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Evaluation of stream sediment contamination by potentially toxic elements around mining and farming areas (SE Nigeria)

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Enrichment Factor

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Abstract

In this work, the concentrations of the potentially toxic elements in stream sediments in SE Nigeria were assessed for pollution monitoring in mining, quarrying, and farming areas. The levels of iron, molybdenum, vanadium, copper, lead, zinc, nickel, cobalt, manganese, chromium, barium, and beryllium were determined. The concentrations of the elements were in the order of Fe > Ba > Mn > Cr > Zn > Pb > Cu > Co > Ni > As > Mo. There were significant positive correlations at $P < 0.01$ between Mo and Cu ($r = 0.734$), Mo and Pb ($r = 0.811$), and Cu and Pb ($r = 0.836$). The others were between Cu and V ($r = 0.748$), Pb and V ($r = 0.793$), Fe and V ($r = 0.905$), Fe and Be ($r = 0.703$), V and Be ($r = 0.830$), Cu and Pb ($r = 0.778$), and Fe and V ($r = 0.905$). The geoaccumulation index values were classified as polluted (0-1) to moderately polluted (1-2). The enrichment factors fell into moderate, significant, and very high enrichment. Pb, Co, and Ba attained significant enrichment factors. The potential ecological risk showed a strong risk level "C" in only three locations. Arsenic was a strong factor carrying risk. The potential ecological risk (E^iR) trend was E^iR (AS) > E^iR (Pb)> E^iR (Cu) > E^iR (Co) > E^iR (Cr) > E^iR (V) > E^iR (Ni) > E^iR (Zn). Ba, Pb, and As should be monitored further to determine their source and recommend possible remedial measures. The result of this work could be used to improve water management efficiency and serve as a benchmark of vulnerability assessment of the studied area. This could also be useful for future impact assessment and adequate planning of mining and farming areas. In addition, the result obtained could assist the scientists to make appropriate environmental management strategies to reduce the influence of metal contamination triggered from the mining sites and farming areas both in Nigeria and globally.

1. Introduction

Sediments serve as habitats for aquatic organisms and as their source of nutrients. The erosion of bedrocks and soil results in the settlement of sediments of previous or current natural or anthropogenic processes and components [1, 2]. The data obtained from sediments can provide information on the impact of distinct human activities on a wider ecosystem [2].

Stream sediment analysis is relevant to the assessment of qualities of the total ecosystem of a body of water, coupled with water sample analysis. This has been in practice for many years because it is a reflection of the long-term quality scenario exclusive of the current inputs. In addition, sediments are the ultimate sink of contaminants in an aquatic ecosystem [2]. Monitoring of soil and sediment contamination with trace elements is of interest due to their influence on the ground and surface water, plants, animals, and humans [3]. Trace elements occur naturally in rock-forming minerals and ore minerals; therefore, they can reach the environment from natural processes. Accumulation of trace metals in the upper

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sediments in an aquatic environment can become toxic to sediment dwelling organisms and fish. This can result in death, reduced growth or impaired reproduction, and density of lower species [4, 5]. The accumulation of heavy metals to toxic levels in the environment may stem naturally from geological phenomena such as ore formation, weathering of rocks, and leaching. In addition, increased population, urbanization, industrial activities, agricultural practices, exploration, and exploitation of natural resources are possible sources of trace elements [6].

Sources of heavy metals also include industrial processing of ore metals, disposal of metals, and leaching of metals from garbage and solid waste heaps. Other sources are animal and human excretions, harbor activities such as docking, vessel repair facilities, anti-fouling, vessel paints, anti-corrosion materials, and petroleum exploration. These operations introduce lead, copper, zinc, cadmium, chromium, and other metals into coastal waters [7, 8]. Heavy metal pollution of the aquatic environments is one of the critical issues due to their toxic and persistent characters [9]. Natural processes of heavy metal input and geological weathering of rocks and soil directly to surface waters is usually the largest natural source. In comparison, anthropogenic sources are mainly from industrial processing, urban sewage, mining activities, and agricultural runoffs [10, 11]. Trace metal geochemistry in sediments is important because they constitute the host of contaminants and have a long residence time compared with water. Analysis of trace elements in sediments determines the extent, distribution, origin, and possible risks due to the presence of these metals [12, 13]. Different authors elsewhere utilized stream sediment geochemistry for assessing heavy metal contamination. Tijani and Onodera [14] investigated groundwater quality in the Osogbo Township in Nigeria. Rodrigues and Formoso [15] used geoaccumulation index to assess heavy metals in stream sediments affected by tannery activities. Shruti *et al*. [16] assessed heavy metals in stream sediments in the Atoya river basin using the contamination factor, enrichment factor (EF), potential ecological index (E^iR), and geoaccumulation index. In addition, Ayari, *et al*. [17] and Nnabo [18] used the metal enrichment factor and pollution indices to assess heavy metal contamination in surface water and stream sediments. Singovszka and Balintova [11] assessed the ecological risk of stream sediments in the rivers of eastern Slovakia using the potential ecological index (PERI). This consisted of degree of contamination (C_D), toxic response factor (T_R), and potential ecological risk factor (E^iR). Heavy metal contamination in stream sediments using the geoaccumulation factor, enrichment factor, and ecological potential index in Niger Delta in Nigeria is in Onunugbo and Avwiri [19]. Similar research works were carried out by Cocker [20] and Atunes *et al*. [21].

Oban Massif and parts of the Mamfe Mbayment were characterized by a network of streams and river channels such as Ayuk, Aroi, Essai, Aboyeri, and Calabar River. The geochemistry of stream sediments both for the environmental and the mineral exploration studies in the area has not been properly investigated. Hence, this work was carried out to address the need for environmental consideration of stream sediments in the studied area. Heavy metal accumulation in stream sediments has a longer residence time than in water. Heavy metal detection in stream sediment is mostly above the limit compared with water. Stream sediment contamination with heavy metals in this work would be a better guide for groundwater management. The outcome of this work would be helpful for water management studies by the scientists in other parts of the world. Agricultural activities such as cultivation of farmlands and application of fertilizers are common in the study. In addition, quarrying and mining of solid minerals such as barite are common industrial activities in the area. The trace element content exerts an overwhelming influence on sediment and soil quality and its use in cultivation for food production [22]. Hence, the assessment of metal contamination is of vital importance in farming areas. Pockets of mining, quarrying, and agricultural activities going on the Oban Massif and Mamfe Mbayment underscore the need to evaluate stream sediment contamination in the area.

The main goal of this work was to investigate the distribution of heavy metal contents in stream sediments of the studied area. The specific objectives of this research work include (1) evaluation of the heavy metal concentrations in stream sediments, (2) assessment of contamination using indices such as the geoaccumulation factor and enrichment factor, (3) determination of the ecological risk in sediments (RI), and (4) identification of natural and anthropogenic sources of metals. This work will serve as a standard for sediment and water quality monitoring around the mining and farming areas on a global scale. It is also useful for evaluating

stream sediment contamination using multiple criteria such as Sediment Quality Guideline (SQG), pollution indices, and bivariate statistics. The integrated approach adopted in this work would produce the results that are more credible. The results of this work will improve the water management efficiency and provide a benchmark of vulnerability assessment of the studied area and for the future impact assessment and adequate planning of mining and farming areas.

1.2. Description of studied area

The studied area covers Oban Massif and Mamfe Mbayment (Figure 1). This area is located between the latitudes N05^0 18' 57.7'' and N05^0 45' 26.8'' and the longitudes E08^0 34' 39.39'' and E08^0 05' 20.5'' (Figure 1). The area covers the Oban hills and forest, which have a common boundary with Cameroon in the east. The western part of this area has a common boundary with the Ebonyi state along the Cross River channel. Calabar Flank bounds the area in the south and Mamfe Mbayment in the north (Figure 1).

This study possesses the features such as highlands and their flanking lowlands with areal extent in the ratio 1 to 5 of low lands to highlands. The highlands have elevations in excess of 400 m above sea level, by contrast; the lowlands have elevations with an average of 30 m. The crystalline basement complex has an average height of 150 m rising gradually from south northwards, and falls away towards the north. The eastern part has prominent isolated hills with an estimated height of 200 m above the sea level. The hills rise steeply and abruptly, frequently traversed by V-shaped valleys and densely forested even at the highest peaks. In the western Flank of Oban Massif and Mamfe Mbayment, there is a subdued topography characterized by the proliferation of human settlements, while in the western Flank of the Oban Massif, there are swamps along the banks of the extensive rivers crisscrossing the area (Figure 2). Depressions and gullies due to erosion and weathering are ubiquitous in the Oban Massif area. Farming and mining activities are common in the area. Barite open-mine site is situated at Ibogo in Oban Massif at an elevation of 131 m (Figure 2).

The drainage of the study comprises the main Cross River, Calabar River, and Great Kwa River. The Calabar River takes its source from the Oban hills and empties into the Cross River Estuary. Generally, weathering of fractures and joint trends controls the drainage around the area. Drainage in the Oban Massif is mainly southwards, seawards, and northwards to join the upper course of the Cross River in the Ikom depression. Notable rivers that drain the area include Inyang Ita, Udem, Ebe, Kwa, River Akparam, Ifunkpa Effurat, and Ekenge Oyenre.

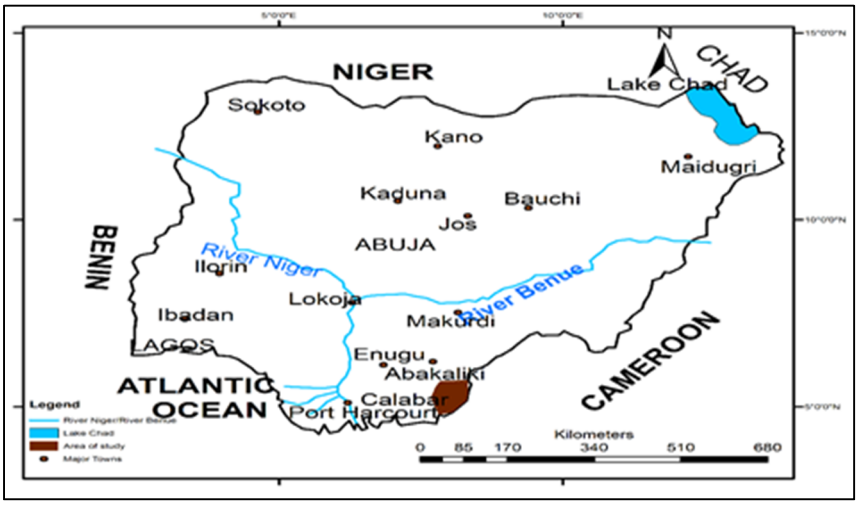

Figure 1. The studied location in the map of Nigeria.

1.3. Geology

From the geochronological data based on lithological units, the Oban Massif is Pre Pan African [23]. Rocks such as garnet, hornblende, gneiss, kyanite gneiss, and biotite gneiss are restricted to the eastern part of the Oban Massif [23]. Amphibolite, schist, phyllites, and granodiorite are dominant in the western Oban Massif. Charnokites with granulite facies metamorphism, metamorphic Isograd, and zones in pelitic schist and gneisses are common in the Uwet area in Oban Massif [24]. The Oban Massif

has a dominance of syntectonic granitoids known as Uwet granodiorite [25]. North of Kwa falls is the Oban Town composed of banded gneisses of Proterozoic age [26]. The sediment/basement contact as exposed at Awi formation lies unconformably on the migmatiite gneiss-quartz complex. Places such as Awi, Ayiebam, Akamkpa, Mbarakom, Calaro estate, Old Netim, Okom Ita, Nsan, and Obung are composed of gneisses associated with quartzite cut by pegmatite (Figure 2). The gneisses are, in part, magmatic, particularly around Ayiebam, Mbarakpa, and Oban Okoroba. The gneisses grade into schist after Okom Ita and Mbarakom. The schist extend westward to the channels of Cross River at Ikot Ana and Ikot Okpora (Figure 2).

Granodiorites are common in the western flank of the Oban Massif and Uwet Area, hence, the name Uwet Granodiorite. Schist in the greenschist facies dominates the lithology of the western part of Uwet, which forms part of the Oban Massif. The schist is green schist facies and most are biotite garnet-bearing phyllites. The granodiorite contains xenoliths and enclaves of other rocks [26]. Eze Aku Group in Mamfe area near Cameroon shows sandstone ridges at Abini and Adim. Basal and more marine part of the ridges are in Idomi and Agwagwune (Figure 2).

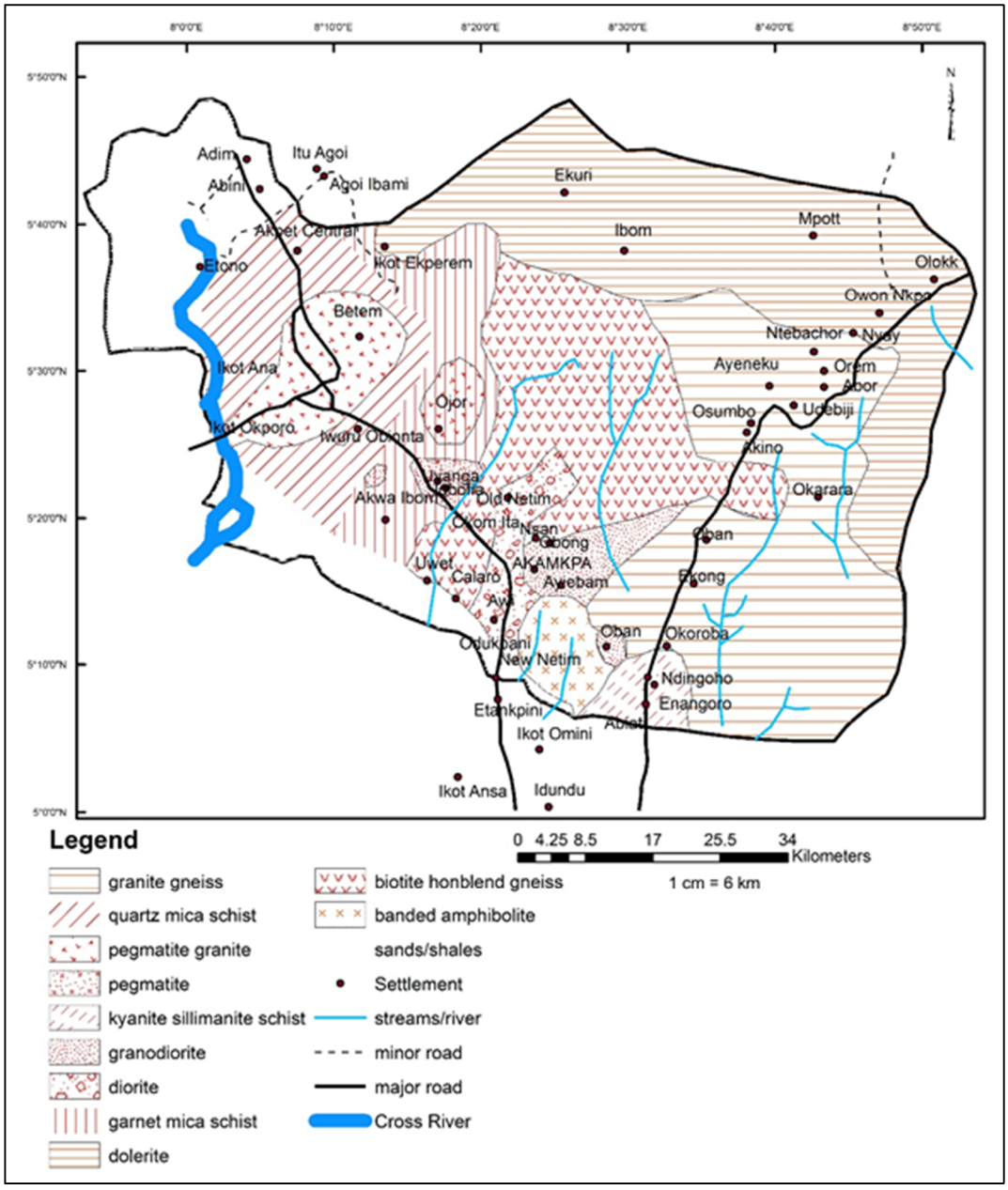

Figure 2. Geological map of the studied area.

2. Materials and method

2.1. Sample collection

The equipment used included the global positioning system Garmin GPS for recording the coordinates of sample points, stainless steel hand trowel for stream sediment sampling, and polyethylene bags. A total of 21 stream sediment samples were collected for analysis (Figure 3). Collection of the sediment samples was along the stream and river channels along Cross River and Calabar River and their tributaries. Sampling point selection was by sampling the bottom stream sediments concentrated around quarries, mines, and farming areas (Figure 3). Collection of the stream sediment samples was by putting them into polyethylene bags using a hand trowel washed with detergent, rinsed and dried before use to minimize contamination. Figure 4 shows an example of the sampling site.

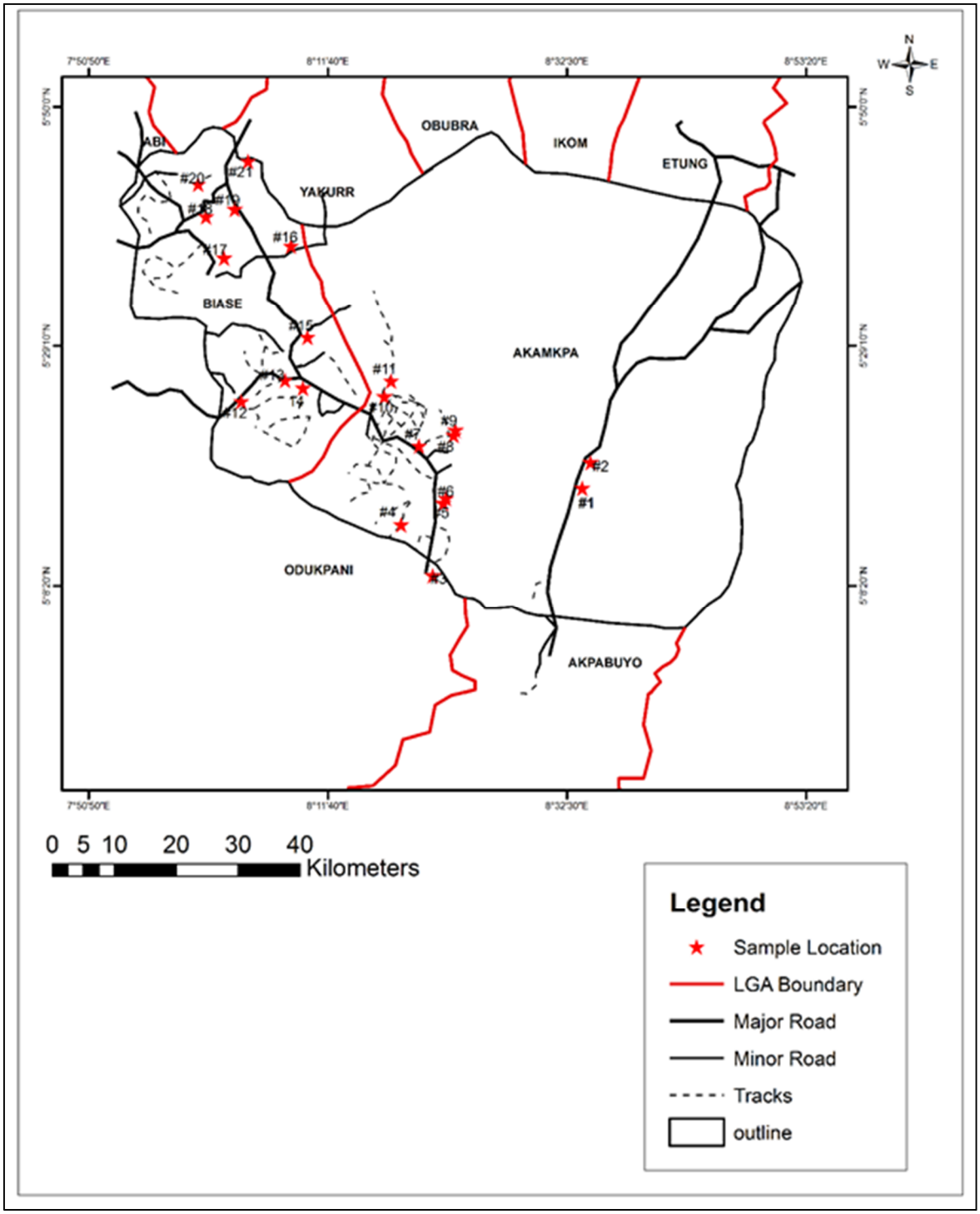

Figure 3. Sample location map of the studied area.

2.2. Sample preparation and chemical analysis

The procedure for sample preparation is as what follows. Dry the sediment samples in the sun for 2 to 3 days, then disaggregate the samples and sieve using an 80 mesh nylon sieve to remove large grains. Grind the sediments properly using an agate mortar and a pestle, and keep the sieved samples in sealed properly labelled envelopes for analysis. In order to have homogenous representative samples of the sediments, homogenize about three sub-samples. From this, finally take the representative samples and keep in a sample cloth specifically for this purpose.

Weigh 10 g of the ground and sieved sediment sample into a porcelain crucible. Add 25 mL of distilled water followed by 1 mL of concentrated nitric acid (4 M) and 3 mL of concentrated hydrochloric acid. Then cover the beakers with glass discs and transfer to a steam bath over a hot plate in a fumed cupboard heated for about 1 h and cool. Filter the digested sample and make up to 50 mL with distilled water. Store the filtrate in plastic bottles for heavy metal analysis. All materials used for sample collection must be non-metallic to avoid sample contamination by metals. Refluxed the mixture at moderate temperatures (< 100 ^{0}C) for 1 h and then evaporate at temperatures ranging between 180 ^{0}C and 190 ^{0}C to dryness, forming a white cake. Leach the white cake residue with 5 M HCl into already calibrated labelled test tubes and make up to 10 mL with deionized water. Then allow the test tubes to stand for a clear aliquot to separate. Cork the test tubes with plastic stoppers. Carry out multi-elemental analysis of the digested samples for trace elements (Mo, Cu, Zn, Ni, Pb, Ba, As, Cr, Co, Mn, V, and Fe) using ICP-Ms. The analysis was done at the ACME Analytical Laboratories at Vancouver in Canada. Assessment of quality assurance and quality control of the analyses was by standard reference material. Table 1 shows the instrumental detection limits reported by the analytical laboratory, and the reference values and percentage recoveries are contained in this table.

Table 1. Reference material and recovery.

Chemical element	Detection limit (mg/kg)	Certified value STSD-1 (µg/g)	Measured value (µg/g)	Recovery (%)
Mo	1	2	1.19	59.5
Cu	1	36	14.07	39.1
Pb	3	165	35.64	21.6
Zn	1	18	47.952	266.4
Ni	1	18	12.58	70
Co	1	14	12.66	70.3
Mn	2	3740	172.14	4.6
V	1	47	75	159.6
Cr	1	28	76.09	271.7
Ba	2	630	1104.95	175.4
As	2	17	5	29.4
Fe	0.01%	3.5	2.99	85.4

2.3. Heavy metal risk determination

Geoaccumulation index assesses the concentration of trace metal contamination in a geological material sample by comparing the current and pre-industrial levels [27].

The heavy metal contamination indices such as geoaccumulation proposed by Muller [28] are given as:

$$\text{I-geo}=\log_2 Cn/1.5B_n \quad (1)$$

where I-geo represents the geoaccumulation index, C_n represents the concentration of the element of interest, and B_n represents the background value of the element. The constant value 1.5 applies due to possible variation in the background data caused by lithological variation.

The enrichment factor of trace metals determines both the natural and the anthropogenic trace metal sources. This helps to evaluate the degree of contamination of stream sediments [29, 30]. The potential ecological risk index (PERI) considers the synergy, toxic level, and concentration of the heavy metals. This further considers the ecological sensitivity of heavy metals and the potential ecological risk of heavy metals [31, 11]. The enrichment factor is given by:

$$EF = \frac{C_y / C_r}{B_y / B_y} \quad (2)$$

where Cx and C_r are the concentrations of the trace metal of concern and the reference element in sediment samples, respectively, and B_x and B_r

are the geochemical background values of the trace metal of concern and the reference element, respectively. In this work, the values of the upper continental crust (UCC) in Taylor and McLennan [32] were the background values used for calculating the enrichment factor.

The ecological Index assess the degree of trace element pollution in sediments according to their toxicity and response to the environment [33]. Calculation of this index is the sum of risk factors of individual trace metals Ei, calculated by:

$$RI = \sum_{i=1}^{n} E_i \quad (3)$$

where Ei is the single risk factor for each trace metal I defined as $E_i = T_i C_i / B_i$, where Ti is the toxic response factor for each trace metal I, as calculated by Hakanson [33], i.e. Cd = 30, As = 10, Pb = Cu = Ni = Co = 5, Cr = V = 2, and Zn =1. C_i is the measured concentration of the trace metal, and Bi is the background value of the trace metal i. Hakanson [33] defined four levels of RI.

In this work, more heavy metals were considered for risk assessment, and world standard guidelines were utilized for sediment pollution studies compared to the previous works cited in the literature. In addition, the Pearson correlation statistics was used for enhanced sediment pollution interpretation. The previous studies on sediment contamination were limited to pollution indices such as the geoaccumulation index, enrichment factor, and ecological indices.

Table 2 summarizes the ecological impact of the indices of individual metals in sediments, contained in Shruti *et al*. [16].

Table 2. Classification of stream sediment pollution.

Geoaccumulation index (after, Muller [27])		
I geo	**Class**	**Pollution intensity**
> 5	6	Very strongly polluted
4-5	5	Strongly to very strongly polluted
3-4	4	Strongly polluted
2-3	3	Moderately to strongly polluted
1-2	2	Moderately polluted
0-1	1	Unpolluted to moderately polluted
0	0	unpolluted

Enrichment factor Sutherland [34]	
Value	**Degree of contamination**
< 2	Depleted to minimal enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
> 40	Extremely high enrichment

Risk grades indexes and grades of potential ecological risk of heavy metal pollution				
E_r^1	Risk grade	RI value	Risk level	Risk degree
$E_r^i < 30$	Slight	$R^i < 40$	A	Slight
$30 \leq E_r^i < 60$	Medium	$40 \leq R^i < 80$	B	Medium
$60 \leq E_r^i < 240$	Strong	$80 \leq R^i < 160$	C	Strong
$120 < E_r^i < 240$	Very strong	$160 \leq R^i < 320$	E	Very strong
$E_r^i \geq 240$	Extremely strong	$R^i \geq 320$	D	Extremely strong

2.4. Data handling

Computation of descriptive statistical parameters such as minimum, maximum, mean, standard deviation, and median from the geochemical data was from SPSS to characterize the distribution of trace metals in the sediments.

The Pearson correlation analysis evaluated trace metal concentration relationships and identified potential natural and anthropogenic sources of trace metals in the sediments.

3. Results and discussion

Table 3 presents a statistical summary of heavy metals in stream sediments. Table 4 presents the principal component analysis. Table 5 shows the corresponding analysis. Table 6 shows the statistical analysis. Correlation statistics is in Table 7. Table 8 shows the sediment Quality Guidelines (SQGs).

Table 3. Detail and statistical summary of heavy metals.

	Mo	Cu	Pb	Zn	Ni	Co	Mn	V	Cr	Ba	As	Fe%
1	1.6	11.8	30.1	39	11.7	7.6	88	62	53	215	4	2.46
2	1.6	11.8	45.6	52	13.8	4.4	130	63	35	466	1	2.74
3	0.5	16	39.2	89	12.6	9.7	419	84	40	817	1	3.18
4	1.4	14.4	41.2	96	17.5	9.1	150	135	61	862	2	4.89
5	1	14.9	36.4	80	43.2	13.3	203	155	96	556	6	5.46
6	3.1	44.1	116.9	56	11.9	2.2	52	228	227	7500	8	5.48
7	0.4	3.9	31.5	12	4.1	9	48	20	17	882	1	1.24
8	0.7	12.9	26.3	73	15.9	9.5	286	61	47	595	3	2.49
9	0.2	5.9	19.2	30	5.5	42.9	140	23	18	536	<1	0.82
10	0.5	12.6	26.4	126	13.8	7.3	252	52	46	598	2	1.98
11	0.5	2.5	4.1	9	1.4	19.5	20	9	8	21	<1	0.68
12	0.6	18.1	29.1	80	15	14.5	470	99	236	577	<1	4.07
13	0.5	9.7	10.1	24	8.7	15.59	102	66	227	337	4	2.53
14	0.6	9.6	7.5	19	8.3	23.5	251	61	94	174	<1	1.56
15	0.7	10.7	24.7	69	17.2	10.9	390	46	39	788	<1	2.26
16	3.1	30.7	53.5	40	7.4	2.2	61	160	106	3770	15	4.99
17	0.7	9.3	9.8	39	8.8	16.8	241	35	63	175	2	2.04
18	0.1	12.2	19.8	12	2.5	7.6	13	8	6	646	<1	0.39
19	3.2	12.2	35.3	37	18.7	8.9	224	148	117	3003	14	11.13
20	0.2	4.9	11.9	12	4	27	66	21	36	627	<1	0.62
21	3.9	27.2	129.9	13	22.1	4.3	9	39	26	59	7	1.68
Mean	1.19	14.07	35.64	47.952	12.58	12.66	172.14	75	76.09	1104.95	5	2.99
STDEV	1.14	9.627	32.04	33.15	9.025	9.52	136.92	58.81	71.41	1725.46	4.61	2.44
Median	0.7	12.2	29.1	39	11.9	9.5	140	61	47	595	3.5	2.46
Min	0.1	2.5	4.1	9	1.4	2.2	9	8	6	21	1	0.39
Max	3.9	44.1	129.9	126	43.2	42.9	470	228	236	7500	15	11.13

Table 4. Principal component analysis.

	Mo	Cu	Pb	Zn	Ni	Co	Mn	V	Cr	Ba	As	Fe
1	-0.1827	-0.5045	-0.7313	0.0392	0.2174	-0.1272	-0.6243	0.0714	-0.1542	-0.4301	0.0131	-0.1126
2	0.2131	-0.1477	-1.2593	-0.0107	0.0112	-0.3437	-0.3892	0.1230	-0.1422	-0.2163	-0.2385	-0.0855
3	0.2281	1.9770	-0.4748	-0.2525	-0.0987	-0.9449	0.8173	0.1540	-0.5986	0.0204	-0.0993	0.2334
4	1.3418	1.2281	-0.9533	-0.4917	0.9719	-0.1732	-0.1791	-0.1742	0.3812	-0.6907	-0.2575	0.1870
5	1.8697	2.4926	-1.1540	0.2394	1.3334	1.9878	-0.7908	-0.3748	0.0698	0.5147	0.1706	0.0350
6	6.5208	-1.4604	1.4345	-1.2891	0.1625	-0.3430	0.5640	-0.4394	0.1502	0.4792	-0.1536	-0.0324
7	-1.6742	-1.3728	-0.6051	-0.4804	0.1713	-0.6028	-0.5260	0.0639	-0.1847	0.4625	-0.5182	0.0346
8	-0.2326	1.2623	-0.5805	0.0212	0.0296	-0.4578	0.0866	0.0473	-0.2090	0.1204	0.0814	-0.1296
9	-2.8241	-0.4126	0.5973	-1.0422	0.7273	1.2570	1.7116	-0.0985	0.3479	-0.1809	-0.0272	-0.0791
10	-0.4894	1.7520	-0.6495	0.2344	-0.8226	-1.2298	0.2787	-0.3722	1.3360	-0.0489	0.1655	-0.0785
11	-2.8642	-1.4967	-0.1531	-0.5375	0.2489	-0.0983	-0.2793	0.2188	0.2241	-0.0994	0.0549	0.0195
12	0.3165	2.3075	1.7324	-0.1896	-1.9644	0.2218	-0.0162	-0.2053	-0.3161	-0.1520	0.0317	0.0995
13	-0.9553	-0.2879	1.7186	-0.4741	-0.8631	0.6256	-1.4119	-0.6141	0.0499	-0.2431	-0.1252	-0.1231
14	-1.5326	0.1892	0.7876	-0.6589	0.0352	0.6101	0.0777	0.3359	-0.7079	-0.2163	0.1666	0.0806
15	-0.5227	1.6576	-0.5695	0.0138	-0.2453	-0.3773	0.3870	0.5109	-0.5187	0.3943	-0.0095	-0.3106
16	3.4137	-1.3905	0.4827	-0.0515	1.0301	-0.7600	-0.1227	0.2992	-0.3107	-0.5567	0.3982	-0.0800
17	-1.4937	-0.1420	1.8225	3.4847	1.1917	-0.5255	0.2852	-0.5246	-0.1270	0.0781	-0.1019	0.0139
18	-1.8857	-1.6485	-0.5361	-0.4381	-0.1936	-0.9456	-0.5030	-0.3401	-0.0496	0.5534	0.4515	0.1785
19	1.5200	-0.3177	0.8908	1.0600	-0.4530	0.5853	-0.3463	1.6746	0.7073	0.1893	-0.0397	0.0920
20	-2.6303	-1.1197	0.4062	-0.7856	0.2343	0.4647	0.2879	0.0073	0.2593	0.1763	0.0291	0.0318
21	1.8637	-2.5654	-2.2060	1.6092	-1.7241	1.1767	0.6928	-0.3629	-0.2071	-0.1544	0.0079	0.0255

Table 5. Corresponding analysis.

	Mo	Cu	Pb	Zn	Ni	Co	Mn	V	Cr	Ba	As	Fe
1	0.0016	0.0118	0.0301	0.0390	0.0117	0.0076	0.0880	0.0620	0.0530	0.2150	0.0040	2.4600
2	0.0016	0.0118	0.0456	0.0520	0.0138	0.0044	0.1300	0.0630	0.0350	0.4660	0.0010	2.7400
3	0.0005	0.0160	0.0392	0.0890	0.0126	0.0097	0.4190	0.0840	0.0400	0.8170	0.0010	3.1800
4	0.0014	0.0144	0.0412	0.0960	0.0175	0.0091	0.1500	0.1350	0.0610	0.8620	0.0020	4.8900
5	0.0010	0.0149	0.0364	0.0800	0.0432	0.0133	0.2030	0.1550	0.0960	0.5560	0.0060	5.4600
6	0.0031	0.0441	0.1169	0.0560	0.0119	0.0022	0.0520	0.2280	0.2270	7.5000	0.0080	5.4800
7	0.0004	0.0039	0.0315	0.0120	0.0041	0.0090	0.0480	0.0200	0.0170	0.8820	0.0010	1.2400
8	0.0007	0.0129	0.0263	0.0730	0.0159	0.0095	0.2860	0.0610	0.0470	0.5950	0.0030	2.4900
9	0.0002	0.0059	0.0192	0.0300	0.0055	0.0429	0.1400	0.0230	0.0180	0.5360	0.0005	0.8200
10	0.0005	0.0126	0.0264	0.1260	0.0138	0.0073	0.2520	0.0520	0.0460	0.5980	0.0020	0.0020
11	0.0005	0.0025	0.0041	0.0090	0.0014	0.0195	0.0200	0.0090	0.0080	0.0210	0.0005	0.0007
12	0.0006	0.0181	0.0291	0.0800	0.0150	0.0145	0.4700	0.0990	0.2360	0.5770	0.0005	0.0041
13	0.0005	0.0097	0.0101	0.0240	0.0087	0.0156	0.1020	0.0660	0.2270	0.3370	0.0040	0.0025
14	0.0006	0.0096	0.0075	0.0190	0.0083	0.0235	0.2510	0.0610	0.0940	0.1740	0.0005	1.5600
15	0.0007	0.0107	0.0247	0.0690	0.0172	0.0109	0.3900	0.0460	0.0390	0.7880	0.0005	2.2600
16	0.0031	0.0307	0.0535	0.0400	0.0074	0.0022	0.0610	0.1600	0.1060	3.7700	0.0150	4.9900
17	0.0007	0.0093	0.0098	0.0390	0.0088	0.0168	0.2410	0.0350	0.0630	0.0170	0.0520	0.0020
18	0.0001	0.0122	0.0198	0.0120	0.0025	0.0076	0.0130	0.0080	0.0060	0.6460	0.0005	0.0004
19	0.0032	0.0122	0.0353	0.0370	0.0187	0.0089	0.2240	0.1480	0.1170	3.0030	0.0140	0.0111
20	0.0002	0.0049	0.0119	0.0120	0.0040	0.0270	0.0660	0.0210	0.0360	0.6270	0.0005	0.0006
21	0.0039	0.0272	0.1299	0.0130	0.0221	0.0043	0.0090	0.0390	0.0260	0.0590	0.0070	0.0017

Table 6. Statistical analysis.

	Mo	Cu	Pb	Zn	Ni	Co	Mn	V	Cr	Ba	As	Fe
Mean	0.0012	0.0141	0.0356	0.0480	0.0126	0.0129	0.1721	0.0150	0.0750	1.0974	0.015	1.7902
STD	0.0011	0.0096	0.0320	0.0332	0.0090	0.0095	0.1369	0.0588	0.0714	1.7301	0.0114	0.2001

3.1. Concentration of heavy metals in stream sediments

The statistical analysis (Table 3) shows that barium recorded the highest mean value of 1104.95 $\pm$ 1729.46 mg/kg. Barium has maximum and minimum values of 3770 mg/kg and 21 mg/kg, respectively. Manganese possesses a mean of 172.14 $\pm$ 133.61 mg/kg, a median value of 140 mg/kg, and maximum and minimum values of 419 mg/kg and 9 mg/kg, respectively (Table 3). A study by Wei *et al*. [35] in Quanghai Tibet Plateau in China showed Mn in stream sediments to be from the inflow by artificial activities such as agriculture and grazing. The concentration of vanadium ranged from 8 mg/kg to 228 mg/kg with the median and mean values of 61 mg/kg and 75 $\pm$ 57.39 mg/kg, respectively. Zinc possessed a mean of 47.95 $\pm$ 32.36 mg/kg with a median of 39 mg/kg, and ranged from 9 mg/kg to 126 mg/kg. The cobalt concentration ranged from 2.2 mg/kg to 23.9 mg/kg with a median of 9.5 mg/kg. The mean level of iron was 2.99 $\pm$ 2.44% and a median of 2.46% with the minimum and maximum values of 0.39% and 1.13%, respectively.

Barium has been found to be associated with rare earth elements bearing minerals because of its trivalent charge. Barium is typically not present in the minerals such as muscovite, $KAl_2(Si.Al)_4O_{10}(OH)_2$, which is representative of the mica group of minerals. The chromium level ranged from 6 mg/kg to 227 mg/kg with a mean of 76.09 $\pm$ 69.69 mg/kg and a median of 47 mg/kg. Nickel recorded a mean of 12.58 $\pm$ 8.81 mg/kg and ranged from 1.4 mg/kg to 18.7 mg/kg with a median of 11.9 mg/kg. The mean concentrations of Cu and Pb ranged from 2.5 mg/kg to 44.1 mg/kg and 4.1 mg/kg to 129.9 mg/kg, respectively. Molybdenum attained a mean of 1.19 $\pm$ 1.12 and ranged from 0.1 mg/kg to 3.9 mg/kg. The arsenic content ranged from < 1 to 15 mg/kg with a mean of 3.67 $\pm$ 4.08 mg/kg and a median value of 2 mg/kg. The mean concentration of heavy metals in stream sediments is in the order Fe > Ba > Mn > Cr > Zn > Pb > Cu > Co > Ni > As > Mo. A sympathetic association may be responsible for the occurrence of these elements in stream sediments in the studied area. The sympathetic association occurs between Cr, Co, and Cu, U, V, and Mo, Ni, Cu, and Cr in ultramafic. We also have V, Cu, Pb, and Zn association in blackshales and phosphorites [36]. Since these rocks are common in the studied area, the concentrations of these elements are elevated in the stream sediments. High concentrations of these elements may also suggest the regional

tectonic features and metallogenic provinces in the studied area [36]. The stream sediment elemental concentration is due to adsorption of trace elements on the sediments particles, which lead to their high concentration. Surface adsorption and ionic attraction may be responsible for trace element enrichment in the sediments [37]. The high concentrations of Ba, Mn, Cr, and V may be traceable to mineralization and anthropogenic input within the studied area. Their sources may be mostly from pockets of mining operations such as the barite mines and quarry sites within the study.

The elements Pb, Zn, Mn, Ba, Cr, V, and Zn showed high mean values and high standard deviations, which is indicative of a heterogeneous spatial distribution. This is evidenced by the lower median values than the mean of these metals. On the other hand, trace element concentrations of Mo, Fe, As, Co, Ni, and Cu concentration generally exhibited low standard deviations, suggesting their homogenous spatial distribution. The mean values of barium and lead were twice the order of magnitude higher than the values of Average Shale Concentration (ASC). The mean values of Mo, Cu, Zn, Ni, Co, Mn, As, V, and Cr were 1, 4, 2, 6, 2, 5, 3, 2, and 1, respectively, order of magnitude lower than the ASC values, while Pb and Ba were twice each order of magnitude higher than their corresponding ASC. The background reference values give an idea of the concentrations expected in surface sediments in the absence of any human activity [38]. The source of Ba is from barium sulfate, and the Pb source is possibly galena (PbS) or fumes from automobile exhaust. Evaluation of environmental degradation around an active mine for tantalum, niobium in Iludun-Oro SW Nigeria by Oyebamiji *et al*. [39] showed that the levels of Pb, Fe, Cu, Ba, and Sr were higher than the background values, indicating that mining activities had an adverse effect on the studied area. In this work, the Pb and Ba mean values exceeded their ASC values, implying anthropogenic input.

3.2. Correlation

For a proper assessment of the provenance of trace metals in the studied area, there is a Pearson correlation matrix between the twelve investigated elements (Table 7). The coefficients show a strong positive correlation at $P < 0.01$. The elements with a strong correlation show common sources, probably bedrock and soil weathering [17]. A strong positive correlation exist between metals, indicating some common geochemical processes such as co-precipitation and adsorption, controlling their spatial variability and bonding to Fe-oxides. A negative correlation suggests that they are associated with volcanic lithic fragments (carbonates and sulfates) and anthropogenic inputs [32].

Table 7. Correlation matrix of heavy metals in stream sediments from the studied area.

	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	V	Cr	Ba	Be
Mo	1											
Cu	**0.734**	1										
Pb	**0.811**	**0.836**	1									
Zn	-0.065	0.212	0.052	1								
Ni	0.311	0.257	0.327	0.503	1							
Co	-0.556	-0.564	-0.536	-0.292	0.441	1						
Mn	-0.297	-0.095	-0.271	0.641	0.310	0.069	1					
Fe	0.598	0.405	0.274	0.309	0.450	-.373	0.214	1				
V	0.600	**0.748**	**0.793**	0.403	0.481	-0.430	0.099	**0.905**	1			
Cr	0.244	0.503	0.194	0.164	0.172	-0.149	0.221	0.485	0.645	1		
Ba	0.583	**0.778**	0.555	0.072	-.007	-0.373	-0.180	0.548	**0.779**	0.500	1	
Be	0.499	0.642	0.413	0.481	0.289	-0.428	0.458	**0.703**	**0.830**	0.610	0.648	1

The highly significant correlation at $p < 0.01$ in this work is between the elements Mo and Cu (0.734), Mo and Pb (0.811), and Cu and Pb (0.836). The others are Cu and V (0.748), Pb and V (0.793), Fe and V (0.905), Fe and Be (0.703), V and Ba (0.779), V and Be (0.830), Cu and Ba (0.778), and Fe and V (0.905). This kind of highly significant correlation at $P < 0.01$ indicates the same or similar source input. It also implies a similar enrichment mechanism, suggesting that the anthropogenic sources of these elements have a close relationship in sediments of Oban Massif. These significant correlations of heavy metals are indicative of a common source of pollution in the streams and rivers. The second group of correlated elements in this analysis at $P < 0.05$ includes Co and Mo (-0.556), Cu and Co (-0.564), Mo and V (0.600), Cu and Cr (0.503), and Cu and

Be (0.642). The others are Pb and Co (-0.536), Zn and Mn (0.641), Fe and Be (0.548), Fe and Cr (0.485), Cr and Be (0.611), Cr and Ba (0.500), and Ba and Be (0.648). This suggests that they have different origins than the first group due to their concentrations and enrichment factors. Positively correlated heavy metals statistically significant ($P < 0.01$) show similar geochemical features [40].

Copper, lead, vanadium, iron, beryllium, and barium positively correlated strongly with other metals, showing the same source of input. Copper is very mobile in the environment, and is found in all forms of plant and animal life in every part of the human body. The mineral sphalerite is the principal source of zinc. The transport and distribution of zinc in the sediment and soil is dependent on the species present and characteristics of the natural background. The increased level of zinc can be traceable to natural occurrence of zin-enriched ores to anthropogenic sources or even through abiotic and biotic processes. Zinc deficiency is marked by retarded growth, loss of taste, and cause of pre-puberty males' hypo-gonadism and decreased fertility [41]. Lead does not undergo bio-magnification, and is not toxic to plants [42]. Many toxic metals are from both the anthropogenic and the natural origin, where they attach to suspended materials. They finally settle onto the sediments harming important microorganisms and indirectly affecting humans. Although some metals such as Zn, Mn, and Cu are essential to the living organisms, above certain levels, they become toxic to biota [43].

Table 8. Stream sediment quality guidelines (mg/kg).

	Mo	Cu	Pb	Zn	Ni	Co	Mn	V	Cr	Ba	As	Fe%
Canadian Guideline	-	16	31	120	16	50	-	90	26	-	6	-
USEPA[a] SQG[b]	-	16	40	95	68	19	30	-	25	-	-	30
US[c] mean value	-	14.2	14.1	62.9	15.1	9.1	760	81.1	-	-	3.9	-
ASC[d]	2	45	20	95	80	20	850	130	90	600	10	4.7
This study	1.20	14.07	35.64	47.95	12.58	12.66	172.14	75.0	76.10	1104.95	5.0	2.99

[a]USEPA United States Environmental Protection
[b]SQG-Sediment quality guideline
[c]US-Agency United States
[d]ASC- Average shale concentration

The chromium mean concentration in sediments (Table 8) failed to comply with the sediment quality guidelines (SQG) USEPA [44] of 25 mg/kg. Copper is only potentially harmful when present in elevated levels in environmental media [45]. The mean level of copper is below the recommended value of 16 mg/kg by SQG for protection of aquatic life. The guideline value for iron by USEPA in sediments is 30 mg/kg. The mean value of iron (2.99%) does not exceed this guideline. Iron is an essential metal for the living organisms and humans. It is a constituent of proteins and enzymes including hemoglobin and myoglobin [46]. Iron deficiency can lead to anemia and fatigue [47]. USEPA [44] contended that consumption of iron water with high Fe levels did not necessarily lead to any negative health effect. This is because the consumption of an elevated concentration of iron in humans is through the consumption of Fe-rich food. The mean value of Pb (35.64 mg/kg) exceeded the recommended level of 31 mg/kg in Canadian guidelines for stream sediment quality (Table 4). The mean values of Pb and arsenic exceeded guidelines for stream sediments by the United States. The mean value of Mn in this study exceeded the USEPA value for stream sediment quality (Table 4). Manganese plays several roles in physiological processes in living organisms including humans. Iron is a major component of enzymes [48]. In domestic water, Mn constitutes a nuisance if present in high concentrations with a characteristic metallic taste and staining properties [49]. The Mn level in the range of 0.24-0.35 mg/L can lead to memory lapses in children who drink water with high Mn concentration [50]. Manganese usually affects the brain and the central nervous system, causing impaired neurological and neuromuscular control among other symptoms. The neurotoxicity implication has been reported for adults over 50 years who drink Mn-rich water [51]. Lead is both a toxic and a non-essential metal having no nutritional value to living organisms. No amount of Pb is safe in drinking water. In this study, Pb possessed a mean level of 35.64 mg/kg, which is above the US mean value of 14.1 mg/kg for sediment quality (Table 5). A high Pb content may have its source from

automobile exhaust. A high concentration of Pb impairs the proper functioning of the reproductive system [52]. The mean values of heavy metals recorded in this study are below those obtained by Adisa and Adekoya [53] in the sediments of River Oyi and its tributary. The mean values of the elements in the study are Cu (10.5 ppm), Co (5.07 ppm), Cr (20.82 ppm), Fe (0.83%), Mn (248.80), Pb (5.79 ppm), Zn (15.06 ppm), and Ni (6.29 ppm). The values are below those obtained by Aladesanmi *et al*. [54] in stream sediments of Ilseha area of Pb (70.80 ppm), Cr (26.27 ppm), Co (11.63 ppm), Zn (81.26 ppm), Ni (113.15 ppm), Mn (24.15 ppm), Fe (663.5 ppm), Cu (170.20 ppm), and Cd (BDL). Both of these studies were carried out in Nigeria. In this study, the mean values of heavy metals recorded were Mo (1.20 mg/kg), Cu (14.0 mg/kg), Pb (35.64 mg/kg), Zn (47.95 kg/kg), and Ni (12.58 ppm). The others are Co (12.66 mg/kg), Mn (172.14 mg/kg), V (75 mg/kg), Cr (76.10 mg/kg), Ba (1104.95 mg/kg), As (5 mg/kg), and Fe (2.99%). The mean levels of Mn, Cr, and Co in this study exceeded those obtained in the Ilesha area, while Cu, Co, Cr, Fe, Pb, and Zn were below the mean levels obtained by Aladesanmi *et al*. [54]. In addition, the nickel levels obtained in this study exceeded concentrations of the same metals in River Oyi and its distributaries. The mean concentrations of heavy metals Zn (201.5 mg/kg), Cu (113.8 mg/kg) Co (14 mg/kg) obtained from Ogbeze in Ibadan, Nigeria by Ladigbolu and Balogun [55] exceeded those recorded in this study, except for chromium (35.9 mg/kg) that was below Cr (76.10 mg/kg) achieved in this study. In addition, stream quality sediments study by Ekwere *et al*. [56] in Cross River State, which this study forms part, Cr is below that obtained in this study. In the research work, elements possessed mean values of Pb (56.5 mg/kg), Zn (108.77 mg/kg), Cr (0.79 mg/kg), and Ni (7.03 mg/kg), and mean levels of elements Pb (0.6-30 mg/kg), Zn (0.80-27 mg/kg), Cr (0.60-3.30 mg/kg), and Ni (1.20-22.50 mg/kg) in Calabar River. The values recorded by these authors are below those obtained in this study. This may be due to the seasonal variations or proximity to areas of anthropogenic activities.

3.3. Heavy metal pollution indexes

3.3.1. Geo-accumulation Index (I-geo)

The geo-accumulation indices for heavy metals such as Mo, Cu, Pb, Zn, Ni, Co, V, Cr, Ba, Be, and Mn were computed, comparing the values with the geo-accumulation index values (Table 3) after Muller [27]. The elements Mo, Cu, Pb, Zn, Ni, Co, V, Cr, Ba, and Mn were classified as unpolluted. On the other hand, the elements Be and Ba were grouped into the moderately polluted class in the stream sediments. The high Ba I-geo values in this study relative to other heavy metals may be due to barium deposit around Biase in the studied area. Figure 4 shows the spatial variation of geo-accumulation index in the studied area. The negative I-geo values and zero values indicated that the sediments were not polluted at all. The metals with values less than one showed that the sediments recorded moderate pollution with such metals [57]. The I-geo values were not similar to the EF values, showing a single origin of heavy metals such as natural source rock weathering. The authors computed geo-accumulation index and enrichment factor, and reported the presence of high levels of Pb in sediments around the mining area.

3.3.2. Enrichment factor (EF)

Enrichment factor is a normalization factor used to investigate the influence and extent of human activities on metals. In this work, iron was a reference element for geochemical normalization as it is one of the main components of the earth's crust. Moreover, iron correlated significantly with V and Be in this work (Table 4). Enrichment factor is the relative abundance of a chemical element in the sediment compared to the bedrock [58]. The baseline concentration of these heavy metals in unpolluted sediments is necessary in order to quantify the enrichment of these heavy metals in the sediments. The worldwide standard by Turekian and Wedepohol [59] are the reference values adopted for unpolluted sediment in this work. Molybdenum possessed EF values less than 2 in most locations except for location 21 that attained an EF value of 8.715, indicating a significant enrichment. The source of Mo may be anthropogenic from mining and quarrying activities around the studied area. The lead EF values ranged from 1.428 to 34.826. Figure 5 shows the spatial variation of enrichment factor in the studied area. The EF values greater than 1.5 suggest that a significant portion of the metals is by sources other than natural weathering processes [16]. The elements Cu, Zn, Ni, Mn, V, and Cr possessed EF values ranging from depletion to minimal to moderate enrichment. Krishna *et al*. [60] in Karnataka India based on geo-accumulation, EF, and pollution index, investigated soil and sediment contamination around chromite mine. The results showed elevated levels of Cr, Ni, and Co in soil samples

around the studied area. Heavy metal levels exceed the Soil Quality Guidelines (SQGs) limit, showing that there is a steady increase of toxic heavy metals risk in the area.

The elements derived naturally have an EF value of nearly unity. Elements of anthropogenic origin have EF values of several orders of magnitude [61]. In [62], EF values exceeding 1.5 show that such heavy metals are from other sources than geogenic. This implies environmental contamination by those particular metals. On this basis, the elements such as Mo, Pb, Zn, Co, V, Cr, Ba, As, and Cu that attained EF values higher than 1.5 in some locations could be ascribed to the anthropogenic input. In addition, high EF values connotes anthropogenic source of trace metals, mainly from activities such as industrialization or deposition of industrial wastes [62]. Elements with strong positive correlation, low concentrations, and low enrichment factors reflect that their main source is from bedrock and soil weathering [17].

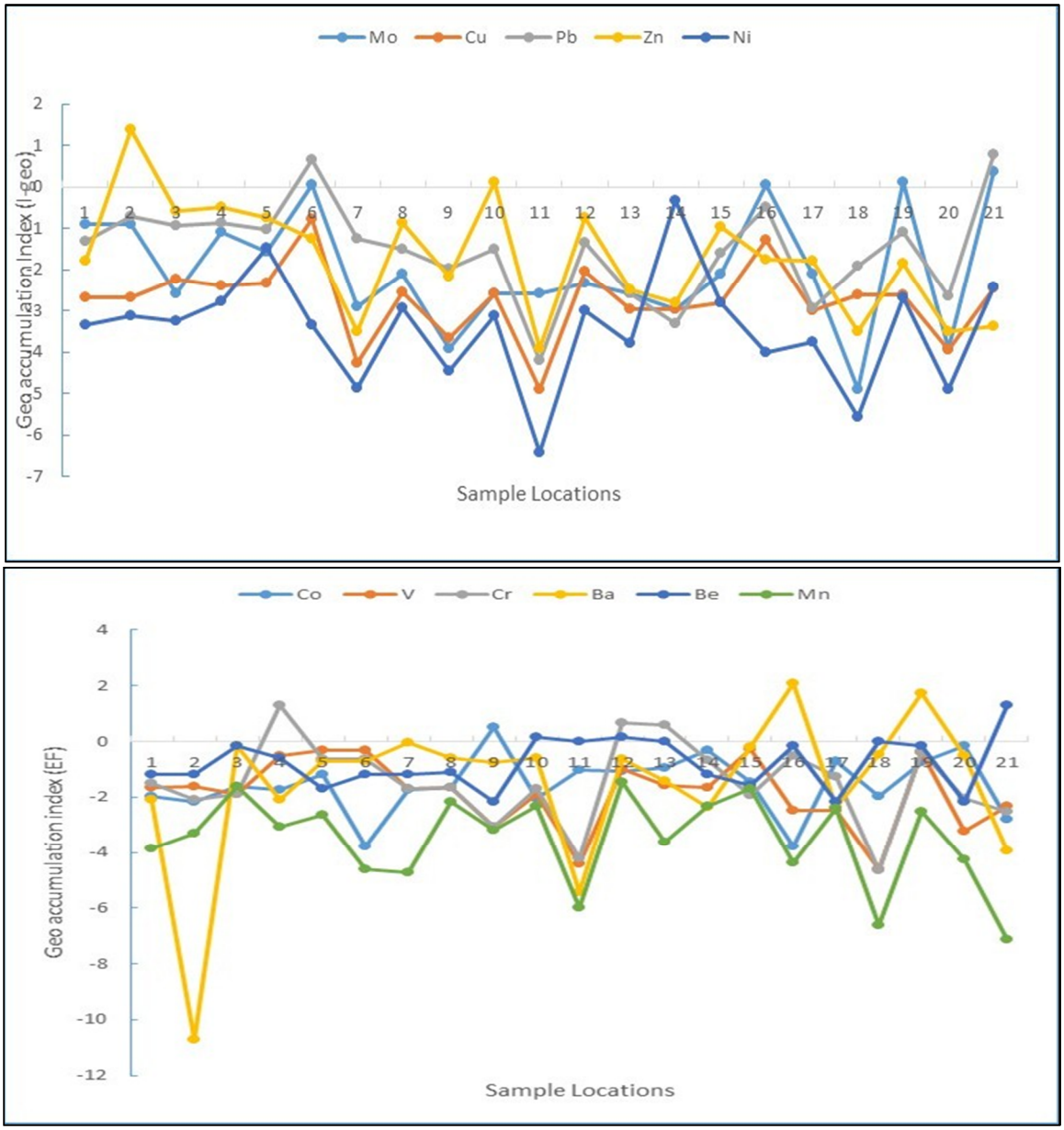

Figure 4. Spatial variation of geo-accumulation index values in the studied area.

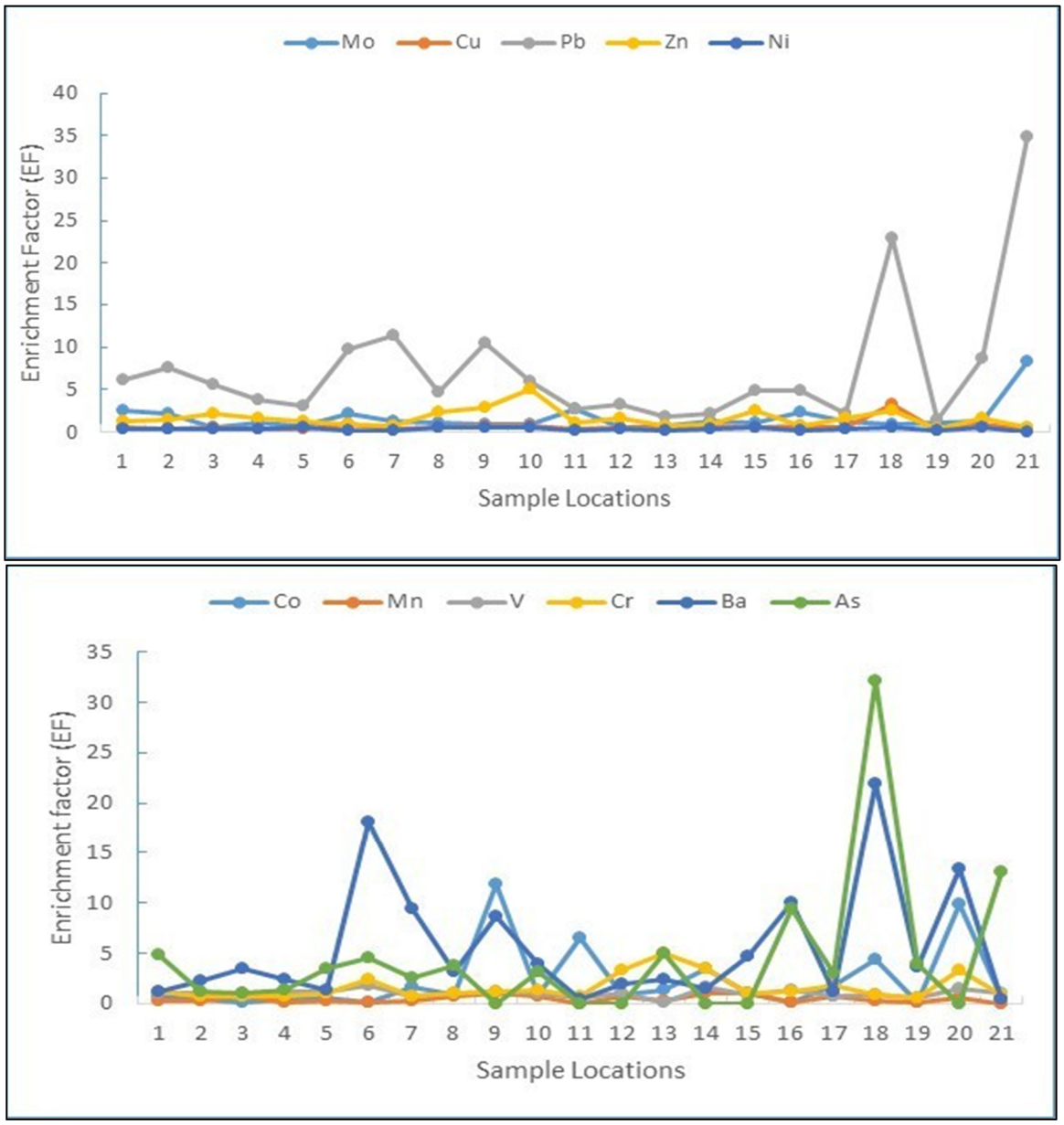

Figure 5. Spatial variation of enrichment factor in the studied area.

3.3.3. Potential ecological risk index (PERI)

PERI is formed by the three modules degree of contamination (C_D), toxic response factor (T_R), and potential ecological risk factor (RI). From Tables 3 and 9, the ecological risk of individual heavy metal arsenic is predominantly slight grade ($E^iR < 30$). Cu, Ni, Co, Cr, V, and Zn possessed E^iR values described as slight in all the sample locations. The comprehensive potential ecological risk index (RI) is classified as risk level "C", which is strong risk degree and medium risk degree risk level B, are in few locations. The rest fall under slight risk degree ($R^i < 40$) risk level A. This implies that there is no very strong risk evidence of stream sediment pollution in the studied area. The potential ecological risk was in the trend of E^iR (As) > E^iR (Pb) > E^iR (Cu) > E^iR (Co) > E^iR (Cr) > E^iR (V) > E^iR (Ni) > E^iR (Zn). Arsenic was the key strong factor for carrying risk because its potential risk factor was up to 83.22 in location 16 and 77.78 in location 19.

RI ranged from 22.18 to 115.82, and this showed that the sediment ecological risk around the studied area was not very strong. Locations 16 and 17 (Figure 6) are around the barite mine sites in the studied area. The high RI values in locations 6 and 21 are also associated with quarrying operations in the study. Variations in mineralogy may generate a low correlation coefficient between metals from the source rock.

The assessment of sediment quality is often fundamental for further management strategies or activities. This sediment quality evaluation often takes the form of risk assessment. This aimed at

defining the probability of various impacts of sediment contamination [63]. The potential ecological risk index has the advantages of considering the heavy metal toxicity, reflecting the comprehensive impacts of different pollutants, and distinguishing quantitatively the level of potential ecological hazard [64]. This method is widely used to evaluate the ecological impacts of heavy metals in the sediments in rivers, lakes, reservoirs, and intertidal zones [65].

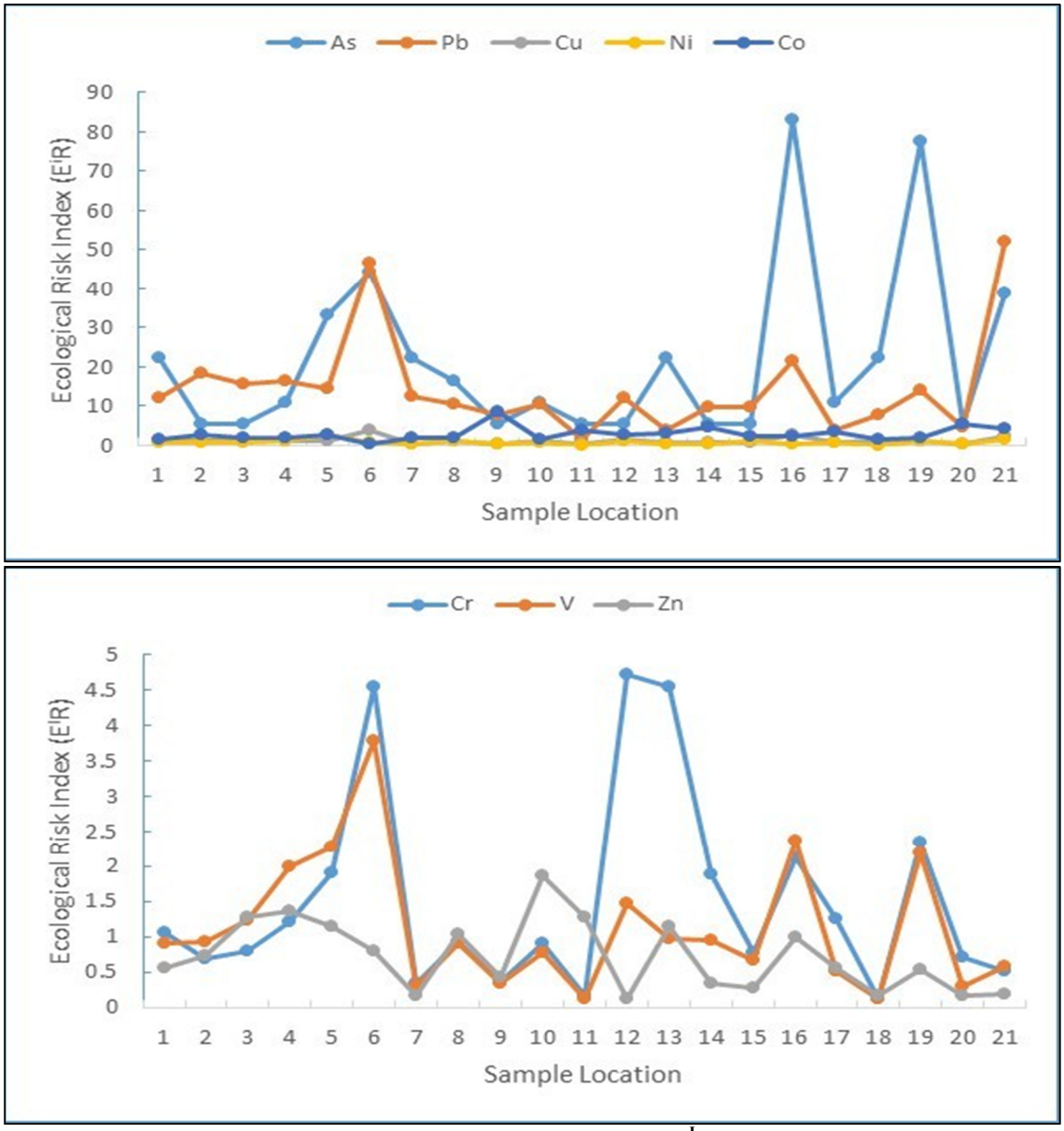

Figure 6. Spatial variation of ecological risk index (E^iR) in the studied area.

4. Conclusions

The concentration of potentially toxic elements analyzed in stream sediments around Oban Massif and Mamfe Mbayment showed that the mean levels of Ba and Pb were twice order of magnitude higher than the values of average shale concentration (ASC). The mean values of Mo, Cu, Zn, Ni, Co, Mn, As, V, and Cr were 1, 4, 2, 6, 2, 5, 3, 2, and 1, respectively, order of magnitude lower than ASC. Comparison with Canadian guideline for stream sediment quality shows that the mean Pb level (35 mg/kg) is higher than the prescribed standard of 31 mg/kg by this standard. In comparison with USEPA for sediment quality, guideline (SQG) manganese recorded a mean value of 172.14 mg/kg, which was above a value of 30 mg/kg recommended by this body for uncontaminated sediment. In comparison with the United States mean values for sediment quality, Co (12.66 mg/kg) and As (5 mg/kg) exceeded the recommended values of Co (9.1 mg/kg) and As (3.9 mg/kg) by this world body. The mean

concentration order of heavy metals in order of magnitude was Fe > Ba > Mn > Cr > V > Zn > Pb > Cu > Co > Ni >>As> Mo.

The Pearson correlation analysis on the stream sediment data showed that a positive significant correlation existed at P > 0.01. Significant correlations existed between Mo and Cu, Mo and Pb, Cu and Pb, Cu and V, Pb and V, Fe and V, Fe, Be, V, and Be, Cu, and Ba and Fe and V. This showed a common source of heavy metals in streams and rivers. Also correlation at P < 0.05 existed between the elements Co and Mo, Cu and Co, Mo and V, Cu and Cr, Cu and Be, Pb and Co, Zn and Mn, Fe and Be, Fe and Cr, Cr and Be, Cr and Ba, and Be and Ba. This showed different origins of heavy metals from the first correlation group.

Computation of stream sediment quality indices showed that geo-accumulation indices ranged from not polluted to moderate pollution with heavy metals. Barium exhibited the highest levels, suggesting barium contamination of stream sediments, which could be by inputs from barium mining in the area. The value of the enrichment factor (EF) showed metal classification from moderate, significant, and very high. Co and Be achieved values in various locations considered to be of significant enrichment. Potential ecological risk index (PERI) exhibited $E^{i}r$ to be slight grade to medium risk. Pb values attained medium risk in some locations, while $E^{i}R$ values of Ni, Co, Cr, V, and Zn slight risk grade. Comprehensive potential ecological risk (RI) showed strong risk level C and medium risk in few locations. The rest of the locations fell under slight risk level A (R < 40). The key strong factor for carrying risk in the study was arsenic. The potential ecological risk was of the order of $E^{i}R$ (AS) > $E^{I}R$ > $E^{i}R$ (Cu) > $E^{i}R$ (Co), $E^{i}R$ (Cr) >$E^{i}R$ (V) > $E^{i}R$ (Ni) > $E^{i}R$ (Zn).

In the light of the foregoing, stream sediments in the study were uncontaminated except for Mn, Co, and As, which exceeded regulatory standards by USEPA, SQG set for sediment contamination. Pb and Ba showed evidence of contamination from computation of pollution indices such as geo-accumulation, enrichment factor, and potential ecological index. These elements required remediation in the studied area.

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References

[1]. Davies, O.A. and Abowie, J.F.N. (2009). Sediment quality of Lower Reaches of Okpoka Creek, Niger Delta: Eur. Jour. Sci. Re. 26 (3): 437-447

[2]. Olunbunmi, F.E. and Olorunsola, O.E. (2010). Evaluation of the status of heavy metal pollution of sediment of Agbabu Bitumen Deposit Area. Nigeria: Eur. Jour. Sci. Res. 41 (3): 373-382.

[3]. Succie, I., Cosma, C., Todica, M., Bolboaca, S.D. and Jantschi, L. (2008). Analysis of soil heavy metal pollution in Central Transylvania: Intl. Jour. Mol. Sci. 9: 434-453

[4]. Akinmosin, A., Osinnowo, O.O. and Oladunjoye, M.A. (2009). Radiogenic components of the Nigerian Tar sand deposits: Earth Sci. Resour. Jour. 13: 64-73.

[5]. Praveena, S.M., Radojevie, M., Abdullah, M.H. and Avis, A.A. (2007). Factor cluster analysis and enrichment study of Mangrove sediments-an example from Mengkabong Sabah. The Malaysian Jour. Analy. Sci. 2 (2): 421-430.

[6]. Ajayi, S.O. and Osibanjo, O. (1981). Pollution studies on Nigerian Rivers, II: Water quality of some Nigerian rivers. Environmental Pollution Series B, Chemical and Physical. 2 (2): 87-95.

[7]. Forstner, U. (1983). Metal concentration in River, Lake and ocwen waters. In Forstner U.&Whiteman, G.T. (eds). Metal pollution in the aquatic Environment Springer Verlag publishers. New York. 109 P.

[8]. Chaerum, S.K., Tazak, K., Aseda, R. and Kogure, K. (2004). Alkane degrading bacteria and heavy metal from Nakohodka oil spill polluted seashore in the area of Japan after five years of remediation. The science report of Kanazawa University. 49 (1-2).

[9]. Zhan, S., Peng, S., Liu, C., Chang, Q.M. and Xu, J. (2010). Spatial and temporal variation of heavy metals in surface sediments in Bohai Bay, North China. Bull. Environ. Cont. Toxic. 84: 482-487.

[10]. Rezaei, A. and Sayadi, M. (2005). Long Term evolution of the composition of surface water from the River Gharasoo, Iran; A case study using a multivariate statistical techniques. Environ. Geochem. Health. 37: 151-261.

[11]. Singovszka, E. and Balintova, M. (2016). Assessment of ecological risk of sediments in rivers of eastern Slovakia. Chem. Eng. Trans. 53: 121-126

[12]. Unlu, S., Topcuoghu, A.B., Kirbasoglu, C. and Yilmax, Y.Z. (2008). Heavy metal pollution in surface sediments and mussel samples in the Gulf of Gemlikk. Environ. Mon. Assess. 144: 169-178.

[13]. Veerasingam, S., Vethamony Murali, R.M. and Fernandes, B. (2015). Depositional record of trace metals and degree of contamination in core sediments from the Maduva estuary mangroveecosystem west coast India. Mari. Poll. Bull. 9 (2): 362-367.

[14]. Tijani, M. and Onodera, S. (2009). Hydrogeochemical assessment of metals contamination in an urban drainage system: case study of Osogbo Township SW Nigeria. Jour. Water Resour. Protect. 1 (3): 164-173.

[15]. Rodrigues, M.L.K. and Formoso, M.L.L. (2016). Geochemical distribution of selected heavy metals in stream sediments affected by tannery activities. Water Air and soil poll. 169: 167-184.

[16]. Shruti, V.C., Rodriguez-Espinosa, D.C., Escobalo-Urias Estefania, M., Martinez, T. and Jonathan, M.P. (2017). Environmental consequences of metal concentration in stream sediments of Atoyal River basin, Central Mexico, Natural and Industrial influences: World Academy of science, Engineering and Technology. Inter. Jour Envi. Toxi. Eng. 11 (1): 44-51

[17]. Ayari, J., Agnan, Y. and Charef, A. (2016). Partial assessment and source identification of trace metal pollution in stream sediments of Oued El Maadene Basin northern Tunisia. Environ. Moni. Assess. 188 (1-2): 397-401.

[18]. Nnabo, P.N. (2016). Surface water contamination by heavy metals from Enyigba Pb-Zn mine District, southeastern Nigeria using metal enrichment and pollution indices. Intl. Jour. Sci. Techno. 5 (1): 8-18.

[19]. Onunugbo, C. and Avwiri, O.G. (2018). Determination of heavy metals concentration in sediments of Bonny River Nigeria. Arch. Current Res. Intl. 11 (4): 1-11.

[20]. Cocker, M.D. (1998). Distribution of selected elements in stream sediments, stream hydro geochemistry and geology of the flinth River Basin Georgia. Georgia Department of Environment and Protection. 78 P.

[21]. Atunes, I.M.H.R., Neiva, A.M.R., Albiquerque, M.T.D., Carvalho, P.C.S., Santos, A.C.T. and Cunha, P.P. (2017). Potential toxic elements in stream sediments, soils and water in an abandoned radium mine (Central Portugal). Environ Geochem Health. 40 (1): 521-542.

[22]. Barbieri, M. (2016). The importance of enrichment factor (EF) and geoaccumulation index (I-geo) to evaluate the soil contamination. Geol. Geo. 5: 1-4.

[23]. Ekwueme, B.N. (2003).The Precambrian Geology and Evolution of the southeastern Nigeria Basin at Complex Calabar University Press. 71 P.

[24]. Ekwueme, B.N. (1993). An easy approach to metamorphic petrology. Calabar University of Calabar Press. 56 P.

[25]. Oden, M.I., Akpama, T.A. and Amah, E.A. (2012). Comparative analysis of fracture lineaments in Oban Massif and Obudu areas, southeastern Nigeria. Jour. Geo. Geol. 4 (2): 36-44.

[26]. Ekwueme, B.N. (1995). The Precambrian geology of Oban Massif geological excursion guidebook to Oban Massif, Mamfe Mbayment and Calabar Flank southeastern Nigeria. 31st annual conference of the Nigerian Mining and Geosciences Society Calabar.

[27]. Muller, G. (1979). Schwarmetalle inden sediment des Rheus Verndragon, Berlin Springer. 1971 P.

[28]. Muller, G. (1969). Index of geo accumulation in sediments of the Rhine River. Geol. Jour. 2: 109-118.

[29]. Bournnaure, H., Douay, F., Sterekeman, T., Villanneau, E., Ciesielski, H., King, D. and Baize, D. (2010). Mapping of anthropogrnic trace elements input, in agricultural topsoil from northern France, using enrichment factors. Geoderma. 157: 165-174.

[30]. Reimann, C. and De Cariat, P. (2000). Flaws of elements enrichment factors (EFs) in Environmental geochemistry. Environ. Sci. Techno. 34: 5084-5091.

[31]. Douay, F., Pelfreme, A., Plaque, J., Fourier, H., Richard, A., Roussel, H. and Girondelot, B. (2013). Assessment of potential Health risk for inhabitants living near a former Lead smelter Part 1 metal concentration in soils, agricultural crops and homegrown vegetables. Environ. Moni. Assess. 185: 3665-3680.

[32]. Taylor, S.R. and McLennan, S.M. (1985). The continental crust. Its composition and evolution Blackwell Oxford. 87 P.

[33]. Hakanson, L. (1980). An ecological risk index for aquatic pollution control, a sedimentological approach. Water Res. 14: 975-1001.

[34]. Sutherland, R.A. (2000). Bed sediments associated trace metals in urban stream, Oahu Hawaii. Environ. Geol. 39: 611-627.

[35]. Wei, W., Ma, R., Sun, Z., Zhou, A., Bu, J., Long, X. and Liu, Y. (2018). Effects of mining activities on the release of heavy metals (HMs) in a typical mountain headwater region, the Qinghai-Tibet Plateau in China. International journal of environmental research and public health. 15 (9): 1987.

[36]. Levinson, A.A. (1974). Introduction to Environmental Geochemistry. Illinois. Applied Publisher. 614 P.

[37]. Horowitz, A.J. and Elrick, K.A. (1987). The relation of stream sediment surface area, grain size and composition to trace element chemistry. Appl. Geochem. 2 (4): 437-451.

[38]. Akoto, O., Bruce, T.N. and Darko, G. (2008). Heavy metals pollution profiles in streams serving the Owabi reservoir. African Jour. Environ. Sci. Techno. 2 (11): 354-359.

[39]. Oyebamiji, A., Amanamba, A., Zafar, T. Adewumi, A.J. and Akinyemi, D.S. (2018). Expected impact of active mining on the distribution heavy metals in soils around Iludun-Oro and its environs southeastern Nigeria. Cogent Environ. Sci. 4: 1495046.

[40]. Mortati, J. and Probst, J.L. (2010). Characteristics of heavy metals and their evaluation in suspended sediments from Piracicaba river basin (Sao Pacilo, Brazil). Revista Brasileira de geociencias. 40 (3): 375-379.

[41]. Obasi, P.N. and Akundinobi, B.E.B. (2015). Geochemical Assessment of heavy metal distribution and pollution status in soil /stream sediment in Ameka mining area of Ebonyi state Nigeria, African Jour. Geosci. Res. 3 (4): 1-9.

[42]. Davies, B.E., Bowman, C., Davies, T.C. and Sellinium, O. (2005). Medical Geology perspectives and prospects. Essential Medical Geology Elsevier Incorporated. 14 P.

[43]. Wendy, N. (2005). Spatial distribution of heavy metals in sediments from the Gulf of Persia Trinidad: Int. Jour. Tropical Biol. 53 (1): 33-40.

[44]. USEPA. (1999). US Environmental Protection Agency Screening Level ecological risk assessment protocol for hazardous waste combustion facilities toxicity reference values. Washington DC. USA. 13 P.

[45]. Guptal, V.B., Anitha, S., Hedge, M.L., Zecca, L., Zecca, L., Garruto, R.M., Ravid, R., Shankar, S.K., Stein, R., Shan Mugavelu, P. and Jagannatha Rao, K.S. (2005). Aluminum in Alzheimeri disease are we still at a crossroad. Cell Mole. Life Sci. 62: 143-158.

[46]. Yip, R. and Dallium, P.R. (1996). Iron in Present Knowledge in nutrition 7th eds. Ziegler E.E Filer L. eds ILSI Press Washington DC USA. pp. 277-292.

[47]. Garvin, K.S. (2015). Health effects of iron in drinking water. Available online. http/www./agwt.org/content/iron. Problems (Accessed on Nov 2015).

[48]. Cross grove, J. and Zheng, W. (2004). Manganese toxicity upon overexposure: NMR Biomed. 17:544-553.

[49]. Ljung, K. and Vahter, M. (2007). Time to reevaluate the Guideline value for manganese in Drinking water. Environ. Health Persp. 115: 1533-1538.

[50]. Kondakis, X.G., Markris, N., Leotsinidis, M., Prinou, M. and Papapetropoulous, T. (1989). Possible effect of high manganese concentration in drinking water. Arch. Environ. Health. 44: 175-178.

[51]. WHO. (2011). Guidelines for drinking water Quality 4th edition WHO Geneva Switzerland. pp. 155-202.

[52]. Adisa, A.L. and Adekoya, J.A. (2016). Assessment of pollution by heavy metals in sediments of River Oyi and its tributaries, southwestern Nigeria: Ife Jour. Sci. 18: 871-886.

[53]. Aladesanmi, O.T., Agboola, F.K. and Adeniyi, I.F. (2016). Distribution of heavy metals in surface sediments from streams and their associated fishponds in Osun state Nigeria: Jour. Health and Poll. 6 (11): 34-46.

[54]. Ladigbolu, A. and Balogun, K.J. (2011). Distribution of Heavy metals in sediments of selected streams in Ibadan Metropolis Nigeria. Intl. Jour. Environ. Sci. 1 (6): 1186-1191.

[55]. Ekwere, A., Ekwere, S.J. and Obim, V. (2013). Heavy metal geochemistry of stream sediments from parts of the Niger Delta Basin, southeastern Nigeria: RMZM&G. 60: 205-210.

[56]. Huu, H.H., Rudy, S. and Van Damme, A. (2010). Distribution and contamination status of heavy metals in estuarine sediments near Cau Ong habour H-Long Bay, Vietnam. Geol. Belgica. 13:37-47.

[57]. Hernandiz, L., Probst, A. and Ulrich, E. (2003). Heavy metal distribution in some French forest soils: Evidence for atmospheric contamination: The Sci. Total Environ. 312: 195-210.

[58]. Waserman, G.A., Liu, X., Paruez, F., Ahsan, H., Lewy, D., Factor Litvak, P., Kline, J., Van Green, A., Slavkovich, V., Lolacono, N.J. (2006). Water Manganese exposure and children's intellectual function in Arachazer, Bangladesh. Environ. Health Persp. 114: 124-129.

[59]. Turekian, K.K. and Wedepohol, K.H. (1961). Distribution of elements in some major units of the earth crust: Geol. Soc. Ame. Bull. 72 (2): 175-192.

[60]. Krishna, K., Murthy, N. and Kurakalve, R.M. (2013). Assessment of heavy metal contamination in soils around chromite mining areas Nuggihalli, Karnataka, India. Environ. Earth Sci. 70: 699-708.

[61]. Saffari, A., Ataei, M., Sereshki, F. and Naderi, M. (2019). Environmental impact assessment (EIA) by using the Fuzzy Delphi Folchi (FDF) method (case study: Shahrood cement plant, Iran). Environment, Development and Sustainability. 21 (2): 817-860.

[62]. Selvam, A.P., Priya, S.L., Banerjee, K., Hariharan, G., Purvaja, R. and Ramesh, R. (2012). Heavy metal assessment using geochemical and statistical tools in the surface sediments of Vembanad

Lake, Southwest Coast of India. Environmental monitoring and assessment. 184 (10): 5899-5915.

[63]. Apitz, S.E. and Power, E.A. (2002). From risk assessment to sediment management, an international perspective. Jour. Soils Sediment. 2 (2): 61-66

[64]. Cobett, C. and Goldbough, P. (2002). Phytocheletins and Metallothineins: Roles in heavy metal detoxification and homeostasis: Annus Rev Plant Biol. 53: 159-182.

[65]. Diaz-de-Alba, M., Galindo_Riano, M.D., Casnueva-Marinco, M.J., Garia-Vergas, M. and Kosore, C.M. (2011). Assessment of the metal pollution potential, toxicity and speciation of sediments from Algeciras Bay (Southern Spain) using chemo metric tools. Jour. Haz. Mater. 190: 177-187.

Evaluation of stream sediment contamination by potentially toxic elements around mining and farming areas (SE Nigeria)

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Abstract:

In this work, the concentrations of the potentially toxic elements in stream sediments in SE Nigeria were assessed for pollution monitoring in mining, quarrying, and farming areas. The levels of iron, molybdenum, vanadium, copper, lead, zinc, nickel, cobalt, manganese, chromium, barium, and beryllium were determined. The concentrations of the elements were in the order of Fe > Ba > Mn > Cr > Zn > Pb > Cu > Co > Ni > As > Mo. There were significant positive correlations at $P < 0.01$ between Mo and Cu ($r = 0.734$), Mo and Pb ($r = 0.811$), and Cu and Pb ($r = 0.836$). The others were between Cu and V ($r = 0.748$), Pb and V ($r = 0.793$), Fe and V ($r = 0.905$), Fe and Be ($r = 0.703$), V and Be ($r = 0.830$), Cu and Pb ($r = 0.778$), and Fe and V ($r = 0.905$). The geoaccumulation index values were classified as polluted (0-1) to moderately polluted (1-2). The enrichment factors fell into moderate, significant, and very high enrichment. Pb, Co, and Ba attained significant enrichment factors. The potential ecological risk showed a strong risk level "C" in only three locations. Arsenic was a strong factor carrying risk. The potential ecological risk (E^iR) trend was E^iR (AS) > E^iR (Pb)> E^iR (Cu) > E^iR (Co) > E^iR (Cr) > E^iR (V) > E^iR (Ni) > E^iR (Zn). Ba, Pb, and As should be monitored further to determine their source and recommend possible remedial measures. The result of this work could be used to improve water management efficiency and serve as a benchmark of vulnerability assessment of the studied area. This could also be useful for future impact assessment and adequate planning of mining and farming areas. In addition, the result obtained could assist the scientists to make appropriate environmental management strategies to reduce the influence of metal contamination triggered from the mining sites and farming areas both in Nigeria and globally.

Keywords: Stream Sediment, Potentially Toxic Elements, Geoaccumulation Index, Enrichment Factor, Potential Ecological Risk.