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Heavy Metals in Water and Sediment of the Lower Ikpoba River, Benin City, Nigeria

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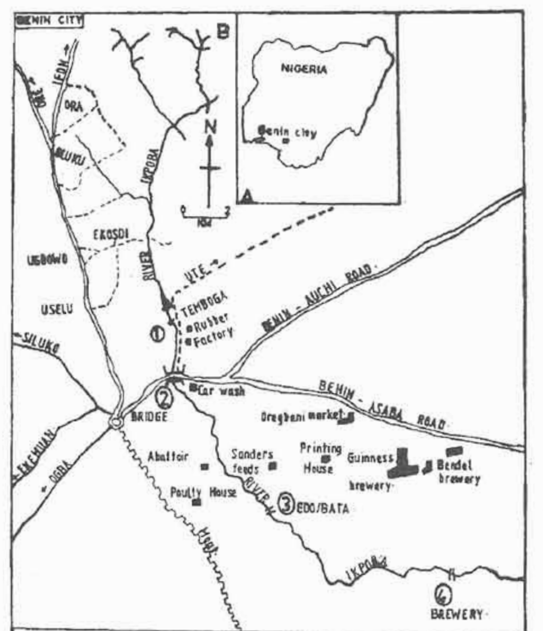
Heavy metals concentrations in the water and sediment at four zones on the lower Ikpoba river in Benin City, Nigeria were investigated by using the flame atomic absorption spectrophotometry technique. Mean concentrations (μg/l) were as Cd (0.73), Cr (0.40), Cu (1.30), Fe (4.00), Pb (0.90), Mn (3.10), Ni (2.05) and Zn (1.20). Mean metal concentrations (μg/g dry wt.) in the sediment samples were as follows: Cd (1.50), Cr (0.90), Cu (1.90), Fe (7.90), Pb (3.30), Mn (4.60), Ni (3.95) and Zn (4.70). Concentrations were of Cd and Pb water exceeded the limits recommended by WHO for portable drinking water. The metal concentrations in the river water were higher during the dry seasons in all the zones when water was used in greater demand by the urban population, there was no significant difference ($P>0.05$) between the concentrations of metals in the river water during the dry and rainy season in the months of sampling.

Key words: Heavy metals, Water sediments, Ikpoba river, Flame atomic absorption spectrophotometry.

Introduction

In Nigeria, industrial activities have given rise to untreated wastes from processing factories located in cities which are being discharged into inland water bodies. These have resulted to stench, discolouration and a greasy oily nature of such water bodies (Mombeshora *et al* 1981). Toxic and hazardous materials from the wastes are settled in the river water and bottom sediments and constitute health hazards to the urban population that depend on the water as a source of supply for domestic uses. The levels of chemicals including those of heavy metals are concentrated in the organic matter of the sediment, which influence the adsorption of metallic elements (Tada and Suzuki 1982). Moore and Sutherland (1981) recorded a significant correlation between the levels of lead, manganese, mercury, nickel and the organic matter content of bottom sediments.

The drainage network in Benin City of Nigeria is dominated by the Ikpoba river and tributaries (Rivers Okhuaihe and Eruvbi). The river flows through the centre of the city draining areas, that have upto 80% of the city's total vehicular traffic volume with many processing factories. The heavy metals concentrations in Nigerian rivers and lagoons have been investigated and because the main aim of this study was to determine the levels of selected heavy metals in the lower Ikpoba River.



Source: Federal surveys Nigeria 1964

Fig 1. The study area, A. Nigeria map showing Benin city; B. The study river showing the four sampling zones.

Materials and Methods

Study area. The study area including the sampled zones had earlier been described (Oguzie 1999) and are presented in Fig 1.

Two litres of water samples were taken monthly during the rainy and dry months of the year at three sites in each zone between April 1991 and June 1992 in polyethylene bottles and this was acidified to pH 1.5 with nitric acid (APHA 1980). Sediment samples were also collected with a bottom "grab" sampler (Hydro-Bios) and treated as described by Ajayi and Mombeshora (1989). Percent total organic matter of sediments were determined by using the modified Walkley and Black method. The final determination point of the different samples were taken to avoid contamination of samples and to minimize loss of analyte by adsorption onto the walls of the containers.

Water samples were digested with preconcentrated nitric acid (Parker 1972). Sediment samples were air dried at 40°C and digested by the nitric acid-perchloric acid method described (Adams *et al* 1980). Atomic absorption spectrophotometer was used for the analysis of cadmium, chromium, copper, lead, manganese, nickel and zinc by the solvent extraction method described (Mombeshora *et al* 1981a). All metals were chelated with 2.0 ml of 1% (w/v) ammonium-1-pyrrolidine dithio-carbamate (APDC) under acid conditions and extrated by 4.0 ml of methylisobutyl ketone (MIBK).

The concentration of iron was determined by the Orthophenonthroline method (Allen 1989). 12.5 ml aliquot of each of the sample was placed in a flask and added 1.25ml of hydroxylamine hydrochloride, 2.5ml of 10% sodium citrate and 1.25ml of orthophenonthroline. Contents of the flask were mixed and filled upto 25ml and allowed to stand for 2 hours. The percent absorbance was read at 465nm wave length twisly.

The standard deviation for duplicate metal samples was less than 10%. Precision studies and recovery experiments on metal samples spiked with authentic releasing agents were carried out with satisfactory results as a part of the analytical data and quality assurance. Procedural blanks were carried through the entire experiments from sample collections to analyse by using de-ionized water. For ten sample replicates, the coefficient of variation and average % recovery obtained were as follows: Cd 16.0%, 88%; Cr 8.0%, 90.0%; Cu 10.0%, 93.0%; Pb 14.0%, 86.0%; Mn 8.0%, 92.0%; Ni 12.0%, 90.0% and Zn 15.0%, 90.0%. The limits of detection were as follows: Cd 0.01 μg/g; Cr 0.05 μg/g; Cu 0.5 μg/g; Pb 0.05 μg/g; Mn 0.5 μg/g; Ni 0.02 μg/g and Zn 0.02 μg/g. Analysis of variarance (ANOVA) and T- test were used in all cases for mean comparisons at 5% level of significance.

Results and Discussion

Table 1 shows the mean percent total and range of organic matter content of the sediments.

The mean percent total organic matter of the sediment was higher at all the various zones during the rainy months (April – October) of sampling compared with values recorded during the dry season months (November – March). However, t-test computations showed no significant differences ($p > 0.05$) in the mean percent total organic matter of the sediment at the various zones during the seasons of sampling (with t-calculated value, 1.413 lower than t-tabulated value of 2.776). This might suggest a relatively high percentage of organic matter content of the sediment during the dry months which are comparable to level transported to the river by flood run-off water during the rainy months of sampling. Table 2 presents mean concentration values (μg/l) of heavy metals in the water while Table 3 shows similar values (μg/gdry wt) of heavy metals in the sediment at the various zones. Each value is the mean of two replicate analysis of duplicate samples taken from one zone.

Results show that metal values in the water are comparatively lower than corresponding values in the sediment.

The highest mean concentration values of Cr (0.59μg/l); Cu (1.41 μg/l); Fe (4.89 μg/l) and Mn (0.417 μg/l) in water were recorded at Temboga. While the highest mean concentrations of Cd (0.83μg/l); Pb (0.95 μg/l); Ni (2.28 μg/l) and Zn (1.47 μg/l) were recorded at Edo/Bata. The lowest metal values for Cd, Cr, Fe and Ni were recorded at the Bridge while the lowest concentrations of Cu (0.98 μg/l) and manganese (0.19 μg/l) were recorded at Edo/Bata.

In the sediment, the highest mean concentration values of Cd (1.86 μg/g); Cr (1.17 μg/g); Cu (2.27μg/g) and Ni (4.20 μg/g) were recorded at the Brewery while the highest concentration values of Fe (9.75 μg/g); Mn (0.47μg/g) at Temboga and Pb (4.50 μg/g) in Bridge and Zn (6.20μg/g) were recorded at Edo/ Bata.

The lowest concentrations of Cd (0.97 μg/g); Cr (0.63μg/g); Fe (6.08 μg/g) and Ni (3.61μg/g) in the sediment were recorded at the Bridge. The relatively high mean concentrations of Cr, Cu at Brewery and Fe, Mn were recorded in the water at Temboga. This may be attributed to the low water pH previously reported by Oguzie (1999). The high level of Fe

Table 1

Mean values (μg/g. dry wt) of % total and range of organic matter content of sediment

	Zone 1 (Temboga)	Zone 2 (Bridge)	Zone 3 (Edo/Bata)	Zone 4 (Brewery)
Mean	2.46 ± 0.11	2.26 ± 0.15	2.36 ± 0.10	2.53 ± 0.08
Range	2.30 - 2.62	2.05 - 2.47	2.20 - 2.55	2.38 - 2.63
DS Mean	2.40 ± 0.06	2.14 ± 0.08	2.26 ± 0.05	2.47 ± 0.01
Range	2.35 - 2.50	2.05 - 2.23	2.20 - 2.30	2.45 - 2.48
RS Mean	2.49 ± 0.11	2.33 ± 0.13	2.41 ± 0.08	2.56 ± 0.08
Range	2.30 - 2.62	2.15 - 2.47	2.25 - 2.55	2.38 - 2.63

DS, Dry Season; RS, Rainy Season.

Table 2
Concentration values of heavy metals (μg/l) in water at the sampled zones

Zones		Heavy Metals							
		Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Temboga (1)	Ds	1.09	0.47	1.36	5.13	0.82	4.83	1.14	1.52
	Rs	0.65	1.64	1.44	4.78	0.83	4.58	2.14	0.94
	Mean	0.80bc	0.59c*	1.41b*	4.61a*	0.83bc	4.70a*	1.81ab	1.14b
Bridge (2)	Ds	0.95	0.36	1.40	4.00	0.72	0.552	1.40	1.71
	Rs	0.47	0.28	1.24	2.76	0.92	0.246	1.93	1.04
	Mean	0.63c	0.34c	1.29b	3.17a	0.85bc	0.360a	1.75ab	1.27b
Edo/Bata (3)	Ds	0.89	0.64	0.80	4.72	0.84	2.55	2.12	1.67
	Rs	0.79	0.35	1.07	4.03	1.00	1.65	2.36	1.37
	Mean	0.83bc*	0.54c	0.98bc	4.26a	0.95bc*	1.95ab	2.28ab	1.47b*
Brewery (4)	Ds	1.29	0.44	1.16	3.79	0.44	2.83	2.61	0.80
	Rs	0.38	0.53	1.29	3.49	1.01	2.39	2.28	1.02
	Mean	0.68c	0.50c	1.25b	3.59a	0.82bc	2.54ab	2.44ab*	0.95bc

(Means in the same row with the same letters are not significantly different (p>0.05),*Zone with highest concentration of a particular metal, DS, Dry season, RS, Rainy season.

Table 3
Concentration values of heavy metals (μg/g dry wt) in the sediment at the sampled zones

Zones		Heavy Metals							
		Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Temboga (1)	Ds	1.43	1.11	1.84	9.79	3.16	5.17	3.26	3.72
	Rs	1.24	1.14	2.35	8.923	2.27	4.59	4.27	3.34
	Mean	1.30bc	1.13c	2.18b	9.75a*	2.57b	4.78ab*	3.93ab	3.46b
Bridge (2)	Ds	1.20	0.64	1.96	7.86	5.04	7.34	2.76	4.80
	Rs	0.85	0.62	1.62	5.19	4.23	3.33	4.04	5.34
	Mean	0.97c	0.63c	1.73bc	6.08a	4.50ab*	4.67ab	3.61b	5.16a
Edo/Bata (3)	Ds	1.66	0.82	1.75	9.50	3.68	6.49	3.44	7.13
	Rs	1.68	1.13	1.32	7.87	3.05	3.60	4.40	5.73
	Mean	1.67bc	1.03c	1.46bc	8.41a	3.26b	4.57ab	4.08ab	6.20a*
Brewery (4)	Ds	2.36	1.22	2.57	8.41	3.51	3.24	3.54	4.36
	Rs	1.61	1.15	2.12	6.90	2.29	4.76	4.53	3.70
	Mean	1.86c*	1.17c*	2.27b*	7.40a	2.70b	4.23ab	4.20ab*	3.92ab

(Means in the same row with the same letters are not significantly different (p>0.05), *Zone with highest concentration of a particular metal; DS, Dry season; RS, Rainy season.

and Mn recorded in the sediment may not be unconnected with the sand dredging and filling operations in the zone at the time of sampling (Oguzie 1996). The physical process of dredging according to Sly (1977), could help to release pore solutions (rich in heavy metals) into the sediment.

Significant correlations were recorded between Cr in water and sediment ($r = 0.452$, $P < 0.05$), Cr in water and Cu in sediment ($r = 0.665$, $P < 0.05$), Fe in water and sediment ($r = 0.875$, $P < 0.05$), Fe in sediment and Cd in water ($r = 0.636$, $p < 0.05$), Mn in water and sediment ($r = 0.516$, $P < 0.05$). Significant correlations were also recorded between Mn in sediment and Cu in water and between Mn in sediment and Fe in water ($r = 704$, $P < 0.05$).

Sediment samples taken at zone 2, (Bridge) have the highest mean concentration value of Pb (4.50μg/g). This might suggest the predominance of Pb compounds associated with gasoline and fumes from vehicular traffic which, according to Oguzie (1996) characterize the zone. Lagerwerff and Specht (1970) reported the burning of gasoline and fossil fuels as sources of Pb in urban aerosols and roadside dusts which get flushed into the aquatic environment through flood run-off and atmospheric precipitation. Significant correlations were not recorded between Pb in water and sediment ($r = 0.146$, $P > 0.05$) but they were recorded with Cd in water ($r = -0.444$, $P < 0.05$).

The low metals (Cd, Cr, Fe and Ni) values recorded in water at the zone may be attributed to the fast flow rate of the river and non-uniform sedimentation of particulate materials previously reported by Oguzie (1999).

In Table 2 the relatively high Cd (0.83 μg/l); Pb (0.95μg/l) and Ni (2.28 μg/l) values recorded in water at zone 3 (Edo/Bata) which might suggest possible complex formation of metal ions with synthetic (NTA and EDTA) chelating agents and used in detergents. According to Oguzie (1996), the inhabitants of the zone carry out laundry activities in the river and possible bioavailability of metals chelates could occur. This finding is supported by Sammanidou and Fytianos (1990) on studies of heavy metals in river sediments of Northern Greece. No significant correlation was recorded between Cd in water and sediment ($r = 0.066$, $P > 0.05$). Significant correlations were recorded between Pb in sediment and Cd in water ($r = -0.604$, $P < 0.05$) and between Ni in sediment and Cr in water ($r = 0.420$ $P < 0.05$). The concentration of Zn was highest both in the water and sediment at Edo/Bata when compared with those of the other three zones. The high Zn value recorded in the water (1.47μg/l) and sediment (6.20μg/g) respectively. This zone might suggest the influx of slaughter effluents composed of dungs and other excretory products. According to Forstner and Prosi (1979), Zn is a product of animal food and is readily concentrated in excretions with adult animals excreting an average of between 7 and 20mg Zn daily.

Moderate enhancement of Pb (0.82 μg/l) and Zn (0.95μg/l) in water and of Cd (1.86 μg/g); Cr (1.17μg/g); Cu(2.27μg/g) and Ni (4.20μg/g) in the sediment taken at the Brewery during the sampling period may be attributed to the relatively high percent organic matter content of the sediment and the bioturbation of the upper sediment layers by tubificid worms and aquatic insects larval previously reported at the zone by Oguzie (1996). Though, no significant difference ($P > 0.05$) was recorded in the mean percent total of organic matter of the sediment at the various zones, the sediment at the Brewery had the highest concentrations of Cd, Cr, Cu and Ni. According to Oguzie (1996), the sediment posseses a characteristic muddy texture caused by the degradation of brewery products by soil organisms. This finding is supported by the studies of Tada and Suzuki (1982) which showed that the adsorption process of heavy metals is more pronounced in sediment composed of fine bottom mud and rich in organic matter.

The relatively low mean concentration values recorded for most of the metals in the water and sediments at the various zones especially during the rainy seasons that might suggest possible dilution of river water by urban run-off water. Though, there are variations in the mean concentration values of the metals in the water and sediment at the various zones during the seasons of sampling, no significant differences ($P > 0.05$) were recorded in the concentration values of the metals at the various zones during the periods of sampling (Tables 2 and 3).

The reported mean concentration values of heavy metals in the sediment of the lower Ikpoba river were lower than values reported for sediments obtained from the Niger Delta (Kakulu and Osibanjo 1988) and the Lagos lagoon sediment (Okoye *et al* 1991).

The total mean concentration values for Cd (0.74μg/1) and Pb (0.86μg/1) reported for water in the present study were higher than the mean Cd (0.094μg/1) and Pb (0.47μg/1) concentrations reported for the Ikpoba reservoir water by Fuferyin (1994). The mean values, were lower than Cd (2.29 μg/1) and Pb (1.08μg/1) concentrations reported for the Warri river water by Egborge (1991), but it exceeded the limits recommended for Cd (0.01μg/1) and Pb (0.05μg/1) in drinking water by the World Health Organisation (WHO 1984). This finding clearly suggests that the Ikpoba river water in Benin City, is unfit for human consumption.

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