

Provenance and Heavy Metals Concentrations in the Bedrocks and Sediments of Okemesi/Ijero District, Southwestern Nigeria

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ABSTRACT

An assessment was conducted on the bedrocks and sediments of Okemesi/Ijero area using geochemical approach in order to establish the concentration of heavy metals; determine the level of enrichment and develop their geo-accumulation index. Field studies of the bedrocks were carried out, and provenance of the sediments was determined. Thirty-five bedrocks and sediment samples were collected for this study in a grid-controlled sampling method. The samples were dissolved using Lithium Tetraborate fusion method followed by HCl and HF acid digestion. Field studies revealed that the sediments were derived from the weathering of the bedrocks such as quartz-biotite-schists, banded gneisses, granite gneisses, biotite gneisses, calc gneisses, porphyritic granites, charnockites, massive/schistose quartzites and mica schists which are the dominant lithologic units in the study area while intermediate rock is attributed as the probable source of sediments. The concentration of Cu, Pb, Zn and Ti were found to be higher in both bedrocks and sediments more than the background. Positive correlation occurred between Pb, Cu and Zn indicating a common lithogenic source in the sediments and bedrocks but Fe and Ti were discovered to be anthropogenically and extremely enriched in the sediments. The enrichment factors of the heavy metals showed moderate to significant enrichment (EF- 5-20) for Pb (28.95%), Cu (73.68) and Zn (2.63%) in bedrocks and Cu (45.7%), Pb (82.86%) and Nb (54.29%) in sediments. However, gold mineralization potentials in the study area is very high based on moderate to significant enrichment of its pathfinder elements in the bedrocks and sediments of the studied areas.

Key words: Bedrocks, Sediments, Heavy metals, Geo accumulation index (Igeo), Enrichment factor (EF).

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INTRODUCTION

Bedrocks and sediments are veritable media for mineral prospecting and exploration because they host mineral deposits, especially when the rock is fresh. Such mineral deposits include metallic, non-metallic, precious and base metals. Due to mechanical breakdown of the rocks, the heavy minerals in them migrate from the primary geochemical environment to a basin of deposition which

is covered with sediments forming placer or paleo-placer deposits. Also, geological processes peculiar to plate boundaries give specific tectonic settings which in turn control the origin, emplacement and distribution of metallic mineral deposits. Sources of heavy metals in sediments/soils include vehicle emissions (Harrison et al., 1981; Lau and Wong, 1982; Yassogiu et al., 1987;

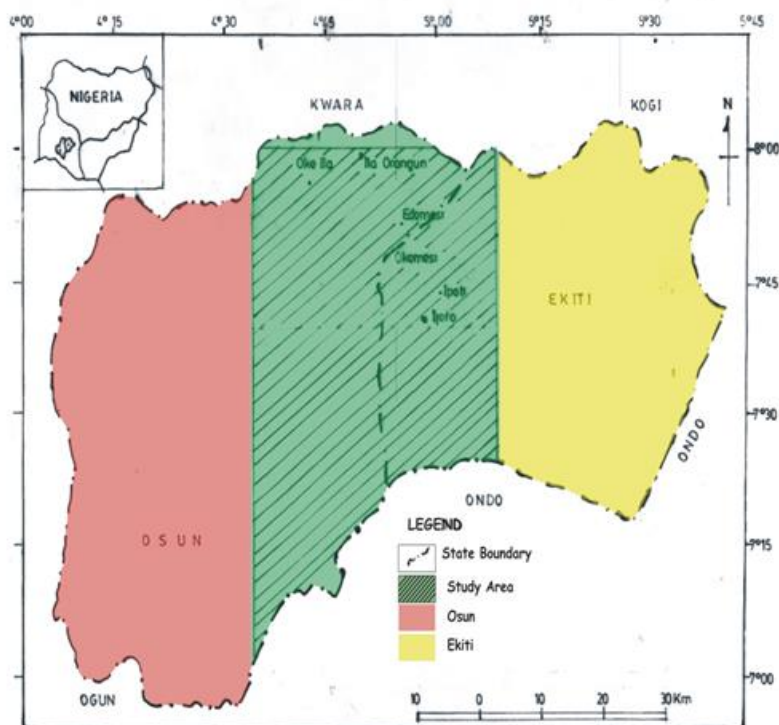


Figure 1. Map of Osun and Ekiti, southwestern Nigeria showing the study area (inset: Map of Nigeria showing Osun and Ekiti States).

Sutherland et al., 2000), industrial waste (Schumacher et al., 1997) and the deposition of dust and aerosol from atmospheric contamination (Simmonson, 1995; Thornton, 1991; Tiller, 1992). Most heavy metals in high concentrations have an adverse effect on human health; they accumulate in the body causing heavy metal poisoning which is a co-factor in many other diseases (Hammond, 1982; Nriagu, 1988; Thacker et al., 1992; Schwatz, 1994; Ballinger, 1995; Paterson et al., 1996). Therefore, this study is aimed at determining the heavy metal contents in the bedrocks and sediments of Okemesi/Ijero area to provide baseline geological and geochemical information on the abundance of these metals subsequent to their exploration.

LOCATION AND ACCESSIBILITY

The study area lies within latitudes $7^{\circ} 45'N$ and $8^{\circ} 00'N$ and longitudes $4^{\circ} 52'E$ and $5^{\circ} 08'E$. It covers part of the topographic map sheet No. 243 (Ilesha N.E. 1:50,000) and sheet No. 244 (Ado N.W. 1:50,000). The study areas cover parts of Ekiti and Osun, southwestern Nigeria with a total surface area of 821.4km^2 (Figure 1). Major towns in the area include Okemesi and Ijero Ekiti. Other towns include Epe, Ikoru, Efon, Ipoti, odo-owa, Ayegunle, while those in Osun State are Oke-ila, Ilupeju, Edemode, Orangun and Oba-sinkin. The areas which fell within

Osun, southwestern Nigeria can be rated moderately motorable due to interconnectivity of roads while areas within Ekiti can be rated poor because there are only minor roads and footpaths which are not motorable. Localities within Ekiti are mainly small villages with linear settlement along the road, while nucleated settlement predominates in Osun. Also, villages and towns have major, minor roads and also footpaths which are inter-linked to one another.

REGIONAL GEOLOGY OF THE STUDY AREA

The study area lies within the crystalline basement complex of southwestern Nigeria. The area is underlain by rocks typical of the basement complex as gneisses, migmatites, granites, quartzites, schists, pegmatites and metasediments ranging from Precambrian to Paleozoic age. The dominant rock type in the study area is the quartzites of the Efon Psammite Formation which occurs mostly as massive quartzites, schistose quartzites and quartz schists. The Efon Psammite Formation which extends to Okemesi (Hubbard, 1966; De Swardt, 1953; Dempster, 1967) is a belt of quartzites, quartz schist and granulites which occurs largely east of Ilesha and runs for nearly 180 km in a general NNE-SSW direction.

This environment like other areas within the Nigerian basement complex was subjected to the Pan African

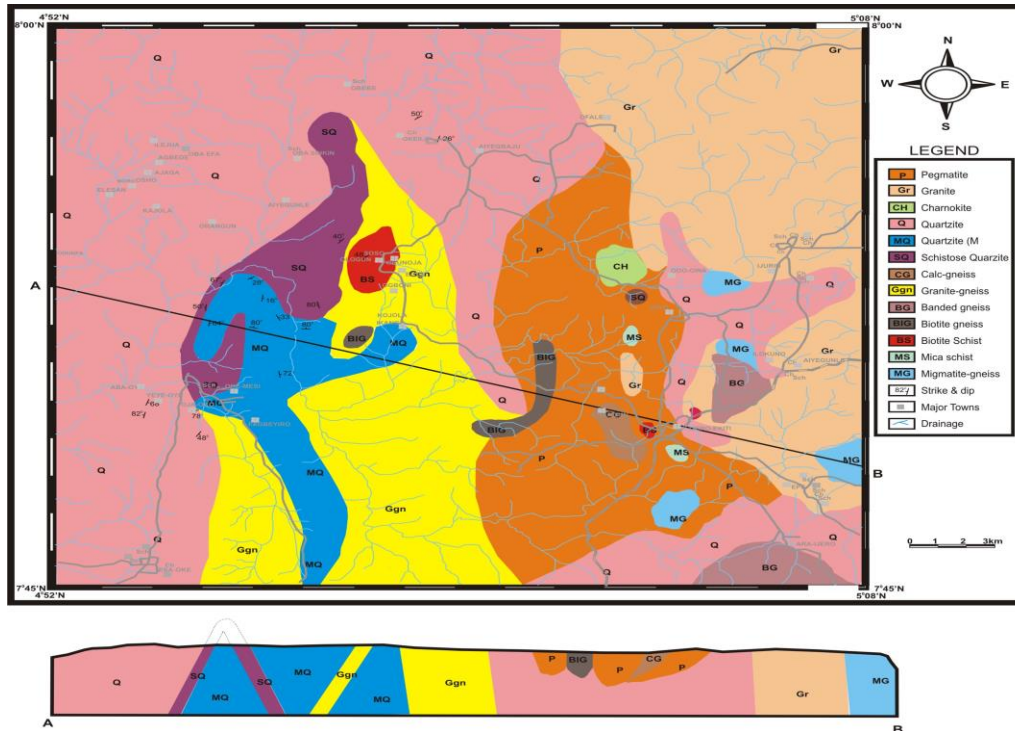


Figure 2. Geologic and cross-sectional map of the study area.

orogenic event about 600 ± 150 Ma (Ajibade et al., 1980). The different lithologies in the study area have been subjected to deformation which led to the development of synformal structures on the metamorphic rocks. The structures include fractures, foliations, veins and folds. The general trend of the folds and foliations is NNE-SSW direction. In Ijero area, the field work carried out also revealed that the area is underlain by the Precambrian rocks of the basement complex which are migmatite-gneiss, gneisses, metasediments-mica-schists, quartzites, calc-silicates, pegmatites and Pan African granites. In the area covered by this study, low-lying mica-schist is found to the west and the migmatites and gneisses occur to the east. The granites occur in the south and the charnockites, in the northwestern sector of the area. The schists and the intruding pegmatites have been highly weathered to the low lying terrain and in some places as rubbles and boulders. Exposures of schists is however noticeable within some built up areas. The charnockites occur as spherical boulders; in some places, they form large inselbergs with discrete exfoliation surfaces. Two varieties were observed: coarse grained and fine-grained. The two sometimes occur within the same vicinity. Fresh samples are bluish to dark-green in colour while the weathered ones, show dark brown stains of chemical weathering process. Granites form prominent outcrops in the southern area. Rocks found in Ikoro Ekiti include charnockite, quartzite, schist, schistose quartzites and migmatite. Some areas

are predominated by paraschists with their associated meta-igneous rocks have been migmatized to various degrees. The granites exhibit both intrusive and replacement characteristics, while the charnockite form an elongated N-S trending topography which ranges from fine grained to coarse grained porphyritic granites. The various rock units mapped in the course of field work were compiled to produce a geologic and cross-section map of the study area (Figure 2). The sediments in the study areas are derived from the weathering of these rocks.

MATERIALS AND METHODS

The methods adopted for this research work is divided into two aspects namely field and laboratory operations. The field operation is essentially geologic mapping of the study area to determine the underlying bedrock units. The geologic mapping was carried out at a scale of 1:50,000 using grid-controlled sampling method at a sampling density of one sample per 4sqkm^2 for the collection of stream sediments and rock samples. Thirty-five (35) rock and stream sediment samples were obtained. The rock samples were collected from different localities in the studied area, after which they were labeled accordingly to avoid mix up (Figure 3). The location of each outcrops were determined with the aid of a Global P ositioning S ystems (GPS) and the lithologic

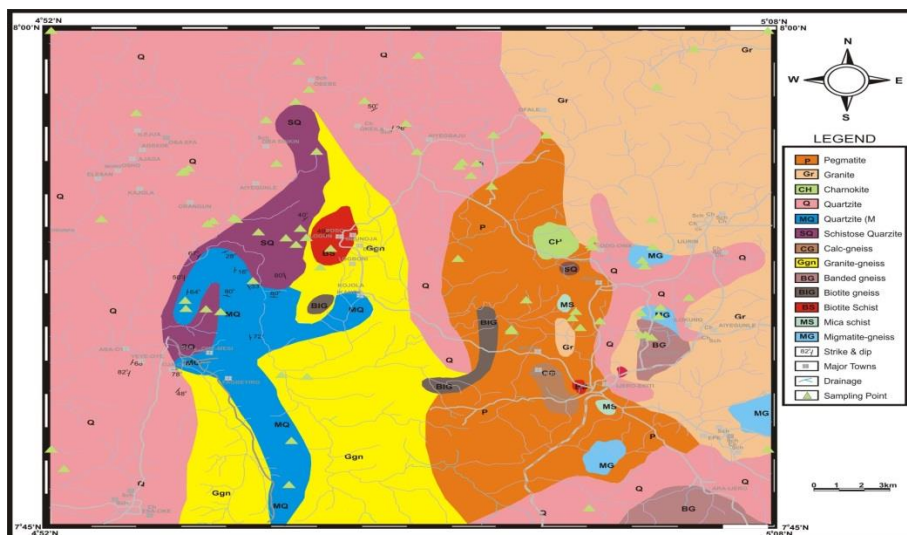


Figure 3. Rock samples collection points.

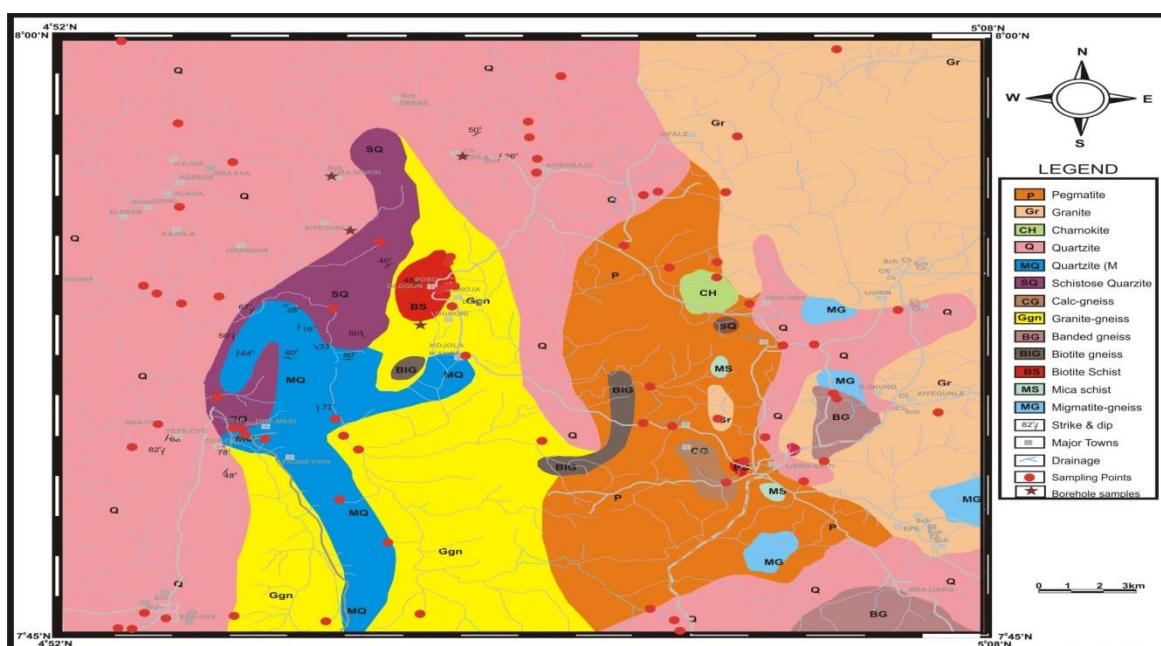


Figure 4. Stream sediments sampling points.

and field description of each samples were correctly recorded in the field notebook. The samples were bagged and transported to Petroc Laboratory, No.2, Shasa Road, Ibadan, where it was pulverized and crushed using standard procedures and were later digested using the total digestion method. 40 g of the digested samples were packaged into containers provided and properly labeled, and were sent to ACME Laboratories, East Vancouver, Canada for geochemical analysis to determine the major oxides using atomic absorption spectroscopy (AES) while the trace and rare earth

elements were determined using inductively coupled mass spectrometry (ICP-MS). Sediment samples were taken at a depth of 20 to 25 cm (Figure 4); they were bagged and labeled to avoid mix up before transportation to the laboratory.

The geographical locations of each sample collected were noted and recorded in the field notebook. Also the characteristic features of the stream sediments collected were also recorded in the field notebook. The laboratory operations involve pulverization and homogenizing the stream sediment samples using a pulverizer to allow to

crush the coarse particles in the sediments after which the milling machine was used for further pulverization until the samples became very fine in size (-15 μm). 40 g of the homogenized sample was analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Samples were dissolved using Lithium Tetraborate fusion method followed by HCl and HF acid digestion (Watts and Johnson, 2010). This digestion method was chosen to provide a more aggressive dissolution of refractory minerals than a standard mixed-acid method. The sediment samples were placed in a sample container which was properly labeled. The digested samples from both areas were transferred to ACME Laboratories, East Vancouver, Canada. The elements analyzed for include Mo, Cu, Pb, Zn, Ag, Fe, Bi, Cr, Ti, Ni and Nb, respectively.

RESULTS AND DISCUSSION

The geological map revealed the dispositions of the various rock units in the area. Also, from the geological map, migmatites are the oldest rocks in the study area, a few lithologies such as the pegmatites, mica schists, charnockites and granites occur as intrusive bodies within the migmatite-gneiss, and others such as granite-gneiss, calc-gneiss etc form discrete, disseminated and linear bodies within the massive quartzites and the schistose types. The strike values of the quartzites (schistose and massive) range from 024- to 046^o in some places. Also, the rocks dip in the western direction, with values such as 40 to 80^oW in some areas of study, while other areas also dip in the eastern direction with dips such as 72 to 80^oE, respectively.

The high dip values could be attributed to several episodes of deformation that characterize the rocks in the area which is manifested in the brittle nature of the quartzites that display several joints and fracture sets which also control the drainage pattern in the area. Also, the existences of structures in the area are also justified as seen on the cross-section map which confirmed the presence of folding on the rocks especially on the schistose quartzites. The type of fold here is an antiform. The ratio of the major, trace and rare earth elements in the stream sediments is presented in Table 1. $\text{Al}_2\text{O}_3/\text{TiO}_2$ is essentially used to infer the source rock composition. $\text{Al}_2\text{O}_3/\text{TiO}_2$ increases from 3 to 8 for mafic igneous rocks, from 8 to 21 for intermediate rocks and 21 to 70 for felsic igneous rocks (Hayashi et al., 1997). Accordingly, the average $\text{Al}_2\text{O}_3/\text{TiO}_2$ obtained from the stream sediments (8.75) suggests intermediate rock as the probable source rock for the stream sediments. Ratios such as La/Co, Th/Co, Cr/Th, Cr/Zr, Ti/Zr, Ba/Sr, Zr/Y, La/Y, La/Th and La/Lu are significantly different in mafic and felsic rocks, and can therefore provide information about the provenance of the sediments.

The high ratio of La/Co, Th/Co, Cr/Th, Ba/Sr, Zr/Y, La/Y, La/Lu and La/Th probably suggests felsic source rock. There is existence of high complexes of mafic/ultramafic in the source region such as biotite gneiss, biotite schist, charnockites and quartz-biotite schist in the source region. The multivariate statistical results of the rock geochemical data (Table 2) revealed that Mo mean value is 0.2, standard deviation (0.11), threshold (0.26) and anomaly (0.35). Cu mean value is 6.74, standard dev. (3.47), threshold (9.86), anomaly (10.81), followed by Pb with 6.68, standard deviation (2.27), threshold (8.13), anomaly (11.29). Zn has a mean value of 15.16, standard deviation (9.15), threshold (23.5) and anomaly (23.5). Ag has 33.75 mean value, standard deviation (61.64), threshold (50), and anomaly (188). Ni mean value from the result is 2.91, standard deviation (1.99), threshold (5.1), anomaly (7.1). Co has 1.63, standard deviation (0.74), threshold (2.6), anomaly (2.9). Fe has 0.79 mean value, standard deviation (0.19), threshold (1.07) and anomaly (1.08), Bi has 0.08, standard deviation (0.03), threshold (0.2), anomaly (6.14), Ag has 33.75 mean value, standard deviation (61.64), threshold (50), and anomaly (188), Ni mean value from the result is 2.91, standard deviation (1.99), threshold (5.1), anomaly (7.1), Ti mean value is 0.27, standard deviation (0.11), threshold (0.38), anomaly (0.42).

The mean concentrations of Cu, Pb, Zn, Ni, Bi, Ag and Fe in the study area revealed their enhanced concentration when compared with background concentration. From the results obtained (Table.3) three sets of elements can be deduced from the table. The first set of trace elements belongs to elements showing high concentration values in the rocks such as Ba, Ce, and Mn. These elements are indicative of the environment of deposition and may be derived from the granites, massive quartzites and pegmatites in the study area. This is followed by another set of elements of moderate concentration such as Ag, Sr, La, Va and Cr, which may be indicative of variations of parent rock type. Although, most of the. Elements such as Ba, Mn, Cr, U, Zr, Ce and Rb and Sr show high values which could be product of pegmatite, quartzite and migmatite-gneiss mineralization. The anomalously high concentration of Ba, U, Rb in the rocks of this group is an indication of pegmatite mineralization.

The suspected rocks are pegmatites, granite-gneiss and migmatite gneiss with a few granite bodies. Table.4 presents the multivariate statistical values for the sediments. The results obtained showed that Zr, Mn, Ba and Ce have very high concentration values. Their sources are sediments obtained from Esa-oke-17, Esa-oke-2 and Babaorioke 8b, respectively. The high concentration values must have originated from the parent rocks hosting these elements, which are now weathered and transported into the streams. Other trace elements with moderate concentration in the streams are

Table 1. Provenance table of the sediments in the study area (%).

Sample	La/CO	Th/CO	Cr/Th	Cr/Zr	Ti/Zr	Ba/Sr	Zr/Y	La/Y	La/Th	La/Lu	Al ₂ O ₃ /TiO ₂	Na ₂ O/K ₂ O
Agbagbara	15.13	4.77	2.90	1.34	0.03	8.00	4.33	6.35	3.17	908	1.41	0.21
baba iyabo	3.59	1.32	9.15	1.49	0.02	6.45	9.41	4.17	2.73	208.5	0.86	0.13
Baba Orioke 8b	21.89	21.59	0.51	0.33	0.01	5.03	8.98	5.91	1.01	810	10.08	0.20
Baba Orioke 8c	10.17	17.07	0.75	0.32	0.00	4.06	11.99	3.01	0.60	213.5	15.97	0.44
Ede 1	5.35	1.40	2.89	0.47	0.00	11.83	5.01	3.09	3.83	190.6	14.33	0.16
Ede 2	3.14	0.86	1.40	0.29	0.01	10.92	4.78	3.60	3.65	272.75	9.59	0.17
Effon 1	29.83	8.74	1.04	0.42	0.00	4.23	3.77	5.12	3.41	0	11.51	0.19
Effon Okemesi												
3C	10.44	3.28	2.37	0.26	0.01	5.64	8.67	3.08	3.19	188	3.69	0.13
Effon Okemesi	44.90	13.07	0.37	0.12	0.01	7.62	5.63	6.11	3.44	1302	0.88	0.23
Effon Okemesi 2	26.48	7.79	0.86	0.17	0.01	8.38	8.86	6.15	3.40	874	0.37	0.19
Esa Oke 2	48.69	15.46	0.55	0.17	0.01	6.30	5.71	5.70	3.15	0	7.21	0.07
Esa Oke 3	13.92	4.92	0.94	0.38	0.01	4.50	4.31	4.89	2.83	0	3.00	0.39
Esa Oke 6	21.61	7.97	0.47	0.19	0.01	7.26	3.67	4.17	2.71	378.25	6.46	0.16
Esa Oke 14	3.31	1.22	5.43	0.84	0.02	6.90	9.43	3.96	2.71	285	1.15	0.14
Esa Oke 17	41.00	18.61	0.22	0.13	0.01	6.96	5.16	6.96	2.20	912.25	0.73	0.20
Ido - Ile 2	6.59	1.66	3.13	0.41	0.01	4.60	6.15	3.24	3.98	0	4.67	0.22
Ikoru - Okemesi	7.12	2.42	1.00	0.40	0.01	7.73	6.61	7.87	2.94	413	4.14	0.17
Ijero - Ipoti River	4.38	2.59	0.73	0.07	0.00	3.97	17.67	2.95	1.69	0	29.44	5.53
Ilokun 1	17.00	8.44	0.63	0.28	0.00	6.78	5.40	4.77	2.02	527	9.87	0.19
Iroko 16	4.31	1.63	2.81	0.92	0.01	4.86	5.07	4.38	2.65	0	10.77	0.45
Kajola 16	5.13	2.99	2.36	1.11	0.02	6.25	5.57	4.49	1.72	364	0.97	0.11
Odo												
Abidogun	7.84	3.15	1.38	1.58	0.01	18.50	1.85	5.27	2.49	748.5	12.27	0.06
Ofale Road	2.13	0.80	2.08	0.50	0.00	7.48	5.19	3.33	2.68	221.5	12.86	0.11
Okemesi 2	68.17	15.83	0.53	0.04	0.00	5.25	18.71	5.68	4.31	0	2.94	0.10
Okemesi 3	34.67	8.33	1.80	0.36	0.00	4.50	6.78	5.62	4.16	0	7.77	0.17
Okemesi 4	13.13	3.53	0.94	0.05	0.00	6.87	22.29	4.80	3.72	0	2.22	0.07
Okemesi 6	10.08	3.29	1.14	0.26	0.01	5.44	7.84	5.50	3.06	484	1.76	0.20
Okemesi 9	26.56	5.56	2.40	0.26	0.01	2.31	13.03	6.83	4.78	0	2.42	0.11
Omi Osa	5.07	0.79	6.36	0.52	0.00	6.78	6.75	3.55	6.45	0	27.01	0.18
River Akola	154.67	38.78	0.14	0.06	0.00	9.86	3.36	5.87	3.99	1392	2.30	0.07
River Elewu	63.88	23.32	0.21	0.10	0.01	6.28	4.36	5.53	2.74	798.5	4.94	0.27
River Eri	1.96	0.56	3.10	0.62	0.01	10.03	4.96	3.47	3.50	350	5.91	0.21
River Isa 7C	10.55	7.18	0.25	0.10	0.00	10.34	5.48	3.18	1.47	0	66.18	0.10
River Oyi	11.19	3.84	0.59	0.38	0.01	9.19	3.70	6.89	2.91	985	2.93	0.16
Oke - Ila 1	13.47	2.84	2.13	0.74	0.01	6.65	3.42	5.62	4.75	0	7.59	0.21

Zn, Cu, Pb, Th, Sr, La and Rb. These are pathfinder elements and are likely to have originated from the pegmatite intrusions into the main lithology in the area. However, there is positive and negative correlations between some of the heavy metals in the bedrocks such as Cu and Pb (0.022), Cu and Zn (0.909), Pb and Zn (0.909), Fe and Zn (0.929), Ni and Cr (-0.128) in the bedrocks (Table 5) while Cu and Pb (0.571), Pb and Zn (0.184), Mn and Fe (0.87) in the sediments (Table.6). The positive correlated showed that they were likely contributing simultaneously (closely associated). Poorly correlated elements might have different geochemical factors influencing their concentrations in rocks and sediments.

A common approach to estimate how much rocks and sediments are impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor

(EF) for metal concentrations above un-contaminated background levels (Huu et al., 2010). The EF method normalizes the measured heavy metal content with respect to a samples reference such as Fe, Al or Zn (Mendiola et al., 2008). The EF of a heavy metal in sediment can be calculated with the following formula: (Huu et al., 2010). $EF = [C_n (\text{sample}/C \text{ normalizer}) Al / [C \text{ metal}/C \text{ normalizer}] \text{ control}$ C metal and C normalizer are the concentrations of heavy metal and normalizer in sample and in unpolluted control. EF can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure, and to assess the degree of anthropogenic influence. Five contamination categories are recognized on the basis of the EF as follows: (Sutherland, 2000). EF < 2 is deficiency to minimal enrichment, EF 2 to 5 is moderate enrichment, EF 5 to 20 is significant

Table 2. Multivariate statistics of bedrocks in the study area (1).

Cluster group I								Cluster group I							
Element	Mean	Median	Stdev.	Skewness	Kurtosis	Threshold	Anomaly	Element	Mean	Median	Stdev.	Skewness	Kurtosis	Threshold	Anomaly
Mo	0.20	0.19	0.11	-0.05	-0.02	0.26	0.35	Sb	0.88	0.15	1.99	2.80	5.55	0.2	6.14
Cu	6.74	6.04	3.47	0.05	-1.32	9.86	10.81	Bi	0.08	0.07	0.03	0.75	11.40	0.09	0.13
Pb	6.68	6.52	2.27	0.33	0.64	8.13	11.29	V	16.13	15.56	6.21	0.19	-0.30	22.5	26
Zn	15.16	12.60	9.15	1.40	2.12	23.5	34.5	Ca	0.02	0.02	0.02	0.79	11.81	0.039	0.004
Ag	33.75	10.50	61.64	2.37	6.83	50	188	P	0.01	0.01	0.00	0.81	11.99	0.014	0.00
Ni	2.91	2.25	1.99	1.69	3.15	5.1	7.1	La	28.63	21.80	16.44	1.43	1.98	39	63.3
Co	1.63	1.45	0.74	0.77	0.28	2.6	2.9	Cr	10.13	10.56	3.69	-0.29	-0.52	13.8	15
Mn	107.25	111.13	34.36	-0.22	0.05	122	132.5	Mg	0.01	0.01	0.01	0.73	11.89	0.03	0.03
Fe	0.79	0.74	0.19	-0.58	4.74	1.07	1.08	Ba	60.88	61.50	20.68	0.21	0.71	66	103
As	1.00	1.00	0.40	0.29	-0.22	1.3	1.7	Ti	0.27	0.28	0.11	-0.57	7.35	0.38	0.42
U	1.45	1.25	0.72	0.99	1.92	1.2	1.8	Al	1.08	0.90	0.55	0.89	0.57	1.5	1.58
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Na	0.03	0.02	0.03	2.92	11.97	0.028	0.0031
Th	8.06	5.75	5.59	1.60	3.02	12.8	20.1	K	0.25	0.19	0.19	2.32	9.88	0.34	0.71
Sr	11.63	11.31	2.45	-1.22	1.54	14.6	15	W	0.33	0.30	0.12	0.41	-0.82	0.47	0.50
Cd	0.01	0.01	0.01	0.73	11.89	0.03	0.003	Zr	58.71	49.25	35.94	1.48	2.15	90	134.7
Sn	1.81	1.30	2.44	2.91	8.36	1.70	8.2	Ce	60.53	44.28	32.77	1.34	1.52	86.1	128.09
Sc	1.34	0.95	0.79	1.31	1.61	2.00	2.9	Rb	13.45	11.69	11.87	2.70	8.26	12	43.6
Y	5.91	5.91	2.63	0.65	0.54	6.80	7.4								

Table 3. Multivariate statistical results of bedrocks in the study area (II).

Cluster group II								Cluster group II							
Element	Mean	Median	Stdev.	Skewness	Kurtosis	Threshold	Anomaly	Element	Mean	Median	Stdev.	Skewness	Kurtosis	Threshold	Anomaly
Mo	0.61	0.40	0.58	2.02	4.76	1.5	2.6	Sb	0.19	0.12	0.27	3.78	15.24	0.38	1.32
Cu	13.15	11.59	6.51	1.24	2.03	25	32.5	Bi	0.30	0.15	0.50	4.17	18.10	0.47	24.2
Pb	29.42	25.67	19.25	1.37	1.82	70	78.8	V	43.10	42.00	22.80	0.50	0.01	78	96
Zn	32.00	26.40	20.05	1.34	1.83	76.5	88	Ca	0.20	0.18	0.11	1.00	1.14	0.38	0.5
Ag	14.30	0.00	17.94	0.59	-1.64	39.5	46	P	0.04	0.03	0.04	2.67	8.01	0.094	0.18
Ni	10.82	9.50	8.37	2.05	5.69	22	40	La	89.21	81.80	75.98	2.48	8.04	160.5	395
Co	10.43	6.60	10.31	2.09	4.10	35	42.5	Cr	42.35	34.50	30.98	1.57	3.63	82	142.5
Mn	658.55	490.00	458.88	0.67	-0.96	1420	1624	Mg	0.13	0.12	0.11	1.91	5.47	0.25	0.5
Fe	2.75	2.22	1.96	1.82	4.16	5.8	9.06	Ba	599.20	336.00	724.99	2.23	4.43	2355	2750
As	1.54	1.30	1.33	1.86	3.36	4.5	5.5	Ti	0.85	0.64	0.67	2.05	4.91	1.75	3.07
U	10.87	4.35	24.01	4.32	19.00	18.5	115.4	Al	3.99	3.42	2.48	0.73	-0.28	9	9.6
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Na	0.56	0.34	0.89	3.58	14.01	1.6	4.15
Th	38.64	28.35	35.63	2.43	7.29	78	172.8	K	1.92	1.68	1.23	0.44	-1.07	3.7	4.4
Sr	102.85	40.50	166.74	2.79	7.32	498	675	W	1.90	0.80	4.47	4.22	18.30	0.35	21.6
Cd	0.08	0.05	0.13	3.91	16.24	0.16	0.62	Zr	105.20	106.70	58.04	0.97	1.53	170.25	270.75
Sn	2.83	1.85	4.10	4.14	17.91	3.75	22	Ce	201.07	169.73	172.26	2.56	8.44	344	840
Sc	4.12	3.30	3.25	2.22	5.75	9.20	15.8	Rb	93.48	89.90	58.03	0.45	-0.37	160.5	230
Y	18.56	13.95	12.09	1.22	1.25	36.00	53.0								

Table 4. Multivariate statistical results of sediments in the study area.

Element	Cluster group I							Element	Cluster group I						
	Mean	Median	Stdev.	Skewness	Kurtosis	Threshold	Anomaly		Mean	Median	Stdev.	Skewness	Kurtosis	Threshold	Anomaly
Mo	0.20	0.19	0.11	-0.05	-0.02	0.26	0.35	Sb	0.88	0.15	1.99	2.80	5.55	0.2	6.14
Cu	6.74	6.04	3.47	0.05	-1.32	9.86	10.81	Bi	0.08	0.07	0.03	0.75	11.40	0.09	0.13
Pb	6.68	6.52	2.27	0.33	0.64	8.13	11.29	V	16.13	15.56	6.21	0.19	-0.30	22.5	26
Zn	15.16	12.60	9.15	1.40	2.12	23.5	34.5	Ca	0.02	0.02	0.02	0.79	11.81	0.039	0.004
Ag	33.75	10.50	61.64	2.37	6.83	50	188	P	0.01	0.01	0.00	0.81	11.99	0.014	0.00
Ni	2.91	2.25	1.99	1.69	3.15	5.1	7.1	La	28.63	21.80	16.44	1.43	1.98	39	63.3
Co	1.63	1.45	0.74	0.77	0.28	2.6	2.9	Cr	10.13	10.56	3.69	-0.29	-0.52	13.8	15
Mn	107.25	111.13	34.36	-0.22	0.05	122	132.5	Mg	0.01	0.01	0.01	0.73	11.89	0.03	0.03
Fe	0.79	0.74	0.19	-0.58	4.74	1.07	1.08	Ba	60.88	61.50	20.68	0.21	0.71	66	103
As	1.00	1.00	0.40	0.29	-0.22	1.3	1.7	Ti	0.27	0.28	0.11	-0.57	7.35	0.38	0.42
U	1.45	1.25	0.72	0.99	1.92	1.2	1.8	Al	1.08	0.90	0.55	0.89	0.57	1.5	1.58
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Na	0.03	0.02	0.03	2.92	11.97	0.028	0.0031
Th	8.06	5.75	5.59	1.60	3.02	12.8	20.1	K	0.25	0.19	0.19	2.32	9.88	0.34	0.71
Sr	11.63	11.31	2.45	-1.22	1.54	14.6	15	W	0.33	0.30	0.12	0.41	-0.82	0.47	0.50
Cd	0.01	0.01	0.01	0.73	11.89	0.03	0.003	Zr	58.71	49.25	35.94	1.48	2.15	90	134.7
Sn	1.81	1.30	2.44	2.91	8.36	1.70	8.2	Ce	60.53	44.28	32.77	1.34	1.52	86.1	128.09
Sc	1.34	0.95	0.79	1.31	1.61	2.00	2.9	Rb	13.45	11.69	11.87	2.70	8.26	12	43.6
Y	5.91	5.91	2.63	0.65	0.54	6.80	7.4								

Table 5. Correlation showing inter-elemental relationships in the bedrocks.

Control variables	Pb	Zn	Ag	Ni	Co	Mn	Fe	As	V	Ca	Cr
Pb	1	0.909	-0.05	-0.128	-0.453	0.843	0.87	0.506	0.652	0.89	0.458
Zn	0.909	1	0.131	-0.113	-0.486	0.979	0.929	0.213	0.668	0.862	0.544
Ag	-0.05	0.131	1	-0.141	-0.245	0.154	0.008	-0.008	-0.126	-0.083	0.068
Ni	-0.128	-0.113	-0.141	1	0.395	0.01	-0.117	-0.159	-0.122	-0.077	-0.152
Co	-0.453	-0.486	-0.245	0.395	1	-0.427	-0.451	-0.222	-0.343	-0.431	-0.339
Mn	0.843	0.979	0.154	0.01	-0.427	1	0.935	0.079	0.714	0.864	0.557
Fe	0.87	0.929	0.008	-0.117	-0.451	0.935	1	0.138	0.88	0.948	0.672
As	0.506	0.213	-0.008	-0.159	-0.222	0.079	0.138	1	-0.033	0.247	-0.207
V	0.652	0.668	-0.126	-0.122	-0.343	0.714	0.88	-0.033	1	0.894	0.697
Ca	0.89	0.862	-0.083	-0.077	-0.431	0.864	0.948	0.247	0.894	1	0.561
Cr	0.458	0.544	0.068	-0.152	-0.339	0.557	0.672	-0.207	0.697	0.561	1

Table 6. Correlation showing inter-elemental relationships in the sediments.

Control variables	Pb	Zn	Ag	Ni	Co	Mn	Fe	As	Cr	V	Ca
Pb	1	0.184	0.599	0.241	0.278	-0.084	-0.132	-0.17	0.303	0.44	0.477
Zn	0.184	1	-0.04	0.225	0.345	0.53	0.178	-0.028	-0.011	0.166	-0.012
Ag	0.599	-0.04	1	-0.151	-0.33	-0.54	-0.287	-0.809	-0.037	0.124	-0.156
Ni	0.241	0.225	-0.151	1	0.778	0.758	0.579	0.119	0.817	0.827	0.687
Co	0.278	0.345	-0.33	0.778	1	0.807	0.482	0.409	0.628	0.515	0.784
Mn	-0.084	0.53	-0.54	0.758	0.807	1	0.759	0.376	0.652	0.575	0.432
Fe	-0.132	0.178	-0.287	0.579	0.482	0.759	1	0.199	0.778	0.577	0.275
As	-0.17	-0.028	-0.809	0.119	0.409	0.376	0.199	1	0.042	-0.168	0.522
Cr	0.303	-0.011	-0.037	0.817	0.628	0.652	0.778	0.042	1	0.91	0.533
V	0.44	0.166	0.124	0.827	0.515	0.575	0.577	-0.168	0.91	1	0.406
Ca	0.477	-0.012	-0.156	0.687	0.784	0.432	0.275	0.522	0.533	0.406	1
Cu	0.571	0.346	0.322	0.693	0.675	0.532	0.416	-0.327	0.743	0.801	0.401

Table 7. Enrichment factor of heavy metals in the bedrocks.

Sample	EF (Mo)	EF (Cu)	EF (Pb)	EF (Zn)	EF (Ag)	EF (Fe)	EF (Bi)	EF (Cr)	EF (Ti)	EF (Ni)	EF (Nb)
Aba Francis	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	10000.000	2.000	260.500
Arapate	0.016	0.172	6.915	0.067	0.003	0.033	0.010	0.003	133.779	0.548	0.950
Baba Ori Oke 8b	0.025	1.294	2.872	0.848	0.029	0.468	0.014	0.083	10953.058	0.871	0.853
Idao 2	0.026	0.546	9.997	0.597	0.003	0.256	0.009	0.153	6109.510	1.605	1.044
Ido-Ile 3A	0.025	2.021	8.336	1.045	0.005	0.378	0.036	0.153	7677.054	0.020	0.003
Ido-Ile 3	0.362	0.714	7.274	0.143	0.024	0.060	0.065	0.024	6904.762	0.119	0.208
Ijero lepidorite	0.186	0.942	4.802	0.093	0.023	0.093	0.052	0.023	6744.186	0.512	27.000
Ijero pegmatite	0.035	0.121	0.793	3.584	0.005	0.121	0.164	0.005	503.778	0.020	0.574
Ijero 5A	0.020	0.049	3.487	0.042	0.005	0.015	0.034	0.003	64.935	0.679	0.003
Ijero 5B	0.424	1.480	2.580	0.040	0.040	0.040	0.040	0.040	800.000	0.520	0.120
Iloko L1	0.596	1.533	8.667	0.311	0.044	0.200	0.144	0.089	4888.889	0.133	0.044
Ilokun 4	1.815	0.923	6.615	0.154	0.154	0.154	0.385	0.154	3076.923	1.385	1.769
Ilokun 4C	0.244	2.940	4.130	0.140	0.020	0.370	0.045	0.060	3000.000	1.320	6.410
Ikoru 6	0.115	2.176	4.477	0.827	0.006	0.471	0.013	0.041	9246.677	0.015	0.003
Iroko Ekiti	0.457	2.190	7.381	0.048	0.048	0.071	0.060	0.048	7142.857	0.810	2.179
Iroko 2	0.054	0.131	9.064	0.184	0.007	0.099	0.003	0.006	1487.102	0.118	0.798
ODO Owa 1	0.025	0.240	4.890	0.688	0.003	0.345	0.008	0.025	7520.891	0.153	0.797
Oke - Ila Granite	0.041	0.177	4.743	0.681	0.005	0.428	0.009	0.040	8908.046	0.147	0.705
Oke - Ila 1	0.043	0.402	3.449	0.533	0.003	0.304	0.003	0.040	6943.164	0.012	0.339
Oke - Ila 8	0.020	0.028	3.631	0.609	0.004	0.206	0.004	0.007	2134.831	0.015	0.987
Okemesi Road	0.012	0.043	4.738	0.262	0.003	0.080	0.009	0.003	1094.017	0.068	0.905
Okemesi Li	0.054	0.443	5.001	0.920	0.003	0.460	0.009	0.017	9608.128	0.099	0.003
Okemesi 2 (ferruginous)	0.503	0.657	5.514	0.057	0.057	0.171	0.100	0.114	6857.143	0.343	0.586
Okemesi 3	0.101	0.429	2.227	0.050	0.017	0.151	0.017	0.050	7731.092	0.739	1.542
Okemesi 5	0.034	2.209	2.202	0.192	0.029	0.253	0.007	0.110	13630.137	0.048	0.007
Okemesi 6	0.244	0.361	1.389	0.028	0.028	0.028	0.028	0.028	2222.222	2.444	2.340
Okemesi L9	0.050	0.640	2.818	0.333	0.014	0.146	0.007	0.084	6945.607	0.285	0.613
Okemesi L14	0.031	0.420	3.327	0.375	0.005	0.195	0.005	0.056	5924.051	0.390	0.506
Okemesi L15	0.088	0.249	4.114	0.300	0.005	0.159	0.007	0.058	6472.149	0.366	0.175
Okemesi L19	0.022	0.635	2.575	0.394	0.009	0.143	0.008	0.040	4008.909	0.049	0.063
Osun Epe-Ekiti	0.186	0.960	1.727	0.020	0.034	0.101	0.020	0.020	6060.606	0.303	9.056
Itawure 20A	0.036	0.152	3.933	0.402	0.002	0.243	0.003	0.009	4887.892	0.007	0.002
Itawure 20B	0.280	1.060	1.600	0.040	0.040	0.080	0.040	0.040	2800.000	0.520	0.530
Itawure 2C	0.275	2.410	2.614	0.036	0.024	0.410	0.024	0.024	11084.337	0.241	0.175
SOSO	0.263	0.382	2.868	0.079	0.026	0.092	0.039	0.026	8421.053	0.184	0.046
Itawure 20A	0.280	1.060	1.600	0.040	0.040	0.080	0.040	0.040	2800.000	0.120	0.040
Itawure 20A	0.290	2.020	1.686	0.039	0.039	0.039	0.039	0.039	2352.941	0.039	0.069

enrichment, EF 20 to 40 is very high enrichment and EF > 40 is extremely high enrichment. As the EF values increase, the contributions of the anthropogenic origins also increase (Sutherland, 2000).

Index of Geo-accumulation (Igeo) has been used widely to evaluate the

degree of metal contamination or pollution in terrestrial, aquatic and marine environment (Tijani and Onodera, 2009), while the geo-accumulation index (Igeo) of a metal in sediment can be calculated with formula: (Mediola et al., 2008; A saah a nd Abimbola, 2005). Igeo

Table 8. Statistical Summary of the enrichment factor of heavy metals in the bedrocks.

Metals	Min	Max	Aver	Stdev
EF (Mo)	0.012	1.815	0.224	0.341
EF (Cu)	0.028	2.940	0.898	0.793
EF (Pb)	0.793	9.997	4.190	2.415
EF (Zn)	0.020	3.584	0.411	0.621
EF (Ag)	0.002	1.000	0.049	0.163
EF (Fe)	0.015	1.000	0.215	0.192
EF (Bi)	0.003	1.000	0.068	0.172
EF (Cr)	0.003	1.000	0.075	0.162
EF (Ti)	64.935	13630.137	5598.398	3449.514
EF (Al)	1.000	1.000	1.000	0.000
EF (Ni)	0.007	2.444	0.466	0.589
EF (Nb)	0.002	260.500	8.701	42.796

Table 9. Percentage EF for some heavy metals in the bedrocks.

Class	EF <2	EF= 2- 5	EF=5-20	EF = 20-40	EF >40
Metals	Deficiency to mineral enrichment	Moderate enrichment	Significant enrichment	Very high enrichment	Extremely high enrichment
Mo	100	0	0	0	0
Cu	18.4	73.68	7.92	0	0
Pb	18.4	52.6	28.95	0	0
Zn	97.37	2.63	0	0	0
Ag	100	0	0	0	0
Fe	100	0	0	0	0
Bi	100	0	0	0	0
Cr	100	0	0	0	0
Ti	0	0	0	0	100
Ni	94.74	5.26	0	0	0
Nb	84.21	5.26	5.26	2.63	2.63

= $\text{Log}_2 C_{\text{metal}} / 1.5 C_{\text{metal (control)}}$ Where C metal is the concentration of the heavy metal in the enriched sample and C metal (control) is the concentration of the metal in the unpolluted sample or control. The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the sediments (Mediola et al., 2008). The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows: (Huu et al., 2010). $I_{\text{geo}} < 0$ = means uncontaminated, $0 \leq I_{\text{geo}} < 1$ means uncontaminated to moderately contaminated, $1 \leq I_{\text{geo}} < 2$ means moderately contaminated, $2 \leq I_{\text{geo}} < 3$ means moderately to strongly contaminated, $3 \leq I_{\text{geo}} < 4$ means strongly contaminated, $4 \leq I_{\text{geo}} < 5$ means strongly to very strongly contaminated and $I_{\text{geo}} \geq 5$ means very strongly contaminated.

The EF and I_{geo} were estimated for Mo, Cu, Pb, Zn, Ag,

Fe, Bi, Cr, Ti, Ni and Nb which are the precious and base metals in the rock and stream sediments. (Tables 7 and 10), their statistical summaries are also presented in Tables 8 and 11, respectively. The distribution of the metal content in both rock and stream sediment are shown in Figures 5 and 6, while the percentage EF the heavy metals in the bedrocks and sediments are presented in Tables 9 and 12. The geo-accumulation index for both rocks and stream sediments and their statistical summaries are presented in Tables 15, 13, 14 and 16, respectively. However, there is extremely high enrichment of Fe and Ti (100%) in the stream sediments followed by moderate to significant enrichment of Cu, Pb, Zn, Cr and Nb (Table 12) while the bedrock is extremely enriched in Ti coupled with moderate to significant enrichment of Cu, Pb and Zn (Table 7).

These results confirmed that the bedrocks and stream sediments have commercial deposits Cu, Pb and Zn mineralization which can be mined at a profit if proper

Table 10. Enrichment factor of heavy metals in sediments.

Samples ID	EF (Mo)	EF (Cu)	EF (Pb)	EF (Zn)	EF (Ag)	EF (Fe)	EF (Bi)	EF (Cr)	EF (Ti)	EF (Ni)	EF (Nb)
Agbagbara	0.11963	10.4673	7.25234	1.6729	0.00935	13504.7	0.0771	0.7757	160467	0.8785	10.6379
baba lyabo	0.05714	9.61429	8.07143	2.84286	0.02857	22000	0.07857	2	262571	1.92857	9.25357
Baba Orioke 8b	0.03571	2.3	13.4571	0.41786	0.00357	2785.71	0.02143	0.14643	22464.3	0.33929	2.22679
Baba Orioke 8c	0.03166	1.86454	11.9863	0.36986	0.00304	2085.24	0.01979	0.16438	14185.7	0.40791	8.38965
Ede 1	0.0449	3.60544	4.9229	0.87982	0.00227	4206.35	0.02438	0.16327	15805	0.88889	2.37528
Ede 2	0.08787	3.05706	5.65621	1.20399	0.00499	8231.1	0.02425	0.11983	23623.4	0.57347	2.42511
Effon 1	0.12033	4.11382	3.63008	0.52033	0.00813	9065.04	0.02033	0.17073	19674.8	0.65041	1.7439
Effon Okemesi 3C	0.07536	7.14493	5.12319	0.78986	0.01522	5507.25	0.03623	0.2029	61304.3	0.73913	3.27174
Effon Okemesi	0.12394	6.3662	19.4085	1.33803	0.02817	18028.2	0.07746	0.39437	257183	0.3662	11.0352
Effon Okemesi 2	0.22	18.225	39.825	4.275	0.055	61750	0.1375	1.1	619500	0.85	12.1125
Esa Oke 2	0.02667	5.14286	5.37619	0.87143	0.08952	3380.95	0.03095	0.10476	31428.6	0.2381	1.32857
Esa Oke 3	0.10411	13.5753	8.71233	1.80822	0.0274	12191.8	0.03425	0.32877	75616.4	0.79452	3.55479
Esa Oke 6	0.10876	1.99326	5.68989	0.63146	0.00854	9033.71	0.01573	0.11685	35056.2	0.44045	2.32697
Esa Oke 14	0.05113	7.8797	6.67669	1.25564	0.01504	16391	0.04135	0.85714	196992	1.59398	3.40226
Esa Oke 17	0.06701	7.92386	14.3198	1.48223	0.01777	24517.8	0.04569	0.36548	310863	0.58883	10.0178
Ido - Ile 2	0.08861	6.10759	4.51899	1.40506	0.01266	6772.15	0.02848	0.18987	48481	0.89873	3.35443
Ikoro - Okemesi	0.03657	2.07202	7.20499	0.59557	0.00554	6786.7	0.01801	0.15512	54736.8	0.52632	3.64127
Ijero - IpotiRiver	0.01026	0.80235	1.51709	0.52778	0.00214	1474.36	0.12927	0.0235	7692.31	0.09615	106.838
Ilokun 1	0.07	2.3025	10.3625	0.53	0.0075	4500	0.01875	0.165	22950	0.36	2.15625
Iroko 16	0.04903	3.52581	6.73548	0.83871	0.00645	5774.19	0.02097	0.17419	21032.3	0.62581	1.24194
Kajola 16	0.02564	11.359	10.5385	2.78205	0.02564	28974.4	0.07051	1.28205	232821	1.89744	0.60897
Odo Owa Abidogun	0.07614	5.55682	4.96307	1.01136	0.00313	8380.68	0.03906	0.2358	18465.9	1.11648	2.42543
Ofale Road	0.15811	3.30079	6.24882	0.7937	0.00724	14252	0.0252	0.21732	17606.3	0.68031	2.0063
Okemesi 2	0.04762	5.19048	7.92857	0.95238	0.14524	13809.5	0.04762	0.2381	77142.9	0.47619	9.04762
Okemesi 3	0.19661	3.9322	4.62712	1.20339	0.0339	10169.5	0.04237	0.30508	29152.5	0.37288	1.72881
Okemesi 4	0.07586	9.2069	9.93103	5.94828	0.03448	11206.9	0.05172	0.17241	102069	0.55172	4.13793
Okemesi 6	0.07	8.44167	8.4	1.49167	0.01667	12833.3	0.0375	0.3	128500	0.68333	4.45833
Okemesi 9	0.22069	7.12069	7.56897	2.06897	0.03448	18620.7	0.06034	0.41379	93448.3	0.62069	2.57759
Omi Osa	0.06129	1.64516	6.55645	0.5	0.01613	4435.48	0.02419	0.1129	8387.1	0.20968	0.7621
River Akola	0.06857	3.5	10.0143	0.31429	0.05429	7285.71	0.04286	0.14286	98285.7	0.34286	3.57857
River Elewu	0.03121	2.78014	10.4291	0.35816	0.00851	2907.8	0.01596	0.08511	45886.5	0.1844	2.90071
River Eri	0.1118	4.49068	7.26708	0.8323	0.00621	8726.71	0.02019	0.19255	38323	0.86957	2.20497
River Isa 7C	0.03636	3.59626	7.93316	0.37968	0.00535	1871.66	0.0107	0.02139	3422.46	0.09091	0.84225
River Oyi	0.06292	3.47753	7.06742	0.8427	0.01124	9606.74	0.02528	0.22472	77191	0.57303	3.80899
Oke - Ila 1	0.05675	3.70242	7.65744	1.2872	0.00692	6955.02	0.01211	0.17993	29827	0.38754	1.63668

Where EF = Enrichment Factor.

estimation of their reserves is determined. Pb has significant enrichment of 28.95% in the rock and may occur as Lead II sulphide (PbS) or Copper II sulphide (CuS) in the rock or may occur as copper and niobium-tantalum mineralization in the study areas. The extremely high enrichment of Fe and Ti (100%) in the sediments can be attributed to the intense weathering of the

rocks rich in aluminosilicate minerals such as feldspar, olivine and micas which are transported to the stream bed. Also, the extreme enrichment of titanium in the sediment is as a result of weathering of granites, gneisses and transportation and accumulation of the weathered minerals in the stream bed over a geologic time.

Table 11. Statistical summary of EF of heavy metals in the sediments.

Metals	Min	Max	Aver	Stdev
EF (Mo)	0.0102	0.2206	0.0808	0.0526
EF (Cu)	0.8023	18.225	5.5824	3.7734
EF (Pb)	1.5170	39.825	8.7879	6.3569
EF (Zn)	0.3142	5.9482	1.2863	1.1577
EF (Ag)	0.0021	0.1452	0.0217	0.02837
EF (Fe)	1474.36	61750	11372.1	10971.7
EF (Bi)	0.0107	0.1375	0.0407	0.0299
EF (Cr)	0.0213	2.0000	0.3383	0.4053
EF (Ti)	3422.46	619500	93204.5	12289
EF (Ni)	0.0909	1.9285	0.6526	0.4360
EF (Nb)	0.6089	106.838	6.9731	17.678

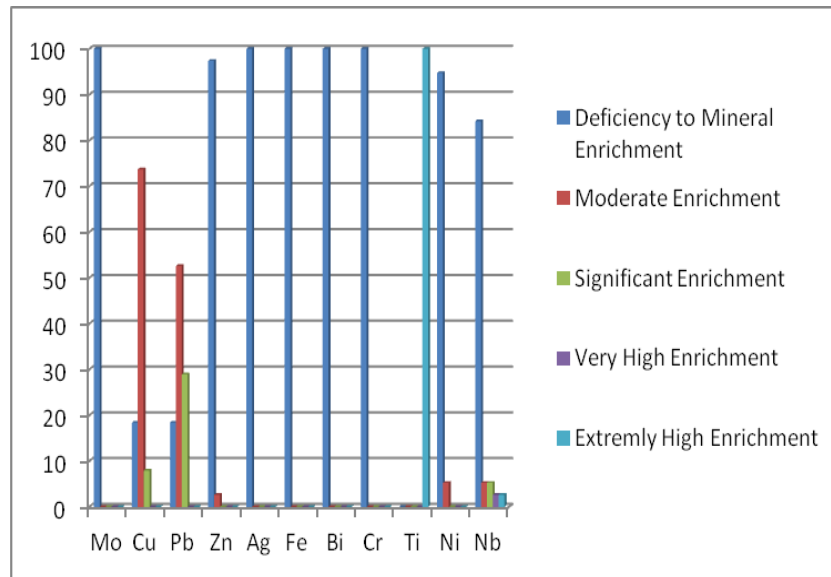


Figure 5. Distribution of heavy metals in the bedrocks.

The geo-accumulation indexes for both rocks and stream sediments also confirmed that metal enrichment in the rocks and stream sediments such as Fe, Ti and Cr are from anthropogenic sources and their index of geo-accumulation ranges from uncontaminated to moderately contaminate. However, the possibility of gold mineralization in the studied area is very high if further geochemical investigation is carried out, as this research has provided baseline geochemical information for further investigation in the studied areas.

CONCLUSION

Bedrock and stream sediments have provided a valuable media for exploration of valuable minerals in that fresh rock samples can provide unusual results from

geochemical analysis which may lead to mineralization, and can be used for recognizing valuable host rocks. It can also be used for outlining a primary halo of elements associated with mineralization, while stream sediments on the other hand serves as a basin for placer deposits or paleo placer deposits, which may constitute an ore due to mechanical dispersal of unweathered heavy minerals from the parent rocks which migrate into the stream bed in form of discrete, detrital mineral grains and become buried under the sediments. A quick look at the results of EF for the rocks revealed a significant enrichment in Ti (100%) with moderate and significant enrichment of Cu and Pb having 73.68 and 52.6%, respectively. Whereas in the stream sediments, there is extremely high enrichment of Fe and Ti (100%) with significant enrichment of Cu and Pb (45.7 and 82.6%). Titanium enrichment is very high in all the rock sampling locations

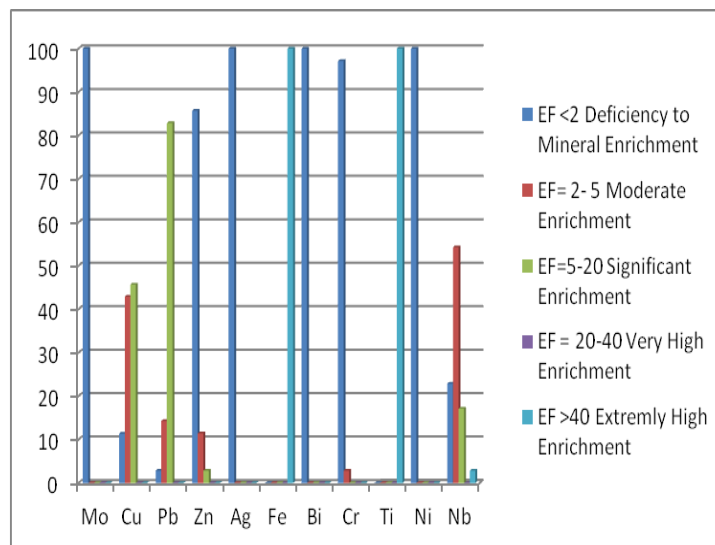


Figure 6. Distribution of heavy metals in the sediments of the study area

Table 12. Percentage EF for some heavy metals in sediments.

Class	EF < 2	EF= 2- 5	EF=5-20	EF = 20-40	EF >40
Stream sediments	Deficiency to mineral enrichment	Moderate enrichment	Significant enrichment	Very high enrichment	Extremely high enrichment
Mo	100	0	0	0	0
Cu	11.4	42.9	45.7	0	0
Pb	2.86	14.28	82.86	0	0
Zn	85.7	11.43	2.86	0	0
Ag	100	0	0	0	0
Fe	0	0	0	0	100
Bi	100	0	0	0	0
Cr	97.14	2.86	0	0	0
Ti	0	0	0	0	100
Ni	0	0	0	0	0
Nb	22.86	54.29	17.14	0	2.86

Table 13. Geo-accumulation index of heavy metals in sediments of the study area.

Sample ID	IgeoMo	Igeo Cu	Igeo Pb	Igeo Zn	Igeo Ag	Igeo Fe	Igeo Bi	Igeo Cr	Igeo Ti	Igeo Al	Igeo Ni	IgeoNb
Agbagbara	-1.67094	-0.52481	-0.68417	0.678822	2.425969	2.585837	-2.35655	1.742987	1.058679	2.455353	-0.20296	0.084266
baba lyabo	-2.17609	-0.74602	-0.82198	0.724822	2.726999	2.613489	-2.53264	1.970037	1.088254	2.271067	-0.04576	-0.16056
Baba Orioke 8b	-1.77815	-0.76515	0.00208	0.494155	2.425969	2.318063	-2.49485	1.436693	0.622559	2.873127	-0.19837	-0.17713
Baba Orioke 8c	-1.76112	-0.78693	0.021189	0.510545	2.425969	2.261659	-2.46009	1.556303	0.492295	2.942504	-0.04899	0.468308
Ede 1	-1.48149	-0.37263	-0.23737	1.0148	2.425969	2.694313	-2.24159	1.681241	0.667142	3.070407	0.417195	0.048183
Ede 2	-1.2896	-0.54404	-0.27682	1.051281	2.669007	2.886115	-2.34358	1.447158	0.741939	2.970657	0.127105	-0.04255
Effon 1	-1.60789	-0.86988	-0.92421	0.232149	2.425969	2.473244	-2.87506	1.146128	0.207724	2.515874	-0.273	-0.64054
Effon Okemesi 3C	-2.06215	-0.88118	-1.02564	0.162365	2.447158	2.005752	-2.87506	0.970037	0.450249	2.264818	-0.46852	-0.61834
Effon Okemesi	-2.1347	-1.21992	-0.73581	0.102662	2.425969	2.232149	-2.83367	0.970037	0.78438	1.976197	-1.06215	-0.37896
Effon Okemesi 2	-2.1347	-1.01233	-0.67285	0.357935	2.467361	2.517636	-2.83367	1.166331	0.91698	1.726999	-0.94564	-0.58771
Esa Oke 2	-2.33099	-0.84164	-0.82237	0.38739	3.399097	1.976197	-2.76112	0.865301	0.342423	2.447158	-0.77815	-0.8274
Esa Oke 3	-2.19837	-0.87899	-1.0716	0.245513	2.425969	2.074329	-3.17609	0.90309	0.264818	1.988262	-0.71369	-0.85886
Esa Oke 6	-1.39434	-0.92714	-0.4716	0.573645	2.704722	2.729165	-2.72893	1.238882	0.716003	2.773299	-0.18487	-0.25785
Esa Oke 14	-2.24667	-0.8547	-0.92665	0.347655	2.425969	2.463395	-2.83367	1.579784	0.94118	2.24879	-0.15079	-0.61738
Esa Oke 17	-1.95861	-0.68166	-0.42466	0.590322	2.669007	2.808886	-2.61979	1.380211	1.309914	2.419405	-0.41266	0.022236
Ido - Ile 2	-1.93305	-0.89053	-1.02136	0.471292	2.425969	2.154323	-2.92082	1	0.407108	2.323596	-0.32483	-0.54873
Ikoro - Okemesi	-1.95861	-1.00116	-0.45992	0.457377	2.425969	2.514105	-2.76112	1.271067	0.818666	2.682446	-0.19837	-0.15424
Ijero - IpotiRiver	-2.09691	-0.99942	-0.72277	0.818666	2.425969	2.264818	-1.49125	0.865301	0.380211	3.096215	-0.52288	1.726999
Ilokun 1	-1.63202	-0.9108	-0.25754	0.451275	2.60206	2.380211	-2.69897	1.342423	0.485721	2.726999	-0.31876	-0.33724
Iroko 16	-1.89734	-0.83644	-0.55533	0.539912	2.425969	2.377792	-2.76112	1.255273	0.337126	2.6163	-0.18932	-0.68754
Kajola 16	-2.77815	-0.92763	-0.96019	0.461398	2.425969	2.479047	-2.83367	1.522879	0.781995	2.017033	-0.30686	-1.59631
Odo Owa Abidogun	-1.35002	-0.28266	-0.33174	0.977419	2.467361	2.895791	-2.1347	1.742987	0.636822	2.972511	0.418301	-0.04064
Ofale Road	-1.07745	-0.55367	-0.27649	0.827369	2.787697	3.081587	-2.36991	1.662758	0.571321	2.927712	0.158362	-0.16783
Okemesi 2	-2.77815	-1.5366	-1.35262	-0.273	2.910269	1.888367	-3.273	0.522879	0.033424	1.748188	-1.17609	-0.69322
Okemesi 3	-2.01472	-1.50957	-1.4389	-0.0238	2.425969	1.90309	-3.17609	0.778151	-0.24159	1.895791	-1.1347	-1.2644
Okemesi 4	-2.43573	-1.14752	-1.11464	0.662758	2.425969	1.937852	-3.09691	0.522879	0.2952	1.888367	-0.97197	-0.89279
Okemesi 6	-2.1549	-0.86945	-0.8716	0.377792	2.425969	2.312459	-2.92082	1.079181	0.710963	2.20412	-0.56331	-0.54465
Okemesi 9	-1.97197	-1.25911	-1.2326	0.20412	2.425969	2.158362	-3.02996	0.90309	0.256878	1.888367	-0.92082	-1.09836
Omi Osa	-2.19837	-1.56543	-0.96497	-0.08267	2.425969	1.865301	-3.09691	0.669007	-0.46009	2.21836	-1.06215	-1.29757
River Akola	-2.3979	-1.4859	-1.02934	-0.53264	2.704722	1.832509	3.09691	0.522879	0.360467	1.970037	-1.09691	-0.87419
River Elewu	-2.1347	-0.98075	-0.40657	0.12926	2.50515	2.038753	-2.92082	0.90309	0.634813	2.575188	-0.76112	-0.36025
River Eri	-1.52288	-0.71489	-0.50585	0.553074	2.425969	2.573645	-2.76112	1.31527	0.614194	2.632795	-0.02996	-0.42174
River Isa 7C	-1.94564	-0.74634	-0.40274	0.277227	2.425969	1.970037	-2.97197	0.425969	-0.36991	2.69781	-0.94564	-0.77469
River Oyi	-2.02996	-1.08337	-0.77538	0.30103	2.425969	2.357935	-2.92082	1.124939	0.660865	2.375359	-0.46852	-0.44177
Oke - Ila 1	-1.86434	-0.84568	-0.53008	0.695482	2.425969	2.428135	-3.02996	1.238882	0.458386	2.585837	-0.4279	-0.59814

Where Igeo = Index of geo-accumulation.

Table 14. Statistical summary of Geo-accumulation index of heavy metals in sediments.

	Min	Max	Aver	Stdev
IgeoMo	-2.7781	-1.0774	-1.9542	0.3851
Igeo Cu	-1.5654	-0.2826	-0.9158	0.3040
Igeo Pb	-1.4389	0.0211	-0.6938	0.3659
Igeo Zn	-0.5326	1.0512	0.4219	0.3445
Igeo Ag	2.4259	3.3990	2.5266	0.2002
Igeo Fe	1.8325	3.0815	2.3444	0.3273
Igeo Bi	-3.273	-1.4912	-2.7495	0.3549
Igeo Cr	0.4259	1.9700	1.1635	0.3927
Igeo Ti	-0.4600	1.3099	0.5136	0.3834
Igeo Al	1.7269	3.0962	2.4281	0.3995
Igeo Ni	-1.1760	0.4183	-0.4509	0.4423
IgeoNb	-1.5963	1.7269	-0.4460	0.5748

Table 15. Geo-accumulation index of heavy metals in bedrocks in the study area.

Sample ID	Igeo (Mo)	Igeo (Cu)	Igeo (Pb)	Igeo(Zn)	Igeo(Ag)	Igeo (Fe)	Igeo(Bi)	Igeo(Cr)	Igeo(Ti)	Igeo(Al)	Igeo (Ni)	Igeo (Nb)
Aba Francis	-2.7782	-3.5740	-3.5740	-1.5740	2.4260	-3.5740	-3.2730	-0.1761	-6.1761	-3.5740	-1.8751	-0.5562
Arapate	-2.0969	-1.8622	-0.2586	-0.2730	2.4260	-2.5740	-2.7959	-0.1761	-5.5740	-1.0984	0.03875	-0.5187
Baba Ori Oke 8b	-1.8337	-0.9160	-0.5699	0.9002	3.4324	-1.3579	-2.5740	1.2863	-3.5906	-1.0281	0.30963	-0.4952
Idao 2	-1.8239	-1.2964	-0.0338	0.7419	2.4260	-1.6246	-2.7959	1.5482	-3.8498	-1.0337	0.56976	-0.413
Ido-Ile 3A	-1.8239	-0.7206	-0.1053	0.9930	2.6931	-1.4486	-2.1675	1.5563	-3.7431	-1.0263	-1.331	-2.972
Ido-Ile 3	-1.5963	-2.0969	-1.0890	-0.7959	2.4260	-3.1761	-2.8337	-0.1761	-4.7137	-1.9508	-1.4771	-2.03
Ijero lepidorite	-1.8751	-1.9666	-1.2591	-0.9720	2.4260	-2.9720	-2.9208	-0.1761	-4.7137	-1.9406	-0.8337	0.09286
Ijero pegmatite	-1.9331	-2.1938	-1.3768	1.2781	2.4260	-2.1938	-1.7611	-0.1761	-5.1761	-1.2763	-1.574	-0.9151
Ijero 5A	-1.9858	-2.3979	-0.5430	-0.4601	2.6163	-2.9208	-2.2518	-0.1761	-5.8751	-1.0855	0.14406	-2.972
Ijero 5B	-1.7528	-2.0058	-1.7645	-1.5740	2.4260	-3.5740	-3.2730	-0.1761	-5.8751	-2.1761	-1.0621	-2.4949
Iloko L1	-1.6510	-2.0362	-1.2840	-0.7289	2.4260	-2.9208	-2.7611	0.1249	-5.1347	-2.2218	-1.699	-2.972
Ilokun 4	-1.7063	-2.7959	-1.9406	-1.5740	2.4260	-3.5740	-2.8751	-0.1761	-5.8751	-2.7611	-1.2218	-1.9113
Ilokun 4C	-1.6918	-1.4067	-1.2591	-0.7289	2.4260	-2.3069	-2.9208	0.3010	-5.0000	-1.8751	-0.3565	-0.4661
Ikoru 6	-1.1871	-0.7069	-0.3935	0.8731	2.7377	-1.3713	-2.6446	0.9700	-3.6805	-1.0445	-1.4771	-2.972
Iroko Ekiti	-1.7959	-1.9113	-1.3837	-1.5740	2.4260	-3.3979	-3.1761	-0.1761	-5.0000	-2.2518	-0.9456	-1.3116
Iroko 2	-1.5277	-1.9406	-0.0989	0.2077	2.8062	-2.0621	-3.2730	0.1249	-4.4859	-1.0562	-0.585	-0.552
ODO Owa 1	-1.8239	-1.6395	-0.3296	0.8187	2.4867	-1.4806	-2.8337	0.7782	-3.7447	-1.0189	-0.4357	-0.5152
Oke - Ila Granite	-1.6198	-1.7852	-0.3564	0.8007	2.6564	-1.4008	-2.7959	0.9700	-3.6847	-1.0325	-0.4685	-0.5824
Oke - Ila 1	-1.6320	-1.4568	-0.5238	0.6653	2.4260	-1.5784	-3.2730	0.9379	-3.8220	-1.0615	-1.574	-0.9286
Oke - Ila 8	-2.0458	-2.6990	-0.5875	0.6368	2.5051	-1.8337	-3.2730	0.1249	-4.4202	-1.1475	-1.574	-0.5512
Okemesi Road	-2.2467	-2.4771	-0.4323	0.3096	2.4260	-2.2030	-2.8337	-0.1761	-4.6709	-1.1079	-0.8751	-0.5491
Okemesi Li	-1.5086	-1.3908	-0.3377	0.9270	2.4260	-1.3740	-2.7611	0.6021	-3.6563	-1.0368	-0.6446	-2.972
Okemesi 2 ferrogenous	-1.8337	-2.5133	-1.5895	-1.5740	2.4260	-3.0969	-3.0300	0.1249	-5.0969	-2.3310	-1.3979	-1.9612
Okemesi 3	-2.0000	-2.1675	-1.4518	-1.0969	2.4260	-2.6198	-3.2730	0.3010	-4.5133	-1.7995	-0.5326	-1.0094

Table 15.Cont.

Okemesi 5	-2.0792	-1.0655	-1.0669	-0.1269	3.0544	-2.0058	-3.2730	1.0280	-3.8772	-1.4097	-1.331	-2.972
Okemesi 6	-1.8337	-2.4601	-1.8751	-1.5740	2.4260	-3.5740	-3.2730	-0.1761	-5.2730	-2.0177	-0.2316	-1.0464
Okemesi L9	-1.6990	-1.3893	-0.7457	0.3263	2.9638	-2.0300	-3.0300	1.1249	-3.9560	-1.1956	-0.3436	-0.8061
Okemesi L14	-1.9858	-1.6550	-0.7565	0.2952	2.4260	-1.9886	-3.2730	0.8653	-4.1079	-1.2785	-0.2896	-0.972
Okemesi L15	-1.5580	-1.9019	-0.6844	0.1780	2.4260	-2.0969	-3.1761	0.8653	-4.0897	-1.2987	-0.3372	-1.4535
Okemesi L19	-2.0792	-1.4202	-0.8121	0.3729	2.7270	-2.0689	-3.0300	0.7782	-4.2218	-1.2228	-1.1347	-1.8182
Osun Epe-Ekiti	-1.8144	-1.8973	-1.6421	-1.5740	2.6564	-2.8751	-3.2730	-0.1761	-4.6990	-1.8794	-1	-0.3205
Itawure 20A	-1.5740	-1.7415	-0.3300	0.6800	2.4260	-1.5386	-3.0969	0.4260	-3.8376	-0.9247	-1.699	-2.972
Itawure 20B	-1.9331	-2.1508	-1.9720	-1.5740	2.4260	-3.2730	-3.2730	-0.1761	-5.3310	-2.1761	-1.0621	-1.8498
Itawure 2C	-1.7212	-1.5740	-1.5386	-1.3979	2.4260	-2.3436	-3.2730	-0.1761	-4.5133	-1.9560	-1.1761	-2.1116
SOSO	-1.7782	-2.4127	-1.5366	-1.0969	2.4260	-3.0300	-3.0969	-0.1761	-4.6709	-1.9942	-1.331	-2.7289
Itawure 20A	-1.9331	-2.1508	-1.9720	-1.5740	2.4260	-3.2730	-3.2730	-0.1761	-5.3310	-2.1761	-1.699	-2.972
Itawure 20A	-1.9089	-1.8622	-1.9406	-1.5740	2.4260	-3.5740	-3.2730	-0.1761	-5.3979	-2.1675	-2.1761	-2.7289

Where Igeo = Index of geo-accumulation.

Table 16. Statistical summary of geo-accumulation index of heavy metals in the bedrocks.

Metals	Min	Max	Aver	Stdev
Igeo (Mo)	-2.7781	-1.1871	-1.8289	0.2986
Igeo (Cu)	-3.5740	-0.7069	-1.8821	0.6413
Igeo (Pb)	-3.5740	-0.0338	-1.0653	0.8423
Igeo(Zn)	-1.5741	1.2781	-0.3355	1.0152
Igeo(Ag)	2.4259	3.4324	2.5401	0.2195
Igeo (Fe)	-3.5741	-1.3579	-2.4407	0.7783
Igeo(Bi)	-3.2731	-1.7611	-2.9726	0.3538
Igeo(Cr)	-0.1761	1.5563	0.3201	0.5701
Igeo(Ti)	-6.1761	-3.5906	-4.6319	0.7786
Igeo(Al)	-3.5741	-0.9247	-1.6117	0.6867
Igeo (Ni)	-2.1761	0.5697	-0.9376	0.6800
Igeo (Nb)	-2.9721	0.0928	-1.5481	1.0392

(Table 2), while Cu and Pb enrichment is high in Ilokuno 4C and Idao2 which is underlain by the massive quartzites and granites. Titanium and Iron enrichment is also high in all the sediment sampling locations which could be attributed to the weathering of the bedrock and transportation and accumulation at the bottom of the nearest streams. Therefore Cu mineralization is confirmed in the rocks and stream sediments in the study which may combine with Pb which is also an indication of sulphide ore deposits.

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