

Multivariate Analysis and Contamination Studies of Elemental Profile in Ife/Ijesa Goldmine Tailings, Southwestern, Nigeria

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Abstract. The concentration of metals in the tailings of Ife/Ijesa goldmine, Nigeria was identified by using Proton Induced X-Ray Emission spectrometry as the main analytical tools. A total of 75 samples of the tailings were collected. Correlation, principal component and cluster analyses suggested probable natural and anthropogenic sources of the metals in the tailings. The contamination level of heavy metals was assessed on the basis of geo-accumulation index (I_{geo}), and ecological risk. The analysis of I_{geo} revealed moderately-heavily to heavily extremely contaminated. The value of E_r showed a low level of heavy metals except Cu which shows considerable contamination

Introduction

Mineral resources are abundant in Nigeria and are spread across the 36 states of the federation. In recent year, its exploitation has greatly enhances Nigeria social and economic development positively.

Mining operation is one of the human/industrial activities that gives rise to soil erosion and environmental contamination by generating waste (tailings) during the extraction, beneficiation, and processing of minerals. Scattered tailings on mining site also contaminate the environment (air, water, soil, and wetland sediments) by dissemination of particles carrying metals by wind action and/or by runoff from the tailings after closure [1].

Mining and smelting are two significant aspects of operations that cause heavy metal contamination in the environment due to the activities such as mineral excavation, ore transportation, smelting and refining [2]. Moreover, mining activities contribute to heavy metal pollution of the environment and their progressive accumulation in soils surrounded by mines, which may result in increased heavy metal uptake by plants [3, 4].

Natural geochemical sources of heavy metals include weathering and other pedogenic processes acting on rock fragments, and are usually at relatively low concentrations while anthropogenic sources such as mining and industrial metallurgic process activities are also been reported to increase As, Cd, Cu, Ni, and Zn concentrations in the environment [5-9].

Heavy metal pollution is considered as one of the most critical contaminants in the environmental due to their persistence, toxicity, bioaccumulation and non-biodegradable properties and all these have negative consequence in plants, animals and humans via the food chain [10].

The main purposes of the present study were to: (a) determine total concentrations of elements in mine tailings from different gold mining villages in Ife/Ijesa zone (b) identify their natural or anthropogenic origin by using correlation analysis, principal component analysis (PCA) and cluster analysis (CA), and (c) assess the levels of contamination based on the geo-accumulation index (I_{geo}), and ecological risk (E_r). The results can provide a baseline for use in future environmental impact assessments and to guide pollution mitigation targets in the zone.

Materials and Methods

Study area

This study was carried out in 15 townships in Ife/Ijesa zone, located in the southwestern Nigerian as shown in Fig. 1. Dominant land-use is agriculture, especially cultivation of cash (mainly cocoa, kola, oil palm and plantain) and food crops (including cassava, yam, and fruits).

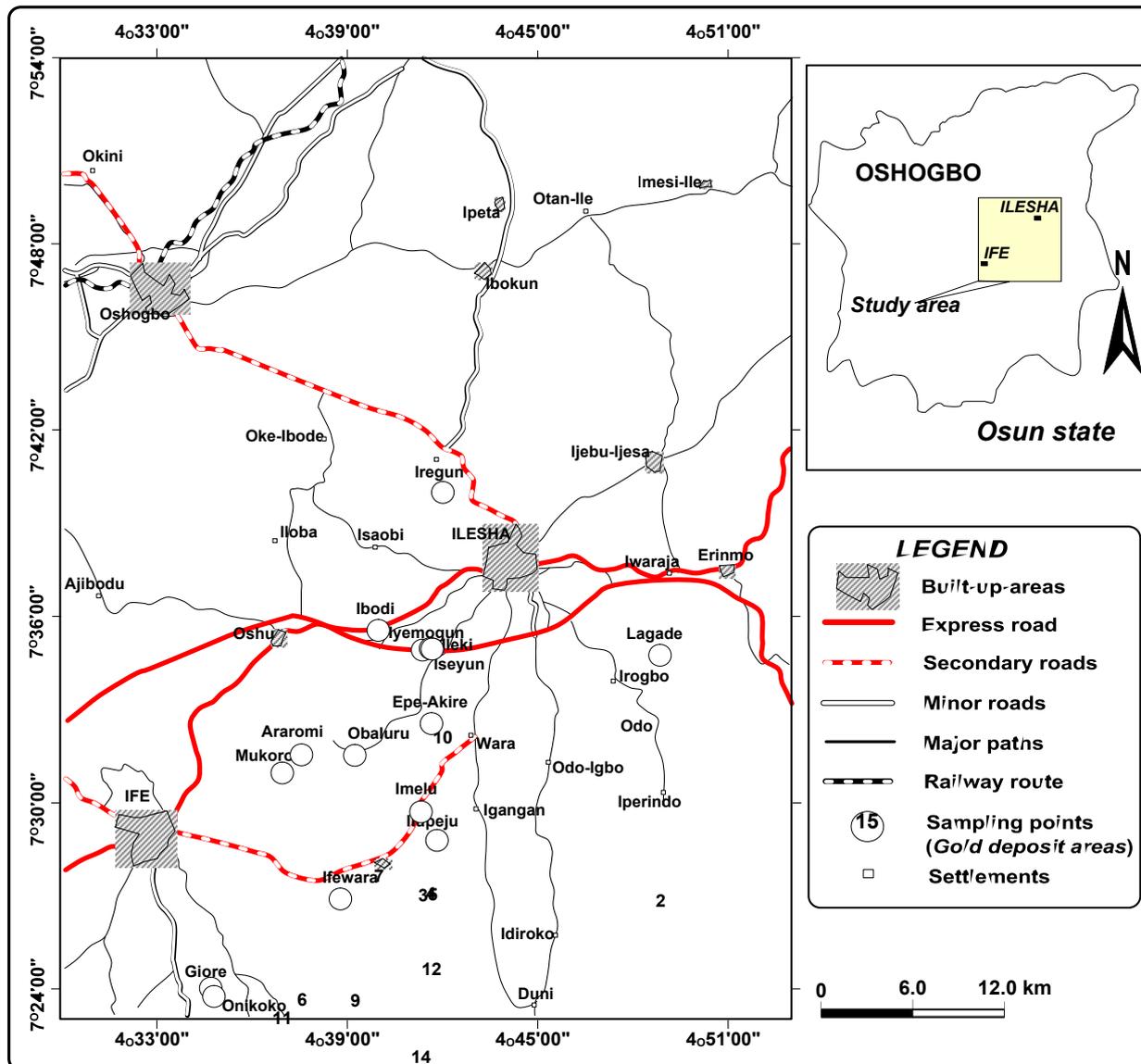


Figure 1. Location map showing the access road to the sampling point and study area (Gold deposit zones) at Ife-Ijesa.

Tailings sampling

A total of 75 tailing samples were collected from different locations which spread across the mining area in Ife/Ilesa geographical zone. The coordinate of each sampling point were taken using GPS. The samples were kept in air tight polyethylene bags. In the laboratory, all the samples were air-dried, ground and passed through a 0.8 mm sieve.

Sample Preparation

The tailings sample were pulverized/crushed to size less than 125nm. Then, drop of toluene acid (binder) was then added to 0.5g of the powdered sample and crushing continued until the mixture was returned to fine powder again. The 0.5g weighed of the crushed sample was compressed under a hydraulic press machine at 10-tone pressure and converted from fine powder to

pellet form. The pellets were carefully labeled, covered with mila and stored in partitioned sample storage plastic container for analysis.

The pelletized soil sample was then analyzed using particle induced x-ray Emission (PIXE) techniques. The PIXE provides a rapid and non-destructive method for the analysis of trace and major elements in geological, environmental and biological samples.

Chemical analysis

The samples were analyzed using Proton Induced X-Ray Emission (PIXE) with a 30 MeV proton beam obtained from the Centre for Energy Research and Development (CERD) ion beam analysis (IBA) facility, with a beam spot of 4 mm in diameter and a low beam current of 3-6 nA. The irradiation was for about 10-20 minutes. A Canberra Si (Li) detector model ESTX 30-150, beryllium thickness of 25 mm, with full width half maximum (FWHM) of 150 eV at 5.9 KeV, with the associated pulse processing electronics, and a Canberra Genie 2000 (3.1) MCA card interfaced to a PC were used for the x-ray data acquisition with respect to the beam direction, the sample's normal was located at 0° and the Si (Li) detector at 45°. The PIXE set-up was calibrated using some pure element standards and NIST geological standard NBS278.

Statistical analysis

To determine the trend of analytical data, correlation analysis, PCA and CA were used. PCA and CA are the most common multivariate statistical methods used in environmental studies [11, 12].

PCA is commonly adopted to extract a smaller number of independent factors (principal components) among available data for analyzing variable relationships [11, 13]. PCA can minimize the number of correlated variables to a smaller set of orthogonal factors, making it easier to interpret a given multidimensional system by displaying the correlations among the original variables. Principal components are those whose eigenvalues exceed 1 [14].

The CA technique consists of an unsupervised classification procedure that involves measuring either the distance or the similarity between objects to be clustered. Objects are grouped into clusters in terms of their similarity. The initial assumption is that the nearness of objects in the space defined by the variables reflects the similarity of their properties [15].

In the current research, statistical analyses such as correlation coefficient, PCA and CA were used for investigating pollutant sources and elucidate the latent relationships between variables/samples using SPSS package version 16.0 for Windows.

Pollution Level Assessment Methods

Geo accumulation index (I_{geo})

The contamination levels of heavy metals in soils were assessed by the geo accumulation index (I_{geo}).

$$I_{geo} = \log_2 [C_n / (1.5B_n)],$$

where C_n is the measured concentration of heavy metal n in the soils, B_n the geochemical background concentration of metal n , and 1.5 is the background matrix correction factor due to lithogenic effects; $I_{geo} \leq 0$, indicate practically uncontaminated; $0 < I_{geo} \leq 1$, indicate uncontaminated-moderate; $1 < I_{geo} \leq 2$, indicate moderately uncontaminated; $2 < I_{geo} \leq 3$, indicate moderately-heavily contaminated; $3 < I_{geo} \leq 4$, indicate heavily contaminated; $I_{geo} > 4$, indicate heavily- extremely contaminated [16].

Ecological risk

The method of determine ecological risk of heavy metals originally introduced by [17]), and has been adopted recently in environmental studies [18]. Hence, the potential ecological risk index (PERI) was calculated to determine the degree of heavy metal pollution in the tailings of gold mining site in Ife/Ijesa zone as follows:

Assessment of soil contamination is performed by the contamination factor (C_f^i) and degree of contamination (C_d) [17].

$$C_f^i = C_s^i / C_n^i, \quad C_d = \sum_i^m C_f^i$$

where C_s^i is the content of metal I, and C_n^i is the reference value, baseline level, or national criteria of metal i.

An ecological risk factor (E_r^i) to quantitatively express the potential ecological risk of a given contaminant also suggested by HAKANSON is

$$E_r^i = T_r^i C_f^i$$

where C_f^i is contamination factor and T_r^i is toxic-response factor of heavy metals i are:

$$T_r^{Zn}=1; T_r^{Pb}=5; T_r^{Cd}=30; T_r^{Cu}=5; T_r^{Ni}=5; T_r^{Cr}=2.$$

$$I_r = \sum_i^n E_r^i = \sum_i^n T_r^i C_f^i = \sum_i^n T_r^i C_s^i / C_n^i$$

The following classes are used to describe risk levels: $C_f \leq 1$, low contamination; $C_f \leq 3$, moderate contamination; $C_f \leq 6$, considerably contaminated; $C_f \geq 6$, very high contaminated. $C_d \leq 8$, low degree of contamination; $C_d \leq 16$, moderate degree of contamination; $C_d \leq 32$, considerable degree of contamination; $C_d \geq 32$, very high degree of contamination. $E_r \leq 40$, low potential ecological risk; $E_r \leq 80$, moderate potential ecological risk; $E_r \leq 160$, considerable potential ecological risk; $E_r \leq 320$, high potential ecological risk; $E_r \geq 320$, very high potential ecological risk. $I_r \leq 150$, low ecological risk index; $I_r \leq 300$, moderate ecological risk index; $I_r \leq 600$, considerable ecological risk index; $I_r \geq 600$, very high ecological risk index.

Results and Discussion

Multivariate analysis results (Principal component analysis)

The PCA was applied to identify possible sources of pollutants in the mine tailings by applying varimax rotation with Kaiser normalization. By extracting the eigenvalues and eigenvectors from the correlation matrix, the numbers of significant factors, the percentage of variance explained by each of them were calculated by using the software package of SPSSv10.0 and the results were given in

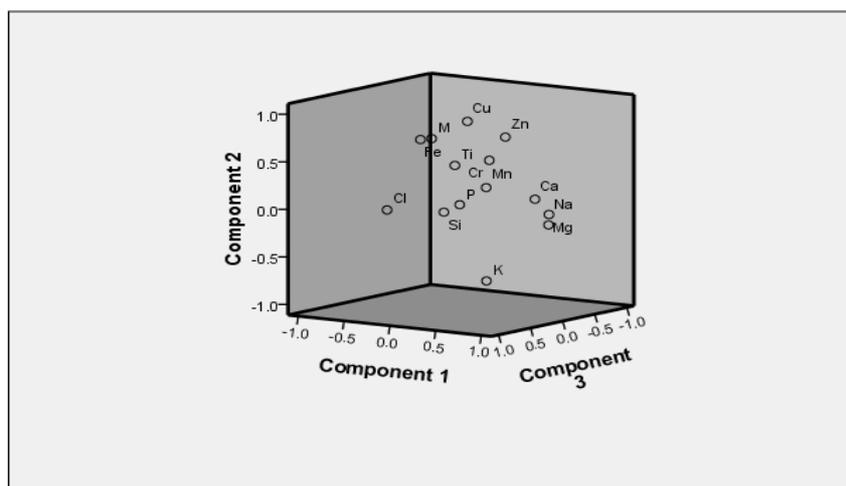
Table 1 as expected, four factors whose eigenvalues > 1 was selected, out of which the three prominent factors were selected for three dimensional plots of the PCA loadings presented in Fig. 2. Principal factors > 0.5 are bolded in each column and the relationship among the fourteen element were readily observed.

Table 1. The result principal component analysis (n=75).

Component	Initial Eigenvalue			Extraction Sum of Square Loading			Rotation Sums of Squared Loading		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.779	41.279	41.279	5.779	41.279	41.279	4.059	28.995	28.995
2	3.257	23.266	64.545	3.257	23.266	64.545	3.725	26.610	55.605
3	1.676	11.974	76.519	1.676	11.974	76.519	2.371	16.933	72.538
4	1.004	7.170	83.689	1.004	7.170	83.689	1.561	11.151	83.689
5	.917	6.553	90.242						
6	.591	4.224	94.467						
7	.225	1.606	96.073						
8	.183	1.304	97.377						
9	.140	.997	98.374						
10	.112	.798	99.172						
11	.057	.404	99.576						
12	.053	.376	99.953						
13	.007	.047	100.000						

Table 2. Pearson's correlation coefficients matrix among the metals concentration in the tailings.

	Na	Mg	Al	Si	P	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn
Na	1													
Mg	0.771837	1												
Al	-0.32588	-0.45025	1											
Si	-0.17953	-0.21892	-0.03132	1										
P	0.443778	0.492115	-0.17694	-0.07555	1									
Cl	-0.29363	-0.15655	-0.15495	0.134093	0.621672	1								
K	0.249032	0.086345	-0.40848	0.303291	-0.21956	-0.25644	1							
Ca	0.762026	0.902993	-0.34452	-0.19745	0.651164	0.084039	-0.08416	1						
Ti	0.097922	0.098616	0.040315	-0.37019	0.340364	0.270605	-0.64252	0.309743	1					
Cr	0.213096	0.540872	-0.09073	-0.43269	0.473404	0.298001	-0.53944	0.66529	0.488272	1				
Mn	0.531115	0.653837	-0.18551	-0.28245	0.86786	0.432326	-0.36397	0.78756	0.523843	0.677412	1			
Fe	-0.15674	-0.06257	0.548985	-0.17695	0.532378	0.467916	-0.70169	0.115756	0.417118	0.52364	0.502279	1		
Cu	-0.07099	0.120011	0.360185	-0.1446	0.269415	0.16913	-0.74667	0.326247	0.465234	0.633502	0.479434	0.656551	1	
Zn	0.240594	0.40578	0.055191	-0.13754	0.267779	0.022806	-0.60682	0.556967	0.591801	0.767561	0.507556	0.391583	0.761909	1

Component Plot in Rotated Space**Figure 2.** PCA results in the three dimensional space plot of loadings of the first three principal components.

At Table 3, the first factor explains 29% of the total variance and load heavily on Na, Mg, Ca and Mn while the second factor explain 27% of total variance and loads on Cr, Al, Fe, Cu and Zn. Also, third factor explains 17% of the total variance and load on Cr, Cl and P. Fig. 2 shows that, heavy metals in the three dimensional PCA loading plot, are separated by a large distance which may suggest that the elements are poorly correlated and have different sources which may be natural or anthropogenic source. The main anthropogenic source in the area is mineral exploration.

Table 3. Varimax rotated loadings and communalities for the gold mine tailing samples (n=75, only those larger than 0.1 are shown and loading > 0.6 are bold).

Element	Rotated Component Matrix				Communalities
	1	2	3	4	
Na	.879				.805
Mg	.954				.919
Al		.619			.664
Si					.845
P	.526	.166	.772		.900
Cl		.070	.958		.941
K	.138				.858
Ca	.936	.180	.182		.950
Ti	.129	.467	.279	.581	.650
Cr	.497	.557	.268	.391	.782
Mn	.669	.330	.562	.219	.920
Fe		.748	.493		.817
Cu	.143	.907	.104		.857
Zn	.462	.754		.157	.808
% Variance	28.995	26.610	16.933	11.151	83.689

Cluster Analysis

Before CA, the variables were standardized by means of Z-scores; then Euclidean distances for similarities in the variable were calculated. The CA results are shown in Fig. 3 as a dendrogram. The cluster has three bigger subgroup; the first group contains only the variables Na, Zn, Cl, Cr, Cu, P, Mn, Mg and Ca. The second one includes K and Ti. The third one contains Al and Fe.

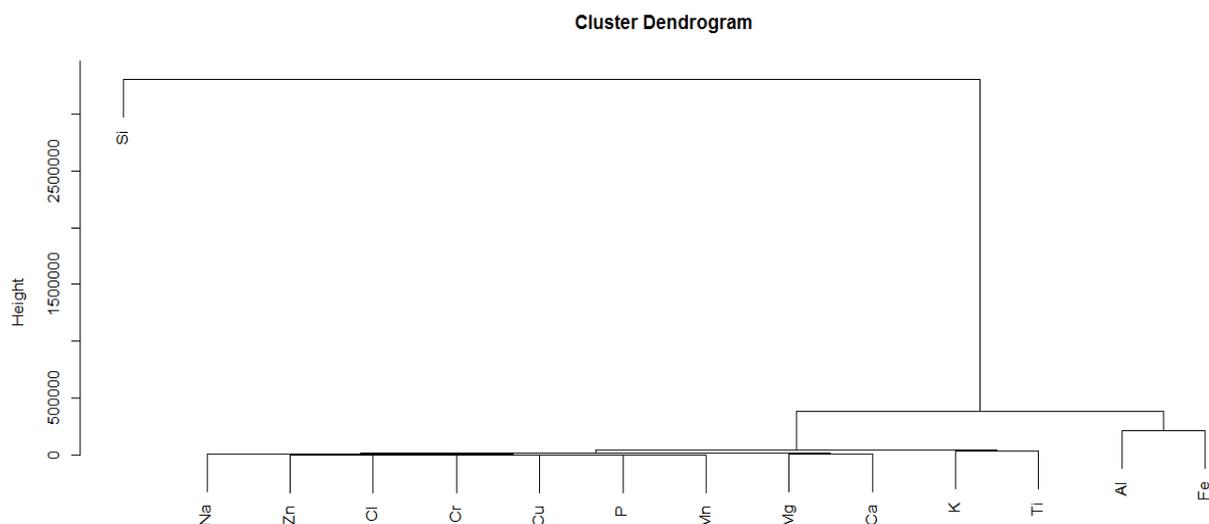


Figure 3. Dendrogram results from ward's method of hierarchical cluster analysis of 13 elements and 75 samples. Similarities have been calculated from Euclidean distance.

Geo-accumulation index and Ecological risks analysis

The I_{geo} stands for “contamination” level, and the E_r for “pollution” level. Thus, it can be seen that the I_{geo} method is best applied to accumulation levels of individual metals, while the potential ecological risk index describes the ecological risk caused by pollutants [18]. The results of geo-accumulation evaluation as shown in Table 4 indicated that Cr, Mn, Cu, Zn, Pb, Ni had moderately-heavily to heavily extremely contaminated in the tailings, but their ecological risks were relatively low. On the other hand, these metals are not at health-threatening levels, but their environmental accumulation merits more attention. To produce more comprehensive and accurate assessment results, both assessment methods should be used when evaluating the environmental quality.

The E_r results of six heavy metals (“except Fe, which lacked a toxic response factor”) in Ife/Ijesa goldmine tailings are shown in Table 5 and Fig. 4a & 4b respectively. The average E_r values of heavy metals showed decreasing order of: Cu>Cr>Mn>Zn>Ni>Pb. The results indicated that the concentration range of Cu have low and considerable potential ecological risk respectively; while Cr, Mn, Zn, Ni and Pb have low potential risk. Based on these results, most sampling locations shows low ecological risk index, which means these metals, may not have adverse effect on the ecosystem.

Table 4. The Values of I_{geo} for Each Metal.

Heavy Metal	I_{geo} value
Cr	5.7818
Mn	4.0349
Cu	7.46
Zn	3.95
Pb	3.99
Ni	2.76

Table 5. The value of C_f , C_d , E_r and I_r for studied heavy metals in Ife/Ijesa goldmine tailings.

Location	C_f							C_d	E_r						I_r
	Cr	Mn	Fe	Cu	Zn	Pb	Ni		Cr	Mn	Cu	Zn	Pb	Ni	
IF	3.02	2.13	1.78	22.5	1.19	18.2	0	48.82	6.04	2.13	112.5	1.19	91	0	212.86
L	6.29	0.74	1.73	4.5	1.19	0	0	14.45	12.58	0.74	22.5	1.19	0	0	37.01
IS	4.93	1.15	2.15	27.6	1.02	0	0	36.85	9.86	1.15	138	1.02	0	0	150.03
IY	7.12	1.34	1.33	34.7	3.69	5.6	0	53.78	14.24	1.34	173.5	3.69	28	0	220.77
ILK	8.38	1.31	3.06	41.4	3.15	0	0	57.3	16.78	1.31	207	3.15	0	0	228.24
AR	5.4	2.32	0.92	12.4	1.16	0	0	22.2	10.8	2.32	62	1.16	0	0	76.28
IB	6.45	1.41	0.95	6.85	1.61	0	0	17.27	12.9	1.41	34.25	1.61	0	0	50.17
G	1.64	0.53	1.15	12.6	1.06	0	2.89	19.87	3.28	0.53	63	1.06	0	14.45	82.32
OB	6.67	3.12	3.74	20.9	1.24	0	0	35.67	13.34	3.12	104.5	1.24	0	0	122.2
IR	3.19	0.52	0.34	1.5	0.45	0	0.83	6.83	6.38	0.52	7.5	0.45	0	4.15	19
MU	11.12	4.13	2.24	36.3	2.76	0	1	57.55	22.24	4.13	181.5	2.76	0	5	215.63
E	2.43	0.33	0.92	3.43	0	0	0	7.11	4.86	0.33	17.15	0	0	0	22.34
ON	7.76	3.36	1.58	18.36	3.18	0	2.61	36.85	15.52	3.36	91.8	3.18	0	13.05	126.91
IM	3.31	1.58	0.97	11.57	0.84	0	2.5	20.77	6.62	1.58	57.85	0.84	0	12.5	79.39
II	4.81	0.64	0.65	10.14	0.63	0	0.39	17.26	9.92	0.64	48.1	0.63	0	1.95	61.24

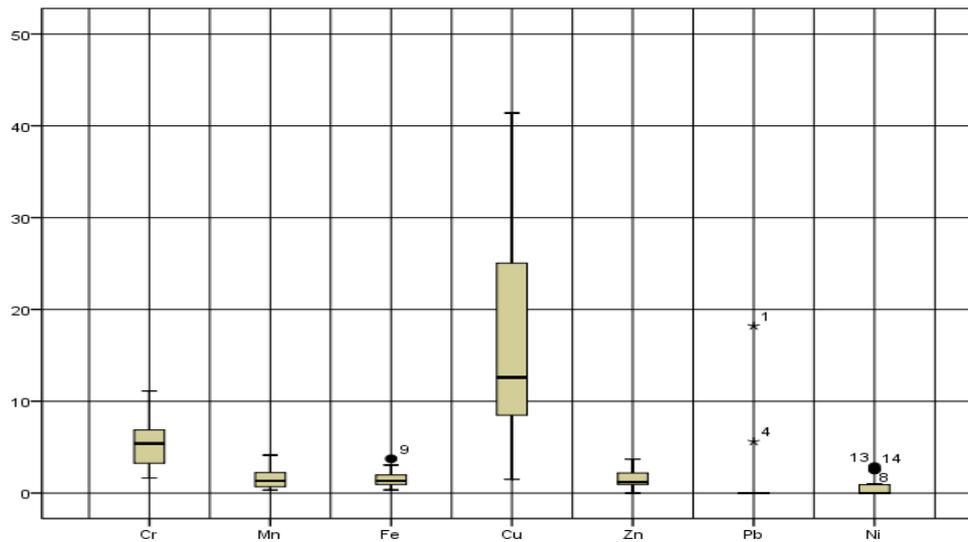


Figure 4a. Box plots of C_f for studied heavy metals in Ife/Ijesa goldmine tailings.

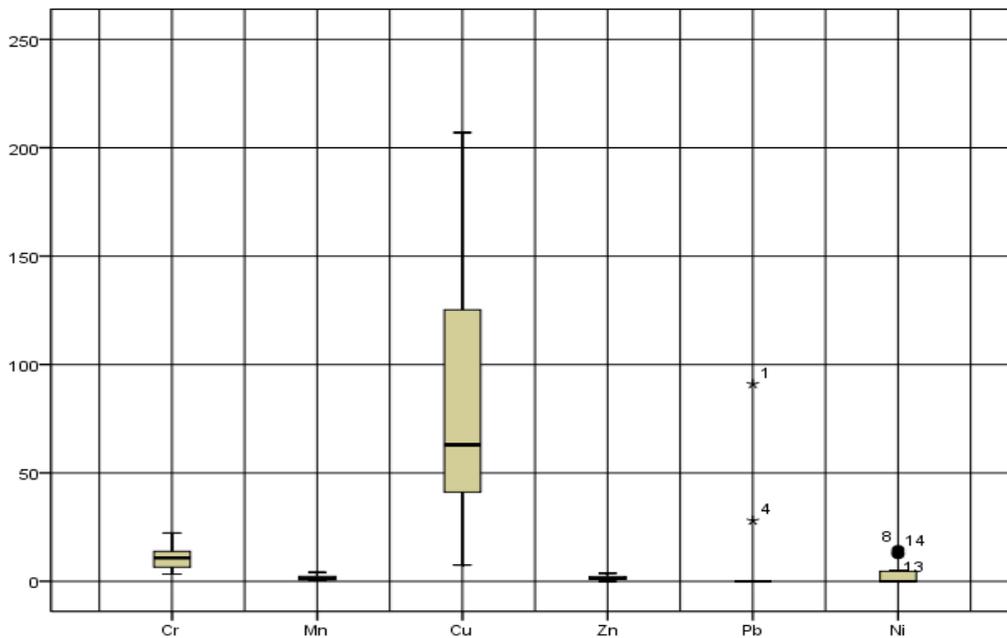


Figure 4b. Box plots of E_r for studied heavy metals in Ife/Ijesa goldmine tailings.

Conclusion

Multivariate analysis is a reliable tool for characterizing and prediction of tailings behavior. PCA shows that natural and geochemical source are possible means of contamination in the tailings. The analysis of I_{geo} of all the element examined indicated moderately-heavily to heavily extremely contaminated while the E_r of all elements showed a low level of heavy metals except Cu which shows considerable contamination and should of concern to the environmental policy maker.

Conflict of Interest

The authors declare that there is no conflict of interest in this manuscript.

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