



Preliminary Geochemical Assessment of Asa River Sediments, North Central Nigeria

Omotoso*¹, O. A., Ojo. O. J²., Okebaram, U. D¹., Alebiosu, M. T¹.

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

²Department of Geology, Federal University Oye-Ekiti, Nigera.

*Corresponding Author: Dr. O. A. Omotoso: deletoso2002@yahoo.co.uk +2348067780267

Abstract

Preliminary geochemical assessment of Asa river sediments has been carried out with the aim of evaluating the concentrations, extent of contamination and possible sources of metals in the sediments using XRF and ICP-MS techniques. Geochemical results of major oxides show that SiO₂ has the highest value (range=72.4 to 94.1%; average=85.66%), others ranged from 0.01% in Cr₂O₃, P₂O₅ and MnO₂ to 11.6 % in Al₂O₃. Enrichment of the major oxides according to UCC, PAAS and NASC shows that only SiO₂ is highly enriched in the sediments (1.3, 1.36 and 1.32 respectively) while others have values less than 1 (that is they are depleted in the sediments). Weathering indication parameters indicate some degree of intensive weathering. Ba, Sr and Zr have the highest average concentrations (1043, 138 and 1155ppm respectively) above other trace elements. Ba, Hf and Zr are highly enriched in the sediments (2.09; 1.9), (15.13; 4.7), (7.22;6.08) according to ASC and UCC average values respectively, while the rest are depleted with values <1. Ce has the highest average value of 29.08ppm above other rare earth elements. Ce may be sourced from glauconites. Tm has the lowest average value (0.18ppm). Rare earth elements show enrichment values <1, meaning that they are depleted in the sediments. Metals/elements ranged from low contamination factor to very high contamination factor, low degree of contamination to very high degree of contamination and the geo-accumulation index ranged from practically no contamination to moderately contaminated. Contamination Factors revealed the influence of both anthropogenic and geogenic on the metal concentrations in the sediments.

Keywords: Geochemistry, Asa River Sediments, Enrichment, Contamination Factor, Weathering Indications

Introduction

River sediments are transported from distant and nearby geological terrains, having information of different geological formations. These sediments are constantly undergoing stages of weathering thereby losing some of their minerals into the water phase. In some cases, the sediments serve as sinks for heavy metals derived from various anthropogenic activities around the vicinity of the river thereby increasing the concentrations of metals in the sediments (Tijani *et al.*, 2007). The pollution of sediments as a result of industrial wastes and other wastes is one of the problems faced by the developed

as well as developing nations. Contamination by potentially toxic elements in the environment is one of the main problems for human health and environment quality because these elements are indestructible and most of them have toxic effects on live organisms when they exceed certain level. River sediment contamination also takes place when toxic chemicals are released into the public drainage system or disposal of effluents by various industries. Some of these elements are not bio-degradable and their presence in streams, lakes, river etc., causes bio-accumulation in living organism leading to chronic health problems in animals, plants and human beings. These metals/elements are

released into the river system by natural and anthropogenic sources.

Asa river water serves Ilorin metropolis and its environs potable water supply despite various industrial and agricultural practices in the area. There is the need to assess the levels of various ions in the sediments so as to know the fate of the sediments and the water for the said purpose.

Materials and Methods

Samples Preparation and Laboratory Analysis

A total of 12 sediment samples were collected from Asa River using random sampling methods because of inaccessibility of certain part of the river (Figure 1). 5 samples out of the 12 were subjected to geochemical analysis. The samples were sun dried in an open air. The samples were also pulverized in the department of Geology and mineral sciences, University of Ilorin, Nigeria and later sent to ACME laboratory, Canada for geochemical analysis using XRF and ICP-MS for major oxides and trace/rare earth elements determination respectively.

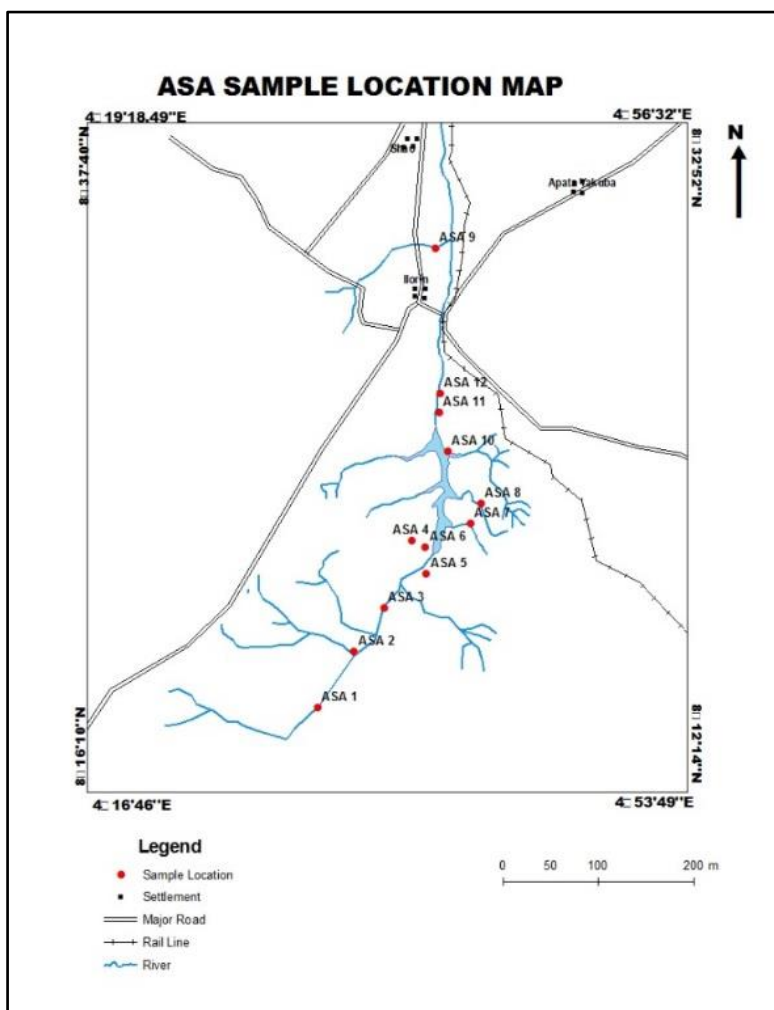


Figure 1: Location map of the study area showing sampling points

Data Evaluation

Assessment of Metal Contamination in Sediments

For the assessment and quantification of the level of contamination in the sediments the following quantitative contamination indices were adopted to illustrate the concentration trends and also to allow easy comparison among the measured parameters:

Contamination Factor (CF): This is the single index determined by the relation:

$C_F = C_M / B_M$ (C_F = contamination factor of the element of interest; B_M = background concentration in this study; C_M = concentration of the element in the sample). Contamination factor has four categories which include: < 1 low contamination factor; 3-6 = considerable contamination factor; > 6 = very high contamination factor (Atiemo *et al.*, 2011).

Degree of Contamination (C_{deg}): This is the sum of all the contamination factors in the sample. It is indicated as: $C_{deg} = \sum (C_M / B_M)$

(C_M = measured concentration in soil/sediment or water; B_M = local background concentration of metal, m within the pristine area of the catchment). Four categories have been defined for the degree of contamination which includes: < 8 = low degree of contamination; 8 – 16 = considerable degree of contamination; > 32 = very high degree of contamination (Atiemo *et al.*, 2011).

Index of Geo-Accumulation (I_{geo}): This is widely used in the assessment of contamination by comparing the level of trace metal obtained to a background

levels originally used with bottom sediments (Muller, 1979) which can also be adopted to soil/sediment contamination (Tijani *et al.*, 2007; Omotoso and Ojo, 2011). It is calculated by:

$I_{geo} = \log_2 [(C_m) / (1.5 * B_m)]$ C_m = measured concentration of metal in soil/sediment or water; B_m = local background concentration (value) of metal, m within the pristine area of the catchment. 1.5 is a factor for possible variation in the background concentration due to lithologic differences. The following classification is given for geo-accumulation index (Huu *et al.*, 2010; Muller, 1979): <0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted and > = extremely polluted.

Weathering Indications

The weathering history of the sources of the sediments were determined through estimation of the chemical weathering of silicates such as the computed 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.

Results and Discussion

Geochemistry of the Major Oxides:

The bulk geochemical results of the sediment samples, their weathering indications, and enrichment are presented in **Table 1**. The analysed value of SiO₂ in the sediments ranged from 72.4 % in ASA-11 to 98.1 % in ASA-3 (Average=85.66 %), Al₂O₃ ranged from 2.82 % in ASA-3 to 11.6 % in ASA-11 (average=5.6 %); Fe₂O₃ ranged from 0.9 % in ASA-3 to 5.11 % in ASA-10 (average=2.59 %); CaO ranged from 0.12 % in ASA-5 to 1.79 % in ASA-11 (average=0.77 %); MgO ranged from

0.05 % in ASA-3 to 0.14 % in ASA-10 (average=0.09 %); Na₂O ranged from 0.21 % in ASA-5 to 1.74 % in ASA-11 (average=0.78 %); K₂O ranged from 0.75 % in ASA-3 to 4.78 % in ASA-11 (average=1.91 %); MnO ranged from <0.01 % in ASA-5 to 0.09 % in ASA-11 (average=0.05 %); TiO₂ ranged from 0.07 % in ASA-3 to 0.71 % in ASA-10 (average=0.3 %) and P₂O₅ ranged from 0.01 % in ASA-3 and ASA-5 to 0.06 % in ASA-10 and ASA-11 (average=0.03 %). P₂O₅ and MnO are strongly deleted in the samples.

Table 1: major oxides (in %) in the investigated sediments, their weathering indication indexes and enrichment based on UCC, PAAS and NASC average values

Major Oxides	ASA-3	ASA-5	ASA-6	ASA-10	ASA-11	Average	Min	Max	Stdev	Enrichment (UCC)	Enrichment (PAAS)	Enrichment (NASC)
SiO ₂	94.1	91.7	91.9	78.2	72.4	85.66	72.40	94.10	9.72	1.30	1.36	1.32
Al ₂ O ₃	2.82	3.02	3.01	7.54	11.6	5.60	2.82	11.60	3.90	0.37	0.30	0.33
Fe ₂ O ₃	0.9	1.1	1.33	5.11	4.52	2.59	0.90	5.11	2.05	0.52	0.36	0.45
CaO	0.31	0.12	0.14	1.47	1.79	0.77	0.12	1.79	0.80	0.18	0.59	0.22
MgO	0.05	0.06	0.06	0.14	0.12	0.09	0.05	0.14	0.04	0.04	0.04	0.03
Na ₂ O	0.53	0.21	0.23	1.19	1.74	0.78	0.21	1.74	0.67	0.65	0.66	0.69
K ₂ O	0.75	1.51	1.43	1.06	4.78	1.91	0.75	4.78	1.64	0.52	0.52	0.48
MnO	0.01	<0.01	0.01	0.07	0.09	0.05	0.01	0.09	0.04	ND	0.35	-
TiO ₂	0.07	0.15	0.13	0.71	0.46	0.30	0.07	0.71	0.27	0.61	0.31	0.38
P ₂ O ₅	0.01	0.01	0.02	0.06	0.06	0.03	0.01	0.06	0.03	0.20	0.20	0.21
Cr ₂ O ₃	<0.01	<0.01	<0.01	0.01	<0.01	0.01	0.01	0.01	-	-	-	-
Ba	0.02	0.07	0.07	0.08	0.3	0.11	0.02	0.30	0.11			
LOI	0.4	0.8	1.1	4	1.6	1.58	0.40	4.00	1.42			
SUM	99.96	98.73	99.43	99.69	99.5	99.46	98.73	99.96	0.46			
CIA	64	62	63	67	58	63	58	67	3			
PIA	71	82	81	71	66	74	66	82	7			
CIW	77	90	89	74	77	81	74	90	8			
SiO ₂ /Al ₂ O ₃	33.37	30.36	30.53	10.37	6.24	22.18	6.24	33.37	12.80			
K ₂ O/Na ₂ O	1.42	7.19	6.22	0.89	2.75	3.69	0.89	7.19	2.85			
Al ₂ O ₃ /SiO ₂	0.03	0.03	0.03	0.10	0.16	0.07	0.03	0.16	0.06			
K ₂ O/Al ₂ O ₃	0.27	0.50	0.48	0.14	0.41	0.34	0.14	0.14	0.14			

The relatively high ratio values of K₂O/Na₂O (range=0.9 to 7.2; average=3.7) of the sediments are attributed to the common presence of K-bearing minerals such as K-feldspar and some micas (McLennan *et al.*, 1983; Nath *et al.*, 2000; Zhang, 2004; Osae *et al.*, 2006). A strong positive correlation coefficient (r=0.83) between K₂O and Al₂O₃ implies that the concentration of the K-bearing minerals has significance influence on Al distributions and suggest that the relative abundance of these elements is primarily controlled by the content of clay minerals (McLennan *et*

al., 1983; Chris *et al.*, 2013). Based on these ratios, some of the sediment samples can be chemically classified as sub-arkose and sub-litharenites. These conclusions are further supported by low Al₂O₃/SiO₂ ratio (range= 0.03 to 0.16; average=0.07) which further assist in classifying some of the samples as being quartz arenites (Pettijohn *et al.*, 1987, Chris *et al.*, 2013).

The enrichment of the major oxides is calculated as a ratio of the respective oxides value to that of the UCC, PAAS and NASC average values. Based on

UCC, PAAS and NASC, SiO₂ has enrichment values of 1.3, 1.36 and 1.32 respectively indicating their level of abundance relative to earth crust composition. However, all the other major oxides have enrichment less than 1, indicating their depletion relative to the earth crust composition. The depletion in the enrichment values of Na₂O, 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 ions concentrations are being controlled by feldspars and they have been depleted in the analyzed sediment samples. This suggests that the minerals containing these oxides have undergone weathering and dissolution into the surrounding water phase. This also implies the destruction of plagioclase as a result of chemical weathering in the source or

during transportation of the sediments samples from the source.

The correlation matrix of the major oxides is presented in Table 2. SiO₂ has a strong negative correlation with Al₂O₃ content (r = -0.98) connoting that much of SiO₂ is present as quartz grains. More so, SiO₂ has strong negative correlation with all the other oxides indicating its recrystallization. Al₂O₃ has strong positive correlation with all the other oxides indicating their source from aluminosilicate minerals (Jin *et al.*, 2006). Low average value obtained for Al₂O₃/SiO₂ confirms quartz enrichment in the studied sediment samples. The average value obtained for K₂O/Al₂O₃ (0.34) confirms the weathering of plagioclase minerals from the sediments and this must have been gained on the water phase in the area (Akarish and El-Gohary, 2011).

Table 2: Correlation matrix of major oxides in Asa River Sediments

Major Oxides	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	MnO	TiO2	P2O5
SiO2	1.00									
Al2O3	-0.98	1.00								
Fe2O3	-0.95	0.89	1.00							
CaO	-0.98	0.97	0.96	1.00						
MgO	-0.93	0.85	1.00	0.93	1.00					
Na2O	-0.95	0.97	0.89	0.98	0.85	1.00				
K2O	-0.74	0.83	0.49	0.66	0.43	0.73	1.00			
MnO	-1.00	0.98	0.95	1.00	0.92	0.97	0.71	1.00		
TiO2	-0.86	0.76	0.97	0.87	0.99	0.77	0.29	0.85	1.00	
P2O5	-0.97	0.92	0.99	0.97	0.98	0.91	0.57	0.97	0.93	1.00

Geochemistry of the Trace Elements

Out of the trace elements analyzed, the following are above detection limits: Ba, Co, Cs, Ga, Hf, Nb, Rb, Sr, Ta, Th, U, V, W, Zr, Mo, Cu, Pb, Zn and Ni. The result of the trace elements analyzed in

sediments of the study area and their descriptive statistical summary is presented in Table 3. Figure 2 also present the ASC-UCC normalized averages of the trace element concentrations in the sediments.

Table 3: Geochemical results of the trace elements in the analyzed sediment samples and their enrichment based on ASE and UCC average values

Trace Elements	Unit	MDL	ASA-3	ASA-5	ASA-6	ASA-10	ASA-11	average	Min	Max	ASE, ppm	UCC	enrichment (ASC)	enrichment (UCC)
Ba	PPM	1	237	710	620	825	2825	1043.40	237.00	2825.00	500.00	550.00	2.09	1.90
Be	PPM	1	<1	<1	<1	<1	1	1.00	1.00	1.00	3.00	3.00	0.33	0.33
Co	PPM	0.2	2.5	1.6	1.7	8.7	3	3.50	1.60	8.70	19.00	10.00	0.18	0.35
Cs	PPM	0.1	0.4	0.3	0.3	0.3	0.3	0.32	0.30	0.40	5.00	3.50	0.06	0.09
Ga	PPM	0.5	5.4	3	3.4	9.5	19.2	8.10	3.00	19.20	19.00	17.00	0.43	0.48
Hf	PPM	0.1	1.7	23.8	21.9	50.5	38.3	27.24	1.70	50.50	1.80	5.80	15.13	4.70
Nb	PPM	0.1	1.3	2.2	3	8.7	20.1	7.06	1.30	20.10	11.00	25.00	0.64	0.28
Rb	PPM	0.1	20.1	26.9	26.5	21	90.3	36.96	20.10	90.30	140.00	112.00	0.26	0.33
Sn	PPM	1	<1	<1	<1	4	<1	4.00	4.00	4.00	6.00	5.50	0.67	0.73
Sr	PPM	0.5	55.4	66.1	67.4	232.7	267.4	137.80	55.40	267.40	300.00	350.00	0.46	0.39
Ta	PPM	0.1	0.1	0.2	0.3	0.6	1	0.44	0.10	1.00	0.80	2.20	0.55	0.20
Th	PPM	0.2	1.1	2.6	3.1	4.6	1.5	2.58	1.10	4.60	ND	-	-	-
U	PPM	0.1	0.3	1.3	1.4	1.4	0.6	1.00	0.30	1.40	3.70	2.80	0.27	0.36
V	PPM	8	9	15	23	67	8	24.40	8.00	67.00	130.00	60.00	0.19	0.41
W	PPM	0.5	1	<0.5	2.6	1.3	1.8	1.68	1.00	2.60	-	2.00	-	0.84
Zr	PPM	0.1	62.1	959.7	876.5	2182.5	1691.9	1154.54	62.10	2182.50	160.00	190.00	7.22	6.08
Mo	PPM	0.1	0.4	0.4	0.5	1.1	0.5	0.58	0.40	1.10	2.60	-	0.22	-
Cu	PPM	0.1	5.8	5.2	6.6	15.7	8	8.26	5.20	15.70	45.00	25.00	0.18	0.33
Pb	PPM	0.1	2	2.3	4.3	9	5.1	4.54	2.00	9.00	-	20.00	-	0.23
Zn	PPM	1	3	3	3	17	30	11.20	3.00	30.00	95.00	71.00	0.12	0.16
Ni	PPM	0.1	2.6	2.1	2.4	11.5	2.1	4.14	2.10	11.50	68.00	20.00	0.06	0.21
As	PPM	0.5	<0.5	<0.5	<0.5	6.9	<0.5	6.90	6.90	6.90	13.00	-	0.53	-
Cd	PPM	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	0.00	0.00	0.30	-	-	-
Sb	PPM	0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.10	0.10	0.10	1.50	-	0.07	-
Bi	PPM	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	0.00	0.00	-	-	-	-
Ag	PPM	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	0.00	0.00	0.07	-	-	-
Au	PPB	0.5	<0.5	<0.5	<0.5	0.6	<0.5	0.60	0.60	0.60	0.40	-	1.50	-
Hg	PPM	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.00	0.00	1.40	-	-	-
Tl	PPM	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	0.00	0.00	20.00	-	-	-
Se	PPM	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-	0.00	0.00	0.60	-	-	-

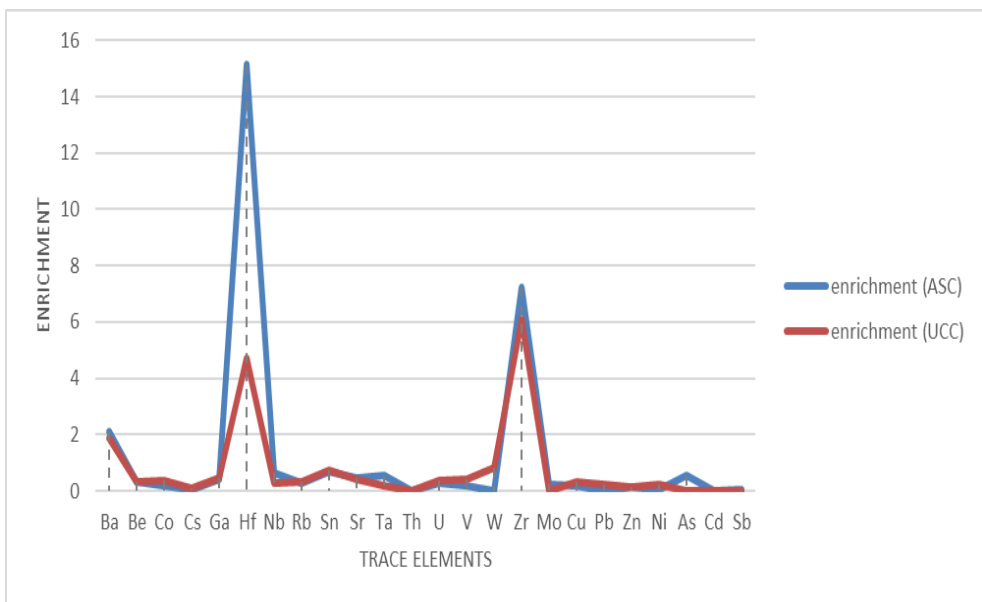


Figure 2: ASC, UCC-normalized averages of trace element concentrations for Asa River sediments (after Taylor and McLennan, 1985)

The trace elements have positive correlation with Al_2O_3 reflecting association of most elements with clay fraction with an exception of Cs having negative correlation ($r=-0.40$)- Akarish and El-Gohary, 2011. The transition metals Co, Ni and V ranged from 1.6 to 8.7 ppm (average= 3.5 ppm), 2.1 to 11.5 ppm (average=4.14 ppm) and 8 to 67 ppm (average=24.4 ppm). It has been reported that these transition metals are mainly concentrated in the clays or metal oxides (Turekian and Michael, 1960; Akarish and El-Gohary, 2011). Positive correlation of Co, Ni, Zn and Cu with Fe_2O_3 ($r=0.78, 0.67, 0.88$ and 0.83) respectively and Al_2O_3 ($r=0.42, 0.25, 1.00$ and 0.48) respectively also connotes that these elements are linked with iron oxides and probably with clay minerals.

The average concentration of each trace metal was compared with UCC and ASC to determine the extent of enrichment of the sediments. The enrichment was calculated by the ratio of individual element concentration in the analyzed sediments to UCC average of equivalent metal. The concentrations of Ba, Rb, Sr and Zr are relatively higher than the other metals. Their respective average concentrations are: 1043, 37, 138 and 1155 ppm. By comparing the trace metals/elements average concentrations with UCC and ASC, it is observed that Ba, Hf and Zr are significantly enriched in the sediments of Asa River sediments because their respective enrichment values are greater one. Others are having enrichment values less than one (depleted). Depletions of these metals

could reflect intensive chemical weathering and recycling. Relatively high value of Sr (range=55.4 to 267.4 ppm; average=137.8) suggests the presence of calcic plagioclase in the sediments (Akarish and El-Gohary, 2011). Almost all the trace elements correlate positively with Al_2O_3 which is a good indication of aluminosilicate minerals association.

Geochemistry of Rare Earth Elements

Table 4 presents the geochemical results and the statistical summary of the rare earth elements in the studied sediments and their comparisons with UCC (Average Upper Continental Crust) and ASC (Average Shale Concentration) average concentrations (Taylor and McLennan, 1985). Tables 5 and 6 also present the correlation matrixes of the rare earth elements with some of the major oxides of the studied sediments. The relatively high concentrations of Ce in the sediments may be from the formation of glauconites (Jarrar *et al.*, 2000). All the enrichment values computed for the rare earth elements are less than one depicting depletion of metals in the sediments phase. The depletion is as a result of intensive chemical weathering of the sediment overtime. All the rare earth elements have strong positive correlation with Al_2O_3 indicating that the source of the elements is from aluminosilicate minerals. Consequently, the good correlation of the rare earth elements with Al_2O_3 also indicates that the rare earth elements are mostly concentrated in the clay fraction (Talyor and McLennan, 1985).

Table 4: Geochemical results of the rare earth elements of Asa River sediments and their enrichment based on ASE and UCC average values

Rare Earth Elements	Unit	MDL	ASA-3	ASA-5	ASA-6	ASA-10	ASA-11	average	Min	Max	ASE, ppm	UCC	enrichment (ASC)	enrichment (UCC)
Y	PPM	0.1	3.4	5.9	6.1	13.5	20.2	9.82	3.40	20.20	26.00	22.00	0.38	0.45
La	PPM	0.1	5	5.3	6.5	18.9	27.3	12.60	5.00	27.30	92.00	30.00	0.14	0.42
Ce	PPM	0.1	12.9	10.9	12.8	53.5	55.3	29.08	10.90	55.30	59.00	64.00	0.49	0.45
Pr	PPM	0.02	1.1	1.22	1.54	4.58	6.64	3.02	1.10	6.64	5.60	7.10	0.54	0.42
Nd	PPM	0.3	3.9	4.4	5.7	17.9	27.3	11.84	3.90	27.30	24.00	26.00	0.49	0.46
Sm	PPM	0.05	0.65	0.78	0.99	2.91	5.19	2.10	0.65	5.19	6.40	4.50	0.33	0.47
Eu	PPM	0.02	0.19	0.2	0.27	0.86	1.77	0.66	0.19	1.77	1.00	0.88	0.66	0.75
Gd	PPM	0.05	0.65	0.81	0.97	2.57	4.59	1.92	0.65	4.59	6.40	3.80	0.30	0.50
Tb	PPM	0.01	0.1	0.14	0.15	0.37	0.66	0.28	0.10	0.66	1.00	0.64	0.28	0.44
Dy	PPM	0.05	0.57	0.87	0.9	2.11	3.83	1.66	0.57	3.83	4.60	3.50	0.36	0.47
Ho	PPM	0.02	0.13	0.22	0.21	0.48	0.83	0.37	0.13	0.83	1.20	0.80	0.31	0.47
Er	PPM	0.03	0.38	0.77	0.68	1.63	2.42	1.18	0.38	2.42	2.50	2.30	0.47	0.51
Tm	PPM	0.01	0.05	0.13	0.12	0.26	0.36	0.18	0.05	0.36	0.20	0.33	0.92	0.56
Yb	PPM	0.05	0.34	0.96	0.91	2	2.39	1.32	0.34	2.39	2.60	2.20	0.51	0.60
Lu	PPM	0.01	0.05	0.18	0.16	0.37	0.42	0.24	0.05	0.42	2.80	0.32	0.08	0.74

Table 5: correlation matrix between the rare earth elements in Asa river sediments

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Y	1.00													
La	0.99	1.00												
Ce	0.93	0.96	1.00											
Pr	0.99	1.00	0.96	1.00										
Nd	0.99	1.00	0.95	1.00	1.00									
Sm	0.99	0.99	0.92	0.99	1.00	1.00								
Eu	0.98	0.98	0.89	0.98	0.99	1.00	1.00							
Gd	0.99	0.99	0.91	0.99	0.99	1.00	1.00	1.00						
Tb	0.99	0.99	0.91	0.99	0.99	1.00	1.00	1.00	1.00					
Dy	0.99	0.98	0.90	0.98	0.99	1.00	1.00	1.00	1.00	1.00				
Ho	0.99	0.98	0.90	0.98	0.99	1.00	0.99	1.00	1.00	1.00	1.00			
Er	1.00	0.99	0.93	0.99	0.99	0.99	0.98	0.99	0.99	0.99	0.99	1.00		
Tm	0.99	0.98	0.93	0.98	0.98	0.97	0.96	0.97	0.97	0.97	0.98	1.00	1.00	
Yb	0.97	0.96	0.94	0.96	0.96	0.94	0.91	0.94	0.94	0.94	0.95	0.98	0.99	1.00

Table 6: correlation matrix between some rare earth elements and the major oxides in the studied sediments

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O
Y	1.00													
La	0.99	1.00												
Ce	0.93	0.96	1.00											
Pr	0.99	1.00	0.96	1.00										
Nd	0.99	1.00	0.95	1.00	1.00									
Sm	0.99	0.99	0.92	0.99	1.00	1.00								
Eu	0.98	0.98	0.89	0.98	0.99	1.00	1.00							
Gd	0.99	0.99	0.91	0.99	0.99	1.00	1.00	1.00						
Al2O3	0.99	1.00	0.94	1.00	1.00	1.00	0.99	1.00	1.00					
Fe2O3	0.89	0.92	0.99	0.92	0.91	0.86	0.83	0.86	0.89	1.00				
CaO	0.95	0.98	0.99	0.98	0.97	0.95	0.93	0.94	0.97	0.96	1.00			
MgO	0.86	0.89	0.97	0.89	0.88	0.82	0.78	0.82	0.85	1.00	0.93	1.00		
Na2O	0.94	0.97	0.95	0.97	0.97	0.96	0.96	0.96	0.97	0.89	0.98	0.85	1.00	
K2O	0.83	0.78	0.58	0.78	0.80	0.85	0.88	0.86	0.83	0.49	0.66	0.43	0.73	1.00

Weathering indications

The intensity of weathering in siliciclastic soils/sediments can be denoted through examination of the relationships among alkali and alkaline earth elements (Nesbitt and Young, 1982). Having known that the upper crust is dominated by the presence of feldspars (Nesbitt and Young, 1982, 1984), the dominant process during chemical weathering and soil/sediment formation is the degradation of mobile feldspars from source rocks to secondary clay minerals. CIA values, ranging from 58 to 67 (average, 63) fall within intermediate silicate weathering and extreme silicate weathering. PIA ranges from 66 to 82 (average, 74) indicating intermediate to extreme silicate weathering and CIW ranges from 74 to 90 (average, 81) indicating extreme silicate weathering. The values of CIA, CIW and PIA obtained reflect high weathering conditions either in the original terrain or during transportation. Furthermore, high CIA values, suggest derivation from a stable cratonic source (Hossain *et al.*, 2010; Akarish and El-Gohary, 2011). Consequently, 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 this resulted in low CaO content (range, 0.12 to 1.79; average, 0.77), especially with increasing PIA values. This suggests 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ is a commonly employed index of sediment maturation in which case the 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. It has been reported that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for the studied samples is 22 (range=6 to 33), indicating matured sediments/soils.

Assessment of Metal Contamination in the studied Sediments

The aim of determining metals contamination in Asa River sediments is to assess the possible environmental impacts of anthropogenic, agricultural activities and the influence of weathering of surrounding rocks on the sediment metals' distributions. The impacts of these activities are evaluated using the following parameters; contamination factor (CF), degree of contamination and geo-accumulation. Several published researches have made use of the Average Crustal Abundance of elements in shale fraction to determine contamination indexes of sediments. Hence, this study has also adopted the same indexes to determine the extent of contamination in the sediment phase of Asa river sediments. The computed contamination indexes for major, trace and rare earth metals are presented in Tables 7, 8 and 9 respectively. The average contaminated factor value (CF=5.49) calculated for Si indicated that it is highly enriched in the sediment phase. Similarly, it depicts more of anthropogenic influence. However, the average values of other major metals are <1 which depicts influence of weathering of aluminosilicate minerals from the rock

types of the study area. The degree of contamination of the major metals is 8.64 which connote considerable degree of contamination. The degree of contamination of the trace elements is 59.29 (very high degree of contamination) according to ASE. The geo-accumulation index for the major metals shows that Si with an average of

1.86 is moderately contaminated while the geo-accumulation of the trace elements shows practically no contamination. The geo-accumulation of the trace elements according to ASE indicates negative values depicting practically no contamination except Hf (2.71) and Zr (1.58) which indicate some extent of contamination.

Table 7: contamination indexes for the major metals in the studied sediments (after average shale concentration)

Contamination Factor											Deg.C
	Si	Al	Fe	Ca	Mg	Na	K	Mn	Ti	P	
Average	5.49	0.37	0.38	0.25	0.03	0.60	0.59	0.33	0.40	0.20	8.64
Min	4.64	0.19	0.13	0.04	0.02	0.16	0.23	0.00	0.09	0.06	7.19
Max	6.03	0.77	0.76	0.58	0.06	1.34	1.49	0.82	0.93	0.37	11.33
Median	5.87	0.20	0.20	0.10	0.02	0.41	0.45	0.09	0.20	0.12	7.36
Stdev	0.62	0.26	0.30	0.26	0.02	0.52	0.51	0.37	0.36	0.16	1.90
Geoaccumulation Index											
	Si	Al	Fe	Ca	Mg	Na	K	Mn	Ti	P	
Average	1.86	-2.28	-2.35	-3.45	-5.57	-1.80	-1.66	-6.09	-2.43	-3.35	
Min	1.63	-3.01	-3.49	-5.27	-6.22	-3.21	-2.68	-20.28	-4.04	-4.59	
Max	2.01	-0.97	-0.99	-1.37	-4.74	-0.16	-0.01	-0.87	-0.70	-2.00	
Median	1.97	-2.91	-2.93	-3.90	-5.96	-1.87	-1.75	-4.04	-2.94	-3.59	
Stdev	0.17	0.94	1.19	1.84	0.67	1.37	1.01	8.07	1.38	1.30	

Table 8: contamination indexes for the trace elements (after Average Shale Concentration)

Contamination Factor	Average	Min	Max	Med	Stdev	Geoaccumulation Index	Average	Min	Max	Med	Stdev
	Ba	2.09	0.47	5.65	1.42		2.04	Ba	0.01	-1.66	1.91
Be	0.07	0.00	0.33	0.00	0.15		-2.17	-2.17	-2.17	-2.17	
Co	0.18	0.08	0.46	0.13	0.16	Co	-3.34	-4.15	-1.71	-3.51	0.99
Cs	0.06	0.06	0.08	0.06	0.01	Cs	-4.56	-4.64	-4.23	-4.64	0.19
Ga	0.43	0.16	1.01	0.28	0.35	Ga	-2.17	-3.25	-0.57	-2.40	1.11
Hf	15.13	0.94	28.06	13.22	10.23	Hf	2.71	-0.67	4.23	3.14	1.95
Nb	0.64	0.12	1.83	0.27	0.71	Nb	-1.93	-3.67	0.28	-2.46	1.59
Rb	0.26	0.14	0.65	0.19	0.21	Rb	-2.78	-3.39	-1.22	-2.99	0.89
Sn	0.13	0.00	0.67	0.00	0.30	Sn	-1.17	-1.17	-1.17	-1.17	
Sr	0.46	0.18	0.89	0.22	0.34	Sr	-2.05	-3.02	-0.75	-2.74	1.10
Ta	0.55	0.13	1.25	0.38	0.46	Ta	-1.89	-3.58	-0.26	-2.00	1.30
U	0.27	0.08	0.38	0.35	0.14	U	-2.70	-4.21	-1.99	-2.09	0.99
V	0.19	0.06	0.52	0.12	0.19	V	-3.47	-4.61	-1.54	-3.70	1.24
W	0.67	0.00	1.30	0.65	0.48	W	-0.93	-1.58	-0.21	-0.97	0.60
Zr	7.22	0.39	13.64	6.00	5.09	Zr	1.58	-1.95	3.18	2.00	2.05
Mo	0.22	0.15	0.42	0.19	0.11	Mo	-2.86	-3.29	-1.83	-2.96	0.60
Cu	0.18	0.12	0.35	0.15	0.10	Cu	-3.15	-3.70	-2.10	-3.35	0.63
Pb	0.23	0.10	0.45	0.22	0.14	Pb	-2.94	-3.91	-1.74	-2.80	0.89
Zn	0.12	0.03	0.32	0.03	0.13	Zn	-4.40	-5.57	-2.25	-5.57	1.62
Ni	0.06	0.03	0.17	0.04	0.06	Ni	-5.01	-5.60	-3.15	-5.41	1.05
As	0.11	0.00	0.53	0.00	0.24	As	-1.50	-1.50	-1.50	-1.50	
Cd	0.00	0.00	0.00	0.00	0.00	Sb	-4.49	-4.49	-4.49	-4.49	
Sb	0.01	0.00	0.07	0.00	0.03	Au	-3.32	-3.32	-3.32	-3.32	
Ag	0.00	0.00	0.00	0.00	0.00						
Au	0.03	0.00	0.15	0.00	0.07						
Hg	0.00	0.00	0.00	0.00	0.00						
Tl	0.00	0.00	0.00	0.00	0.00						
Se	0.00	0.00	0.00	0.00	0.00						
Deg. Of Cont.	59.29	3.98	201.21	22.75	80.71						

Table 9: Table: contamination indexes of rare earth element in the studied sediments (after average shale concentration, 2013)

Contamination Factor																Deg. Cont.
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Average	0.38	0.14	0.49	0.54	0.49	0.33	0.66	0.30	0.28	0.36	0.31	0.47	0.92	0.51	0.08	6.26
Min	0.13	0.05	0.18	0.20	0.16	0.10	0.19	0.10	0.10	0.12	0.11	0.15	0.25	0.13	0.02	2.04
Max	0.78	0.30	0.94	1.19	1.14	0.81	1.77	0.72	0.66	0.83	0.69	0.97	1.80	0.92	0.15	13.65
Med	0.23	0.07	0.22	0.28	0.24	0.15	0.27	0.15	0.15	0.20	0.18	0.31	0.65	0.37	0.06	3.41
Stdev	0.27	0.11	0.39	0.44	0.43	0.31	0.68	0.26	0.24	0.29	0.24	0.33	0.62	0.33	0.06	4.93
Geo-accumulation Index																
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Average	-2.28	-3.82	-2.00	-1.88	-2.06	-2.68	-1.79	-2.74	-2.77	-2.42	-2.59	-1.98	-1.01	-1.86	-4.50	
Min	-3.52	-4.79	-3.02	-2.93	-3.21	-3.88	-2.98	-3.88	-3.91	-3.60	-3.79	-3.30	-2.58	-3.52	-6.39	
Max	-0.95	-2.34	-0.68	-0.34	-0.40	-0.89	0.24	-1.06	-1.18	-0.85	-1.12	-0.63	0.26	-0.71	-3.32	
Med	-2.68	-4.41	-2.78	-2.45	-2.66	-3.28	-2.47	-3.31	-3.32	-2.94	-3.03	-2.28	-1.21	-2.02	-4.54	
Stdev	1.03	1.14	1.19	1.19	1.27	1.31	1.43	1.21	1.13	1.11	1.06	1.06	1.10	1.12	1.23	

The rare earth metals/elements have CF <1 depicting contributions from chemical weathering of the rock types of the area (Tijani *et al.*, 2007). The degree of contamination is 6.26, indicating low degree of contamination. These rare earth elements/metals are associated with aluminosilicate minerals like: biotite, muscovite and plagioclase feldspar.

Conclusion

The preliminary geochemical assessment of Asa River sediments, north central Nigeria has been carried out. SiO₂, Zr and Ce have the highest values among the major oxides, trace elements and rare earth elements concentrations respectively. The values for SiO₂, Al₂O₃, Fe₂O₃, TiO₂, Zr, and SiO₂/Al₂O₃ indicate that the sediments are mineralogically matured. SiO₂, Ba, Hf, Zr are highly enriched with respect to UCC and ASC average values. Computed values for weathering indications indicate some degree of intensive weathering of the sediments. The metals/elements ranged from low contamination factor to very high contamination factor, low degree of contamination to very high degree of contamination and the geo-accumulation index ranged from practically no contamination to moderately contaminated. The Contamination Factors revealed the influence of both anthropogenic and geogenic on the metal concentrations in the sediments.

References

Akarish, A.I.M. & El-Gohary, A.M. (2011). Provenance and Source Area Weathering Derived from the Geochemistry of Pre-Cenomanian Sandstones, East Sinai, Egypt. *Journal of Applied Sciences*, 11: 3070-3088.

Atiemo, M. S., Ofosu, G. F., Mensah, H. K., Tutu, A. O., Linda-Palm, N.D.M. & Blankson, S. A. (2011). Contamination Assessment of Heavy Metals in Road Dust from Selected Roads in Accra, Ghana. *Research Journal of Environmental and Earth Sciences* 3(5): 473-480.

Chris, A., Modupe, M. David, A., Jacob., K. Daniel, A. & Daniel, B. (2013). Geochemistry and provenance of sandstones from Anyaboni and surrounding areas in the voltaian basin, Ghana. *International Research Journal of Geology and Mining (IRJGM)* 3(6):206-212.

Fedo, C. M., Nesbitt, H. W. & Young, G. M. (1995). Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleo-weathering conditions and provenance. *Geology*, 23: 921-924.

Hossain, H. M. Z., Roser, B.P. & Kimura, J. I. (2010). Petrography and whole-rock geochemistry of the Tertiary Sylhet succession, northeastern Bengal Basin, Bangladesh: Provenance and source area weathering. *Sediment. Geol.*, 228:171-183.

- Huu, H.H., S. Rudy & Damme, A.V. (2010). Distribution and contamination status of heavy metals in estuarine sediments near Cau Ong harbor, Ha Long Bay, Vietnam. *Geol. Belgica*, 13(1-2):37-47.
- Jarrar, G., Amireh, B. & Zachmann, D. (2000). The major, trace and rare earth element geochemistry of glauconites from the early Cretaceous Kurnub Group of Jordan *Geochemical Journal*, (34): 207 -222.
- Jin, Z. F., Li, J. Cao, S., Wang & Yu, J. (2006). Geochemistry of Daihai Lake sediments, Inner Mongolia, north China: Implications for provenance, sedimentary sorting and catchment weathering. *Geomorphol.*, 80: 147-163.
- Joo, Y.J., Lee, Y. & Baib, Z. (2005). Provenance of the Qingshuijian Formation (Late Carboniferous), NE China: Implications for tectonic processes in the northern margin of the North China block. *Sediment. Geol.*, 177: 97-114.
- Le Maitre, R.W., (1976). The chemical variability of some common igneous rocks. *J. Petrol.*, 17: 589-637.
- McLennan, S.M., Taylor, S.R., & Eriksson, K.A. 1983. Geochemistry of Archaean shales from the Pilbara supergroup, western Australia, *Geochimica et cosmochimica Acta* 47 (7):1211-1222.
- Muller, G. (1979). Index of geo-accumulation in the sediments of the Rhine River. *Geology Journal*, 2: 108-118.
- Nath, B.N., Kunzendorf, H. and Pluger, W.L. 2000. Influence of provenance, weathering and sedimentary processes on the elemental ratio of the fine-grained fraction of the bed sediments from the Vembanad Lake and the adjoining continental shelf, southwest coast of India, *Journal of Sedimentary Res.* 70:1081-1094.
- Nesbitt, H. W. & Young, G. M. (1984). Prediction of some weathering trends of plutonic and volcanic rocks based on thermodynamic and kinetic considerations. *Geochim. Cosmochim. Acta*, 48: 1523-1534.
- Nesbitt, H. W. & Young, G. M. (1982). Early proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature*, 299: 715-717.
- Omotoso, O.A. & Tijani, M.N. (2011). Preliminary study of hydrochemistry of Eleyele Lake and its Tributaries, Ibadan, Nigeria. Adamawa State University, *Journal of Scientific Research*. 1(2):102-120.
- Osa, S., Asiedu, D.K., Banoeng-Yakubo, B., Koeberli, C. & Dampare, S.B. (2006). Provenance and tectonic setting of late Proterozoic bentonite sandstones of southeastern Ghana: evidence from geochemistry and detrital modes, *Journal of Afri. Earth Sci.* 44:85-96.
- Roser, B. P., Cooper, R. A., Nathan, S. & Tulloch, A. J. (1996). Reconnaissance sandstone geochemistry, provenance, and tectonic setting of the lower Paleozoic terranes of the West Coast and Nelson, New Zealand. *New Zealand J. Geol. Geophys.* 39: 1-16.
- Roy, P. D., Caballero, M. Lozano, R. & Smykatz-Kloss, W. (2008). Geochemistry of late quaternary sediments from Tecocomulco lake, central Mexico: Implication to chemical weathering and provenance. *Chemie der Erde*, 68: 383-393.
- Taylor, S.R. & McLennan, S.M. (1985). *The Continental Crust: Its Composition and Evolution*.

- Blackwell, Oxford, ISBN-13: 978-0632011483, pp: 312.
- Tijani, M.N., Okunlola, O.A. & Ikpe, E.U. 2007. A geochemical assessment of water and bottom sediments contamination of Eleyele Lake catchment, Ibadan, Southwestern Nigeria. 19(1): 105-120.
- Turekian, K.K. & Michael, H.C. (1960). The geochemistry of chromium, cobalt and nickel. *Inter. Geol. Cong.*, 1: 14-27.
- Zhang, K.L. (2004). Secular geochemical variation of the lower cretaceous silica clastic from central Tibet (china) indicate a tectonic transition from continental collision to back-arc rifting, *earth and planetary science letters*, 229:73-89.