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A Preliminary Investigation of Heavy Metals in Periwinkles from Warri River, Nigeria

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Abstract: Periwinkles samples (*Tympanostomus fuscatus*) bought from different major markets in Warri Township were investigated for elemental contaminants. The total levels of iron, copper, barium, lead, cadmium, chromium, nickel and cobalt were determined by atomic absorption spectrophotometry. All the metals except Cr ands Co were present in appreciable quantities in the samples. In descending order of predominance, the overall mean levels (ppm) of the metals in the periwinkles are: Fe (14.67) > Cr (13.59) > Ba (6.46) > Cu (2.06) > Cd (0.57) >Pb (0.05) while Ni and Co were below detection limit. Cluster analysis of the samples predicts a common source for the periwinkles.

Key words: Heavy metals, periwinkles, pollution, flame atomic absorption spectrophotometry

INTRODUCTION

The emission of heavy metals into the biosphere has increased significantly over the natural level owing to human activities such as mining, smelting and fuel burning. This implies that any wastes that are continuously discharged as a result of human activities onto the land or atmosphere will consequently cause metal pollution of water bodies or various components of ecosystem.

Many biological materials have been used as sensitive indicators of heavy metal pollution[1,2]. The usefulness of shell fish as indicators for water pollution has been reported previously[3]. However, there is a need for periodical assessment of accumulation of heavy metals in periwinkles since wastes both domestic and industrial are continuously discharged into Warri River.

With increase diversification in industrialization and particularly with an extensive utilization of crude oil in Nigeria, especially in the Niger-Delta region, the concentration of metal pollutants in Warri River would continue to rise through natural run-off or industrial activities such as disposal of industrial effluents into the nearby stream.

Warri River stretches within latitudes 5°21`-6°00 N and longitudes 5°24`-6°21 E. The outlet of the river to the Atlantic Ocean through the Forcados Estuary made trade between the riverine inhabitants and the Portuguese possible in the 19th century and qualified Warri as the second largest port in Nigeria before 1975.

Warri River supports major commercial activities such as shipping of crude oil, fishery and recreational fishing and prawing. The river has been implicated in heavy metal contaminations in the past[4,5].

The adverse effects of heavy metals in aquatic environment have been documented[6,7]. Strictly speaking, virtually all metals are harmful if the exposure level exceeds permissible limit. Heavy metals endanger public health by being incorporated in the food or being released into water layers which serves as drinking water supply or habitat to some other organisms. Hence, the determination of heavy metals in periwinkles could be used as pollution indicator as well as human metallic burden through aquatic diets since periwinkles are largely consumed by Nigerians especially the people in the Niger-Delta area.

MATERIALS AND METHODS

Apparatus: A computerized buck scientific model 200a/210 atomic absorption spectrophotometer was used.

Reagents and glass ware: All reagents used in this study were analytical grades. Standard solutions of the eight metals were prepared from their respective 1000 ppm stock solution for calibrations. All glass wares and polythene containers were thoroughly washed with hot detergent, then soaked in 20% HNO_3 for 24 h and then rinsed with plenty of distilled water. Triply distilled water stored in all the sample containers were analyzed for metals to check for possible contamination from the samples containers.

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Sample collection: Periwinkles were purchased from four different markets in Warri Township. They are Main, Ekpan, Okere and Udu markets, respectively. The samples were stored at 4°C inside refrigerator until analysis. The analyses of the samples were carried out within five days.

Extraction of sample: Periwinkles weighed 5 g was digested with 20 mL of conc $HNO_3$and 20 mL of water in Macrokjeldal digestion flask. The content was boiled until the volume reduced to about 20 mL. The content was allowed to cool and 10 mL conc. H_2SO_4 was added. The content was boiled again and small quantity of conc. $HNO_3$was added immediately the liquid began to blacken. The addition of conc. HNO_3 was stopped when the liquid no longer blackened but the heating continued until white fumes began to appear. The whole content was cooled and 10 mL 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 polythene bottles. Blank was prepared in the same way but by omitting the sample[8]. The solutions were then analyzed for Fe, Cu, Ba, Pb, Cd, Cr, Co and Ni using the computerized scientific model 200a/20 atomic absorption spectrophotometers. Triplicate samples were digested and analysed.

The instrument working conditions and parameters for the determinations of metals are shown in Table 1.

RESULTS AND DISCUSSION

The result of the analysis of the blank solution and the triply distilled water stored in the sample containers indicate no contamination from the reagents and the sample containers used as all the metals were below their detection limits.

Table 1: Working conditions of Buck Scientific Spectrometer for the determination of metals

Metal	Wave-length (nm)	Slit width (nm)	Lamp current (mA)	Characteristic concentration (mg L^{-1})	Detection limit (mg L^{-1})
Fe	248	2	6.5	0.060	0.020
Cu	247	7	5.0	0.035	0.005
Ba	554	7	6.5	0.008	0.170
Pb	283	7	7.5	0.100	0.080
Cd	228	7	5.5	0.010	0.010
Cr	357	7	6.5	0.050	0.005
Ni	232	2	6.5	0.059	0.020
Co	240	2	6.5	0.048	0.005

Nearly all the metals except Ni and Co were detected in the samples. The concentration ranges were low for most of the metals, thus indicating a uniform distribution in the periwinkles. This idea suggests a common source for the samples irrespective of where they were purchased. For example, the ranges (ppm) were Fe (11.81-18.64), Cu (1.84-2.29), Ba (4.04-10.22), Pb (ND-0.19), Cd (0.49-0.74), Cr (ND-8.34), while Ni and Co were not detected in all the samples (Table 2).

Moreover, the low coefficient of variation obtained in this study and cluster analysis of the samples as shown in Fig. 1 suggest that there is little or no significant difference in the origin of the samples.

In descending order of predominance, the overall mean levels of the metals in the samples are Fe (14.67) > Cr (13.59) > Ba (6.46)> Cu (2.06)> Cd (0.57)> Pb (0.05). The significant high concentration of some of the metals in the *Tympanostomus fuscatus* may be a consequence of their sedentary habit while the existence of some respiratory mechanisms for elimination of accumulated metals in them may be responsible for the non-bioaccumulation of Cobalt and Nickel. This kind of observation has been reported[9].

Table 2: Mean total concentrations of metals in periwinkles

	Metals (ppm)							
Markets	Fe	Cu	Ba	Pb	Cd	Cr	Ni	Co
Main	18.64±1.19	2.29±1.04	4.04±0.95	ND	0.56±0.41	8.34±2.10	ND	ND
Ekpan	13.11±0.22	1.84±0.01	10.22±0.03	ND	0.50±0.01	ND	ND	ND
Okere	15.13±0.46	2.08±0.05	6.23±0.08	ND	0.74±0.02	ND	ND	ND
Udu	11.81±0.81	2.05±0.06	5.35±0.08	0.19±0.01	0.49±0.01	0.01	ND	ND
Overall mean	14.67±2.77	2.06±0.48	6.46±2.44	0.05±0.01	0.57±0.20	2.09±0.56	-	-
CV (%)	18.89	23.3	37.8	20	35.1	33.6	-	-

Values are results of triplicate analysis ND-Not detected

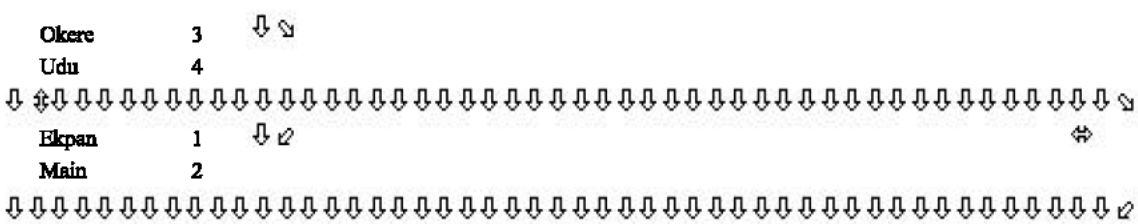

Fig. 1: Cluster analysis of periwinkles samples from different markets

Generally, Mollusks are bottom feeders[3]. Strictly speaking, this study could not demonstrate bioaccumulation because the samples were purchased in various markets in Warri, thereby making their associated water and sediment unknown.

CONCLUSIONS

The result of this study emphasizes the value of constant monitoring of rivers and water bodies receiving effluents in order to forestall cumulative effects of the metals in the river which may lead to sub-lethal consequences in the aquatic fauna and ensuing clinical poisoning to man.

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