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Table of Content: Volume 10 Number 4 May 2018

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Full Length Research Paper

Assessment of the distribution of potentially harmful trace elements in bedrocks and stream sediments of Okemesi-Ijero area, Southwestern, Nigeria

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Assessment and distribution of the concentration of potentially harmful trace elements (PHTEs) is important for environmental health management. The concentrations of thirteen PHTEs were determined in the stream sediments and rocks samples from the underlying bedrock with the use of inductively coupled plasma-mass spectrometry (ICP-MS). Multivariate statistics and principal component analyses were used to identify and characterize trace elemental associations in the system. Trace elements ranged from 0.01 mg/kg as found in Cd concentration to 1591.00 mg/kg as found in Mn. Trace element concentrations vary from one location to another. The geochemistry of the underlying rocks including granite, quartzite and banded gneiss were far lower in metal concentration compared to that of the stream sediments. The concentrations of U (0.40 – 14.40 mg/kg), Mn (51.00 - 1591 mg/kg) and La (7.10 – 364.90 mg/kg) were of great concern to the ecosystem because of their relatively higher values in the stream sediments compared with the control, which is the average earth crust values. The results of enrichment factor and ecological risk index showed that Cu, Pb, As and Cd did not raise any eco-toxicological concern. From the results of the other elements analysed, there were considerable lower metal enrichment in terms of contamination status when compared with the background values. Metals such as Cr, Mn, Pb, Zn, Cu, Ni, V, As, Th, Cd, and La were positively correlated with each other (r = 0.51 - 0.95), which indicated analogous sources of geochemical characteristics. However, from the result, it is seen that there is considerable input of the metal concentration in the stream sediments possibly from man induced activities of these PHTEs in the drainage system of the catchment areas.

Key words: Harmful trace elements, ecological risk, ecosystem, Okemesi, Ijero, stream sediment.

INTRODUCTION

The accumulation of potentially harmful trace elements (PHTEs) has significant effect on human and animal health within an ecosystem. The accumulation of these PHTEs is often aided by weathering of bedrocks that host these elements and also because of increasing mining activities particularly by artisanal miners, where

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environmental control measures are poor, these elements are easily carried as dissolved ions by infiltrating runoff and streams. When the conditions are favourable, these PHTEs are then released and accumulate in stream sediments in either relatively low concentrations or in excessive amounts and migrate in such environment. Chang et al. (2014) noted that the cumulative effects and long-term interactions in these medium negatively affects regional ecosystem safety and poses a threat to humans, animals and plants in such environment. Studies (Berrow, 1991; Mikoshiba et al., 2006; Davies and Abowei, 2009) have shown that bedrock and stream sediments are useful media for the assessment of environmental pollution because accumulated sediments contribute to the quality of surface run-off, rivers as well as ground water. Since stream sediment largely makes up an important component of the river system, its geochemistry has increasingly received attentions because of the potential long-term toxicity occasioned by the presence of harmful elements. Elements such as Pb, Zn, Cd, U, As and Cr etc. are significantly of great concern to the ecosystem.

Assessment of the distribution of such PHTEs in bedrocks and stream sediments is important for the area. It is of particular importance because of the long history of some artisanal mining activities and also for records of intense weathering of rocks which has contributed to sedimentation along stream channels in the area. The selection of bedrock and stream sediment geochemistry for the area is due to the genetic relationship between the two media. It is believed that the underlying bedrocks are the parent hosts of the PTHEs, their natural and artificial disintegration by tropical weathering and mining activities respectively releases these PHTEs as trace elements. The trace elements are then leached into the waters and are quickly incorporated as part of sediments carried by surface run-off and accumulate deep within the layers or bottom of the sediments. Studies (Hansen et al., 1993; Samarghandi et al., 2007; Seshan et al., 2010) have shown that bottom sediments contain significant high concentration of metals.

This study focuses on the assessment of the potentially harmful elements (PHTEs) in the bedrocks and stream sediments along major and minor river systems that drain the study area. Effort was also made to identify the sources of the trace metals enrichment and quantify the status of accumulation for PHTEs discrimination for the studied area. The assessment for the study area is important because the area is occupied by many suburban communities and villages, whose inhabitants depend largely on the streams for drinking as well as for all year round agricultural activities. The area is also notably known to host mineral resources of economic value such as gold, gemstones and industrial minerals (Ayodele, 2012), attracted artisanal mining. The mining activities were indiscriminately carried out in the affected localities of the study area.

Geomorphology and drainage system

The morphology of the landforms is characteristically defined by series of highlands and lowlands, which are the reflection of the underlying geology in the area. The topography is generally characterized by elevations between 250 and 610 m above the sea levels. The northern part of the study area has elevation between 400 and 600 m while the southern parts show elevation ranges of 250 to 400 m. The migmatitic gneiss and quartzite-quartz schist forms major hills, while quartz-mica schist forms dominant low lands. The drainage system has a dendritic drainage pattern and the stream channels appear to be structurally controlled with the rivers flowing southwards except in tributaries where they flow in W-E and E-W directions to join the main rivers flowing south. Notable amongst these rivers are River Yaro, Arire and Obebe in the eastern parts, while River Oya, Isa and Oshun in the western part of the study area.

Geologic setting

The study area is located within Ilesha Schist Belt within latitudes 7° 45'N to 8° 00'N and longitudes 4° 52'E to 5° 08' covering a total surface area of 821.4 km^2. This area is part of the basement complex of Nigeria, which lies within the Pan-African Province of West Africa (Figure 1) between two cratons of Archaean to Lower Proterozoic ages: the West African craton to the west and the Congo craton to the southeast (Turner, 1983). The Nigerian basement represents the southern part of the Trans-Saharan mobile belt (Caby, 2003; Ferre et al., 2002). The Ilesha Schist Belt (ISB) is generally considered as to be relicts of a supracrustal cover which was infolded into the migmatite gneiss complex. Adekoya (1996) indicated that the ISB consist of low to medium grade metamorphic rocks of mainly sedimentary and minor igneous origin, which were presumably deposited on the pre-existing migmatite-gneiss-quartzite basement and are therefore called supra-crustal cover rocks. The ISB is generally underlain by migmatite and gneisses which are overlain by amphibolites, ultramafics and gabbros, quartzites, pelitic and calcareous schists, metavolcanics and minor intrusion of granites and pegmatites (Elueze, 1988; Caby and Boesse, 2001). The dominant rock in the study area (Figure 2b) is the quartzites of the Effon Psammite Formation (Odeyemi, 1993), occurring as massive quartzites and laminated by schistose quartzites and quartz schists within low-lying mica-schist to the west and the migmatites and gneisses to the east. The granites occur in the south and the charnockites in the northwestern sector of the area.

MATERIALS AND METHODS

Collection of samples

Eighty samples comprising forty rocks and stream sediments

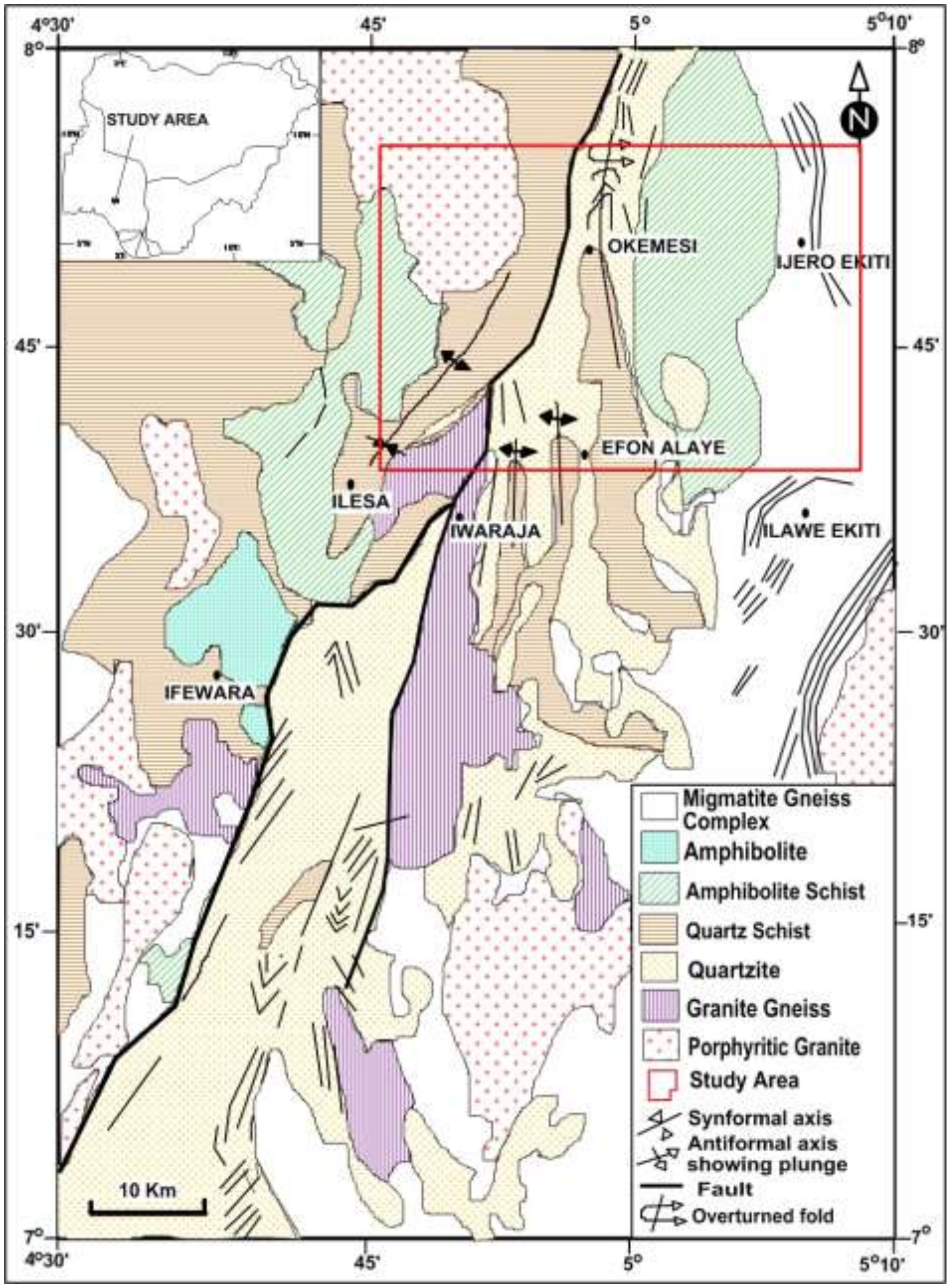


Figure 1. Sketch map of Ilesha Schist belt showing the study area.
Source: Odeyemi (1993).

samples from Okemesi-Ijero area, south western Nigeria were collected (Figure 2) during the dry season between December, 2014 and January, 2015 and analyzed for thirteen PTEs: Mo, Cu, Pb, Zn, Ni, Co, Mn, As, U, Th, Cd, V and La. The rocks and stream sediments samples were depicted by different lithologic areas (Figure 1). The samples were air-dried to constant weight. Dried aliquots were ground (as for rock they were pulverized) and sieved through 0.5 mm mesh as described by Dalman et al. (2006). One gram dry weight was accurately weighed after homogenization, placed into a Teflon digestion vessel (CEM Analytical Matthews, NC, USA). After adding 10 mL of 1:1 (V/V) HNO_3 (65%, Merck, Darnstadt, Germany) into each vessel; they were sealed and placed into a microwave reaction system (MARS, CEM Analytical Matthews). The content was heated to 130°C for 60 min followed by cooling for 10 min. A 5 mL 30% H_2O_2 (Merck, Darnstadt, Germany) were added and the mixture was heated to 130°C for 60 min to complete digestion. The digested samples were allowed to cool, after which they were filtered with filter paper (Whatman No. 144-110, Sigma-Aldrich, Taukirchen, Germany). The filter paper was rinsed with 5% HNO_3 to release the residues of the digested samples. The run off was made-up to 10-mL mark with de-ionized water (Merck, Darnsatdt, Germany). The concentrations of the PTEs were determined by inductively coupled plasma mass spectrometry (ICP-MS), Agilent 7700, Santa Clara, CA, USA). The

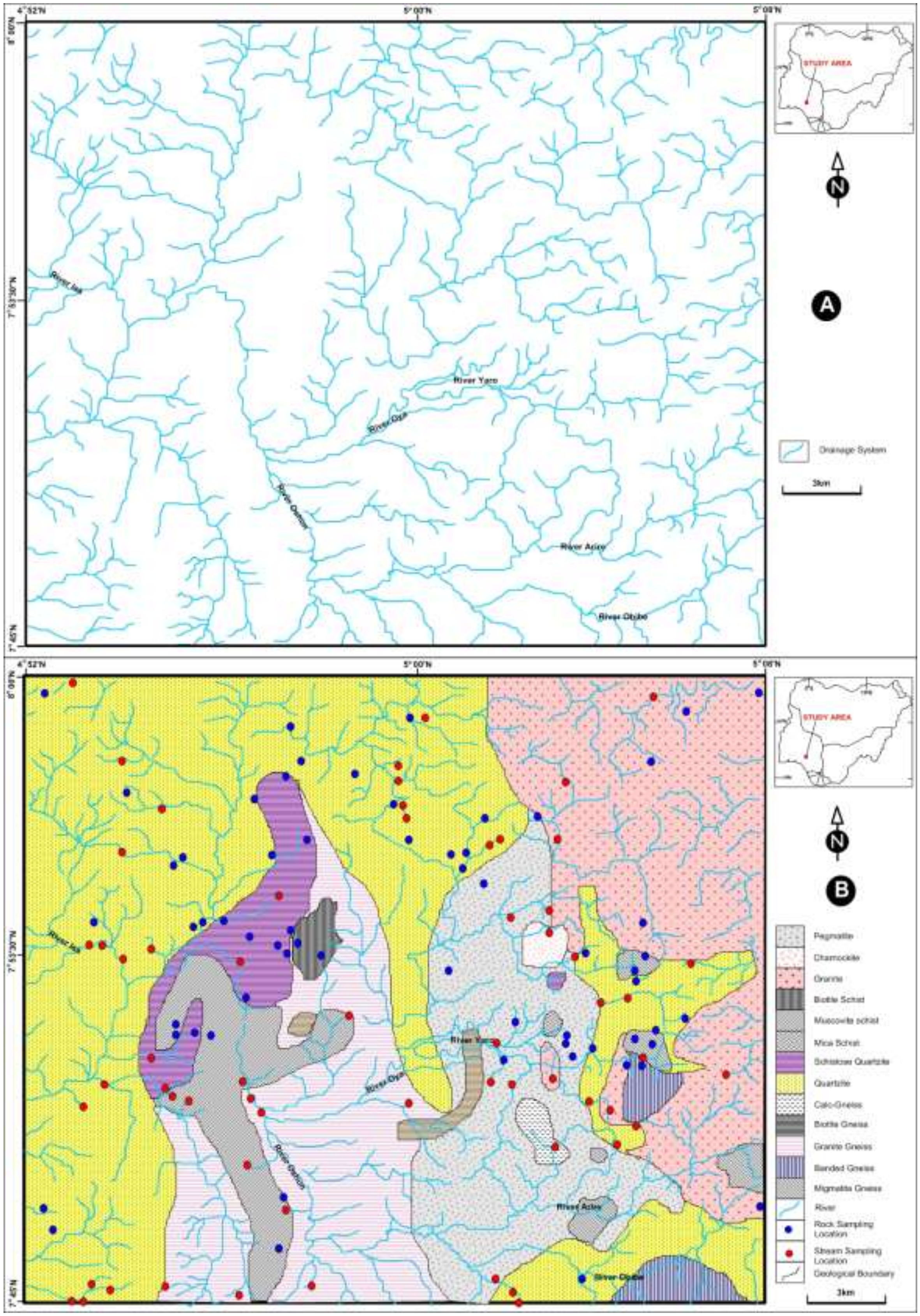


Figure 2. Drainage and geological map of the study area.
Source: (Ayodele, 2012).

Table 1. Concentrations of PTEs (mg/kg) in different rock type and sediment in the study area.

Rock type	Statistical parameter	Mo	Cu	Pb	Zn	Ni	Co	Mn	As	U	Th	Cd	V	La
	Min.	0.00	2.04	2.73	2.20	1.00	0.60	51.00	0.20	0.40	1.10	0.00	7.00	7.10
S/S (n = 80)	Max.	2.51	39.12	78.75	84.40	39.30	41.60	1591.00	5.40	16.40	165.60	0.60	106.00	364.90
	Mean	0.49	11.33	21.17	26.05	8.58	7.52	472.89	1.36	5.35	29.59	0.05	36.51	74.76
	Std.	0.51	7.91	18.35	19.91	9.27	9.13	432.77	1.11	4.93	31.11	0.10	24.78	66.83
	Min.	0.31	0.30	1.29	0.20	0.40	30.90	12.00	0.20	0.10	0.10	0.02	1.00	0.40
BG (n = 4)	Max.	1.95	14.73	30.31	56.00	20.90	75.40	555.00	0.30	6.00	23.50	0.05	54.00	30.60
	Mean	0.80	4.15	14.30	14.90	7.10	44.78	177.50	0.23	2.08	7.43	0.04	14.50	12.03
	Std.	0.77	7.06	13.91	27.42	9.65	20.83	253.63	0.05	2.68	10.82	0.02	26.34	13.85
	Min.	0.44	0.12	0.86	0.20	0.30	24.70	2.00	0.20	0.10	0.10	0.02	1.00	0.20
GN (n = 8)	Max	0.89	9.10	69.38	59.60	30.60	125.60	532.00	1.30	5.00	22.40	0.08	63.00	52.00
	Mean	0.59	2.21	23.99	20.31	7.18	54.64	181.38	0.49	1.90	8.70	0.04	19.38	22.41
	Std.	0.16	2.99	27.53	24.96	10.89	33.75	223.79	0.39	1.90	9.14	0.03	25.22	19.60
	Min.	0.17	0.15	0.80	0.20	0.10	17.10	2.00	0.20	0.20	0.20	0.02	1.00	1.10
Qtz (n = 22)	Max.	0.93	14.27	58.85	73.80	55.70	77.80	651.00	4.20	15.20	30.80	0.24	42.00	61.20
	Mean	0.48	2.12	14.64	15.00	4.96	35.72	147.50	0.90	2.14	6.35	0.05	9.95	20.47
	Std.	0.22	3.10	16.00	21.00	11.67	14.36	192.67	0.91	3.47	8.12	0.05	12.55	15.46

BG= Banded gneiss GN= Granite Qtz= Quartzite Std= Standard deviation S/S = stream sediments.

average value of three measurements was used for the analysis. A certified reference material (International Atomic Energy Agency, IACA 158, for mine sediments) was used for comparison according to Campbell et al. (2008), to evaluate the quality of analytical method. The detection limits of ICP-MS were evaluated with respect to the protocols of Chen and Ma (2001) and were found to range between (0.0001 - 0.1) mg/kg for the thirteen elements considered in this study.

Two distinct indices were used in the assessment of the level of enrichment and ecological risk by PTEs contamination in the stream sediments of Okemesi-Ijero, southwestern, Nigeria. The enrichment factor (EF) for each element was calculated in stream sediments using Equation 1.

$$EF = (Cn/Cref.)/(Bn/Bref) \quad (1)$$

Where Cn is the content of the examined element in the studied environment, Cref is the content of the reference element in the examined environment. Bn is the content of the examined element in the reference or background environment. Bref is the content of the reference element in the reference environment. The background/reference metals that was used for enrichment factor calculation was gotten using Fe as reference for geochemical normalisation according to Daskalakis and O'Connor (1995). EF < 1: no enrichment; 1 < EF < 3: minor enrichment; 3 < EF <5: moderate enrichment; 5 < EF < 10: moderately severe enrichment; 10 < EF < 25: severe enrichment; 25 < EF < 150: very severe enrichment and EF > 150; extremely severe enrichment. The potential ecological risk index is defined in Equation 2 as:

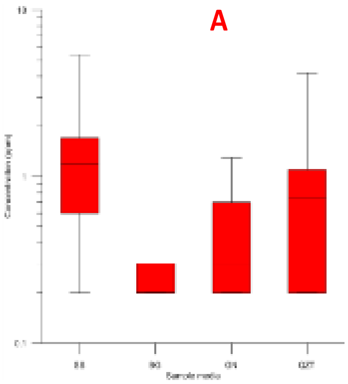
$$ER^i = Tr^i \times C_f^i; C_f^i = C_f^i = C_0^i/C_n^i \quad (2)$$

where Tr^i is the toxic-response factor for a given element (i), which accounts for the toxic requirement and the sensitivity requirement. The geochemical (average composition of shale) was adopted after Turekian and Wedepohl (1961) with Cu (45), Pb (20), As (4.72) and Cd (0.3), all in mg/kg as background values. Cf^i is the concentration factor, Co^i is the concentration of the sediment element i and Cn^i is the value of world shale average.

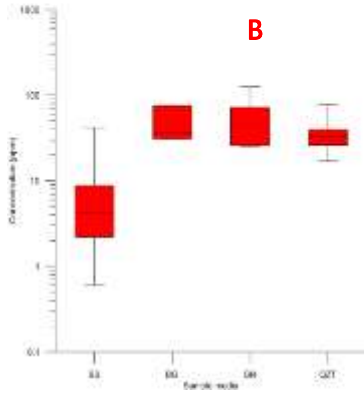
The interrelationship and distribution of PTEs in various rock and stream sediment segments were conducted by Pearson correlation (PC), Principal component analysis (PCA) and boxplot analyses, using Orange 6 and Grapher 8 software packages.

RESULTS AND DISCUSSION

The concentrations of thirteen PTEs (mg/kg) in different rocks type and stream sediment considered in this study are depicted in Table 1. The results showed spatial variation in concentration of the elements from one location to the other with respect to the stream sediments. Also, there were significant variation between the stream sediments and the rocks geochemistry. The mean concentrations of PTEs in stream sediments were found to vary in the order Mn (472.89), La (74.76), V (36.51) Th (29.59), Zn (26.05), Pb (21.17) C\u (11.33), Ni (8.58), Co (7.52), U (5.35), As (1.36) Mo (0.49) and Cd (0.05), all in mg/kg. Comparing the results of PTEs for stream sediments and the rocks analysed in the study area, it was found that most of the elements in the stream sediments have higher concentration than those in the rocks (Table 1 and Figure 3). For instance, the mean concentration of Mn in the stream sediments (mg/kg) is



As



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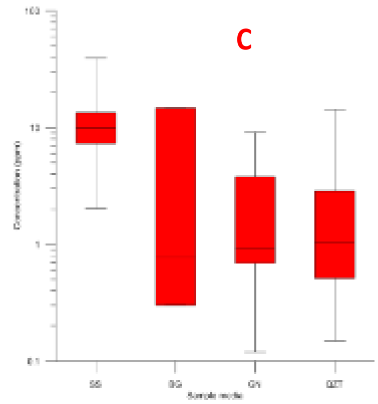

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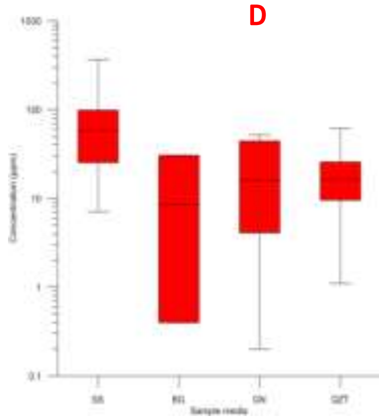

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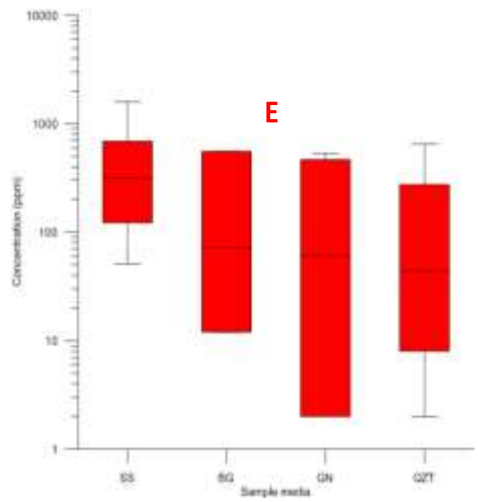

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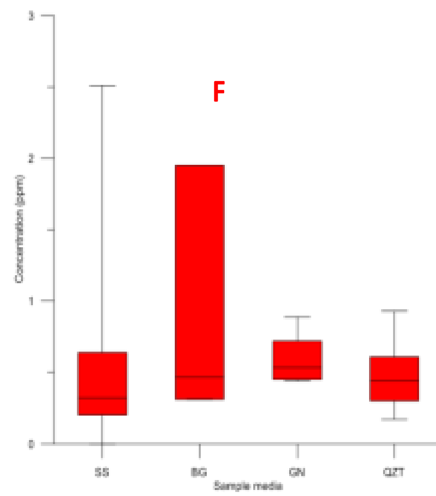

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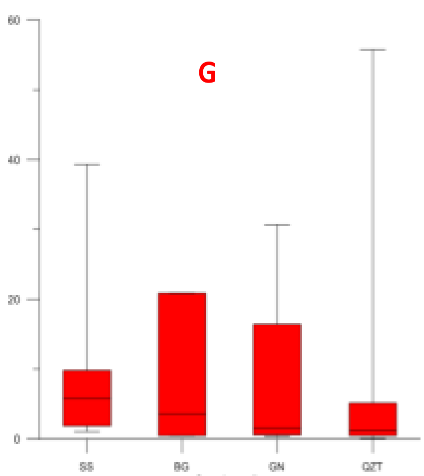
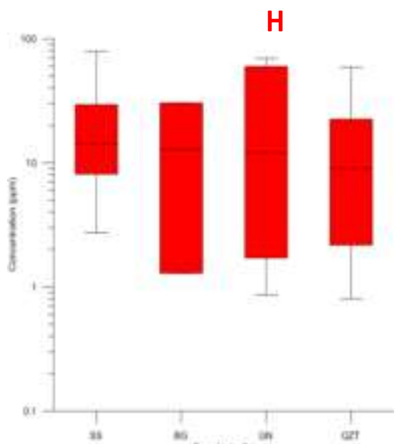
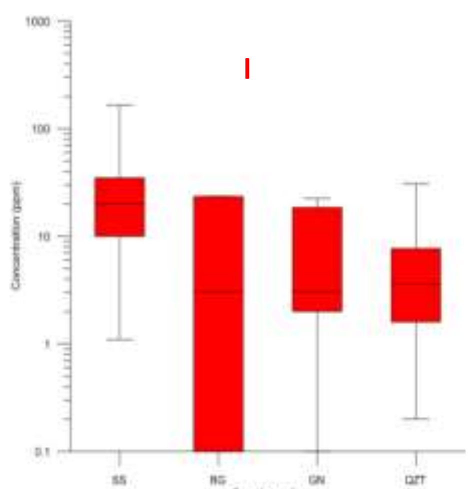


Ni



Pb



Th

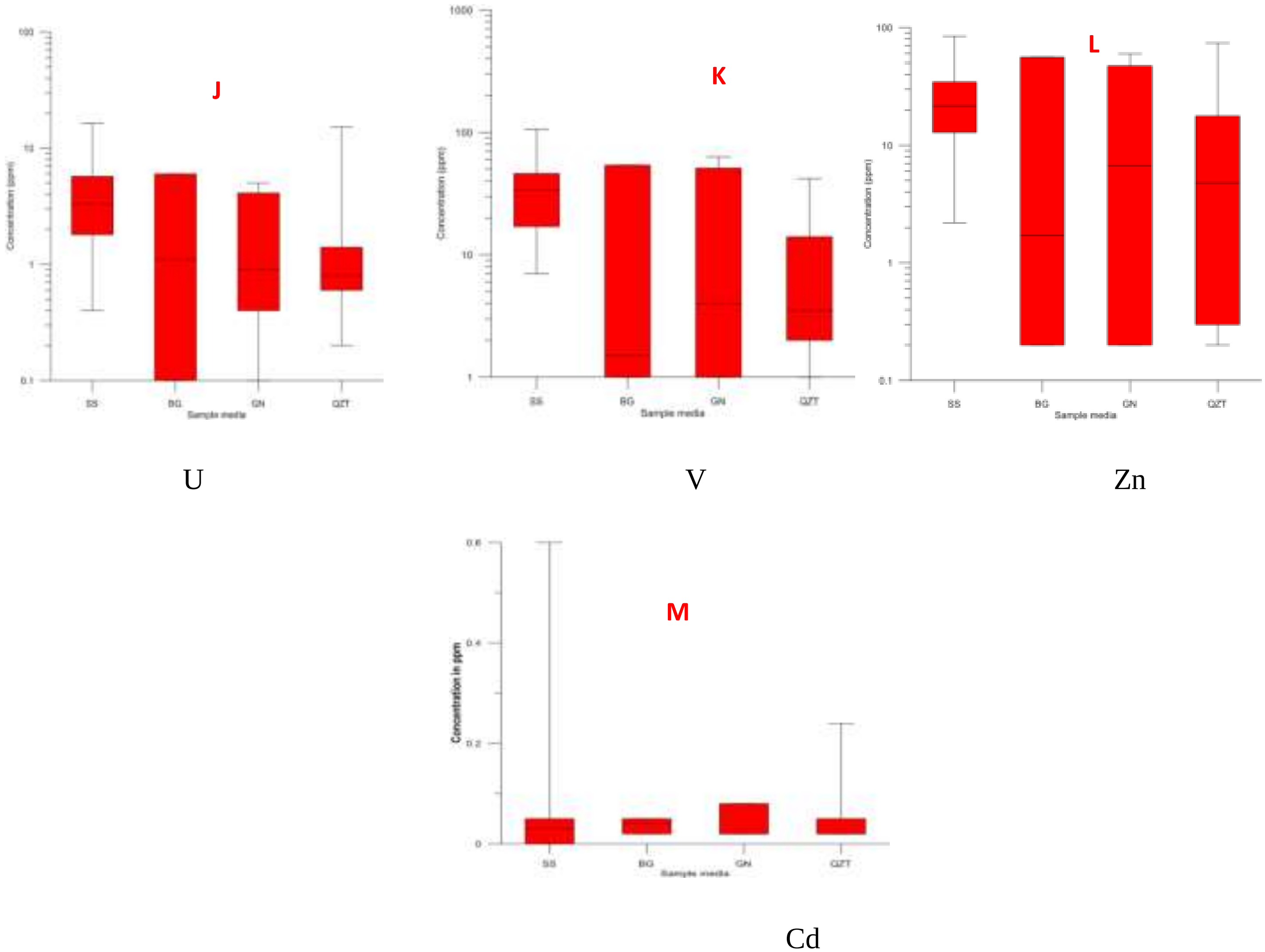


Figure 3. Boxplots of analysed trace elements in ppm concentration (A – M).

472.89 as against Banded gneiss (BG) 177.50, Granite (GN) 181.38 and Quartzites (Qtz) (147.50) respectively. This showed that the enrichment of Mn could be as a result of anthropogenic and geogenic influences. Also, the mean concentration for La from stream sediments is 74.76 mg/kg, while BG, 12.03 mg/kg, GN 22.41 and Qtz 20.47 mg/kg respectively. Generally, these higher trends of concentrations of PTEs were observed al through the sample matrix except for Mo and Co where the concentration were lower in stream sediments. This observation gave credence to the suggestion that sediments are the final repository of PTEs. Similar observations were reported by Nguyen et al. (2017) in their study on the surface sediment sample collected from Seagrass Bed of Khanh Hoa Coast, Vietnam.

Among PTEs considered in this study, Cu, Pb, As and Cd received more attention than others (Kljakovic-Gaspic et al., 2009; Nguyen et al., 2017) as they are main elements of anthropogenic influence on the ecosystems. The enrichment EF and ER (Table 2) were adopted in the assessment of the ecological impact and possible anthropogenic contributions of Cu, Pb, As and Cd. The results of EF varied from between minor enrichment (Pb, As, Cd) to moderate enrichment (Cu) while low potential ecological risk index was obtained.

Inter elemental relationships between stream sediments and bedrocks

The results of PTEs obtained in Table 1 were similarly interpreted using Pearson Correlation (PC) for inter-elemental correlation evaluation. The PC indicated variation in the relationship of the PTEs. From the correlation matrix result, there were relatively wide variations in the correlation coefficient (r) of the studied

Table 2. Enrichment factor and ecological risk index of stream sediment in the study area.

Variable	Cu	Pb	As	Cd
Stream Sediment (mg/kg)	11.33	21.17	1.36	0.05
Mean Conc. in Rock (mg/kg)	2.83	17.64	0.59	0.04
Enrichment Factor (EF)	5.29	1.52	3.20	1.58
Ecological Risk Index (ER)	0.25	1.06	0.29	0.17

Table 3. Correlation coefficients of elements in the stream sediments and rocks of the study area.

Elements	Mo	Cu	Pb	Zn	Ni	Co	Mn	As	U	Th	Cd	V	La
Mo	1.00												
Cu	0.45	1.00											
Pb	0.36	0.41	1.00										
Zn	0.39	**0.51**	0.42	1.00									
Ni	0.37	**0.68**	**0.52**	**0.54**	1.00								
Co	0.33	-0.34	-0.05	-0.11	-0.03	1.00							
Mn	0.39	**0.60**	0.37	**0.54**	0.44	-0.22	1.00						
As	0.43	0.34	0.11	0.18	0.17	-0.13	0.44	1.00					
U	-0.01	0.13	0.13	0.21	0.05	-0.16	0.37	0.07	1.00				
Th	0.17	0.48	0.48	0.22	0.21	-0.33	**0.53**	0.12	0.18	1.00			
Cd	0.08	0.11	0.16	0.25	0.12	-0.04	0.39	0.11	**0.89**	0.13	1.00		
V	**0.52**	**0.87**	0.49	**0.59**	**0.66**	-0.32	**0.69**	0.32	0.11	**0.55**	0.11	1.00	
La	0.18	**0.51**	0.29	0.21	0.22	-0.35	**0.55**	0.22	0.12	**0.91**	0.07	**0.57**	1.00

Significant level of r = 0.50.

PTEs. For example, the r values obtained ranged from −0.01 between U and Mo to 0.91 between La and Th. There were fairly strong to very strong positive correlations as found in the following elements; U, Cu, Ni, Zn, Cd, V and La.

The values of the following PTEs such as Cu and Zn (r = 0.51), Ni and Cu (r = 0.68), Zn and Ni (r = 0.54), were fair, while Cu and V (r = 0.87), Cd and U (r = 0.89) as well as Ni and V (r = 0.66), were considerably strong in correlation. The correlation coefficient of the other PTEs as presented in Table 3 also showed relatively fair significant level of correlation. The result of Principal Component Analyses showed four factors of elemental association. The analyses further buttress the r result (Table 4). From the result, the first group include the following PTEs; Mo, Co, Pb, Zn, Ni, Mn, Th, V and La with a total eigen value of 40%. These elements also showed similar correlation pattern as seen in Table 3, which suggest that these elements might have received enrichment from similar sources, such as from weathered vehicular parts as well as municipal waste that are indiscriminately dumped. Though the elements are generally relatively low in concentration, their presence in any case as earlier stated, could be linked to close or similar sources with the other elements. The second group of the factor is made up of U and Cd, accounting for approximately 14.45% of the total variance. These elements might have been enriched in the sediments by activities relating to similar source draining into the stream. Action of weathering and transport of the underlining rock might have added to the enrichment sources. The third group consists of Mo and Co, which accounted for 13.10% of the total variance. These two elements might have been enriched by activities relating to soil weathering. As occurred alone in the fourth component, with a total eugen value of 8.36%. This occurrence may have been as a result of possibly a combination of rock and soil weathering as well as other domestic wastes and vehicular effluents.

Conclusion

The stream sediments in the Ijero and Okemesi catchment area have been analysed for some selected trace elements, which include; Mo, Cu, Pb, Zn, Ni, Co, Mn, As, U, Th, Cd, V and La. These elements though are naturally present in stream sediments, the knowledge of their relative abundance in some locations are of environmental importance. The relatively high concentration of U, La, and Th are of great concern, owning to the fact that these elements are radiogenic elements and

Table 4. Principal component analyses of the trace elements in stream sediments and rocks in the study area.

Elements	FA-1	FA-2	FA-3	FA-4
Mo	**0.54**	-0.36	**0.51**	0.32
Cu	**0.85**	-0.19	-0.04	-0.04
Pb	**0.62**	-0.12	0.13	-0.38
Zn	**0.67**	-0.03	0.32	-0.25
Ni	**0.68**	-0.27	0.29	-0.37
Co	-0.31	-0.24	**0.64**	0.05
Mn	**0.82**	0.18	0.04	0.20
As	0.43	-0.09	0.16	**0.76**
U	0.32	**0.88**	0.22	-0.02
Th	**0.69**	0.08	-0.55	0.00
Cd	0.33	**0.84**	0.36	-0.01
V	**0.90**	-0.21	-0.05	-0.05
La	**0.68**	0.03	-0.58	0.14
Total	5.20	1.88	1.70	1.09
% of Variance	**40.00**	**14.45**	**13.10**	**8.36**
Cumulative %	40.00	54.45	67.54	75.90

FA: Factor analysis.

their presence in such environmental media can be harmful to the biota in general and to human in particular through food chain such as direct consumption of the stream water or through all year round consumption of consumable plants like vegetables and cereals that are grown in wetlands. The relatively high concentration of Pb, Zn and Cr, though not to an alarming rate, but their enrichment with a concentration of two to four folds higher than the bedrock concentration showed that these elements are of significant environmental concern.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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