and Student T-test.

RESULTS AND DISCUSSION

Comparative Seasonal Variation of Water samples

The comparative data analysis of water samples showed that Cr, Hg, As, Ca, and Pb were in high concentration in rainy season in the respective order of Pb > Ca > Hg > Cr > As with Pb being 3.42mg/l while As is 0.33mg/l with %CV of 109% and 93.93% respectively (Table 1). In dry season Cd, Co, Zn, and Fe, were in high concentration in their respective order of Fe > Zn > Cd > Co with Fe being 4.98mg/l while Co is 0.73mg/l with %CV of 59.63% and 110.95% (Table 1).

Comparison of water sample concentration values for both seasons showed that Hg and Ca had a mean value of 1.98mg/l and 3.06mg/l with %CV of 169.19% and 127.45% respectively. This confirmed that Hg and Ca had highest concentration in rainy season while other elements had high and low values (Table 1and fig 5 and 8).

Co in dry season had a mean of 0.73mg/l and %CV of 110.95% higher; Although Pb, Cr and As had low mean values when compared to that of rainy season, their %CV of 153%, 73.91% and 123.80% respectively were very high in dry season.

The possible explanation to these was that during rainy season there was increase in run-off water from various locations such as battery chargers workshop, mechanical workshop, bioremediation site, seaport, junk yard, dump site, jetty, market places, abattoir; other activities include non-point spillage of petrol motor diesel oil, effluent and emission from various production industries, fumes, sewage as well as oil pollution due to sabotage or equipment failure e.t.c [12]. As a result of washing by rain, there was increase in dilution of the river water, increase in flow of sediment, short residence time, increase in upwelling and continuous water exchange.

During rainy season, there was twice increase in dilution and immense volume of the river water was passed out into the sea; the influx had a lot of force but only a short residence time. The short residence time of the influx meant that most of the input materials were discharged into sea, leaving a comparatively small quantity in the river [13].

The high flow conditions enhances rapid transportation of sediment, thus sediment is likely one more important mechanism for removing heavy metals and other pollutants from the river at high tide [14].

However, during dry season when the influx of run-off water from various locations was reduced there was decrease in dilution effect with increase in heavy metals concentration due to high evaporation, low tide and with increased particle settling velocity as well as little or no upwelling and poor ions or water exchanged.

These processes coupled with other activities which occur mostly during the dry season period such as heavy drilling, dredging, pilling, sand filling, and underwater pipe laying; these operations open up the natural source of the these element to the aquatic environment there by leading to heavy metal pollution of the aquatic environment [12].

Other activities which also occurred within this period of dry season are non-point spillage of petrol motor diesel oil, effluent and emission from various production industries, fumes, sewage as well as oil pollution are also sources of heavy metal pollution of the river within the dry season period.

Nevertheless the accumulation of these heavy metals by aquatic organism and man by way of food chain; when above human tolerant level may lead to health effects such as dermatitis, dizziness, nausa, carcinogenesis, brain damage, kidney damage, behavioral disorder and even death [15]. This called for a periodic monitoring and impact statement on the level of pollution of Warri river. From WHO standard, most of the metals had concentrations very much above the recommended standards (Table 1)

Comparative Seasonal Variation of Samples of Crab sample

Comparative study of the data obtained from by analysis of crab sample revealed that Co, Cr, As and Ca were of higher concentrations during the rainy season in the order Ca > Co >As > Cr; with Ca being 4.16mg/g while Cr was 0.99mg/g (Table 2).

During the dry season Cd, Hg, Fe, Na, Zn and Pb were in high concentration in the crab sample in the order Fe > Na > Pb > Hg > Zn > Cd; with Fe being 6.26mg/g while Cd was 1.05mg/g (Table 2 and fig 7 and 1).

A comparison of concentration values of crab samples for both season showed that As, Cr and Ca had mean values of 0.44mg/g, 0.72mg/g and 2.39mg/g with %CV of 129.54%, 137.50% and 115.06% respectively higher in rainy season compared to others having either low or high %CV. Although Co had a high mean value but its variation was low compare to its dry season value.

Pb, Hg and Cd in dry season had a mean of 1.75 mg/g, 0.99 mg/g and 0.61mg/g with %CV of 122.85%, 105.05% and 83.60% respectively higher. Although, Fe and Zn had high variation in rainy season, their concentrations had being kept low by the action of the river already explained above [13].

Reasons for these variation was that, during the rainy season the prevailing environmental condition such as excess run- off water from various locations, sewage, emission e.t.c. bring to the river huge amount of nutrients through which the aquatic organism by way of accumulation and bio-accumulation ingest in these heavy metals either by adsorption or absorption. However the cleansing ability of the river had helped to reduce the level of heavy metals concentration which would have been ingested by the aquatic organism [16].

Dry season values on the other hand, showed that the crab sample had higher concentration values as compared to crab samples in rainy season. Thus, this clearly showed that the numerous marine conditions and industrial activities associated with dry season period was solemnly responsible for the pollution of the aquatic environment of Warri river within this period.

Comparing crab and water samples in rainy season showed that both samples were indeed polluted, the concentration of certain metal in both samples were higher than WHO standard except for Ca. However As, Zn, Co, Cr and Cd were higher in concentration in crab sample while Pb, Hg, Fe, As were higher in concentration in water samples in rainy season (Table 1 and 2).

On the other hand Comparing crab and water samples in dry season showed that both samples were indeed polluted, the concentration of certain metal in both samples were higher than WHO standard except for Ca. However As, Hg, and Cr were higher in concentration in crab sample while Pb, Fe Zn Co Cd were higher in concentration in water sample in dry season (Table 1 and 2).Reasons for these could be that, during the rainy season the prevailing environmental condition such as excess run- off water from various locations, sewage, emission e.t.c. bring to the river huge amount of nutrients through which the aquatic animal by way of accumulation and bio-accumulation acquire in these heavy metals either by adsorption or absorption [16].

Comparing crab sample in dry season and water samples in rainy season result showed that both samples were indeed polluted, the concentration of certain metal in both samples were higher than WHO standard except for Ca. However the concentration of Fe, As, Zn, Co and Cd were higher in concentration in crab sample in dry season while Pb, Hg, and Cr were higher in concentration in water sample in rainy season (Table 1 and 2).

On the other hand comparing crab samples in rainy season and water samples in dry season, result showed that both samples were indeed polluted, the concentration of certain metal in both samples were higher than WHO standard except for Ca and Na. However the concentration of As, Co, Cr, Hg and Cd were higher in concentration in crab samples in rainy season while Fe, Zn, Cd, Hg, and Pb were higher in concentration in water sample in dry season (Table 1 and 2). Thus, this clearly showed that the numerous marine conditions and industrial activities associated with both dry and rainy season periods were solemnly responsible for the pollution of the aquatic environment of Warri river within the sampling period.

From correlation analysis conducted at significant level of 0.05, some elemental pairs were significantly correlated with each other, whereas the rest of elemental pairs showed no significant correlation with each other. Elemental association may signify that each paired elements had identical source or common sink in the samples [17]. The inter-metal relationships for essential and non-essential metals have been regarded as indicative of similar biogeochemical pathways for metal accumulation in aquatic animal [17].

The results of t-test for water samples showed that, 30.00% of the parameters had significant difference between the two seasons at 95% confidence level, while 70.00% of the parameters had no significant difference. The results of t-test for crab samples showed that, 20.00% of the parameters had significant difference between the two seasons at 95% confidence level, while 80.00% of the parameters had no significant difference.

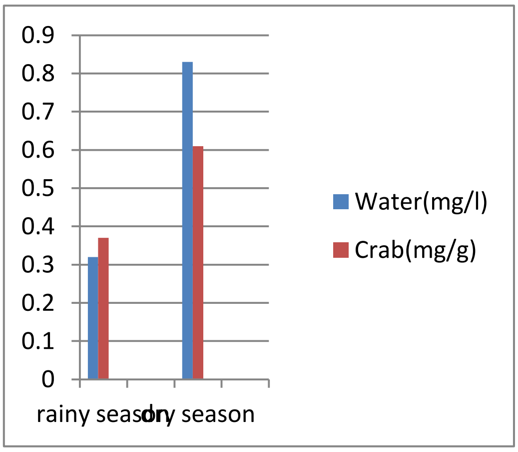
Table 1: SEASONAL VARIATION OF HEAVY METALS FOR WATER SAMPLES. (mg/l)

	Rainy season					Dry season					
Elem Ent	Mean	SD	Range	Variance	CV %	Mean	SD	Range	Variance	%CV	WHO Std
Cd	0.32	0.28	2.0 - 0.00	0.07	87.50	0.83	0.58	1.75 - 0.22	0.33	69.87	0.003 mg/l
Cr	0.49	0.06	0.90 – 0.00	3.6 x 10^{-03}	12.24	0.23	0.17	0.62 - 0.00	0.02	73.91	
Co	0.66	0.52	1.90 – 0.00	0.27	78.78	0.73	0.81	2.63 – 0.01	0.65	110.95	
Zn	0.42	0.30	0.90 – 0.00	0.09	71.42	1.57	0.87	2.73 – 0.04	0.75	55.41	5.0 mg/l
Hg	1.98	3.35	9.82 – 0.00	11.22	169.19	0.59	0.76	2.41 – 0.03	0.57	128.81	
As	0.33	0.31	0.99 – 0.00	0.09	93.93	0.21	0.26	0.62 – 0.00	0.06	123.80	0.05 mg/l
Fe	0.54	0.51	1.54 – 0.00	1.00	94.44	4.98	2.97	9.58 – 0.50	8.82	59.63	
Ca	3.06	3.90	2.11 – 0.00	15.21	127.45	0.28	0.24	0.74 – 0.00	0.05	85.71	75 mg/l
Pb	3.42	3.76	9.89 – 0.01	14.13	109.94	2.27	3.49	9.58 – 0.00	12.18	153.74	0.05 mg/l

Table 2: SEASONAL VARIATION OF HEAVY METALS FOR CRAB SAMPLES. (mg/g)

	Rainy season					Dry season					
Elem Ent	Mean	SD	Range	Varianc e	%CV	Mean	SD	Range	Varianc e	%CV	WHO Std
Cd	0.37	0.28	2.0 – 0.00	0.07	75.67	0.61	0.51	1.60 - 0.02	0.26	83.60	0.003m g/g
Cr	0.72	0.99	0.90 – 0.00	9.80	137.5 0	0.37	0.26	0.87 – 0.01	0.06	70.27	
Co	1.16	1.19	1.90 – 0.00	1.41	102.5 8	0.70	0.92	9.82 – 0.16	0.84	131.42	
Zn	0.65	0.84	0.90 – 0.00	0.70	129.2 3	0.71	0.56	1.95 – 0.01	0.50	70.42	5.0 mg/g
Hg	0.59	0.58	9.82 – 0.00	0.33	98.30	0.99	1.04	2.88 – 0.08	1.08	105.05	
As	0.44	0.57	0.99 – 0.00	0.32	129.5 4	0.37	0.28	0.87 – 0.01	0.07	75.67	0.05mg/ g
Fe	0.48	0.73	1.54 – 0.00	0.53	182.5 0	4.02	3.86	9.82 – 0.16	14.89	96.01	
Ca	2.39	2.75	2.11 – 0.00	7.56	115.0 6	0.90	0.57	1.77 – 0.20	0.32	63.33	75 mg/g
Pb	0.67	0.41	9.89 – 0.01	0.16	61.19	1.75	2.15	8.25 – 0.00	4.62	122.85	0.05 mg/g

Comparative seasonal variation of heavy metals



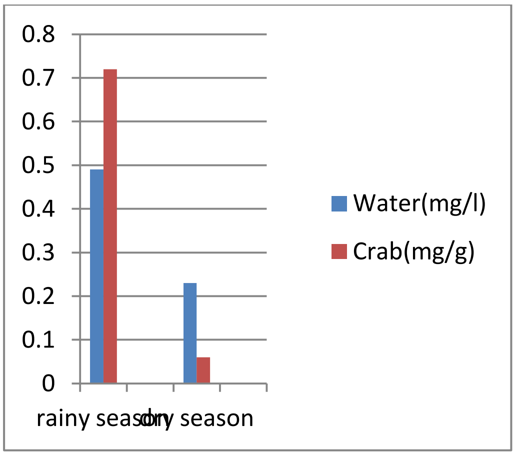
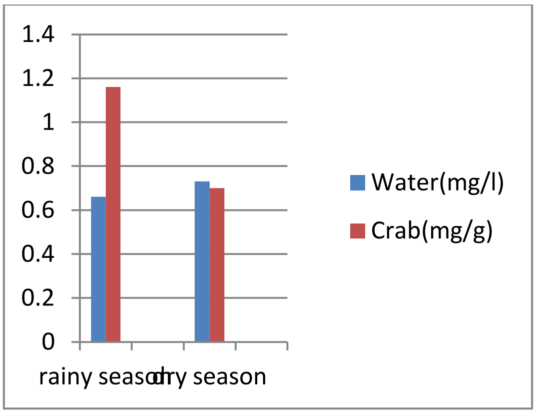


Fig 1. Comparative seasonal variation for Cd.

Fig 2. Comparative seasonal variation for Cr.



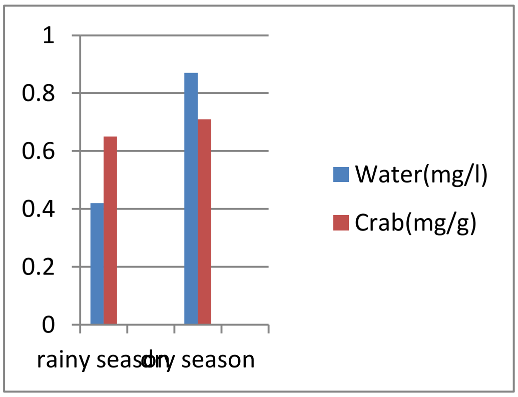
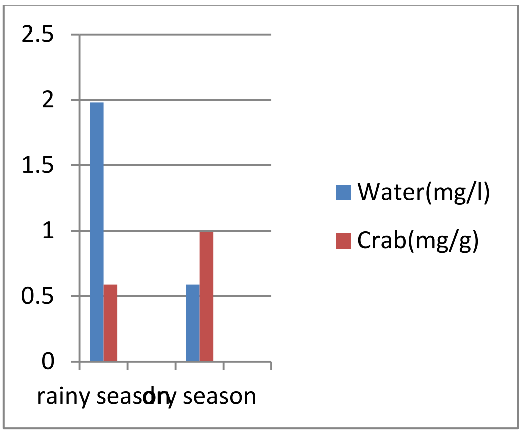


Fig 3. Comparative seasonal variation for Co. **Fig 4. Comparative seasonal variation for Zn.**



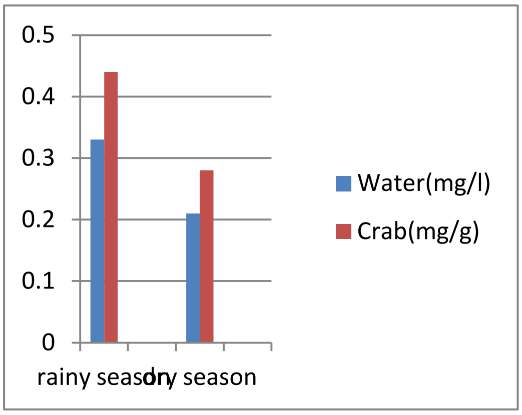


Fig 5. Comparative seasonal variation for Hg. **Fig 6. Comparative seasonal variation for As.**

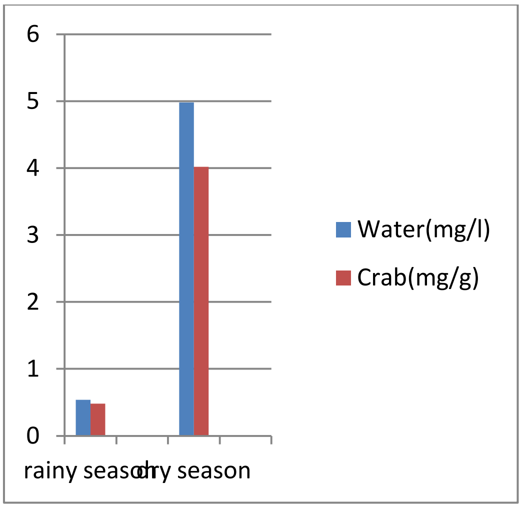
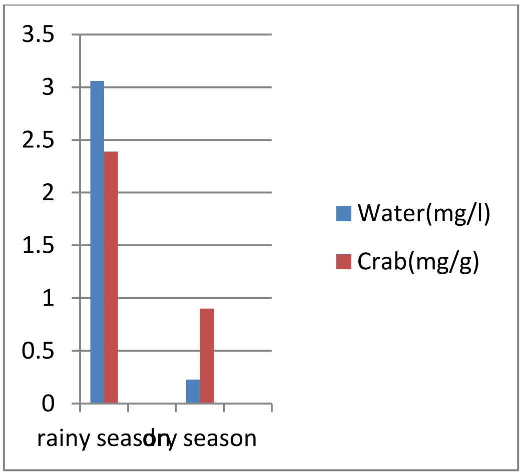


Fig 7. Comparative seasonal variation for Fe.



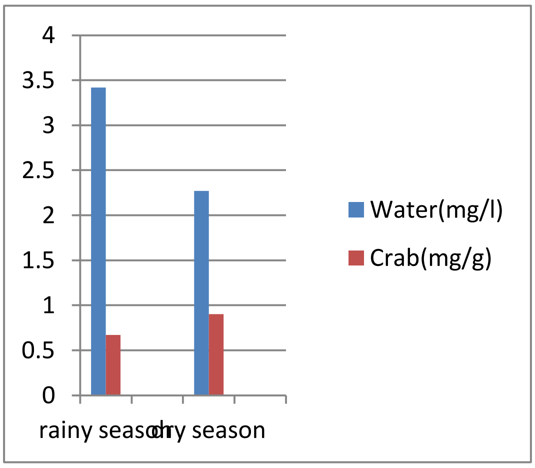


Fig 8. Comparative seasonal variation for Ca. **Fig 9. Comparative seasonal variation for Pb.**

CONCLUSION

From the result and discussion, it was obvious that Warri river had high mean level of Cd, Hg, and Pb which lead to serious pollution of the bottom dweller "crab". The crab samples had a bio-accummulation of the Cd, Hg and Pb. These heavy metal pollutants are traceable to urban and industrial waste dumped in this Warri river. High concentrations associated with high coefficient of variation suggested anthropogenic sources for Cd, Cr, Co, Zn, Hg, As, Fe, Na, Ca and Pb. The present observation indicated that the two samples (water and crab) were indeed polluted when compared with the WHO (1972) and FEPA (1991) standard for heavy metal in water and aquatic organism.

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