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Distribution Pattern of Some Heavy Metals Pollutants in the Bottom Sediment of Ekpan Creek, Warri, Delta State, Nigeria

Okojie V. U[1]. Osuide M.O. Ebu S. and Ize-iyamu O.k. Ph.d

[1] Department of Chemistry,
Ambrose Alli University, Ekpoma
Email : usi4life@yahoo.com

Abstract : Ekpan creek was sampled at three selected locations and the samples analysed for some heavy metals to determine the concentration speciation and distribution pattern of the metals. The sediments were obtained specifically at upstream, effluent zone and downstream of the river in the industrial location. The metals distribution pattern of the river clearly indicates the source of pollution to be land – based and implicates the industries in the adjacent area as the most likely source. Correlation studies suggest that some of them are strongly associated indicating a common source for the coupled metals. The main concentration level of bio-available fraction of Pb, Cu, Cd and Zn in bottom sediments along the length of the creek were 28.89 ± 1.05 Mg/kg, 14.54 ± 4.06 Mg/kg, 12.92 Mg/kg 1.08 Mg/kg and 64.92 ± 3.84 Mg/kg

Keywords : Sediment, Speciation, Ekpan Creek, distribution pattern.

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1. Introduction

The study of heavy metal concentration in water bodies is a function of the substrate sediment, composition and the water chemistry, sediment serves as a sink to heavy metals in a polluted river system. The interaction between heavy metals and sediments matrix are important to the understanding of the environmental impact and the distribution, bioavailability and toxicity of the metals are best described , when the chemical fractionation in the sediment is known. The total concentration of the metal is not enough to predict the bioavailability of a metal in relation to its phytotoxicity, Fatoki, et al 2002. A great mass of waste water and solid waste containing toxic metals are directly disposed into Ekpan River. However no attempt has been made in any previous work to establish specifically the sources and distribution, including the forms of these pollutants in the river.

Therefore this study attempts to investigate whether pollution is occurring in the river especially the sediments and identify the sources of the pollution and the extent of damage to the coastal system. The behaviour of trace metal in the sediments depends on the fraction and the concentration which is often determined by sequential fractionation, procedures used to understand the fate of trace metal in terms of chemical species, mobility and availability in the water environment. The five – stage extraction scheme of Tessier et al. 1979, is very important in this case. All extractions scheme involve the use of extractants with different chemical properties under suitable pH conditions at each stage of extraction. To achieve this objective, sequential extraction of Cu, Zn, Cd and Pb from the bottom sediment of Ekpan Creek shall be carried out following the modified sequential scheme of Tessier et al 1995.

The term speciation of heavy metals in bottom sediments of natural and man-made water reservoirs refers to quantitative and qualitative differentiation The criteria of division into various forms can be different, e.g. (1) functional - forms available for organisms living in water, mobile forms, exchangeable cations (2) operational – according to procedures, reagents and extractant used for their isolation, identification and determination and (3) according to the element oxidation state in specific compounds, Ure et al, (1993), and Zerbe et al 1995

The speciation of metal in bottom sediments has been the subject of interest for a long time, however the first work in which a complete scheme of operational differentiation of metal forms by sequential extraction was proposed by Tessier et al (1979) in which he identified and defined five fractions. The fractions are exchangeable, Metal bound to carbonates, bound to organic matter and metal in other forms. To separate particular fraction Tessier et al applied various extractants system. Later other authors introduced certain modifications both in the division into fraction and in the method of sequential extraction. Welte et al, 1983, and Fernex et al 1986 . Although metal speciation and solubility affect the mobility, bioavailability and toxicity of metals significantly, the sequential extraction method elaborated by Tessier et al (1979), has some shortcomings, it is the most widely used method to study the geochemical occurrence of metals in sediments, Peng et al 2005. To access the mobility and bioavailability of Cd, Cu, Pb, and Zn, five step sequential extraction method was performed to determine the geochemical distribution of Cd, Pb, Cu and Zn in sediments collected from zone 1 to zone 3, of the Ekpan creek.

(1) Sampling

The river sediment was collected at three different locations along the river course with the aid of the stainless bottom sediment grab (Auckman grab). Each grab content was immediately emptied into the polythene bag and stored in an ice-chilled 50ml capacity cooler and taken to the laboratory for analysis. Air dried sample were finally homogenized by grinding using agate mortar (Adekola et al 2003).

(2) Sampling Points

The entire creek was divided into three points based on facilities, structure and human activities that could impact on the water and sediment qualities. Such activities are direct raw sewage disposal, laundering and bathing. Also dumping of household materials, metal scraps and recipients of strong runoff from Nigerian National petroleum Corporation (NNPC) housing estate which links Edjeba.

2. Method of Analysis

Heavy Metals Fraction (Speciation): some metals such as Pb, Cd, Cu and Zn were chosen for the speciation study. The procedure of Tessier et al (1979, 1983 and 1985) was selected for this study. In this method, metals are separated into six operationally defined fraction.

Water soluble, exchangeable, bound to carbonate, bound to manganese – oxide bound to iron oxide, bound to organic matter and residual fraction.

The sequential extraction is as follows :

Step 1 : Exchangeable Fraction : one gram of the dried sediment sample was extracted using 20ml of 1m NH_4 OAC (pH = 7) with stirring at room temp. for 30 minutes (continuous agitation).

Step 2 : Bound to Carbonates: the residue from step 1 was continually extracted with 20ml of sodium acetate (NaoAc) pH 5.0 adjust with acetic acid (HOAC) for 5 hours with continuous agitation.

Step 3 : Bound to Mn – oxide: the residue from step 2 was continually extracted with 20ml of 0.1m NH_2OH. HCL in 0.01M HNO_3 (pH 2.0) for 30 minutes with continues agitation, at room temp.

Step 4 : Bound to Fe – oxides: The residue from 0.04M NH_2 OH. HCL in 25% (v/v) acetic acid (HOAC) for 6 hours with continuous agitation at 96^{0}C.

Step 5 : Bound to Organic Matter: The residue from step 4 was continually extracted at 85^{o}C with 10ml of 30% H_2O_2 for 5 hours with occasional agitation adjusted to pH 2.0 with HNO_3 cooled at room temp. and extracted with 15ml of 3.2m NH_4OAC in 20% HNO_3 (v/v) for 30 minutes with continuous agitation.

Step 6 : Residual Fraction : the residue from step 5 was digested with a mixture of conc, Hcl and HNO_3 for 10 hours while the soluble fraction was digested with 30 ml water only for 10 hours with continuous agitation.

The metals Cd, Pb, Cu, and Zn in the above supernatant solutions were determined with flame atomic absorption spectrophotometer scientific model 210 CVP. The selective extraction was conducted in certrifuge tubes (poly propylene) to minimize losses of solid materials.

3. Results and Discussion

Table 1 : Distribution pattern and chemical fractions of some trace metal pollutants in the bottom sediment of ekpan creek, effurun in zone 1

Form/phase	Pb	Cu	Cd	Zn
Water soluble	2.81	0.80	2.75	3.07
Exchangeable	10.73	3.60	2.40	15.63
Carbonate bound	6.40	5.64	4.53	11.67
Fe – Mn oxide Reducible	4.43	4.38	1.90	23.08
Organically bound	3.75	0.12	1.34	11.51
Residual	12.80	3.37	0.42	7.52
Total fractionated	40.92	17.91	13.34	72.48
Potentially availability	28.10	14.54	12.92	64.92
Total metal (acid Digestion)	42.55	8.37	12.99	70.24

Analysis of the data obtained shows that Cd occurred mainly in the residual fraction and in the form bound to organic matter and in much smaller amount in the form of oxide Only small amount of Cd were detected in the exchangeable and bound to carbonate fractions. These result are similar to the distribution of Cd among particular fractions reported for bottom sediment in literature Pb was found mainly in the form bound to hydrated Iron oxide than in the residual fraction and bound to carbonates. In a smaller amount, it was found bound to organic matter and exchangeable form. A similar distribution of Pb forms among the five fraction was observed as shown in Figure 1.

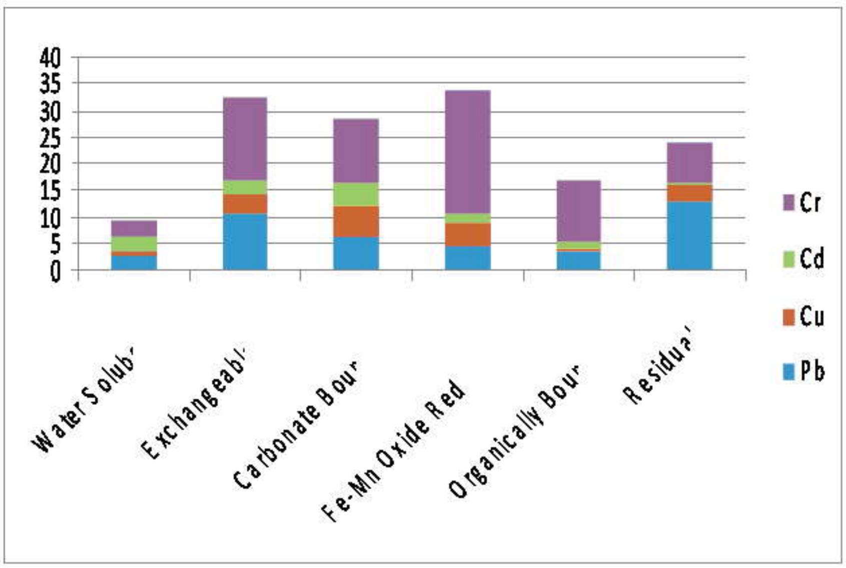

Figure 1 : Heavy metals fractions in zone 1

Table 2 : Heavy Metals form and their concentration in Zone 2

Form/Phase	Pb	Cu	Cd	Zn
Water soluble	4.83	0.24	2.91	2.87
Exchangeable	5.78	3.41	2.88	13.42
Carbonate bound	6.48	5.64	3.61	9.89
Fe Mn oxide reducible	5.25	5.75`	2.23	23.65
Organically bound	5.95	8.53	2.97	16.22
Residual	10.4	2.51	1.45	5.45
Total fractionated	38.69	26.08	16.05	71.5
Potentially available	28.29	23.57	14.6	66.05
Total metal (acid Digestion)	36.81	27.02	17.11	69.99

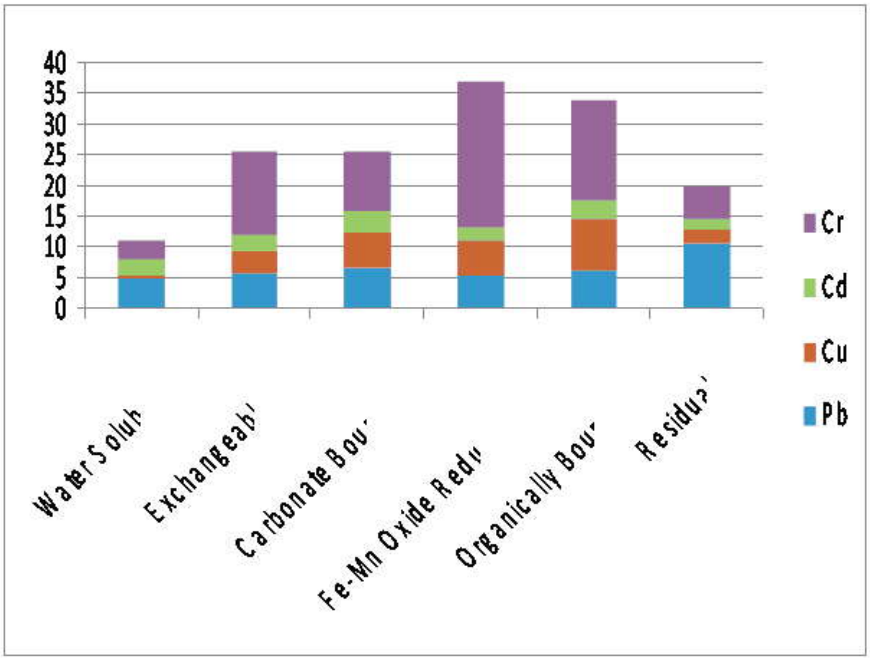

Figure 2 : Heavy metals fractions in zone 2

Zn in the sediment was mainly found in the residual fraction and in that bound to organic matter, while in smaller amounts in the fraction bound to hydrated iron and manganese oxides. Copper as well as Cd was mainly found in the residual fraction. Much fewer amounts of this metal were bound to organic matter and hydrated oxides of iron and manganese. The distribution of Cu forms among particular fractions were similar both in sediments from zone 1 and zone 3 upstream areas and the effluent zone as shown inFigure 2 and Figure 3.

The concentration of heavy metals were high for the metals, thus indicating a lack of uniform distribution in the sediment. For example in the upstream area, Cu ranged from 18.37 to 27.02 with the highest values at the effluent point. These higher values at the effluent point imply that industrial activities are responsible for elevated levels of metal in the Ekpan Creek sediment. The values at different sampling points show Cu to be the most abundant metal in all the three locations followed by Zn and Pb as shown inFigure1, Figure 2 and Figure3. The value of Zn is higher at the effluent of location 2 than other locations being a major pollutant from the activity of the iron and steel company and the high levels of Pb are due to the composition of metal ions in drilling mud and the use of Pb as anti knocle in petrol.

Table 3 : Heavy Metals form and their concentration in Zone 3

Form/Phase	Pb	Cu	Cd	Zn
Water soluble	4.43	0.31	2.85	5.94
Exchangeable	3.70	2.15	3.09	15.35
Carbonate bound	8.25	8.41	3.54	11.33
Fe Mn oxide reducible	7.75	6.81	2.46	11.47
Organically bound	6.28	3.75	3.59	16.22
Residual	12.23	1.61	2.29	5.29
Total fractionated	42.64	23.04	17.82	65.60
Potentially available	30.41	21.43	15.53	60.31
Total metal (acid Digestion)	40.28	24.88	18.07	63.10

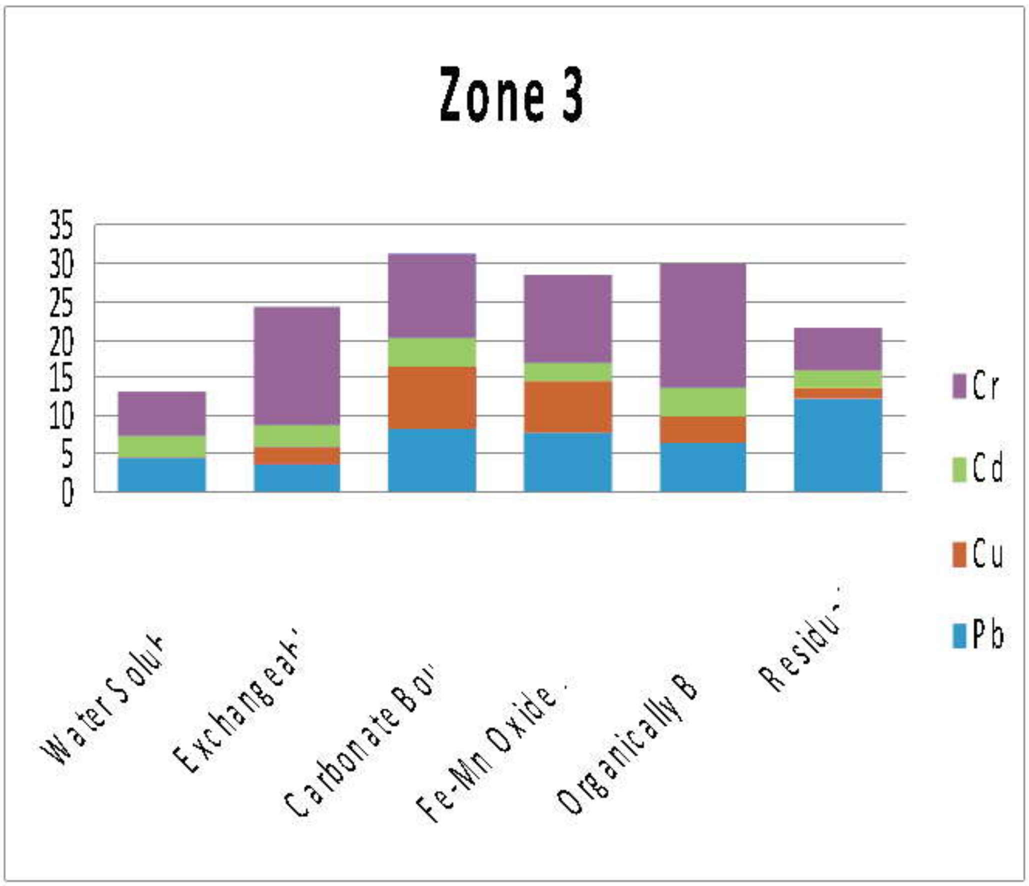

Figure 3 : Heavy metals fractions in zone 3

Table 4 : Total concentration of heavy metals (Mg/g) in sediment of ekpan creek

Location	Pb	Cu	Cd	Zn	PH
Upstream	42.45	18.27	12.99	70.24	4.82
Effluent point	43.09	19.88	18.04	64.15	4.56
Down stream	38.81	27.02	17.11	63.1	5.08
Rang	38.81-43.09	18.27-27.02	12.99-18.04	63.10-70.24	3.08-7.56

Table 5 : Correlation matrix of heavy metals concentration in the various SAMPLES

	Cd	Zn	Cu	Pb
Cd	1	0.63	0.26	0.61
Zn	0.63	1	0.79	-0.19
Cu	0.26	0.79	1	-0.19
Pb	0.61	0.07	-0.19	1

Table 6 : Correlation matrix of total heavy metals concentration and chemical properties such as ph, do and conductivity.

	Cd	Zn	pH	Cu
pH	-0.564	-0.114	0.554	0.196
%C	-0.127	0.242	0.152	0.298
Conductivity	-0.266	0.222	0.394	0.329

The correlation between the value of Cd, Cu, Pb and Zn were investigated (as shown in table 5). Apparently, Cd, Cu, Pb and Zn correlated with each other very significantly ($P<0.01$) indicating that heavy metals were released from the same sources. It was also found that relationship between pH %C, Cd, Cu and Pb were significant and the correlation coefficient R^2 is 0.0318 for Cd and 0.3070 for Pb. It showed that both organic matter, and metals originated from terrestrial sources. At the same time, strong association between metals and organic carbon induced similar characteristics of migration in aquatic environment. Zn has negative relationship with Cd and Cu. The possible reason for this difference is that Cd and Cu mainly originated from anthropogenic activities whereas Pb and cu were controlled by natural processes.

Linear Regression Equation

pH	=	9.218 + (- 1.675) Cd (R^2 = 3.318)	**
	=	7.220 + (- 0.0029) Pb (R^2 = 0.376)	**
	=	0.7.612 + (- 0.0576) Cr (R^2 = 0.0131)	**
	=	6.5536 + (- 0.0031) Cu (R^2 0.0395)	ns
Do	=	- 0.208 + (0.2762) Cr (R^2 = 0.0590)	ns
	=	4090 + (- 0 0018) Pb (R^2(0.0234)	ns
	=	3.049 + (0.0105) Cu (R^2 = (0.0886)	ns
Conductivity	=	54.513 + (- 17.362) Cd ($R^2$0.0659)	ns
	=	- 7.5199 + (2.5426) Cr (R^2 = 0.0492)	ns
	=	36.3762 + (- 0.0476) Pb (R^2 = 0.1558)	**
	=	20.764 + (0.1164) Cu (R^2 = 0.1085)	**

However the values of the studied metals was a result of physical or chemical phenomenon such as mobility, adsorption or co-precipitation of metals or existence of some respiratory mechanism by aquatic fauna to eliminate accumulated metal ions in the river. All the metal exceeded the allowable limits for aquatic culture. This may explain why there is drastic reduction in marine organism nowadays than pre-industrial times. This ascertion agrees with the study of *Tetsola et al 2004,* who found low biomass of fish in Ekpan river Comparing results of this study with previous investigations, there is apparently an increase in the periodical accumulation of the metals in the river. This suggests that industrialization must have contributed a fair amount of these metals to the river.

The distribution of metal species associated with different geochemical fraction is a critical parameter to assess the potential mobility and bioavailability of heavy metals in sediments. Risk assessment code (RAC) established by Perin et al (1985) was used to evaluate the risk of Cd, Cu and Pb in sediment of Ekpan Creek. RAC is mainly the sum of exchangeable and carbonate fractions for assessing the availability of metals in sediments. From the study, the sum of exchangeable and carbonate bound fraction of Cd, Cu, Pb and Zn were 6.21%, 8.4%, 12% and 13.2% respectively. This suggests that Cd has posed a very high risk to local environments while Cu and Pb were at medium risk level. The results showed that total metal concentration at the sampling points at zone 1 to zone 3 were significantly different. In a sense, this difference can represent the migration distance of pollutants from the creek (estuary) to offshore.

Therefore, dynamic variation and stability of metal forms can be investigated in seaward migration process of pollutants through analyzing the relationships between percentage metal speciation and total metal concentration in sediment of Ekpan creek.

The results showed that some forms of metals correlated significantly with total metal concentrations in sediments. On one hand the percentage of exchangeable Cd, Cu bond to carbonate and organic matter and Pb associated with organic matter deceased with the reduction of total Cd, Cu and Zn concentration in sediments

4. Conclusion

The heavy metals concentration of Ekpan Creek sediment has been fractionated to determine the environmental impact of Pb, Cu, Zn and Cd. At present, the contributions of Cd and Pb to the bioavailable fraction is high and may be transferred into the food chain through gradual leaching to water and uptake by aquatic plants or fish. The appreciable contents of these metals associated with the exchangeable and the iron-oxide fractions shows that their availability is susceptible to pH. Therefore, these levels are of environmental concern in relation to the consumption of aquatic animals especially fish from this creek. The investigation of wood treatment chemical from the wood factories and effluent from Nigeria National Petroleum Co-operation (NNPC) must be analysed in order to understand the contribution of these heavy metals from these sources.

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