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Source, Contamination Assessment and Risk Evaluation of Heavy Metals in the Stream Sediments of Rivers around Olode Area SW, Nigeria

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ABSTRACT

In order to investigate the source, contamination, and risk of heavy metals such as Pb, Zn, Cu, Ni, Co, Fe, Mn, and Cr, twelve (12) stream sediments and ten (10) rock samples were collected from pegmatite mining sites at Olode and its environs inside Ibadan, Southwestern Nigeria. The average values and order of abundance obtained followed the pattern: Mn (595.09) > Ba (80) > Cr (50.82) > V (45.09) > Zn (29.73) > Cu (13.82) > Co (13.82) > Sr (10.46) > Ni (9.73) > Pb (9.09) > Fe (1.59). These were greater than the background values, indicating that mining has a negative impact on the study area, as indicated by the high coefficient of variation and correlation values (> 0.6) for Copper-Lead (0.929), Copper-Vanadium (0.970), Copper-Chromium (0.815), Lead-Vanadium (0.884), and others. On the basis of the enrichment factor (EF), the Olode sediments show extremely high enrichment for Mn and Ba in the research region. Cu and Ni are most likely to blame for the elevated contamination levels, according to CF values. The degree of contamination (CD), pollution load index (PLI), pollution index (PI), and modified pollution index (MPI) all revealed high levels of contamination in all stream sediment samples, whereas Igeo shows that the Olode stream sediments are "practically uncontaminated to extremely contaminated by Ni, Co, and Mn". Ni and Cu are the major regulating factors that are most likely causing the possible Er[i]. As a result, these findings give important information for conducting appropriate ecological management research.

Keywords: Olode; Heavy metals; Stream sediments; Risk assessment; Contamination indices

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ARTICLE INFO

Received: 12 September 2022 | Revised: 18 March 2023 | Accepted: 21 March 2023 | Published Online: 13 April 2023

DOI: https://doi.org/10.30564/jees.v5i1.5060

CITATION

Okonkwo, S.I., Idakwo, S.O., Kolawole, M.S., et al., 2023. Source, Contamination Assessment and Risk Evaluation of Heavy Metals in the Stream Sediments of Rivers around Olode Area SW, Nigeria. Journal of Environmental & Earth Sciences. 5(1): 65-84. DOI: https://doi.org/10.30564/jees.v5i1.5060

1. Introduction

River sediments are a primary transporter of heavy metals in the aquatic environment all over the world. Sediments are the mixture of mineral and organic debris that act as a final sink for heavy metals released into the environment. Due to their consistency, non-degradability, and toxic nature, the presence of these heavy metals in stream sediments has been shown to be a significant environmental problem [1,2]. According to Lei [3], the most harmful toxic metals in the environment are Cr, Cu, Cd, Pb, and As. These metals enter the environment through anthropogenic processes (e.g. mining and indiscriminate dumping of mine wastes) or geogenic processes (e.g. weathering of parent rocks) [4-7]. While some of these metals are necessary for individual survival, only minute amounts are required, according to international organizations such as the World Health Organization (WHO) and the Environmental Protection Agency (EPA) [8,9]. Sediment quality has recently been regarded as a key indicator of pollution because it is a major sink for a variety of pollutants [8]. Heavy metals are carried by contaminated sediments into the water body, resulting in a reduction in water quality [10-13].

Several researchers, including but not limited to: Atgin [14]; Salah et al. [12]; Adamu, et al. [15]; Oyebamiji, et al. [16]; Kolawole, et al. [17]; Boroumandi, et al. [18]; Madukwe, et al. [19]; Adewumi and Laniyan [13] have carried out extensive research into heavy metal contamination in sediments. The findings revealed the accumulation of heavy metals in sediments from various environments and places around the globe. Despite this, there is a paucity of published studies on the distribution and sources of heavy metals in stream sediments near the Olode mining area, and Nigeria has yet to adopt a strategic policy aimed at coordinating and monitoring environmental management and long-term development [20,21]. The study is aimed at assessing the degree of heavy metal concentrations in stream sediments of the study area in order to identify the level of metal pollution, source of heavy metal contamination and appraise the risks associated with heavy metals.

2. Materials and methods

2.1 Study area

Within the Ibadan sheet 261 S.E., the research area is located in the south-western section of Nigeria, between latitudes 7° 08'N and 7° 13.30'N and longitudes 3° 55'E and 3° 59'E. In the area, there are two significant mining operations [22]. They are in the Oluyole Local Government Area of Oyo State, in the Gbayo and Falansa localities (**Figures 1A and 1B**). The terrain is undulating, with elevations varying from 300 to 500 feet above sea level. Pegmatites and associated rocks are usually found as flat tabular masses and are found in low-lying areas. The majority of the streams flow south, but tributaries flow southeast and southwest, draining into the Omi and Opedi rivers, respectively. The majority of streams and their tributaries dry up during the dry season, with the exception of a few perennial streams. The climate of the research region is tropical rainforest, with a wet season that lasts from March to October and a dry season that lasts from November to March. Annual rainfall varies from 788 mm to 1844 mm [23]. Temperatures range from 23 to 32 degrees Celsius, indicating a high-temperate climate [22].

2.2 Sample collection and geochemical analysis

In total, 12 stream sediment samples were collected, with a geochemical sampling of active stream sediments using the natural drainage system in the study area at an interval of about 1 km (**Figure 1A and 1B**; **Table 1**), with samples taken at meanders and from the center of stream courses to obtain more recent and active sediments. A Global Positioning System (GPS) Margillean 315, 2000 model was used to appropriately locate the sample sites on the topographical map. To avoid particle loss when the flow velocity was high, sediment samples were collected in a plastic cup.

Hand trowels were utilized to collect at each spot where the flow velocity was low. Organic materials and bank sediments were strictly avoided. The bedrock and its surroundings were also recorded. The

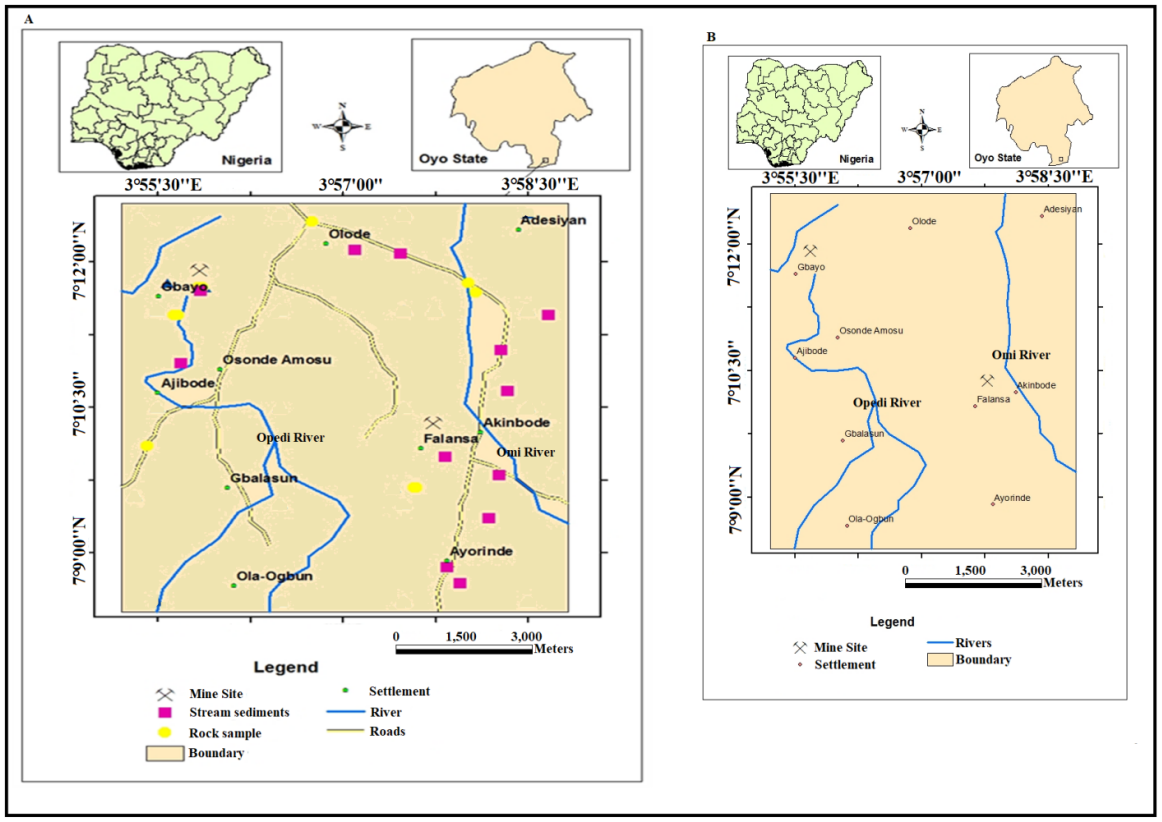


Figure 1. Map of the study area showing: A) Different sampling (media) points and B) Drainage patterns (Adapted from Okonkwo et al. [22]).

Table 1. Stream sediments description (hand specimen) and sample locations.

Sample Numbers ↓	Co-ordinates		Sample Description		pH	Bedrock
	Latitude	Longitude	Grain Size	Colour		
SS01	7°12’07”N	3°57’06”E	gritty	Dark-brown	7	Pegmatite
SS02	7°12’05”N	3°57’28”E	Smooth to fine	Dark brown	8	Pegmatite
SS03	7°11’51”N	3°58’10”E	Smooth to fine	Greyish-white	8	Pegmatite
SS04	7°11’27”N	3°58’40”E	Smooth to fine	Brown	7	Pegmatite
SS05	7°10’40”N	3°58’20”E	Smooth to fine	Brownish-white	7	Pegmatite
SS06	7°11’05”N	3°56’15”E	gummy to sticky	Dark –grey	8	Pegmatite
SS07	7°09’59”N	3°57’50”E	Smooth to fine	Brown	8	Pegmatite
SS08	7°09’48”N	3°58’15”E	Smooth to fine	Brown	7	Pegmatite
SS09	7°09’21”N	3°58’11”E	Smooth to fine	Greyish white	7	Pegmatite
SS10	7°08’50”N	3°57’50”E	Smooth to fine	Grey	8	Pegmatite
SS11	7°08’41”N	3°57’43”E	gritty	Brown	7	Pegmatite
SS12	7°11’42”N	3°55’51”E	gummy to sticky	Greyish-white	8	Pegmatite

texture of the samples was characterized in hand specimens, with the majority of the samples being fine and medium-grained (**Table 1**). The pH of the streams where the sediment samples were taken was measured in situ using a pH indicator paper with a pH range of 1 to 11 (**Table 1**). The samples were collected in thick polythene bags and labelled.

Air-dried stream sediment samples were desegregated, sieved, and divided into size fractions with sieve size fractions of 1180 m, 1000 m, 850 m, 600 m,

425 m, 300 m, 212 m, 180 m, 150 m, 100 m, and 63 m. Aqua regia was used to digest 0.5 g of crushed stream sediment samples (100 m) (3 part HCl and 1 part HNO_3) and the trace elements (Pb, Ba, V, Sr, Zn, Cu, Ni, Co, Fe, Mn, and Cr) were determined using the Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP AES) in the ACME Laboratory (Bureau Veritas Mineral Laboratories) in Canada, following a near-total inclusion by hydrofluoric-perchloric acid. The analytical methods were performed with precision in accordance with Dulski's recommendations [24]. These data produced acceptable results, with precision values for various elements ranging from 1% to 10%.

In eight sample locations (Olode, Gbayo, Osonde, Onipede, Sanku, Falansa, Moleke, and Olojuoro), ten rock samples were obtained (**Figures 1A, 2** and **Table 2**). The major research area, pegmatites mining regions, are Falansa and part of Gbayo, whereas non-mining areas are Olode, part of Gbayo, Olojuoro, Onipede, Osonde, and Moleke, despite the fact that these areas were blasted for gemstone (Beryl) but were later abandoned because nothing was discovered [22]. The rock samples were pulverized and placed in cellophane paper, which was then carefully sealed, tagged, and packaged for trace elemental (Pb, Ba, V, Sr, Zn, Cu, Ni, Co, Fe, Mn, and Cr) analysis in ACME Laboratory (Bureau Veritas Mineral Laboratories) utilizing Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP AES).

Table 2. Rock descriptions (hand specimen) and sample locations.

Serial Numbers	Co-ordinates	Texture	Mineralogy	Rock type	Location
LO 1= (RR01)	Lat. 7°12'25"N Long. 3°56'46"E Elevation 541 ft	Medium coarse grained	Quartz, feldspar, muscovite, and biotite	Pegmatite	Olode
LO 2= (RR02)	Lat. 7°11'47"N Long. 3°58'01"E Elevation 451 ft	Medium grained	Quartz, biotite, and feldspar	Granite gneiss	Ori-Oke Olojuoro
LO 3= (RR03)	Lat. 7°11'40"N Long. 3°58'04"E Elevation 461 ft	Medium grained	Quartz, biotite, and feldspar	Granite granite	Ori-Oke Olojuoro
LO 4= (RR04) & (RR05)	Lat. 7°9'40"N Long. 3°57'25"E Elevation 365 ft	Course grained	Quartz, muscovite, biotite, beryl, feldspar(mica) dark-brown, specks of garnet	Pegmatite and mica schist	Falansa Mine
LO 5= (RR06) & (RR07)	Lat. 7°11'27"N Long. 3°55'36"E Elevation 443 ft	Course grained	Quartz, muscovite, feldspar(mica), brown pitches of garnet with very limited amount of biotite	Pegmatite and mica schist	Gbayo (Active and abandoned mine)
LO6= (RR08) & (RR09)	Lat. 7°11'44"N Long. 3°55'50"E Elevation 448 ft	Medium to course grained	Quartz, feldspar, biotite, and medium grained size muscovite	Pegmatite and mica schist	Gbayo (an abandoned mine)
LO 7	Lat. 7°10'30"N Long. 3°55'59"E Elevation 459 ft	Medium grained	Quartz, biotite and feldspar	Granite gneiss	Sanku
LO 8= (RR10)	Lat. 7°10'06"N Long. 3°55'25"E Elevation 437 ft	Medium grained	Quartz, biotite, and feldspar	Granite gneiss	Onipede

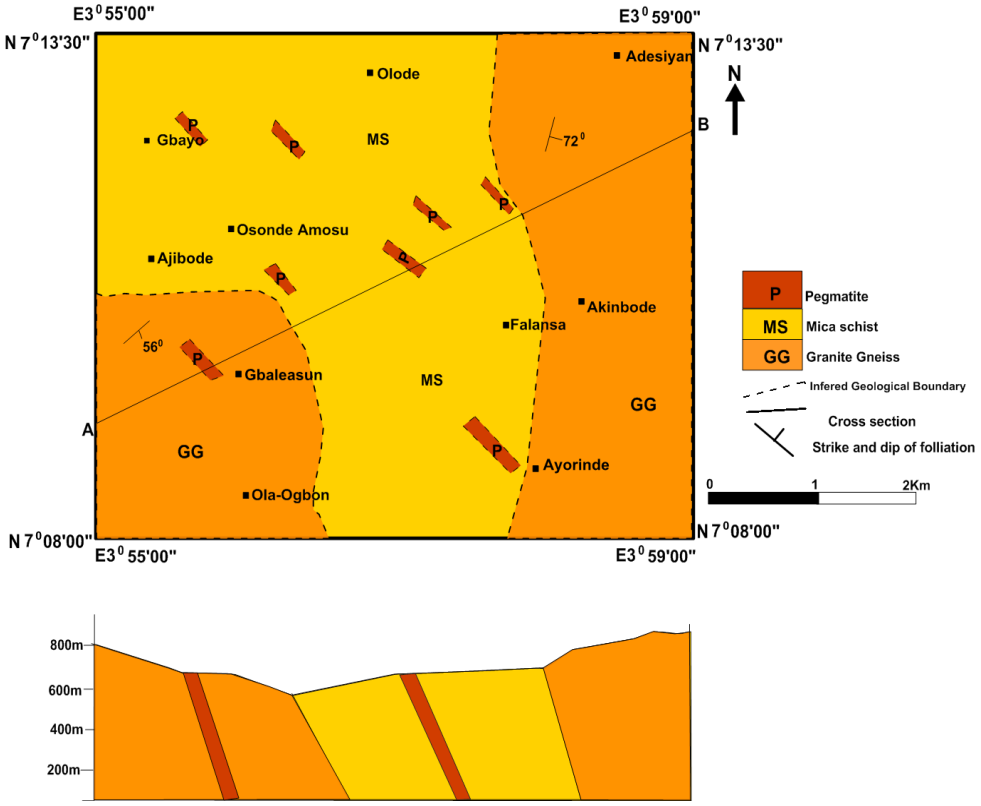


Figure 2. Geological map of the study area (Adapted from Okonkwo et al. [22]).

2.3 Assessment of metal contamination

Single-element pollution indices

Single pollution indices are employed in the assessment of metal contamination because they show how concentrated an element is in a certain location in comparison to a background. As an example:

Contamination factor (Cf) is a quantitative evaluation of the contaminant's level and sources. The following is how CF is assessed:

$$\mathbf{Cf = C_m Sample / C_m Background}$$

where C_mSample = concentration of a given metal in the sediment, C_mBackground = Background value of the metal of interest at a site [25,26]. The following four classes were established (**Table 3**).

Table 3. Contamination factor (CF) and level of contamination [27].

Contamination Factor (CF)	Contamination Level
CF < 1	Low contamination
1 ≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF > 6	Very high contamination

Enrichment factors (Ef) are a useful indicator of contamination status and level in the research environment [28]. As seen below, the EF computation compares each value to a certain (control sample) background level in order to identify possible sources:

$$\mathbf{EF = (Me/Fe)_{Sample}/(Me/Fe)_{background}}$$

where $(Me/Fe)_{sample}$ = the metal to Fe ratio in the sample under study; $(Me/Fe)_{background}$ is the natural background value of metal to Fe ratio. We used metal background values from roughly 4.5 kilometers away for this study. Iron was chosen as a normalization factor since its natural sources (1.5 percent) have a significant influence on its input [29]. **Table 4** shows the many types of enrichment factors.

Table 4. Enrichment factor (EF) categories [30].

Enrichment factor (EF)	Enrichment factor (EF) Categories
EF < 2	Deficiency to minimal enrichment
2 ≤ EF < 5	Moderate enrichment
5 ≤ EF < 20	Significant enrichment
20 ≤ EF < 40	Very high enrichment
EF ≥ 40	Extremely high enrichment

The Igeo index is used to classify and identify environmental control exerted by anthropogenic

activities. Igeo was determined using the following formula:

$$\mathbf{I_{geo} = Log_2\ [C_mSample/(1.5 \times C_m\ Background)]}$$ [26]

where C_mSample = measured concentration of an element in the sediment sample and C_mBackground = geochemical background value. To account for possible fluctuations in baseline values for a specific metal in the environment as well as very modest anthropogenic influences, a factor of 1.5 was utilized. Muller [31] recognized seven levels of qualification (**Table 5**).

Table 5. Muller's classification for geo-accumulation index (Igeo).

Igeo Values	Class	Sediment Quality
≤ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 6	6	Extremely polluted

Multi-element pollution indices

Due to some inherent limitations that single-element pollution indices have, multi-element pollution indices were also used [32]. The followings are the most common and regularly used:

The contamination degree (Cd) is calculated as the sum of contamination factors (CF of the study region) for all elements examined, as shown below [27].

$$\mathbf{C_d} = \sum_{i=1}^{n} \mathrm{Cf}^{i}\Sigma$$

This is intended to establish a standard of overall effluence intensity in surface layers in a specific area.

Pollution Index (PI) equation derived by Hakanson [27] and Nemerow [33] is as follow:

$$PI = \sqrt{\frac{(\mathrm{Cf_{average}})^2 + (\mathrm{Cf_{max}})^2}{2}}$$

where $Cf_{average}$ = average of contamination factor and Cf_{max} = maximum contamination factors. Categories for PI are: PI < 0.7—Unpolluted, 0.7 < PI < 1—Slightly polluted, 1 < PI < 2—Moderately polluted, 2 < PI < 3—Severely polluted, PI > 3—Heavily polluted.

Modified Pollution Index (MPI): In their calculation, Brady et al. [25] used enrichment factors instead of contamination factors.

$$MPI = \sqrt{\frac{(\mathrm{Ef_{average}})^2 + (\mathrm{Ef_{max}})^2}{2}}$$

where $Ef_{average}$ = average of enrichment factors and Ef_{max} = maximum enrichment factor.

Categories for MPI are: MPI < 1—Unpolluted, 1 < MPI < 2—Slightly polluted, 2 < MPI < 5—Moderately polluted, 3 < MPI < 5—Moderately-heavily polluted, 5 < MPI < 10—Severely polluted and MPI > 10—Heavily polluted.

PI and MPI are both used in the same way. This takes into account background concentrations as well as the sediments' complex, non-conservative behaviour [27,33,25].

The pollution load index (PLI) provides a simple but relative method of evaluating an area's suitability for human well-being. Tomlinson et al. [34] devised this method, and the degree of metal pollution in the research area was determined using the formula below:

$$\mathbf{PLI = (CF_1\ X\ CF_2\ X\ CF_3\ X\ .....CF_n)^{1/n}}$$

where Cf1 = CF, n = number of metals. According to Brady et al. (2015), the degree of heavy metal risk assessed by PLI is mainly divided into PLI < 0.7—Unpolluted; 0.7 < PLI < 1—Slightly polluted; 1 < PLI < 2—Moderately polluted; 2 < PLI < 3—Severely polluted; PLI > 3—Heavily polluted.

The ecological risk index (ERI) is a useful technique for determining heavy metal pollution in soil and its ecological and environmental consequences. The ecological risk factor (Er^i) can be stated mathematically using the following equation:

$$\mathbf{Er = Tr^i * C^iF}$$

where Tr^i = toxic-response factor for a given element; Hakanson [27] defined a "toxic-response factor" (Tr) for a specific substance and found values of 30, 5, 5, 5, 2, 1, 1 for Cd, Cu, Pb, Ni, Cr, Zn, and Mn, respectively; C^if = contamination factor.

The potential ecological risk index (PERI) is expressed after Wang et al. [35] as:

$$R.I = \sum_{i=1}^{6} Er^i$$

where R.I = requested potential ecological risk index for the environment and Er^i is the ecological risk factor for a given element i to semi-quantitatively determine the pollution level in an area.

3. Results and discussion

3.1 Heavy metals concentration in the stream sediments

Table 6 shows the results of the geochemical analysis of stream sediment. Copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), cobalt (Co), manganese (Mn), strontium (Sr), vanadium (V), cadmium (Cd), chromium (Cr), barium (Ba), and iron (Fe) were among the heavy metals evaluated in this work (Fe). For the most part, the concentrations of heavy metals were found to have a relatively wide range of values.

Table 7 shows the descriptive statistics for the obtained data set relating to the stream sediments under research in Olode and its environs, as well as background geochemical data. Cu, Pb, Zn, Ni, Co, Mn, Sr, V, Cr, and Ba have mean concentrations of 16.25, 10.60, 27.83, 9.00, 13.90, 553, 9.83, 42.08, 47.42, 74.5, respectively. Heavy metal mean values were higher than background values (samples collected 4 km away from the mining site at Ayorinde), indicating that mining activities had an impact on the study area. Although the abundance of these heavy metals analysed in stream sediments was Mn > Ba > Cr > V > Zn > Cu > Co > Pb > Sr > Ni > Fe, the highest metal concentrations were found in rock and stream sediment samples from the mine area, particularly from abandoned mines in Gbayo. The coefficient of variation (CV), a powerful tool for measuring relative variability, was used in this work to compare the degree of variation from one data sequence to the next [12-14,18,19,22]. Sr had the lowest CV of 6.12, followed by V and Cr with 85.08 and 92.13 percent, respectively. Pb, Ni, Cu, and Ba had CVs of 110.30, 111.1, 114.58, and 119.79 percent, respectively, while Zn Mn and Co had CVs of 124.69, 148.00, and 171.22 percent. Cr, Pb, Ni, Cu, Ba, Zn, Mn, and Co exhibited a CV of over 90%. Although sampling methods and preparations with analytical techniques may be responsible for the large coefficient variation across the area under investigation, the obtained CV (CV < 90%) values of heavy metals dominated by anthropogenic sources are generally greater than (CV > 90%) dominated by geogenic sources [19,13,22] (**Table 7**).

Table 6. Concentration (ppm) of heavy elements in the stream sediment samples around Olode Pegmatite Mine.

Locations	Gbayo	Gbayo	Olojuoro	Olojuoro	Akinbode	Olojuoro	Falansa	Adeoro	Agbeja	Elerin	Gbayo
Sample Numbers	SS01	SS02	SS03	SS04	SS05	SS06	SS07	SS08	SS10	SS11	SS12
Cu	12	33	7	6	8	17	14	8	14	59	15
Pb	7	13	5	3	8	5	12	5	3	40	8
Zn	19	36	16	13	13	18	88	16	16	55	37
Ni	11	48	3	3	2	4	11	3	7	9	6
Co	6	85	1	4	3	3	13	4	8	22	3
Mn	121	4330	36	188	148	76	690	157	193	447	160
Sr	17	31	6	4	4	12	10	5	8	13	5
Cd	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
V	28	90	21	13	27	65	43	15	24	135	35
Cr	46	161	18	12	29	36	54	14	34	113	42
Ba	91	354	21	25	23	53	75	24	71	107	36
Fe	0.97	4.29	0.42	0.52	0.89	1.32	1.51	0.57	0.91	4.98	1.08

All values are in part per milliom (mg/kg) except Fe in %.

Table 7. The summary of chemical parameters of the stream sediment samples of Olode area.

Elements	Min.	Max.	Mean	STD	Coefficient of variation (%)	Background value	WHO
Cu	2	59	16.25	18.62	114.58	2	25
Pb	3	40	10.6	9.61	110.30	3	----
Zn	7	88	27.83	22.32	124.69	7	123
Ni	1	48	9	8.10	111.1	1	20
Co	2	85	13.90	23.80	171.22	2	---
Mn	36	4330	553	33.82	148	90	---
Sr	3	31	9.83	7.57	6.12	3	----
V	9	135	42.08	35.80	85.08	9	----
Cr	10	161	47.42	43.69	92.13	10	25
Ba	14	354	74.5	89.24	119.79	14	---
Fe	0.42	4.98	1.59			0.33	

3.2 Spatial distribution/variation of heavy metals

In order to evaluate the likely sources of enrichment and identify possible hotspot sections of the study area with high metal concentrations, the spatial distribution/variation of heavy metals was investigated for both stream sediment and rock samples [36,22] (**Figure 3**).

Copper concentrations in rock and stream sediment samples are 30 and 16.25 ppm on average, respectively (**Figure 3A**). Falansa (122,1 ppm) and Gbayo (122,1 ppm) have high copper values in their rocks (95.6 ppm). All of these were collected in the research region near the operating and abandoned mines of Falansa and Gbayo.

Lead concentrations in rock samples average 2.81 ppm, whereas stream sediment samples average 10.60 ppm (**Table 7** and **Figure 3B**). The highest Lead concentration in rock samples (10.7 ppm) was found in the Onipede area, implying that the concentration of Lead in the research area is due to anthropogenic sources such as waste dumps, incineration point leaching, atmospheric deposition, and the use of agrochemicals [13,22].

Zinc concentrations of 72 ppm were found in rocks at Gbayo and 88 ppm in sediments near Falansa (**Table 7** and **Figure 3C**). Many of the high zinc concentrations were found in rock and stream sediment samples taken near abandoned mines. The existence of high zinc values in the studied area could possibly be due to an anthropogenic source [22].

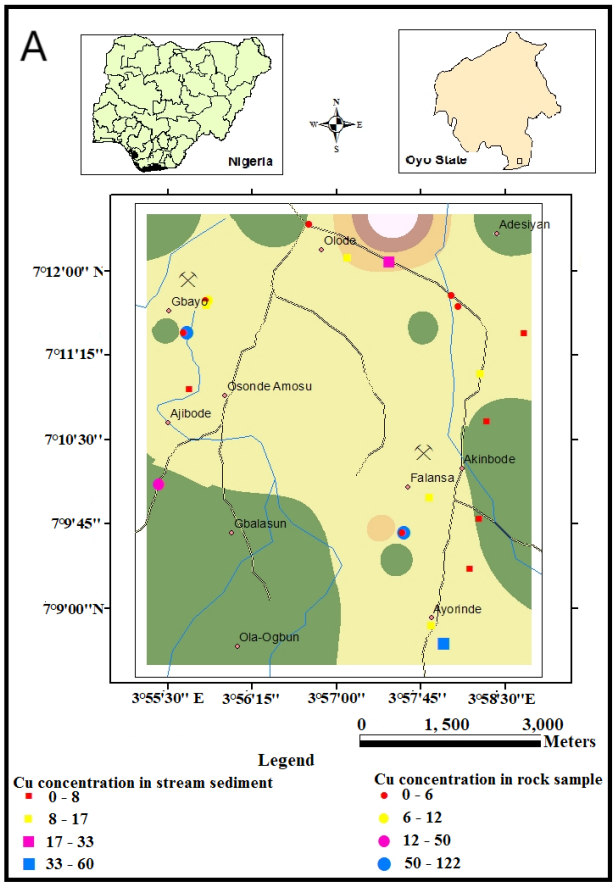
Nickel concentrations were moderately high in the area of the mine and the abandoned Falansa mines (**Table 3** and **Figure 3D**). Nickel concentrations in rock samples average 58.67 ppm, while stream sediment samples average 9.00 ppm (**Table 7**).

Cobalt concentrations in rocks and stream sediment samples average 9.67 and 13.91 ppm, respectively (**Table 7** and **Figure 3E**). The locations with high Cobalt concentration values in the sediment in Gbayo have the highest with 85 ppm, which could be caused by anthropogenic sources such as waste dump sites, leaching from incineration points, discharge from domestic waste, agro-chemicals, and others, but these are evidently very low in the rock samples of the areas, limiting the sources to lithogenic sources (**Figure 3E**).

Extraordinarily high manganese concentration values were found in stream sediments from Gbayo, with the highest concentration of (4330 ppm). The occurrence of extremely high manganese concentrations in the area is likely due to run-off from the habitats (**Table 3** and **Figure 3F**).

In rock and stream sediment samples, the average levels of strontium were found to be 221.12 ppm and 9.83 ppm, respectively (**Table 7**). The amount of strontium in the rocks in the research area is higher than in stream sediment samples, indicating that the metal derives from a natural (geogenic) source in the rock types studied [18].

Furthermore, substantial strontium concentrations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Cu concentration in stream sediment
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33 - 60
Cu concentration in rock sample
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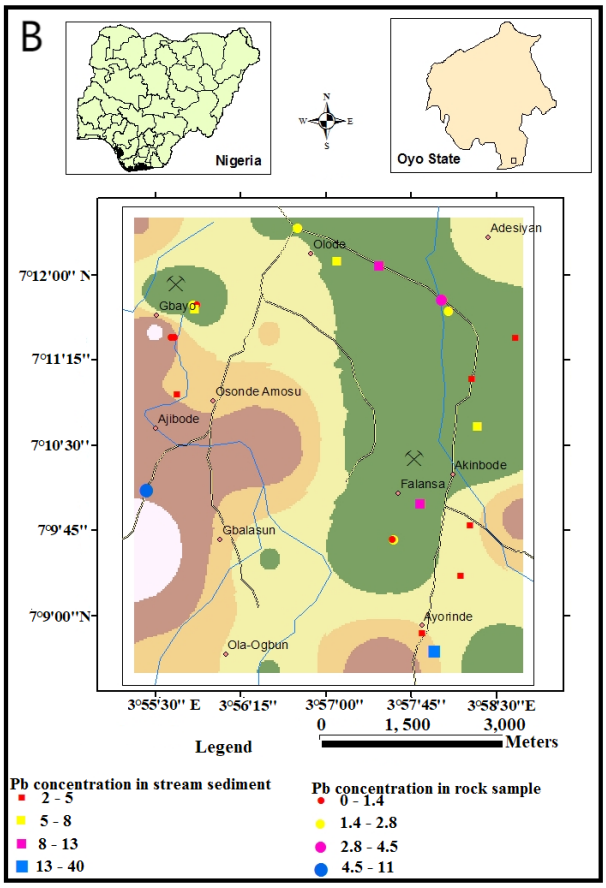
6 - 12
12 - 50
50 - 122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Pb concentration in stream sediment
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5 - 8
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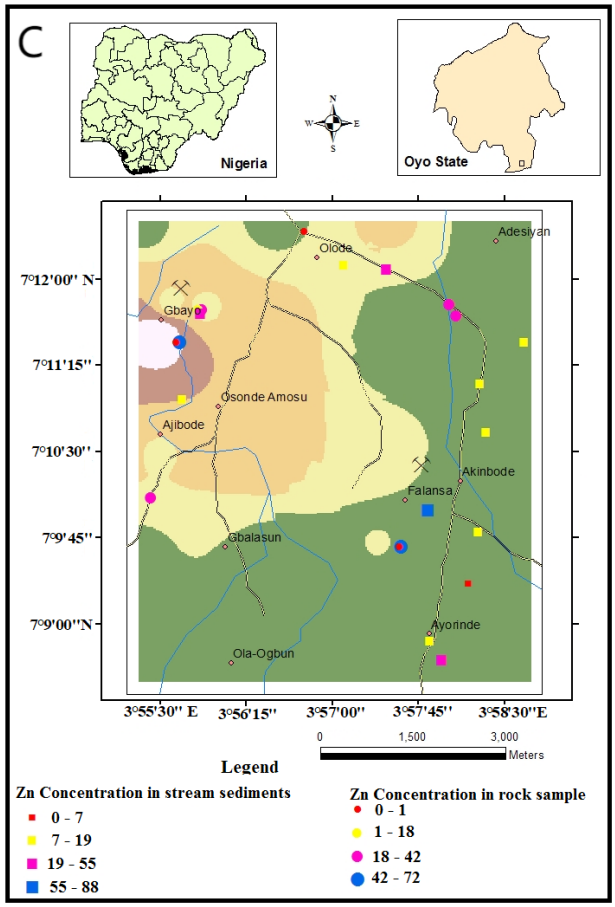
13 - 40
Pb concentration in rock sample
0 - 1.4
1.4 - 2.8
2.8 - 4.5
4.5 - 11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3°56'15''
3°57'00''
3°57'45''
3°58'30''E
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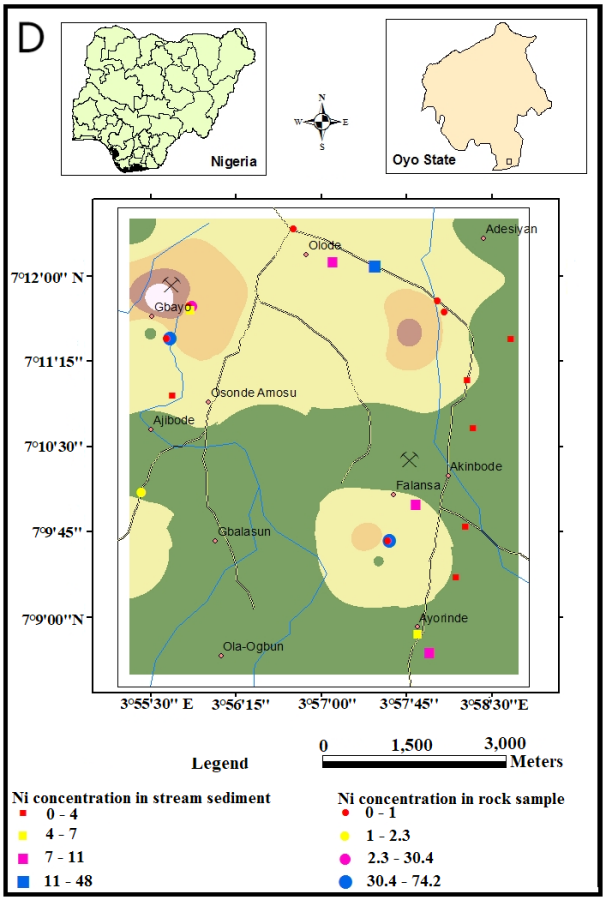
Zn Concentration in stream sediments
0 - 7
7 - 19
19 - 55
55 - 88
Zn Concentration in rock sample
0 - 1
1 - 18
18 - 42
42 - 72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3°57'00''
3°57'45''
3°58'30''E
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Meters
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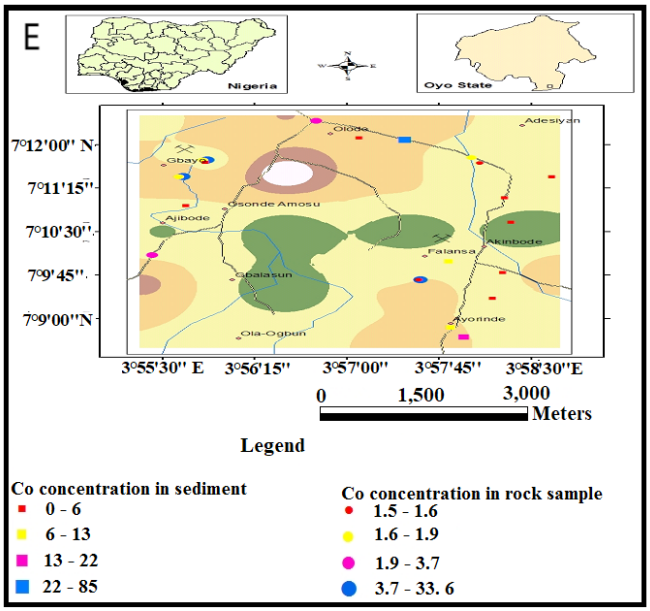
Ni concentration in stream sediment
0 - 4
4 - 7
7 - 11
11 - 48
Ni concentration in rock sample
0 - 1
1 - 2.3
2.3 - 30.4
30.4 - 74.2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3°57'45"
3°58'30"E
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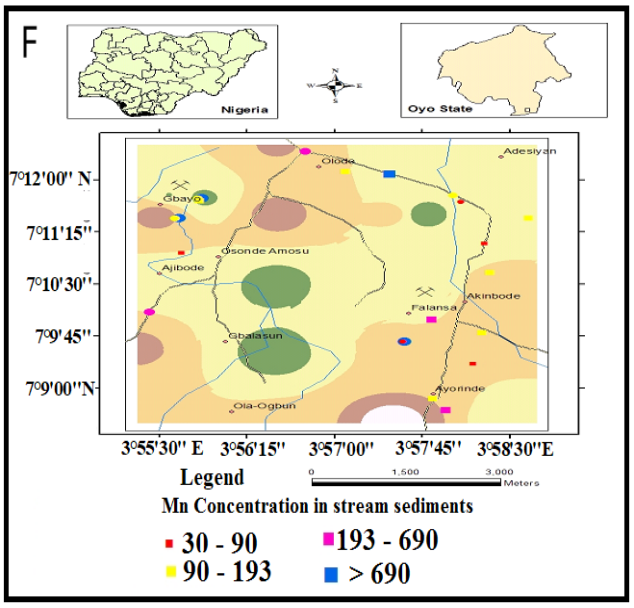
3,000
Meters
Legend
Co concentration in sediment
0 - 6
6 - 13
13 - 22
22 - 85
Co concentration in rock sample
1.5 - 1.6
1.6 - 1.9
1.9 - 3.7
3.7 - 33. 6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3°57'45"
3°58'30"E
Legend
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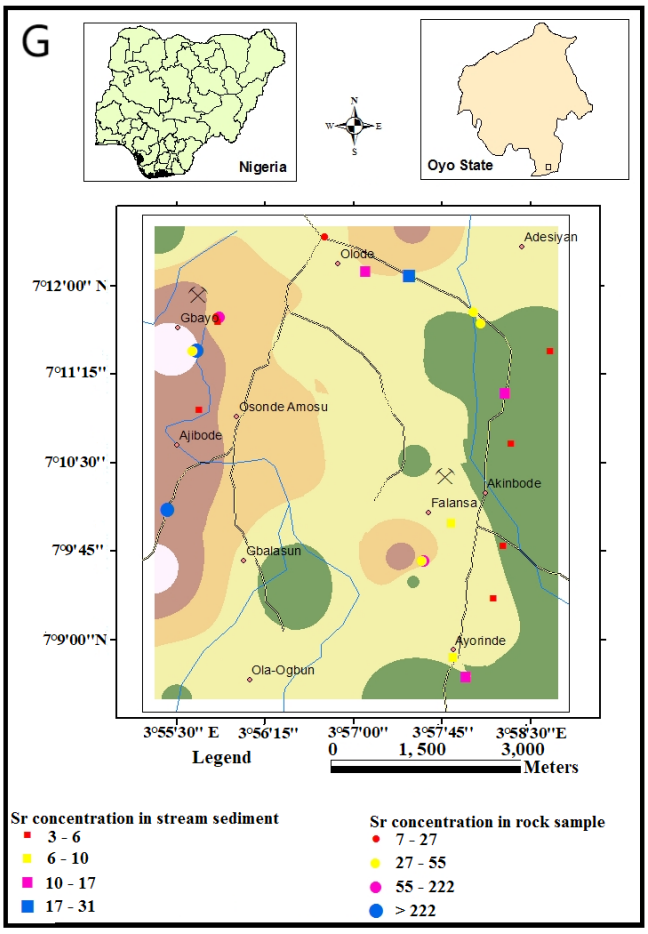
Meters
Mn Concentration in stream sediments
30 - 90
90 - 193
193 - 690
> 690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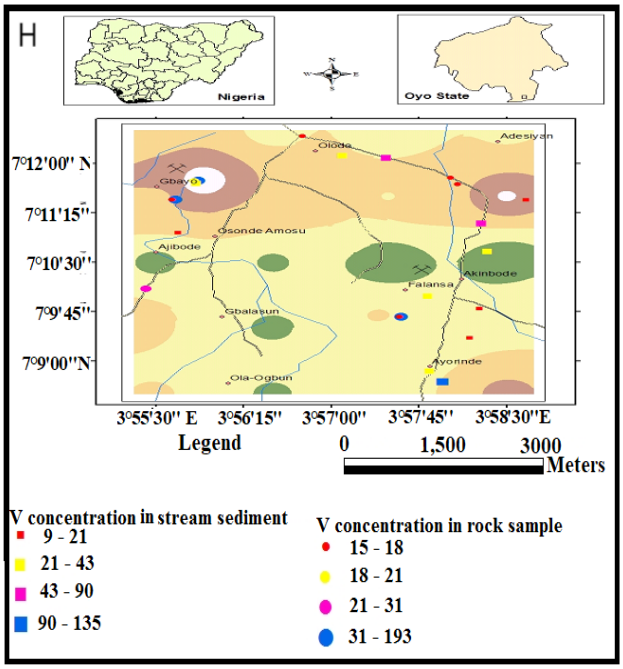
3°58'30"E
Legend
0
1, 500
3,000
Meters
Sr concentration in stream sediment
3 - 6
6 - 10
10 - 17
17 - 31
Sr concentration in rock sample
7 - 27
27 - 55
55 - 222
> 222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3°56'15"
3°57'00"
3°57'45"
3°58'30"E
Legend
0
1,500
3000
Meters
V concentration in stream sediment
9 - 21
21 - 43
43 - 90
90 - 135
V concentration in rock sample
15 - 18
18 - 21
21 - 31
31 - 193

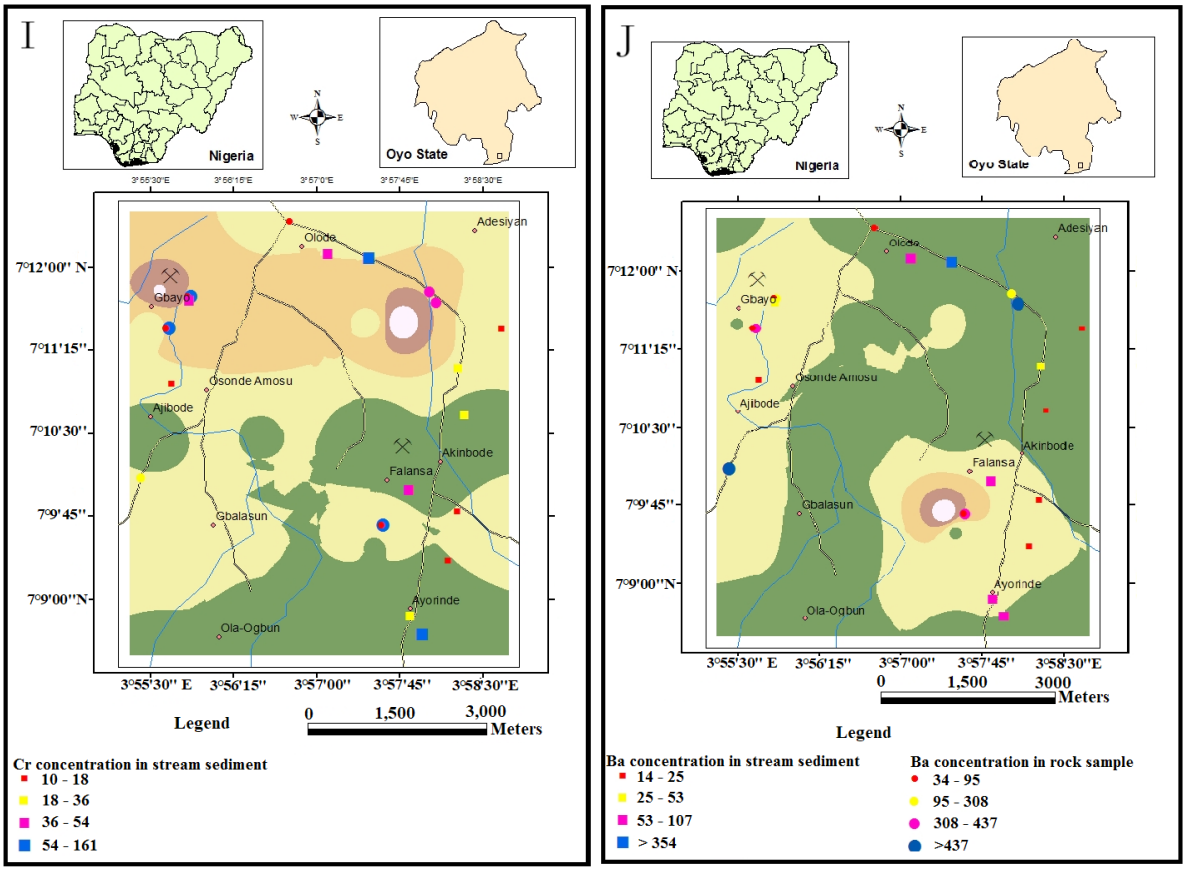

Figure 3. Map of the study area showing distribution of : (A) Copper, (B) Lead, (C) Zinc, (D) Nickel, (E) Cobalt, (F) Manganese, (G) Strontium, (H) Vanadium, (I) Chromium and (J) Barium in the stream sediment and rock samples within the study area (Modified after Okonwo et al. [22]).

were found in rock samples collected in Onipede (864.7 ppm), Gbayo (685.8 ppm, 213.5 ppm), and Falansa (222.3 ppm). It's worth noting that the levels of strontium in all of the stream sediment samples are modest (**Figure 3G**).

Vanadium concentrations of 193 ppm, 173 ppm, and 170 ppm were found in rock samples, while 135 ppm, 90 ppm, and 65 ppm were found in stream sediment samples from the research area, indicating a natural (geogenic) contribution of this metal from the rock types to the environment (**Figure 3H**).

High chromium concentration levels were found to be centered around the stream sediment samples, with high concentration values in Gbayo (161 ppm) and Elerin (113 ppm) (**Table 7** and **Figure 3I**). Chromium compounds attach to soil and are unlikely to travel to groundwater, but they persist in water sediments.

Barium levels were found to be high in rock and stream sediment samples collected in the Falansa, Gbayo, Ayominde, Olojuoro, Onipede, and Ajibode locations. The rock samples had high concentration levels of 737 ppm, 594 ppm, 437 ppm, 412 ppm, 308 ppm, and 209 ppm, whereas the stream sediment samples had 107 ppm and 354 ppm (**Table 7** and **Figure 3J**). Vomiting, abdominal cramps, diarrhea, difficulty breathing, elevated or lowered blood pressure, numbness around the face, and muscle weakness can all be symptoms of exposure to this metal. High blood pressure, heart rhythm abnormalities, paralysis, and death are all possible side effects of consuming large doses of barium [13].

The stream sediments showed a low concentration of Fe (**Table 6**).

3.3 Heavy metal sourcing

To determine the contribution of various factors

to the concentrations of metals in the samples and so infer the sources of metal pollution, the data were subjected to Pearson's correlation statistical analysis [13,22] (**Table 8**). High positive and significant correlation values (> 0.65) were discovered in the acquired data for stream sediment samples from Olode and its vicinity; Copper-Lead (0.929), Copper-Vanadium (0.970), Copper-Chromium (0.815), Lead-Vanadium (0.884), Lead-Chromium (0.660), Nickel-Cobalt (0.978), Nickel-Manganese (0.979), Nickel-Strontium (0.925), Nickel-Chromium (0.875), Nickel-Barium (0.989), Cobalt-Manganese (0.986), Cobalt-Strontium (0.884), Cobalt-Chromium (0.905), Cobalt-Barium (0.982), Manganese- Chromium (0.838), Manganese-Barium (0.961), Strontium-Chromium (0.878), Strontium-Barium (0.950), Vanadium-Chromium (0.840), and Chromium-Barium (0.917) (**Table 8**). These significant correlation values indicate that the origin of metals in the studied area is strongly linked to abandoned mine water, mining activities, and emissions from fossil fuel combustion, among other things [22].

Nickel, Manganese, Copper, Lead, Chromium, Vanadium, Barium, and Cobalt have high correlation values, indicating that these metals were anthropogenically added to stream sediment samples. However, the strong correlations between Nickel-Cobalt (0.978), Nickle-Manganese (0.979), Nickel-Strontium (0.925), Nickel-Barium (0.989), Manganese-Barium (0.961), Strontium-Barium (0.950), Chromium-Barium (0.917) imply a natural (geogenic) contribution of metals from the rock types observed in the research area [36,13].

Zinc, Copper, Cadmium, and Lead are frequently found together in geochemical research [37,38]. Lead had weak positive correlation values with Zinc, Cobalt, and Manganese, indicating that these metals may have contributed to the stream sediment samples from various undefined sources, both naturally and anthropogenically, whereas Lead had high correlation values with Copper, Vanadium, and Chromium, indicating that these metals may have come from a natural source.

3.4 Single-element indices

To determine the environmental effects, a quantitative analysis of heavy metal pollution estimation surrounding the pegmatite mining site in Olode and its vicinity was conducted using single-element indices [13]. These indices used include:

Contamination factor

The result for this index, as shown in **Table 9**, was calculated by comparing the measured heavy metal concentration with background values for stream sediments collected in an uninterrupted area inside the research area at Ayorinde, about 4 kilometers from the Falansa mine. On average, the CF values found were in the following order: Cu > Co > Mn > V > Ba > Cr > Zn > Pb. The results for these metals ranged from extremely low to very high contamination (CF = CF1; 1CF > 6) (**Table 4**), indicating that their prevalence was anthropogenic [18].

Table 8. Correlations matrix for heavy metals in stream sediment samples of Olode area.

	Cu	Pb	Zn	Ni	Co	Mn	Sr	V	Cr	Ba
Cu	1									
Pb	0.929	1								
Zn	0.497	0.575	1							
Ni	0.450	0.235	0.296	1						
Co	0.537	0.334	0.287	0.978	1					
Mn	0.402	0.200	0.250	0.979	0.986	1				
Sr	0.552	0.333	0.285	0.925	0.884	0.853	1			
V	0.970	0.884	0.515	0.499	0.580	0.463	0.619	1		
Cr	0.815	0.660	0.487	0.875	0.905	0.838	0.878	0.840	1	
Ba	0.548	0.323	0.290	0.989	0.982	0.961	0.950	0.593	0.917	1

Table 9. Contamination factor (CF) for the heavy metals of Olode stream sediments.

	Cu	Pb	Zn	Ni	Co	Mn	Sr	Cd	V	Cr	Ba
SS01	6	2.33	2.71	11	3	1.34	5.67	1	3.11	4.6	6.5
SS02	16.5	4.33	5.14	48	42.5	48.11	10.33	1	10	16.1	25.29
SS03	3.5	1.67	2.89	3	0.5	0.4	2	1	2.33	1.8	1.5
S004	3	1	1.86	3	2	2.09	1.33	1	1.44	1.2	1.79
SS05	4	2.67	1.86	2	1.5	1.64	1.33	1	3	2.9	1.64
SS06	8.5	1.67	2.57	4	1.5	0.84	4	1	21.67	3.6	3.79
SS07	7	3	12.57	11	6.5	7.67	3.33	1	4.78	5.4	5.36
SS08	4	1.67	2.28	3	2	1.74	1.67	1	1.67	1.4	1.71
SS10	7	1	2.29	7	4	2.14	2.67	1	2.67	3.4	5.07
SS11	39.5	13.33	7.86	9	11	4.97	4.33	1	15	11.3	7.64
SS12	7.5	12.33	5.29	6	1.5	1.78	1.67	1	3.89	4.2	2.57
Range	3-39.50	1-13.33	1.86-12.57	2-48	0.5-42.5	0.4-48.11	1.33-10.33	1	1.44-21.67	1.2-16.10	1.5-25.29
CD	106.5	45	47.32	107	76	72.72	38.33	11	69.56	55.9	62.86

*CD = Degree of contamination.

The enrichment factor (EF)

Table 10 shows the heavy metal concentrations found in the Olode stream sediments.

EF is a tool that can be used to compare areas by providing a concise assessment of geochemical trends [39]. The computed enrichment factor for all heavy metals was EF < 2, showing a lack of minimal enrichment in diverse places.

The geo-accumulation index (Igeo)

The obtained calculated Igeo values, based on background values are listed in **Table 11**. The Igeo values for each heavy metal are: Cu (−1 to 3), Pb (−1 to 3), Zn (−1 to 3), Ni (−1 to 5), Co (−1 to 5), Mn (−1 to 6), Sr (0-3), V (0-3), Cr (0-4) and Ba (−1 to 4) (**Figures 4-8**). The Igeo values for the Olode stream sediments were in the following sequence of abundance: Mn > Co > Ni > Cr > Ba > Sr > Ba > Pb > Zn. Obtained values for Cu, Pb, Zn, Sr, V, Cr and Ba revealed practically uncontaminated to "moderately to heavily" contaminated except values for Ni, Co and Mn that indicated practically uncontaminated to extremely contaminated [31,26] (**Table 11**).

Table 10. Calculated enrichment factors of heavy metals in Olode stream sediments.

Sample Numbers	SS01	SS02	SS03	SS04	SS05	SS06	SS07	SS08	SS10	SS11	SS12
Unit	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Cu	2.04	1.3	2.75	1.9	1.48	2.13	1.53	2.32	2.54	1.96	2.29
Pb	1.19	3.03	1.96	0.95	1.48	0.63	1.31	1.45	0.54	1.3	1.22
Zn	3.23	1.38	6.29	4.13	2.41	2.25	9.62	4.63	2.90	1.85	5.65
Ni	1.87	1.85	1.18	0.95	0.37	0.5	1.2	0.87	1.27	0.3	0.92
Co	1.01	3.27	0.39	1.27	0.57	0.38	1.42	1.16	1.45	4.42	0.46
Mn	20.58	166.56	14.14	59.66	27.44	9.5	75.4	45.45	35	14.81	24.45
Sr	2.89	1.19	2.36	1.27	0.74	1.5	1.09	1.45	1.45	0.43	0.76
Cd	0.09	0.02	0.02	0.2	0.09	0.06	0.05	0.14	0.09	0.02	0.08
V	4.76	3.46	8.25	4.12	5.01	8.13	4.67	4.34	4.35	4.47	5.35
C r	7.83	6.20	7.07	3.80	5.38	4.5	5.9	4.05	6.17	3.74	6.42
Ba	15.48	13.62	8.25	7.93	4.26	6.63	8.20	6.94	12.87	3.55	5.5

Table 11. Geo-accumulation index of Olode sediments.

Metals	Igeo range in the Sediments	Interpretation
Cu	–1 to 3	Practically uncontaminated to "moderately to heavily" contaminated
Pb	–1 to 3	Practically uncontaminated to "moderately to heavily" contaminated
Zn	–1 to 3	Practically uncontaminated to "moderately to heavily" contaminated
Ni	–1 to 5	Practically uncontaminated to extremely contaminated
Co	–1 to 5	Practically uncontaminated to extremely contaminated
Mn	–1 to 6	Practically uncontaminated to extremely contaminated
Sr	0-3	Practically uncontaminated to "moderately to heavily" contaminated
V	0-3	Practically uncontaminated to "moderately to heavily" contaminated
Cr	0-4	Practically uncontaminated to "moderately to heavily" contaminated
Ba	–1 to 4	Practically uncontaminated to "moderately to heavily" contaminated

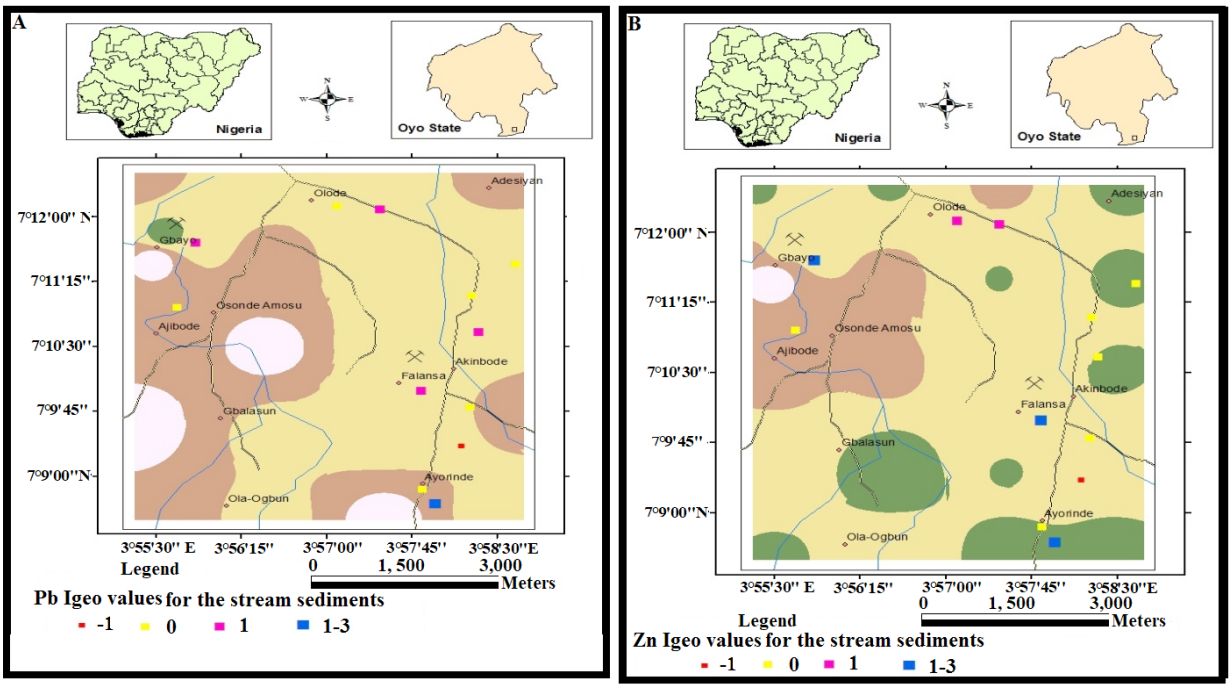

Figure 4. Igeo maps of : A) Lead and B) Zinc within the study area.

3.5 Multi-element pollution indices

The following indices were employed due to some inherent limitations that single-element pollution indices [32].

The degree of contamination (CD)

The degree of contamination (CD) is obtained by adding all of the computed CFs for each metal (**Table 9**), ranging from moderate to extremely high, signifying a significant human influence. With the exception of Cd, which is moderately contaminated, all of the heavy metals tested exhibited very high levels of contamination, indicating a worrying anthropogenic input as a result of mining and probably increased agricultural activity in the studied area.

Pollution load index (PLI)

The pollutant load index (PLI) was used to properly assess the level of environmental contamination caused by mining activity [34,40,22]. All of the PLI values obtained for the Olode stream sediments were more than one (**Table 12**). This indicates that the sampling site is significantly polluted/degraded, implying anthropogenic contamination. This index (PLI), which gives a simple, comparative approach

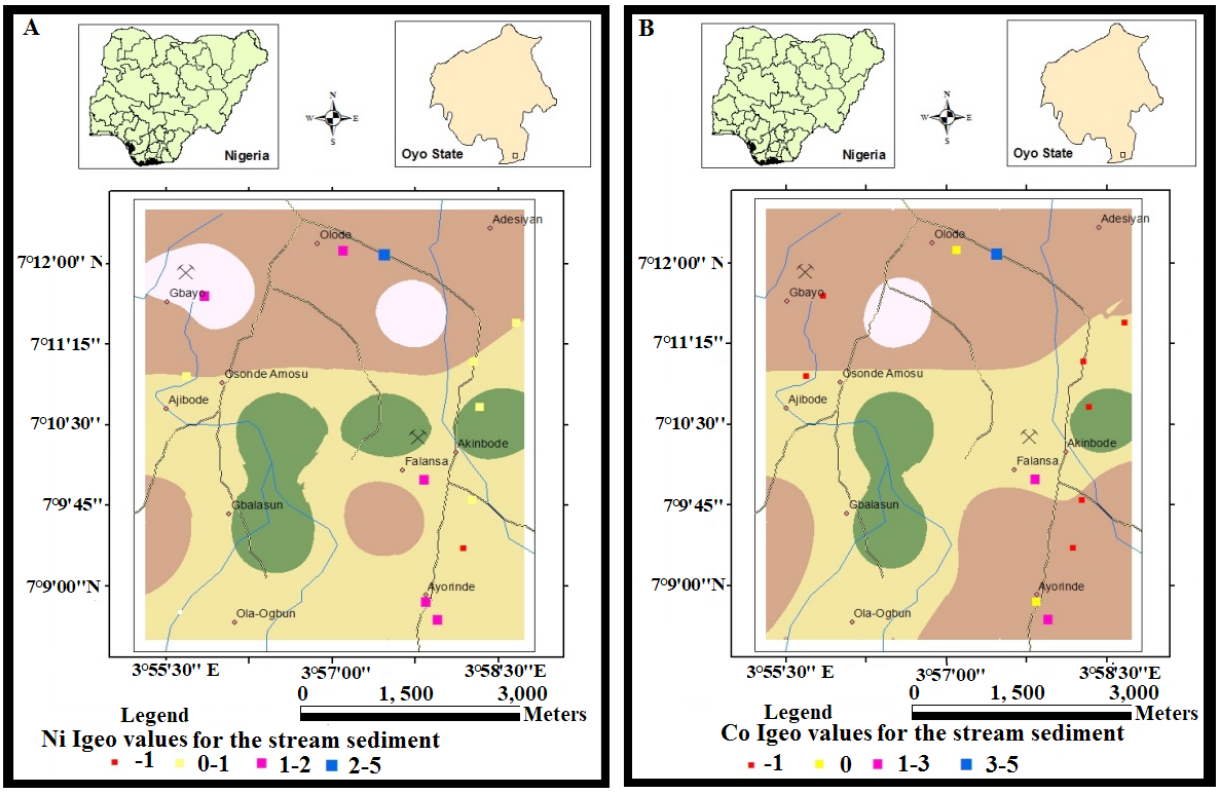

Figure 5. Igeo maps of A) Nickel and B) Cobalt within the study area.

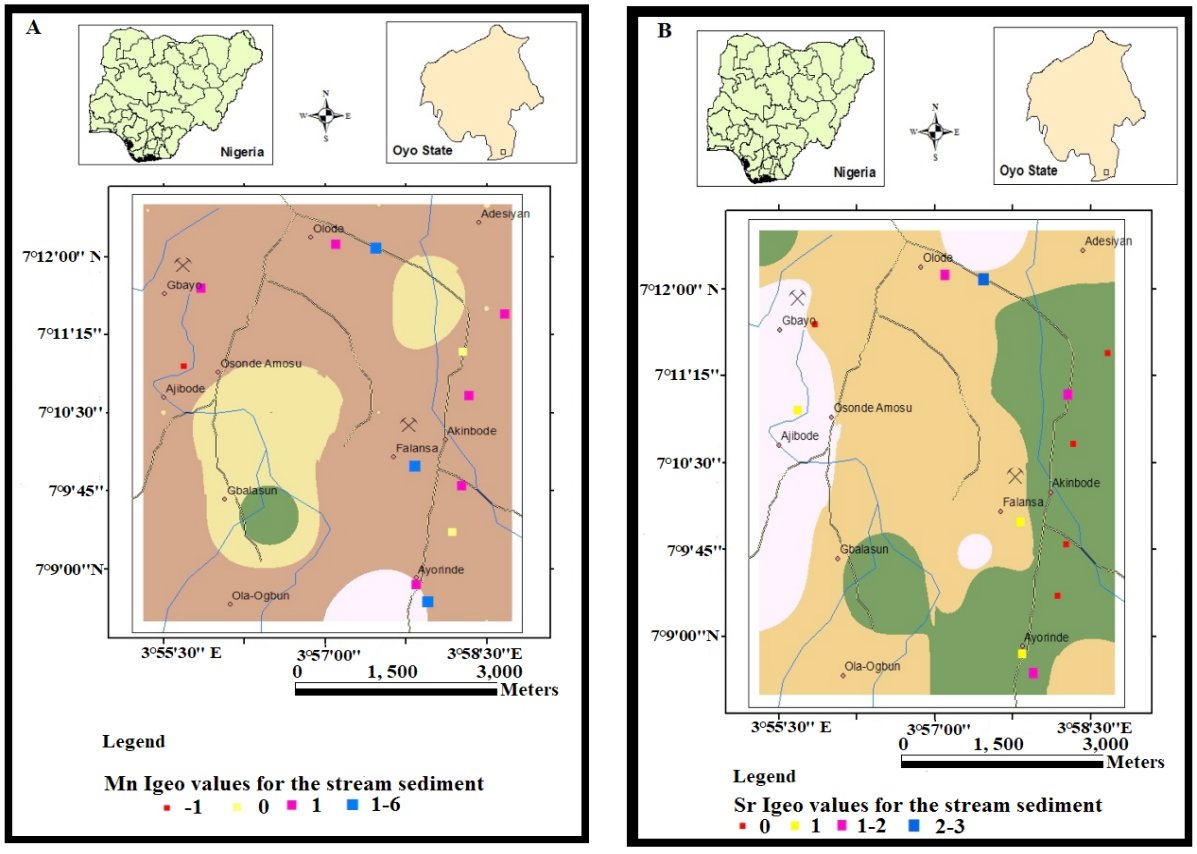

Figure 6. Igeo maps of A) Manganese and B) Strontium within the study area.

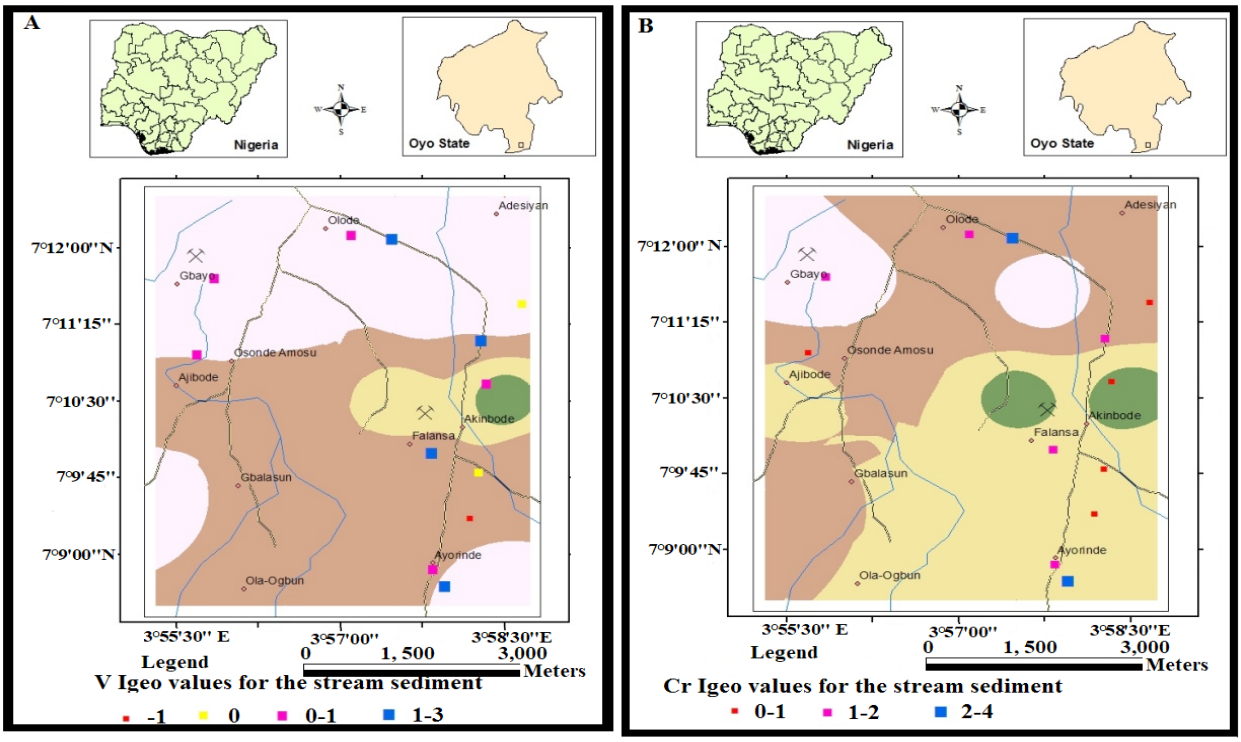

Figure 7. Igeo maps of A) Vanadium and B) Chromium within the study area.

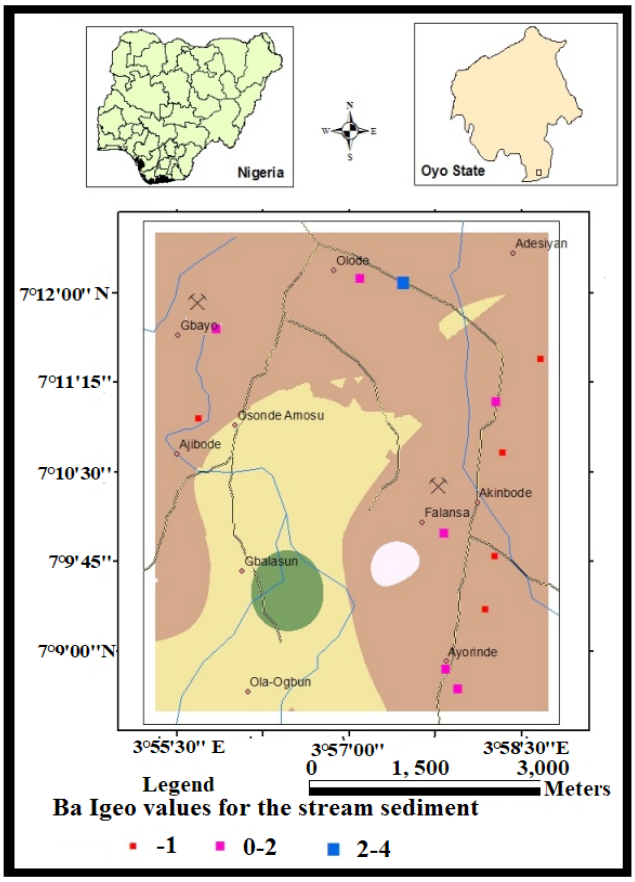

Figure 8. Igeo maps of Barium within the study area.

to measuring the degree of heavy metals contamination in a site, states that PLI = 0 indicates perfection, PLI = 1 indicates just baseline levels of pollutants, and PLI > 1 indicates progressive site deterioration [34,40].

Pollution Index (PI)

The Olode stream sediments can be classified according to the PI categories. SS03 and SS04 were moderately polluted (1PI2), SS05 and SS08 were severely polluted (2PI3), while the remaining eight samples (8) were significantly polluted (PI > 3) (**Table 12**). Thus, PI appeared to have an advantage over other underestimating indices, as it easily classifies high-risk sediments within a specific area/site of habitation [26,13].

Modified Pollution Index (MPI)

The MPI clearly distinguishes between three levels of pollution: moderately contaminated (2MPI5; SS 06), "moderately-heavily polluted" (Severely polluted; SS 03), and the other ten samples heavily polluted [27,33,25] (MPI > 10; S7, S10, S13, and S19; **Table 12**). This shows that 83.33% of the area under investigation was heavily polluted implying great

anthropogenic contribution.

Table 12. Pollution Load Index (PLI), Pollution Index (PI) and Modified Pollution Index values for heavy metals in Olode stream sediments.

Sampling sites	PLI	PI	MPI
SS01	85.14	5.91	10.66
SS02	39.48	20.18	83.78
SS03	1.02	1.98	7.46
S004	3.25	1.75	30.09
SS05	6.13	2.27	13.89
SS06	40.34	52.33	2.01
SS07	30.96	7	38,02
SS08	2.93	2.24	22.96
SS10	30.96	3.91	17.78
SS11	29.66	20.55	7.57
SS12	2.46	6.53	12.46

Pollution Load Index: PLI < 0.7—Unpolluted; 0.7 < PLI < 1—Slightly polluted; 1 < PLI < 2—Moderately polluted; 2 < PLI < 3—Severely polluted; PLI > 3—Heavily polluted.

Pollution Index: PI < 0.7—Unpolluted, 0.7 < PI < 1—Slightly polluted, 1 < PI < 2—Moderately polluted, 2 < PI < 3—Severely polluted, PI > 3—Heavily polluted.

Modified Pollution Index: MPI < 1—Unpolluted, 1 < MPI < 2—Slightly polluted, 2 < MPI < 5—Moderately polluted, 3 < MPI < 5—Moderately-heavily polluted, 5 < MPI < 10—Severely polluted and MPI > 10—Heavily polluted.

Ecological risk evaluation

Table 13 displays the value of the ecological risk index. The results demonstrated that the potential Er^i for heavy metals in Olode stream sediments followed a pattern of heavy metal contamination: Cu > Ni > Cd > Pb > Mn > Zn (**Table 8**). For all of the heavy metals in the sediment, the obtained potential Er^i values indicated a low to moderate ecological danger.

4. Conclusions

In Olode and its environs, southwestern Nigeria, a combination of geochemical tests, statistical approaches, and eight indices were utilized to identify heavy metal sources and assess pollution in stream sediments inside an active and abandoned mining site. The goal of this study was to determine the distribution of heavy metals in stream sediments, as well as the level of pollution, ecological danger, and potential sources of heavy metals. In order to investigate the source, contamination, and risk of heavy metals such as Pb, Zn, Cu, Ni, Co, Fe, Mn, and Cr, twelve (12) stream sediments and ten (10) rock samples were collected from pegmatite mining sites at Olode and its environs inside Ibadan, Southwestern Nigeria. The average values and order of abundance obtained followed the following pattern: ppm Mn (595.09) > Ba (80) > Cr (50.82) > V (45.09) > Zn (29.73) > Cu (13.82) > Co (13.82) > Sr (10.46) > Ni (9.73) > Pb (9.09) and Fe (1.59). The mean values

Table 13. Ecological risk index of heavy metals in the Olode stream sediments.

Sample	Cu	Pb	Zn	Ni	Mn	Cd	Cr	RI
SS01	30	11.65	2.71	55	1.34	30	9.2	139.9
SS02	82.5	21.65	5.14	240	48.11	30	32.2	459.6
SS03	17.5	8.35	2.89	15	0.4	30	3.6	77.74
S004	15	5	1.86	15	2.09	30	2.4	71.35
SS05	20	13.35	1.86	10	1.64	30	5.8	82.65
SS06	42.5	8.35	2.57	20	0.84	30	7.2	111.46
SS07	7	3	12.57	11	7.67	1	5.4	47.64
SS08	20	8.35	2.28	15	1.74	30	2.8	80.17
SS10	35	5	2.29	35	2.14	30	6.8	116.23
SS11	197.5	66.65	7.86	45	4.97	30	22.6	374.58
SS12	37.5	61.65	5.29	30	1.78	30	8.4	174.62
Average	45.86	19.36	4.30	44.64	6.61	27.36	9.67	157.81

Category: $Er^i < 40$—Low potential ecological risk; $40 \leq Er^i \leq 80$—Moderate potential ecological risk; $80 \leq Er^i \leq 160$—Considerable potential ecological risk; $160 \leq Er^i \leq 320$—High potential ecological risk; $Er^i > 320$—Very high ecological risk at hand for the substance in question.

for the heavy metals were higher than the background values, indicating that mining activities have a negative impact on the study area, as evidenced by the high coefficient of variation and correlation values (> 0.6). Copper-Lead (0.929), Copper-Vanadium (0.970), Copper-Chromium (0.815), Lead-Vanadium (0.884), Lead-Chromium, Nickel-Cobalt, Nickel-Manganese, Nickel-Strontium.

Based on the enrichment factor (EF), the Olode sediments show exceptionally significant enrichment for Mn and Ba when compared to other sediments in the research area. Cu and Ni are most likely responsible for the high contamination, according to contamination factor (CF) values. According to Igeo, the Olode stream sediments are practically uncontaminated to extremely contaminated by Ni, Co, and Mn, as measured by the degree of contamination (CD), pollution load index (PLI), pollution index (PI), and modified pollution index (MPI). Ni and Cu are the major regulating factors that are most likely causing the possible Er^{i}. Even though the results for the different indices varied, the combined eight (8) indices supplied us with an all-encompassing picture of heavy metal dangers in the Olode stream sediments. This aids in the development of an appropriate ecological management strategy for reducing the impact of heavy metal contamination from active and abandoned mining sites in Nigeria and other similar places.

Author Contribution

Authors whose names appear on the submission have contributed sufficiently to the scientific work. It is the M.Sc research of the first author supervised by the fourth author, research article drafted by the second and third authors respectively.

Conflict of Interests

The authors declare no conflict of interest.

Funding

The authors did not receive support from any organization for the submitted work.

References

[1] Wuana, R.A., Okeimen, F.E., 2011. Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. International Scholarly Research Notices. Article ID 402647.
DOI: https://doi.org/10.5402/2011/402647

[2] Islam, S., Ahmed, K., Al-Mamun, H., et al., 2019. Sources and ecological risk of heavy metals in soils of different land uses in Bangladesh. Pedosphere. 29(5), 665-675.
DOI: https://doi.org/10.1016/S1002-0160(17)60394-1

[3] Lei, M., Zhang, Y., Khan, S., et al., 2010. Pollution, fractionation, and mobility of Pb, Cd, Cu, and Zn in garden and paddy soils from a Pb/Zn Mining area. Environmental Monitoring and Assessment. 168(1-4), 215-222.
DOI: https://doi.org/10.1007/s10661-009-1105-4

[4] Lottermoser, B., 2007. Mine wastes: Characterization, treatment and environmental impacts. Springer: New York. pp. 1-290.

[5] Fashola, M.O., Ngole-Jeme, V.M., Babalola, O.O., 2016. Heavy metal pollution from gold mines: environmental effects and bacterial strategies for resistance. International Journal of Environmental Research and Public Health. 13(11), 1047.
DOI: https://doi.org/10.3390/ijerph13111047

[6] Finkelman, R.B., Orem, W.H., Plumlee, G.S., et al., 2018. Applications of geochemistry to medical geology. Environmental geochemistry: Site characterization, data analysis and case histories. Elsevier: Amsterdam. pp. 435-465.
DOI: https://doi.org/10.1016/b978-0-444-63763-5.00018-5

[7] Ayuso, R.A., Foley, N.K., 2018. Lead and strontium isotopes as monitors of anthropogenic contaminants in the surficial environment. Environmental geochemistry: Site characterization, data analysis and case histories. Elsevier: Amsterdam. pp. 307-362.
DOI: https://doi.org/10.1016/b978-0-444-

63763-5.00013-6

[8] Zarei, I., Pourkhabbaz, A., Khuzestani, R.B., 2014. An assessment of metal contamination risk in sediments of Hara Biosphere Reserve, southern Iran with a focus on application of pollution indicators. Environmental Monitoring and Assessment. 186, 6047-6060.

[9] Kumar, S., Trivedi, P.K., 2016. Heavy metal stress signaling in plants. Plant metal interaction. Elsevier: Amsterdam. pp. 585-603. DOI: https://doi.org/10.1016/b978-0-12-803158-2.00025-4

[10] Zhang, W., You, M., Hu, Y., 2016. The distribution and accumulation characteristics of heavy metals in soil and plant from Huainan coalfield, China. Environmental Progress & Sustainable Energy. 35(4), 1098-1104. DOI: https://doi.org/10.1002/ep.12336

[11] Atkinson, C., Jolley, D., Simpson, S., 2007. Effect of over-lying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from metal contaminated marine sediments. Chemosphere. 69(9), 1428-1437. DOI: https://doi.org/10.1016/j.chemosphere.2007.04.068

[12] Salah, E.A., Turki, A.M., Mahal, S.N., 2015. Chemometric evaluation of the heavy metals in urban soil of Fallujah City, Iraq. Journal of Environmental Protection. 6, 1279-1292.

[13] Adewumi, A.J., Laniyan, T.A., 2020. Contamination, sources and risk assessments of metals in media from Anka artisanal gold mining area, Northwest Nigeria. Science of the Total Environment. 718(137235), 1-14.

[14] Atgin, R.S., El-Agha, O., Zararsız, A., et al., 2000. Investigation of the sediment pollution in Izmir Bay: Trace elements. Spectrochimica Acta Part B. 55, 1151-1164. DOI: https://doi.org/10.1016/S0584-8547(00)00231-7

[15] Adamu, C.I., Nganje, T.N., Edet, A., 2014. Heavy metal contamination and health risk assessment associated with abandoned barite mines in Cross River State, south-eastern Nigeria. Environmental Nanotechnology, Monitoring & Management. 3, 10-21. DOI: http://dx.doi.org/10.1016/j.enmm.2014.11.001

[16] Oyebamiji, A., Odebunmi, A., Ruizhong, H., et al., 2018. Assessment of trace metals contamination in stream sediments and soils in Abuja leather mining, southwestern Nigeria. Acta Geochimica. 37(4), 592-613. DOI: https://doi.org/10.1007/s11631-017-0256-1

[17] Kolawole, T.O., Olatunji, A.S., Jimoh, M.T., et al., 2018. Heavy metal contamination and ecological risk assessment in soils and sediments of an Industrial area in Southwestern Nigeria. Journal of Health and Pollution. 8(19), 1-16.

[18] Boroumandi, M., Khamehchiyan, M., Nikoudel, M.R., et al., 2019. Evaluation of soil pollution sources using multivariate analysis combined with geostatistical methods in Zanjan Basin, Iran. Geopersia. 9(2), 293-304. DOI: https://doi.org/10.22059/GEOPE.2019.263512.648406

[19] Madukwe, H.Y., Ibigbami, O.A., Obasi, R.A., 2020. Assessment of trace and rare earth element levels in stream sediments in Ijero-Ekiti Area, Southwest Nigeria. Nature Environment and Pollution Technology. 19(2), 421-439.

[20] Aina, A.T., Salau, A.T. (editors), 1992. The challenge of sustainable development in Nigeria. An NGO Report Prepared for the United Nations Conference on Environment and Development; 1992 Jun 1-12; Rio de Janeiro, Brazil. NEST: Nigeria. pp. 16-44.

[21] Bell, R.G., Rusell, C., 2002. Environmental policy for developing countries. Issues in Science and Technology. 18(3), 63-70.

[22] Okonkwo, S.I., Idakwo, S.O., Ameh, E.G., 2021. Heavy metal contamination and ecological risk assessment of soils around the pegmatite mining sites at Olode area, Ibadan southwestern Nigeria. Environmental Nanotechnology, Monitoring & Management. 15, 100424. DOI: https://doi.org/10.1016/j.enmm.2020.100424

[23] Egbinola, C.N., Amobichukwu, A.C., 2013. Climate variation assessment based on rainfall and

temperature in Ibadan, South-Western, Nigeria. Journal of Environment and Earth Science. 3(11), 32-45.

[24] Dulski, P., 2001. Reference materials for geochemical studies: new analytical data by ICP-MS and critical discussion of reference values. Geostandards Newsletter. 25(1), 87-125. DOI: https://doi.org/10.1111/ggr.2001.25.issue-1

[25] Brady, J.P., Ayoko, G.A., Martens, W.N., et al., 2015. Development of a hybrid pollution index for heavy metals in marine and estuarine sediments. Environmental Monitoring and Assessment. 187(5), 306.

[26] Qingjie, G., Jun, D., Yunchuan, X., et al., 2008. Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. Journal of China University of Geosciences. 19(3), 230-241. DOI: https://doi.org/10.1016/S1002-0705(08)60042-4

[27] Hakanson, L., 1980. An ecological risk index for aquatic pollution control a sedimentological approaches. Water Research. 14(8), 975-1001. DOI: https://doi.org/10.1016/0043-1354(80)90143-8

[28] Feng, H., Han, X., Zhang, W.G., et al., 2004. A preliminary study of heavy metal contamination in Yangtze River Intertidal Zone Due to urbanization. Marine Pollution Bulletin. 49(11-12), 910-915. DOI: https://doi.org/10.1016/j.marpolbul.2004.06.014

[29] Tippie, V.K., 1984. An environmental characterization of Chesapeake Bay and a frame work for action. The estuary as a filter. Academic Press: New York.

[30] Mmolawa, K., Likuku, A., Gaboutloeloe, G., 2011. Assessment of heavy metal pollution in soils along roadside areas in Botswana. African Journal of Environmental Science and Technology. 5(3), 186-196.

[31] Muller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. GeoJournal. 2(3), 108-118.

[32] Duodu, G.O., Goonetilleke, A., Ayoko, G.A., 2016. Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. Environmental Pollution. 219, 1077-1091. DOI: https://doi.org/10.1016/j.envpol.2016.09.008

[33] Nemerow, N.L., 1991. Stream, lake, estuary, and ocean pollution. Van Nostrand Reinhold: New York. pp. 472.

[34] Tomlinson, D., Wilson, J., Harris, C., et al., 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgolnder Meeresuntersuchungen. 33, 566-575.

[35] Wang, Z., Wang, Y., Chen, L., et al., 2015. Assessment of metal contamination in coastal sediments of the Maluan Bay (China) using geochemical indices and multivariate statistical approaches. Marine Pollution Bulletin. 99(1-2), 43-53. DOI: https://doi.org/10.1016/j.marpolbul.2015.07.064

[36] Li, C., Lu, F.Y., Zhang, Y., et al., 2008. Spatial distribution characteristics of heavy metals in street dust in Shenyang city. Ecology Environment. 17(2), 560-564.

[37] Buchauer, M.J., 1973. Contamination of soil and vegetation near a Zinc smelter by Zn, Cd, Cu and Pb. Environmental Science and Technology. 7, 131-135.

[38] Ward, N.E., Brooks, R.R., Reeves, R.D., 1976. Cd, Cu, Pb and Zn in soils, stream sediments, waters around tin mine. New Zealand Journal of Science. 19, 81-99.

[39] Sinex, S., Helz, G., 1981. Regional geochemistry of trace elements in Chesapeak Bay sediments. Environmental Geology. 3, 315-323. DOI: https://doi.org/10.1007/BF02473521

[40] Chakravarty, M., Patgiri, A., 2009. Metal pollution assessment in sediments of the Dikrong River, N. E. India. Journal of Human Ecology. 27(1), 63-67.