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HEAVY METALS ASSESSMENT OF SELECTED SOILS IN OWO TOWNSHIP, SOUTHWESTERN NIGERIA

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Abstract

Heavy metal assessment of selected soils in Owo Township, Ondo state was carried out. Thirteen sampling sites were chosen from the study area. The samples were collected using the international acceptable standard for collecting soils for geochemical study. To determine the level of heavy metals pollution in this area, Enrichment Factor (EF), Geo-accumulation (*Igeo*) and Pollution Load Index (PLI) was used. The results show that the area has a background (EF, < 1) to significant enrichment (EF, 5-20) which implies that they are unpolluted (*Igeo*, <0) to moderately polluted (*Igeo*, 1-2). We proposed a sub-classification for the PLI. Based on this, the results shows that some of the areas are not polluted, while some are polluted. Statistical methods such as correlation and cluster analysis were used to show the relationship between metals, pH and Eh in the soils. Fe has a positive but weak correlation with Mn (r = 0.143) and Pb (0.064). There exist a strong correlation with Cu (r = 0.456).The strongest relationship occur between Cu and Pb (r = 0.881). Cluster analysis shows that the heavy metals are generated from mixed sources or retention phenomena. It also shows that most of the areas have the same source of pollution.

Keywords: *Heavy metals; Pollution; Owo; Soils; Background; Statistical analysis.*

Introduction

Heavy metals have been recognized to be a major source of pollution which affects soils and are introduced into the environment through natural phenomena and human activities within the environment. Physical and chemical weathering are the major processes that affect both consolidated and unconsolidated geomaterials. Manmade processes that affect the environments include industrial wastes, application of fertilizers, metal sheets, wire and pipeand the burning of coal and wood in the environment (Sekabira *et al.,* 2010).These heavy elements could be involved in adsorption, co-precipitation and complex formation (Okafor and Opuene, 2007). The co-precipitation of these elements especially the heavy metals could account for the accumulation of heavy metals in sediments(Sekabira *et al.*, 2010). The rates at which soils and other geomaterials are being polluted in recent years have been a source of great concern to the world. It has continued to threaten the health safety and environment of the world populace. Owo town is not as industrialized as other major cities in Nigeria such as Lagos, Ibadan, Kaduna and Kano cities.

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Therefore, less pollution due to industrial factors are not likely to be much when compared to these industrialized cities. However, with increasing population of the area, industrialization is bound to be on the increase. This will lead to more pollution.

Hence, the objectives of this research will be to determine the concentration of selected heavy metals in the soils of Owo Township, determine the level of pollution in the soils of the study area, establish the relationship between the elements and physical properties of the soils, establish the relationship between the elements contained in the soil. To achieve this, correlation analysis of data and hierarchical (dendograms) diagrams are used. Also we propose a subdivision to the Pollution Load Index.

Materials and Methods

This study was carried out on the selected soils of Owo township ($5^o32'$N, $7^o8'$E and $5^o38'$N, $7^o16'$E) (Figure 1). Owo is an ancient town in Ondo state, southwestern Nigeria. It is about 45km from Akure, the capital of Ondo state. The study area has a tropical rainforest climate, with high humidity and warmth and high to moderate relief. The area has a temperature of approximately between 30^oC-35^oC.

Geology of the study area

The Owo area forms part of the southern margin of the southwestern section of the Nigeria Basement Complex which comprises of the gneiss-schist complex and migmatite-gneiss complex. Studies have shown that the migmatite-gneiss is made up of biotite-hornblende-gniess with intercalated amphibolite which have been variably affected by migmatization and metasomation. The differentiated gneiss-schist complex have been observed to have pelitic schist (undifferentiated) and quartzite mainly which have evolved over three or four major tectonic cycles of metamorphism and reactivation (Rahaman, 1976).

However, the lithostratigraphic unit of the study area is dominantly quartz. The quartz is thinly to thickly bedded of local micaeous and contains minor amounts of muscovite, pebbly layers of smoky quartz. The quartzite region mainly trends N-S across the study area. The pelitic schist trend along the N-W region, it form the low relief area and it is largely overlay by lateritic soil derived from the quartzite ridge which is covered with high vegetation in the study area.

Sampling and chemical analysis

In this study, thirteen (13) sampling sites were selected (Figure 1) within the study area and soils samples were collected using a hand trowel at a depth of 30cm. The samples were collected in polythene bags and transported into the laboratory for further analysis. After the collection of each sample, the hand trowel was washed with detergent, rinsed and dried before each use so as to minimize contamination. Soil samples were dried in an oven at 65^oC overnight,sieved mechanically using 0.5mm sieve, was homogenized and ground to 0.063mm fine powder because metals are known to adhere to fine particles (Sekabira *et al*., 2010).

1.25g of each was digested with 20ml aqua regia (HCl/HNO_3 3:1) in beaker (open-beaker digestion) on a thermostatically controlled hotplate. The digest were heated to near dryness and cooled to ambient temperature. Then 5.0ml of hydrogen peroxide was added in parts to complete the digestion and the resulting mixture heated again to dryness in a fume cupboard. The beakers walls were washed with 10ml of de-ionised water. Pb, Cu, Mn and Fe heavy metal were then analyzed by direct aspiration of the sample solution into the Atomic Absorption Spectrometer (AAS). Soil pH and Eh was measured in a suspension of 1:2 sediment to water ratio using a calibrated pH meter.

Assessment of soil contamination

Enrichment Factor (EF) of the soil was calculated as proposed by Simex and Helz (1981). It was used to assess the degree of contamination and to understand the distribution of the elements of anthropogenic origin of individual elements in the soil. To achieve E.F. data, Fe was chosen as a normalizing element since it is widely used as a reference material (Loska *et al*., 2003).Other reference materials that are usually used are Al and Mn (Ong and Kamaruzzaman, 2009).

$$\text{Enrichment Factor} = \frac{\frac{Cn}{Fe}\text{ Sample}}{\frac{Cn}{Fe}\text{ Background}}$$

where Cn is the concentration of element “n”. The background value is that of average shale (Turckian and Wedepohl, 1961; Sekabira *et al*., 2010). Elements which are naturally occurring have an EF value of near unity, while elements of anthropogenic sources have EF values of several orders of magnitude. Six categories are recognized: ≤1 background concentration; 1-2 depletion to minimal enrichment; 2-5 moderate enrichment; 5-20 significant enrichment; 20-40 very high enrichment and >40 extremely high enrichment(Sutherland, 2000; Sekabira *et al*., 2010).

Pollution Load Index (PLI) was evaluated as indicated by (Sekabira *et al.*, 2010).Pollution Load Index = $(CF_1{*}CF_2{*}\ldots{*}CF_n)^{1/n}$, where n is the number of metals (four present in this study) and CF is the ContaminationFactor. The Contamination Factor can be gotten from:

$$\text{Contamination Factor (CF)} = \frac{\text{Metal Concentration in Soils}}{\text{Background values of the metal}}$$

where the PLI value is greater 1, pollution is established, whereas when PLI is less than 1, it indicates no pollution(Seshan *et al*, 2010). However, we propose a sub-classification of this pollution index as follows; <1 unpolluted, >1 polluted. The polluted areas can then be subdivided into, 1-3 moderately polluted, 3-4 heavily polluted, 4-5 very highly polluted and >5 extremely polluted. Geo-accumulation Index (*Igeo*) was used to assess heavy metals in soils as introduced byMuller (1969) and used by Sekabira *etal* (2010) to measure the degree of metal pollution in sediment studies.(Chakravarty and Patigiri, 2009)

$$\text{Igeo} = \log 2 \frac{Ca}{1.5\ Bn}$$

where Ca is the measured concentration of a heavy metal in soil samples, Bn is the geochemical background value in average shale of element n and 1.5 is the background matrix correction due to terrigenous effects. The geo-accumulation index classification consists of seven classes, 0-6, ranging from background concentration to heavily polluted; <0 (class 0) background concentration; 0-1 (class 1) unpolluted; 1-2 (class 2) moderately polluted; 3-4 (class 4) heavily polluted; 4-5 (class 5) highly to very highly polluted; 5-6 (class 6) very highly polluted (Kumar and Edward, 2009).

Several statistical analyses were carried out to effectively deduce the impact of the elements in the study area.Pearson correlation’s method of analysis was used to analyze and establish inter-elemental relationship and physico-chemical characteristics of the soil samples. Cluster Analysis (CA) was performed to classify elements of different sources on the basis of their similarities using dendograms and to identify relatively homogenous groups of variables with similar properties.

Result and Discussion

Heavy metal distribution in the selected soil samples

Average contents of heavy metals and physicochemical parameters of individual elements in the soil of the studied area are given in table 1. The pH (figure 2) ranged between 5.91and 6.20. Mean heavy metal contents in the selected soil ranged from 336.08 to 1,525.11mg/g Mn; 16,250.17mg/g Fe; 20.95 to 112.45mg/g and 14.01 to 322.08mg/g Pb. The highest concentration of Mn (figure 4)occurs at Ijebu and Okedogbon soils, while it has lowest concentration in the Achievers University Permanent Site (P.S) soil. The highest concentration of Fe (figure 5) occurs in Iyere community soil and lowest in the Ehinogbe community soil. The concentration of Cu (figure 6)is greatest at the Ijebu community soil and lowest in the Achievers P.S soil. The concentration of Pb is high at Ijebu community soil and lowest in the Achievers P.S soil. At the Achievers Mini campus area, Achievers University P.S, Emure market, Ehinogbe, Isuada, Saint Louis Grammar School, Okegun, Iyere and Rufus Giwa Polythenic the concentrations of metals are in the order Fe>Mn>Cu>Pb. However in Federal Medical Centre, Oja Koko and Ijebu soils the order of concentration is in the order Fe>Mn>Pb>Cu.

Heavy metal pollution

The results showed that heavy metal can be assessed with respect to world surface rock averages(Chakravarty and Patigiri, 2009) or the widely used average shale (Shyamalendia*et al.*, 2001; Ong and Kamarazzan, 2009). The source of pollution is therefore determined by normalizing the geo-accumulation values to the reference element. The degree of pollution in soils can be assesses by determining the enrichment factor and indices such as the pollution load index and geo-accumulation index. Variations of EF, Igeo and PLI in the selected soils are as shown in figure 8a-c.

Enrichment Factor (E.F): enrichment factors values are shown in figure 8a. Mn has an enrichment between 0.19 and 2.88 which implies that they are of anthropogenic origin but exist as a background concentration to moderate enrichment in the soil. Mn has background concentration at the Achievers University Permanent site, Achievers mini campus, Emure market, Isuada, Oja Koko, Iyere and Rufus Giwa Polythenic soils. However, in Saint Louis Grammar School, Ogbomo and Ijebu soils, Mn has depletion to minimal enrichment. In Federal Medical Center, Okegun and Ehinogbe soils Mn has a moderate enrichment. Cu has enrichment between 0.097 to 2.65 which implies an anthropogenic source of pollution. It has a background concentration at AMC, AO, IAD, LGS, IRE, OWG and EOE. At EMT, FOD, OGB, OJI and OKG it has depletion to minimal enrichment. However at IJB, it has a moderate enrichment. Pb has enrichment between 0.701 and 16.10. In AO, EOE and LGS soils it has backgroundconcentration, while in AMC, FOD, IAD, OKS and OWG soils it has depletion to moderate enrichment. In OGB, IRE and EMT soils it has a moderate enrichment. In OJI and IJB it has a significant enrichment.

Geo-accumulation (Igeo):The geo-accumulation index of the study area shows that Mn has a value less than 1(Figure 8b). This indicates that although Mn shows a background concentration and does not show sign of pollution in the soils of the study area it does not in any way pollute the soils. The same goes for Fe that has geo-accumulation values that are less than 1. Cu also has *Igeo* values that are less than 1. This implies that Mn, Fe and Cu are derived from the subsurface rocks in the study area. However, Pb has *Igeo* values that are less than 1 except in IJB where it is greater 1. The source of Pb in the areas except IJB is from the subsurface rocks, while its concentration in IJB may be from surface runoff. Even with greater than1 *Igeo* value, Pb does not still contribute pollution in the area.

Pollution Load Index (PLI)

Pollution Load Index (PLI) (Figure 8c) shows that AMC, EOE, FOD and LGS show no traces of pollution, while the other nine sampling sites show traces of pollution. From our proposed sub-classification, we can further subdivide the polluted areas. With this we can say that AO, EMT, IAD, OGB, OJI, IJB, OKS, IRE and OWG are moderately polluted.

Statistical analysis of data

Correlation analysis of data

The correlation of the data was carried out to determine the relationships that exist between the elements under study. In achieving this bivariate and partial correlation was carried out (Table 2, 3 and 4). The bivariate correlation shows that a positive correlation exist between pH and Mn and Eh. pH/Mn

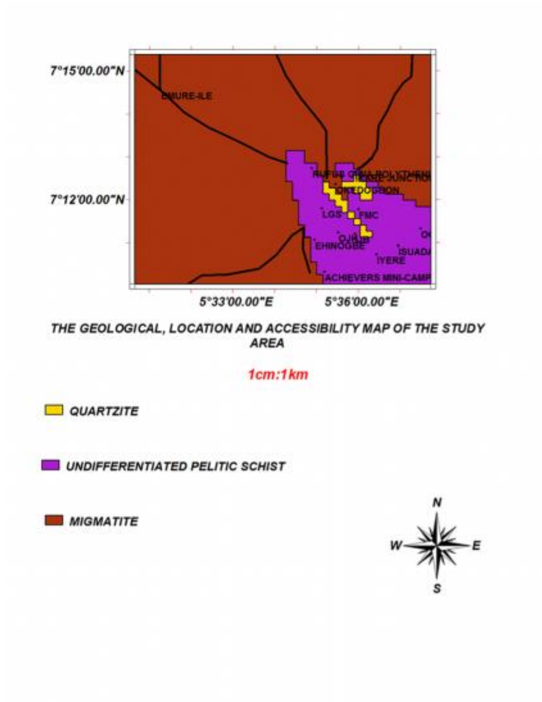

Figure 1: Geological, location and accessibility map of the study area

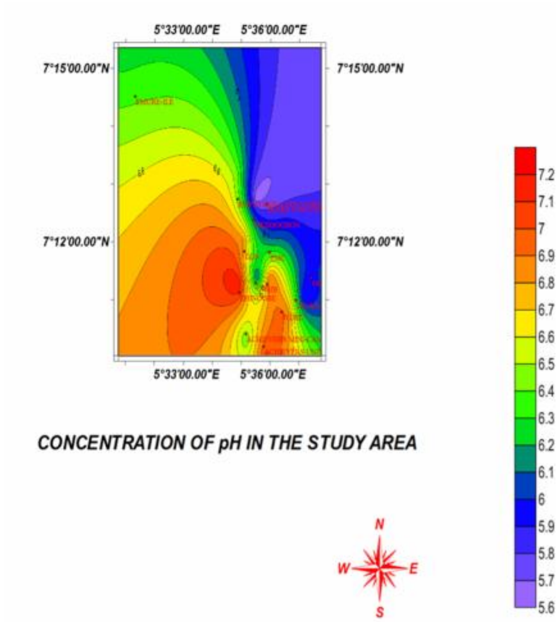

Figure 2: Concentration of pH in the study area

(r = 0.512), pH/Fe (r = -0.386), pH/Cu (r=-0.340), pH/Pb (r=-0.66), pH/Eh (0.319). Fe has a positive but weak correlation with Mn and Pb, Fe/Mn (r=0.143), Fe/Pb (0.064). However, Fe as a strong correlation with Cu (r = 0.456). The strongest relationship occur between Cu and Pb (r = 0.881). The correlation clearly shows that although the source of pollution in the soils of the study area is anthropogenic they were actually generated from different anthropogenic sources. The partial correlation was used to confirm the results from the bivariate correlation. Using Fe as the control, the result confirms the positive but weakly correlation that exists between the pH and Mn and Eh. It also confirms that a negative correlation occurs between Mn and Cu and weak relationship between Fe and Mn (Table 3). It also confirms that a good relationship exists between Cu/Pb and Cu/Fe.

Table 1: Mean values of physical parameters and heavy metal content in the selected Owo township soils.

S/N	NAME	pH	Eh	Mg/g Mn	Mg/g Fe	Mg/g Cu	Mg/g Pb
1.	Achievers University Permanent Site. (AMC)	7.02	90.00	1140.01	64250.03	43.72	26.04
2.	Achievers Mini Campus (AO)	6.40	63.00	336.08	23875.22	21.54	14.01
3.	Emure Market (EMT)	6.23	83.00	1485.06	80250.13	83.55	91.53
4.	Ehinogbe (EOE)	7.21	41.00	864.12	16250.17	29.08	17.04
5.	Federal Medical Centre (FOD)	6.09	88.00	755.17	18500.22	20.95	22.02
6.	Isuada (IAD)	5.89	78.00	975.24	77750.06	51.42	28.04
7.	St. Louis Grammar School. (LGS)	6.78	74.00	920.36	29500.34	35.42	19.55
8.	Ogbomo (OGB)	6.03	49.00	1525.11	44250.42	44.15	53.56
9.	Oja koko (OJI)	6.05	73.00	920.36	48750.08	74.92	155.04
10.	Ijebu (IJB)	6.93	97.00	1525.11	4,375.15	112.45	322.08
11.	Okedogbon (OKS)	5.64	37.00	1275.17	24375.15	37.65	20.09
12.	Iyere (IRE)	6.88	75.00	391.55	111000.11	64.15	42.55
13.	Rufus Giwa Polytechnic (OWG)	6.45	81.00	1, 195.44	71000.02	40.55	37.56
	Average Shale			850.00	46,000.00	45.00	20.00

Table 2: Bivariate correlation for elements and pH in the soil of the study area.

	pH	Mn	Fe	Cu	Pb	Eh
Ph	1					
Mn	0.512	1				
Fe	-0.386	0.143	1			
Cu	-0.340	-0.012	0.456	1		
Pb	-0.66	-0.72	0.064	0.881**	1	
Eh	0.319	0.298	0.418	0.465	0.439	1

** Correlation significant at the 0.01 level (2-tailed).

Table 3: Partial correlation for elements and pH in the soil of the study area significant at two-tail using pH as the control parameter.

Control	Variables	Mn	Fe	Cu	Pb	Eh
pH	Mn	1				
	Fe	0.431	1			
	Cu	0.201	0.374	1		
	Pb	-0.44	0.04	0.915	1	
	Eh	0.176	0.607	0.633	0.972	1

Table 4: Partial correlation for elements and pH in the soil of the study area significant at two-tail using Fe as the control parameter.

Control	Variables	Mn	Cu	Pb	Eh	pH
Fe	Mn	1				
	Cu	-0.880	1			
	Pb	-0.820	0.959	1		
	Eh	0.265	0.340	0.454	1	
	pH	0.622	-0.200	-0.450	0.551	1

Cluster analysis.

The dendograms (Figure9)clarifies the influence and association of the cluster and groupings by their relative elemental concentration at each sampling sites. It was also used to determine locations that have common source of pollution (Figure10). Therefore, on the basis on of similarity coefficients, Cu, Pb, Mn and Fe originated from mixed sources or retention phenomena. Mn and Fe may have originated from the bedrock in the area as suggested from the geology of the area, while Cu may have been generated from outside the study area, it may have been greatly influenced by pH and Eh.Pb may be have been generated from either in-situ or external sources. Figure 4 shows that OGB and IJB, IJB, OJI, EOE and FOD, FOD, AO, OKG, LGS, EMTand IAD, IAD, OWG and AMC and IRE may have the same source of pollution. This shows that some areas are especially affected by different source of pollution in the way they overlap other groups. IJB, FOD and IAD show this tendency of different sources of pollution.

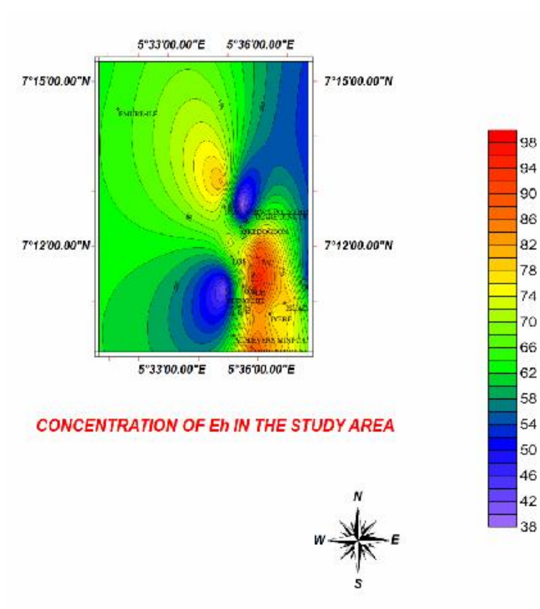

Figure 3: Concentration of Eh in the study area

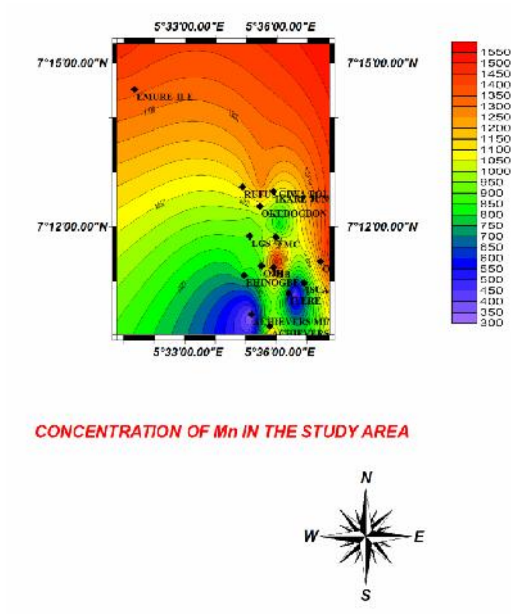

Figure 4: Concentration of Mn in the study area

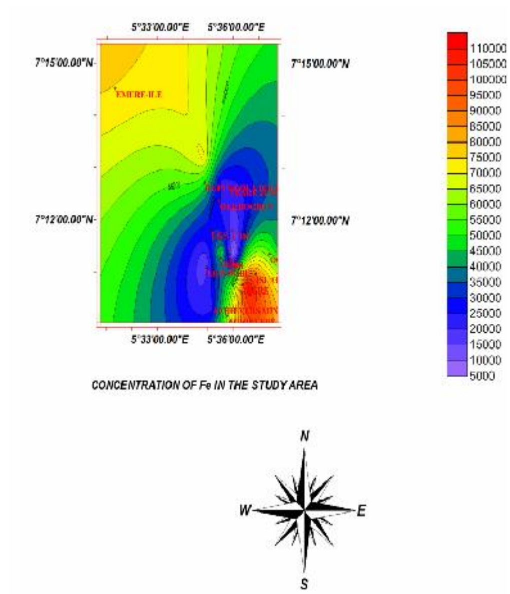

Figure 5: Concentration of Fe in the study area

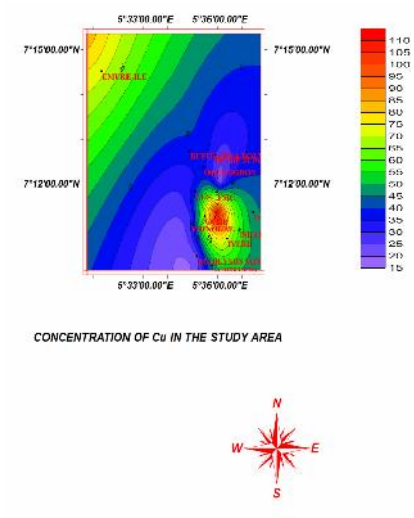

Figure 6: Concentration of Cu in the study area

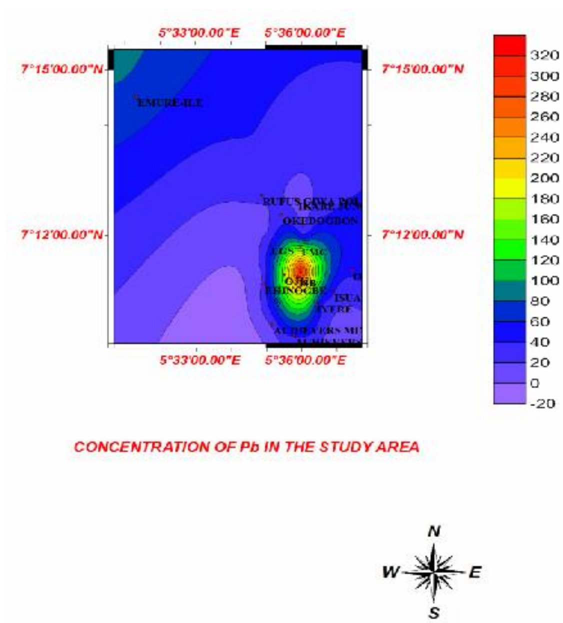

Figure 7: Concentration of Pb in the study area

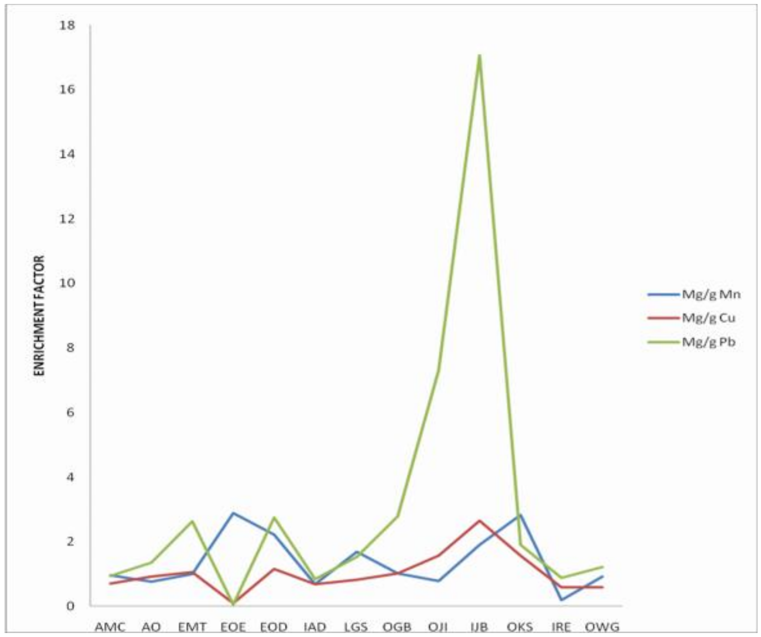

Figure 8a: Enrichment Factor of the study area

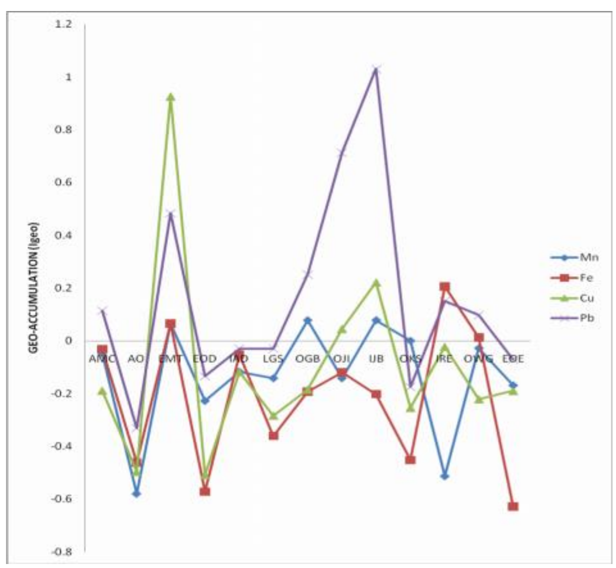

Figure 8b: Geo-accumulation values of the study area

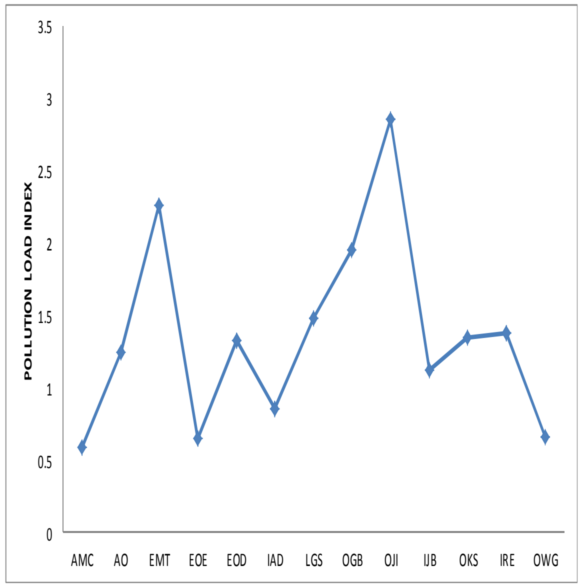

Figure 8c: Pollution Load Index of the study area.

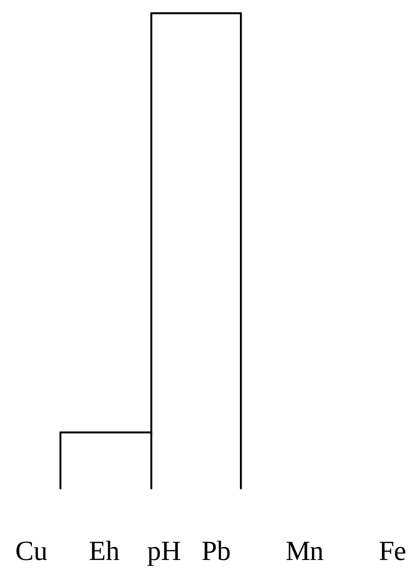

Figure 9: Dendogram showing relationship between the elements, pH and Eh in the soils of the study area.

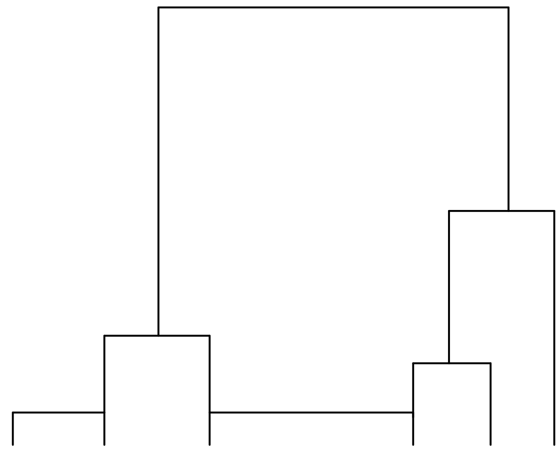

Figure 10: Dendogram showing the relationship between the sampling points to the source of pollution.

Conclusions

Thirteen soil samples taken from Owo Township were analyzed using standard geochemical techniques. The Enrichment Factor (EF), Pollution Load Index (PLI) and Geo-accumulation Index (*Igeo*) was used to assess the level of pollution in the soils. Attempt was made to subdivide the categories of Pollution Load Index (PLI) as introduced by Seshan *et al* (2010).

The results of the analysis shows that the soils have pH which range between 5.91 and 6.20, with mean heavy metal contents in the selected soils ranging between 391.55 to 1,525.11 mg/g Mn; 16,250-111,000.11 mg/g Fe; 20.95 to 112.45 mg/g Cu and 14.01 to 322.08 mg/g Pb.Enrichment Factor (EF) values shows that Mn has an enrichment between 0.19 and 2.88 which implies that they are of anthropogenic origin but exist as a background concentration to moderate enrichment in the soils. Geo-accumulation (*Igeo*) shows that all the metal have an Igeo value less than 1 except in Ijebu soils where Pb has Igeo value greater than 1. This indicates that although most of the metals show background to moderate concentration, their presence does not show sign of pollution in the sites of the study area. Pollution Load Index (PLI) shows that AMC, EOE, FOD and LGS show no traces of pollution whereas the others shows some traces of pollution. With our proposed sub classification of PLI, we classified these as moderately polluted.

Correlation of the analysis result using bivariate and partial correlation show that positive correlation exist between pH and Mn and Eh, while Fe has a positive but weak correlation with Cu. Cu and Pb has the strongest correlation in the soil. Cluster analysis using dendograms shows that Cu, Pb, Mn and Fe originated from mixed sources (i.e anthropogenic and natural) or relation phenomena.

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