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Heavy Metal Pollution Assessment of Sediments of River Gora in Minna, North-Central Nigeria: Statistical Approach

S.O. Obaje[1*] I.A. Akpoborie[2] F.C. Ugbe[2]
1.Department of Earth Sciences, Salem University, P.M.B. 1060, Lokoja, Nigeria
2.Department of Geology, Delta State University, P.M.B. 1, Abraka, Nigeria
* E-mail of the corresponding author: isolobaje2004@yahoo.com

Abstract
The main aim of this study is the assessment of the concentration and pollution levels of heavy metals in the sediments of River Gora. The result of the samples in ppm was exported from Microsoft Excel to SPSS Version 20. Twelve heavy metals from 24 locations were subjected to principal component analysis (PCA). Before PCA was done, the suitability of the data for factor analysis was assessed. Four component factors extracted revealed the following heavy metal associations, namely: component 1 (Fe, Cr, Sr, Cu and Zn), component 2 (Fe, Cu, V, Mo, Zn, As and Mn), component 3 (Ni, Sr, Cu, Pb, As and Mn) and component 4 (Ni, Sr, Zn and Sb). While some of the heavy metals were from lithogenic origin, others were from anthropogenic and mixed sources. The computed enrichment factors revealed that V, Cu, Mo, Sb, Fe and Mn are enriched while Cr, Ni, Zn, As, Sr and Pb suffered depletion in the study area. The results revealed the pollution index for V, Cr, Ni, Cu, Zn, As, Sr, Mo, Pb, Fe and Mn on scale of unpolluted to moderately polluted without environmental health risk; however, Sb indicated extremely high pollution level.

Keywords Heavy Metals, Pollution Index, Health Risk, River Gora, Minna, Nigeria

1. Introduction

The main aim of this paper is to assess the concentrations and pollution levels of V, Cr, Ni, Cu, Zn, As, Sr, Mo, Pb, Sb, Fe and Mn from sediments from River Gora and use statistical approach to process the data into useful interpretational format using SPSS Version 20. According to Wikipedia [1] define a heavy metal as any metal or metalloid of environmental concern. Criteria used to define heavy metals included density, atomic weight, atomic number, or periodic table position. Examples of heavy metals are Cr, Co, Ni, Cu, Zn, As, Ag, Cd, Sb, Hg, Pb, etc. (Wikipedia, 2014). The study area lies between latitude $9^{0}33^{'}$N and $9^{0}34^{'}$N and longitude $6^{0}34^{'}$E and $6^{0}35^{'}$E in Minna area of North-central Nigeria. Accessibility to the sampling locations is via Chanchaga-Tegina road, minor roads, footpaths and the river channel (Fig. 1).

The study area is covered by “guinea woodland savannah” vegetation. This vegetation comprises typical combinations of tall grasses, shrub and scattered trees with denser tree cover along drainage channels. Cotton and sugar plantations are found in the study area. The vegetation cover helps to prevent wind-scoring of unconsolidated soils during the wet season, but not during the dry season (Iloeje, 1991).

1.1. Geology of Study Area

The study area is underlain by the Precambrian Basement Complex of North-Central Nigeria. The Basement Complex is one of the three major litho-petrological components that make up the geology of Nigeria. The Nigerian Basement Complex forms a part of the Pan-African mobile belt and lies between the West African and Congo cratons and south of the Tuareg Shield (Black, 1980; Grant et al., 1969). It is intruded by the Mesozoic Calc-alkaline ring complexes (Younger Granites) of the Jos Plateau and is unconformably overlain by Cretaceous and Recent sediments. The Nigerian Basement Complex was affected by the Pan-African (600 ± 150 Ma) orogeny and it occupies the reactivated region which resulted from plate collision between the passive continental margin of the West African craton and the active Pharusian continental margin (Burke and Dewey, 1972).

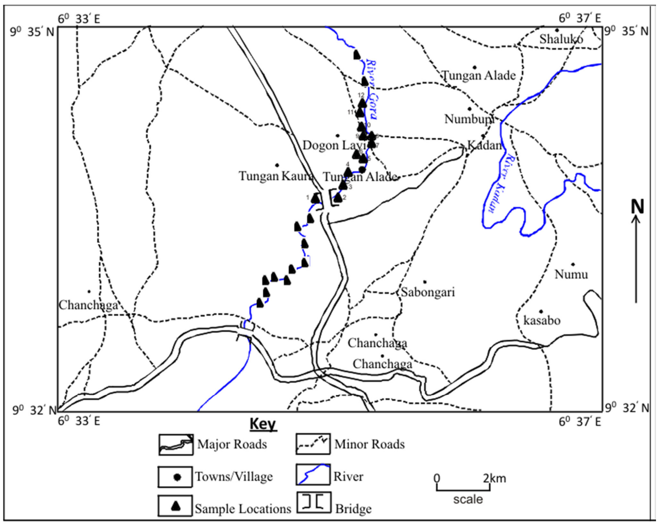

Figure 1. Road Map of Study Area showing Sampling Locations

The Basement rocks are believed to be the results of at least four major orogenic cycles of deformation, metamorphism and remobilisation corresponding to the Liberian (2,800 ± 200 Ma), the Eburnean (2,000 ± 200 Ma), the Kibaran (1,100 ± 200 Ma), and the Pan-African cycles (600 ± 150 Ma). The first three cycles were characterized by intense deformation and isoclinals folding accompanied by regional metamorphism, which was further followed by extensive migmatization. The Pan-African deformation was accompanied by a regional meta-induced syntectonic granites and homogenous gneisses. Late tectonic emplacement of granites and granodiorites and associated contact metamorphism accompanied the end stages of this last deformation. The end of the orogeny was marked by faulting and fracturing (Gandu et al., 1986). The granitic emplacement was probably controlled by fractures within the Basement, and also showed outcrop pattern indicating that the Older Granite cut across all other structures with sharp and chilled contact. Within the Basement Complex of Nigeria, four major petro-lithological units are distinguishable, namely: Migmatite-Gneiss-Quartzite Complex, Schist belts, Pan-African Granitoids, and under-formed acid and basic dykes (Dada, 2006).

The dominant lithologic unit in River Gora area is schist. The area has undulating topography comprising high hills and valleys with covered vegetation. The highest elevation within the area is about 240 meters above mean sea level. The area is drained principally by River Gora. The drainage pattern of the area is dendritic. Most of the streams that drain the area are seasonal. Several quartz veins cross-cut the schist rocks in the area.

2. Materials and Methods

The research method involved fieldwork and laboratory sample preparation and analysis. In the field, the following materials were used, namely: location map, plastic samplers, plastic panning bowls, set of sieves, Global Positioning System (GPS), digital camera, kraft envelops, nylon bags, plastic hand gloves, permanent markers, field notebook and rubber boots. In the laboratory, the following materials were used, namely: weighing balance (model: ScoutPro SPU601 S/N-7123270179), brush, set of sieves, sieves shaker (STSJ-4 digital high frequency sieves shaker: S/N-100064) and cardboard. The fieldwork involved the collection of River Gora sediments and the recording of the geographical coordinates of the sediments sampling points using GPS. Twenty-four stream sediments taken at depths of 30-50 cm with the aid of plastic sampler were wet sieved and packed into labeled brown kraft envelopes, left to sun dry and transported to field base camp for onward transportation to the laboratory.

Sample preparation via dry sieving was carried out in the Department of Geology Laboratory of the Delta State University, Abraka, South-southern Nigeria. 10 g from 63 µm fractions of each sample were taken to the National Geochemical Laboratory of the Nigerian Geological Survey Agency in Kaduna, North-western Nigeria for X-Ray Fluorescence spectrometric analysis. The stream sediment samples were crushed to less than 63 microns with the aid of a Tema vibrating mill before sieving to 60 µm. Beads for major element analysis expressed in oxide weight percent were prepared by first drying the pulverized samples in an oven at 110 ^{0}C for 24 hours to remove moisture content. 5 grams of the dry sample was weighed in the silica crucible and then ignited in the furnace at 1,000 ^{0}C for 2 to 3 hours for the calcination of impurities in the sample powder. Thereafter, samples were removed from the furnace and allowed to cool to room temperature in desiccators. Each ignited sample powder was weighed again to determine the weight of calcinated impurities which were H_2O^-, H_20^+ and CO_2. 1 gram of stored ignited sample powder and exactly 5 times of flux (x-ray flux-type)

66%:34% (66% lithium tetraborate: 34% lithium metaborate) was added to lower the vitrification temperature. The weighed mixture was properly mixed in a Platinum dish and ignited in the pre-set furnace (Eggon-2 Automatic Fuse Bead Maker) at 1,500 ^{0}C for 10 minutes to form glass bead. Each glass bead was labeled and slotted into the computerized XRF (Epsilon-5 Panalytical model) for major oxide analysis measured in weight percentages. The trace elemental analysis was carried out using compressed powder pellets. The pellets were prepared by weighing 3 grams of oven-dried samples and 3 grams flux (cellulose-powder) added as a binder and dispersive agent and shaken in small plastic containers for 12 minutes. The appropriately blended mixture was then compressed by applying pressure of 1,500 kgm^{-2} electronic compressors. The pellets were placed in the computer programmed X-Ray Fluorescence spectrometer (XRF) and the conditions for trace elemental analysis were set to give the result in part per million (ppm).

3.0 Results and Discussion

In descending order of mean concentrations, the heavy metals analyzed are; Sr (181.50 ppm), V (112.33 ppm), Cr (43.87 ppm), Cu (42.42 ppm), Zn (39.58 ppm), Sb (14.17 ppm), Ni (12.75 ppm), Fe (9.43 ppm), Mo (4.75 ppm), As (2.50 ppm), and Mn (0.19 ppm) (Table 1). Fe concentration in the study is 135 times enriched in comparison to its crustal baseline concentration. Sb is 35 times higher than its crustal concentration. Additionally, Mo, Cu and V have 4.32, 1.52 and 1.16 times, respectively, than their crustal baseline concentrations. On the other hand, Cr, Ni, Zn, As, Sr, Pb and Mn have lesser concentrations in comparison to their crustal baseline concentrations (Table 2). Assessment of the heavy metal pollution using Geoaccumulation Index indicated that V, Cr, Ni, Cu, Zn, As, Sr, Mo, Pb, Fe and Mn are below zero and occupied 0-1 Igeo value and Igeo class of 1 which indicated unpolluted to moderately polluted (Tables 3 and 4). On the other hand, Sb have Igeo value of > 5 in Igeo class 6 that indicated extremely polluted. Sb concentration in the study area is of environmental concern (Tables 3 and 4).

V has positive correlation with Cr, Ni, Zn, As, Sr, Sb, Fe and Mn but negatively correlated with Cu, Mo and Pb. On the other hand, Fe is positively correlated with V, Cr, Ni, Cu, Zn and As but negatively correlated with Sr, Mo, Pb and Sb. Mn is positively correlated with V, Ni, Zn, Sr and Fe but negatively with Cr, Cu, As, Mo, Pb and Sb. Lastly, As is positively correlated with V, Cr, Cu, Zn, Pb, Sb and Fe but negatively with Ni, Sr, Mo and Mn (Table 5).

To decipher the factors responsible for the heavy metal concentration and association, factor analysis and principal component analysis were used after the result of the samples in ppm was exported from Microsoft Excel to SPSS Version 20. Twelve heavy metals from 24 locations were subjected to principal component analysis (PCA) involving three steps, namely: initial, extraction and rotation. Prior to the application of the principal component analysis, the appropriateness of the data for factor analysis was carried out. The correlation matrix generated indicated the presence of many coefficients of 0.3 and above. The use of the Kaiser-Meyer-Oklin (KMO) measure of sampling adequacy gave 0.724 to 0.972 (Table 6) that was interpreted to be very good to excellent because the recommended baseline value of 0.6 was exceeded. Furthermore, the Bartlett's test of sphericity yielded statistical significance that further strengthened validity of the factorability of the correlation matrix of the heavy metal concentrations in the study area. Four component factors were extracted from the Principal Component Analysis using eigenvalues greater than 1 and they explained 33.40%, 25.94%, 13.17% and 12.18% of the variance, respectively. The cumulative per cent of the variance of the initial eigenvalues and extracted sums of squared loading was 84.68% (Table 7). Additionally, the scree plot (Fig. 2) revealed a clear break after the fourth component and that further established the retention of the four components for further analysis and interpretation using Varimax with Kaiser Normalization and rotated solution. The four component solution revealed the cumulative per cent of the variance as 25.20%, 48.13%, 69.79% and 84.68% for components 1, 2, 3 and 4, respectively (Table 8). The Varimax with Kaiser Normalization and rotated solution gave cumulative per cent (84.68%) of rotation sums of squared loading for component 4 (Table 9) which was consistent with the values revealed in the unrotated Principal Component Analysis extraction loading (Table 8). Using factor scores, outliers were eliminated from the data set. The Chronbach's alpha reliability of summated scale indicated that heavy metals from mixed origin registered impact on the internal consistency of the scale. The Principal Component Analysis was validated by splitting the entire samples into two using 519,447 as the random number seed. Each of the split was computed at less or equal to 0.50. The first split revealed that the absence of outlier had no impact on the internal consistency of the variables (Table 10), while the second split revealed otherwise (Table 11). Rotated Principal Component Analysis solution (Table 9) gave the following heavy metal associations given as components, namely: component 1 (Fe, Cr, Ni, Sr, Cu and Zn), component 2 (Fe, Cu, V, Mo, Zn, As and Mn), component 3 (Ni, Sr, Cu, Pb, As and Mn) and component 4 (Ni, Sr, Zn and Sb). Fe appeared in components 1 and 2, while Cu appeared in component 1, 2 and 3. On the other hand, Ni and Sr appeared in components 1, 3 and 4; while Zn appeared in components 1, 2 and 4. Conversely, Mn appeared in components 2 and 3. The results revealed that four factors controlled the heavy metal distribution in the study area.

The correlation matrix corroborated with the inference made with the Principal Component Analysis that the heavy metals from lithogenic origin are Cr, As, Fe and Mn, while those from anthropogenic origin are Sb, Zn, and Sr. On the other hand, those from mixed origin are V, Ni, Mo, Pb, Sb, Zn, Sr and Cu. The computed enrichment factors revealed that V, Cu, Mo, Sb, Fe and Mn are enriched while Cr, Ni, Zn, As, Sr and Pb are depleted in the study area. Finally, the pollution index for V, Cr, Ni, Cu, Zn, As, Sr, Mo, Pb, Fe and Mn indicated that they do not pose any environmental health risk, with the exception of Sb that has extremely high pollution level.

Table 1. Results of Geochemical Analysis of Samples with all Elements in ppm in comparison to published Upper Crust Concentrations in ppm; n=24

Element	**This Study**				**Upper Continental Crust**			
	Min.	**Max.**	**Mean**	**Std. Dev.**	**A**	**B**	**C**	**D**
V	40.00	150.00	112.33	29.22	98.00	107.00	53.00	97.00
Cr	10.00	108.00	43.87	32.12	80.00	85.00	35.00	92.00
Ni	3.00	30.00	12.75	9.35	38.00	44.00	19.00	47.00
Cu	21.00	56.00	42.42	10.74	32.00	25.00	14.00	28.00
Zn	8.00	96.00	39.58	30.55	70.00	71.00	52.00	67.00
As	1.00	5.00	2.50	1.17	4.40	1.50	2.00	4.80
Sr	12.00	319.00	181.5	86.60	266.00	350.00	316.00	320.00
Mo	0.50	21.00	4.75	2.13	0.78	1.50	1.40	1.10
Pb	2.00	48.00	9.25	13.47	18.00	17.00	17.00	17.00
Sb	9.00	26.00	14.17	4.59	0.30	0.20	0.31	0.40
Fe	5.20	14.55	9.43	2.80	0.07	0.05	0.05	0.07
Mn	0.05	0.31	0.19	0.08	4.16	3.50	3.19	3.93

A: Gao et al. (1975); B: Taylor and McLennan (1985, 1995); C: Wedepohl (1995); D: Rudnick and Gao (2003)

Table 2. Enrichment Factor of Heavy Metals in Study Area

Element	Enrichment Ratios, ER		
	Min.	Max.	Mean
V	0.41	1.55	1.16
Cr	0.11	1.17	0.48
Ni	0.06	0.64	0.27
Cu	0.75	2.00	1.52
Zn	0.12	1.43	0.59
As	0.21	1.04	0.52
Sr	0.04	1.00	0.57
Mo	0.46	19.09	4.32
Pb	0.12	2.82	0.54
Sb	22.50	65.00	35.43
Fe	74.29	207.86	134.71
Mn	0.6	4.00	2.45

Table 3. Class Interpretation of Index of Geoaccumulation of Trace Elements (after Muller (1969)

I_{geo} Value	I_{geo} Class	Pollution Intensity
> 5	6	Extremely polluted
4-5	5	Strongly to extremely polluted
3-4	4	Strongly polluted
2-3	3	Moderately to strongly polluted
1-2	2	Moderately polluted
0-1	1	Unpolluted to moderately polluted
0	0	Unpolluted

Table 4. Index of Geoaccumulation of Trace Elements in River Gora Sediments (n=24)

Element	Index of Geoaccumulation, I_{geo}		
	Min.	Max.	Mean
V	0.08	0.31	0.23
Cr	0.02	0.24	0.10
Ni	0.01	0.13	0.05
Cu	0.15	0.40	0.30
Zn	0.02	0.29	0.12
As	0.04	0.21	0.11
Sr	0.01	0.20	0.11
Mo	-0.52	1.11	0.46
Pb	0.02	0.57	0.11
Sb	4.52	13.05	7.11
Fe	-0.01	0.44	0.23
Mn	-0.40	1.72	0.30

Table 5. Pearson Correlation Coefficient of Sediment Samples from River Gora

Correlation Coefficient Matrix												
	V	Cr	Ni	Cu	Zn	As	Sr	Mo	Pb	Sb	Fe	Mn
V	1											
Cr	0.365	1										
Ni	0.307	0.461	1									
Cu	-0.348	0.529	0.236	1								
Zn	0.672	0.429	0.677	-0.056	1							
As	0.253	0.202	-0.179	0.207	0.353	1						
Sr	0.036	-0.434	-0.270	-0.510	-0.160	-0.477	1					
Mo	-0.786	-0.365	-0.321	0.248	-0.494	-0.259	0.056	1				
Pb	-0.314	0.245	-0.444	0.443	-0.262	0.558	-0.515	0.222133	1			
Sb	0.223	0.078	0.368	0.205	0.602	0.119	0.249	-0.07554	-0.24643	1		
Fe	0.393	0.699	0.715	0.253	0.580	0.205	-0.597	-0.57898	-0.10674	-0.01104	1	
Mn	0.115	-0.368	0.081	-0.531	0.060	-0.251	0.194	-0.25571	-0.65902	-0.09583	0.225893	1

Figure 2. Scree Plot of Eigenvalues vs Component Numbers for River Gora Samples

Table 6. Kaiser-Meyer-Oklin (KMO) Measure of Sampling Adequacy (Communalities)

	Initial	Extraction
V	1.00	.847
Cr	1.00	.724
Ni	1.00	.915
Cu	1.00	.864
Zn	1.00	.881
As	1.00	.801
Sr	1.00	.810
Mo	1.00	.799
Pb	1.00	.934
Sb	1.00	.886
Fe	1.00	.972
Mn	1.00	.729

Table 7. Total Variance Explained: Initial Eigenvalues

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.007	33.396	33.396	4.007	33.396	33.396
2	3.112	25.935	59.331	3.112	25.935	59.331
3	1.580	13.169	72.500	1.580	13.169	72.500
4	1.462	12.180	84.680	1.462	12.180	84.680
5	.834	6.950	91.630			
6	.427	3.556	95.186			
7	.249	2.076	97.262			
8	.186	1.550	98.812			
9	.129	1.076	99.887			
10	.011	.095	99.983			
1	.002	.017	100.000			
12	1.18E-16	9.882E-16	100.000			

Table 8. Unrotated Principal Component Matrix

	Component			
	1	2	3	4
V	.694	-.381	-.387	
Cr	.718	.433		
Ni	.752		.528	
Cu		.767	.486	
Zn	.852			.333
As	.344	.484	-.540	.395
Sr	-.423	-.674		.395
Mo	-.699	.313	.460	
Pb		.889	-.316	
Sb	.350		.499	.697
Fe	.865			-.464
Mn		-.718		-.433

Table 9. Rotated Principal Component Matrix

	Component			
	1	2	3	4
Fe	.881	.419		
Cr	.763			
Ni	.750		-.393	.422
Sr	-.711		-.438	.335
Cu	.599	-.503	.452	
V		.885		
Mo		-.885		
Zn	.393	.627		.577
Pb			.903	
As		.451	.770	
Mn		.391	-.730	
Sb				.936

Table 10. Total Variance Explained: Split Without Outlier

Component	Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %
1	3.024	25.200	25.200
2	2.752	22.934	48.134
3	2.599	21.655	69.789
4	1.787	14.891	84.680

Table 11. Total Variance Explained: Split With Outlier

Component	Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %
1	4.619	38.490	38.490
2	4.380	36.498	74.988
3	3.001	25.012	100.000
4	4.723	3.936E-15	100.00

4. Conclusion and Recommendations

4.1 Conclusion

In this paper, the importance of the application of statistics in geochemical data analysis and interpretation has been demonstrated. The concentrations and pollution levels of V, Cr, Ni, Cu, Zn, As, Sr, Mo, Pb, Sb, Fe and Mn were assessed using various methods. The application of multivariate statistics revealed heavy metal associations in the study area were controlled by four component factors, namely: component factor 1 (Fe, Cr, Ni, Sr, Cu and Zn), component factor 2 (Fe, Cu, V, Mo, Zn, As and Mn), component 3 (Ni, Sr, Cu, Pb, As and Mn) and component 4 (Ni, Sr, Zn and Sb). Fe appeared in component factors 1 and 2, while Cu appeared in component factors 1, 2 and 3. On the other hand, Ni and Sr appeared in component factors 1, 3 and 4; while Zn appeared in component factors 1, 2 and 4. Conversely, Mn appeared in component factors 2 and 3. Heavy metals of lithogenic origin are Cr, As, Fe and Mn, while those from anthropogenic origin are Sb, Zn, and Sr. On the other hand, those from mixed origin are V, Ni, Mo, Pb, Sb, Zn, Sr and Cu. The computed enrichment factors also revealed that V, Cu, Mo, Sb, Fe and Mn were enriched while Cr, Ni, Zn, As, Sr and Pb were depleted in the study area. Finally, the pollution index for V, Cr, Ni, Cu, Zn, As, Sr, Mo, Pb, Fe and Mn indicated that they do not pose any environmental health risk, with the exception of Sb that has extremely high pollution level.

4.2 Recommendation

The following recommendation is proffered:
That soil, rock and water samples should be taken for detailed geochemical assessment of heavy metals and their mobility Pattern in the study area

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