



Assessment of Heavy Metals Bioavailability in Stream Sediments around A Gold Mining Environment in South-western Nigeria

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Abstract: In order to estimate environmental effects and the associated health risk of some of the metals determined in stream sediment samples in the mining area, the abundance of fractions of some of these metals: Cd, Pb, Fe, Cr and Cu that are bioavailable were determined using the modified Tessier extraction scheme. X-ray fluorescence spectrometer (XRF) was used in determining the total concentration of metals in sediments while metals concentrations in extracted fractions were determined with the use of atomic absorption spectrophotometer (AAS). Results obtained revealed different metals to be partitioned in different percentages in the fractions. The bulk of the metals were retained in the residual fraction for metals like Pb, Cd, Cr and Fe while only Cu has a greater percentage of the metal retained in the fraction bound to organic matter and sulphide and this is due to the affinity of the metal to organic compounds reacting to form stable complexes. Partitioning of the metals in the labile fractions is a measure of their bioavailability in sediments to benthic organisms.

Key Words: Extraction, Bioavailability, Fractions, Partitioning, Residual, Mobility Factor.

Introduction

The sediment is usually a sink of various chemical contaminants, both organic and inorganic including heavy metals in different chemical forms (Samir & Ibrahim, 2008). The release of such contaminating specie into water becomes hazardous to benthic dwelling organisms especially when their concentration is above certain tolerable limits (Jones *et al*, 1981). Total concentration of metals and metalloids in sediments and other environmental facets in the past have been determined using various techniques in order to measure their toxicity and otherwise in such environments to different organisms. However, it is not the proportion of the total concentration in samples that matters but the amount that is available for accumulation by the organisms. Only a small portion of heavy metals and metalloids in sediments is bioavailable, hence, measuring the total concentration will not be good enough to determine their contamination and potential health risks (Violante *et al*, 2010, Badaway & El-Motaium, 2000). Since these metals are not in a fixed concentration in the sediment, biological and chemical reasons may cause a change in their form within the sediment-water phase (Sharmin *et al*, 2010).

Availability of the metals is determined by the partitioning of the metal complexes into different fractions: dissolved, exchangeable, carbonates, iron-manganese oxide, organic and crystalline, which are affected by factors such as pH, biological processes, redox state and other environmental factors (Salomons, 1995). Chemical separation of these metals into different fractions and specie is of paramount importance in the determination of their toxicity and availability to aquatic organisms, hence this study.

These metals are sequentially extracted through a number of procedures involving some steps. Most commonly used are the modified 4-step standard, measurement and testing program (SM&T, formerly BCR scheme, modified by Raur *et al.*, 1999), the Hall scheme (Hall *et al.*, 1996) and the 5-step Tessier extraction scheme

Tessier *et al.* (1979) which has been modified recently by Baffii *et al.* (1998) according to the European Community of Bureau of Reference (BCR 701). The modified Tessier sequential extraction scheme is a three step procedure involving selectively extracting the metals over the following three

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phases: exchangeable metals and bound to carbonates, metals bound to Fe- Mn oxides and hydroxides and metals bound to organic matter and sulphides (Marco *et al*, 2005).

Materials and Methods

Sample collection: sediment samples were randomly collected from different locations covering 12 villages namely: Mokuro, Oke-Ora, Okutu-Omo, Oko-Ogboni, Alaba, Itagunmodi, Ariyelepe, Alaba-Oke, Iyere, Igun, Aba-Isobo and Sabo mining environments in South West, Nigeria. Fig 1 shows the map of Osun state and the sampling sites. Samples were collected with stainless steel trowel; stones and plant debris were discarded. In order to have a homogeneous representative sample of the sediment, about 3 sub samples were collected from each sampling site. The subsamples collected were homogenized from where a representative sample was finally taken and kept in a sample cloth particularly sown for the purpose. The sediment samples were air dried for 2 to 3 days, sieved to remove large grains, properly grinded in an agate mortar and kept in labelled bags for analysis. From each sample 13 mm diameter and 1 mm thick pellets were made with Spec-caps by applying 10 Ton pressure with hydraulic pelletizing machine. Pellets made were used for the XRF analysis to determine the total concentration of heavy metals in the samples.

Sequential Extraction Procedure: Five (Cd, Pb, Fe, Cr and Cu) of the metals among the priority metals listed in bioavailability studies by the U.S. Environmental Protection Agency (McKinney and Rogers, 1992) were selected for the study. The sequential extraction was carried out by the modified Tessier *et al.* (1979) as prescribed by Baffi *et al.* (1998). This is made up of the exchangeable and bound to carbonate fraction (F1), fraction bound to Fe-Mn oxides (F2) and the fraction bound to organic and sulphides (F3). Each of the stages was extracted appropriately. The exchangeable and bound to Carbonate Fraction was extracted using 1g of the sample weighed into a 50mL plastic bottle. 25mL of acetic acid was added and shaken for 6Hrs at room temperature; the sample was then removed from shaker and centrifuged at 3000rpm for 10 minutes after which the supernatant was decanted in clean bottles and refrigerated pending analysis. The residue was washed with 20mL of distilled water, shaken for 15 minutes and centrifuged at 3000rpm for 10minutes, this was again decanted and the supernatant in this case discarded while the residue was preserved for the next stage. The reducible fraction bound to Fe/Mn Oxide was extracted using approximately 25ml of hydroxylamine hydrochloride solution added to the residue of stage 1. The mixture was shaken for 6Hrs and later centrifuged at 3000rpm for 10 minutes. This was then carefully decanted and the supernatant stored in the refrigerator pending AAS analysis. The washing procedure was repeated while the residue obtained was used for stage 3. 10mL of 8.8M Hydrogen Peroxide was added to the residue from stage 2. The mixture was digested at 85⁰C for 1Hr in a water bath with the cover open until the volume reduces to about 5mL. Additional 10mL of the peroxide was added to digest the mixture further for another 1Hr at the same temperature until the volume again reduces to about 5mL of the initial volume. To the cooled mixture, 25mL of 2M ammonium acetate was added and shaken for 6hrs at room temperature, centrifuged at 3000rpm and decanted. The supernatant was kept for AAS analysis (PG 990 Model) to determine the oxidizable fraction bound to soil organic matter.

The residual fraction included in the mineral structure of the sample particles was obtained by from the residue obtained in stage 3 and analyzed using Eclipse III, X-ray fluorescence spectrometer (XRF) by AMPTEK INC. MA; USA).

Results and Discussion

Results of total elemental concentrations and the sequential extraction scheme are as presented in Tables 1, 2, 3, 4 and 5 respectively. Table 1 shows that stream sediment samples of dry season has greater percentage of the Cd metal retained in the residual fraction. The percentage of the metal in this fraction ranges from 55.9% in samples from Oko-Ogboni to 71.8% in Itagunmodi (Figure 2). The lowest percentage of 5.3% was extracted in the exchangeable and bound to carbonate fraction. This observation was the same for samples from seven (7) villages namely: Mokuro, Oke-Ora, Okutu-Omo, Oko-Ogboni, Igun, Itagunmodi and Alaba-Oke while in the other five (5) villages (Alaba, Ariyelepe, Iyere, Aba-Isobo and Sabo), samples showed a higher percentage (25.3%, 27.8%, 17.8%, 29.2% and 15.9%) of the metal in the fraction bonded to organic matter and sulphides with highest percentages in the residual fraction.

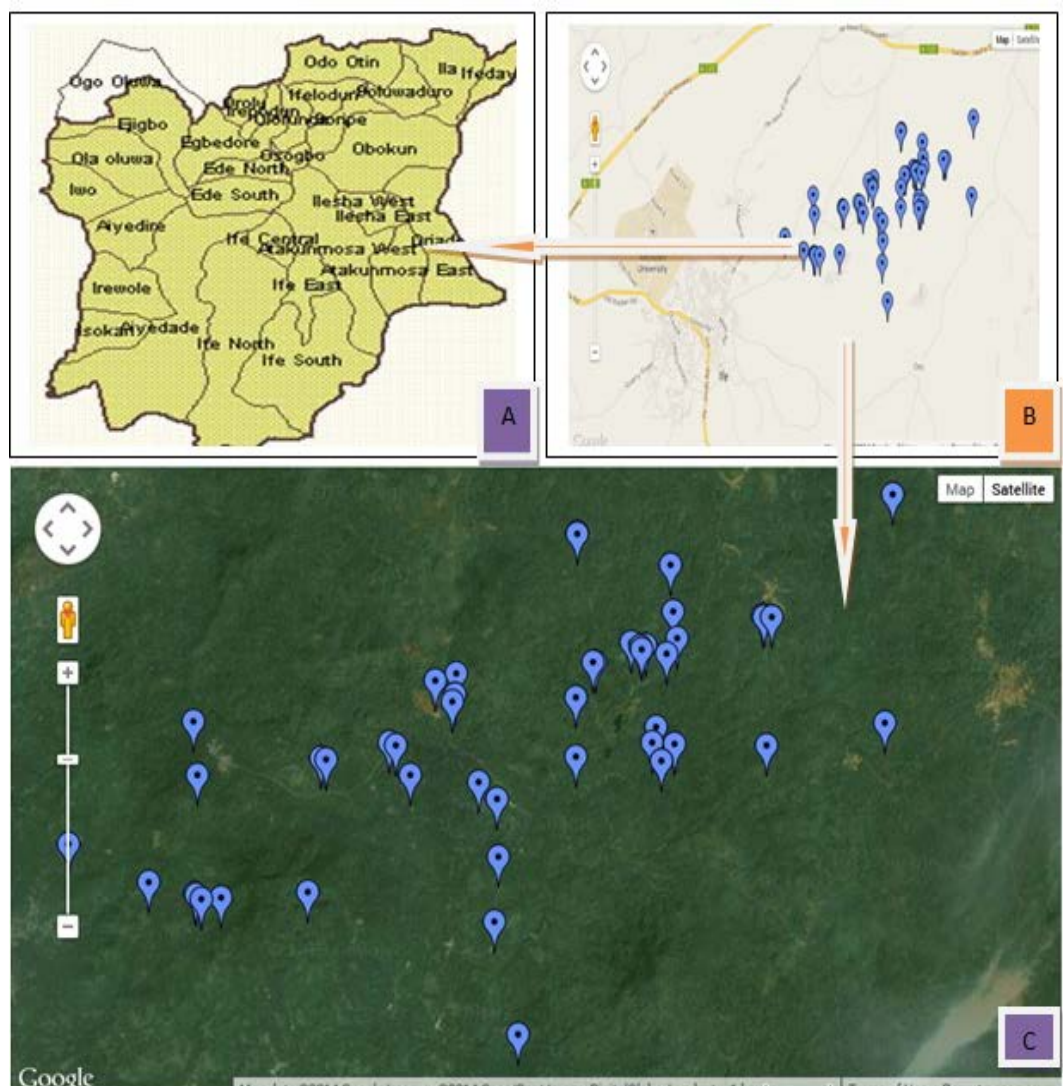


Figure 1. Map of Osun State (A) showing the sampling area (B) and the sampling points (C)

Table 1: Mean Concentration (mg/kg) of Cadmium in Different Stages of Extraction

Locations	Cd									
	Dry Season					Wet Season				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
Mokuro	5.711 ±	0.302 ±	0.910±	0.886 ±	3.113 ±	4.312±	0.162±	0.229 ±	0.082±	3.739±
	1.033	0.077	0.081	0.073	0.652	0.991	0.021	0.034	0.033	0.903
Oke Ora	5.932 ±	0.381 ±	0.900±	0.648±	3.801±	4.510±	0.199±	0.402±	0.508±	3.201±
	1.301	0.074	0.079	0.052	0.825	0.779	0.052	0.094	0.020	0.613
OkutoOmo	4.542 ±	0.271 ±	0.921±	0.233±	2.817±	0.055±	0.200±	0.620±	0.536±	3.671±
	0.877	0.054	0.088	0.027	0.708	0.710	0.061	0.102	0.027	0.520
Okoogboni	4.007 ±	0.201 ±	0.773±	0.092±	2.241±	3.811±	0.161±	0.582 ±	0.280±	2.588±
	0.792	0.019	0.051	0.012	0.710	0.601	0.043	0.075	0.015	0.468
Alaba	5.644 ±	0.286 ±	0.824±	1.427±	2.507±	4.341±	0.110±	0.611 ±	0.298±	3.322±
	1.002	0.081	0.091	0.110	0.720	1.111	0.062	0.109	0.019	0.940
Ariyelepe	5.64 ±	0.27 ±	0.79 ±	1.567 ±	2.671 ±	3.897 ±	0.166	0.520	0.37 ±	2.82 ±
	1.216	0.076	0.08	0.129	0.93	1.099	±0.051	±0.072	0.05	0.93
Iyere	4.498 ±	0.221±	0.609±	0.802±	2.466±	3.755±	0.114±	0.491±	0.395±	2.705±
	0.997	0.071	0.052	0.064	0.810	0.591	0.022	0.073	0.052	0.444
Aba Isobo	5.054 ±	0.185±	0.601±	1.477±	2.391±	3.908±	0.095±	0.891 ±	0.100±	2.922±
	0.908	0.031	0.061	0.100	0.716	0.600	0.021	0.174	0.013	0.392
Sabo	4.111 ±	0.091±	0.291±	0.652±	2.577±	4.001±	0.027 ±	0.822 ±	0.156±	2.916±
	0.653	0.010	0.037	0.059	0.547	0.501	0.009	0.113	0.019	0.360
Igun	6.418 ±	0.377±	1.520±	0.293±	4.714±	3.907±	0.189 ±	1.228±	0.511±	2.921±
	1.297	0.102	0.213	0.022	0.960	0.991	0.088	0.810	0.022	0.071
Itagunmodi	6.809 ±	0.389±	1.411±	0.079 ±	4.888±	4.200±	0.203±	0.943 ±	0.021±	3.002±
	1.315	0.100	0.093	0.010	1.112	0.711	0.090	0.099	0.007	0.515
Alaba Oke	4.503±	0.186±	0.220±	0.196±	3.801±	2.911±	0.097±	0.698±	0.209±	1.891±
	1.009	0.079	0.041	0.021	0.868	0.560	0.011	0.091	0.021	0.437

In the wet season however, the residual fraction had the highest percentage of the metal in all the samples in the range of 64.96% in samples from Alaba-Oke to 86.7% in samples from Mokuro village. Higher percentages were found in the fractions bound to Fe and Mn oxides and hydroxides with metal percentage ranging from 5.3% in Mokuro to 24% in samples from Alaba- Oke village while the exchangeable and bound to carbonate fractions had the lowest percentages of the metal in all the samples except the ones from Mokuro and Alaba-Oke where the fraction bound to organic matter and sulphides has the lowest percentage of the metal

The speciation result of lead (Pb) (Table 2) in dry season showed a similar trend in sediment samples of eleven villages. The highest percentage of the metal was found in the residual fraction and the values ranged from 35.8% in Igun to 49.3% (Figure 3) in samples collected from Oko-Ogboni village. The exception comes from extracted sediment from Itagunmodi in which the percentage of the toxic metal in residual fraction was the lowest (0.49%). The highest percentage (51.6%) of the sample was found in fraction bound to Fe and Mn oxides and hydroxides and only 14.2% and 33.6% was retained in the exchangeable and bound to carbonate fraction as well as the fraction bound to organic matter and sulphides respectively.

Table 2: Mean Concentration (mg/kg) of Lead in Different Stages of Extraction

Locations	Pb									
	Dry Season					Wet Season				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
Mokuro	4.380±0.312	0.555±0.098	1.114±0.154	0.611±0.100	2.005±0.960	2.114±0.410	0.128± 0.011	0.511± 0.096	0.371±0.022	1.004±0.281
Oke-Ora	4.500±0.991	0.719±0.091	1.310±0.162	0.813±0.110	1.558±0.628	3.116±0.811	0.181± 0.037	0.581± 0.088	0.300±0.031	1.953±0.663
Okuto-Omo	4.005±0.800	0.511±0.078	0.976±0.110	0.631±0.113	1.818±0.499	4.011±0.511	0.316± 0.069	0.843± 0.101	0.511±0.087	2.301±0.254
Oko-Ogboni	3.951±1.001	0.422±0.056	0.919±0.078	0.559±0.062	1.951±0.805	3.310±0.388	0.200± 0.043	0.982± 0.071	0.404±0.043	1.674±0.231
Alaba	4.475±1.101	0.623±0.071	1.388±0.174	0.412±0.091	1.892±0.765	3.712±0.200	0.911± 0.044	0.833± 0.081	0.371±0.052	1.557±0.023
Ariyelepe	4.473±0.789	0.621±0.073	0.880±0.092	1.002±0.210	1.753±0.414	2.187±0.510	0.199± 0.012	0.811± 0.077	0.330±0.042	0.817±0.379
Iyere	3.991±0.900	0.400±0.042	0.660±0.081	0.871±0.116	1.960±0.661	2.872±0.311	0.186± 0.061	0.771± 0.080	0.440±0.029	1.455±0.141
Aba-Isobo	4.008±0.803	0.331±0.054	0.711±0.088	1.100±0.122	1.796±0.539	2.891±0.300	0.188± 0.059	0.610± 0.072	0.600±0.066	1.473±0.103
Sabo	4.218±0.823	0.611±0.079	0.900±0.155	0.771±0.102	1.906±0.487	2.342±0.271	0.164± 0.023	0.700± 0.084	0.611±0.076	0.837±0.088
Igun	5.005±1.322	0.810±0.091	1.444±0.441	0.917±0.100	1.794±0.690	4.089±0.400	0.500± 0.098	1.117± 0.108	0.343± 0.042	2.109±0.152
Itagunmodi	5.447±1.326	0.772±0.088	2.811±0.985	1.833±0.082	0.027±0.171	4.991±0.518	0.339± 0.061	1.231± 0.155	0.471± 0.100	2.910±0.202
Alaba-Oke	3.961±0.552	0.200±0.021	0.886±0.102	0.844±0.072	2.011± .357	3.003±0.299	0.180± 0.018	0.934± 0.099	0.519± 0.089	1.370±0.093

Table 3. Mean Concentration (mg/kg) of Iron in Different Stages of Extraction

Locations	Fe									
	Dry Season					Wet Season				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
Mokuro	39.588	2.133±0.1	2.611±0.1	7.112	27.632±0.5	26.113	1.333	3.913	4.118	16.549
	±1.020	12	31	±0.241	36	±2.711	±0.087	±0.133	±0.171	±2.320
Oke-Ora	36.112±2.1	2.001±0.0	1.832±0.0	5.554±0.1	26.125	17.755	1.002±0.0	3.331±0.1	4.011±0.1	8.411
	16	98	61	16	±1.841	±2.911	76	28	38	±2.569
Okuto-Omo	32.008	1.502±0.0	1.220±0.0	6.612	22.474	17.855	1.220	4.110	6.221	4.504
	±2.023	71	31	±0.432	±1.489	±1.643	±0.062	±0.204	±0.271	±1.106
Oko-Ogboni	30.072	1.709±0.0	1.099±0.0	4.661	22.303±1.4	22.543	1.401	4.901	5.611	10.230
	±2.015	84	21	±0.435	75	±9.911	±0.092	±0.250	±0.299	±0.270
Alaba	39.311	1.459±0.0	1.199±0.0	7.331	29.122±2.0	29.877	0.980	2.776	2.901	23.120
	±3.031	40	48	±0.931	15	±2.198	±0.023	±0.099	±0.110	±1.966
Ariyelepe	39.289	2.711±0.0	0.877±0.0	4.554	30.147±1.4	29.651	1.576	3.996	4.100	19.879±2.2
	±2.023	93	90	±0.430	10	±2.712	±0.112	±0.151	±0.165	84
Iyere	31.700	1.711±0.0	2.611±0.0	5.110	21.268±0.6	20.559	1.443	4.551	4.580	9.985
	±1.033	39	81	±0.601	01	±1.900	±0.022	±0.231	±0.239	±1.408
Aba-Isobo	28.990	1.155±0.0	3.710±0.0	2.008	20.122	25.810	0.875	1.970	1.982	20.783
	±1.028	22	92	±0.078	±0.836	±2.099	±0.031	±0.077	±0.081	±1.910
Sabo	28.979	1.100±0.0	3.811±0.0	5.088	18.880	25.771	0.801	1.884	3.209	19.677
	±2.024	41	56	±0.618	±1.309	±1.800	±0.020	±0.071	±0.108	±1.601
Igun	41.098	3.011±0.0	5.822±0.1	2.788	29.277	33.851	1.600	4.111	4.887	22.253
	±3.039	80	87	±0.203	±2.569	±1.077	±0.144	±0.281	±0.293	±0.359
Itagunmodi	42.077	3.400±0.0	5.710±0.1	2.109	30.758±2.7	36.800	2.511	5.552	5.745	21.024
	±3.043	91	32	±0.098	22	3±.901	±0.220	±0.771	±0.782	±2.128
Alaba-Oke	24.886±2.0	1.077±0.0	3.931±0.0	1.907±0.0	17.911	15.008±2.0	0.156±0.0	0.089±0.0	0.1±0.041	14.443
	39	42	99	70	±1.828	09	44	10	2	±1.914

The fraction bound to Fe and Mn oxides and hydroxides has the highest percentage of the non-essential metal in sediment samples of nine (9) villages namely Mokuro (25.4%), Oke-Ora (29.1%), Okutu-Omo (24.4%), Oko-Ogboni (23.3%), Alaba (31%), Sabo (21.3%), Igun (21.9%), Itagunmodi (51.6%) and Alaba-Oke (22.4%) (Fig 3), except in samples from Alaba, the exchangeable and bound to carbonate fraction in samples from all the villages has the lowest percentage ranging from 5% in Alaba-Oke to 16.2% in Igun village. However, sediment samples from Ariyelepe, Iyere and Aba-Isobo had the highest percentage of lead in the fraction bound to organic matter and sulphides with 22.4%,

21.8% and 27.4% richness respectively. In the wet season, a simple pattern is maintained in which the highest percentage of the total concentration of the metal is in the residual fraction in all the villages with percentages ranging from 0.57% to 51.9% in samples from Itagunmodi and Oko- Ogboni respectively. Fraction bound to Fe and Mn has a relatively higher percentage of the metal in all the samples except the one at Alaba village where the exchangeable and bound to carbonate fraction is higher (24%) in the total concentration.

Table 4. Mean Concentration (mg/kg) of Copper in Different Stages of Extraction

Locations	Cu									
	Dry Season					Wet Season				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
Mokuro	4.532± 0.330	1.034 ±1.101	0.411 ±0.031	2.154± 0.166	0.903± 0.035	4.611± 0.300	1.200 ±0.087	0.210 ±0.011	2.105 ±0.104	1.096 ±0.098
Oke Ora	4.822± 0.381	1.300 ±0.121	0.482 ±0.043	2.109± 0.159	0.911± 0.058	4.188± 0.391	1.287 ±0.089	0.203 ± 0.014	1.997 ± 0.098	0.701± 0.190
Okutu	3.778±	0.879	0.255	2.088±	0.536±	2.813±	0.652	0.174±	1.833±	0.144±
Omo	0.300	±0.078	±0.019	0.115	0.088	0.311	±0.054	0.012	0.099	0.146
OkoOgboni	3.602± 0.274	0.877 ±0.075	0.264 ±0.023	2.177± 0.122	0.254± 0.054	3.442± 0.201	0.641 ±0.055	0.189± 0.021	2.044± 2.051±	0.528± 0.063
Alaba	4.941± 0.498	2.052 ±0.221	0.713 ±0.062	1.502± 0.088	0.664± 0.127	2.833± 0.291	0.811 ±0.077	0.331± 0.041	1.308± 0.087	0.323± 0.086
Ariyelepe	4.938± 0.432	2.022 ±0.218	0.689 ±0.054	1.433± 0.079	0.774 ±0.081	4.099± 0.210	1.270 ±0.045	0.274± 0.036	2.051± 0.056	0.484 ±0.073
Iyere	3.407± 0.315	1.098 ±0.100	0.410 ±0.067	1.504± 0.088	0.355± 0.060	2.892± 0.233	0.790 ±0.061	0.188± 0.019	1.543± 0.092	0.321± 0.061
Aba Isobo	3.769± 0.300	1.100 ±0.100	0.413 ±0.065	1.802± 0.091	0.404± 0.044	3.033± 0.238	0.600 ±0.061	0.192± 0.023	2.100± 0.101	0.111± 0.053
Sabo	3.998± 0.388	0.899 0.081	±0.044	0.107	0.155	0.201	±0.053	0.015	0.091	0.042
Igun	6.117± 0.391	2.399 ±0.137	±0.064	0.072	0.118	5.911± 0.355	1.809 ±0.100	0.416± 0.077	3.310± 0.085	0.336± 0.093
Itagunmodi	6.623± 0.400	2.508 ±0.119	±0.101	0.089	0.091	6.448± 0.441	2.277 ±0.210	0.316± 0.087	3.166± 0.100	0.649± 0.044
Alaba Oke	3.570 ± 0.221	1.088 ±0.063	±0.048	0.050	0.006	2.848± 0.161	0.887 ±0.038	0.251± 0.029	1.433± 0.040	0.267± 0.054

Table 5: Mean Concentration (mg/kg) of Chromium in Different Stages of Extraction

Locations	Cr									
	Dry Season					Wet Season				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
Mokuro	1.118 ±0.521	0.021 ±0.006	0.024 ±0.005	0.204± 0.011	0.819 ±0.499	1.000± 0.300	0.019 ±0.008	0.033± 0.011	0.211± 0.020	0.717 ±0.261
Oke-Ora	1.277 ±0.305	0.032 ±0.007	0.029 ±0.004	0.322± 0.021	0.844 ± 0.273	1.211± 0.143	0.021± 0.010	0.031± 0.012	0.251± 0.027	0.878 ± 0.094
Okuto- Omo	1.002 ±0.071	0.019 ±0.003	0.026 ±0.006	0.198 ±0.010	0.719± 0.052	0.665± 0.100	0.016 ± 0.007	0.022 ± 0.010	0.320 ± 0.061	0.307 ± 0.022
Oko- Ogboni	0.889 ±0.034	0.014 ±0.005	0.020 ±0.008	0.300 ±0.011	0.505 ± 0.010	0.321 ±0.107	0.011 ±0.003	0.016 ±0.005	0.185 ±0.021	0.089 ± 0.078
Alaba	1.102 ±0.085	0.025 ±0.009	0.033 ±0.010	0.271 ± 0.014	0.753 ± 0.052	0.442 ± 0.100	0.022 ± 0.008	0.027 ± 0.004	0.198 ± 0.034	0.185 ± 0.054
Ariyelepe	1.100 ±0.088	0.022 ±0.007	0.035 ±0.009	0.310 ± 0.032	0.713 ±0.04	0.410 ± 0.055	0.021 ± 0.007	0.038 ± 0.013	0.211 ± 0.020	0.129 ±0.015
Iyere	0.992 ±0.076	0.019 ±0.004	0.024 ±0.006	0.299 ± 0.033	0.630 ± 0.033	0.500 ± 0.081	0.010 ± 0.003	0.011 ± 0.004	0.287 ± 0.020	0.172 ± 0.054
Aba-Isobo	3.111 ±0.481	0.441 ±0.020	0.472 ±0.033	1.221 ± 0.071	0.947 ± 0.357	2.041 ± 0.198	0.035 ± 0.010	0.037 ± 0.012	1.360 ± 0.101	0.569 ± 0.075
Sabo	1.001 ±0.089	0.017 ±0.006	0.022 ±0.005	0.241 ± 0.043	0.711 ± 0.035	0.519 ± 0.108	0.013 ± 0.005	0.010 ± 0.006	0.288 ± 0.034	0.198 ± 0.063
Igun	3.455 ±0.501	0.500 ±0.034	0.551 ±0.041	1.111 ± 0.082	1.158 ± 0.344	2.012 ± 0.111	0.041 ± 0.013	0.036 ± 0.010	1.207 ± 0.038	0.718 ± 0.005
Itagunmodi	4.002 ±0.301	0.410 ±0.051	0.440 ±0.056	1.204 ± 0.121	1.238 ±0.073	2.711 ± 0.201	0.019 ± 0.007	0.030 ± 0.011	1.338 ± 0.103	1.320 ± 0.080
Alaba-Oke	2.511 ±0.211	0.100 ±0.030	0.118 ±0.036	0.970 ± 0.073	1.313 ± 0.072	0.884 ± 0.194	0.020 ± 0.009	0.022 ± 0.007	0.431 ± 0.049	0.3811 ± 0.129

In the speciation result obtained for Fe metal (Table 3) during the dry season, the residual fraction in all the villages recorded the highest percentages of the total concentrations ranging from 71.972% to 73.099% in samples from Alaba-oke and Itagunmodi respectively. Of the mobile fractions, the fraction bound to organic matter and sulphide (F3) recorded the highest percentages in sediment samples from Mokuro (17.9%), Oke-Ora (15.4%), Okutu-Omo (20.7%), Oko-Ogboni (15.5%), Alaba (7.9%), Ariyelepe (11.6%), Iyere (16.1%) and Sabo villages (17.6%) respectively while the lowest percentage of the essential metal were associated with the exchangeable and bound to carbonate fraction in Mokuro, Iyere, Aba-isobo, Sabo, and Alaba- Oke villages and in F2 (fraction bound to Fe-Mn oxides) in Oke-Ora, Okutu-Omo, Oko-Ogboni, Alaba and Ariyelepe

villages, for the dry season. This pattern was not found in samples from Aba-Isobo, Igun and Itagunmodi where the highest percentage of the metal was associated with the fraction bound to Fe and Mn oxides and hydroxides. However, the speciation result for the metal in samples of wet season followed the same pattern with higher percentages of the metal associated with the fraction bound to organic matter and sulphide (except for samples in Alaba-Oke) while the lowest percentages occur in exchangeable and bound to carbonate fraction. However large percentages of the metal were still retained in the residual fraction.

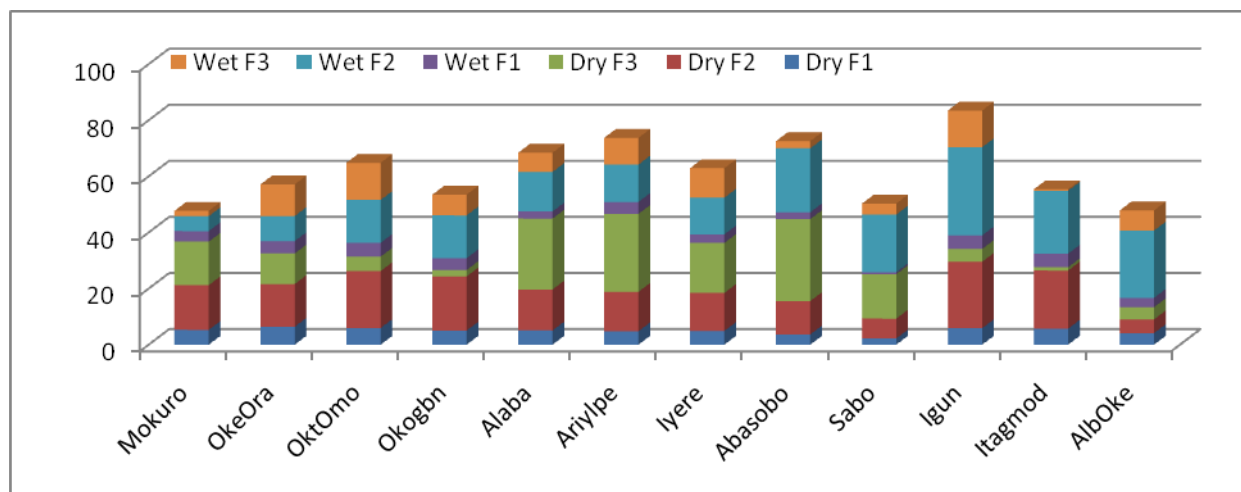


Figure 2. Percentages of Cd in the Fractions for Dry and Wet Seasons

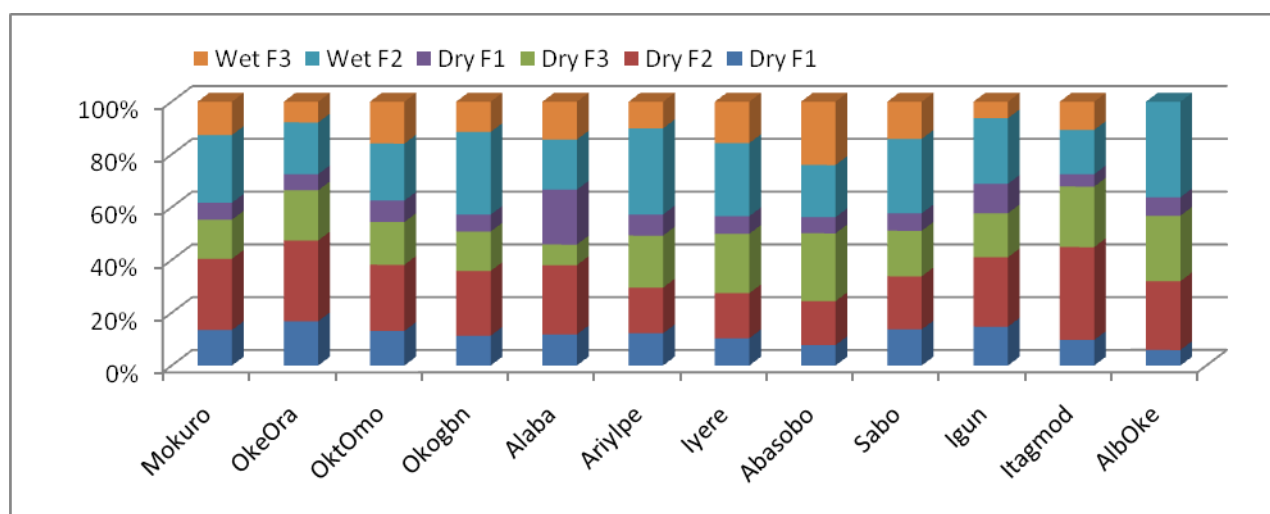


Figure 3. Percentages of Pb in the Fractions for Dry and Wet Seasons

The speciation result (Table 4) obtained for Cu showed the element to be highly mobilized in the fraction bound to organic matter and sulphide (F3). The greater percentages of the total concentration of Cu obtained for this stage were in all the samples of dry season with percentages ranging from 43.2% in Itagunmodi to 44.1% in Iyere village. In the exchangeable and bound to carbonate fraction, percentage of the total concentration ranges from 22.8% in Mokuro to 41.5% in samples collected from Alaba village. The same trend was maintained in the sequential extraction steps recorded for sediment sample in all the villages for the wet season where the percentages of the metal in the total concentration was greater in the oxidizable fraction bound to organic matter and sulphides. In all the samples the percentages of the element in the total concentration observed in the residual fraction is low. This observation will not be surprising considering the affinity of Cu for organic matter indicating its association with organic compounds (Tamunobereton *et al*, 2010). The element can react to form very stable complexes with organic compounds (Marco *et al*, 2005).

In the dry season (Table 5), the residual fraction showed the highest percentages of Cr metal in the total concentration in all the villages except Aba-Isobo. The percentage enrichment of the metal in this fraction ranges from 30.4% at Aba-Isobo to 73.3% at Mokuro. In the labile fractions, the fraction bound to organic matter and sulphide (F3) in all the samples for the season has the highest percentage of the metal than other labile fractions, it ranges from 18.2% in samples from Mokuro village to 39.3% in samples from Aba Isobo. Except the samples from Oke-Ora village, all other samples varied in the percentage of the element in the total concentration as $F1 < F2 < F3$ (where F1 is the exchangeable and bound to carbonate, F2 is the fraction boundable to Fe and Mn oxides and hydroxide fraction and F3 is the fraction bound to organic matter and sulphide). The percentages in F1 ranges from 1.57% in samples from Oko Ogoni to 14.5% in samples collected from Igun while F2 ranges from 2.14% to 15.9%. In the wet season, the same pattern is repeated for samples collected from Mokuro and Oke-Ora, Samples from all other sites had the highest percentage of the metal in the labile fractions (with the pattern: $F3 > RF > F2 > F1$) with the fraction bound to organic matter and sulphides having the highest enrichment of the metals. Though F1 has the lowest concentration of Cr in all the labile phases, manmade and chemical actions may force the metal back into water and increase its mobility and availability to organisms.

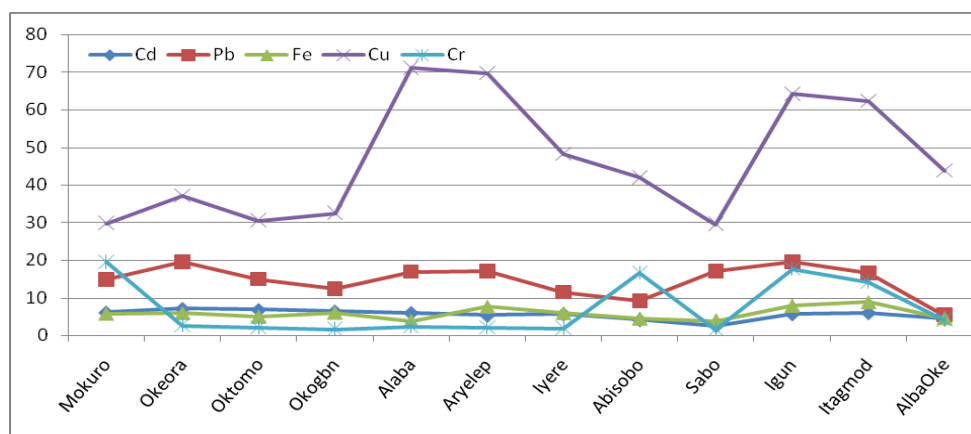


Figure 4. Metals mobility Factor (%) in different Sample locations During the dry Season

Mobility of Metals in the Sediment Samples

Toxic metals get into aquatic organisms through direct ingestion of metal-contaminated sediments or metals in solution; hence, determination of the metals mobility form in stream sediments is important in explaining the pathway to aquatic and higher organisms. The mobility factor (MF) is a measure of the relative amount of the easily mobilizable metals in the sediment was determined according to:

$$MF = (F1) / (F2 + F3 + RF)$$

(Where F1 is the exchangeable and bound to carbonate fraction, F2 is the fraction boundable to Fe-Mn oxides, F3 is the fraction boundable to organic and sulphides and RF is the residual fraction) the result revealed Cu metal as having the highest mobility factor of all the metals for both seasons (Fig iv and v) in all the villages making it the most potentially bioavailable. Despite the lower concentration of the metal recorded in the exchangeable and carbonate bounded fractions, the high MF indications that geologic and environmental factors played important role and could be responsible for the re-mobilization of the metal from the fraction bound to organic matter and sulphide (F3) where highest concentration of the metals were found. The MF of Cu ranged from (29.2 – 71.2) % in the dry season and (23.2-53.9) % in the wet season. For Pb, the MF is in the range of (5.3- 19.5) % in the dry season and (6.3-32.9) % in the wet season. Cd have a MF ranging from (2.5-7.1) % in the dry season and (2.4-5.1) % in the wet season, Fe (3.8-8.8) % for dry season and (1.1-8.2) % for wet season while for Cr, the MF values ranged from (1.7-19.6) % in the dry season and (0.5-6.8) % in the wet season. MF values for the metals increases in the following order $Cd < Fe < Cr < Pb < Cu$ (dry season) and $Cr < Cd < Fe < Pb < Cu$ (wet season). Generally, the MF values obtained for the dry season were higher than those of the wet season probably due to dilution effect as a result of rain run-off and less

mining activity during the wet season. High values of mobility factor have been linked to higher bioavailability of metals (Ahumada *et al*, 1999; Yusuf, 2007, Kabala & Singh, 2001).

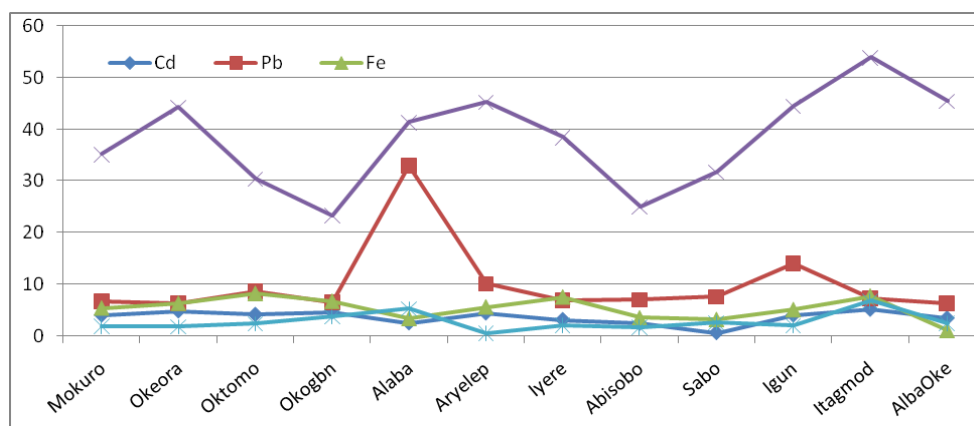


Figure 5. Metals mobility Factor (%) in different Sample locations During the wet Season

Conclusion

This study revealed different metals to be partitioned in different percentages in the exchangeable and bound to carbonate, bound to Fe and Mn oxides and hydroxides and bound to organic matter and sulphide fractions. The bulk of the metals in sediments samples from the study area were retained in the residual fraction for metals like Pb, Cd, Cr and Fe limiting their mobility and availability while only Cu has a greater percentage of the metal retained in the fraction bound to organic matter and sulphide and this is due to the affinity of the metal to organic compounds reacting to form stable complexes. For the non-essential heavy metals Pb and Cd, the low concentrations recorded in the labile fractions reduces their bioavailability and limits the potential risk as pollutants in the sediments due to their toxicity, the bulk of the metals are retained in the residual fractions.

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References

- Ahumada I, Mendoza J, Ascar L, (1999) Sequential extraction of heavy metals in soils irrigated with wastewater *Commum. Soil Sci. Plant Anal.*, **30**, 1507-1519
- Baffi F, Iannim C, Soggia F, Magi E, (1998) Evaluation of the Acetate buffer Attack of a Sequential Extraction Scheme for Marine Particulate Metal Speciation Studies by Scanning Electron Microscop[y with Energy Dispersive X-ray Analysis. *Anal. Chim., Acta*, **360**, 27-34.
- Badaway SH, El-Motaium RA, (2000) Fate of Some Heavy Metals in Sandy Soil Amended with Sewage Sludge and their Accumulation in Plants. ICEHM2000, Cairo University, Egypt September, 483–494
- Hall GEM, Vaive JE, Beer R, Hoashi M, (1996) Selective leaches revisited, with emphasis on the amorphous Fe Oxyhydroxide phase extraction. *J. Geochem. Expl.*, **56**: 59–78.
- Jones RA, Mariani GM, Lee GF, (1981) Evaluation of the Significance of Sediment-Associated Contaminants to Water Quality, Proc. Am. Water Resources Assoc. Symposium, Utilizing Scientific Information in Environmental Quality Planning, AWRA, Minneapolis, MN, pp. 34-45.
- Kabala C and Singh BR, (2001) Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *J. Environ. Quality*, **30**, 485–492.
- Marco R, Serena M, Roberto F, Juan AC, (2005) Metal Speciation and Environmental Impact on Sandy Beaches due to El Salvador Copper Mines. *Marine Pollution Bulletin*, **50**, 62-72.
- McKinney J, Ron R, (1992) Metal bioavailability: *Environ. Sci. & Tech.*, **26**, 1298-1299.
- Ngole VM, (2011) Using soil heavy metal enrichment and mobility factors to determine potential uptake by vegetables. *Plant Soil Environ.*, **57**, 75–80

- Raure G, Lopez-Sanchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A and Quevauviller PH, (1999) Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* 1, 57-61
- Salomons W, (1995) Environmental impact of metals derived from mining activities: Processes, predictions, prevention: *J. Geochem. Expl.*, 52, 5-23.
- Samir MS and Ibrahim MS, (2008) Assessment of Heavy Metals Pollution in Water and Sediments and their Effect on *oreochromis niloticus* in the Northern Delta Lakes, Egypt. 8th international symposium on tilapia in aquaculture, 475.
- Sharmin S, Zakir HM, Naotatsu S, (2010) Fractionation Profile and mobility pattern of trace metals in sediments of Nomi River, Tokyo, Japan. *J. Soil Sci. & Environ. Manag.* 1, 1-14.
- Tamunobereton-ari I, Uko ED and Omubo-Peppie VB, (2010) Anthropogenic Activities-Implications for Groundwater Resource in Okrika, River State, Nigeria. *Res. J Appl. Sci.* 5, 204-211.
- Tessier A, Campbell PGC and Bisson M, (1979) Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Anal Chem.* 51, 844-851.
- Vaněk A, Borůvka L, Drábek O, Mihaljevič M, Komárek M, (2005) Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry. *Plant Soil Environ.*, 51, 316-321.
- Violante A, Cozzolino V, Perelomov L, Caporale AG, Pigna M, (2010) Mobility and Bioavailability of Heavy Metals and Metalloids in Soil Environments. *J. Soil. Sci. Plant Nutr.* 10, 268 – 292.
- Yusuf KA, (2007) Sequential extraction of lead, copper, cadmium and zinc in soils near Ojota Wastesite. *J. Agron.*, 6, 331-337