GEOCHEMICAL ASSESSMENT OF INFLUENCE OF URBANIZATION ON HEAVY METAL ENRICHMENT IN STREAM SEDIMENTS OF ONDO TOWN, SOUTHWESTERN NIGERIA

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ABSTRACT

Trace element enrichment and pollution caused by urbanization with its associated effects increasingly becoming a great threat to environmental and human health. This paper, sediments from streams that drain Ondo town were sampled to evaluate the potential effects of urbanization on trace element accumulation in stream sediments. Fifty (50) samples of stream sediments samples were collected along the main stream and other adjoining streams in the town, wet sieved, digested and analyzed by Inductively coupled plasma- Atomic emission spectrometer (ICP-AES) for trace element (Cu, Zn, Pb, Cd, Cr,).. The result of the concentration of trace elements in ppm showed in the order of distribution: Cu (1-114); Pb (3-214); Zn (8-1332); Ni (1-17); Co (1-20); Mn (26-1699); Th (3-16); Sr (5-145); Cd (0.5-1.4); V (3-188); La (11-51); Cr(2-116); and Ba (40-337). From the result, several hot-spot areas were identified. These hot-spots were identified to be located close to areas where activities like, vehicle related workshops, road junctions, municipal waste, abattoir and farm gardens. Except for some of the elements, such as Cd, Sr and Th, which shows low concentration, the rest of the heavy metals in the stream sediments had two to three folds of magnitude of the concentration compare with the limits values of Granite, Migmatite and Average Shale samples. Principal component analyses (PCA) and geoaccumulation Index (Igeo) of the compositional data, slightly shows presence of metal contamination except Cd, Sr and Th which are ascribed to anthropogenic activities. Pb, Zn, Cu, Cr, Mn, Ni and V positively correlated with each other (R= 0.51-0.95), which indicate analogous sources of geochemistry characteristics.

KEYWORDS: Ondo town, Sediment, Geo-accumulation index, Urbanization, Hot-spot.

INTRODUCTION

As the world's urban population continues to grow, it becomes increasingly imperative to understand the dynamic interactions between human activities and the urban environment. The development of urban environmental geochemistry has yielded a significant volume of scientific information about geochemical phenomena found uniquely in the urban environment, such as the distribution, dispersion, and geochemical characteristics of some toxic and potentially toxic trace metals as stated by (Wong,et al, 2006 Gbadebo, 2007, Baruah and Khare, 2009; 2010, Lee, et al., 2005). Urban activities have a significant negative impact on the environment, particularly on aquatic resources as well as other biota. Stream Sediments are classic materials that are derived from the parent bed rock, as well as sand and deposited particles. Most sediments that are often transported through streams with continues transportation to various location or depositional environment, serve as ecologically important systems that provide diverse habitats for aquatic biota but because of their usefulness, physico-chemical characteristics and their relative flows, they are susceptible to contaminant retention, that may eventually lead to potentially harmful elements. Stream suspended and bottom sediments contain significant high concentration of metals than those found in the host water, because they serve as sink for these elements which may directly affect overlying waters, shallow ground water, as well as vegetation around the area, affecting human and livestock lives. (Samarghandi, et. al. 2007; Seshan et. al. 2010, Olatunji and Abimbola 2010, Baruah and Khare, 2010, Yaun, et al., 2011). Hence stream sediment becomes important media for assessing the influence of urban growth. Ondo metropolis is one of the many cities in Nigeria that have continued to witness tremendous growth in human population, which has also led to increase in her associated consumables. Market places, high waste generated, increased vehicular activities, raw material processing industries, sawmill abattoir and waste metal recycling company. All these activities result in generation and accumulation of waste, which eventually finds it ways into most of these drainages because of obvious non- regulation of waste disposal by government authorities. Ondo metropolis is the second largest city in ondo state, with a dentritic drainage system, where most of these streams empty into the Isalewa river which is the main river in the city. All

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runoff surface waters that cannot percolate or infiltrate into the ground, empty into this river, with attendant redistribution of sediments in the river channels. The city lies within longitudes **7°.00'** to **7°. 06'** and Latitude **4° 47'** to **4°. 53'.** (Fig 1) it is connected in the south through road by Ore, in the East by Akure, in the north by Ileluji and in the west by Ile-Ife, Okegbo town, with an average distance of between 25km to 45km to all these cities. The city cover's an average land area of 40km². The city is made up of towns like Surulere, Valentino, Funbi-Fagun, Ademalagun express way, Yaba, Sabo, Oka, Itanla, Nipakala, and many others towns that developed to form the city.

The objectives of this study were to determine the concentrations of metals in the stream sediments that drain the study area, to assess the geochemical distribution of these elements as well as evaluate for pollution status of the elements using statistical quantification indices.

The geology of the study area consists of Precambrian igneous and metamorphic rocks (Migmatite, Igneous and Quartzite) that is at discreet location seen as low lying outcrop in some areas, while in some other areas, they occur as massive and extensive. The mineralogy consists of Biotie, feldspar, quartz and muscovite minerals.
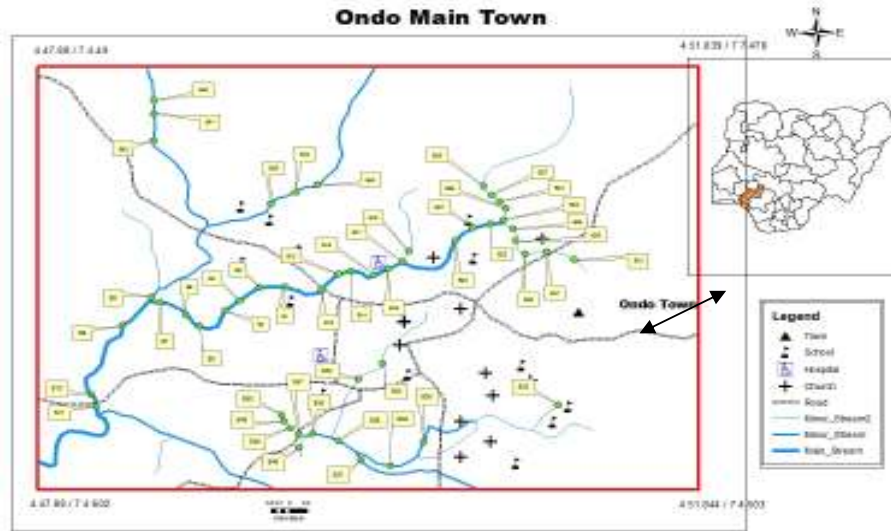

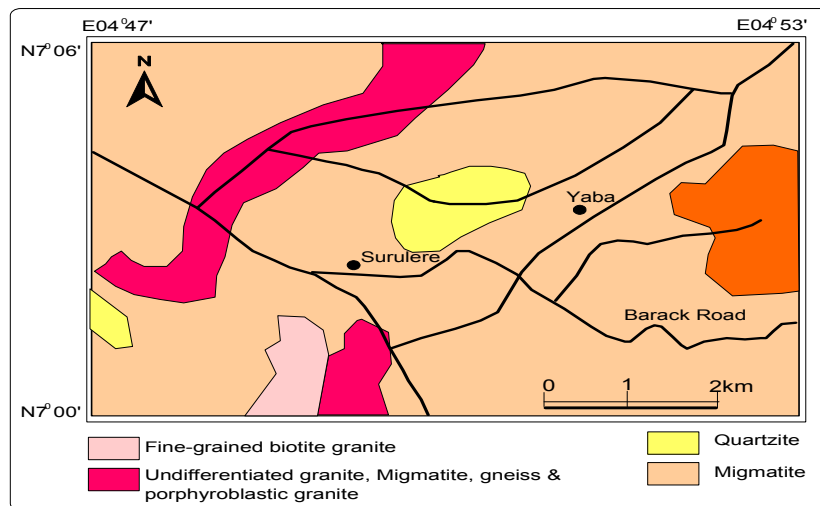**Fig1:** Sampling locations of the study area (Modified Sheet 263, Federal Survey Nigeria, 1968)

Fig2: Geologic map of the study area (Modified after NGSA generalised geologic map of Nigeria, 2006)

2. MATERIALS AND METHODS

A total of fifty (50) stream sediment samples were collected from some of the streams that traverse the study area, including the main stream which is known as Isalewa River (fig. 2). The samples were collected at interval of between 200m to 300m using plastic packer to avoid contamination of samples. At each site, 3-4 sub-samples in the area of about 10m radius from both sides of the river's sampling point, were obtained and mixed to yield a composite

sample and wet sieving was carried out at each location using <200um sieve mesh to get the silt-clay fraction.

The wet samples were stored in the field in a plastic bottle of 75cl. All the samples were allowed to settle down, and the suspended water was decanted. After-ward, they where air dried and homogenized in an agate mortar, disaggregated, ground and further sieved with < 63um for subsequent sample digestion and chemical analyses. The samples where digested using, Aqua-regia digestion (0.5ml H_2O,).6ml concentrated HNO_3 and 1.8ml HCL) for 2hours at 95^oC. Thereafter, the samples were cooled and then diluted to 10ml with deionize water and homogenized, then they were analyzed to determine the constituents of the elements using inductively coupled plasma- optical emission spectroscopy (ICP-OES) at the Geochemical Laboratory of ACME laboratory Limited, Vancouver, Canada. pH, Electrical Conductivity (EC) and Total Dissolve Solid (TDS) values were obtained with a standard multi physico-chemical determinant meter (Hach Eco40 multi Milwaukee), from slurries prepared using 20g of samples and 20ml of distilled water

3.   RESULTS AND DISCUSSION

It is interesting for the proper understanding of the effect of urbanization on surface earth media, using the background as a measure is of importance. Hence the natural (normal) concentration of trace elements in sediments is of great interest, which will be needed to assess the degree of sediment contamination in other to evaluate the sediment quality, which is a prerequisite for sustainable land use and management. As we already know, there is no one natural background level for any solid material, in or on the earth, because the earth is characterized by non-homogenous, according to (Eby 2004, Hamzeh et al. 2011). So, in environmental geochemistry studies, natural background values must be evaluated on a local scale. Using published work on the average values of soils, sediments, rock and water can be conventionally accepted. In this work, the average   shale   concentration,   the   elemental concentration two main rock types that underlain the study area (i.e Granite and Migmatite rocks) as well as relative variation on trace elements from one location to another particularly these location that of low human activities were used to measure enrichment status of the sediments in the study area.

The statistic summary result of trace element concentration in (units: ppm) of Ondo stream sediments is presented in (Table:1). The stream sediments showed a significant heterogeneity in the concentrations of the elements being studied, with the obvious spatial variation of concentratons from one sample location to another.

Mn exhibits the highest concentration in (unit: = ppm) in the stream sediments(range = 26-1699, arithmetic mean ± standard deviation= 519.6 ± 322.2), followed by Zn, (8-1332, mean 489.9 ± 359.6), Ba (40-300 mean152.6 ± 55.4,), Pb (3-214, mean 78.7 ± 48.4), V(3-188, mean 59.2 ± 25.1), Sr (5-145, mean 43.6 ± 31.8), Cr (2-116, mean 36.6 ± 16.8), Cu (1-114, mean 36.5 ± 26.3), La (11-51, mean 30.1 ± 8.5), and Co (1-20, mean 20 ± 3.1). The mean concentration were below 8.9 ppm for Ni, below 10.2ppm for Th and below 0.7ppm for Cd.

Comparing the results of the concentration of trace elements in the various locations with the analised results from two dominant rock types in the study area i.e the migmatite and granitic rock as well as the concentration of uncontaminated average shale values, shows that stream sediment in ondo town, are enriched in some locations of the trace element investigated. Arithmetic mean concentration of stream sediments were three times higher for Zn and Pb, two times higher for Cd compare to those of stream sediments (Table1). Again when one observe comparatively, the concentration of the studied elements in the two rock types are lower than the mean concentration for Cu, Pb, Zn and the other elements being studied. From the results, it is observed for Mn, with the exception of location's (SS) 2, 40, 41, 43, 45 and 49, which has elemental concentration less than 120ppm. The other locations have concentration higher than 250ppm, with the highest location in SS9 (1699ppm). Other hot spots are in location (SS) 1, 4, 7, 11, 26, 34, 36, 44 and 49.

Zn concentration in the study area are relatively high in most locations. Few location with low elemental concentration include (SS) 2, 26, 27, 28, 30, 40, 41, 42, 42, 43, 44, 45,49 and 50. These areas have elemental concentration lower than 200ppm. All other locations are characterized with high Zn concentration higher than 200ppm. Some of the hot spots include, (SS) 1, 20, 32, 34, 35, 37, 39, 48, and 33. With the highest in location 33 (1332ppm). These locations have Zn concentration higher than 800ppm.

Lead (Pb) concentration determined in the study area are found to be high in similar locations compare to Zn and Mn locations that are observed to be hot spot, showing the same trend of elemental concentration. With the exception of locations (SS) 2, 10, 26, 27, 28, 40, 41, 42, 43, 44, 45,and 49, which have Pb concentration lower than 45ppm. Other locations have Pb concentration higher than 50pp. some of the hot spots include locations 12, 13, 23, 25, 32, 33, 35, 37, 39, 47 and 48. The higher concentration is in location 33 (214ppm). The other elements i.e Ba, V, Cr, Ni, Co, La, Th, Sr, and Cd, also shows spatial distribution of trace metal concentration from the samples analyses. These distributions align with the effect of urban activities, (areas close to waste dump, vehicular activities, farm lands, domestic emissions, wear and tear of vulcanized rubber tires) areas of high elemental concentration almost follow the same trend for most of the metals observed. The relative pervasive general metal enrichment in almost all the locations for Pb, Mn and Zn suggest high effect of urban activities. Severe contamination appear to be of the same trend in most localities for Mn, Zn and Pb, suggesting noticeable pollution in the major stream of the area which drain North to South of the city, because of its high influx of waste   draining   into   the   main   stream.

Table1: Descriptive statistics of trace element concentration (ppm) in stream sediment of the study area

Elements	N	Minimum (ppm)	Maximum (ppm)	Mean	Std. Deviat	ASC (ppm)	MGT ppm	GT ppm
Cu	50	1	114	36.5	26.3	50	10	20
Pb	50	3	214	78.7	48.4	20	50	13
Zn	50	8	1332	489.9	359.6	90	100	77
Ni	50	1	17	8.9	3.8	80	<2	5
Co	50	1	20	5.4	3.1	20	4	4
Mn	50	26	1699	519.6	322.2	850	62	81
Th	50	3	16	10.2	2.6	12	3.5	6.0
Sr	50	5	145	43.6	31.8	400	391	230
Cd	50	0.5	1.4	0.7	0.3	0.3	<0.5	<0.5
V	50	3	188	59.2	25.1	130	13	
La	50	11	51	30.1	8.5	40	39	5.3
Cr	50	2	116	36.6	16.8	100	<2	21
Ba	50	40	337	152.6	55.4	600	82.7	61
EC (us/cm)	50	89	211.0	158.4		-		
TDS (Mg/L)	50	66.8	158.3	118.8		-		
pH	50	5	8.4	7.0		-		

*ASC: Average Shale Concentration after Turekian and Wedepohl (1961)
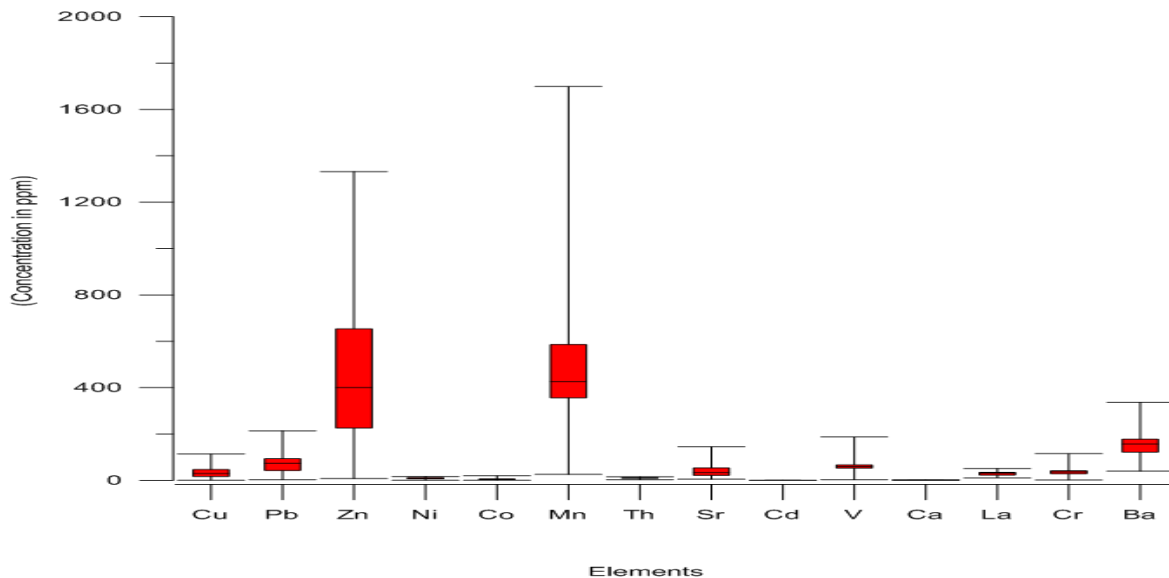MGT: Migmatite
GT: Granite

Fig3: Boxplots of the total concentrations (ppm) of trace elements in stream sediments. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution

3.2   Statistical Analyses

The results were further analyzed by statistical interpolations to ascertain trace elements relations in the stream sediments of the study area, between the various metal concentrations of the sediment samples. In the present study, both Pearson Correlation (PC) and Principal Component Analysis (PCA) were carried out using Origin and SPSS software package. In order to study the general characteristics of the stream sediments in Ondo town, the concentrations of trace metals content of the stream sediments were used as the input data in the PC and PCA.

The Pearson correlation showed a wide variation in the interelemental relationship both for the scatter plot and Correlation coefficients of the trace elements, fig4 (a-e) and Table 2. For the elemental relationship, there is a fair coefficient of determination (R^2) between Mn and Co (R^2 = 0.4179), Ni and Cr (R^2 = 0.4855) and Zn and Pb (R^2 = 0.5821). While there is strong correlation between Cu and Pb (R^2 = 0.6106) and Zn and Ni (R^2 = 0.6704). These elements show close affinity suggesting analogous source of enrichment in the stream sediment.

The correlation matrix for the data obtained (**Table 2**) shows a wide variation in the correlation coefficient (r) between element pairs. For example, the r values range from −0.01 between Th and Zn to 0.95 between V and Cr. Fairly strong to very strong positive correlation occurs among Pb, Cu, Zn, Ni and Sr. positively correlated with each other. Considerable high

correlation were found between Pb and Cu (R = 0.78), Zn and Cu (R = 0.93), Zn and Pb (0.76), Ni and Cu (R = 0.85), Ni and Pb (R= 0.70), Ni and Zn (R= 0.82), Cd and Sr (R = 0.87) and Cr and V (R= 0.95). Other elements also showed fair to strong correlation as summarized in (Table 2).

Also the result obtained from the various PCA i.e (Factor analyses, three component plot and two component plot), (Table3, fig5a&b) further found elemental association three and two component factors of association respectively. Factor analyses revealed three group of trace element, (Table3). the first group is made up of   Cu, Pb, Zn, Ni, Sr, Cd, Cr and Ba, accounting for 45% total variance of eigen value. These elements as also found in the correlation values (Table2), may have been enriched by same sources, most likely from domestic waste, effuents and vehicle related waste. The second group is made up of Co, Mn, Th and La, accounting for approximately 22.8% of the total variance. These elements may have been enriched in the sediments by activities relating to similar pollution source draining into the stream (e.g. urban waste). The third group consist of V and Cr, which account for

15.2% of the total variance. These two element main have been enriched in the sediment by same source, activities relating to soil weathering and leachate from automobile activities and other urban consumables like additives in chemical products. Table 4; shows summary of factor Analyses of the trace elements in stream sediements of Ondo town.

Applying the three and two plots of principal component analyses (PCA) enabled us to find out further that the same trace elements cluster close to each other i.e. those elements that are likely to be from analogous sources cluster together as summarily seen in fig 4(a&b). for the three component loading, Cd, Sr, Cu, Zn, Pb and Ni load close to each other suggesting similar source of enrichment. While La, Th, Mn, and Co load close to each other, also suggesting same source of enrichment. Ba appear on it own, suggesting an entire different source of enrichment. Also for the two component plot, it is observed that, the elements plot on two sides. These element further correlate base on the likelihood of their enrichment being from similar sources, fig4(a&b)
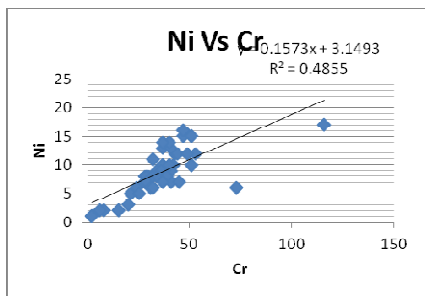
(a)
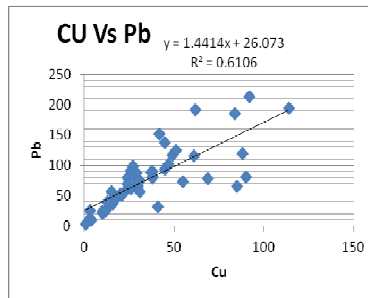
(b)
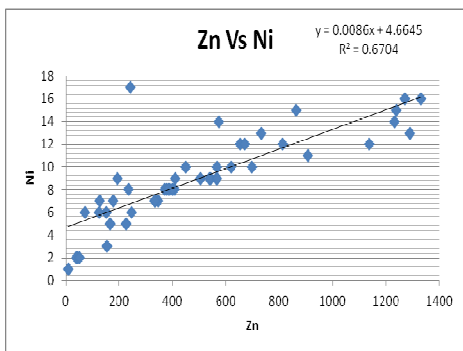
(C)

(d)

(e)

Fig4(a-e): Relationship between some of the trace elements in the stream sediments of the study area.
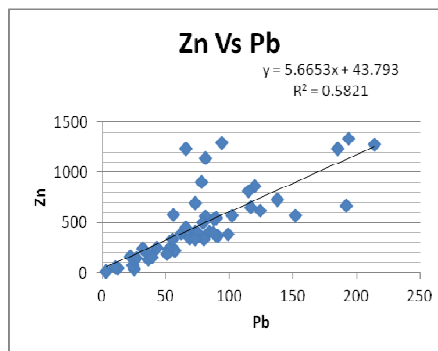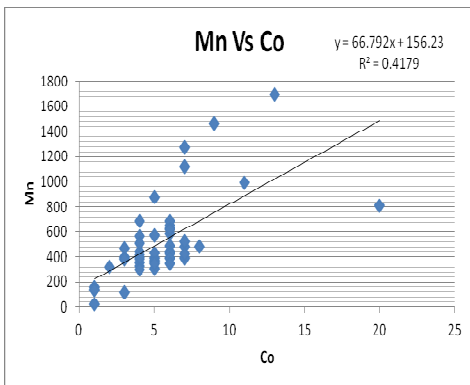
Table 2: Correlation coefficients of stream sediments in the study area

	Cu	Pb	Zn	Ni	Co	Mn	Th	Sr	Cd	V	La	Cr	Ba
Cu	1												
Pb	**0.78**	1											
Zn	**0.93**	**0.76**	1										
Ni	**0.85**	**0.70**	**0.82**	1									
Co	0.01	0.02	0.20	0.24	1								
Mn	-0.02	0.04	0.03	0.12	**0.65**	1							
Th	-0.04	0.13	-0.01	0.29	0.38	0.27	1						
Sr	**0.87**	**0.57**	**0.86**	**0.68**	-0.02	-0.03	-0.20	1					
Cd	**0.91**	**0.70**	**0.87**	**0.72**	-0.09	-0.11	-0.10	**0.87**	1				
V	0.29	0.18	0.18	**0.64**	0.24	0.13	**0.55**	0.12	0.15	1			
La	-0.10	0.02	0.06	0.17	**0.69**	0.48	**0.61**	-0.11	-0.18	0.19	1		
Cr	0.42	0.29	0.29	**0.70**	0.12	0.04	0.39	0.25	0.30	**0.95**	0.02	1	
Ba	0.40	0.45	**0.59**	0.42	**0.64**	**0.54**	0.03	0.45	0.35	-0.05	**0.51**	-0.05	1

Table 3: Summary of factor Analyses of the trace elements in stream sediments of the study area

| Extraction Method: Principal Component Analysis.			
Elements	1	2	3	4
Cu	**0.96**	-0.18	0.01	-0.03
Pb	**0.79**	-0.04	-0.06	-0.36
Zn	**0.95**	-0.07	-0.19	-0.09
Ni	**0.92**	0.20	0.24	0.00
Co	0.17	**0.82**	-0.33	0.19
Mn	0.09	**0.69**	-0.36	0.37
Th	0.09	**0.72**	0.38	-0.47
Sr	**0.88**	-0.28	-0.17	0.13
Cd	**0.89**	-0.31	-0.05	-0.07
V	0.40	0.47	**0.75**	0.19
La	0.07	**0.83**	-0.24	-0.29
Cr	**0.50**	0.29	**0.75**	0.25
Ba	**0.53**	0.42	-0.66	0.07
% of Variance	45.40029	22.80217	15.26634	5.329084
Total	6.356041	3.192304	2.137288	0.746072
Cumulative %	45.40029	68.20246	83.4688	88.79789
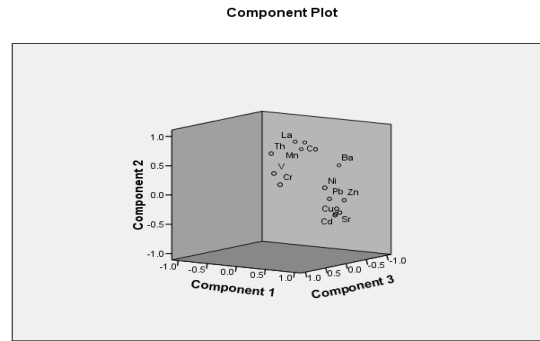
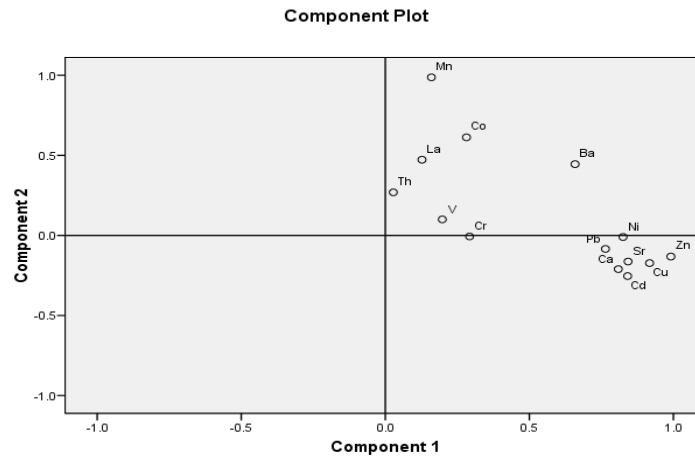**Fig5a:** Plot of the three principle component for the trace elements

Fig5b: Plot of the two principle component for the trace elements concentration in stream sediments

The stream sediment quality assessment of the contamination status were evaluated using Geo-accumulation index. This method has been used successfully by researchers (Muller, 1979, Forstner and Wittmann, 1983 and Odewande and Abimbola, 2008) to determine the quality of the geo materials. It is expressed as

$I_{geo} = Log_2 Cn/1.5B_n$

Where I_{geo} represent the geo-accumulation index, C_n represent measured concentration of the element in the sediment, B_n represent the background value (where for this paper, the average shale value) and 1.5 is the backgraund matrix correlation. It is classified into six (6) classes (Muller, 1979), ranging from unpolluted to very highly polluted. The summary and details of the calculated Igeo from selected metals in the study area is presented in fig4(a and b)

Table4a: Detailed Geo-accumulation Index Calculated for selected elements in stream sediments of Ondo town.

S/N	Ig Cu	Ig Pb	Ig Zn	Ig Cd
SS1	1.75	2.82	4.43	2.00
SS2	-3.74	-2.15	-2.91	1.32
SS3	0.85	2.58	2.47	1.32
SS4	0.96	2.77	2.62	1.32
SS5	0.17	2.10	1.91	1.32
SS6	1.07	2.74	2.66	1.32
SS7	1.02	2.66	2.77	1.58
SS8	0.85	2.37	2.52	1.32
SS9	1.17	2.45	2.77	1.58

SS10	0.35	1.69	2.04	1.32
SS11	0.58	1.96	1.97	1.32
SS12	1.88	3.13	3.45	2.17
SS13	1.75	3.37	3.61	1.81
SS14	1.51	2.75	3.18	1.58
SS15	1.51	2.60	3.23	1.81
SS16	1.47	2.72	3.16	1.81
SS17	1.12	2.71	2.74	1.32
SS18	0.72	2.04	2.48	1.32
SS19	0.96	2.22	2.70	1.32
SS20	2.75	2.60	4.25	2.70
SS21	1.17	2.31	2.90	1.58
SS22	1.22	2.07	3.26	2.00
SS23	1.66	3.51	3.24	2.17
SS24	1.62	1.26	2.01	1.32
SS25	2.19	3.11	3.76	2.70
SS26	0.26	1.47	1.56	1.32
SS27	0.07	1.43	1.07	1.32
SS28	-0.42	0.72	1.47	1.32
SS29	2.04	2.45	3.54	2.46
SS30	0.66	1.94	1.69	1.32
SS31	2.37	2.55	3.92	2.32
SS32	2.66	3.79	4.37	2.81
SS33	3.10	3.86	4.47	2.70
SS34	2.67	2.31	4.36	2.70
SS35	2.79	4.00	4.41	2.70
SS36	1.51	2.57	3.07	2.32
SS37	1.82	2.94	3.24	2.46
SS38	1.02	2.89	2.68	1.58
SS39	2.72	3.17	3.85	2.70
SS40	-2.15	-0.15	-0.45	1.32
SS41	-2.15	0.91	-0.66	1.32
SS42	-0.42	0.85	0.24	1.32
SS43	-0.15	0.91	1.04	1.32
SS44	-0.15	1.02	1.33	1.32
SS45	-1.74	-0.42	-0.23	1.32
SS46	1.22	2.49	2.73	1.32
SS47	1.94	3.22	3.37	2.17
SS48	2.22	3.85	3.48	2.32
SS49	0.04	1.55	1.35	1.32
SS50	1.17	2.45	2.48	1.81

Table 4b: summary of Geo-accumulation index calculated for selected metals in Ondo town stream sediments.

Metal	Igeo Range	Interpretation
Cu	0 - 3	Unpolluted – highly polluted
Pb	0 - 4	Unpolluted – very highly polluted
Zn	0 – 4	Unpolluted – very highly polluted
Cd	0 - 2	Unpolluted – moderately polluted.

CONCLUSION

A total of 50 stream sediments samples in Ondo town were examined for Cu, Pb, Zn, Cr, Ni, Mn, Ba, Th, La, Sr, Co, V and Cd. High concentration of metals were generally found, especially Mn, Zn, and Pb. These indicate that these metals may be potentially hazardous to the environment. Elevated metal concentrations were found at locations close to active commercial and human waste discharges into the stream, indicating anthropogenic effect. Comparing the determined elemental result with the background result, there is a considerable elemental enrichment in the stream sediments to between 4 to 6folds in most of the location greater than the background. Further pollution level quantification of the trace metals revealed that Pb, Zn and Cu have reached significant pollutant status in the stream sediments of Ondo town as observed in the calculated geo-accumulation index which is seen that Pb and Zn are ranging from uncontaminated to very highly contaminated while Cu and Cd is ranging from uncontaminated to highly contaminated and moderately contaminated respectively.

ACKNOWLEDGEMENTS

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