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Evaluation of the Source of Heavy Metals in Stream Sediments of Itapaji-Ekiti, Southwest Nigeria; Insights from Provenance, Risk Assessment and Statistical Analysis

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Abstract

This study investigates the geochemical composition of stream sediments in parts of sheet 244, Ado-Ekiti, to understand rock-water-soil interactions, sediment provenance, and potential contamination. Seventeen sediment samples were collected from streams and rivers at a depth of 15–25 cm, air-dried for five days, stored in labeled bottles and analyzed using X-ray fluorescence. Results show that SiO_2 is the most abundant oxide (71.29 wt. %), indicating highly siliceous sediments. Lower SiO_2 concentrations in some samples may result from mineral substitution or leaching of aluminosilicate minerals. Al_2O_3 levels suggest abundant feldspars and micas, while low K_2O and Na_2O concentrations indicate minimal clay mineral content and feldspar leaching. The Na_2O/Al_2O_3 vs K_2O/Al_2O_3 discriminant diagram showed a positive correlation, while binary plots indicate sediment provenance from mafic to felsic igneous rocks. Heavy metal analysis showed moderate contamination by Cr and Cd, with Pb exhibiting considerable contamination factors, leading to an overall low to moderate degree of contamination. The likely sources are sewage effluent discharge and/or agricultural chemical use, which pose risks to water quality, soil health, and aquatic ecosystems. This study underscores the need for continuous monitoring and mitigation strategies to minimize heavy metal pollution and protect environmental and public health in the region.

Keywords: Heavy Metals; Itapaji-Ekiti; Provenance; Risk assessment; Stream Sediment

1.0 Introduction

Sediments symbolize the critical basins for heavy metals in the environment (Gibbs *et al.,* 1977; Adewumi and Laniyan, 2020). Stream sediments are fine mineral deposits and silt located on the streambed. In excess amounts, they can fill in the habitat spaces between stream cobbles and rocks where aquatic organisms live and breed, suffocating the organisms. Stream sediments are combinations of sediments, soils, and rock fragments from the drainage basin upstream of the collection site (Mikoshiba *et al.,* 2006; Laniyan and Adewuni, 2023). A detailed knowledge of the geology of an area, the processes of rock weathering, and sediment formation necessitates a comprehensive understanding of the geochemical movements of elements during weathering and sediment redistribution processes. It is known that factors such as geological setting and mineralogy have a resilient impact on the chemical characteristics of stream sediments and natural waters, affecting the distribution or dispersion of metals (Sahoo *et al.,* 2014; Oyebamiji *et al.,* 2018, Oyebamiji *et al.,* 2024). However, the extent to which these factors interact within active sedimentation processes has received limited attention.

Elements may be mobilized due to natural processes (such as weathering and erosion of geological formations) and man-made activities (land use practices and culture). The movement and bioavailability of these trace elements in the environment greatly depend on some physicochemical characteristics of the environment like pH, organic matter content, speciation or chemical form, and electrical conductivity (Teng *et al.,* 2009; Equeenuddin *et al.,* 2013; Popoola, 2025). Only 30% of the lithosphere is dry land, and the upper surface is affected by some degree of chemical decomposition or physical weathering (Carroll, 1970). The natural processes dominate in sub-Saharan regions through the water-rock-sediment interactions that start and move forward during chemical weathering towards equilibrium by dissolving or leaching bedrock minerals into the solution, eventually settling in sediments.

The mixing of major and trace elements within the environment due to their solubility rate warrants the determination and examination of stream sediments. Heavy metal pollution has become a serious environmental problem in recent times as it has greatly increased the discharge of pollutants to receiving water bodies, which eventually settle in bottom sediments (Oguzie, 2002; Laniyan and Adewumi, 2019). The danger of heavy metals has been aggravated due to their relatively high toxicity and persistent nature in the environment (Aboud and Nandini, 2009). Sediments act as a major reservoir of metals and as a source of contaminants in aquatic environments under favourable conditions (Sarkar *et al.* 2014; Harikrishnan *et al.* 2017; Adewumi *et al.* 2024). This study, therefore, aims to assess the provenance, geochemical characteristics, and potential contamination sources of heavy metals in the stream sediments of Itapaji-Ekiti and its environs.

2.0 Study Area

2.1 Location and Accessibility

The study area falls in part of Ekiti State, Southwestern Nigeria. The areas are Iye, Itapaji and Omu-Titun (Figure 1). There are good road network systems linking the towns to each other. The towns are generally accessible with a good road network, with a few settlements having very bad roads, which posed little difficulty in accessing the areas. The rivers and streams are located mostly near the main roads.

2.2 Drainage and Climate Setting

The proliferation of many smaller channels usually marks the drainage system over the areas of the basement complex rock. The drainage is generally dendritic, while the channels of these smaller streams are dry for many months, especially from November to May. Rivers like Atu, Agboro, Ele, and Afe, among others, were encountered during the mapping. Annual rainfall is about 1300 mm to 1500 mm, and its distribution is bimodal within the hydrologic year. The first peak occurs in June to July, while the second peak occurs in September to October rainy season. The two wet seasons are normally separated by a draught (August break), while the dry season is defined by little or no rainfall between November and April (Ayoade, 1977).

The study areas enjoy tropical climates with two distinct seasons: rainy and dry. The rainy season prevails from April to October, while the dry season is prevalent from November to March. Temperature ranges between 21 °C and 28 °C with high humidity. The South-Westerly and North East trade winds blow in the rainy and dry seasons, respectively. Tropical rain forests exist in the South while guinea savannah predominates in the Northern peripheries. The areas were sparsely vegetated when the mapping and sample collection were carried out in the middle of December.

3.0 Materials and Methods

3.1 Field Sampling

Several notable streams and rivers, including Atu, Agboro, and Ele, were mapped, and sediment samples were collected during fieldwork. Some stream and river channels exhibited rock exposures, while others contained thick sediment deposits. A magnet test on the sediments showed minimal attraction, suggesting potential mineralization in the area. Seventeen stream sediment samples (Figure 1) were randomly collected from various locations at 20–25 cm depth using a hand trowel and shovel, maintaining a minimum spacing of 200 m. The samples were prepared for analysis by air drying for five days to remove moisture. Organic debris and coarse particles were manually removed before grinding the sediments into a homogeneous mixture using a porcelain mortar and pestle. The ground samples were then sieved through a 2 mm mesh to eliminate coarse materials. To minimize environmental contamination during sample collection and preparation, all equipment was thoroughly cleaned before and after use to prevent cross-contamination. Samples were collected using non-reactive tools, and polythene bags were used to avoid external contamination. Strict handling measures were followed during grinding, sieving, and storage to maintain the geochemical purity of the sediments.

3.2 Geochemical Analysis

The samples were treated following the digestion method of Mekonnen *et al.* (2012), using 37 % hydrochloric acid and 69.5 % nitric acid to break down the matrix and release elements for analysis. The treated samples were placed in Ziploc bags and transported to the laboratory for analysis. Major element concentrations were determined using X-ray fluorescence (XRF) at the Department of Chemistry, University of Fort Hare, South Africa.

For the heavy metal analysis, sediment samples were dried in an oven at 105 °C overnight, sieved mechanically using a 0.5 mm sieve, homogenized, and ground to 0.063 mm fine powder. After which, 1.25 g of each sample was digested with 20 mL aqua

regia in a beaker on a thermostatically controlled hot plate. The digest was heated to near dryness and cooled to ambient temperature. Then, 5.0 mL of hydrogen peroxide was added in parts to complete the digestion, and the resulting mixture was heated again to achieve near dryness in a fume cupboard. The resulting digest was allowed to cool, transferred into a 50 mL standard flask, and made up to the mark with de-ionized water. Heavy metal elements were then analyzed by direct aspiration of the sample solution into a Perkin-Elmer model 2380 flame atomic absorption spectrophotometer (AAS).

3.3 Contamination Assessment

3.3.1 Contamination Factor

Several pollution indices were calculated to assess the degree of heavy metal contamination in the stream sediments. The contamination factor (CF) was determined using the equation:

$$CF = \frac{C_{metal}}{C_{background}} \; (1)$$

where C_{metal} is the concentration of the metal in the sediment sample and $C_{background}$ is the background concentration (average crustal abundance or local background values). CF values were classified as: CF < 1 (low contamination), $1 \leq CF < 3$ (moderate contamination), $3 \leq CF < 6$ (considerable contamination), and $CF \geq 6$ (very high contamination).

3.3.2 Pollution Load Index

The pollution load index (PLI) was calculated as the geometric mean of all contamination factors:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots CF_n)^{1/n} \; (2)$$

where n is the number of metals analyzed. PLI > 1 indicates polluted sediments while PLI < 1 suggests unpolluted conditions.

3.4 Provenance Analysis

Provenance discrimination was performed using established geochemical discrimination diagrams and elemental ratios. to distinguish between felsic, intermediate, mafic, and ultramafic source rocks. Major element compositions were plotted on the TiO_2 versus Al_2O_3 binary plot to distinguish between granitic and basaltic source rocks. The TiO_2-K_2O-P_2O_5 ternary plot is used to assess source rock composition. Principal Component Analysis (PCA) and cluster analysis were performed to identify element associations and potential sources. Correlation matrices were constructed to examine inter-element relationships and distinguish between natural geochemical associations and anthropogenic inputs.

4.0 Results

From the results of the geochemical analysis for the major oxides on the stream sediments (Table 1) and the statistical data (Table 2), the following major elements were analyzed, namely: SiO_2, Al_2O_3, Fe_2O_3, TiO_2, K_2O, CaO, MgO, MnO, P_2O_5, Na_2O and Cr_2O_3 respectively. The results revealed that SiO_2 (silica) was found to have the highest concentration among the major oxides analyzed in the stream sediments, with values ranging from 51.46 to 71.29 wt. % and mean concentration of 62.40 wt. % as shown in (Figure 2). The highest concentration of SiO_2 was detected in sample S15, which has a high concentration value of 71.29 wt. %. This showed that the sediments were highly siliceous. The lowest silica concentration was detected in sample S5 with a value of 48.07 wt. %. This could be attributed to substitution by a less stable SiO_2 in the mineral framework (Deer *et al.,* 2013) or as a result of intensive leaching of aluminosilicate minerals such as mica, feldspar, and clay minerals from the parent rock (Nesbitt *et al.,* 1980).

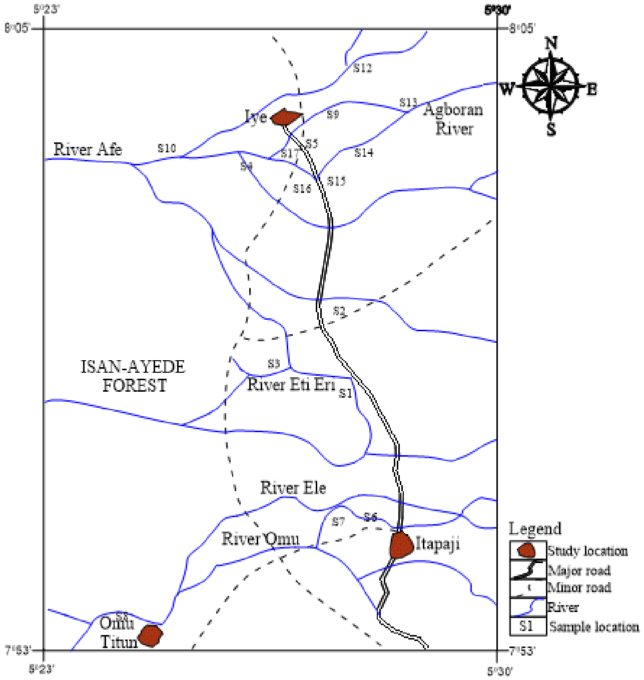


Figure 1: Map showing stream sediment sampling locations

The concentration values of Al_2O_3 in the stream sediments range from 11.44 to 18.87 wt. % with an average value of 13.93 wt. %. The values were high in samples S2, S4, and S5, with their concentration being 18.87 wt. %, 16.53 wt. % and 17.92 wt. % respectively. The abundance of Al_2O_3 in the sediments indicated the presence of abundant feldspars and micas. Aluminum is a conservative element and a major constituent of clay minerals (Rudnick and Gao, 2014). Fe_2O_3 concentration values range from 3.17-19.72 wt. % with an average value of

7.94 wt. %. The values were moderately high in samples S2, S6, and S7, with values of 14.14 wt. %, 11.35 wt. % and 11.88 wt. % respectively. The stream sediments were moderately enriched in Fe_2O_3 with a mean value of 7.94 wt. %. This could be due to the oxidizing conditions the sediment might have gone through (Poulton and Canfield, 2011) or moderately to low concentrations of iron-bearing minerals in the parent rock (Meng *et al.,* 2015).

CaO values range from 0.29-1.34 wt. % and mean concentration of 0.67 wt. %. The highest concentration of CaO in the sediments was found in samples S5 and S17, with concentration values of 1.34 wt. % and 1.21 wt. % respectively. As shown in Table 1, the concentration of CaO was considerably low. This is an indication of the calc-alkaline precursor of the surrounding rocks. Calcium oxide (CaO) is one of the numerous elements that may probably have originated from the calcium-rich amphibole mineral, i.e., hornblende with the chemical formulae $\{Ca_2 (Mg_4Al) (Si_7Al)\}$ contained in the charnockitic rocks in some parts of the study area.

K_2O and Na_2O values range from 1.78-7.89 wt. % and 0.22-1.47 wt. % respectively. The highest concentrations of K_2O and Na_2O were found in samples S10 and S17, with concentration values of 7.49 wt. % and 1.47 wt. % respectively. Generally, the concentrations of K_2O and Na_2O were very low, with an average concentration of 4.67 wt. % (K_2O) and 0.76 wt. % (Na_2O). This indicated that a relatively small proportion of clay minerals were present (Meng *et al.* 2015), and the broken-down feldspars might have leached away (Dixon and von Blanckenburg, 2012).

The occurrence of other major elements was in minute concentration. For instance, the concentration of MgO values in the stream sediments ranges from 0.14 to 0.58 wt. % with an average value of 0.35 wt. %. The highest concentration of MgO in the sediments was found in samples S7 and S11, with concentration values of 0.58wt. % and 0.56 wt. % respectively, while samples S8 and S14 accounted for the lowest concentration of MgO with values of 0.17 wt. % and 0.14 wt. % respectively. The concentration of MgO in the stream sediments was significantly low. The sediments were derived from parent rocks containing moderate to low concentrations of amphibole, olivine, and serpentine. MgO in the stream sediments was formed through erosion, leaching, and other related weathering activities of the ferromagnesian minerals in the amphibolites.

TiO_2 ranges from 0.28-4.12% and has a mean concentration of 1.36%, while major elements such as Cr_2O_3, MnO, and P_2O_5 accounted for the lowest concentration of major elements in wt. % from the samples analyzed. MnO contents range from 0.03 to 0.27 wt. % and an average of 0.13 wt. %. P_2O_5 concentration ranges from 0.05 to 0.24 wt. % and mean value of 0.13 wt. % while Cr_2O_3 had the lowest concentration, ranging from 0.01 to 0.02 wt. % and mean value of 0.01 wt. %.

Table 1: The geochemical result of the stream sediments of the study area.

Sample ID	Al_2O_3	CaO	MgO	Na_2O	K_2O	Cr_2O_3	Fe_2O_3	MnO	P_2O_5	SiO_2	TiO_2	L.O.I.	Sum of Conc.
S1	12.14	0.75	0.37	0.76	4.45	0.01	5.64	0.10	0.13	66.55	1.47	7.73	100.10
S2	18.87	0.34	0.24	0.41	2.95	0.02	14.14	0.18	0.16	51.46	1.74	9.42	99.93
S3	12.76	0.70	0.30	0.77	4.57	0.01	6.89	0.07	0.13	64.80	1.17	7.75	99.92
S4	16.53	0.69	0.30	1.08	7.89	bdl	3.85	0.19	0.08	64.41	0.28	4.31	99.61
S5	17.92	1.34	0.42	0.44	3.52	bdl	3.17	0.03	0.24	48.07	0.52	25.40	101.07
S6	11.44	0.67	0.31	1.01	4.78	0.01	11.35	0.16	0.14	64.85	0.98	4.17	99.87
S7	12.76	0.89	0.58	0.82	4.72	0.01	11.88	0.27	0.17	61.11	1.57	5.55	100.33
S8	13.88	0.45	0.17	0.75	5.87	0.01	6.77	0.09	0.12	64.04	1.55	5.91	99.61
S9	14.36	0.40	0.29	0.53	5.39	0.01	4.49	0.03	0.10	65.43	0.67	8.66	100.36
S10	14.97	0.90	0.22	1.29	7.49	0.01	6.08	0.13	0.15	64.08	0.65	3.51	99.48
S11	15.41	0.43	0.56	0.56	3.75	0.01	9.07	0.05	0.10	60.54	0.90	8.88	100.26

S12	13.68	0.47	0.47	0.54	4.10	0.01	5.15	0.06	0.08	66.31	1.04	7.85	99.76
S13	12.19	0.37	0.27	0.29	2.83	0.01	9.36	0.13	0.10	62.84	2.37	9.51	100.27
S14	11.55	0.29	0.14	0.22	1.78	0.02	19.72	0.23	0.11	52.84	4.12	9.16	100.18
S15	12.82	0.53	0.29	0.78	5.55	0.01	4.48	0.12	0.05	71.29	0.47	3.40	99.79
S16	12.18	0.99	0.42	1.21	4.64	bdl	4.35	0.12	0.17	69.14	1.87	4.60	99.69
S17	13.34	1.21	0.52	1.47	5.13	0.01	8.55	0.24	0.14	63.12	1.83	4.17	99.73

* bdl: below detectable limit

The discriminant diagram of the SiO_2 vs CaO plot (Figure 3) showed a very weak correlation between the SiO_2 and CaO of 0.005. It inferred that there was no significant relationship between the two determinants. On the P_2O_5 vs CaO discrimination diagram (Figure 4), the relationship between both elements was presumably significant and had a positive correlation. Also, the discriminant diagram of Na_2O/Al_2O_3 vs K_2O/ Al_2O_3 plots (Garrels and Mackenzie, 1971) presented a positive correlation between the two ratios (Figure 5).

The geochemical results of the concentration of heavy metals in the stream sediments around the Itapaji-Ekiti are presented in Table 3, while the statistical data are shown in Table 4 and Figure 6. The concentration of Cd in the samples ranged from 0.72ppm to 0.20ppm (avg. 0.32ppm), Pb concentration varied from 91.16ppm to 34.86ppm (avg. 55.14ppm), Ni varied from 41.30ppm to 11.12ppm (avg. 22.35ppm), Zn varied from 91.55ppm to 29.90ppm (avg. 48.96ppm), Cr varied from 170.33ppm to 29.91ppm (avg. 95.70ppm), Ba varied from 2208.83ppm to 690.05ppm (avg. 1278.51ppm), As varied from 7.25ppm to 1.26ppm (avg. 3.75ppm), V varied from 390.44ppm to 50.41ppm (avg. 140.34ppm) and Cu varied from 52.55ppm to 15.40ppm (avg. 27.70ppm). Consequently, arranging the metals in descending order of mean content in this area yields the sequence: Ba >V > Cr > Pb > Zn > Cu > Ni > As > Cd. The concentrations of these heavy metals are similar to the study of (Tchounda *et al.* 2019) in Cameroon and (Harikumar *et al.* 2010) in India, except for Pb and Cr, which are significantly higher.

The threshold effect concentration (TEC) represents the standard of chemical concentrations to which values below would not adversely affect sediment-dwelling organisms (MacDonald *et al.,* 2000). TEC provides an accurate basis for predicting the absence of sediment toxicity. As a result, the mean concentrations of Cd, Ni, Cu and Zn in all sediment samples were lower than the proposed TECs, indicating that these metals had no harmful effects. Elevated Ni and Cu values above the TEC were noticed in S2, S7, S11 and S14, while all the samples had values below TEC for Cd and Zn. On the other hand, the mean concentrations of Cr and Pb were higher than the TEC, and the values of these heavy metals exceeded the TEC values for all the samples. These indicated that these metals had harmful effects.

Table 2: Summary of the statistical data of the major elements for stream sediment.

Major elements	**Max**	**Min**	**Mean**	**Range**	**Standard deviation**
Al_2O_3	18.87	11.44	13.93	7.43	2.181
Cr_2O_3	0.02	0.01	0.01	0.01	0.004
Fe_2O_3	19.72	3.17	7.94	16.55	4.354
K_2O	7.89	1.78	4.67	6.11	1.552
Na_2O	1.47	0.22	0.76	1.25	0.357
MgO	0.58	0.14	0.35	0.44	0.131
CaO	1.34	0.29	0.67	1.05	0.310
MnO	0.27	0.03	0.13	0.24	0.073
P_2O_5	0.24	0.05	0.13	0.19	0.044
SiO_2	71.29	48.07	62.40	23.22	6.173

TiO_2	4.12	0.28	1.36	3.84	0.918

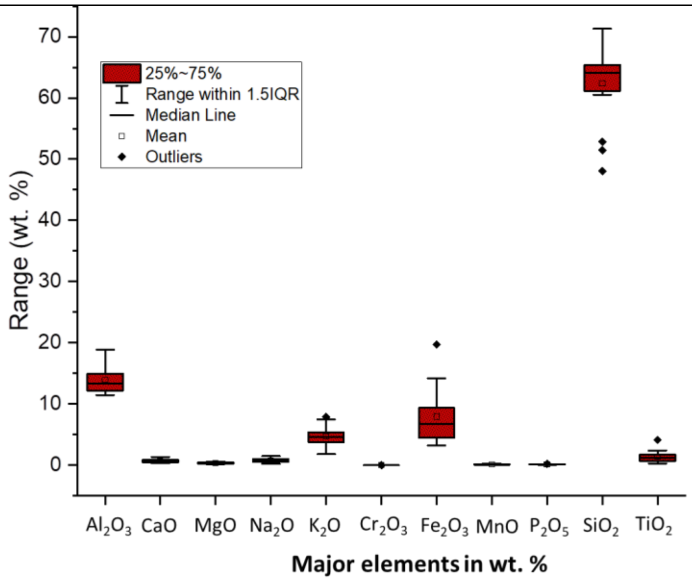


Figure 2: A boxplot of the mean concentration of the major elements.

Table 3: Heavy Metal concentration results in stream sediment samples

Sample ID	Pb	Ba	Cd	As	Ni	Cu	Zn	V	Cr
S1	45.80	1155.72	0.49	3.67	17.25	22.58	42.07	97.20	72.36
S2	73.49	787.13	0.30	7.25	41.30	52.55	51.08	232.67	170.33
S3	47.44	1149.60	0.29	3.92	19.37	26.38	40.55	118.43	109.33
S4	91.16	2208.83	0.10	2.09	11.12	15.40	36.51	63.24	29.91
S5	34.86	987.99	0.21	1.26	15.68	21.20	91.55	50.41	39.65
S6	50.93	1151.13	0.10	5.48	16.69	30.29	29.90	216.32	111.80
S7	40.36	1278.38	0.10	4.01	37.24	32.39	64.00	179.48	141.31
S8	52.62	1343.20	0.36	3.43	16.96	29.65	55.61	97.81	80.51
S9	59.60	1450.24	0.10	3.10	17.08	16.75	42.91	83.73	80.07
S10	63.66	2105.86	0.10	2.83	12.86	20.48	33.09	98.05	64.49
S11	54.12	1150.10	0.23	3.50	28.03	35.92	56.98	156.49	146.45
S12	46.07	1308.83	0.32	2.47	20.80	21.30	45.68	92.98	87.87
S13	45.38	848.93	0.22	3.18	28.39	27.46	53.09	177.44	98.41
S14	65.11	690.05	0.27	5.83	38.00	45.97	65.65	390.44	161.72
S15	62.09	1380.98	0.20	1.86	17.94	19.48	31.96	85.59	63.94
S16	55.19	1239.42	0.72	6.03	18.74	15.47	40.58	81.26	66.68
S17	49.52	1498.34	0.20	3.92	22.49	37.77	51.17	164.26	102.03

Table 4: Summary of statistical presentation of heavy metals in the stream sediment.

Heavy Metals	Max	Min	Range	Mean	Threshold effect Concentration (TEC)
Pb	91.16	34.86	56.30	55.14	35.80
Ba	2208.83	690.05	1518.78	1278.51	-
Cd	0.72	0.20	0.52	0.32	0.99

As	7.25	1.26	6.00	3.75	-
Ni	41.30	11.12	30.18	22.35	22.70
Cu	52.55	15.40	37.16	27.70	31.60
Zn	91.55	29.90	61.65	48.96	121.0
V	390.44	50.41	340.03	140.34	-
Cr	170.33	29.91	140.43	95.70	43.40

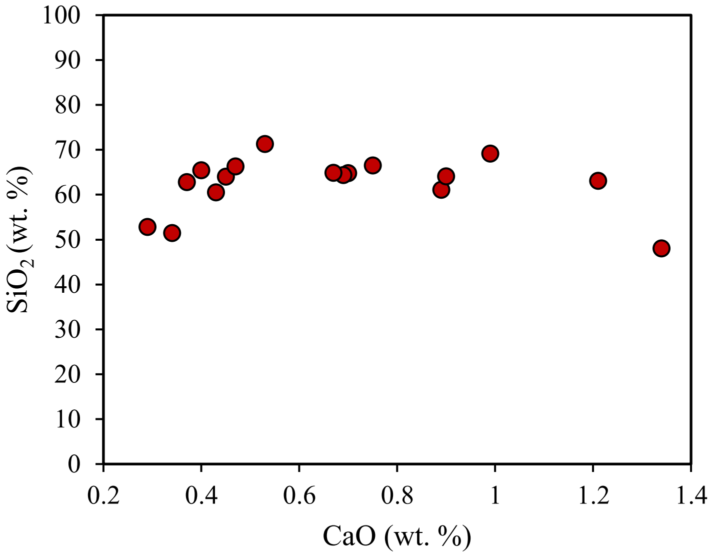


Figure 3: A discriminant diagram of SiO_2 vs CaO plot.

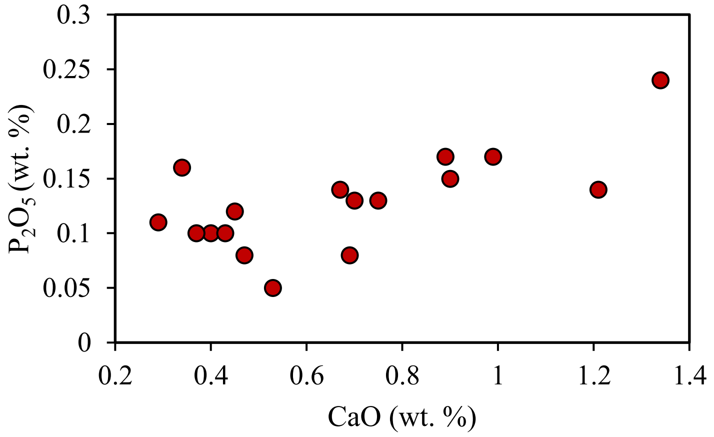


Figure 4: A discriminant diagram of P_2O_5 vs CaO plot.

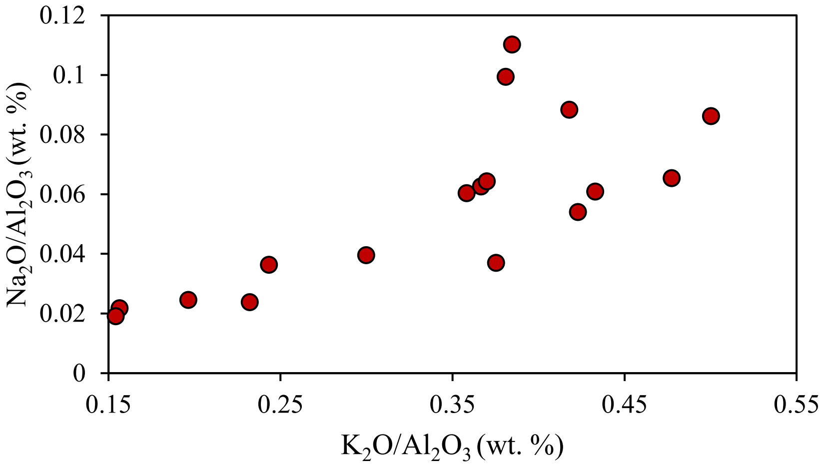


Figure 5: A discriminant diagram of Na_2O/Al_2O_3 vs K_2O/Al_2O_3 plots (Garrels and Mackenzie, 1971).

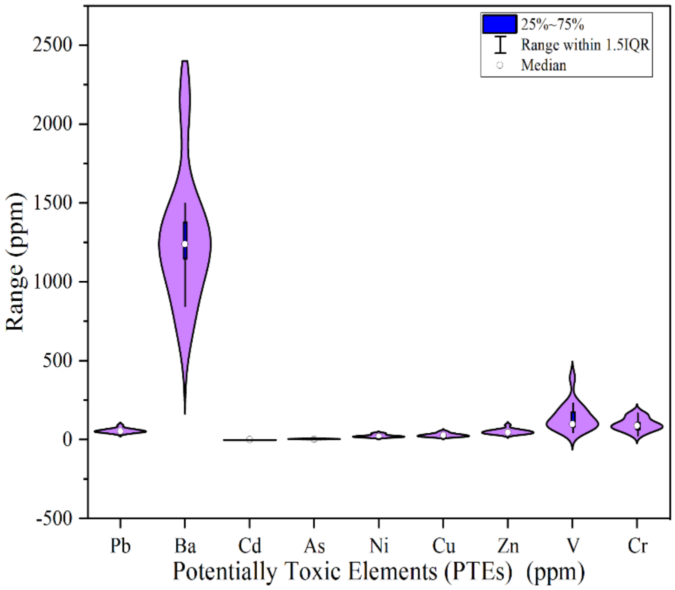


Figure 6: A boxplot of the mean concentration of heavy metals in the stream sediments

5.0 Discussions

5.1 Provenance and tectonic settings of the stream sediments

The Al_2O_3/TiO_2 ratios of most clastic rocks are essentially used to infer the source rock composition (Hayashi *et al* 1997). They suggested that Al_2O_3/TiO_2 ratio range of 3 – 8wt% for mafic igneous rocks, 8 – 21wt% for intermediate rocks, and 21 – 70wt% for felsic igneous rocks. In the study areas, the Al_2O_3/TiO_2 ratios of the stream sediments vary between 2.8 and 59.0wt% (Table 5), inferring a diverse provenance that includes mafic, intermediate, and felsic igneous rocks. This wide range of ratios suggests that the sediments were derived from a heterogeneous source terrain, likely reflecting the complex tectonic and geological history of the region. Similar findings have been reported in other studies, such as those by McLennan *et al.* (1993) and Condie (1993), who emphasized the role of tectonic settings in controlling sediment composition.

Among the analyzed stream sediment samples, four samples (24 %) fall within the range of mafic igneous rocks (3-8wt. %), while eight samples (47%) align with intermediate igneous rocks. Additionally, 5 samples (29 %) correspond to felsic igneous rocks. The distribution of source rock compositions in the stream sediments is illustrated in Figure 7. This mixed provenance is significant because it provides insights into the region's geological evolution, suggesting that the area has experienced multiple phases of magmatic activity and tectonic uplift. Such findings are consistent with studies in other regions with similar geological settings, such as the work of Bhatia and Crook (1986), who highlighted the importance of provenance analysis in reconstructing tectonic histories.

The TiO_2 versus Al_2O_3 (Amajor, 1987) further supports these interpretations. This plot is commonly used to differentiate between granitic (felsic) and basaltic (mafic) source rocks. When applied to the studied stream sediments, the samples plot within fields indicative of intermediate to felsic provenances (Figure 8). This finding aligns with the Al_2O_3/TiO_2 ratios and reinforces the conclusion that the sediments are derived from a mix of igneous sources. The predominance of intermediate to felsic compositions is particularly significant because it suggests that the region may have been influenced by continental arc magmatism or collisional tectonics, as discussed by Taylor and McLennan (1985).

The TiO_2-K_2O-P_2O_5 (AKF) plot of (Garrels and Mackenzie, 1971) for samples in the study area, showed further confirms the predominantly igneous origin of the stream sediments (Figure 9). This is consistent with the geochemical signatures observed in other regions with active or ancient magmatic activity, such as the studies by Nesbitt and Young (1982) on sedimentary provenance. The igneous origin of the sediments is significant for understanding the region's rock-water-soil interactions, as it implies that weathering and erosion of igneous bedrock have played a major role in shaping the geochemical composition of the stream sediments.

Table 5: The Al_2O_3/TiO_2 ratios of stream sediments in the study area to infer the source rock composition (Hayashi *et al.,* 1997).

S/N	**Sample ID**	**Al_2O_3**	**TiO_2**	**Al_2O_3/TiO_2**
1	S1	12.14	1.47	8.3
2	S2	18.87	1.74	10.8
3	S3	12.76	1.17	10.9
4	S4	16.53	0.28	59.0
5	S5	17.92	0.52	34.5
6	S6	11.44	0.98	11.7
7	S7	12.76	1.57	8.1
8	S8	13.88	1.55	9.0
9	S9	14.36	0.67	21.4
10	S10	14.97	0.65	23.0
11	S11	15.41	0.90	17.1
12	S12	13.68	1.04	13.2
13	S13	12.19	2.37	5.1
14	S14	11.55	4.12	2.8
15	S15	12.82	0.47	27.3
16	S16	12.18	1.87	6.5
17	S17	13.34	1.83	7.3

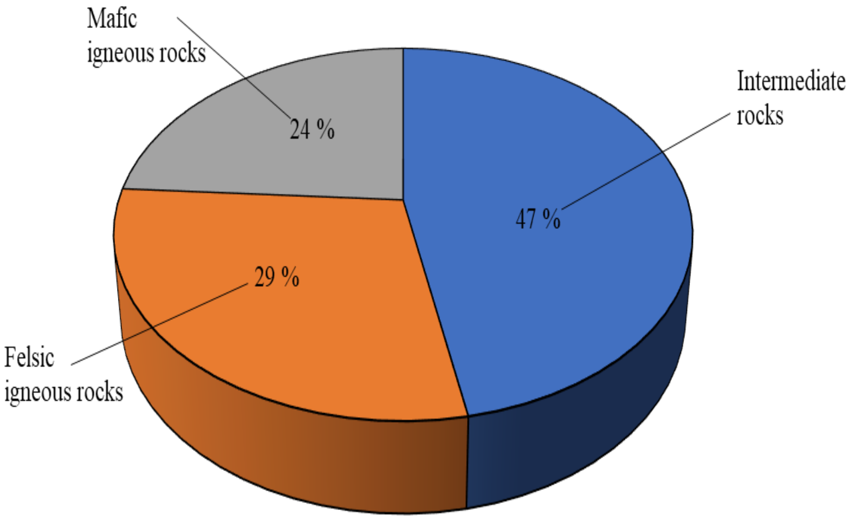
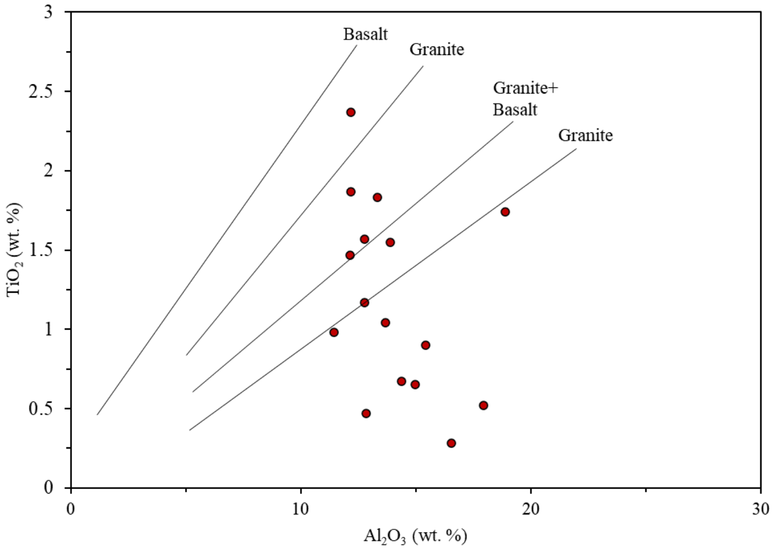


Figure 7: Percentage source rock composition in the stream sediments (Hayashi *et al.,* 1997).



Fiure 8: The TiO_2 versus Al_2O_3 binary plot to distinguish between granitic and basaltic source rocks (Amajor, 1987).

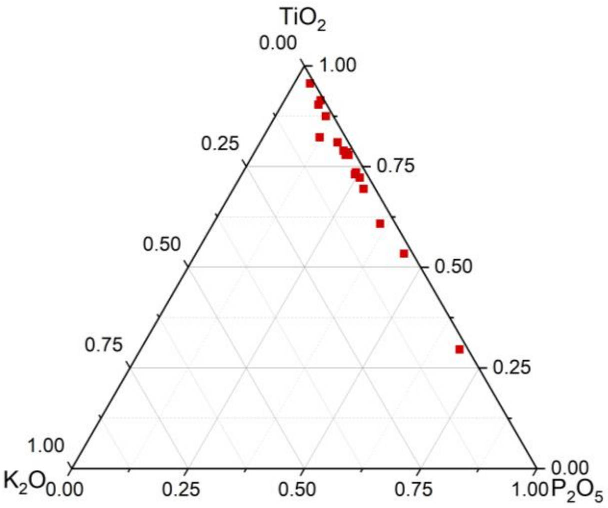


Figure 9: TiO_2-K_2O-P_2O_5 plot of Stream sediments in the study area (Garrels and Mackenzie, 1971).

5.2 Indices of Sediment Contamination

5.2.1 Heavy Metal Concentration in the Sediments

Heavy metals concentration in bottom sediments is an unbiased and reliable index of water contamination and total anthropogenic load (Perin et al., 1997). To evaluate the contamination of metals in sediments, a comparison is made with the background value and sediment quality guidelines (SQG) given in Table 6 below, calculation of indices of contamination such as the contamination factors (CF), degree of contamination (DC) and the Pollution Load Index (PLI) were employed.

The background values refer to the average concentration of heavy metals in uncontaminated sediments suggested by Martin and Meybeck (1979) and are as follows: Pb = 16, Cu = 32, Zn = 127, Cr = 71, Cd = 0.2. The heavy metal concentrations and the statistical table of heavy metal concentration in sediments for each sampling location for this study are shown in Tables 3 and 4, respectively. The mean concentration of the metals was: Pb: 55.14 ppm; Cd: 0.32 ppm; Cr: 95.70 ppm; Cu: 27.70 ppm; Zn: 48.96 ppm dry weights, allowing to arrange the metals from higher to lower mean content in this area as: Cr>Pb > Zn > Cu> Cd.

Table 6: USEPA Guidelines for sediments (ppm dry weights)

				Present study	
Metal	**Not polluted**	**Moderately polluted**	**Heavily polluted**	**Mean**	**Interpretation**
Pb	<40	40 - 60	>60	55.14	Moderately Polluted
Cd	….	…	>6	0.32	Not polluted
Cr	<25	25 - 75	>75	95.70	Heavily polluted
Cu	<25	25 - 50	>50	27.70	Moderately polluted
Zn	<90	90 - 200	>200	48.96	Not polluted

Comparing these values to the Sediment Quality Guidelines (Table 6), the concentrations of Zinc (Zn) and Cadmium (Cd) can be classified as unpolluted, Lead (Pb) and Copper (Cu) are moderately polluted, and Chromium (Cr) heavily polluted. The high concentrations of Cr in sediments could be attributed to effluent discharges from sewages and the use of chemicals in agricultural activities in the catchment area. The high levels of Cu and Pb in sediments could also be attributed to the run-off from using chemicals containing copper in agricultural activities. This indicates that most inhabitants living within the catchment area were mainly farmers who used fertilizer and chemicals to cultivate their vegetables and cocoa. Chemicals used in farming mostly contain heavy metals such as lead, which accumulate in the soil. Moreover, grease and soap from car washing activities could contain some heavy metals, and these degrade water quality as most of the communities in the catchment use these rivers for domestic, recreational, farming, fish farming, and the washing of vehicles. The use of various iron salts as coagulants in water treatment could also lead to high lead concentrations in this water.

5.2.2 The Contamination Factor (CF)

The contamination factor is used to determine and to get a fair idea of the extent of anthropogenic pollution and accumulation of heavy metals in the sediments at the various sampling locations. In this study, the world surface rock average proposed by Martin and Meybeck (1979) is considered background concentration for the Contamination factor calculation. The Contamination factor (CF) at various points in the stream and rivers is shown in Table 7 below.

Table 7: Table showing the calculated contamination factor for the sediments

Sample ID	**Contamination Factor (CF)**				
	Pb	**Cu**	**Zn**	**Cr**	**Cd**
S1	2.86	0.71	0.33	1.02	2.45
S2	4.59	1.64	0.40	2.40	1.50
S3	2.97	0.82	0.32	1.54	1.45
S4	5.70	0.48	0.29	0.42	0.50
S5	2.18	0.66	0.72	0.56	1.05
S6	3.18	0.95	0.24	1.57	0.50
S7	2.52	1.01	0.50	1.99	0.50
S8	3.29	0.93	0.44	1.13	1.80
S9	3.73	0.52	0.34	1.13	0.50
S10	3.98	0.64	0.26	0.91	0.50
S11	3.38	1.12	0.45	2.06	1.15
S12	2.88	0.67	0.36	1.24	1.60
S13	2.84	0.86	0.42	1.39	1.10
S14	4.07	1.44	0.52	2.28	1.35
S15	3.88	0.61	0.25	0.90	1.00
S16	3.45	0.48	0.32	0.94	3.60
S17	3.10	1.18	0.40	1.44	1.00
Max	5.70	1.64	0.72	2.40	3.60
Min	2.18	0.48	0.24	0.42	0.50
Range	3.52	1.16	0.48	1.98	3.10
Mean	3.45	0.87	0.39	1.35	1.27

Hakanson (1980) classified Contamination Factors into four groups: $CF < 1$ refers to a low contamination factor; $1 \leq CF < 3$ refers to a moderate contamination factor; $3 \leq CF < 6$ refers to the considerable contamination factors; $CF \geq 6$ refers to a very high contamination factor as shown in Table 8.

From the result, the calculated contamination factor (Cf), lead (Pb), had values ranging from a low value of 2.18 to a highest value of 5.70 (Mean = 3.45). Copper (Cu) also obtained a low contamination value of 0.48 and a highest value of 1.64 (Mean-0.87). Contamination factor (Cf) value for Zn also ranged from 0.24 to 0.78 (Mean = 0.39). Chromium (Cr) also obtained a low contamination value of 0.42 and the highest value of 2.40 (Mean = 1.35), and CF values for Cadmium (Cd) ranged from 0.50 to 3.60 (Mean-1.27). The Mean values of the concentration factor (C.F) for the above-stated metals in the analyzed sediments are interpreted as follows: Cu and Zn have low contamination, Cr and Cd have moderate contamination, while Pb has a considerable contamination factor based on Hakanson (1980) classification.

Table 8: Classification and terminologies used for the Contamination Factor of metals (Hakanson, 1980)

Contamination Factor (CF)	**Description**
CF < 1	Low degree of contamination
1 < CF < 3	Moderate degree of contamination
3 < CF < 6	Considerable degree of contamination
CF > 6	Very high degree of contamination

The variation in the result of these heavy metals is that they are not fixed permanently due to changing environmental conditions; they may be released to the water column by various remobilisation processes (Allen and Martynov, 1995). This phenomenon poses a risk of secondary water pollution by heavy metals under sediment disturbance and/or changes in sediment chemistry.

5.2.3 The Degree of Contamination (DC)

The degree of contamination value is the contamination status of the sediment in the study, giving a standardized description of sediment contamination (Hakanson, 1980). The degree of contamination (DC), defined as the sum of all contamination factors for a given basin, was also used in the study. For the description of the degree of contamination, the following classification and terminologies were adopted (Hakanson, 1980): Dc < 7 low degree of contamination; 7< Dc <14 moderate degree of contamination; 14≤ Dc <28 considerable degree of contamination; Dc > 28 very high degree of contamination. The summary of the classification and terminologies used by Hakanson (1980) is shown in Table 9.

The degree of contamination (DC) result obtained in this study is presented in Table 10. For this study, the degree of contamination (DC) for all the samples ranges from a low degree of contamination to a moderate degree of contamination. This suggests low input of heavy metals from anthropogenic sources.

Table 9: Classification and Terminologies Used for the Degree of Contamination (DC) of Metals (Hakanson, 1980)

Degree of contamination (DC)	**Description**
DC < 7	Low degree of contamination
7< DC <14	Moderate degree of contamination
14≤ DC <28	Considerable degree of contamination
DC > 28	Very high degree of contamination

Table 10: Degree of contamination of river sediments in the study area

Sample ID	**Degree of Contamination**	**Interpretation**
S1	7.37	Moderate Degree of Contamination
S2	10.53	Moderate Degree of Contamination
S3	7.10	Moderate Degree of Contamination
S4	7.37	Moderate Degree of Contamination
S5	5.17	Low Degree of Contamination
S6	6.44	Low Degree of Contamination

S7	6.52	Low Degree of Contamination
S8	7.59	Moderate Degree of Contamination
S9	6.22	Low Degree of Contamination
S10	6.29	Low Degree of Contamination
S11	8.16	Moderate Degree of Contamination
S12	6.75	Low Degree of Contamination
S13	6.61	Low Degree of Contamination
S14	9.66	Moderate Degree of Contamination
S15	6.64	Low Degree of Contamination
S16	8.79	Moderate Degree of Contamination
S17	7.12	Moderate Degree of Contamination

5.2.4 The Pollution Load Index (PLI)

The pollution load index (PLI) for the sediments at each site was evaluated following the method of Tomlinson *et al.* (1980). This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution and can be expressed as:

The calculated PLI for this study indicates that the sediments are both polluted and non-polluted (Table 11). Stream sediment Samples S4, S5, S6, S9, S10, S12, S16, and S15 have low Pollution Load Index and are characterized not to be polluted based on classification by Seshan et al. (2010) while Samples S1, S2, S3, S7, S8, S11, S13, S14, and S17 are considered to be polluted. It is noted in Table 11 below that the Pollution Load Index for samples S2, S11, and S14, with PLI values of 13.24, 14.93, and 11.46, respectively, are excessively high compared to others. These samples are, therefore, regarded to be heavily polluted. High PLI values in samples S2, S11, and S14 result from the high concentration of chromium and lead in the samples.

5.3 Multivariate statistical analysis

The statistical relationship concerning dissimilar elements is frequently adopted to decide whether the considered elements have a common source, and it is commonly reflected that elements with an obvious positive correlation may display similar sources. Correlation coefficient values between 0.9 and 1 are considered very high, correlation coefficients between 0.7 and 0.9 are deemed high, between 0.5 and 0.7 are moderate, 0.3–0.5 low correlation, and < 0.3 low correlation (Hugh, 1993). High correlation coefficients specify the occurrence of comparable geochemical processes, influences, and responses affecting metal distributions. Cross-elemental association in the stream sediments proposes diverse geochemical processes accountable for the metal composition in the samples. In the stream sediment samples, a strong positive correlation exists between As-Ni (0.601), As-Cu (0.649), As-V (0.669), As-Cr (0.698), Ni-Cu (0.829), Ni-V (0.769), Ni-Cr (0.890), Cu-V (0.822), Cu-Cr (0.884) and V-Cr (0.885) suggesting that these elements could originate from same source (Table 12). Also, a strong negative correlation was observed between Ba and other elements such as Ni, Cu, Zn, V, and Cr, suggesting that these elements may have originated from different sources.

The principal component (PC) analysis for stream sediments revealed a three-component model, as presented in Table 13. The PC1 consisted of the following metals: As, Ni, Cu, Zn, V, and Cr. It accounted for 51.71% of the variance (Figure 10). The PC2 consists of the following metals, Pb and Ba, accounting for 19.48% of the total variance. Ba displayed a negative correlation with the other elements, so it can be inferred that they were anthropogenically influenced. In PC3, Cd accounted for 14.48% variance, and Cd was poorly correlated with other elements. It may have been formed by adsorption of the metal by its oxide in the samples. Even though the statistical analysis might group the elements, they remained anthropogenically introduced into the samples.

Table 11: Pollution load index of river sediments in the study area

Sample ID	Pollution Load Index	Interpretation
S1	2.05	Polluted
S2	13.24	Polluted
S3	2.13	Polluted
S4	0.20	Non-Polluted
S5	0.74	Non-Polluted
S6	0.70	Non-Polluted
S7	1.55	Polluted
S8	3.34	Polluted
S9	0.46	Non-Polluted
S10	0.37	Non-Polluted
S11	14.93	Polluted
S12	1.68	Polluted
S13	1.92	Polluted
S14	11.46	Polluted
S15	0.65	Non-Polluted
S16	2.19	Polluted
S17	2.57	Polluted

Hierarchical Cluster Analysis (HCA) is universally used to investigate the causes of pollution or the sources of associated elements. The results of HCA can reveal the interactions among the analyzed elements, between and within the groups. The elements from varied origins are grouped according to the maximum and minimum levels of clustering similarity. HCA can frequently be employed as a secondary method to corroborate the results of PCA analysis and simplify the grouping of variables. The results of HCA for the stream sediments studied are shown in Figure 11. These elements can be classified into three groups: (1) As-Ni-Cu-Zn-V-Cr.; (2) Pb-Ba; and (3) Cd. The results of the correlation coefficient and the PCA agreed well with the cluster analysis and hence helped to interpret the data. The linkage and clustering pattern of the trace elements in the media indicated three clusters. This was generally consistent with the PCA results.

Table 12: Pearson correlation matrix for the elements in the stream sediments

	Pb	Ba	Cd	As	Ni	Cu	Zn	V	Cr
Pb	1								
Ba	0.446	1							
Cd	-0.166	-0.327	1						
As	0.168	-0.479	0.373	1					
Ni	-0.033	**-0.655**	0.009	**0.601**	1				
Cu	0.056	**-0.574**	-0.079	**0.649**	**0.829**	1			
Zn	-0.440	**-0.490**	-0.012	-0.111	0.395	0.325	1		
V	0.107	**-0.567**	-0.113	**0.669**	**0.769**	**0.822**	0.184	1	
Cr	-0.045	**-0.612**	-0.055	**0.698**	**0.890**	**0.884**	0.186	**0.825**	1

Table 13: The result of principal component analysis for stream sediments in the study area

	Coefficients of PC1	**Coefficients of PC2**	**Coefficients of PC3**
Pb	-0.041	0.653	-0.004
Ba	-0.357	0.360	-0.159
Cd	0.041	-0.217	0.799
As	0.348	0.244	0.425
Ni	0.428	0.004	-0.104
Cu	0.425	0.107	-0.144
Zn	0.169	-0.530	-0.327
V	0.409	0.182	-0.111
Cr	0.434	0.108	-0.072
Eigenvalue	4.654	1.753	1.303
Percentage of Variance	51.71%	19.48%	14.48%
Cumulative	51.71%	71.19%	85.66%

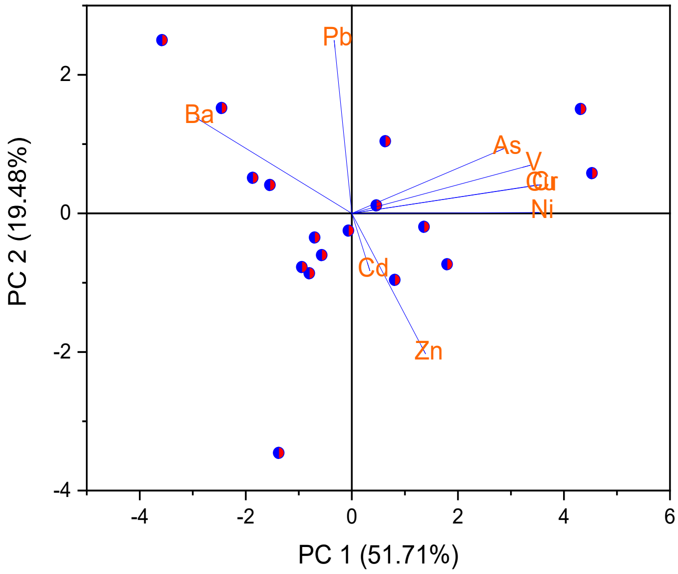


Figure 10: Two-dimensional principal component loading plot of the PCA results for stream sediments

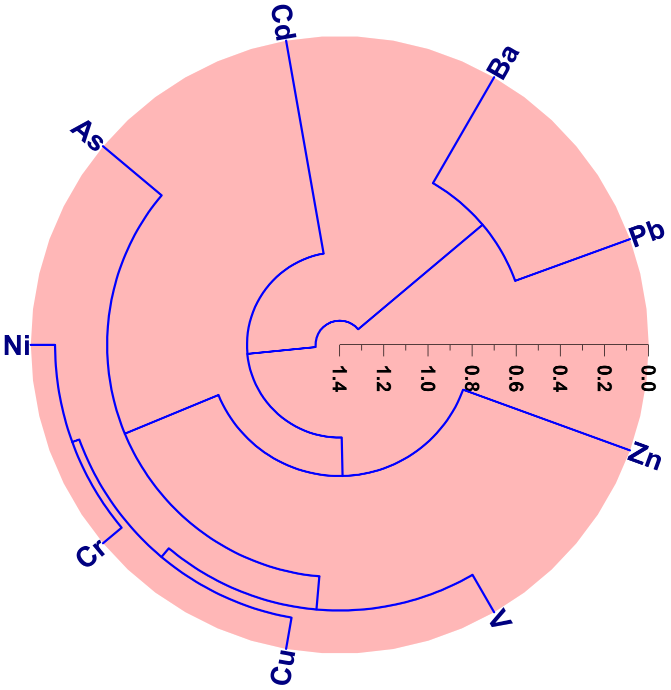


Figure 11: Dendrogram of HCA of the concentration of elements in the stream sediment

5.4 Implications for Contamination and Environmental Risks

Despite the geochemical data pointing to a natural igneous provenance, the potential influence of anthropogenic contamination cannot be overlooked. Agricultural activities, sewage discharge, and industrial effluents introduce heavy metals and other pollutants into stream sediments (Alloway, 2012; Li *et al.,* 2014). For instance, elevated levels of heavy metals such as Pb, Cd, and Zn in some samples may reflect contamination from agricultural runoff (e.g., fertilizers and pesticides) or untreated sewage. Studies by Huang *et al.* (2007) and Wei and Yang (2010) have demonstrated similar contamination patterns in regions with intensive agricultural and urban development.

The broader environmental and public health risks associated with heavy metal contamination in stream sediments are significant. Heavy metals can accumulate in the food chain, posing risks to local communities that rely on stream water for drinking, irrigation, or fishing (Wuana and Okieimen, 2011). For example, cadmium and lead are known to cause severe health issues, including kidney damage, neurological disorders, and developmental problems in children (Järup, 2003). The potential for heavy metal contamination in the study area is particularly concerning, given the reliance on local water resources for agriculture and domestic use. This highlights the need for further investigation into the sources and extent of contamination and the implementation of mitigation measures to protect public health and the environment.

6.0 Conclusions

The study revealed that silica is the dominant oxide in the stream sediments, indicating that the sediments are highly siliceous. The abundance of Al_2O_3 in the sediments indicated the presence of abundant feldspars and micas, while the low concentration of K_2O implies a relatively small proportion of clay minerals due to the leaching of broken-down feldspars. The discriminant diagrams indicate that the sediments are largely of igneous origin, with their provenance ranging from mafic to intermediate to felsic igneous rocks.

The findings also highlight the presence of moderate contamination by Cr and Cd and considerable contamination by Pb, with a low to moderate overall degree of contamination. These heavy metals pose potential environmental and health risks, likely stemming from anthropogenic activities such as effluent discharges from sewage systems and the use of agricultural chemicals in the area. The Pearson correlation and hierarchical cluster analysis confirmed significant positive associations among selected metals, suggesting common sources or similar geochemical behaviors.

These findings highlight the need for proactive environmental management strategies to mitigate heavy metal contamination in the study area. Given the moderate contamination levels of Pb and Cr, continuous monitoring programs should be implemented to track heavy metal concentrations in stream sediments over time. Promoting public awareness and adopting improved waste management practices, including proper disposal of industrial and sewage effluents, are essential to prevent further contamination and ensure the sustainability of the ecosystem and the well-being of local communities.

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