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Geochemical studies of heavy metals in stream sediments around Oguro, southwestern Nigeria

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ABSTRACT

This study evaluates the geochemical characteristics and contamination status of stream sediments in Oguro, Southwestern Nigeria, with emphasis on heavy metal distribution and potential sources. Twelve sediment samples were analysed for Cr, V, Co, Ni, Cu, Zn, Pb, Th, Zr, Mo, and Ti using Inductively Coupled Plasma Mass Spectrometry (ICP–MS). Contamination levels were quantified through the Geo-accumulation Index (I_geo), Contamination Factor (CF), Enrichment Factor (EF), and Pollution Load Index (PLI), complemented by multivariate statistical techniques. The results reveal that Cr, V, Ni, Th, and Zr are largely geogenic, whereas Cu, Zn, Pb, and Co exhibit high spatial variability (CV > 96%) and markedly elevated I_geo (>12), CF (>3), and EF (>40), indicating significant geogenic enrichment. Principal Component Analysis (PCA) and Ward-linkage hierarchical clustering identified dominant assemblages of anthropogenic clusters of transition and heavy metals and geogenic grouping. Although basin-wide PLI values remain generally low (<0.5), localised hotspots, particularly at stations L5 and L6, approach regulatory thresholds, underscoring potential ecological risks. Conclusively, this investigation establishes a robust geochemical baseline for environmental quality monitoring and offers critical insights for sediment management in transitional agro-urban watersheds.

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Introduction

Heavy metals are naturally occurring elements characterized by high atomic weights and densities exceeding 5 g/cm^3. While trace levels of elements such as iron (Fe), zinc (Zn), and copper (Cu) are essential for biological and metabolic processes, others including lead (Pb), cadmium (Cd), and mercury (Hg) are highly toxic even at very low concentrations [1]. Elevated levels of these metals may originate from both natural geogenic processes and diverse anthropogenic activities, resulting in significant environmental and public health concerns. Stream sediments are key transport and depositional media for heavy metals within aquatic ecosystems. They play a vital role in geochemical cycling, as they can adsorb, accumulate, and subsequently release contaminants into the water column under varying environmental conditions. Once deposited, these metals may persist for extended periods, thereby posing long-term risks to aquatic organisms, soil fertility, water quality and ultimately human health. In Southwestern Nigeria where anthropogenic pressures are increasing, it is crucial to evaluate the extent of heavy metal contamination in stream sediments, particularly in rural and peri-urban environments such as Oguro. Such assessments provide critical insights into environmental quality and associated ecological and human health risks.

Several Nigerian case studies have documented the distribution and implications of heavy metals in stream sediments. Investigations of the Osun and Erinle Rivers in Southwestern Nigeria revealed considerable enrichment of Cd, Cu, Ni, Pb, Zn, Co, Cr, V, and Mn, with contamination levels markedly higher

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in urban areas than in suburban catchments [2, 3] reported that sediments derived from metasediments and schistose rocks of the Iseyin–Oyan River Schist Belt exhibited elevated concentrations of As, Co, Mo, Mn, Pb, Zn, Cu, Cr, Ni, and Fe, reflecting a strong lithogenic influence of the underlying bedrock. In contrast, the Abakaliki Pb–Zn ore district in Ebonyi State displayed abnormally high Fe, Zn, Cu, Pb, and Cr contents, which were attributed to intensive mining activities, underscoring the impact of anthropogenic factors in heavy metal redistribution [4]. Additional studies in Ibadan identified indiscriminate refuse dumping and urban runoff as dominant contributors to Pb, Zn, Cu, and Cd enrichment, while Ni, Co, and Cr were largely associated with geogenic origins [5, 6].

Oguro, located in Southwestern Nigeria, is a predominantly agrarian community where residents rely heavily on streams for drinking water, irrigation, and domestic activities. The area is characterised by fertile soils and a dense network of streams feeding into larger water systems. However, the intensification of agricultural practices, inadequate waste management systems, and emerging urbanisation pressures may contribute to heavy metal contamination of local water bodies. Given the tendency of heavy metals to bioaccumulate in aquatic organisms and enter the human food chain, determining their levels and distribution within stream sediments is a pressing environmental and public health necessity.

The geochemical investigation of stream sediments, therefore, provides an indispensable framework for monitoring environmental quality, identifying sources of contamination, and evaluating ecological and human health risks. Against this background, the present study investigates the concentration of heavy metals in stream sediments from Oguro, Southwestern Nigeria. This study is targeted at quantifying the concentrations of selected heavy metals in the sediments, identifying their possible geogenic and anthropogenic sources, and evaluating the magnitude of contamination and its potential environmental implications.

Study area

The study was conducted in Oguro located at approximately N07^0 55’ 00” to N08^0 00’ 00” and longitude E 04^0 12’ 00” to E04^0 15’ 00 in the southwestern part of Nigeria, an area characterised by a predominantly agricultural land. The area is known for its fertile soils, which support various crops, including cassava, yams, and maize. Oguro is situated within a tropical climate zone, with distinct wet and dry seasons. About 1260 mm of precipitation falls annually. Precipitation is lowest in January, with an average of 8 mm. The greatest amount of precipitation occurs in September with an average of 199 mm. The terrain is predominantly flat with some rolling hills, and the region is drained by several small streams that feed into larger rivers in the vicinity. These streams are susceptible to pollution due to the proximity of farmlands and rural settlements. Figure. 1 presents a map of the study area, illustrating the locations of the sampling points. The streams in this area are crucial sources of water for both domestic use and irrigation, which makes them vulnerable to contamination from agricultural runoff and other anthropogenic activities.

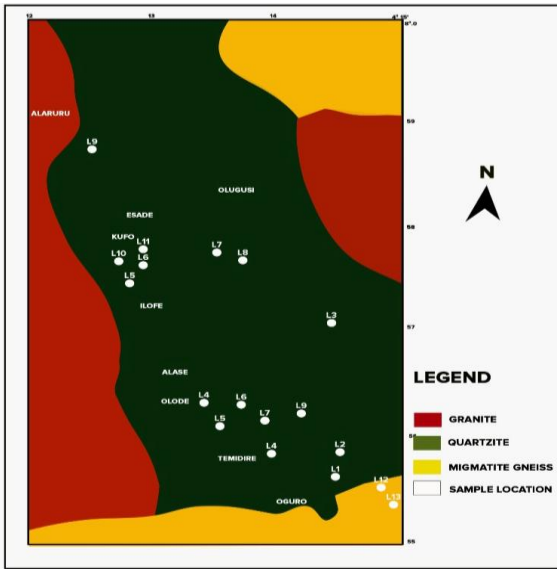

Figure 1: Geological map of the study area

Materials and methods

Sampling procedure

Stream sediment samples were collected from twelve (12) distinct streams around the Oguro area, as detailed in Figure 1 and presented in Table 1. Sampling points were selected based on proximity to potential sources of contamination, such as agricultural fields, settlements, and agro-allied activities like palm oil/kernel processing and cassava mills. The sampling locations were spread across the study area to ensure representative data from various regions.

Sampling was conducted during the rainy season to capture the heavy metal concentrations in the sediment during a period of possible increased runoff and erosion. Active sediments were collected from the

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surface portion within the stream channels and banks where flow velocity of the stream is low. At each site, three samples were taken at different points along the stream to account for spatial variability. The coordinates of each sampling point were recorded using a handheld Global Positioning System (GPS) device. The study area was separated into two (2) catchment areas. The first catchment area comprising six (6) sampling points is located around the central part of the study area are surrounded by villages like Olugusi, Kufo, Ilofe and Esade. Background sample was collected at Alaruru, a rural community of about 2 km north of the first catchment area. The second catchment area is made up of agrarian villages like Alase, Olode, Temidire and Oguro towards the south, its background sample was collected around Otamokun towards the East and about 2 km away from the second catchment area. The background samples are collected over similar basement rock as the main samples and are also derived from locations where similar anthropogenic activities (mostly farming) take place.

Sample preparation

The collected sediment samples were transferred into clean, pre-labelled polyethene bags and transported to the laboratory for analysis. In the laboratory, the samples were air-dried at room temperature for 24 hours. Once dried, the samples were sieved through a 2 mm mesh to remove large debris, such as plant material and rocks. The sieved samples were then ground using a mortar and pestle to ensure uniformity before geochemical analysis.

Table 1:Coordinates of sampling points of stream sediments

Sample Location	Sample Locality	Latitude	Longitude
L1	Oguro	7⁰ 55'56"	4⁰ 14'24.5"
L2	-	7⁰ 57'1.5"	4⁰ 14'21.2"
L3	Temidire	7⁰ 55'44.1"	4⁰ 13'50.4"
L4	Ilofe	7⁰ 57'26.2"	4⁰ 12'42.3"
L5	Kufo	7⁰ 57'29.3"	4⁰ 14'42.1"
L6	-	7⁰ 57'36.9"	4⁰ 13'28.1"
L7	-	7⁰ 57'36.8"	4⁰ 13'34.1"
L8	Alaruru	7⁰ 58'37.4"	4⁰ 13'26.4"
L9	Kufo	7⁰ 57'29.3"	4⁰ 12'44.7"
L10	Kufo	7⁰ 57'28.3"	4⁰ 12'47.9"
L11	Oguro	7⁰ 55'27.1"	4⁰ 14'40.3"
L12	Aye	7⁰ 57'25.9"	4⁰ 15'4.3"

Geochemical analysis

The sediment samples were analyzed for a range of heavy metals, including Chromium (Cr), Vanadium (V), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Titanium (Ti), Lead (Pb), Thorium (Th), Zirconium (Zr), Molybdenum (Mo) The analysis was carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), at the wet geochemistry laboratory, Department of Geological Sciences, University of Cape Town, South Africa. These techniques are commonly employed for their sensitivity and accuracy in detecting trace amounts of heavy metals in environmental samples. For each heavy metal analysed, the instrument was calibrated using standard solutions of known concentration. Quality control measures were taken throughout the analysis process, including the use of blanks, duplicates, and certified reference materials (CRMs) to ensure reliability and precision of the results.

Data analysis and interpretation

The concentrations of heavy metals in the sediment samples were measured and reported in parts per million (ppm). The data were statistically analysed using IBM SPSS 28 to determine the spatial distribution of heavy metals across the study area. This statistical software package was employed because of its robustness, flexibility and user-friendly capacity for multivariate data analysis. It was also adopted due to its versatility in interpreting complex geochemical datasets. The statistical analysis includes descriptive statistics, such as mean, range, and standard deviation. Also, various contamination indices such as Contamination factor, Geo-accumulation index, Degree of contamination, Enrichment factor and Pollution Load Index were also used for the quantification of the impact of selected metals in the study area [7, 8, 9, and 10].

The geoaccumulation index (I_geo), was calculated using the formula:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \cdot B_n}\right) \quad (1)$$

where: Cn = measured concentration of the element in the sediment, Bn = geochemical background value of the element and the factor 1.5 accounts for natural variations in the background levels. The contamination factor (CF) is the ratio obtained by dividing the mean concentration of each metal in the soil by the baseline or background value (concentration in uncontaminated soil).

$$CF = \frac{C_n}{B_n} \quad (2)$$

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where: Cn = measured concentration of the element in the sample and Bn = background concentration [11].

The Contamination Factor (CF) is classified into four categories as follows: CF < 1 indicates low contamination; 1 ≤ CF ≤ 3 denotes moderate contamination; 3 < CF < 6 represents considerable contamination; and CF ≥ 6 signifies very high contamination.

The enrichment factor is calculated using

$$EF = \frac{\left(C_n / C_{ref}\right)}{\left(B_n / B_{ref}\right)} \quad (3)$$

C_n = concentration of the element in the sample, C_{ref} = concentration of the reference element in the sample (in this study, Titanium (Ti) is used), B_n = average crustal abundance of the element, B_{ref} = crustal average of the reference element (Ti = 3300ppm).

The Pollution Index is calculated using

$$\mathrm{PLI} = \left(\prod_{i=1}^{n} CF_i\right)^{1/n} \quad (4)$$

Where, CF_i Contamination Factor for the iii-th metal, n = number of metals considered.

PLI is defined according to 3 categories: PLI > 1 indicates pollution; PLI = 1 is baseline; PLI < 1 suggests no pollution.

Results and discussion

Results of geochemical analysis for stream sediment of the study area are presented in Table 2.

Table 2: Heavy metals concentration (ppm) for stream sediment of the study area (n = 12)

Sample Location	Cr	V	Co	Ni	Cu	Zn	Pb	Th	Zr	Mo	Ti
L1	5	6	0.8	1	2.5	6.1	3.5	5.4	0.4	0.19	< 0.02
L2	9	14	2.8	1.1	2.4	6.1	8.2	2.4	0.8	0.33	0.03
L3	36	26	0.6	1.7	25.7	24.7	6.3	3.8	1.8	0.62	< 0.02
L4	9	6	0.5	0.9	3.7	7.5	4.4	9.9	0.7	0.21	< 0.02
L5	42	45	1.9	2.7	9.7	32.9	13.3	32.8	3	0.81	0.03
L6	26	43	14.9	11.3	169	147	44.4	5.7	1.8	0.92	0.17
L7	6	6	1.3	1.1	8.9	14.8	6.3	14.4	0.3	0.15	0.03
L8	14	15	2.1	1.4	4.3	20.1	7.4	5.9	0.4	0.25	< 0.02
L9	13	16	4.6	3.1	9.6	14.5	8.4	7.4	1.1	0.23	0.05
L10	9	8	2	1.8	5.4	19.8	9.9	28.1	0.5	0.18	0.02
L11	14	13	1.6	1.9	4.1	20.3	9.4	40.3	0.6	0.29	0.02
L12	28	41	3.9	4.1	8.4	32.6	14.6	9	0.8	0.65	0.07

Descriptive statistics

The statistical characterisation of heavy metals in stream sediments from the Oguro area offers a crucial understanding of their geochemical behaviour, provenance, and potential anthropogenic influence. The comparison between mean elemental concentrations and established crustal averages [11] reveals both natural and anthropogenically-enhanced geochemical signatures.

Chromium (Cr), Vanadium (V), and Nickel (Ni) exhibit significantly lower average concentrations in Oguro sediments compared to their global crustal values (Table 3). Specifically, Cr has a mean of 17.58 ppm (90 ppm crustal), V at 19.92 ppm (135 ppm), and Ni at 2.68 ppm (80 ppm). These low values, in combination with moderate to high coefficients of variation (70–108%), indicate that these elements are predominantly geogenic, likely derived from silicate-dominated source rocks lacking ultramafic contributions. Their dilution within finer sediment fractions or leaching under variable redox conditions also contributes to the low concentrations.

Conversely, Copper (Cu) and Zinc (Zn) demonstrate considerable variability and moderately high mean values—21.14 ppm and 28.87 ppm, respectively (Table 3). Although still slightly below crustal benchmarks (55 ppm for Cu, 70 ppm for Zn), their high coefficients of variation (Cu: 222%, Zn: 133%) imply localised enrichment, possibly from inputs such as mining activities, metal-based agriculture (e.g., fertilisers and fungicides), or domestic wastewater discharge. The pronounced variability underscores spatial heterogeneity in pollution sources, particularly for Cu.

Lead (Pb) and Cobalt (Co) present similar characteristics, with Pb averaging 11.34 ppm (20 ppm crustal) and Co at 3.08 ppm (25 ppm). Their distribution patterns, especially Pb's CV nearing 96% suggest mixed origin, with both geogenic weathering and low-level anthropogenic sources playing roles.

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Table 3: Descriptive analysis of heavy metal concentration (ppm) in the stream sediments

Element	Mean (ppm)	Median (ppm)	Std. Dev.	Min	Max	Coeff. of Variation (%)	Crustal Average (Taylor 1964) ppm
Cr	17.58	13.50	12.34	5.00	42.00	70.18	90
V	19.92	14.50	15.04	6.00	45.00	75.53	135
Co	3.08	1.95	3.93	0.50	14.90	127.37	25
Ni	2.68	1.75	2.88	0.90	11.30	108.00	80
Cu	21.14	6.90	46.99	2.40	169.00	222.24	55
Zn	28.87	19.95	38.30	6.10	147.00	132.67	70
Pb	11.34	8.30	10.90	3.50	44.40	96.14	20
Th	13.76	8.20	12.71	2.40	40.30	92.35	12
Zr	1.02	0.75	0.80	0.30	3.00	78.89	170
Mo	0.40	0.27	0.27	0.15	0.92	67.37	1.2

The Pb levels, while below crustal averages, are elevated compared to pristine background levels expected in uncontaminated sediments, hinting at subtle contamination.

Thorium (Th) and Zirconium (Zr) behave conservatively, with Th (13.76 ppm) marginally exceeding its crustal average (12 ppm), and Zr (1.02 ppm) markedly lower than expected (crustal Zr -17 ppm). These elements are commonly associated with resistant minerals such as zircon and monazite, reflecting a strong lithogenic control. The moderate variability in Th (CV: 92%) is likely driven by differential input from felsic lithologies or sediment sorting processes.

Molybdenum (Mo), with a mean of 0.40 ppm compared to a crustal average of 1.2 ppm, remains uniformly distributed (CV: 67%). Its low concentration and minimal variability imply limited influence from industrial or geochemical anomalies and a predominantly background geogenic origin. Generally, the data indicate that Cr, V, Ni, and Th are controlled predominantly by natural processes, particularly parent rock composition and sediment transport dynamics. In contrast, Cu, Zn, Pb, and to some extent Co show spatially heterogeneous distributions indicative of anthropogenic modification, consistent with observations from geochemically similar environments [12, 13].

Correlation analysis

Pearson correlation analysis was conducted to quantify inter-element relationships and elucidate potential common sources or geochemical behaviours among the heavy metals (Table 4). A strong and statistically significant correlation ($r > 0.95$) was observed among Pb, Zn, Ni, Co, and Cu, indicating a common source of anthropogenic origin. This co-enrichment pattern reflects shared pathways such as industrial runoff, vehicular emissions, or urban waste deposition. Titanium, employed as the geochemical normaliser, exhibited high positive correlation with Ni, Co, and Pb ($r \approx 0.95–0.98$), further affirming its conservative behaviour and geochemical stability in the sedimentary environment. Conversely, Th demonstrated weak or negative correlation with most trace metals, implying a distinct lithogenic source and limited anthropogenic influence. These correlations provide critical insights into geochemical partitioning and pollutant provenance within the stream channel or the drainage system.

Table 4: Correlation analysis of stream sediment samples

Element	Cr	V	Co	Ni	Cu	Zn	Pb	Th	Zr	Mo
Cr	1.000									
V	0.885	1.000								
Co	0.222	0.556	1.000							
Ni	0.386	0.678	0.972	1.000						
Cu	0.300	0.528	0.934	0.944	1.000					
Zn	0.402	0.646	0.938	0.973	0.978	1.000				
Pb	0.377	0.669	0.962	0.982	0.948	0.985	1.000			
Th	0.134	0.032	-0.223	-0.134	-0.219	-0.098	-0.060	1.000		
Zr	0.878	0.784	0.296	0.409	0.371	0.428	0.418	0.169	1.000	
Mo	0.881	0.962	0.601	0.724	0.652	0.733	0.731	-0.012	0.819	1.000

Geoaccumulation index (I_geo)

The Geoaccumulation Index (I_geo), originally proposed by Müller, was utilized to quantify the degree of heavy metal pollution in stream sediments, referencing average crustal abundances by [11] and using Ti as a conservative lithogenic normalizer (Equ.

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1). Although several entries are marked as "ND" (Not Detected), available data show consistently elevated I_geo values across samples L2, L5, L6, L7, L9 and L12 for metals such as Pb, Zn, Cu, and Th. Pb exhibits I_geo values above 14 in most of these samples (Table 5), indicating "heavily to extremely polluted" according to Müller's classification scheme (Table 6). Zn and Cu show similarly elevated indices (I_geo > 12), particularly in samples L5 and L6, suggesting substantial anthropogenic input likely from domestic waste, agrochemicals, or industrial activities. The values also peak in L11 and L10 (18.66 and 18.14), implying radio-elemental enrichment, possibly linked to natural granitic detritus. The elevated I_geo values in these elements point to localised contamination hot spots within the watershed, which require environmental attention.

Table 5: Geoaccummulation index of stream sediments samples

Sample Location	Cr	V	Co	Ni	Cu	Zn	Pb	Th	Zr	Mo
L1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	12.84	12.94	13.00	10.21	11.64	12.64	14.87	14.00	8.27	13.97
L3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L5	15.06	14.63	12.44	11.51	13.66	15.07	15.57	17.78	10.17	15.27
L6	11.87	12.06	12.91	11.07	15.27	14.73	14.81	12.75	6.94	12.95
L7	12.26	11.72	11.89	10.21	13.53	13.92	14.49	16.59	6.85	12.84
L8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L9	12.63	12.40	12.98	10.97	12.91	13.15	14.17	14.89	7.99	12.72
L10	13.43	12.72	13.10	11.51	13.39	14.92	15.73	18.14	8.17	13.69
L11	14.06	13.43	12.78	11.59	13.00	14.96	15.66	18.66	8.44	14.37
L12	13.26	13.27	12.26	10.89	12.23	13.84	14.49	14.69	7.05	13.73

Table 6: Muler geoaccummulation index classification

Class	I_geo Range	Pollution Intensity	Description
0	I_geo ≤ 0	Unpolluted	Natural background levels; no enrichment.
1	0 < I_geo ≤ 1	Unpolluted to moderately polluted	Slightly enriched above background levels; possible minor anthropogenic input.
2	1 < I_geo ≤ 2	Moderately polluted	Clear enrichment; likely anthropogenic influence.
3	2 < I_geo ≤ 3	Moderately to heavily polluted	Significant anthropogenic contribution.
4	3 < I_geo ≤ 4	Heavily polluted	Strong enrichment; serious contamination concern.
5	4 < I_geo ≤ 5	Heavily to extremely polluted	Very high levels of enrichment.
6	I_geo > 5	Extremely polluted	Severe pollution often indicates industrial or urban waste dominance.

Contamination factor (CF)

Contamination Factors (CFs) were calculated to assess the degree of anthropogenic disturbance for each individual metal relative to its natural abundance (Equation 2). It is a key diagnostic index used to classify the contamination intensity of an individual metals in sediment. Most metals recorded CF values below 1 (Table 7), suggesting generally low contamination levels, particularly for Cr, V, Ni, and Zr. However, Cu, Zn, Pb, and Th exhibit moderate to very high CF values across several locations. Notably, sample L6 shows very high CFs for Cu (3.07), Zn (2.10), Pb (2.22), and Mo (0.61) (Table 7), indicating considerable to very high contamination (Table 8), consistent with anthropogenic metal enrichment. Sample L11 records the highest CF for Th (3.77), reflective of a potential natural radiogenic source or possibly industrial inputs. The variability in CFs among sites further highlights the heterogeneous distribution of contaminants within the stream system and the influence of both natural geochemical processes and human-induced activities.

Pollution load index (PLI)

The Pollution Load Index (PLI), a composite metric of overall contamination status, was computed as the nth root of the product of individual CFs (Equation 4). It integrates the cumulative effect of multiple contamination factors to provide a single pollution metric. Values less than 1 indicate no overall pollution, whereas values above 1 reflect progressive deterioration (Table 10). All samples reported PLI values below 0.5, with sample L6 (0.459) and L5 (0.242) being the most polluted (Table 9). Although these

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Table 7: Contamination factor of stream sediment samples

Sample Location	Cr	V	Co	Ni	Cu	Zn	Pb	Th	Zr	Mo
L1	0.06	0.05	0.03	0.01	0.05	0.09	0.18	0.51	0.02	0.13
L2	0.10	0.11	0.11	0.02	0.04	0.09	0.41	0.22	0.04	0.22
L3	0.40	0.2	0.02	0.03	0.47	0.35	0.32	0.36	0.01	0.41
L4	0.10	0.05	0.02	0.01	0.07	0.11	0.22	0.93	0.03	0.14
L5	0.47	0.35	0.08	0.04	0.18	0.47	0.67	3.07	0.02	0.54
L6	0.29	0.33	0.59	0.17	3.07	2.10	2.22	0.53	0.01	0.61
L7	0.07	0.05	0.05	0.02	0.16	0.21	0.32	1.35	0.01	0.1
L8	0.16	0.12	0.08	0.02	0.08	0.29	0.37	0.55	0.02	0.17
L9	0.14	0.12	0.18	0.05	0.17	0.21	0.42	0.69	0.01	0.15
L10	0.10	0.0	0.08	0.03	0.09	0.28	0.50	2.62	0.03	0.12
L11	0.16	0.1	0.06	0.03	0.07	0.29	0.47	3.77	0.03	0.19
L12	0.31	0.32	0.16	0.06	0.15	0.46	0.73	0.84	0.05	0.43

Table 8: Contamination factor classification

CF	1 ≥ CF ≥3	3 < CF < 6	CF ≥ 6
Low Contamination Factor	**Moderate Contamination Factor**	**Considerable Contamination Factor**	**Very High Contamination Factor**

Table 9: Pollution index of stream sediment samples

Sample Location	PLI
L1	0.050715
L2	0.075871
L3	0.142559
L4	0.062603
L5	0.242467
L6	0.459502
L7	0.075385
L8	0.093282
L9	0.13011
L10	0.104038
L11	0.120583
L12	0.193488

Table 10: Pollution index classification

PLI Range	Pollution Level	Interpretation
PLI < 1.0	No pollution (baseline)	Indicates low contamination; metal levels are within natural background levels.
PLI = 1.0	Baseline level of pollution	Represents the threshold between unpolluted and polluted conditions.
1.0 < PLI ≤ 2.0	Moderate pollution	Suggests some anthropogenic influence; early signs of contamination.
2.0 < PLI ≤ 3.0	Heavy pollution	Indicates significant anthropogenic contamination.
PLI > 3.0	Very heavy pollution	Severe pollution is often linked to industrial, mining, or urban discharge sources.

values fall within the "unpolluted to moderately polluted" range, the relatively higher PLI in these samples, in conjunction with high I_geo and EF values, suggests localised contamination zones that may function as pollutant sinks. The low PLI in samples like L1 (0.05), L4 (0.06), and L7 (0.07) confirms background or minimally impacted conditions likely due to limited human activity in those areas. These findings

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emphasise the importance of integrated assessment frameworks, as individual metal concentrations may be high, but their combined effect can vary in environmental significance.

Enrichment Factor (EF)

Enrichment Factor (EF) analysis, using titanium as the immobile reference element, was performed to differentiate between natural and anthropogenic contributions (Equ 3). The rationale for adopting Ti as a reference element is due to the nonavailability of Fe, Al and Sc among the elements considered for analysis. The EF values calculated for several metals are exceedingly high in samples L5-L12. Specifically, EFs for Pb exceed 45,000 in samples L5 and L10–L11 (Table 11), placing them well into the "extremely high enrichment" category (Table 12), signifying severe anthropogenic influence. Similarly, Zn, Cu, and Mo show EFs ranging from 10,000 to over 50,000, strongly indicating external sources such as urban runoff, metal waste dumping, and possibly e-waste leakage. Elevated Th EFs, especially in L11 (621,448), suggest a concentrated input of radioactive heavy minerals, likely linked to felsic lithologies or mining residues. The high EF values across multiple sites suggest the presence of multiple, overlapping contamination sources, both geogenic and anthropogenic, contributing to sediment quality degradation in the study area.

Principal Component Analysis (PCA) with Varimax Rotation

The PCA was conducted to identify the underlying geochemical factors controlling the distribution of heavy metals in stream sediments around Oguro. Varimax rotation was employed to maximise the loading variance and improve the interpretability of the extracted principal components. Three components were retained based on eigenvalues > 1 and cumulative variance exceeding 96.21% (Table 13). Principal Component 1 (PC1) accounts for 63.31% of the total variance and shows strong positive loadings for Pb, Zn, Cu, Ni, and Co, with moderate influence from Mo (Table 13). The close association of these metals indicates a dominant anthropogenic origin, likely linked to urban activities, vehicular emissions, solid waste disposal, and agricultural runoff. These elements are frequently introduced into fluvial systems through municipal discharges, industrial effluents, and phosphate-based fertilisers [14, 15]. The strong loading of Pb and Zn, in particular, aligns with typical patterns in areas impacted by traffic-related pollution and domestic waste [16]. The clustering of these metals under a single component indicates they are co-mobilised in the environment, often associated with fine-grained particles and organic matter.

Principal Component 2 (PC2), accounting for 20.89% of the total variance, is characterised by high loadings of Cr, V, Zr, and Mo, suggesting a lithogenic signature governed by mineralogical composition and natural geochemical processes. These metals are typically associated with lithogenic sources, derived from the weathering of ultramafic to mafic bedrock, heavy mineral enrichment, and resistant mineral phases such as chromite and zircon [17, 18]. Cr and V are common in basic igneous rocks, while Zr is a key constituent of zircon, a highly stable detrital mineral. The presence of Mo may also reflect a lithological control, but could suggest minor input from low-temperature hydrothermal processes or diagenetic remobilisation in anoxic environments. The dominance of these elements in PC2 indicates a geogenic control, representing the mineralogical and geological background signature of the basin, particularly in less disturbed upstream sections of the catchment.

Principal Component 3 (PC3) accounts for 9.00% of the variance and is uniquely dominated by Th (Thorium). Thorium is a naturally occurring, immobile element predominantly hosted in resistant minerals such as monazite and thorite. It is commonly used as a tracer for natural radioactive sources and is rarely influenced by anthropogenic activity [19]. Its behaviour is primarily controlled by the mechanical weathering of Th-bearing accessory minerals and subsequent deposition in sedimentary systems [20]. The exclusivity of Th in this component suggests a distinct radio-elemental control, likely indicative of localised enrichment from granitic or high-grade metamorphic terrains. Hence, PC3 reflects a natural radiogenic signature, which is important for understanding background radiation levels and detrital input in the region.

Table 11: Enrichment Factor Classification

EF<1	EF 1-2	EF 2-5	EF 5-20	EF20-40	EF >40
Background of enrichment	Depletion enrichment	Moderate enrichment	Significant enrichment	Very high enrichment	Extremely high enrichment

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Table 12: Enrichment factor of stream sediment samples

Sample Location	Cr	V	Co	Ni	Cu	Zn	Pb	Th	Zr	Mo
L1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	11000	11846	12320	1779	4800	9585	45100	24672	463	24200
L3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L5	51333	38076	8360	4367	19400	51700	73150	337196	1736	59400
L6	5607	6420	11569	3225	59647	40764	43094	10340	183	11905
L7	7333	5076	5720	1779	17800	23257	34650	148037	173	11000
L8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L9	9533	8123	12144	3008	11520	13671	27720	45644	382	10120
L10	16500	10153	13200	4367	16200	46671	81675	433317	434	19800
L11	25666	16500	10560	4610	12300	47850	77550	621448	521	31900
L12	14666	14868	7354	2842	7200	21955	34414	39652	198	20428

Table 13: PCA of stream sediments samples

Element	PC1	PC2	PC3
Cr	0.115	1.026	0.068
V	0.443	0.906	0.009
Co	1.007	0.147	-0.133
Ni	0.987	0.307	-0.054
Cu	0.993	0.208	-0.136
Zn	0.990	0.310	-0.017
Pb	0.995	0.297	0.025
Th	-0.118	0.088	1.034
Zr	0.190	0.927	0.116
Mo	0.526	0.887	-0.028
Cum. %	63.31	87.20	96.21
Var . %	63.31	20.89	9.00

Therefore, PC1 reflects a multi-source anthropogenic input, emphasising the impact of human activities on the stream sediment chemistry in the Oguro area.

The Hierarchical Cluster Analysis (HCA), based on Ward's linkage and Euclidean distance metric (Figure 2), was employed to identify geochemical associations among heavy metals in stream sediments of the Oguro catchment. This multivariate approach facilitates the classification of elements based on the similarity of their spatial distribution patterns and potential source pathways.

The resulting dendrogram delineates two primary clusters. The first cluster, composed of Pb, Zn, Cu, Ni, and Co, indicates a strong inter-element correlation and suggests a common anthropogenic origin. These metals are widely reported as markers of urban, industrial, and agricultural pollution, often introduced into fluvial systems through runoff, vehicular emissions, or improper waste management [21, 14]. Their proximity within the cluster suggests co-mobilisation under similar geochemical conditions, likely associated with organic matter or fine sediment fractions [15]. This grouping is consistent with PCA and correlation results and reflects the influence of localised contamination sources in the Oguro area.

The second cluster, comprising Cr, V, Mo, and Th, appears at a greater rescaled distance, indicating less statistical similarity with the anthropogenic cluster. These elements are typically of lithogenic origin, naturally derived from the weathering of parent rocks and resistant mineral phases such as chromite and monazite. Their clustering pattern implies a geochemical behaviour governed more by sediment mineralogy and regional geology than by anthropogenic input [17, 18]. Zirconium (Zr**)** emerges as a distinct outlier, forming an independent branch in the dendrogram. This reflects its conservative

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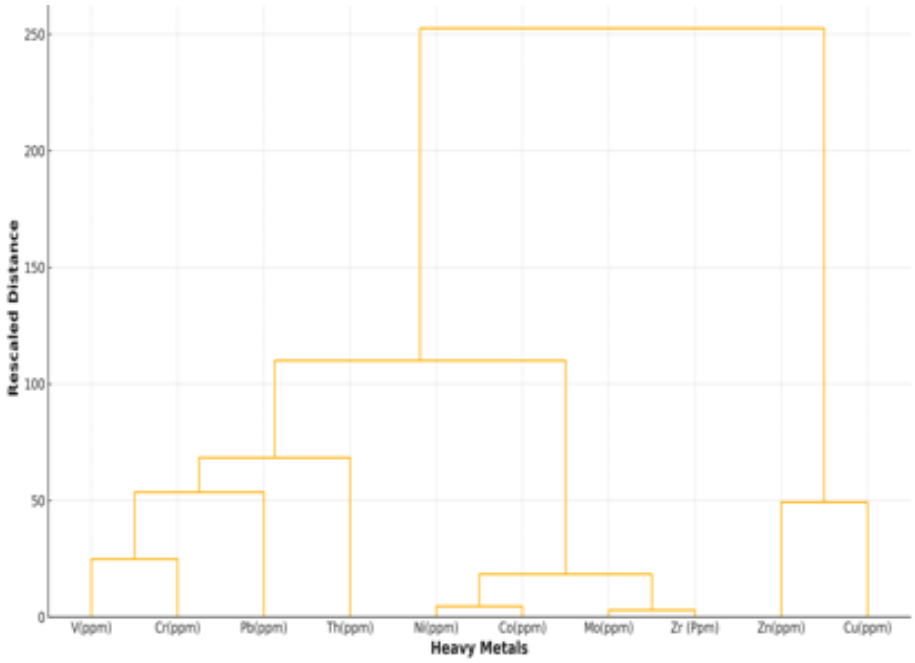

Figure 2: Hierarchical cluster analysis (HCA) dendrogram of heavy metals

behaviour and confinement to highly resistant detrital minerals such as zircon, which are geochemically stable and not readily altered or redistributed under normal surface conditions [20]. The independence of Zr from both anthropogenic and lithogenic clusters underlines its reliability as a tracer of sediment provenance and mineralogical control.

Ecological and Human Health Implications.

The environmental risk measured concentrations were benchmarked against sediment quality guidelines [22]. Table 14 presents the mean concentrations of selected heavy metals in comparison with established Threshold Effect Levels (TELs) and Probable Effect Levels (PELs), providing a benchmark for assessing potential ecological risks in the sediment matrix.

Table 14: Sediment quality guidelines (tel/pel) versus measured mean concentrations.

Metal	Mean Concentration (ppm)	TEL (ppm)	PEL (ppm)
Pb	11.34	35	128
Cu	21.14	18	197
Zn	28.87	123	271

The Probable Effect Levels (PELs) for Pb, Cu and Zn are (128 ppm, 197 ppm and 271 ppm). While mean values remain below PELs, samples L5 and L6 approach 50–75 % of these thresholds for Cu and Pb (Table 1), suggesting potential adverse effects on benthic fauna under episodic loading. Elevated EF and I_geo for Pb and Cu indicate bioavailable fractions capable of bioaccumulating in fish and entering the human food chain [23]. Consequently, implementation of riparian buffer zones, optimised agrochemical practices, and enhanced community waste management is recommended to mitigate these emerging ecological and public health risks.

Conclusion

The geochemical assessment of Oguro stream sediments reveals that, while background concentrations of lithogenic elements such as Cr, V, Ni, Th, and Zr largely conform to Taylor's (1964) crustal baselines, significant pollutants including Cu, Zn, Pb, and Co exhibit pronounced spatial heterogeneity (CVs > 96 %), elevated geoaccumulation indices (I_geo > 12), contamination factors (CF > 3), and extreme enrichment factors (EF > 40), identifying discrete anthropogenic hotspots driven by agricultural runoff, domestic effluents, and vehicular emissions. Although the composite Pollution Load Index (PLI < 0.5) indicate that the broader catchment remains within minimally disturbed thresholds, multivariate analyses elucidate two dominant source regimes: a mixed-source anthropogenic cluster (Pb,

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Zn, Cu, Ni, Co) and a geogenic assemblage (Cr, V, Mo, Th, Zr). The convergence of Principal Component Analysis and Ward-linkage hierarchical clustering reinforces the delineated groupings, highlighting the co-mobilisation of anthropogenically derived metals and the geochemical stability of lithogenic tracers.

These results not only identify priority areas for targeted remediation but also establish a robust methodological framework for future environmental monitoring and risk mitigation in semi-urban, agriculturally intensive watersheds.

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