HEAVY METAL DEPOSITS IN PERIWINKLES (*Tympanotonus fuscatus and Pachymelania aurita*) AND SEDIMENTS FROM THREE WATER BODIES IN AKWA IBOM STATE, NIGERIA

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ABSTRACT

Heavy metal contents of two species of periwinkle (*Tympanotonus fuscatus* and *Pachymelania aurita*) from three water bodies (fresh and brackish waters) were studied to determine the concentration of these substances in the biospecimens. Samples of water, sediment and periwinkles were analyzed for eight elements (Pb, Cu, Fe, Mn, V, Cd, Ni and Zn). The metals decreased in concentration from sediment through periwinkle to water (sediment> periwinkle > water). The concentration of the elements above showed a decreasing sequence Fe>Mn>Zn>Cu>Ni>V>Pb>Cd. In dry season, water samples indicated higher levels of Fe, Ni, V and Cu consistently in the three studied areas while Mn was higher only in wet season at two water bodies. Comparison of fresh and brackish samples indicated significant differences (P<0.05) in element concentrations with brackish water dominating in both seasons. In wet season, fresh water periwinkle showed higher values. Periwinkles from fresh water showed biomagnifications of >1 in Zn, Cu, Mn and V while Fe and Ni indicated values of <1 in all. This indicated that the concentration of Zn, Cu, Mn and Vn observed in the biospecimens were inimical to human health, as such, pollution and anthropogenic activities of these water bodies should be monitored.

INTRODUCTION

Heavy metal pollution is one of environmental problems faced by most communities throughout the world today. Most of these metallic pollutants are produced independently or in compounds through natural phenomena such as rock weathering or tectonic movements like earthquake or volcanic eruption. Anthropogenic sources include industrial, agricultural and technological activities/leachates of solid wastes mostly (Umoren and Udousoro,2009). Tropical climates of high temperatures and heavy rainfall throughout the year could lead to elevated leaching rates and accumulation of heavy metals (Sin *et al*., 2016). Water resources which are among the most critical natural resources (Shanbehzadeh *et al*., 2014) are the main sinks of these pollutants from untreated municipal sewage and surface runoff. As such, the concentrations in water bodies and wetlands are likely to be higher than deposits on land. This makes it a great concern in one's efforts to create a sustainable environment that can protect lives. Meanwhile the kinetics of these heavy metals in soil (sediment in this study) is determined by their chemical forms (Zauyah *et al.,* 2004, Petit and Rucandio, 1999, Davidson *et al*., 1999 and Tack and Verloo, 1995) and soil properties e.g texture and organic matter contents (Chlopecka *et al.*, 1996).

The investigation of the entry sources, effects and control of pollutants in rivers mostly has always been the interest of environmental scientists as this can affect human health through recreational activities, washing, drinking and fishing (Shanbehzadeh *et al.*, 2014).Metallic pollutants are reported to be harmful to organism (Bahazan an Ishat, 2015) but some of the elements are micronutrients for metabolic activity in organism (Karadede – Akin and Unlu 2006, Prabu, 2009). It is therefore pertinent that the concentrations of most of these elements should be highly monitored. The pollutants pass through different trophic levels into human body.

Although they would be biotransformed and biodegraded along the route in body tissues to prevent or reduce their noxious effects, the bioconcentrations of the non degradable ones is of human interest. The Niger Delta region of Nigeria, otherwise described as the Nigerian oil bloc, is rich in aquatic resources. There are many industries (oil and non oil) located within this area. The industrial effluents (untreated) finally enter the surrounding water bodies enrouting to the sea. Most of the pollutants observed in this region are metals and mineral hydrocarbons (Essien *et al.,* 2006, Ebong *et al.,* 2006) according to Ubabukoh (2009) experts report high levels of mercury in the breast milk of woman in Lagos and other riverine areas of Nigeria (part of which is the Niger Delta region). This report therefore become a prelude to determine the occurrence and biomagnifications of some of the metallic pollutants in periwinkles. Periwinkles as a biospecimen in this study is a common and affordable protein source and a favourite delicacy in most communities in the Niger Delta region particularly the riverine communities (Ekanem and Otti,1997, Nwabueze *et al.*,2011). It is a source of income and the shell is used in feed formulation (Powell *et al.,* 1985 Oyenekan, 1987). Periwinkle is a highly recommended food item because of its high iodine content. Moreover, the study will assist in assessing the pollution status of these water bodies.

MATERIALS AND METHODS

Study Areas

The sampling stations were at Odio and Ukpenekang within the Qua Iboe River Estuary (Fig. 1) and Odu Itu along Cross River system (Fig.2). Details of Qua Iboe River Estuary has been reported by Ebong *et al.,* (2004) and Udo *et al*., (2016). Detail description of Cross River system is included in the reports of Moses (1988) and Ekanem and Adegoke (1995).

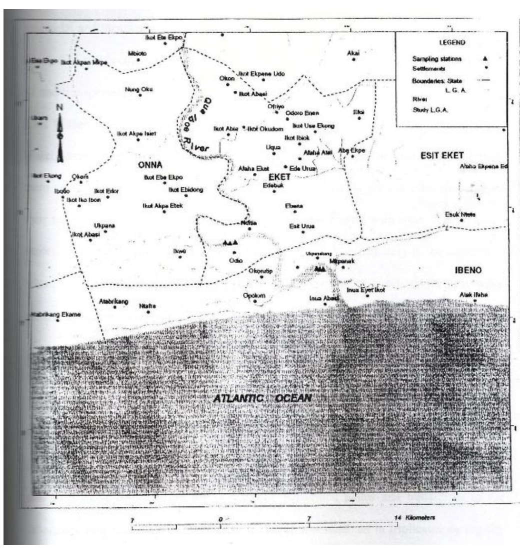

Fig. 1. Map of Qua Iboe River Estuary.

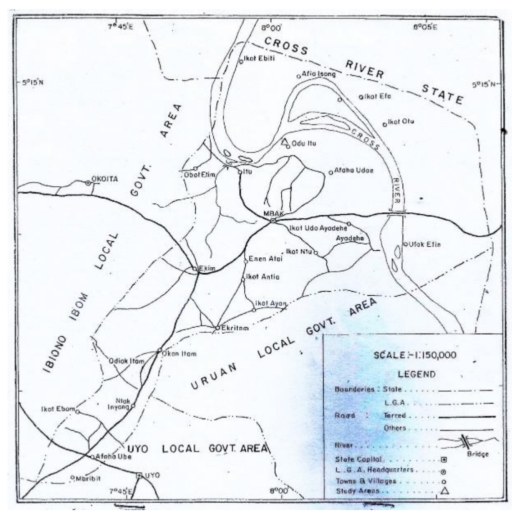

Fig. 2. Map of Cross River System.

Collection and Treatment of Samples

(1) Intertidal sediment samples were collected with a 6.5cm, diameter Auger to a depth of 10cm. Each sediment sample was stored in a separate transparent plastic jar with tight fitting lid labeled and taken to the laboratory for analysis.

(2) Water samples were collected with clean 1 litre capacity plastic bottle below the water surface. 1.5 ml of HNO_3 was added for the preservation of the elements.

(3) The periwinkle *Tympanotonus fuscatus* was handpicked from the mangrove swamps in Qua Iboe River estuary while Pachymelania *aurita* was collected from the floor of Cross River. The sample were collected monthly in triplicates for each station for dry (December **-** February) and wet (July – September,) seasons.

Determination of Heavy Metal Contents

Each water sample was filtered into a 100ml flask and HNO_3 was added. The samples were analyzed with Atomic Absorption Spectrophotometer (AAS Unicam 939) using the methods of American Public Health Association (APHA) (1999) and Radojevic and Bashkin (1999).

Sediment samples were each oven dried at $70^0 – 80^0$c for 48 hours. It was crushed and sieved to obtain <63µm grain sizes. This was digested as described by Ito *et al*, (2003) and Radojervic and Bashkin (1999). The digested solution stayed overnight before filtration. The filtrate was transferred into 100ml volumetric flask and made up to the mark with 0.5m HNO_3 (Burning and Bani, 2001). Determination of the heavy metal was then done using APHA (1999).

T. fuscatus and *P. aurita* were separately boiled in water for 5 minutes and the flesh tissues were pulled out from the shell. These were dried in oven at 60^0c and allowed to cool (Ndifon *et al*,,, 1997).The dried tissues were ground to powder using electric blender and 5.0g of each ground substance was digested and treated according to the procedure of Radojevic and Bashkin (1999). Analysis of the filtrate for heavy metals was done using AAS.

Determination of Biomagnification

Biomagnification quotient (BMQ) or bioconcentration factor (BCF) of each element was determined to ascertain the harmful level of the heavy metals in the tissues of biospecimens. This was obtained by the formula:

$$\frac{Qpd}{Qpy}$$

where: Qpd = the quantity of element in predator (biospecimens)
Qpy = the quantity of the element in prey (sediment)
values >I were considered inimical

RESULTS

The eight heavy metals studied were detected in water, sediment and periwinkle samples collected from the three stations (Tables1, 2, 3).

Table 1: Heavy metal concentrations in water from the three sampling stations in dry and wet seasons (value = x ± SD mg/kg)

Parameters	Seasons	Stations		
		Ibeno	Eket	Itu
Fe	Wet	0.262 ± 0.041	0.045 ± 0.004	0.210 ± 0.009
	Dry	2.705 ± 0.849	0.490 ± 0.077	1.470 ± 0.040
Zn	Wet	0.016 ± 0.003	0.009 ± 0.000	0.005 ± 0.001
	Dry	0.113 ± 0.085	0.065 ± 0.082	0.043 ± 0.028
Cd	Wet	0.002 ± 0.001	<0.001	<0.001
	Dry	0.003 ± 0.003	0.003 ± 0.003	0.009 ± 0.006
Mn	Wet	0.715 ± 0.061	0.874 ± 0.260	0.024 ± 0.004
	Dry	0.011 ± 0.004	0.002 ± 0.001	0.037 ± 0.022
Cu	Wet	0.017 ± 0.001	0.008 ± 0.001	0.012 ± 0.004
	Dry	0.161 ± 0.032	0.140 ± 0.037	0.005 ± 0.001
Pb	Wet	0.011 ± 0.002	0.006 ± 0.001	0.003 ± 0.001
	Dry	0.008 ± 0.001	0.003 ± 0.001	0.001 ± 0.001
Ni	Wet	0.011 ± 0.002	0.027 ± 0.030	0.002 ± 0.001
	Dry	0.036 ± 0.016	0.032 ± 0.001	0.078 ± 0.023
V	Wet	0.009 ± 0.002	0.005 ± 0.001	0.002 ± 0.001
	Dry	0.020 ± 0.003	0.029 ± 0.002	0.075 ± 0.019

Table 2: Heavy metal concentrations in sediment from the three sampling stations in dry and wet seasons (values = x ± SD mg/kg)

Heavy Season Metal		Stations		
		Ibeno	Eket	Itu
Fe	Wet	4783.000 ± 50.990	4632.666 ± 68.187	2578.17 ± 1795.860
	Dry	1280.000 ± 51.890	1360.000 ± 1.416	1116.370 ± 115.590
Zn	Wet	236.000 ± 36.066	92.126 ± 7.491	35.683 ± 3.037
	Dry	41.710 ± 17.340	99.116 ± 27.687	74.397 ± 4.060
Cd	Wet	0.288 ± 0.027	0.167 ± 0.012	0.159 ± 0.025
	Dry	1.570 ± 0.300	2.660 ± 0.345	1.110 ± 0.385
Mn	Wet	146.223 ± 46.919	349.666 ± 84.021	193.700 ± 29.960
	Dry	76.270 ± 33.220	161.233 ± 5.512	92.597 ± 10.780
Cu	Wet	36.783 ± 10.014	25.530 ± 2.012	23.370 ± 9.818
	Dry	7.640 ± 3.582	10.616 ± 1.677	13.700 ± 3.201
Pb	Wet	4.849 ± 1.261	2.112 ± 0.827	0.843 ± 0.168
	Dry	4.250 ± 0.438	1.760 ± 0.233	1.925 ± 0.123
Ni	Wet	8.566 ± 2.114	11.450 ± 0.674	3.370 ± 0.485
	Dry	9.903 ± 1.669	28.000 ± 7.338	4.932 ± 1.164
V	Wet	6.612 ± 1.721	4.648 ± 0.369	1.890 ± 0.027
	Dry	5.526 ± 0.669	15.986 ± 3.807	3.326 ± 1.354

The trend of occurrence of the elements showed by the three media was in the order of sediment> periwinkles>water except at Itu where periwinkles showed some higher values than sediment in Mn, Zn and Cu. The differences were statistically significant at $P<0.05$.The concentrations of the elements showed a decreasing sequence of Fe > Mn > Zn > Cu > Ni > V > Pb > Cd.s

Table 3: Heavy metal concentrations in periwinkle from the three sampling locations in dry and wet seasons (values = x ± SD mg/kg)

Heavy Season Metal		Stations		
		Ibeno	Eket	Itu
Fe	Wet	1542.666 ± 224.673	1843.000 ± 89.543	1770.666 ± 166.737
	Dry	474.266 ± 123.762	393.600 ± 178.752	419.800 ± 78.622
Zn	Wet	132.210 ± 49.728	123.166 ± 4.368	253.333 ± 16.358
	Dry	71.750 ± 5.414	71.886 ± 6.750	166.333 ± 3.189
Cd	Wet	0.060 ± 0.035	0.081 ± 0.008	0.059 ± 0.001
	Dry	4.622 ± 0.365	5.188 ± 0.519	0.656 ± 0.124
Mn	Wet	148.340 ± 76.241	150.667 ± 0.865	403.533 ± 82.204
	Dry	38.753 ± 5.081	78.990 ± 11.735	225.233 ± 18.531
Cu	Wet	54.603 ± 11.074	0.119 ± 0.007	47.950 ± 4.471
	Dry	38.210 ± 4.755	33.500 ± 15.759	32.510 ± 11.011
Pb	Wet	0.130 ± 0.042	37.390 ± 1.543	0.091 ± 0.002
	Dry	2.769 ± 0.483	2.235 ± 0.222	1.363 ± 0.504
Ni	Wet	1.593 ± 0.208	3.855 ± 0.183	6.188 ± 0.232
	Dry	5.226 ± 2.364	1.721 ± 1.039	1.928 ± 0.636
V	Wet	1.033 ± 0.131	3.372 ± 0.412	4.790 ± 0.564
	Dry	2.193 ± 0.373	3.941 ± 0.531	4.309 ± 0.182

Seasonal Variations in Heavy Metal Concentrations

There were seasonal variations in heavy metal levels in water, sediment and periwinkles from the study stations. In dry season, water contained higher levels of Fe, Ni, V and Cu consistently in the three stations whereas Mn was higher in wet season at two stations. For instance, the quantity of Fe recorded for Ibeno was 2.705±0.849mg/kg, Eket (0.490± 0.077mg/kg) and Itu (1.470±0.040mg/kg) for dry season against 0.262± 0.041, 0.064± 0.004 and 0.210± 0.009mg/kg recorded during wet season for the three stations respectively (Table 1).These values were significant at $P<0.05$. Three were no significant difference in Zn and Cd concentration in dry and wet seasons.

Sediment samples recorded higher dry season concentration of Cd in all stations and for Ni and V at Eket and Pb at Itu only. Mn, Fe, Zn and Cu dominated the wet season with Mn and Fe indicated as 146.230±46.900, 349.666 ±84.021, 193.700±29.960 and 4783.000±50.990, 4632.666±68.187,2578.170±1795.860mg/kg respectively (Table 2).

Periwinkles indicated significant wet season concentration in Fe, Mn, Ni and Zn. Fe was higher in the 3 stations whereas Mn, Ni and Zn were higher in Eket and Itu Stations. Cadmium was higher in dry season at all stations while Pb was significantly high in dry season at Ibeno and Itu (Table 3).

Variations in heavy metal concentrations with sample sites

The metals were detected at the three sites studied. There were variations in the concentrations in both seasons. There were no significant differences in concentration of Cd and Cu in water, Fe and Cd in sediments and Fe in periwinkle. There were weak differences in the concentrations of Ni and V in water and Ni in sediment (Table 2).Comparison of samples from Ibeno (brackish water) with Itu (fresh water), indicates some significant differences also. In dry season, concentration of Fe, Cu and Pb were higher in Ibeno water than Itu, while in the brackish sediment, Fe, Pb, Ni and V indicated higher values. Its periwinkles also showed higher concentrations in Cd, Pb and Ni (Table 3). During wet season, Ibeno water indicated higher concentrations in Fe, Zn, Mn, Pb, Ni and V. Sediments indicated higher values in Fe, Zn, Cd, Pb, Ni, V. In contrast periwinkles from Itu showed significantly higher concentration in Fe, Zn, Mn, Ni and V in all cases tested (Table 3).

Biomagnification (Bioconcentration)

Biomagnifications quotient showed values greater than 1 (>1) in nine out of sixteen test analyzed from Itu while Eket and Ibeno indicated 6 and 4 elements respectively (Table 4). Zn, Cd, Mn, Cu, Pb, V and Ni showed higher values. The values for Fe was <1 in all samples tested.

Table 4: Biomagnifications Quotient of the elements from the three sampling stations in wet and dry seasons

		Stations		
Metal	Season	Ibeno	Eket	Itu
Fe	Dry	0.37	0.28	0.57
	Wet	0.32	0.39	0.46
Zn	Dry	1.72	1.24	2.34
	Wet	0.56	1.34	7.09
Cd	Dry	2.21	1.94	0.58
	Wet	0.21	0.50	0.38
Mn	Dry	0.51	0.49	2.43
	Wet	1.02	0.43	2.08
Cu	Dry	5.00	3.15	2.37
	Wet	1.49	0.01	2.05
Pb	Dry	0.49	1.27	0.71
	Wet	0.03	17.69	0.11
Ni	Dry	0.53	0.06	0.39
	Wet	0.19	0.34	1.84
Vn	Dry	0.39	0.25	1.29
	Wet	0.16	0.73	2.53

Values > 1 are harmful

DISCUSSION

Result of the analysis of water, sediment and periwinkles in these water bodies indicate the occurrence of Fe, Zn, Mn, Pb, Cu, Cd, Ni and V metals. Some of the metals could come from untreated municipal sewage, runoffs and abattoir wastewater. Others come from agricultural activities and leachates from solid waste decays within and around these water bodies. The deposits of the heavy metals was higher in the sediment than the periwinkles, while water contained the least. Similar observations were made by Aderinola (2004), Davies *et al.* (2006)

and Opaluwa *et al.* (2017).Physicochemical parameters of these water bodies could enhance the precipitation of these elements in sediment creating an alluvial sink for the pollutants. The occurrence of the elements showed a decreasing order of Fe > Mn > Zn > Cu > Ni > V > Pb > Cd. According to the Priority List of Harzardous Substances (Baharom and Ishak, 2015), Pb, Cd and Ni were the top elements while Zn, Cu and Mn were the least.

Seasonal comparisons indicated higher concentrations in dry than wet seasons in most of the water metals contrary to the reports of Olowoyo (2011). This is due to increasing evaporation by dry season high temperatures and heavy dilution from rainfall at wet seasons (Obasahan and Equavon, 2008 and Ahmed *et al.* 2010). Few elements in wet season indicated some higher concentrations in sediments and periwinkles. This could be due to leachates brought in by runoff from wet season rains and consequent deposition in the sediments and uptake by the biospecimens. This probably means that the quantity of heavy metals in water bodies increases more because of the influx from runoff but the quantity per unit volume makes it to seem less compared to hot seasons.

The water bodies studied contained the heavy metals tested but at different concentrations. The sediments and periwinkles also contained these elements. Comparison of Ibeno (brackish water) with Itu (fresh water) indicated higher concentration of some heavy metals in brackish water and sediments than fresh water whereas the fresh water periwinkles contained significantly higher concentrations of Zn, Mn, and V in dry and wet season than samples from brackish water. This indicates that the fresh water organisms are equally at risks of heavy metals like their counterparts in brackish and marine waters.

The downstream effects of Qua Iboe river system is observed through the higher concentrations of most of the heavy metals in Ibeno than Eket samples (Tables 5 a and b). This is probably caused by increasing influxes from surface runoffs and adjoining streams/water bodies downstream. Similar observations had been reported by Shanbehzadeh *et al.* (2014). However, sediment and periwinkle samples deviated from this profile in some elements. The sediment of the river at Eket contained higher concentrations of Fe, Zn, Cd, Mn, Ni and V than the sediment at Ibeno. Also periwinkles obtained from Eket contained more Mn and V than downstream samples. These high deposits upstream occurred in dry season. Probably the dry season water (which contains more metals) tidally increased metal concentrations in the sediments which the periwinkles detritivorously ingested.

Table 5a: Dry season variations in heavy metal concentrations, Ibeno *vs* Itu stations (values are calculated t, P <0.05 = 2.132).

Medium	Heavy metals							
	Fe	Zn	Cd	Mn	Cu	Pb	Ni	V
Water	2.53[a]	1.35	1.58	1.97	7.85[a]	4.41[a]	2.60[b]	3.11[b]
Sediment	2.24	3.18[b]	1.85	0.81	1.53	4.06[a]	4.24[a]	2.53[a]
Periwinkle	0.64	26.06[b]	17.67[a]	16.82[b]	0.82	3.53[a]	2.32[a]	8.94[b]

[a] = Ibeno high, [b] = Itu high

Table 5b: Wet season variations in heavy metal concentrations, Ibeno *vs* Itu stations (values are calculated t, P <0.05 = 2.132).

Medium	Heavy metals							
	Fe	Zn	Cd	Mn	Cu	Pb	Ni	V
Water	2.14[a]	5.43[a]	ND	19.58a	1.83	5.23[a]	7.31[a]	6.18[a]
Sediment	2.13[a]	9.58[a]	6.08[a]	1.47	1.65	5.48[a]	4.16[a]	4.75[a]
Periwinkle	1.41	4.01[b]	0.05	3.94b	0.97	1.61	25.67[b]	13.88[b]

[a] = Ibeno high, [b] = Itu high

Table 6a: Wet season variations in heavy metal concentrations, Ibeno *vs* Eket stations (values are calculated t, P< 0.05 = 2.132).

Medium	Heavy metals							
	Fe	Zn	Cd	Mn	Cu	Pb	Ni	V
Water	8.35[a]	4.05[a]	ND	1.03	15.58[a]	3.87[a]	6.91	3.10[a]
Sediment	1.02	6.76[b]	7.12[a]	3.66	1.91	3.14[a]	2.25[a]	1.93
Periwinkle	2.15[a]	0.31	1.02	0.05	8.52[a]	41.82[a]	14.15[a]	9.37[a]

[a] = Ibeno high, [b] = Eket high

The concentrations of these elements in water were not significantly different from the quantities recommended for drinking water by World Health Organisation (WHO) except in few cases. Considering the sediment (which is the main sink) and the periwinkles, the biomagnifications quotients of some metals were greater than 1 (Table 4). The quantity of Cd (0.05mg/kg) and Pb (0.03mg/kg) as maximum concentration limits in fish tissues recommended by EU regulation of 2006 were far less than the values observed in periwinkle (Table 3). Consumption of periwinkles obtained from these stations can probably and significantly constitute some health problems to man.

Table 6b: Dry season variations in heavy metal concentrations, Ibeno *vs* Eket stations (values c

Medium	Heavy metals							
	Fe	Zn	Cd	Mn	Cu	Pb	Ni	V
Water	4.49[a]	10.34[a]	ND	3.14[a]	0.73	7.43[a]	0.43	3.87[b]
Sediment	2.63[b]	3.04[b]	4.13[b]	4.37[b]	1.30	30.36[a]	4.19[b]	4.68[b]
Periwinkle	0.29	0.02	1.54	5.72[b]	0.49	1.74	2.35[a]	4.66[b]

calculated t, P<0.05 = 2.132). [a] = Ibeno high, [b] = Eket high

REFERENCES

Aderinola, O.J., Clarke, E.O., Olarinmoye, O.M., Kusemiju, V. and Amatekhai, M.A.(2009). Heavy metals in surface water, sediment, fish and periwinkles of Lagos lagoon. *American-Eurasian J. Agric. Environ. Sci.* 5(5):609-617.

Ahmad, M.K., Islam, S., Rahman, S., Haque, M.R. and Islam, M.M. (2010). Heavy metals in water, sediment and some fishes of Buriganga River, Bangladesh. *Inter. J. Environ. Research* 4(2): 321-332

American Public Health Association (APHA)(1989). *Standard methods for the examination of water and waste water*. 17th ed. Washington DC. pp 203-216.

Baharom, Z.S. and Ishak, M.Y. (2015). Determination of heavy metals accumulation in fish species in Galas River, Kelantan and Beranang mining pool, Selangor. *Procedia Environtl. Sci.* 30:320-325

Birining, K and Baird, D. (2001). Survey of heavy metals in sediments of the Swatkoy river estuary, Port Elizabeth, *South African Water SA*. 24(4): 461-466

Chlopecka, A., Bacon, J.R., Wilson, M.J. and Kay, J. (1996). Forms of Cadmium, Lead and Zinc in contaminated soils from Southwest Poland. *J. Environ. Qua*l. 25:69-79

Davidson, C.M., Ferreira, P.C.S and Ure, A.M. (1999). Some sources of variability in application of the three-stage sequential extraction procedure recommended by BCR to industrially contaminated soil. *Feresenius J. Anal. Chem*. 363: 446-451

Davies, O.A., Allison, M.E., and Uyi, H.S. (2006). Bioaccumulation of heavy metals in water, sediment and periwinkle (*Tympanotonus fuscatus* var radula) from the Elechi creek, Niger Delta. *African J. Biotech* 5(10): 968-973

Ebong, G.A., Itah ,B.N., Nyong, A.B and Benson, N.U. (2006). Seasonal changes in water quality of Qua Iboe river estuary and its associated creeks in Ibeno, Nigeria. *J App. Sci*. 9(2): 6462-6482.

Ebong, g. A., Udoessien, E.I. and Ita, B. N. (2004). Seasonal variations of heavy metals concentrations in Qua Iboe River estuary, Nigeria. *Global J. Pure Appl. Sci*. 10 (4) 611-617.

Ekanem, E. O. and Adegoke, G. O. (1995). Bacteriological study of West African clam (*Egeria radiata*) (Lamrach) and their overlying waters. *Food Mirobiol*. 13: 381-385.

Ekanem, E.O and Otti, B.N. (1997). Total plate count and coli form levels in Nigerian periwinkles from fresh and brackish water. *Food Control*. 8:81-89

Essien, J.P., Benson, U. and Antai, S.P. (2006). Seasonal dynamics of physicochemical properties and heavy metals burden in mangrove sediments and pelagic column of Qua Iboe estuary. *Nig. Res. J. Environ. Toxicology* 9:329-345

Karadede-Akin, H. and Unlu, E. (2007). Heavy metal concentrations in water, sediment, fish and some benthic organisms from Tigris River. Turkey. *Environ. Monit. Assess*. 131:323-337.

Moses, B. S. (1988). Growth, mortality and potential yield of Bonga, *Ethmalosa fimbriata* (Bodwich, 1825) of Nigerian inshore waters. *Fish. Res*. 6:233- 247.

Ndifon, P.M., Ayuki, A.A., Ebenso, I.E. and Ndifon, C.O. (1997). Microbial flora and some biochemical constituents of periwinkle (*Tympanotonus* sp) flesh sold in Calabar markets. *Global J.Pure and App.Sci*. 3(2): 206-213

Nwabueze, A.A., Nwabueze, E.O and Okonkwo, G.N. (2011). Levels of petroleum hydrocarbons and some heavy metals in tissues of *Tympanotonus fuscatus* periwinkles from Warri river of Niger Delta area of Nigeria. *J. App.Sc. Environ. Manage*. 15(1): 75-78

Obasohan, E.E. and Eguavoen, O.I. (2008).seasonal variations of bioaccumulation of heavy metals in a freshwater fish (*Erpetoichthys calabaricus*) from Ogba River, Benin City, Nigeria. *Indian J. Anim. Research*. 42(3):171-179

Olele, N.F., Falodun,E.D and Wangboje, O.M.(2013). Some heavy metals in surface water, sediment and fish (*Clarias gariepinnus*) from Ikpoba River, Benin city, Edo state, Nigeria. *J. Agric. Sc. Environ*. 13(1)

Olowoyo, D.N (2011). Heavy metals concentration in periwinkle (*Littorina littorea*) and Tilapia (*Tilapia zilli*) from the coastal water of Warri, Nigeria. *Am. J. Food and Nut*. 1(3): 102-108

Onwuli, D.O., Gospel, A., Brown, H. and Amadi, F.C. (2014). The concentration of Lead in periwinkle (*Tympanotonus fuscatus*) and river sediments in Eagle Island River, Port Harcourt, Rivers State, Nigeria. *Am. J. Environ. Protection*. 2:37-40

Opaluwa, O.D., Aremu, M.O., Ogbo, L.O., Magaji, J.I., Odiba, I.E. and Ekpo, E.R. (2017). Assessment of heavy metals in water, fish and sediments from UKE stream, Nassarawa State, Nigeria. *Curr. World Environ*. 8: 1-15

Oyenekan, J. A. (1985). Benthic macro-faunal communities of Lagos Lagoon, Nigeria. *Nigerian J. Sci*. 20: 45-51

Petit, M.D and Rucandio, M.I. (1999). Sequential extraction for determination of Cadmium distribution in coal fly ash, soil and sediment samples. *Anal. Chem. Acta*. 401: 283-291

Powell, C. B., Hart,I. and Deekae, S. N. (1985). Market survey of the periwinkle (Tympanotonus fuscatus) in the Rivers state: sizes, prices, trade routes and exploitation levels. In: Ajayi, T. O. and Ita I. (eds). *Proc. of the Fisheries society of Nigeria, Kainji*. 55-90

Prabu, P.C. (2009). Impact of heavy metal contamination of Akaki river of Ethiopia on soil and metal toxicity on cultivated vegetable crops. *J. Environ. Agric. And Food Chem*. 8(9): 818-827

Radojevic, M. and Bashkin, U.N. (1999). *Practical Environmental Analysis*. The Royal Society of Chemistry. Cambridge. pp 253-256

Shanbehzadeh, S., dastjerdi, M.V., Hassanzadeh, A. and Kiyanizadeh, T. (2014). Heavy metals in water and sediment: A case study of Tembi river. *J. Environ. Pub. Health*.http://dx.doi.org/10.1155/2014/858720.

Sim, S.F., Ling, T.Y., Nyanti, L., Gerunsin, N., Wong, V.E and Kho, L.P. (2016). Assessment of heavy metals in water, sediment and fishes of a large Tropical hydroelectric dam in Sarawak, Malaysia. *J. Chem*. http://dx.doi.org/10.1155/2016/8923183.

Tack, F.M.G. and Verloo, M.G. (1995). Chemical speciation and fractionation in soil and sediment heavy metal analysis: A review. *Int. J. Environ. Anal. Chem*. 59: 225-238

Ubabukoh, O. (2009). Breastfeeding: Rethinking the exclusive options. *The Punch Newspaper* (Nigeria). Dec. 10, 17 (20, 535):3.

Udo, M. T. and Daniel, U. I. (2016). Sexual dimorphism and biometric notes of the Schlegel's Goby, *Porogobius schlegelii* (Gunther, 1861) (Teleostei: Gobidae) in the Qua Iboe River estuary, south eastern Nigeria. *Nigerian J. Agric Food Environ.* 12(4). 212-217.

Umoren, I. U. and Udousoro, I. I. (2009). Fractionation of Cd, Cr, Pb and Ni in roadside soils in Uyo, Niger Delta Region: Nigeria using the optimized BCR sequential extraction technique. *Environmentalist.* 29: 280-286.

Zauyah, B., Juliana, B., Noorhafizah, R., Fauziah, C. I. and Rosenami, A. B. (2004). Concentration and speciation of heavy metals in some cultivated and uncultivated ultisols and inceptisols in Peninsular Malaysia. In: *3rd Australian New Zealand soils conference.University of Sydney, Australia.*