

Geochemical characteristics of sediments in river Niger fadama, central Nigeria

O.A. Omotoso^{1*}, O.J. Ojo² and M.T. Alebiosu¹

¹ Department of Geology and Mineral Sciences, University of Ilorin, Ilorin, Nigeria

² Department of Geology, University of Oye-Ekiti, Nigeria

* e-mail: deletoso2002@yahoo.co.uk

Abstract: Floodplain also known as Fadama in Nigeria is a large centre of agricultural activities but usually faced with challenges of contamination. This study focused on the floodplain of River Niger at Jebba, Central Nigeria and the objectives of the study were to assess the geochemical characteristics of the sediments as well as their weathering indications. Thirty sediment samples were randomly collected over the entire Fadama and subjected to pulverization and geochemical analysis using X-ray Fluorescence (XRF) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for major oxides, trace and rare earth elements determinations. The geochemical results show that the average concentrations of the major ions (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO Na₂O, K₂O, MnO, TiO₂, P₂O₅, and Cr₂O₃) are: 66.14 wt%, 13.16 wt%, 4.48 wt%, 0.57 wt%, 0.56 wt%, 0.59 wt%, 1.86 wt%, 0.07 wt%, 0.99 wt%, 0.06 wt% and 0.01 wt% respectively. According to Upper Continental Crust Average Concentration (UCC), the major ions are depleted in the sediment except TiO₂ that is enriched having an average value of 1.98; the trace elements are also depleted in the sediments except Ba, Co, Cs, Ga, Hf, U, V and Zr that are enriched having average values greater than 1; and the rare earth elements are highly enriched in the sediments with average values greater than unity. The weathering indications show that CIA, PIA and CIW give average values of 80, 89 and 92, respectively. This shows that the sediments have undergone intensive weathering. The intensive weathering of the sediments would have contributed to the concentration of metals in the water phase. Contamination Factor and Enrichment Factor of the sediments show that the sediments are enriched in trace and rare earth elements from geogenic and anthropogenic sources.

Key words: Floodplain / fadama, sediments, major oxides, trace elements, rare earth elements, weathering indications

1. INTRODUCTION

Interestingly, Fadamas are located or are formed on the floodplains of paleo-channels of streams which may or may not have been abandoned by such rivers. Fadamas are centres of large-scale agricultural activities involving dry season farming which are supported by irrigation. Waters (surficial or sub-terrestrial) are derived from flowing streams within the alluvial plains or drawn from tube wells and bore-holes, sunk into the alluvial deposits. Actually, floodplains are termed by different local names all over the world. In Nigeria, it is called *Fadama* (derived from Hausa native name meaning an irrigable land). In this ecosystem, different activities take place within the organisms and their respective aquatic environments. The influence of man and animals (rearing of cattle) also play a major role in the condition of the ecosystem. The accumulation of potentially toxic elements in the environment can be detrimental to the aquatic ecosystem, terrestrial system very close to the wet area and man. Hence, the identification and quantification of trace metals contamination and mobilization in these environments are essential tools to raise environmental scientific issues (Bowen, 1979; Forstner and Wittmann, 1983; Sutherland, 2000; Tijani et al., 2007).

In some developing countries like Nigeria, soil and sediments are at risk of contamination due to rapid and unplanned urbanization, industrialization and indiscriminate disposal of domestic, industrial, agricultural and mining wastes (Ramesh et al., 1995; Subramanian, 2000; Mohan et al., 2000; Singh et al., 2005; Kumaresan and Riyazddin, 2006; Kumar et al., 2006; Singh et al., 2007, 2011; Akoto et al., 2016). This would definitely have hazardous effect on the surface and groundwater in the area. Public ignorance of environment and related considerations, lack of

provisional basic social services, indiscriminate disposal of anthropogenic wastes, unplanned application of agrochemical and discharges of improperly treated sewage/industrial effluents, lead to excess accumulation of contaminants on the land surface and contamination of water resources (Singh et al., 2011). Subsurface leaching of contaminants from landfills and pit latrines cause severe degradation, not only to the soil and sediments but also to the surface and groundwater quality in rural and urban areas. Adsorption/dispersion processes in the soil zone, degrees of evaporation/recharge and lateral inter-mixing of groundwater determine the level of contaminations in both groundwater and surface water. Furthermore, heavy metals are of high ecological significance due to their tendency of self-purifications. They however accumulate in soils or sediments and enter the food chain (Loska and Wiechula, 2003).

Trace metals in soil/sediments are usually derived from both natural (geogenic) and artificial (anthropogenic) sources (Tijani et al., 2007; Naseem et al., 2010). Dissolved metals in solution that are by nature introduced into the aquatic system come primarily from rock/mineral weathering as well as soil erosion or leaching while such dissolved metals move through aquatic environments independent of human activities and sometimes without any detrimental effects. However, due to heavy agricultural practices, rapid growth in population and urbanization, exploration and exploitation of natural resources and lack of adherence to environmental regulations, the level of these metals has increased in the environment over the past decades through various human activities (Widianarko et al., 2000; Tijani et al., 2004, 2007; Omotoso et al., 2011). Both water and sediments (soils) can be employed as indicators for trace elements indicators (Ajayi et al., 1990; Sutherland, 2000; Tijani et al., 2007). At this juncture, for effective control and management of floodplains for agriculture, domestic and industrial purpose, there is the need for clear understanding of the inputs, sources and the distributions of these metals into the floodplain (Fadama) system.

2. THE STUDY AREA

The area of study is River Niger Floodplain at Jebba, Central Nigeria. The area lies between latitude 9° 11' 29'' N to 9° 07' N and longitude 4° 48' E to 4° 52'' E (Figures 1 and 2). It falls within western part of sheet 181 Jebba SE. Jebba is one of the ancient cities in Nigeria. The study area is located across the basement complex of Nigeria and Bida basin. The basement rocks comprise of migmatite gneiss, quartzite complex, porphyritic granite, granitoids and minor acid dykes while the sedimentary terrain consists essentially of sandstones, conglomerates and claystones of Campanian to Maastrichtian age (Okonkwo, 1992; Omotoso and Ojo, 2012). The total area covered in the present work is about 50 km². The present study area is usually flooded whenever the water-way of Hydro-electrical Power station is opened. Farmers in the area loss their crops to flooding and materials are deposited on the floodplain yearly. Hence, the present study deals with the geochemistry and the weathering indications of sediments on the floodplain from which the levels of trace and major elements are determined. The sources of contamination of the sediments have been assessed in this research based on the geochemical data of sediments in the study area and from their computed contamination indexes.

3. METHODOLOGY

A total of thirty sediment samples were randomly collected from designated points (using the GPS) on the floodplain by scooping with clean plastic container. The samples were packed in polythene bags and labeled accordingly. The sediments were sampled for mineralogical and geochemical analyses. The samples were sun dried in a clean environment and contamination from external activities was highly monitored and reduced. Drying was carried out to reduce the moisture content of the sediment samples and prevent coagulation of the soil particles. Pulverization of sediment samples was done in Geology Laboratory, University of Ilorin, Nigeria. The sediment sample was grinded into powder prior to laboratory analysis. Acetone was used to prevent cross

contamination between the sediment samples. Geochemical analysis was carried out in ACME laboratory Canada.

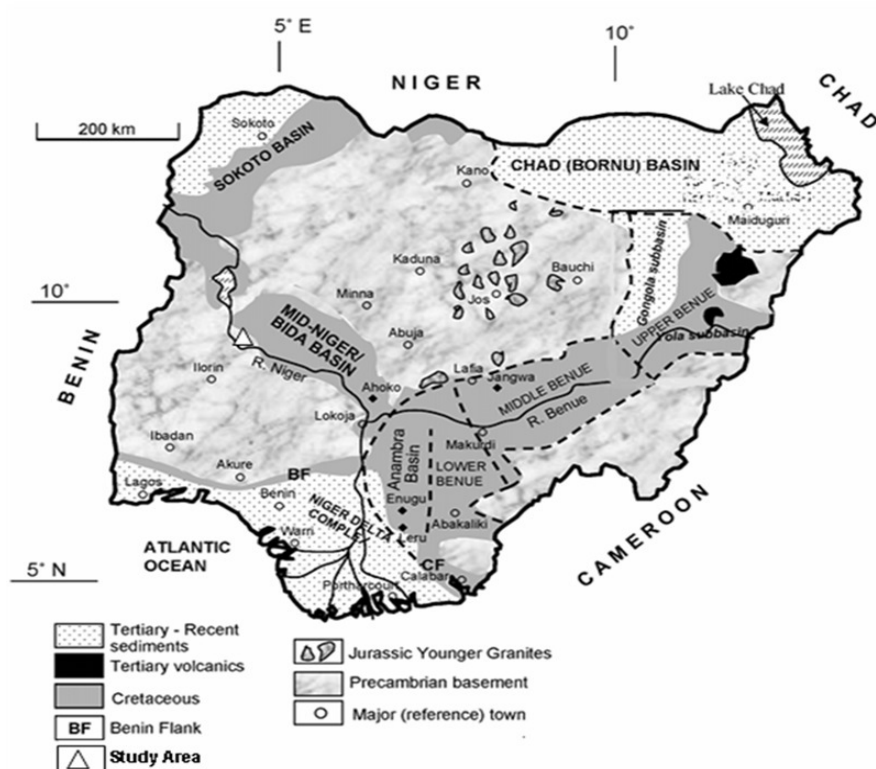


Figure 1. Geological map of Nigeria showing the location of the study area (Obaje, 2004)

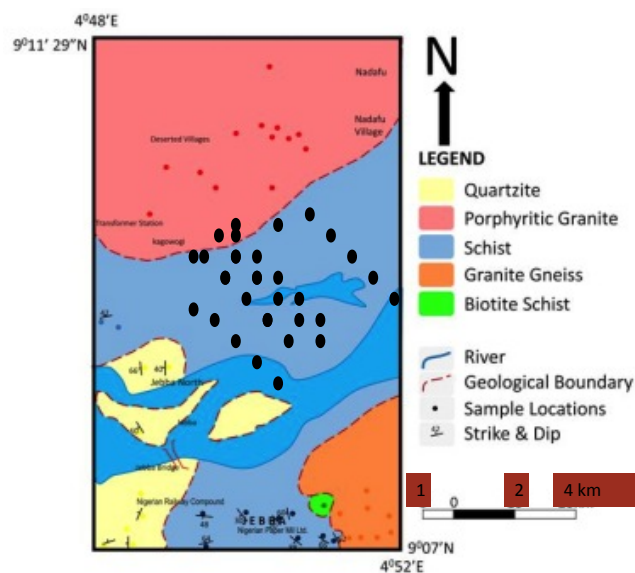


Figure 2. Local geological map of the study area showing sampling points on the floodplains

4. RESULTS AND DISCUSSION

4.1 Geochemistry of sediments in the study area

4.1.1 Major oxides

The bulk geochemistry of the major elements of thirty samples of the River Niger Floodplain

sediment is presented in Table 1 with their descriptive statistical summary. The sediments are rich in SiO_2 with an average concentration of 66.14%. They have low contents of CaO (average 0.57%), MgO (average 0.56%), Na_2O (average 0.59%), K_2O (average 1.86%), MnO (average 0.07%), TiO_2 (average 0.99%), P_2O_5 (average 0.06%) and Cr_2O_3 (average 0.01%). Relative concentration of TiO_2 reflects abundance of Ti-bearing minerals (biotite, ilmenite, titanite and titaniferous magnetite) in the analyzed samples (Akarish and El-Gohary, 2011; Armstrong-Altrin et al., 2004). P_2O_5 , Cr_2O_3 and MnO are strongly depleted in the samples.

The enrichment values of the major oxides are computed as a ratio of the respective oxides to that of UCC average values and this is presented in Table 2. SiO_2 has an enrichment value of 1.0022 indicating the level of abundance relative to earth crust composition. All the major oxides have enrichment values less than unity except TiO_2 that has value greater than one. The depletion in Na_2O , MnO and CaO indicates that the sediments have suffered from intensive weathering and recycling (Joo and Baib, 2005; Jin et al., 2006; Akarish and El-Gohary, 2011). Ca, Na and K concentrations are controlled by feldspars and they are depleted in the analyzed sediment samples. This means that the minerals containing these oxides have undergone weathering and dissolution into the water phase. It also suggests the destruction of plagioclase due to chemical weathering in the source or during transportation of the samples from the source. SiO_2 has a strong negative correlation with Al_2O_3 ($r=-0.98$) depicting that much of SiO_2 is present as quartz grains. Low values of $\text{Al}_2\text{O}_3/\text{SiO}_2$ (range 0.06-0.4, average 0.21) confirm quartz enrichment in the studied samples. TiO_2 and MgO follow the trend of Al_2O_3 indicating that they are associated with micaceous clay minerals (Akarish and El-Gohary, 2011). This is further confirmed by their correlation with Al_2O_3 (i.e. Al_2O_3 has positive strong correlation with TiO_2 , $r=0.68$ and MgO, $r=0.86$). This shows that they are associated and most likely from the same source. Furthermore, Al_2O_3 have positive correlation with Fe_2O_3 ($r=0.74$), CaO ($r=0.29$), P_2O_5 ($r=0.64$) and Cr_2O_3 ($r=0.74$). However, Al_2O_3 has negative correlation with Na_2O ($r=-0.21$) and K_2O ($r=0.16$) which depicts different origin, (Table 3). This suggests that most of the oxides result from aluminosilicate minerals like the plagioclase feldspars and mica group minerals (Jin et al., 2006).

4.1.2 Trace elements

The following trace elements were analyzed for in the sediments of the study area: Ba, Be, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, U, V, W, Zr, Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi, Ag, Au, Hg, Tl and Se. Their descriptive statistical summary is presented in Table 4. The correlation matrix of the trace elements in the sediments is also presented in Table 5 and Figure 3 illustrates ASC –UCC-normalized averages of trace elements concentrations in the sediments phase.

Based on the alert values (an alert value is the maximum prescribed limit for the concentration of metals/elements in sediments/soils) the average concentration of V (84.2 ppm) exceeded the alert value of 50 ppm (Atiemo et al., 2011). The main feature of the trace element distributions is the generally positive correlation with Al_2O_3 , reflecting association of most elements with the clay fraction with the exception of Hf having negative correlation ($r=-0.88$) (Akarish and El-Gohary, 2011). The exception in Hf might probably be that they are not from the same source. The transition metals Co, Ni and V, respectively, range from 3.7-32.50 ppm (average 11.94 ppm), 3.6-27.70 ppm (average 14.4 ppm) and 29-134 ppm (average 84.17 ppm). These transition metals are mainly concentrated in the clays or metal oxides (Turekian et al., 1960; Akarish and El-Gohary, 2011). V is positively and strongly correlated with Fe_2O_3 ($r = 0.79$) and TiO_2 ($r = 0.76$). Generally, it is adsorbed on kaolinite and also may be associated with iron oxide minerals (Hirst, 1962; Akarish and El-Gohary, 2011). Positive correlations of Co, Ni, Zn, Cu and V with both Fe_2O_3 ($r = 0.78$, 0.82, 0.73, 0.63, 0.79 and 0.73, respectively) and Al_2O_3 ($r = 0.46$, 0.89, 0.90, 0.93, 0.95 and 0.90, respectively) also indicate that these elements are linked with iron oxides and probably with clay minerals.

Table 1. Major Oxides in the investigated sediments and the computed enrichment values

Sample ID	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	Na ₂ O %	K ₂ O %	MnO %	TiO ₂ %	P ₂ O ₅ %	Cr ₂ O ₃ %	Ba %	LOI %	SUM %
	0.1	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.001	0.01	-5.11	0.01
1	76.9	9.69	3.44	0.44	0.41	0.43	1.58	0.06	0.77	0.02	0.008	0.06	6.33	100.09
2	71.6	9.58	5.55	0.46	0.33	0.64	2	0.33	0.85	0.07	0.003	0.09	7.63	99.16
3	71.6	9.56	6.45	0.47	0.25	0.76	2.02	0.04	0.66	0.05	0.01	0.08	7.42	99.37
4	84.6	6.14	1.83	0.49	0.2	0.68	1.91	0.04	0.83	0.03	0.004	0.06	2.44	99.25
5	81.4	7.32	2.41	0.64	0.29	0.68	2.07	0.07	0.99	0.02	0.004	0.06	2.9	98.85
6	51.6	19.07	6.79	0.67	1.01	0.24	1.16	0.06	1.03	0.08	0.011	0.06	17.66	99.47
7	66.7	13.27	5.37	0.42	0.53	0.52	1.61	0.05	0.96	0.11	0.011	0.05	9.54	99.18
9	69.7	11.54	4.08	0.39	0.3	0.5	1.86	0.03	0.96	0.04	0.011	0.06	9.76	99.18
10	66.3	13.29	5.85	0.51	0.45	0.52	1.8	0.03	1.04	0.04	0.013	0.07	9.23	99.19
11	64.2	11.37	3.23	0.61	0.56	0.47	1.71	0.06	0.86	0.08	0.012	0.07	16.27	99.47
12	53.4	17.85	3.8	0.59	0.56	0.29	1.09	0.03	0.74	0.07	0.011	0.07	20.99	99.5
16	66.4	14.42	3.46	1.29	0.69	1.97	3.68	0.07	0.99	0.04	0.006	0.18	5.8	99.06
17	57.5	16.17	6.18	1.05	1.12	0.97	2.48	0.15	1.16	0.1	0.01	0.12	12.75	99.72
18	48.8	19.49	9.54	0.88	1.43	0.56	1.95	0.14	1.2	0.07	0.013	0.09	15.43	99.56
19	72.2	10.99	4.64	0.55	0.46	0.65	1.67	0.06	0.94	0.09	0.007	0.06	6.96	99.27
20	77.5	8.75	2.61	0.67	0.29	0.53	1.74	0.04	0.86	0.03	0.008	0.06	6.06	99.1
21	62	15.25	5.08	0.4	0.58	0.46	2.06	0.05	1.34	0.05	0.014	0.07	11.27	98.59
22	58.6	15.75	4.09	0.44	0.66	0.42	1.86	0.05	1.14	0.1	0.012	0.06	16.19	99.35
26	52	18.08	5.25	0.41	0.85	0.35	1.74	0.06	1.14	0.15	0.018	0.07	19.18	99.26
27	62.1	15.01	3.64	0.44	0.61	0.38	1.88	0.03	1.23	0.07	0.012	0.07	13.28	98.71
28	69.6	12.82	4.79	0.48	0.49	0.6	1.91	0.08	1.04	0.03	0.01	0.06	6.98	98.93
29	63.4	15.51	4.67	0.46	0.62	0.54	2.24	0.04	1.33	0.05	0.014	0.08	9.87	98.87
30	52.3	19	7.06	0.48	0.76	0.22	1.3	0.07	1.02	0.11	0.015	0.06	17.11	99.46
31	79.8	7.6	1.85	0.58	0.26	0.66	1.81	0.03	0.73	0.03	0.008	0.06	5.22	98.64
32	48.9	19.76	6.61	0.83	1.09	0.23	1.26	0.06	1.11	0.07	0.012	0.07	19.37	99.37
33	56.9	16.48	6.42	0.57	0.56	0.78	1.63	0.07	1.09	0.09	0.01	0.09	14.55	99.26
35	66.6	11.76	2.58	0.72	0.38	1.25	2.3	0.05	0.79	0.08	0.01	0.12	12.75	99.36
37	78.4	9.36	2	0.31	0.26	0.37	1.52	0.03	1	0.04	0.008	0.05	5.81	99.17
38	66	14.3	3.67	0.45	0.56	0.55	2.06	0.04	1.21	0.04	0.012	0.07	10.11	99.07
39	87.3	5.47	1.51	0.39	0.15	0.58	1.79	0.03	0.7	0.01	0.006	0.06	1.41	99.38
average	66.14	13.16	4.48	0.57	0.56	0.59	1.86	0.07	0.99	0.06	0.01	0.07	10.68	99.23
minimum	48.80	5.47	1.51	0.31	0.15	0.22	1.09	0.03	0.66	0.01	0.00	0.05	1.41	98.59
maximum	87.30	19.76	9.54	1.29	1.43	1.97	3.68	0.33	1.34	0.15	0.02	0.18	20.99	100.09
stdev	10.75	4.15	1.89	0.21	0.30	0.34	0.47	0.06	0.18	0.03	0.00	0.03	5.39	0.32
UCC	60.60	15.90	6.70	6.40	4.70	3.10	1.80	-	0.70	0.10	-	-	-	-

Table 2. Enrichment values of the major oxides in the sediments of the investigated area (Krauskopf and Bird, 1995)

Major oxide	Average (present work) in ppm	UCC(ppm)	*Enrichment Values
SiO ₂	66.14	66	10022
Al ₂ O ₃	13.16	15.2	0.87
Fe ₂ O ₃	4.48	5	0.9
CaO	0.57	4.2	0.14
MgO	0.56	2.2	0.25
Na ₂ O	0.59	12	0.49
K ₂ O	186	3.7	0.5
MnO	0.07	ND	-
TiO ₂	0.99	0.5	198
P ₂ O ₅	0.06	0.15	0.39
Cr ₂ O ₃	0.01	ND	-

ND=not
determined

* Enrichment value is the ratio of concentration of the element in the analyzed sediment sample to the average concentration of the element in the upper continental crust.

The average concentration of each trace element was compared with UCC and ASC (Average Shale Concentration) to determine the degree of enrichment. The enrichment was computed by the ratio of individual element concentration in the analyzed sediment sample to UCC average of equivalent element. The concentrations of Ba, Rb, V, Sr and Zr are relatively higher than other trace elements. Ba ranges from 484 to 1595 ppm (average 663.77 ppm), Rb ranges from 53.6 to 138.5 ppm (average 88.11 ppm), V ranges from 29 to 134 ppm (average 84.17 ppm), Sr varies between 85.6 to 481.2 ppm (average 145.05 ppm) and Zr ranges from 169.2 to 1138 ppm (average

572.2 ppm). By comparing the trace elements average concentrations with UCC, it has been discovered that Ba, Co, Cs, Ga, Hf, U, V and Zr are significantly enriched in the sediments of River Niger floodplain at Jebba because their respective enrichment values is greater than one. However, other trace elements like Be, Nb, Rb, Sn, Sr, Ta, W, Cu, Pb, Zn and Ni are less enriched in the sediments having enrichment values less than one. Depletions of these elements may reflect intense weathering and recycling. Low Sr content is generally related to low CaO content, probably due to the lack of calcic plagioclase (Akarish and El-Gohary, 2011). Rb, Sn, Sr, Ta, U, V, Cu, Pb, Zn, Ni, Co, Cs, Ga and Ba correlate positively with Al_2O_3 which is an indication of aluminosilicate minerals (e.g. feldspar and mica) association.

Table 3. Correlation Matrix of the Major Oxides

Major Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	Cr ₂ O ₃
SiO ₂	1.00										
Al ₂ O ₃	-0.98	1.00									
Fe ₂ O ₃	-0.76	0.74	1.00								
CaO	-0.29	0.29	0.22	1.00							
MgO	-0.86	0.86	0.75	0.52	1.00						
Na ₂ O	0.22	-0.21	-0.19	0.66	-0.10	1.00					
K ₂ O	0.19	-0.16	-0.16	0.54	-0.02	0.89	1.00				
MnO	-0.13	0.06	0.38	0.22	0.23	0.14	0.17	1.00			
TiO ₂	-0.55	0.63	0.43	0.06	0.59	-0.15	0.15	0.04	1.00		
P ₂ O ₅	-0.71	0.64	0.51	0.06	0.54	-0.16	-0.20	0.20	0.30	1.00	
Cr ₂ O ₃	-0.74	0.74	0.50	-0.15	0.54	-0.41	-0.25	-0.30	0.56	0.56	1.00

Table 4. Statistical summary of Trace elements in sediments of the study area with their enrichment values

Trace Elements	UCC (ppm)	ASE (ppm)	present work average	Enrichment (UCC)	Enrichment (ASC)
Ba	550	500	663.77	1.21	1.33
Be	3	3	2.76	0.92	0.92
Co	10	19	11.94	1.19	0.63
Cs	3.5	5	3.61	1.03	0.72
Ga	17	19	17.42	1.02	0.92
Hf	5.8	1.8	14.42	2.49	8.01
Nb	25	11	20.23	0.81	1.84
Rb	112	140	88.11	0.79	0.63
Sn	5.5	6	2.70	0.49	0.45
Sr	350	300	145.05	0.41	0.48
Ta	2.2	0.8	1.48	0.67	1.85
U	2.8	3.7	4.07	1.45	1.10
V	60	130	84.17	1.40	0.65
W	2	-	1.59	0.79	ND
Zr	190	160	572.20	3.01	3.58
Mo	-	2.6	0.19	BDL	0.07
Cu	25	45	20.66	0.83	0.46
Pb	20	-	13.86	0.69	ND
Zn	71	95	33.43	0.47	0.35
Ni	20	68	14.40	0.72	0.21
As	ND	13	0.89	ND	0.07
Cd	ND	0.3	BDL	ND	ND
Sb	ND	1.5	BDL	ND	ND
Bi	ND	-	0.18	ND	ND
Ag	ND	0.07	BDL	ND	ND
Au	ND	0.4	1.27	ND	3.17
Hg	ND	1.4	0.02	ND	0.01
Tl	ND	20	0.23	ND	0.01
Se	ND	0.6	0.60	ND	1.00

ND= not determined, UCC=upper continental average composition, ASC=average shale concentration

4.1.3 Rare earth elements

Table 6a presents the statistical summary of the rare elements and their comparison with UCC (Average Upper continental crust) average concentrations (Talyor and McLennan, 1985). All the enrichment values computed for the rare earth elements are greater than one, depicting high enrichment of these elements in the sediment phase. The reason for the high enrichment values is

due to the influence of various anthropogenic activities in the area like: farming, rearing of animals, application of fertilizer, manure etc. Figure 4 presents the ASC-UCC-normalized averages of rare earth elements concentrations and Table 6b shows the enrichment of the rare earth elements compared with ASC (Average Shale Concentration). All the rare earth elements are highly enriched in the sediments phase except La, Tb, Ho and Lu that are depleted. Furthermore, the average concentrations of the elements in Jebba sediments are generally lower than the average values of granite-gneiss except element Yb (3.2 ppm) having a lower concentration. However, the average values are depleted in granite, quartzite and schist/biotite schist except Eu having higher concentration in schist/biotite schist (1.8 ppm). The enrichment of these elements in the sediment phase could also be attributed to the weathering of these crystalline rocks most especially the granite-gneiss. The good positive correlation (Table 7) of the rare elements with Al_2O_3 confirms that the rare elements are mostly concentrated in the clay fractions.

Table 5. Correlation matrix of trace elements in the sediments of the analyzed samples with some major oxides

	SiO_2	Al_2O_3	Ba	Be	Co	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Ni	V	Fe_2O_3	Zn	Cu	Pb	TiO_2
SiO_2	1.00																		
Al_2O_3	-0.98	1.00																	
Ba	-0.07	0.07	1.00																
Be	-0.73	0.67	0.19	1.00															
Co	-0.50	0.46	0.27	0.60	1.00														
Cs	-0.94	0.96	0.01	0.57	0.46	1.00													
Ga	-0.97	0.99	0.03	0.64	0.53	0.96	1.00												
Hf	0.93	-0.88	-0.02	-0.66	-0.42	-0.86	-0.87	1.00											
Nb	-0.65	0.72	0.08	0.18	0.28	0.78	0.71	-0.54	1.00										
Rb	-0.79	0.79	0.43	0.50	0.46	0.84	0.79	-0.72	0.73	1.00									
Sn	-0.64	0.67	-0.29	0.40	0.12	0.69	0.66	-0.60	0.49	0.38	1.00								
Sr	-0.07	0.06	0.95	0.25	0.14	-0.03	0.01	-0.02	-0.05	0.35	-0.27	1.00							
Ni	-0.90	0.89	-0.06	0.59	0.57	0.88	0.92	-0.81	0.57	0.73	0.51	-0.06	1.00						
V	-0.92	0.95	-0.04	0.55	0.52	0.96	0.96	-0.81	0.80	0.78	0.64	-0.09	0.89	1.00					
Fe_2O_3	-0.76	0.74	0.62	0.62	0.78	0.71	0.78	-0.68	0.42	0.56	0.39	0.01	0.82	0.79	1.00	0.73	0.68		
Zn	-0.92	0.90	0.07	0.59	0.55	0.93	0.93	-0.83	0.67	0.86	0.54	0.04	0.92	0.91	0.73	1.00	0.89		
Cu	-0.95	0.93	-0.03	0.60	0.39	0.95	0.94	-0.89	0.69	0.79	0.62	-0.03	0.90	0.92	0.68	0.94	1.00		
Pb	-0.93	0.90	0.23	0.68	0.52	0.88	0.89	-0.84	0.68	0.82	0.54	0.25	0.81	0.85	0.73	0.88	0.89	1.00	
TiO_2	-0.55	0.63	0.03	0.12	0.26	0.73	0.62	-0.43	0.94	0.70	0.43	-0.10	0.53	0.76	0.43	0.61	0.59	0.57	1.00

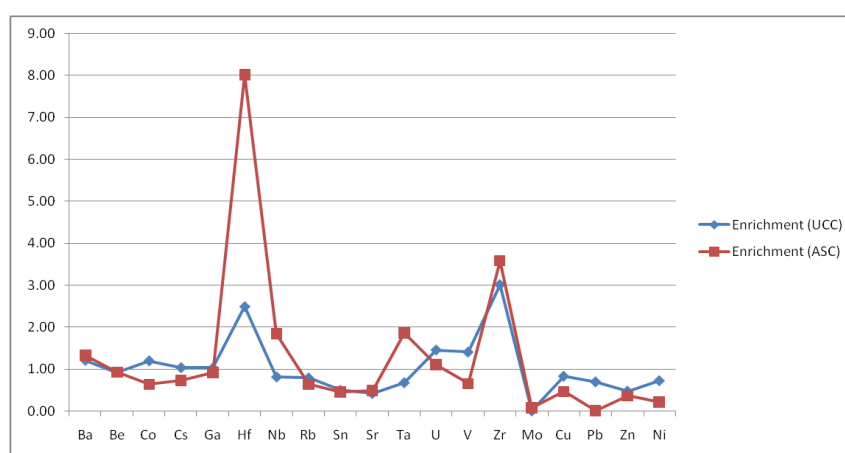


Figure 3. ASC, UCC-normalized averages of trace element concentrations for Jebba floodplain sediments (after Taylor and McLennan, 1985)

4.2 Source area weathering

The intensity of weathering in siliciclastic sediments/soils can be designated by examining the relationships among alkali and alkaline earth elements (Nesbitt and Young, 1982). Since the upper crust is dominated by the presence of feldspars (Nesbitt and Young, 1982, 1984), the dominant process during chemical weathering and soil formation is the degradation of mobile feldspars from source rocks to secondary clay minerals. These chemical signatures are ultimately transferred to sedimentary records and supply a useful means for monitoring the original composition and following weathering conditions. The weathering history of the sources of siliciclastic sediments can be determined through estimation of the chemical weathering of silicates such as the calculated values of Chemical Index of Alteration (CIA), Plagioclase Index of Alteration (PIA) and Chemical

Index of Weathering (CIW) (Nesbitt and Young, 1982; Fedo et al., 1995). Where, $CIA = Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O) \times 100$, $PIA = (Al_2O_3 - K_2O) / (Al_2O_3 + CaO^* + Na_2O - K_2O) \times 100$ and $CIW = Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O) \times 100$, in molecular proportions.

Table 6a. Descriptive statistical summary of rare elements (in ppm) in the sediment of the study area showing UCC, enrichment values computed in the investigated area

Analyte	UCC (ppm)	Jebba sediments (average in ppm)	min	max	stdev	Enrichment
Th	ND	15.22	8.40	20.40	3.22	-
Y	22	32.46	19.70	44.60	7.01	1.48
La	30	51.16	22.50	83.90	16.57	1.71
Ce	64	104.68	53.00	163.90	32.02	1.64
Pr	7.1	11.52	5.51	18.50	3.61	1.62
Nd	26	43.10	21.60	71.40	13.63	1.66
Sm	4.5	7.77	3.88	11.75	2.25	1.73
Eu	0.88	1.63	0.67	2.70	0.57	1.85
Gd	3.8	6.92	3.44	9.93	1.98	1.82
Tb	0.64	0.99	0.55	1.39	0.26	1.55
Dy	3.5	6.01	3.18	9.13	1.52	1.72
Ho	0.8	1.16	0.68	1.59	0.27	1.44
Er	2.3	3.32	2.04	4.68	0.67	1.44
Tm	0.33	0.51	0.30	0.68	0.10	1.53
Yb	2.2	3.34	1.98	4.22	0.58	1.52
Lu	0.32	0.52	0.35	0.74	0.09	1.62

Table 6b. Average rare earth elements concentrations of Jebba Floodplain sediments normalized against UCC-ASC (after Taylor and McLennan, 1985)

Analyte	UCC (ppm)	ASC (ppm)	Present work average (ppm)	Enrichment (UCC)	Enrichment (ASC)
Th	ND	ND	15.22	ND	ND
Y	22	26	32.46	1.48	1.25
La	30	92	51.16	1.71	0.56
Ce	64	59	104.68	1.64	1.77
Pr	7.1	5.6	11.52	1.62	2.06
Nd	26	24	43.10	1.66	1.80
Sm	4.5	6.4	7.77	1.73	1.21
Eu	0.88	1	1.63	1.85	1.63
Gd	3.8	6.4	6.92	1.82	1.08
Tb	0.64	1	0.99	1.55	0.99
Dy	3.5	4.6	6.01	1.72	1.31
Ho	0.8	1.2	1.16	1.44	0.96
Er	2.3	2.5	3.32	1.44	1.33
Tm	0.33	0.2	0.51	1.53	2.53
Yb	2.2	2.6	3.34	1.52	1.28
Lu	0.32	2.8	0.52	1.62	0.19

ND= not determined, UCC=upper continental average composition, ASC=average shale concentration

Table 7. Correlation matrix between the rare earth elements of the sediments in the investigated area

Parameters, ppm	Th	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	1															
Y	0.86	1.00														
La	0.81	0.80	1.00													
Ce	0.82	0.87	0.98	1.00												
Pr	0.83	0.86	0.99	0.99	1.00											
Nd	0.81	0.84	0.99	0.99	0.99	1.00										
Sm	0.86	0.91	0.97	0.98	0.99	0.98	1.00									
Eu	0.81	0.87	0.97	0.99	0.99	0.98	0.98	1.00								
Gd	0.87	0.94	0.94	0.97	0.97	0.96	0.99	0.97	1.00							
Tb	0.88	0.97	0.89	0.94	0.93	0.92	0.97	0.94	0.99	1.00						
Dy	0.88	0.97	0.84	0.89	0.88	0.87	0.94	0.90	0.96	0.98	1.00					
Ho	0.85	0.99	0.79	0.86	0.85	0.84	0.91	0.87	0.94	0.98	0.97	1.00				
Er	0.78	0.95	0.65	0.73	0.71	0.70	0.80	0.73	0.83	0.89	0.93	0.94	1.00			
Tm	0.76	0.92	0.60	0.69	0.67	0.66	0.75	0.69	0.78	0.85	0.87	0.91	0.95	1.00		
Yb	0.67	0.84	0.54	0.54	0.52	0.52	0.61	0.53	0.65	0.73	0.75	0.82	0.89	0.93	1.00	
Lu	0.53	0.72	0.28	0.37	0.35	0.34	0.45	0.35	0.49	0.58	0.62	0.70	0.82	0.86	0.91	1.00

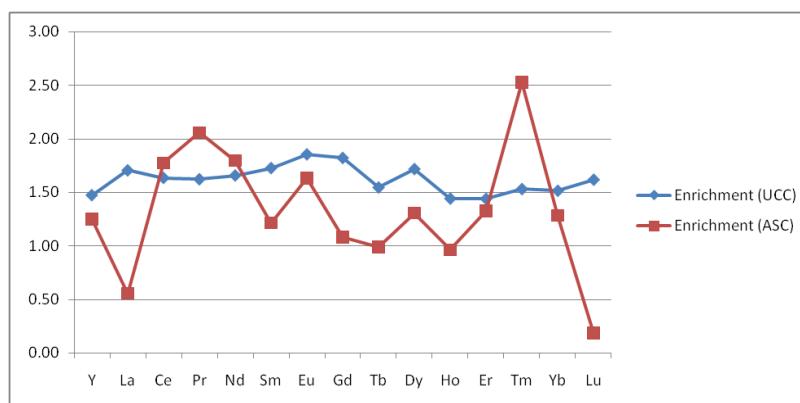


Figure 4. ASC, UCC-normalized averages of rare earth element concentrations for Jebba floodplain sediments (after Taylor and McLennan, 1985)

The CIA values, ranging from 66.46 to 90.48 fall within intermediate silicate weathering and extreme silicate weathering. On the average (80.08), it falls on the extreme silicate weathering. Similarly, PIA ranges from 76.71 to 96.20 (average 89.37) – intermediate to extreme silicate weathering and CIW ranges from 81.56 to 96.45 (average 91.17) –extreme silicate weathering. The values of CIA, CIW and PIA obtained reflect high weathering conditions either in the original terrain or during transportation. In addition, high CIA values, suggest derivation from a stable cratonic source (Hossain et al., 2010; Akarish and El-Gohary, 2011). The variations in the computed CIA, PIA and CIW values may be due to the different concentrations of alumina in samples rather than variable degrees of source area weathering. Also, PIA values indicate that the plagioclases feldspar in the possible parent rock displayed high weathering condition and resulted in low CaO content (range 0.31-1.29 wt %; average 0.57 wt %), especially with increasing PIA values. This implies that with increasing chemical weathering the sediments/soils are steadily depleted in plagioclase and enriched in secondary aluminous clay minerals (Roy et al., 2008; Akarish and El-Gohary, 2011).

The following elemental ratios were used as markers to delineate the intensities of chemical weathering in the samples: Al/Na, Al/K and K/Na (Roy et al., 2008; Akarish and El-Gohary, 2011). According to Roy et al. (2008), Akarish and El-Gohary (2011), plots of CIA values against Al/Na, Al/K and K/Na elemental ratios support the intermediate to extreme chemical weathering (Figure 5).

The following mobile elements: Na₂O (0.59 wt %), K₂O (1.86 wt %), MgO (0.56 wt %) and P₂O₅ (0.06 wt %) were depleted compared to UCC which is reliable with the loss through sedimentary processes. The depletion in Al₂O₃ (13.16 wt %) and enrichment in SiO₂ (66.12 wt %) relative to the UCC may be due to sedimentary sorting and loss of small grain-sized clays (Al₂O₃-rich and SiO₂ –poor) and retention of sand-size composition (Al₂O₃-poor and SiO₂-rich) (Borges et al., 2008; Akarish and El-Gohary, 2011).

The SiO₂/Al₂O₃ is a commonly employed index of sedimentary maturation. Values increase because of increase of quartz at the expense of less resistant components such as feldspar and lithic fragments during sediment transport and recycling. The SiO₂/Al₂O₃ ratio is about 3 in basic rocks (basalts and gabbros) and it is around 5 in the acidic end member (granites and rhyolites) (Le Maitre, 1976; Roser et al., 1996; Akarish and El-Gohary, 2011). Ratio more than 5 or 6 in sedimentary rocks provided evidence of sedimentary maturation (Roser et al., 1996; Akarish and El-Gohary, 2011). The average value of SiO₂/Al₂O₃ ratio for the studied samples is 5.98 (range 2.47-15.96), indicating matured sediments/soils.

The low value recorded for K₂O (range 1.09-3.68, average 1.86) in River Niger Floodplain sediments may be attributed to intense chemical weathering (Cox et al., 1995; Akarish and El-Gohary, 2011) which influenced leaching of sediments and removal of alkalis in solution. Very low K₂O/Al₂O₃ ratios (0.06-0.33, average 0.16), probably caused by the presence of high proportion of

kaolinite, possibly indicates moderate to intense chemical weathering of source rocks (Potter et al., 1980).

High ratio of Th/U (range 2.59-6.26, average 3.82) reflects intense weathering condition. The presence of correlation between Th/U and CIA values ($r=0.11$) suggests that the Th/U ratio is probably a reflection of chemical weathering (Akarish and El-Gohary, 2011). The average value of Th/U obtained is similar to the range (2.03-3.24) calculated. They stated that the ratio Th/U probably reflects intensive weathering condition which could be confirmed by the positive correlation with CIA.

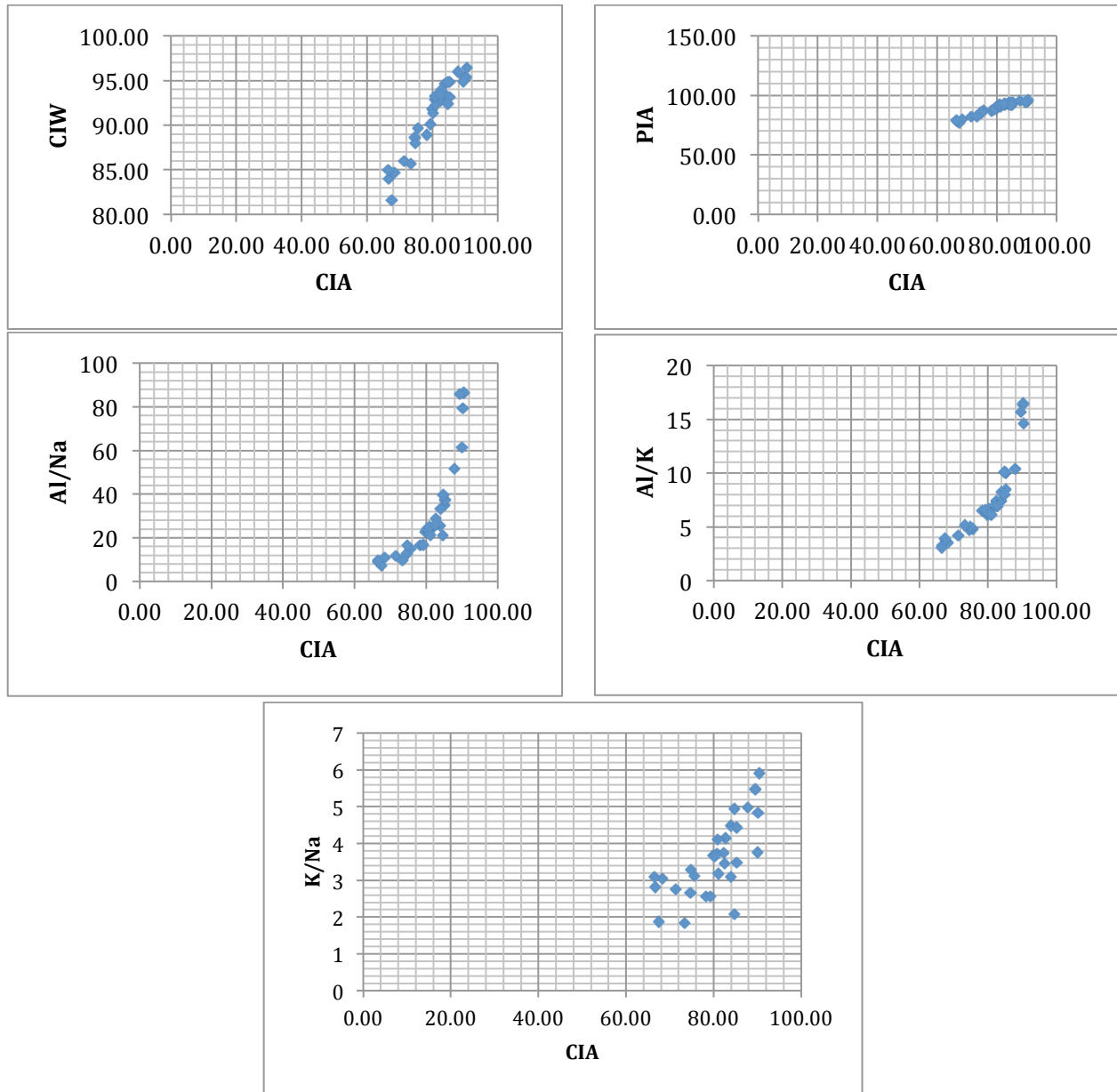


Figure 5. Scattered plots of Chemical Index of alteration (CIA) vs CIW, PIA, Al/Na, Al/K and K/Na showing degree of chemical weathering in River Niger Floodplain sediments

4.3 Assessment of contamination in the sediments phase

The focus on the determinations of trace metals concentrations in the River Niger floodplain sediments is to assess the possible environmental impacts of anthropogenic, agricultural activities and the influence of weathering of surrounding rocks on the metal distributions. The impacts of

these activities are evaluated below using parameters; contamination factor (CF) or anthropogenic factor (AF), degree of contamination, geo-accumulation and enrichment factor. Several published researches have made use of the Average Crustal Abundance of elements in shale fraction, World River Sediment Average (2009) and Average Composition of Basement Rock of SW-Nigeria (compiled by Tijani et al., 2006) to determine contamination indexes of sediments. Hence, this study has also adopted the same index values to determine the contamination indexes in the sediment phase of the study area.

The computed anthropogenic factors for the heavy/trace metals in the sediment with respect to the average compositions of basement rock of SW-Nigeria are presented in Table 8 and the trends of the indexes are illustrated in Figure 6. The three indexes followed the same trend. If the CF is > 1 , it depicts influence of anthropogenic activities and if CF is < 1 it connotes influence of geogenic factors. Therefore, the estimated average contamination factor (CF) of the sediment samples < 1 for Ca, Na, K, P, Cr, Pb, Zn and As reflects geogenic sources for these elements in the sediment while average values of CF > 1 for Si, Al, Fe, Mg, Mn, Ti, Ba, Co, Sr, Cu and Ni reflects enrichment through anthropogenic sources. I-geo > 1 for Si and Mg indicates contamination / enrichment with respect to these metals while I-geo < 1 for Al, Fe, Ca, Na, K, Mn, Ti, P, Cr, Ba, Co, Sr, Cu, Pb, Zn, Ni and As indicates no practical contamination by anthropogenic activities in the area but depicts influence of weathering of the country rocks in the area (Tijani et al., 2007). These elements are associated with silicate minerals like biotite, muscovite and plagioclase feldspar.

Average EF > 1 for Si, Mg, Mn, Ba, Co, Sr, Cu and Ni indicates varying degree of enrichment through possible anthropogenic activities or weathering of silicate mineral rich rocks in the area of study. The trend of the EF is consistent with the results of the estimated AF and I-geo (Figure 6). On the basis of the Contamination Factor (CF), elements Ca, Na, K, P, Cr, Pb, Zn and As have low enrichment/ contamination as a reflection of geogenic inputs. The sediment is moderately enriched/contaminated with respect to Al, Fe, Mn, Ti, Ba, Co, Sr, Cu and Ni; considerably and highly contaminated/enriched with respect to Si and Mg respectively. The contamination indexes are also computed using the average world river sediment. In this case, Si, Ti, Ba, Nb, Ta, U, Zr, Y, La and Ce have CF > 1 reflecting anthropogenic source for these elements/metals. Detailed interpretation for the computed contamination indexes of the respective metals are interpreted and presented in Tables 9a-c.

Table 8. Contamination Indexes for the investigated sediments and interpretations (after Tijani et al. 2006)

Parameters	CF	CF/Source	IGEO	extent of contamination	EF	level of enrichment
Si	4.2	CCF/anthropogenic	1.5	moderately polluted	2.7	moderate enrichment
Al	1	MCF/anthropogenic	-0.6	practically unpolluted	0.6	minimal enrichment
Fe	2	MCF/anthropogenic	0.3	unpolluted to moderately polluted		
Ca	0.7	LCF/geogenic	-1.1	practically unpolluted	0.4	minimal enrichment
Mg	6.6	VHCF/anthropogenic	1.9	moderately polluted	3.3	moderate enrichment
Na	0.2	LCF/geogenic	-3.1	practically unpolluted	0.1	minimal enrichment
K	0.5	LCF/geogenic	-1.6	practically unpolluted	0.3	minimal enrichment
Mn	2.2	MCF/anthropogenic	0.3	unpolluted to moderately polluted	1.1	minimal enrichment
Ti	1.3	MCF/anthropogenic	-0.2	practically unpolluted	0.7	minimal enrichment
P	0.4	LCF/geogenic	-2.2	practically unpolluted	0.2	minimal enrichment
Cr	0.8	LCF/geogenic	-1	practically unpolluted	0.5	minimal enrichment
Ba	1.3	MCF/anthropogenic	-0.3	practically unpolluted	2.8	moderate enrichment
Co	2.9	MCF/anthropogenic	0.8	unpolluted to moderately polluted	5.4	significant enrichment
Sr	1.2	MCF/anthropogenic	-0.4	practically unpolluted	2.7	moderate enrichment
Cu	1.7	MCF/anthropogenic	-0.05	practically unpolluted	3.4	moderate enrichment
Pb	0.2	LCF/geogenic	-3	practically unpolluted	0.4	minimal enrichment
Zn	0.5	LCF/geogenic	-1.9	practically unpolluted	0.9	minimal enrichment
Ni	1.3	MCF/anthropogenic	-0.4	practically unpolluted	2.3	moderate enrichment
As	0.6	LCF/geogenic	-1.4	practically unpolluted	0.9	minimal enrichment

MCF=moderate contamination factor;

LCF= low contamination factor; CCF=considerable contamination factor; VHCF=very high contamination factor.

Table 9a. Contamination indexes of the major element in the investigated sediments (after World River Sediment, 2009)

	Parameters	CF	CF/Source	IGEO	extent of contamination	EF	level of enrichment
Major Elements	Si	1.2	MCF/anthropogenic	-0.3	practically unpolluted	2.9	moderate enrichment
	Al	0.8	LCF/geogenic	-1	practically unpolluted	1.6	minimal enrichment
	Fe	0.5	LCF/geogenic	-1.6	practically unpolluted	-	
	Ca	0.2	LCF/geogenic	-3.3	practically unpolluted	0.3	minimal enrichment
	Mg	0.3	LCF/geogenic	-2.7	practically unpolluted	0.5	minimal enrichment
	Na	0.6	LCF/geogenic	-1.4	practically unpolluted	1.5	minimal enrichment
	K	0.9	LCF/geogenic	-0.8	practically unpolluted	2.1	moderate enrichment
	Mn	0.3	LCF/geogenic	-2.6	practically unpolluted	0.6	minimal enrichment
	Ti	1.3	MCF/anthropogenic	-0.2	practically unpolluted	2.9	moderate enrichment
	P	0.1	LCF/geogenic	-3.7	practically unpolluted	0.3	minimal enrichment
	Cr	0.5	LCF/geogenic	-1.6	practically unpolluted	1.1	minimal enrichment

MCF=moderate contamination factor; LCF= low contamination factor; CCF=considerable contamination factor; VHCF=very high contamination factor.

Table 9b. Contamination indexes of the trace element in the investigated sediments (after World River Sediment, 2009)

	Parameters	CF	CF/Source	IGEO	extent of contamination	EF	level of enrichment
Trace Elements	Ba	1.27	MCF/anthropogenic	-0.3	practically unpolluted	2.85	moderate enrichment
	Co	0.53	LCF/geogenic	-1.67	practically unpolluted	0.99	minimal enrichment
	Cs	0.58	LCF/geogenic	-1.53	practically unpolluted	1.2	minimal enrichment
	Ga	0.96	LCF/geogenic	-0.72	practically unpolluted	1.99	minimal enrichment
	Hf	3.57	CCF/anthropogenic	1.09	moderately polluted	9.62	significant enrichment
	Nb	1.5	MCF/anthropogenic	-0.03	practically unpolluted	-	
	Rb	1.12	MCF/anthropogenic	-0.47	practically unpolluted	2.26	moderate enrichment
	Sn	0.59	LCF/geogenic	-1.42	practically unpolluted	1.25	minimal enrichment
	Sr	0.78	LCF/geogenic	-1.09	practically unpolluted	1.75	minimal enrichment
	Ta	1.17	MCF/anthropogenic	-0.41	practically unpolluted	2.55	moderate enrichment
	Th	1.26	MCF/anthropogenic	-0.29	practically unpolluted	-	
	U	1.23	MCF/anthropogenic	-0.33	practically unpolluted	2.52	moderate enrichment
	V	0.65	LCF/geogenic	-1.29	practically unpolluted	1.3	minimal enrichment
	W	0.8	LCF/geogenic	-1.01	practically unpolluted	1.61	minimal enrichment
	Zr	3.58	CCF/anthropogenic	1.07	moderately polluted	9.27	significant enrichment
	Y	1.48	MCF/anthropogenic	-0.05	practically unpolluted	3	moderate enrichment
	Mo	0.06	LCF/geogenic	-4.71	practically unpolluted	0.12	minimal enrichment
	Cu	0.27	LCF/geogenic	-2.66	practically unpolluted	0.52	minimal enrichment
	Pb	0.23	LCF/geogenic	-2.85	practically unpolluted	0.43	minimal enrichment
	Zn	0.16	LCF/geogenic	-3.44	practically unpolluted	0.3	minimal enrichment
	Ni	0.19	LCF/geogenic	-3.11	practically unpolluted	0.37	minimal enrichment
	As	0.02	LCF/geogenic	-6.04	practically unpolluted	0.04	minimal enrichment
	Bi	0.21	LCF/geogenic	-3.14	practically unpolluted	0.4	minimal enrichment

Table 9c. Contamination indexes of the rare earth element in the investigated sediments (after World River Sediment, 2009)

	Parameters	CF	CF/Source	IGEO	extent of contamination	EF	level of enrichment
Rare Earth Elements	La	1.37	MCF/anthropogenic	-0.21	practically unpolluted	3	moderate enrichment
	Ce	1.42	MCF/anthropogenic	-0.15	practically unpolluted	2.86	moderate enrichment
	Pr	1.45	MCF/anthropogenic	-0.12	practically unpolluted	4.08	moderate enrichment
	Nd	1.34	MCF/anthropogenic	-0.24	practically unpolluted	2.55	moderate enrichment
	Sm	1.27	MCF/anthropogenic	-0.31	practically unpolluted	2.78	moderate enrichment
	Eu	1.26	MCF/anthropogenic	-0.34	practically unpolluted	2.57	moderate enrichment
	Gd	1.32	MCF/anthropogenic	-0.25	practically unpolluted	2.75	moderate enrichment
	Tb	1.21	MCF/anthropogenic	-0.37	practically unpolluted	2.56	moderate enrichment
	Dy	1.41	MCF/anthropogenic	-0.13	practically unpolluted	3.01	moderate enrichment
	Ho	1.31	MCF/anthropogenic	-0.24	practically unpolluted	2.84	moderate enrichment
	Er	1.49	MCF/anthropogenic	-0.04	practically unpolluted	3.3	moderate enrichment
	Tm	1.33	MCF/anthropogenic	-0.2	practically unpolluted	2.73	moderate enrichment
	Yb	1.58	MCF/anthropogenic	0.05	unpolluted to moderately	3.55	moderate enrichment
	Lu	1.48	MCF/anthropogenic	-0.04	practically unpolluted	3.35	moderate enrichment

MCF=moderate contamination factor; LCF= low contamination factor; CCF=considerable contamination factor; VHCF=very high contamination factor.

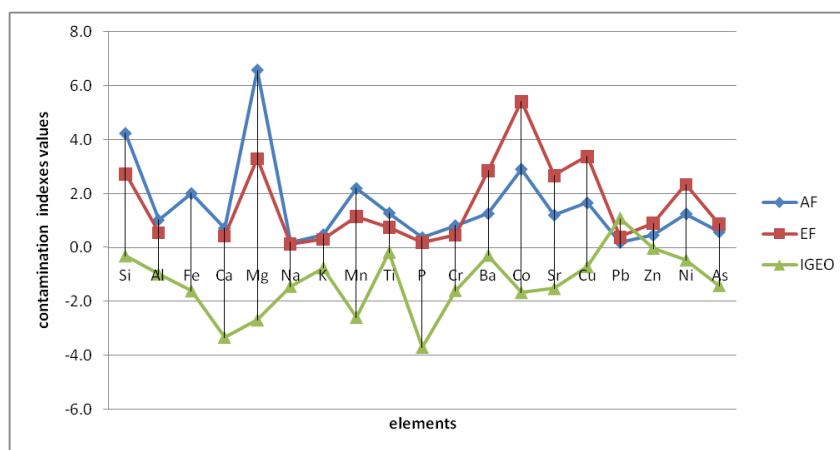


Figure 6. Trace metals contamination trend in sediment with respect to (a) Anthropogenic factor (AF); (b) Geo-accumulation Index (Igeo); (c) Enrichment factor (EF)

5. CONCLUSION

The geochemical characteristics and level of metal contamination of sediments in River Niger Fadama at Jebba have been examined. The geochemical investigation of the sediments revealed that most of the major oxides in the sediments have undergone depletion due to intensive weathering. It is suggested that the weathering products must have found their way into the water phase thereby increasing the elemental compositions of the water. Contamination Indexes obtained revealed that the sediments have experienced certain level of contamination due to geogenic and anthropogenic influences over-time. Some trace elements (Ba, Co, Cs, Ga, Hf, U, V and Zr) are highly enriched in the sediments when compared with UCC average values. The Chemical Index of Alteration, chemical index of weathering, plagioclase index of alteration of sediments indicated that the sources of ions in the sediment phase range from geogenic to anthropogenic (agrochemicals, municipal wastes, etc.) origins.

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