

Original Research Article**Spatial Distribution and Speciation of Heavy Metals in Sediment of River Ilaje, Nigeria****ABSTRACT**

Speciation of heavy metals (Zn, Fe, Cr, Cd, Cu and Pb) was carried out on the top and bottom sediment samples of two sampling sites in river Ilaje, Nigeria during the dry and rainy seasons. The samples were subjected to sequential extraction method and the extracts were analyzed for heavy metals using atomic absorption spectrophotometer. The result shows that Zn and Fe are abundant in reducible fraction, oxidizable fraction and highest in residual fractions in both seasons. The concentrations of Cr and Cd varied greatly with the seasons, while the highest concentration of Pb occurs in residual fraction for both seasons. The concentration of Cu occurs abundantly in oxidizable fraction and residual fraction, Cu and Pb shows a low concentration in exchangeable fraction and carbonate fraction. This study reveals that the mobility and bioavailability of the heavy metals in the sediment for the two seasons are in this order: Fe > Cr > Zn > Pb > Cu > Cd. It was observed that the origin of metals in the environment is likely to be lithogenic.

Keywords: Speciation, heavy metals, fraction, concentration, bioavailability

1. INTRODUCTION

Heavy metals enter into the aquatic environment either through the naturally occurring biogeochemical processes or through anthropogenic sources. These influence the nature of the sediments in the coastal water areas such as the Ilaje coastal area. The Ilaje coastal area of Ondo State, Nigeria lies on Latitude. 5° 50'N – 6° 09'N and Longitude. 4° 45'E – 5° 05'E, river Ilaje is a deltaic region which takes its source from river Oluwa. Ilaje communities depend on the river Ilaje for their economic and domestic activities.

Heavy metal contamination is a major problem because of their toxicity and threat to living organisms and the environment [1]. Heavy metals are being accumulated in urban rivers, estuaries and adjacent coastal zones as a result of urbanization, industrialization, water runoff, landfill leachate e.t.c [2, 3]. Sediments may therefore act as either sources or sinks for metals and this is strongly dependent on their chemical forms [4]. Determination of the total metal concentration may provide information concerning possible pollution levels but generally there are insufficient details for estimating their biological effects, risk of bioavailability, toxicity, capacity for remobilization of heavy metals in the environment. It is the chemical form of metals in the soil that determine its toxicity, mobilization capacity and behavior in the environment

[5, 6, 7, 8,]. The bioavailability, toxicity and distribution of trace metals are best described when the speciation (chemical fractionation) in the soil/sediment is known [9].

2. MATERIALS AND METHODS

2.1 Sampling and Pre-treatment of Sample

A total of 24 sediment samples were collected from two sampling sites (Abereke and Ogogoro) in river Ilaje, Nigeria during the dry (December 2014) and rainy (May 2015) seasons. Sampling points were geo-located using Geographical Position System (GPS) to ensure consistency, top (0-15cm) and bottom (15-30cm) sediment samples were collected using hand hugger, and stored in a polythene bag prior to analysis. The samples were air dried in the laboratory for two weeks, and later pulverized using laboratory mortar and pestle and sieved with 2mm mesh size sieve.

2.2 Multi-Step Sequential Extraction

The sediment samples were subjected to sequential extractions method and heavy metals were associated in five fractions [10]. As stated below:

Fraction 1 (Exchangeable fraction): 1g of sediment samples were extracted at room temperature for 1 hour with 8ml of $MgCl_2$ solution (1M $MgCl_2$) at pH 7. Sediment and extraction solution were thoroughly agitated throughout the extraction using a centrifuge at 4,000rpm. The extracts were decanted from the residue and analyzed for heavy metals using AAS.

Fraction 2 (Bound to carbonates): The residue of Fraction 1 was extracted with 8ml of 1M sodium acetate/acetic acid buffer at pH 5, the extraction process was carried out for 5 hours at room temperature with thorough agitation using a centrifuge at 4,000 rpm. The extracts were decanted from the residue and analyzed for heavy metals using AAS.

Fraction 3 (Bound to iron and manganese oxides): The residue from fraction 2 was extracted under mild reducing conditions using 20ml of 0.04M $NH_2OH.HCl$ in 25% (v/v) acetic acid with agitation at 96°C in a water bath for six hours. The extracts were decanted from the residue and analyzed for heavy metals using AAS.

Fraction 4 (Bound to organic matter and sulphide): The residue from fraction 3 was extracted under a mild oxidizing condition as follows: 3ml of 0.02M HNO_3 and 5ml of 30% (v/v) H_2O_2 , which has been adjusted to pH 2 with HNO_3 , were added to the residue from fraction 3. The mixture was heated to 85°C in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3ml of 30% H_2O_2 , adjusted to pH 2 with HNO_3 , was then added. The mixture was heated again at 85°C for 3 hours with occasional agitation and allowed to cool down. Then 5ml of 3.2M ammonium acetate in 20% (v/v) HNO_3 was added, followed by dilution to a final volume of 20ml with de-ionized water and agitated continuously for 30 minutes. The extracts were decanted from the residue and analyzed for heavy metals using AAS.

Fraction 5 (Residual or inert fraction): The residue from fraction 4 was oven dried at 105°C. Digestion was carried out with a mixture of 5ml conc. Nitric acid (HNO₃, 70% w/w), 10ml of hydrofluoric acid (HF, 40% w/w) and 10ml of perchloric acid (HClO₄, 60%w/w) in Teflon beakers. The digestate was decanted and analyzed for heavy metals using AAS.

After each extraction step, the sample was subjected to centrifugation at 4,000 rpm and the supernatants were separated from the residue in order to ensure selective dissolution and prevent possible interface mixing between the extractants. Analysis of each extract was carried out using atomic absorption spectrophotometer (AAS). Blanks were also used for correction of background and other sources of error.

2.3 Data analysis

Data generated on concentrations of each metal were analyzed for spatial variation using one way analysis of variance (ANOVA) with SPSS package version 20.

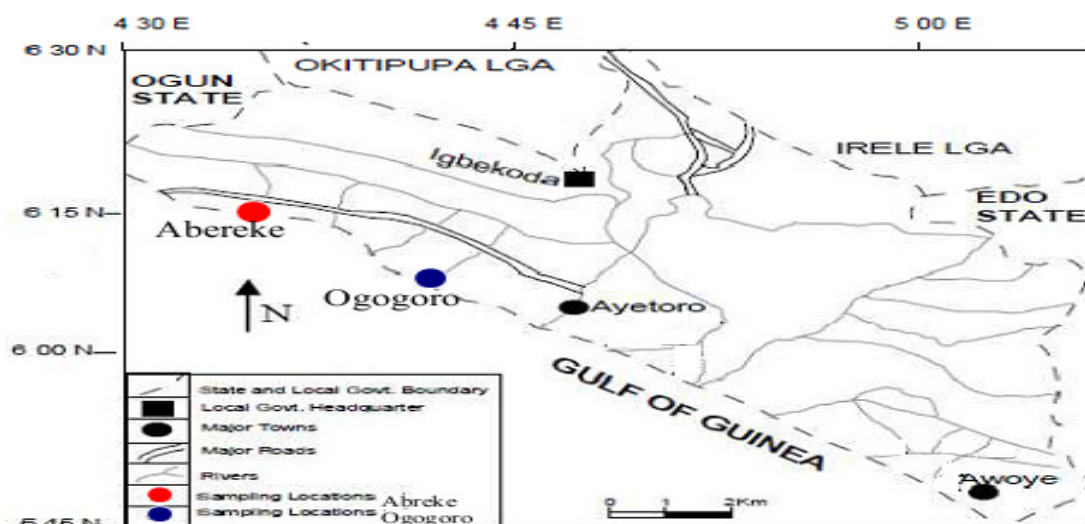


Fig 1: Map of the study area (Ilaje community, Ondo State, Nigeria)

3. RESULT AND DISCUSSION

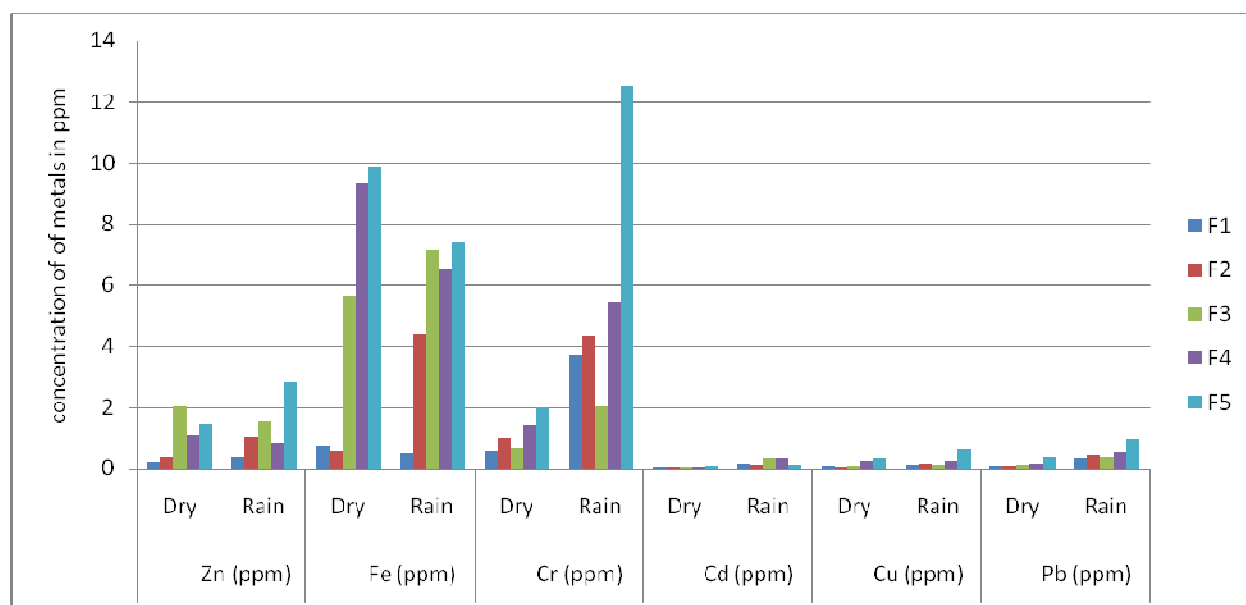
Tables 1-4, shows the results of the sequential extraction of top and bottom sediment samples for both dry and rainy seasons in the 2 sampling sites (Abereke and Ogogoro) in the coastal area of river Ilaje in Ilaje local government area of Ondo State, Nigeria.

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89 Table 2; Concentration of heavy metals in sediment samples at Abereke site (F= fractions, Bottom= 15-
90 30cm)

F ₁	0.17	0.33	0.70	0.50	0.55	3.70	0.03	0.15	0.08	0.12	0.05	0.30
F ₂	0.34	1.01	0.55	4.41	1.00	4.35	0.04	0.11	0.03	0.13	0.06	0.45
F ₃	2.04	1.52	5.65	7.17	0.64	2.03	0.04	0.31	0.07	0.12	0.13	0.40
F ₄	1.06	0.83	9.35	6.55	1.42	5.45	0.05	0.30	0.23	0.23	0.14	0.55
F ₅	1.46	2.82	9.85	7.41	1.97	12.51	0.06	0.12	0.29	0.62	0.34	0.95

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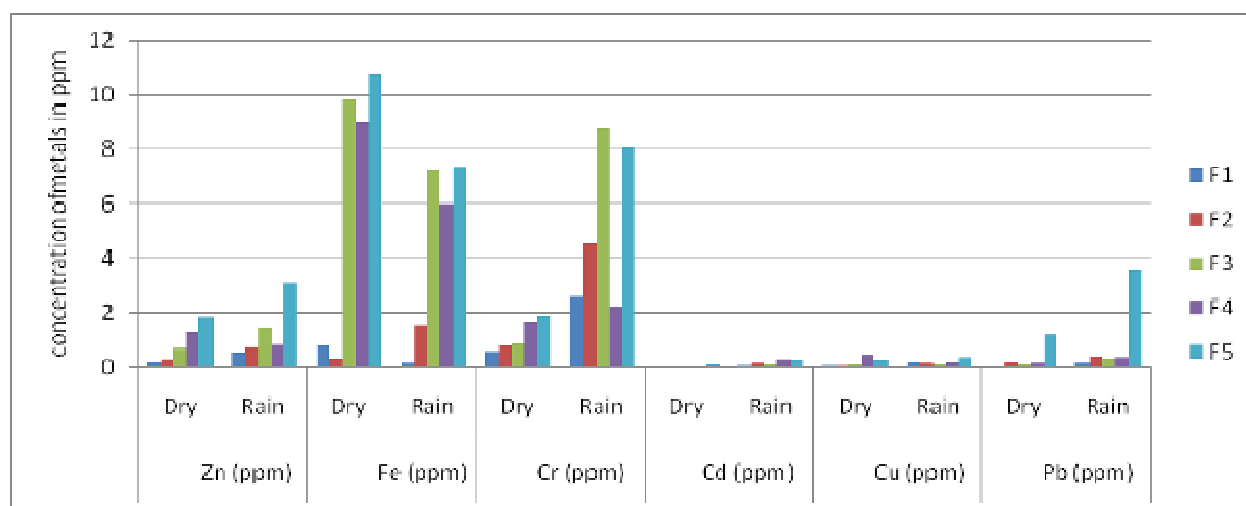
93 Fig 3; a graph of concentration metals in ppm against metals in Abereke bottom sediment samples

94 Table 3; Concentration of heavy metals in sediment samples at Ogogoro site (F= fractions, Top= 0-15cm)

Fraction/h heavy metals	Zn (ppm)		Fe (ppm)		Cr (ppm)		Cd (ppm)		Cu (ppm)		Pb (ppm)	
	Dry	Rain	Dry	Rain	Dry	Rain	Dry	Rain	Dry	Rain	Dry	Rain
F ₁	0.19	0.55	0.75	0.18	0.59	2.57	0.03	0.09	0.06	0.19	0.04	0.15
F ₂	0.30	0.71	0.35	1.54	0.77	4.52	0.03	0.17	0.08	0.16	0.20	0.40
F ₃	0.67	1.48	9.80	7.24	0.85	8.76	0.05	0.11	0.14	0.13	0.11	0.35
F ₄	1.30	0.81	9.00	6.01	1.66	2.22	0.05	0.28	0.47	0.22	0.16	0.40
F ₅	1.83	3.09	10.75	7.35	1.91	8.03	0.13	0.26	0.24	0.38	1.19	3.55

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98 Fig 4; a graph of concentration metals in ppm against metals in Ogogoro Top sediment samples

99 Table 4; Concentration of heavy metals in sediment samples at Ogogoro site (F= fractions, Bottom= 15-
100 30cm)

Fraction/h eavy metals	Zn (ppm)		Fe (ppm)		Cr (ppm)		Cd (ppm)		Cu (ppm)		Pb (ppm)	
	Dry	Rain	Dry	Rain	Dry	Rain	Dry	Rain	Dry	Rain	Dry	Rain
F ₁	0.21	0.57	0.55	0.20	0.40	1.30	0.03	0.16	0.08	0.13	0.05	0.30
F ₂	0.21	0.88	0.35	1.99	0.28	7.41	0.03	0.10	0.10	0.36	0.05	0.35
F ₃	0.93	1.64	8.50	7.20	0.93	8.30	0.05	0.17	0.06	0.13	0.08	0.35
F ₄	0.93	0.95	9.20	6.10	1.21	4.83	0.05	0.28	0.27	0.26	0.17	0.40
F ₅	1.90	3.20	10.60	7.50	1.67	10.21	0.10	0.27	0.22	0.61	0.33	0.70

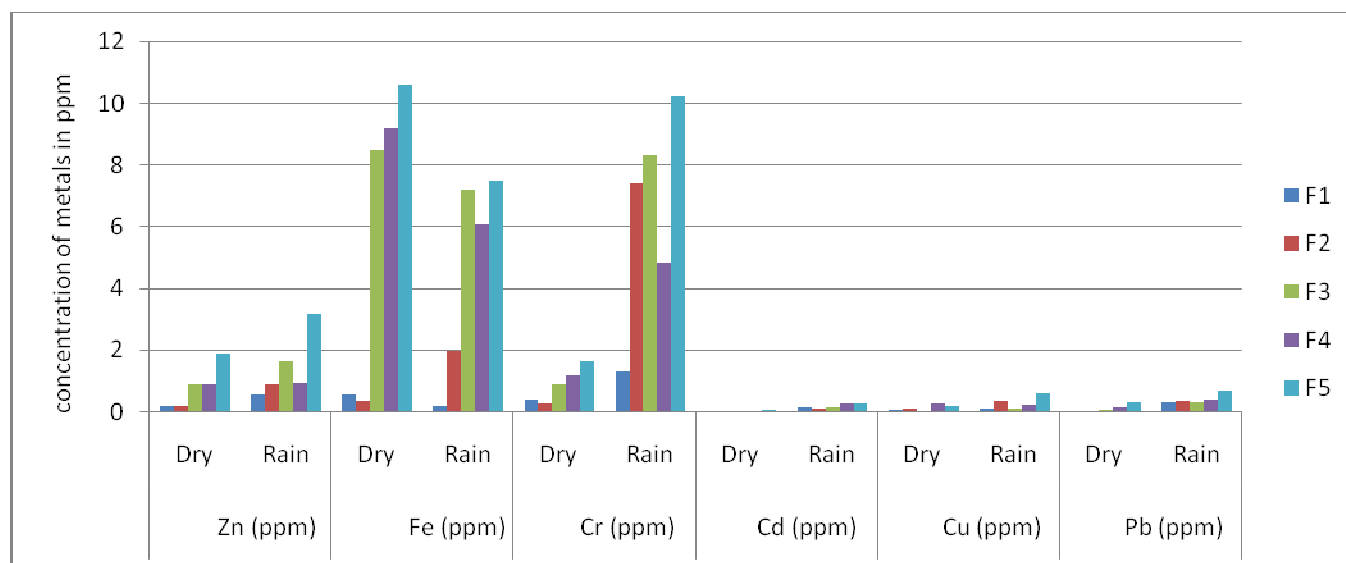


Fig 5; a graph of concentration of metals in ppm against metals in Ogogoro bottom sediment samples

Analysis of the data obtained in the two sampling site shows that in the dry season, all the heavy metals in the top sediment were mostly abundant in the residual fraction in the following order Fe (9.80-10.75ppm) > Cr (1.91-1.98ppm) > Zn (1.60-1.83ppm) > Pb (0.40-1.19ppm) > Cu (0.24-0.35ppm) > Cd (0.13-0.14ppm), while for the bottom sediment it follows the same order Fe (9.85-10.60ppm) > Cr (1.67-1.97ppm) > Zn (1.46-1.90ppm) > Pb (0.33-0.34ppm) > Cu (0.22-0.29ppm) > Cd (0.06-0.10ppm). However, for both top and bottom sediment samples, Fe was also abundant in the bound to organic matter and sulphide fraction (top {6.60-9.00ppm}, bottom {9.20-9.35ppm}) and bound to iron and manganese oxide fraction (top {8.45-9.80ppm}, bottom {5.65-8.50ppm}), while Pb occurs at a very low concentration in the bound to organic matter and sulphide fraction (top{0.40-0.16ppm}, bottom{0.14-0.17ppm}) as well as the bound to iron and manganese oxide fraction (top{0.11-0.19ppm}, bottom{0.08-0.13ppm}). All the heavy metals in the top sediments occurs at a low concentration in the Exchangeable fraction in the following order Fe (0.75-0.95ppm) > Cr (0.59-1.04ppm) > Zn (0.19ppm) > Cu (0.06-0.11ppm) > Pb (0.03-0.04) = Cd (0.03-0.04), while for the bottom sediment was as follows Fe (0.55-0.70) > Cr (0.40-0.55) > Zn (0.17-0.21) > Cu (0.08) > Pb (0.05) > Cd (0.03). Also the heavy metals in the top sediment associated with the bound to carbonate fraction occurs at a low concentration as follows Cr (0.62-0.77ppm) > Fe (0.35-0.40ppm) > Zn (0.23-0.30ppm) > Pb (0.07-0.20ppm) > Cu (0.08-0.10ppm) > Cd (0.03ppm).

In the rainy season, most of the heavy metals in the top sediments have their highest concentration in the residual fraction as follows Cr (8.03-12.40ppm) > Fe (7.35-7.37ppm) > Zn (3.01-3.09ppm) > Pb (0.75-3.55ppm) > Cu (0.38-0.71ppm) > Cd (0.22-0.26ppm), the heavy metals in the bottom sediments follows a similar order Cr (10.21-12.51ppm) > Fe (7.41-7.50ppm) > Zn (2.82-3.20ppm) > Pb (0.70-0.95ppm) > Cu (0.61-0.62ppm) > Cd (0.12-0.27ppm). However, Fe (top {6.01ppm}, bottom {6.10-6.55ppm}) > Cr (top{2.22-3.61ppm}, bottom{4.83-5.45ppm}) > Zn (top{0.81-0.93ppm}, bottom{0.83-0.95ppm}) occurs

abundantly in the bound to organic matter and sulphide fraction, and also in the bound to iron and manganese oxide fraction as follows Cr (top {7.16-8.76ppm}, bottom {2.03-8.30ppm}) > Fe (top {7.01-7.24ppm}, bottom {7.17-7.20ppm}) > Zn (top {1.33-1.48ppm}, bottom {1.52-1.64ppm}). While Pb (top {0.40ppm}, bottom {0.40-0.55ppm}), Cd (top {0.25-0.28ppm}, bottom {0.28-0.30ppm}) and Cu (top {0.22-0.24ppm}, bottom {0.23-0.26ppm}) occurs at a low concentration in the bound to organic matter and sulphide fraction, they also occurs at a low concentration in the bound to iron and manganese fraction as follows Pb (top {0.35ppm}, bottom {0.35-0.40ppm}), Cd (top {0.11-0.26ppm}, bottom {0.17-0.31ppm}) and Cu (top {0.11-0.13ppm}, bottom {0.12-0.13ppm}). All the heavy metals occurs at a very low concentration in the exchangeable fraction Zn (top {0.31-0.55ppm}, bottom {0.33-0.57ppm}), Fe (top {0.18-0.45ppm}, bottom {0.20-0.50ppm}), Cr (top {0.77-2.57ppm}, bottom {1.30-3.70ppm}), Pb (top {0.15-0.20ppm}, bottom {0.30ppm}), Cd (top {0.09-0.18ppm}, bottom {0.15-0.16ppm}) and Cu (top {0.13-0.19ppm}, bottom {0.12-0.13ppm}). They also occurs at a low concentration in the bound to carbonate fraction as follows Fe (top {1.54-3.99ppm}, bottom {1.99-4.41ppm}), Cr (top {2.82-4.52ppm}, bottom {4.35-7.41ppm}), Zn (top {0.71-0.90ppm}, bottom {0.88-1.01ppm}), Pb (top {0.40-0.45ppm}, bottom {0.35-0.45ppm}), Cd (top {0.14-0.17ppm}, bottom {0.10-0.11ppm}) and Cu (top {0.14-0.16ppm}, bottom {0.13-0.36ppm}). This indicates that, there is a visible variation in the concentration of heavy metals in each fraction in relation with the dry and rainy seasons.

4. CONCLUSION

The heavy metals (Zn, Fe, Cr, Cd, Cu and Pb) contents of river Ilaje sediment have been fractionated in order to determine their environmental fate; the following conclusion can be summarized:

Regarding the group of heavy metals and their potential mobility, there is a wide range of spatial variation of heavy metals contents occurring in the top and bottom sediment samples of the two sampling sites for both dry and rainy seasons;

Most of the heavy metals were mainly associated with the bound to iron and manganese, oxidizable and residual fraction, this allow us to predict their mobility and bioavailability in the sediment samples. The residual fraction has the highest concentration, while the exchangeable and bound to carbonate fractions has the lowest concentration. This is an indication of a low bioavailability index;

The increase in the concentration of heavy metals within some fractions during the rainy season could be attributed to possible anthropogenic activities.

The present study of the mobility and bioavailability of heavy metals in sediment of river Ilaje by a sequential extraction procedure has provided vital information in addressing serious environmental problems of bioaccumulation and biomagnifications of heavy metals which could possible occur in aquatic organisms of Abereke and Ogogoro fishing communities as a result of anthropogenic activities. Further work should be carried out on both flora and fauna of the rivers.

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