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CHARACTERIZING TRACE ELEMENTS IN SOILS AND ROCKS IN THE AGRICULTURAL AREAS OF LABUNWA, SOUTHWESTERN NIGERIA

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ABSTRACT

Trace element (TE) concentrations in subsoils and underlying bedrocks of Labunwa, Odele area, were determined to ascertain the enrichment level and distribution of the TEs. Twenty-one subsoils (at 30 – 100 cm) and 13 rock samples were collected, pulverised and digested using aqua regia and total digestion, respectively. The samples were analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The mean TE concentrations in ppm for the subsoil showed Cu (40.0), Pb (24.2), Zn (56.3), As (0.9) and U (2.7), among other elements, as against the mean concentrations of Granite gneiss (GGN) which showed Cu (22.9), Pb (61.4), Zn (64.6), As (1.0), U (2.6) and Pegmatite (PG), Cu (128.4), Pb (17.0), Zn (108.8), As (1.1), U (1.3) among other TEs. The relatively low concentrations of the TEs in the subsoil compared to the underlying parent rocks suggests that TEs in the subsoil may have been influenced by geogenic factors, such as weathering of the underlying rocks. TEs source apportionments in the subsoil using Bivariant plots, correlation coefficient, Bi-polar and dendogram analyses showed that these TEs are essentially from the underlying GGN and PG in the area. Pollution status indices, I-geo, Contamination factor and PI_N showed that the study area is practically unpolluted. These values suggest that locations with relatively higher concentrations of some TEs are probably due to local enrichment, and because most subsoil TEs are significantly lower in concentrations compared to the underlying bedrock, the area is safe for agricultural activities.

Keywords: Labuwa, Trace Element, Pegmatite, Granite Gneiss, Subsoil.

INTRODUCTION

Soils are heterogeneous mixtures of organic and inorganic materials, formed as a result of the breakdown of biological, chemical and physical materials, which are mobilised by various means of transportation and deposition, forming upper layers of the ground surface. Abou El-Anwar *et al.* (2019) reported that a total of twelve (12) elements, comprising Al, Ca, Fe, K, Ti, O, Mg, Mn, Na, Cr, Ni and Si, constitute approximately 99.4% of the total composition of the soil, while other trace elements make up the remaining. However, the chemistry of the local soils is essentially influenced by factors such as the underlying rocks (pedogenic and lithogenic weathering effects) (Salman, 2013), regional and local climatic conditions, the topography of the environment, transportation mechanisms, among other factors (Gall *et al.*, 2015; Quintero *et al.*, 2017; Li *et al.*, 2019; Rivera-Hernández *et al.*, 2019).

Soils are veritable matrices that accumulate a significant amount of water and other organic and inorganic materials. These phenomena also add to the physical characteristics that the soils exhibit, such as acidity and alkalinity, texture, colour, moisture content, organic matters, structures and shapes, among other physical attributes. These attributes make soils an essential component of the ecosystem, useful for agricultural activities and other economic utilisations. Owning to this strategic relevance of soil to humanity, interest in the understanding of trace element enrichment, distribution and the source apportionment, whether anthropogenic or geogenic, becomes very important for the environmental and health wellbeing of human beings.

Soils are a veritable part of the ecosystem, the understanding of the distribution of trace elements and source apportionment will go a long way in effective management policies formulation (Li *et al.*, 2019). Rocks in crystalline environments mostly undergo weathering to form the overlying soils in such area. In most cases, the chemistry of the overlying soil shows close resemblance to the chemistry of the underlining rocks, except in cases where there is enrichment resulting from anthropogenic inputs or geogenic inputs. Hence, soils can serve as a sink and repository for trace element accumulation, which can record past anthropogenic events. In the same vein, soils can serve as habitats for diverse organisms and plants, a critical ecosystem component.

According to Ahmed *et al.* (2010), trace elements such as As, Pb, Zn, Hg, Cu, Ni, Cr and V can be mobilised by weathering and microbial activities. These elements are largely concentrated in soil silt and clay fractions, possibly due to high adsorption capacity, redox condition, pH, weather conditions such as rainfall, and microbes in soils. Also, carrier phases of the soils can serve as factors that control the mobility and toxic effect of these trace elements in the soil. In the same vein, factors such as adsorption on oxides and hydroxides of Fe and Mn and grain sizes of the soil also control the mobility of trace elements in the soil (Wang *et al.*, 2012, Larrios *et al.* 2012, 2013, Ma *et al.* 2015).

The use of Agrochemicals such as herbicides for weeding, pesticides, and plant fertilizers have been reported to influence the enrichment of trace elements in agricultural land use (Larrios *et al.* 2012, Shi *et al.*, 2015; Gall *et al.*, 2015; Quitero *et al.*, 2017). And such relative enrichment of these trace elements present in the agricultural input might be hazardous when they exceed the permissible limit in the soil.

Agricultural soils are critical assets that need to be monitored, particularly the chemical status. There is the possibility of mobility of such trace elements into the plant and other living things interacting with the soil, hence the need for continuous monitoring.

The works of Owens *et al.* (2016); Li *et al.* (2019) showed the use of Cluster analysis, Principal Component Analysis and other related methods to infer potential sources of trace elements in sediments and soils. These assisted in knowing the source contribution and compositions of the analysed geochemical data. Odukoya and Akande (2015) carried out pollution status assessment of major, trace and rare earth elements (Fe, Al, Ca, Na, Mg, K, P, Ti, Co, Mn, U, Th, Sr, V, La, Cr, Ba, Sc, Ga, Cs, Nb, Rb, Y, Ce, Mo, Pb, Zn, As, Cd, Sb, Sn and Zr) using Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). The environmental risk assessment was quantified using geo-accumulation index (Igeo), Pollution Load Index (PLI) and Contamination Factor (CF). It was observed that all the samples were within the class of low to medium contamination risk range, except samples from Owode Onirin stream catchment, which fell within very high to extremely high risk. Several published works have similarly used statistical inference methods in assessing soils and sediments' elemental enrichment status, whether the geomedia are from geogenic or otherwise (Grba *el al.*, 2015; Udosen *et al.*, 2016; Sako *et al.*, 2018; Melvin *et al.*, 2020). They concluded that the trace element contents of the geo media (soil, sediments and water) were mainly controlled by geochemical processes, particularly by weathering rather than anthropogenic effect. They also found out that there is little or no significant health risk to the exposed population. From the foregoing, it becomes imperative that such agricultural soil is continuously monitored.

The aim of this research is to ascertain the trace element concentration and distribution in the subsoil of Labunwa - Odole and its environs as well as evaluate the possible health risk, if any, that is associated with the concentration level of these selected trace elements in the soil and rocks in the study area.

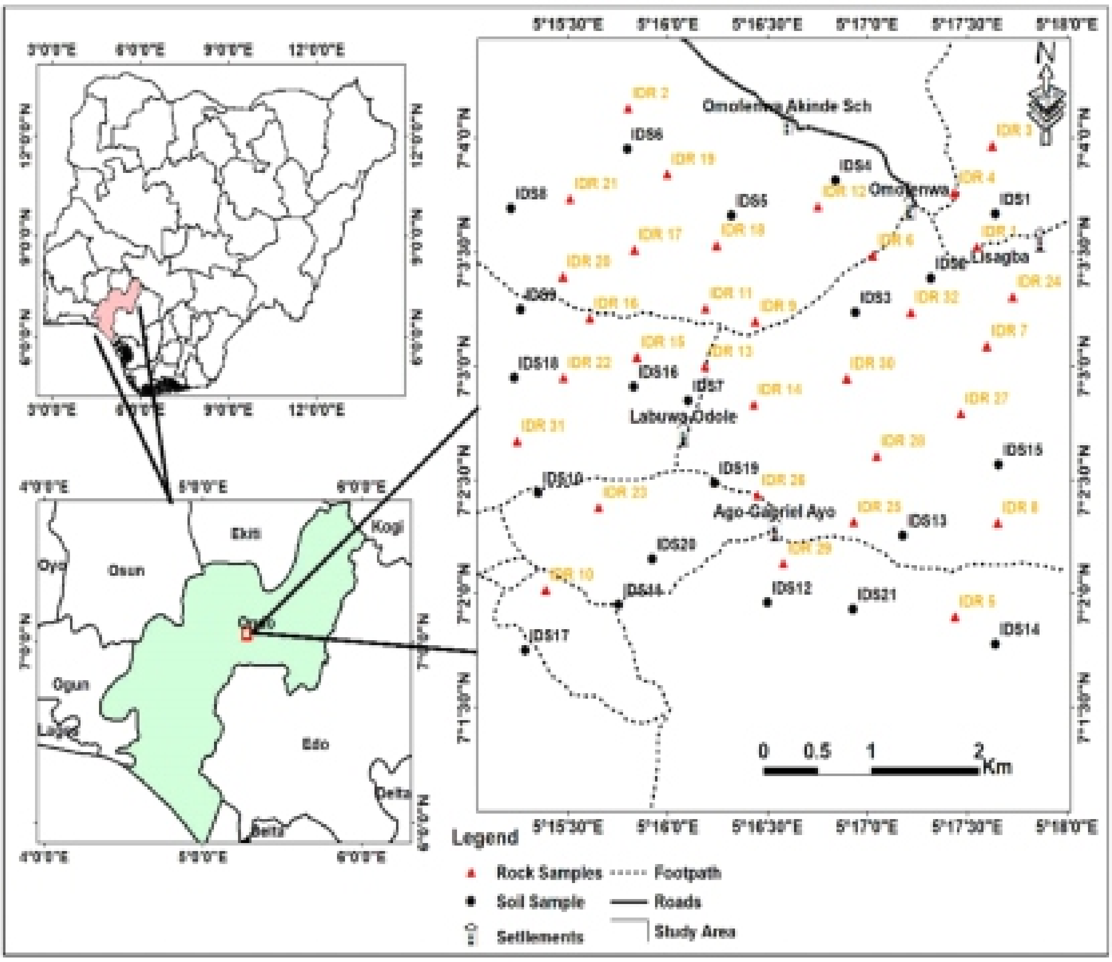


Figure 1: Sampling location map of the study area.

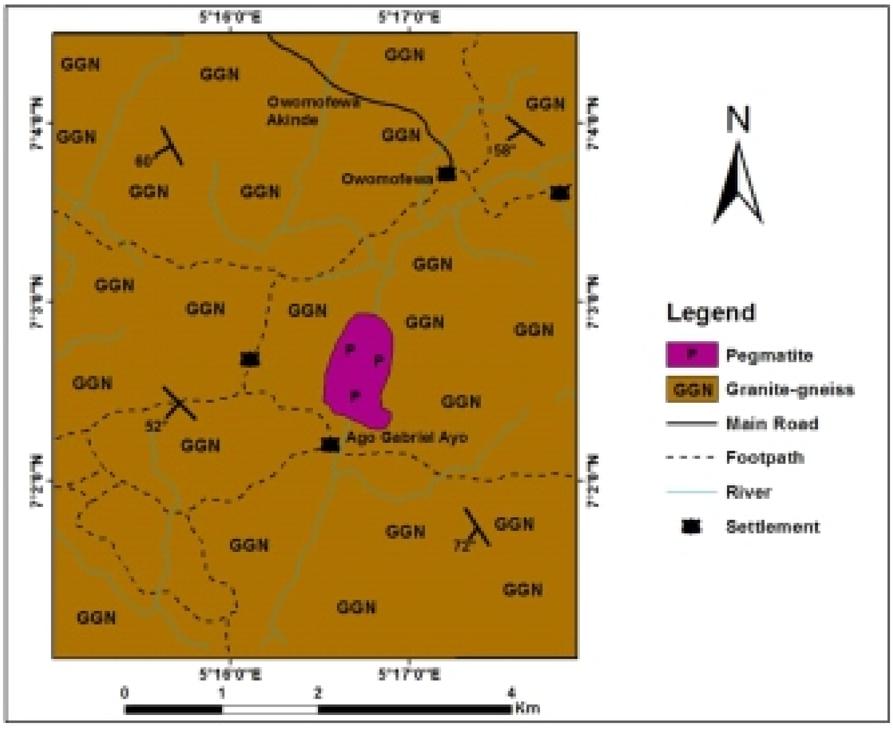


Figure 2: A geologic map of the study area.

STUDY AREA

A field survey was carried out in the agrarian (agricultural farmland) area of cocoa, cassava, yam tuber and other cash crops. The communities in the study area include Omiliyan, Labunwa, Owomofewa, Akinde, Olisaga, Ago-Gabriel and Odole, among other hamLets (Figure 1). The study area is easily accessible from Oda and Idanre towns and lies within the tropical rainforest of the southwestern part of Nigeria. The area is humid, with temperatures varying between 21.1 – 22.3 °C during the rainy season, while it ranges from 31 – 32.1 °C during the dry season and with mean temperature between 26.0 – 28.1 °C (Nicholson, 1981, Abuloye *et al.*, 2017; Omogbai 2010). The rainy (wet) season extends from April to November every year, while the dry season starts from late November to the end of March every year. Because of the relatively abundant rainfall recorded every year characterizes the area by moderate to dense vegetation. The vegetation ranges from shrubs to tall trees; hence plants like cocoa, yam tubers, cassava, and maize are cultivated in this area. Isolated floodplains of small sizes, along the stream channels, also receive non-seasonal cultivation of vegetables.

Geology of the Study Area

Labunwa and environs are underlain by the Precambrian Basement Complex of Southwestern Nigeria. These Precambrian rocks are regionally sub-divided into four major rock types due to tectonostratigraphic basis (Hockey *et al.*, 1963; Oyawoye 1976; McCurry, 1976; Olarewaju 1988; Rahaman 1988). These sub-divisions are Migmatite – Gneiss – Quartzite Complex, the Schist belt, the Older Granites and the Granitoids, which are emplaced as minor felsic and mafic intrusive bodies (Ajibade *et al.*, 1987, Ajibade *et al.*, 2008, Adekoya 1991). The study area, Figure 2, is underlain by two rock types: granite gneiss and pegmatite. The mineral compositions have been described by Rahaman (1988) and Olarewaju (1988).

METHODOLOGY

Twenty–one (21) composite subsoils samples were collected from the B – horizon between 30 – 100 cm depth. Three (3) subsamples were collected from each grid drawn from the topographic sheet before sample collection to obtain the composite samples. The three sub-samples were then mixed to obtain the composite sample (Figure 1). The soil sampling exercise was conducted in February 2019. The collection was done with a hand auger and care was taken (from the B horizon) to ensure that samples were not contaminated. This was achieved by carefully washing the hand auger with detergent, properly rinsing it, and drying it after each sample collection. After that, the collected samples are carefully put in a well-labelled sample bag, the location's coordinates and other necessary observations are recorded in the field notebook. Similarly, at every sample point, a larger diameter cutting head was employed to remove the overburden, shrubs and topsoil and then replaced with a narrower diameter to collect the subsoil. In the same vein, thirty-one (31) representative rock samples were also collected within the study area. These rock samples were collected based on the lithology of the study areas as presented by Awosusi *et al.*, (2019). The soil and rock samples were properly labelled upon sampling in bags and transported to the laboratory for sample preparation.

The soil samples were air-dried at room temperature for eight (8) days. Subsequently, the dried samples were pulverized and sieved using a 053 μm mesh fraction. Furthermore, the sieved samples were digested using a modified partial digestion method (Aqua regia). The digestion process involves gradual input of 5 mL nitric acid (mesh Suprapur of 65%), with the addition of 2 mL hydrochloric acid (Hcl) (merch suprapur 36 °C) and 10 mL of pure water of 18 mΩ/cm specific resistivity) in an ultraclean tube. The samples were heated at 95 °C for two hours, using a microwave oven. The samples were decanted into a 50 mL volumetric flask at the end of heating. Then, the solution was extracted using a disposable syringe filtered through a 0.45 filter membrane. The digested samples were analysed using Inductive Coupled Plasma – Mass Spectrometry (ICP-MS), AVIO200, PerkinElmer, MA USA model. Similarly, thirteen (13) representative samples were further selected from the thirty-one (31) field samples for geochemical analysis for the rock samples. Before ICP-MS analysis, total digestion method, using $HClO_4$, HF. HCl and HNO_3 of different proportions were used for the rock sample digestion. Prior to this, the pulverised rock samples were placed in an ultra-clean baker and shaken in a clean bath for 35 min. The digestion procedures followed the established protocol of the ACME laboratory as well as the published protocols of Makishima and Nakamura, (1997), Murray *et al.* (2000), Cotta and Enzweiler (2011), and Zhengdong *et al.* (2021). 0.15 mL of perchloric acid ($HClO_4$) of 60 wt% and 0.3 mL of conc. HF of 60 wt% were gradually added to 0.5 g of the pulverised rock samples in an ultraclean Teflon plastic bottle. After the addition, the bottles were tightly sealed and agitated in a clean cleanser for about 5 h to mix up and dissolve the samples properly. After that, the bottles were opened using a ceramic hot plate. The samples were gradually dried from an increased temperature of 120 °C through 140 °C to a maximum temperature of 200 °C for 6 h. Then, the degraded samples were again gradually introduced with 0.2 mL of 35 wt% of HCl in other to dissolve the samples completely. Then, the dissolved samples were dried under a temperature of 120 °C for another 6 h and then HNO_3 was added to the dried samples to round up the dissolution process before about 25 mL of 0.5 M of HNO_3 was added to 50 mL bottles before the analysis of trace elements. Subsequently, the digested samples were analyzed using the Inductively Coupled Plasma Mass Spectrometry method (ICP-MS)(AVIO 200, PerkinElmer, MA, USA) at ACME Laboratory, Canada.

The procedures for quality control and assurances were carried out before and in between the analysis of the samples. Following the laboratory (ACME) scientific protocol, these were done using certified reference materials, duplicate samples, and blank samples, following the laboratory (ACME) scientific protocol (Table 1). The geochemical results of the quality control data, 20% of the total soil samples, were analysed, and the result showed very low standard deviation of 10% in between samples analysed (Table 1). Similarly, the minimum detection limit (MDL), analysed samples as shown in Table 1, indicated significantly high sensitivity values, suggesting that the equipment was highly sensitive and was satisfactory for determining the selected trace elements.

Table 1: Quality control data (in ppm) for subsoil and rocks in the study area.

		Pulp Duplicates		Ref. Mat.			Ref. Mat.		
Elm	MDL	IDS14	IDS14	STD DS11	STD OREAS262	BLK	OREAS45E	OREAS25A-4A	BLK
Cu	0.01	0.71	0.69	14.28	0.58	<0.01	804.1	35.2	<0.1
Pb	0.01	20.3	19.92	147.1	115.21	<0.01	19.44	24.03	<0.02
Zn	0.1	17.55	17.71	141.45	56.89	0.02	50.5	46.4	0.3
Ni	0.1	24	33	1634	447	<2	455.2	46.4	<0.1
Co	0.1	15.2	15.4	79.5	62.7	<0.1	61.5	8.1	<0.2
Mn	1	15.7	16.1	13.6	27.4	<0.1	582	472	<1
As	0.1	4.75	4.83	3.13	3.21	<0.01	3.13	3.21	<0.01
U	0.1	0.7	0.6	43.9	34.7	<0.1	43.9	34.7	<0.1
Th	0.1	<0.2	<0.2	125.6	71.2	<0.2	14	14.5	<0.1
Sr	0.5	22.9	24.5	8.2	9.4	<0.1	17	44	<1
Cd	0.01	24.4	25.2	68.9	35.5	<0.5	<0.02	<0.02	<0.02
V	1	0.11	0.13	12.8	1.07	<0.02	327	164	<1
La	0.5	0.014	0.015	0.071	0.041	<0.001	11.4	20	<0.1
Cr	0.5	75	75.9	18.5	15.8	<0.5	986	123	<1
Ba	0.5	0.42	0.42	0.85	1.12	<0.01	262	142	<1
Sc	0.1	<0.1	<0.1	2.8	0.1	<0.1	95.1	11.6	0.1
Se	0.1	59	49	264	169	<5	2.3	2.4	0.7

Blk = Blank; MDL = Minimul Detection Limit; STD = Standard; Ref. Mat. = Reference Material.

Assessment of pollution status in the subsoil

To know the pollution status of the selected trace elements in the subsoil of the study area, pollution quantifications were carried out on the determined elements using Geo-accumulation Index (Igeo), Contamination Factor (CF) and Pollution Load Index equations. These indexes have been widely applied to evaluate the pollution status of trace elements in geo media such as soils, sediments, water, among others, Ayinde *et al*., 2020; Asowata and Olatunji, 2018; Saha and Hossain 2010; Karim *et al*., 2015; Cai *et al*., 2015; Adisa and Adekoya, 2016; Sungur, 2016. The Geoaccumulation Index (Igeo) assessment is evaluated according to Muller 1979, with an equation as stated in equation 1;

$$\mathrm{Igeo} = \log_2(\mathrm{Cn} / 1.5\mathrm{Bn}) \qquad (1)$$

From the equation, Cn means the concentration of trace elements in the subsoil in ppm, Bn represents the background concentration (in ppm), which in this case, the average granite gneiss elemental concentration were used as the background concentrations. 1.5 is a constant used as a factor to minimize variation in the litho materials. Under this evaluation, the classification that ranges from 0 to 5, and it has been adopted to represent the relative pollution status of each element in every location.

- Uncontaminated ($\mathrm{Igeo} \leq 0$)
- Uncontaminated to moderately contaminated ($0 < \mathrm{Igeo} \leq 1$)
- Moderately contaminated ($1 < \mathrm{Igeo} \leq 2$)
- Moderately to heavily contaminated ($2 < \mathrm{Igeo} \leq 3$)
- Heavily contaminated ($3 < \mathrm{Igeo} \leq 4$)
- Heavily to extremely contaminated ($4 < \mathrm{Igeo} \leq 5$)
- Extremely contaminated ($\mathrm{Igeo} > 5$)

Regarding contamination factor (CF), it quantifies the degree of contamination relative to either the average crustal composition of a metal or the measured background value from geologically similar and uncontaminated areas (Ladigbolu and Balogun, 2011). This was also used to assess the relative pollution status of the studied subsoil. The equation of CF follows thus;

$$CF = C_{metal} / C_{background} \qquad (2)$$

where C_{metal} is the concentration of the selected trace element in the study area and $C_{background}$ means the background concentration of the metal in the underlying crystalline rock in the study area. In this study, the average concentrations of the granite gneiss analysed were used as the background concentrations of the trace element. Hakanson (1980), Sutherland, (2000) and Qingjie (2008) classification of CF has been adopted in this study as follows:

- $CF < 1$: Low contamination factor,
- $1 \leq CF < 3$: Moderate contamination factor,
- $\leq CF < 6$: Considerable contamination factor,
- $CF \geq 6$: Very high contamination factor.

Similarly, for the Pollution Load Index (PI_N), equation 3 was also used to assess the pollution index of each sample location complimentarily (Jiang *et al*., 2014)

$$PI_N = \sqrt{\frac{(Cf_{average})^2 + (Cf_{max})^2}{2}} \qquad (3)$$

where,
CF = Contamination Factor
Cmetal = Metal concentration in the subsoil
Cbackground = Natural background value of the metal
n = Number of metals (n= 14)

PI_N is an index for evaluating sediment and soil sample contamination status to trace elements. It represents the number of times the heavy metal concentration in the sediment exceeds the background concentration and gives a summative indication of the overall level of trace element toxicity in a particular sample (Priju and Narayana, 2006).

The pollution load index (PI_N) evaluates how the soil and sediment associated with heavy metal might impact soil micro flora and fauna in the study area. The PI_N value > 1 is polluted whereas PI_N value < 1 indicates no pollution (Chakravarty and Patgiri, 2009; Seshan *et al.,* 2010).

RESULTS AND DISCUSSION

The distributions of the analysed trace elements (Cu, Pb, Zn, Ni, Co, Mn, As, U, Th, Sr, Cd, V, La, Cr, Ba, Sc, and Se) in the subsoil of the study area were found to vary in concentrations (in ppm) from one sample location to the other. The concentrations of Cu in the subsoil ranged from 9.26 ppm, as found in location IDS16, to 76.28 ppm as found in location IDS12. The average (mean) concentration of Cu was 40.00 ppm, with a standard deviation of 20.50. Locations IDS13, IDS19 and IDS7 were found to have a relatively low concentration of 14.82, 17.65 and 15.16 ppm, respectively, while locations IDS4, IDS17 and IDS20 recorded relatively high concentrations of 63.09, 62.05 and 72.54 ppm, respectively. Pb concentrations (ppm) in subsoil ranged from 16.4 as recorded in location IDS16 to 36.6 as found in location IDS2. The mean concentration (ppm) of Pb in the study area was 40.0, with a standard deviation of 5.5. The concentrations of Pb in the subsoil also recorded relatively low values (in ppm) in locations IDS14 (17.55) and IDS19 (18.38). Similarly, Zn exhibited varying concentrations in ppm, in the subsoil of the study area, with the lowest concentration (19.5) recorded in location IDS19, while the highest concentration (134.1) was found in location IDS18. The mean concentration was 56.3 ± 25.8 as the standard deviation. Other locations with relatively low concentrations in ppm were IDS3 (32.0), IDS16 (33.9) and IDS6 (39.0). Relatively higher concentrations were recorded in locations IDS5 (91.2 ppm), IDS21 (74.0 ppm) and IDS20 (75.3 ppm), among other locations. Similar variations in concentrations of the other analysed elements were also observed in the subsoil samples (Table 2). The average concentrations of some of the trace elements in the subsoil were lower than the average concentrations of both the granite gneiss and pegmatite. Such elements include As, Sr and Ba. The concentrations of these elements in the subsoil decrease in the order: Mn>Ba>La>Zn>V>Cu>Cr>Cr>Pb>Co>Sr> Th>Ni>Sc>U>Se>As>Cd.

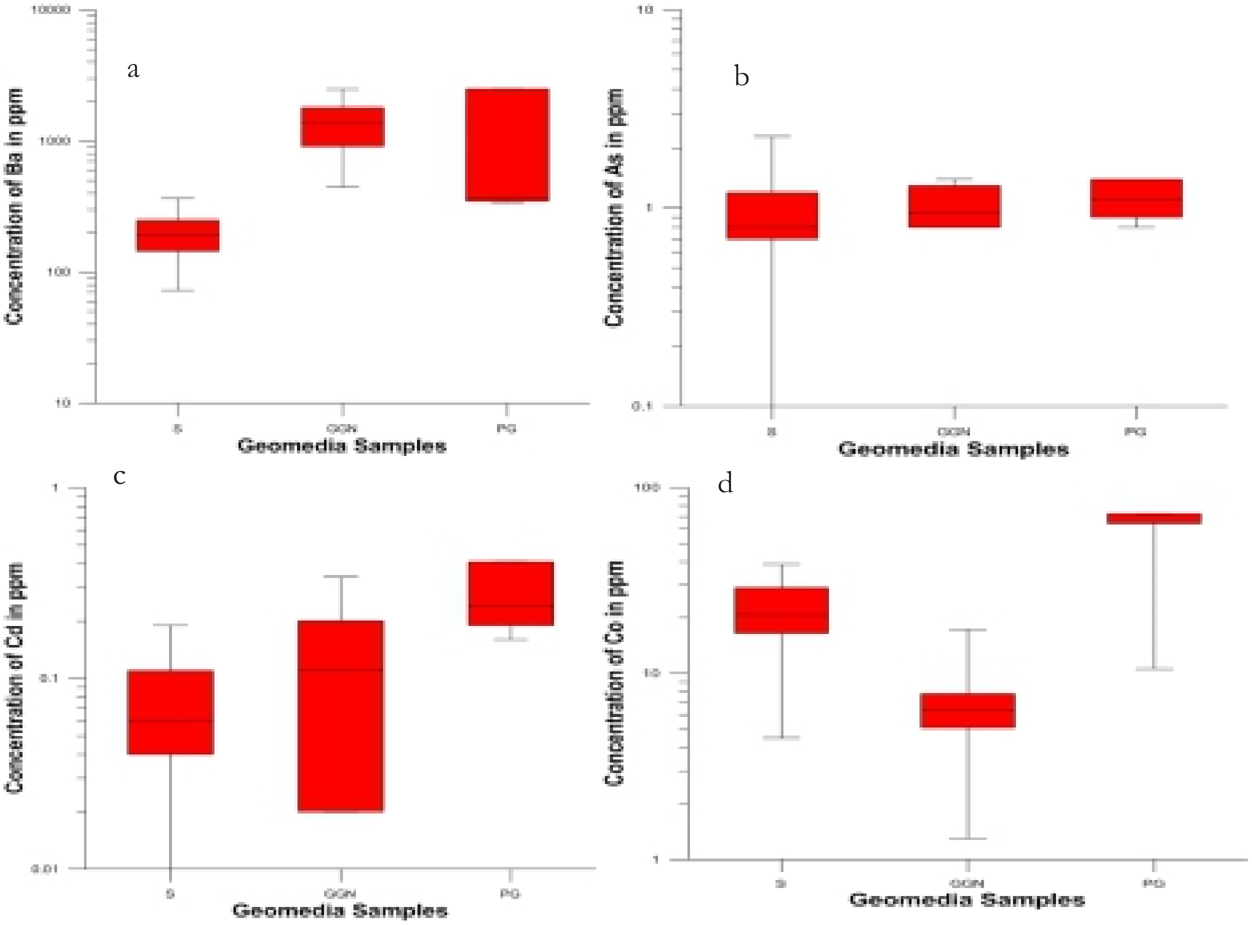
The mean value of As in the subsoil was 0.9 ppm, slightly higher than that in the granite gneiss 1.0 ppm and pegmatite 1.1 ppm (Table 2). Sr in the subsoil also recorded a much lower average of 21.1 ppm than 255.1 and 257.1 ppm in pegmatite and granite gneiss, respectively.

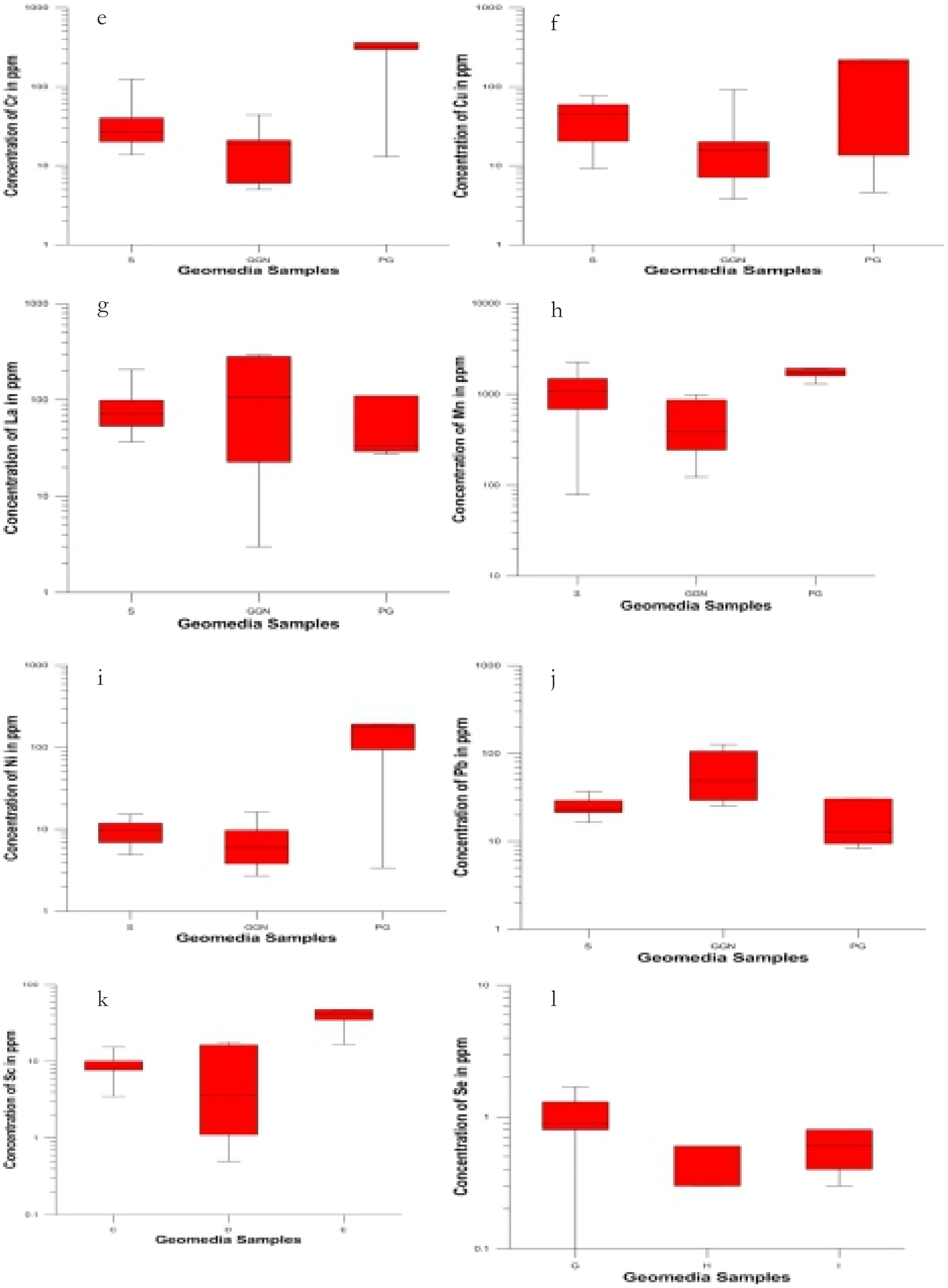
The mean concentration in ppm of Cu in the subsoil (40.0) was found to be far lower than that of pegmatite (128.4), but higher than granite gneiss (22.9). Similar pattern of concentration variation in the subsoil, relative to the underlying rocks (granite gneiss and pegmatite), were observed in Pb, Zn, U, among other elements (Table 2).

A comparative analysis of the trace elements in the subsoils and the two rock types (granite gneiss and pegmatite) underlying the study area were also carried out using the boxplots in Figures 3 (a-q). From the plots, higher concentrations of Ba were found in both the pegmatite and the granite gneiss compared to in the subsoil. Similar trends were recorded in As, Cd, Sr and Zn. However, different enrichment patterns were observed in Co, Cr, Cu, Mn, Ni, Sc, and V. In these elements, pegmatite concentrations were relatively higher than in the subsoil, and the concentrations of these elements were much lower in the granite gneiss. It was also observed that La, Pb, Th and U were found to be higher in concentration in the granite gneiss than in the subsoil. Since the study area is essentially underlain by granite gneiss, covering about 90% of the rock within the study area, it could be inferred that the rock (granite gneiss) may have contributed greatly in the enrichment of the elements in the subsoil through effect of weathering and erosion in the formation the soil in the study area.

Table 2: Results of trace element concentrations (ppm) in the subsoils, granite gneiss and pegmatite rocks.

	Subsoil (*n* = *21)*				PG(*n* = *5)*				GGN (*n* = *8*)			
Elements	Max	Min	Mean	STDV	Max	Min	Mean	Stdv	Max	Min	Mean	Stdv
Cu	76.28	9.26	40.0	20.5	219.6	4.6	128.4	109.3	91.7	3.8	22.9	28.4
Pb	36.6	16.4	24.7	5.5	30.6	8.4	17.0	9.8	126.6	25.5	61.4	37.5
Zn	134.1	19.5	56.3	25.8	145.9	68.0	108.8	35.3	115.1	7.8	64.6	31.2
Ni	15.2	4.9	9.9	3.1	191.6	3.4	130.5	81.4	16.3	2.7	7.3	4.4
Co	38.6	4.5	21.8	8.7	72.4	10.6	56.2	25.7	17.3	1.3	7.2	4.5
Mn	2267	79	1099.3	541.7	1923.0	1303.0	1683.0	243.9	992.0	123.0	468.1	304.4
As	2.3	0.1	0.9	0.5	1.4	0.8	1.1	0.3	1.4	0.8	1.0	0.2
U	4.1	1.3	2.7	0.7	1.6	0.7	1.3	0.4	8.2	0.6	2.6	2.5
Th	30.9	10.6	19.0	5.9	23.9	2.5	9.8	9.9	266.7	2.1	72.7	83.8
Sr	46.5	12.4	21.1	8.3	666.0	127.0	255.2	230.1	503.0	161.0	257.4	107.8
Cd	0.19	0.01	0.1	0.0	0.4	0.2	0.3	0.1	0.3	0.0	0.1	0.1
V	104	31	55.9	25.1	322.0	47.0	214.8	139.1	83.0	4.0	29.4	24.3
La	207	36.6	78.5	37.3	110.1	27.4	51.8	35.1	293.6	3.0	127.7	114.3
Cr	124.2	13.7	36.9	29.9	361.0	13.0	266.2	144.2	44.0	5.0	18.0	12.4
Ba	365.2	72.7	197.6	74.2	2496.0	341.0	788.4	954.8	2485.0	443.0	1338.0	621.0
Sc	15.2	3.5	8.9	2.8	47.3	16.6	36.6	12.0	17.7	0.5	6.9	6.8
Se	1.7	0.1	1.0	0.4	0.8	0.3	0.6	0.2	0.6	0.3	0.5	0.1

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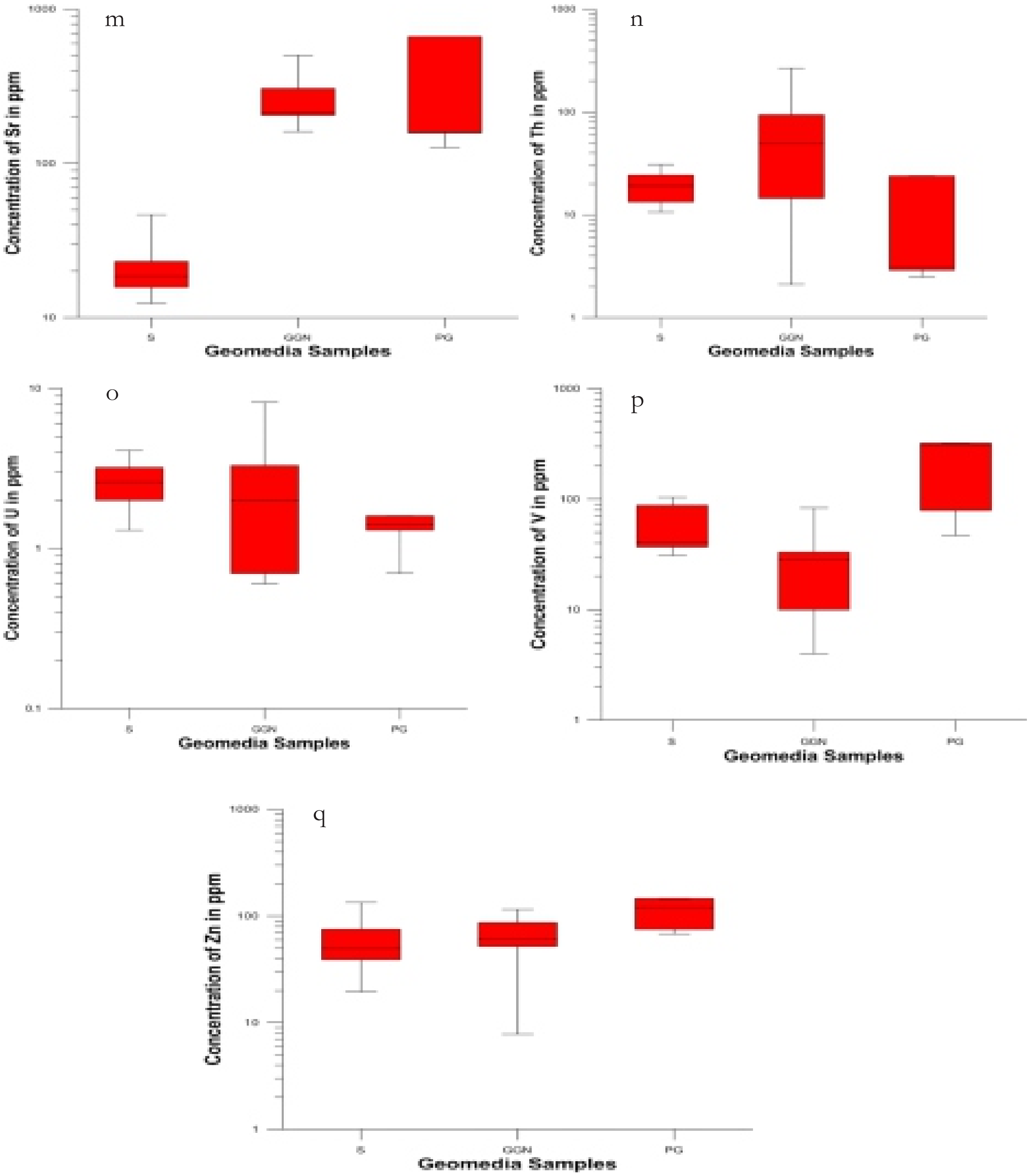


Figure 3: (a-q). Boxplots of the concentrations of the selected trace elements in the studied geomedia (Subsoil, Granite gneiss and Pegmatite). The central box represents 50% of the distribution between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the distribution's Max and Min. values. Also, S represents Subsoil, GGN, Granite Gneiss and PG represents Pegmatite.

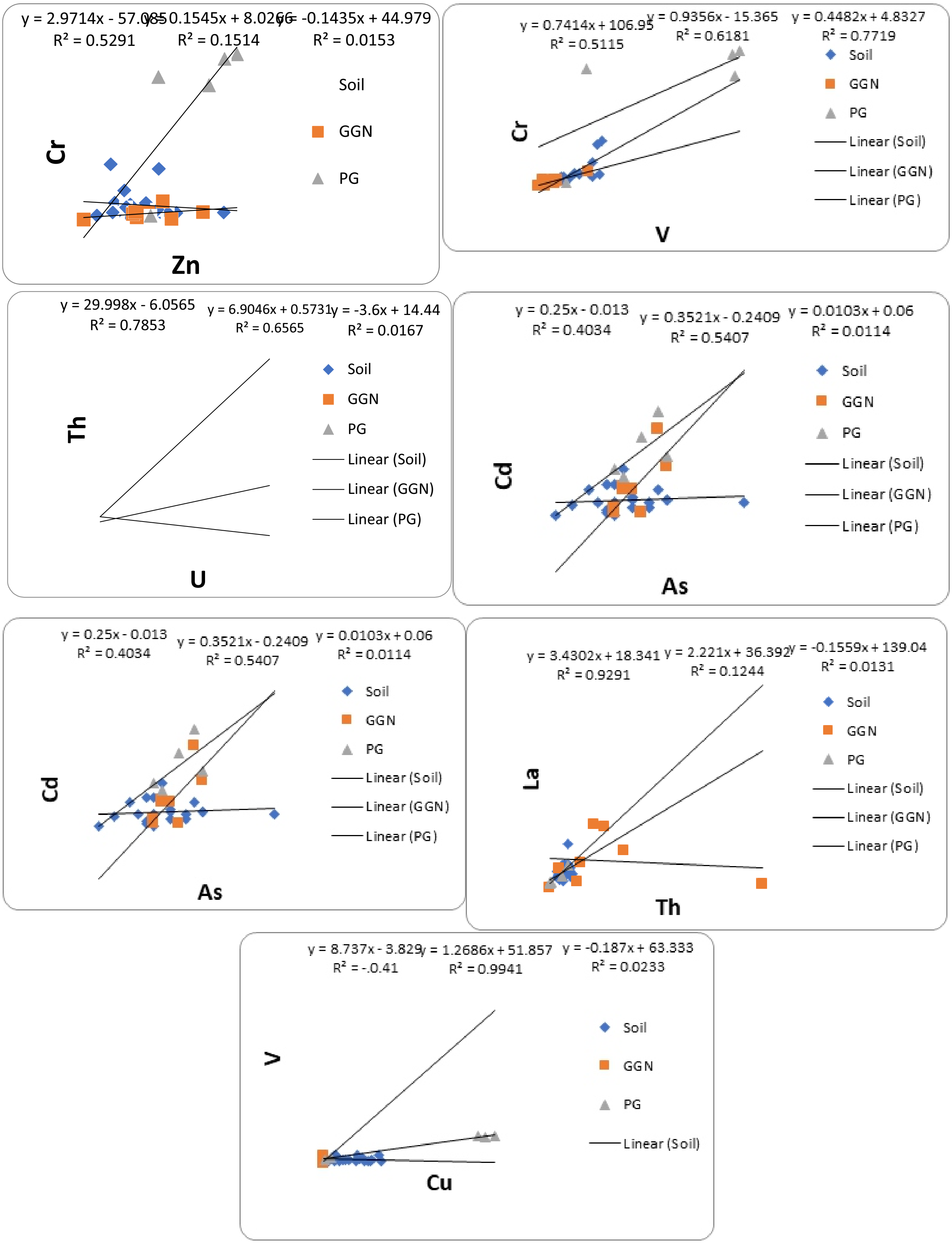


Figure 4: (a-g). Bivariant plots of some selected trace elements in the subsoil, GGN and PG.

Interelemental relationship

The relative association of the trace elements in the geomedia, (subsoil, granite gneiss and pegmatite) were evaluated using Pearson correlation coefficient (Bivariant plots) in Figure 4 (a-g). The coefficient of determination, principal component analysis and cluster (Deodegram) analysis were carried out on the subsoil trace elements.

For the Pearson correlation analysis (R^2), the correlation between Cr and Zn showed a relatively fair R^2 of 0.529 for subsoil, weak R^2 of 0.151 for GGN and very weak R^2 of 0.015 for PGM. The R^2 of Cr and V showed a fair correlation of 0.511 for subsoil and a strong correlation of 0.618 and 0.771 for GGN and PGM, respectively. The R^2 of Th and U had a relatively strong correlation of 0.785 and 0.656 for both subsoil and GGN, but very weak correlation for PGM. The correlation of Cd and As exhibited a relatively fair association of 0.403 and 0.540 for subsoil and GGN, respectively, but a weak correlation of 0.011 for PGM. A strong correlation was observed between Mn and Co. The values of R^2 are 0.680, 0.583 and 0.852 for the subsoil, GGN and PGM, respectively. Similarly, the correlation of La and Th was such that the subsoil showed a very strong R^2 value of 0.929, while a very weak correlation of 0.124 and 0.013 for both GGN and PGM. V and Cu also showed a very strong correlation of 0.994 for GGN but a very weak to the negative correlation of 0.023 and – 0.410 for PGM and subsoil, Figure 4 (a-g). Elemental associations with strong R^2 suggest that these elements may have been enriched in the geomedia by similar sources. On the other hand, elements in the geomedia with relatively weak to negative correlation depict non-similarity of enrichment sources.

The correlation matrix of the trace elements in the subsoil showed varying degrees of correlation (Table 3). From the correlation coefficient (r), it was observed that it ranges from the negative correlation of – 0.4, between Th and Cu, to a very strong correlation of 0.9, between Cd and Mn. Relatively fair to strong correlation were found between Mn/Cu (0.7), As/Pb (0.7), Mn/Zn (0.6), Co/Ni (0.6), La/Zn (0.8), Cr/V (0.8) among others. The relatively fair to strong correction of these trace elements in the subsoils suggests that their enrichment may have been from similar (analogous) sources. Nevertheless, some other elements also showed negative to weak correlation. Examples are: Se/V (-0.4), Se/Cr (-0.3) among others.

The subsoil data were further subjected to Principal Component Anaysis (PCA) with varimax rotation. From the results, a total of five factors with an eigen value greater than 1.0 and accounting for 85.74% of the data variability were extracted and considered appropriate (Table 4). The first factor, Zn, V, La, Cr, Ba, Sc and Se, accounted for 23.04% of the model. This elemental association probably suggests the scavenging activities of hydrous Fe-Oxide on these elements and the lithophile – silicate mineral association in the underlying granite gneiss. This factor, therefore, probably means environmental controls and that the enrichment in the soils may have been from the same source. The second factor, Cu, Co, Mn and Cd, accounted for 20.6% of the variability of the model. The strong positive correlation of Mn with Cu (0.7), Co (0.8) and Cd (0.9) probably indicates the scavenging action of Mn on these elements it is associated with. According to Loganathan and Burau (1973) and Burns (1976), Co and Mn – oxides occur together in the secondary environment due to the substitution of Co with Mn – Oxides and the adsorption of Co on the surface of Mn – oxides. This metal association could be interpreted as an environmental factor. Elemental affinity may have been associated with lithologic association with pegmate veins present in the study area. And since Mn-Oxide can effectively associate with many elements, hence the affinity of Mn with Cu, Co and Cd. The third factor, Ni, Co, U, Th, V and Sc, which accounted for 20.07% of the variability of the model, may be interpreted as a lithological factor. These metal association was probably influenced by in situ weathering of pegmatite veins present in the granite gneiss. Thorium is usually associated with uranium in granitic rocks and pegmatite, with monazite being the possible source of Th. Pb, As and V constitute the fourth factor. This factor accounted for 13.43% of the variability of the model. These elemental associations could be partly due to lithological or mineralization. The source of Pb could be from feldspar in the granite gneiss or probably the pegmatite in the area. Wedephol (1970) has reported the Pb in K-feldspar as the element that can substitute for K. Pb could also be found in other minerals such as quartz, albite, biotite, muscovite, as well as some accessory minerals like beryl, zircon etc. The strong positive correlation between Pb and As could suggest some sulphide mineralization in the underlying gneisses in the area. And the fifth factors were Sr and Ba elements association these two elements accounted for 8.59% of the total Eugen values. These elements have been reported to be in strong affinity with potassium (K) in felsic rocks, which probably may have influenced the relative enrichment of these trace elements in the soil. The Bi-plot (Figure 5) exhibited a similar trend, which showed a strong correlation between La, Ba and Mn; U and Th; Cu and Se and a weak correlation between Cu and Zn. The biplot further revealed two distinct elemental associations with sub-groups such as Ni, U, Th, V and Co; Cu, Mn, Cd; and Zn, La, Ba. These associations are similar to the elemental associations obtained from the PCA analysis, as earlier explained. In the case of the dendrogram, there were four clusters: Cluster I contains Mn, Cd, Cu, Ni, Co and Sr, cluster II showed Zn, Ba, La, and Se. Cluster III showed an association of U, Th and Sc, while Cluster IV contains V, Cr, Pb and As. The outcome of the cluster analysis agrees with the results of the Factor analysis (Figure 6). And the association of these elements, as earlier explained, suggests possibly the same source(s) of enrichment of these elements in the soil samples of the study area.

Table 3: Correlation coefficients of trace elements in the analysed subsoil of the study area.

Cu	Pb	Zn	Ni	Co	Mn	As	U	Th	Sr	Cd	V	La	Cr	Ba	Sc	Se	
1	0.3	0.3	0	0.4	**0.7**	0.1	-0.3	-0.4	0.3	**0.6**	-0.2	0.2	0.2	0.2	-0.1	**0.5**	Cu
	1	0.2	0.1	0.4	0.4	**0.7**	0.2	0.4	0	0.2	0.3	0.2	0.2	0	0.3	0.3	Pb
		1	0.3	0.1	**0.6**	0.2	0.3	0.3	0.2	**0.6**	-0.1	**0.8**	-0.1	**0.8**	**0.5**	**0.6**	Zn
			1	**0.6**	0.3	0.2	**0.7**	0.5	0.4	0.1	**0.5**	0.2	0.2	0.3	0.3	-0.1	Ni
				1	**0.8**	0.3	0.3	0.1	0.2	**0.6**	0.4	0.1	0.4	0.2	-0.1	0.1	Co
					1	0.2	0	-0.1	0.3	**0.9**	-0.1	**0.5**	0.1	**0.5**	0.1	**0.5**	Mn
						1	0.4	**0.5**	0.1	0.1	**0.6**	0.1	0.4	0.1	0.3	0.2	As
							1	**0.8**	-0.1	-0.1	**0.6**	0.1	0.2	0.1	**0.5**	-0.2	U
								1	-0.2	-0.3	**0.5**	0.4	0.1	0.1	**0.7**	-0.1	Th
									1	0.3	0.1	0.1	-0.1	**0.5**	0.1	0.1	Sr
										1	-0.2	0.4	0.1	**0.6**	-0.2	**0.5**	Cd
											1	-0.3	**0.8**	-0.2	0.1	-0.4	V
												1	-0.3	0.6	0.4	**0.5**	La
													1	-0.3	-0.2	-0.3	Cr
														1	0.4	**0.6**	Ba
															1	0.4	Sc
																1	Se

Table 4: Correlation coefficient of trace elements in the subsoil in the study area.

	1	2	3	4	5
Cu		0.72			
Pb				0.865	
Zn	0.818				
Ni			0.803		
Co		0.804	0.409		
Mn		0.91			
As				0.878	
U			0.901		
Th			0.754		
Sr					0.949
Cd		0.85			
V	0.508		0.686	0.411	
La	0.838				
Cr	0.586				
Ba	0.764				0.492
Sc	0.639		0.401		
Se	0.732				
Eigen Total Value	3.916	3.504	3.412	2.282	1.46
% of Variance	23.035	20.613	20.073	13.426	8.588
Cumulative %	23.035	43.648	63.721	77.147	85.735

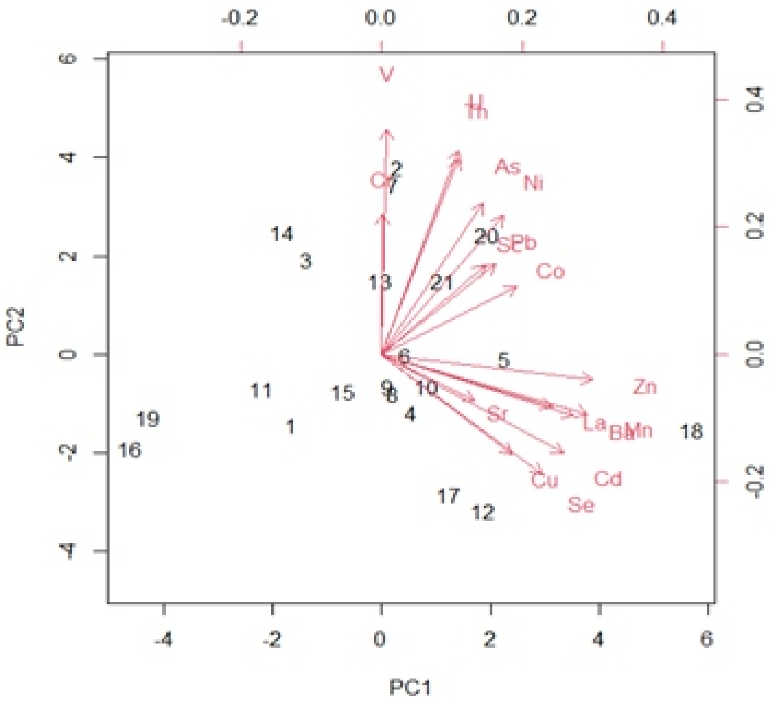
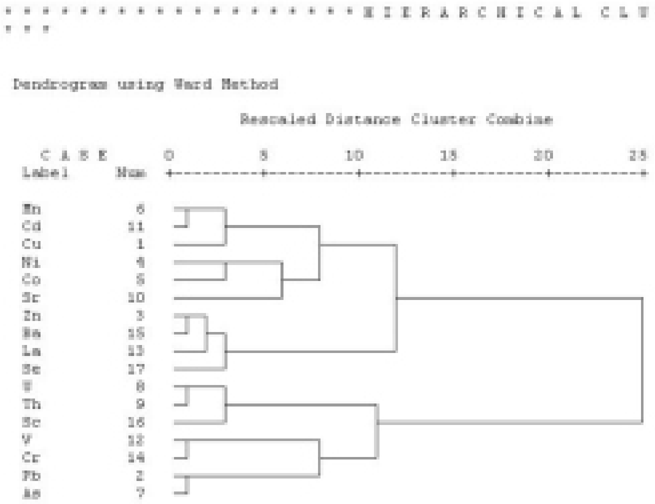


Figure 5: Bi-Polar plot for the selected trace elements.



The four clusters are as follows
Cluster 1: Mn, Cd, Cu, Ni, Co, Sr
Cluster 2: Zn, Ba, La, Se
Cluster 3: U, Th, Sc
Cluster 4: V, Cr, Pb, As

Figure 6: Dendogram plot of the analysed trace elements and sample location, using average linkage (between groups).

Table 5 presents the mean concentration of the trace elements in the subsoil, granite gneiss and pegmatite and the mean concentration of some trace elements in soils of published researched works, particularly in agricultural and urban soils in Nigeria. Also included in the table are concentrations of trace elements from other parts of the world and the average world shale concentration. From the results, mean concentration of Cu in the study area subsoil is found to be higher than the Cu concentration in Agricultural soils, Assiut governorate, Egypt (Abou El-Anwar *et al.*, 2019), the soil of Agricultural Sites in Sri Lanka (Jayawardana *et al.*, 2013), Cerrado Soils, Brazil (Marques *et al.*, 2004), Agricultural Soil in Dexing area (Teng *et al.* 2010), Background Concentrations of Trace and Major Elements in California Soils (Bradford *et al.*, 1996) as well as the Average Earth Crust metal concentration (Turekian and Wedepohl, 1961). But with lower Cu concentration in Agricultural Soil of Aswan area, South Egypt (Darwish and Pollmann, 2015), and top and subsoil of Ile - Ife area (Asowata and Akinwumiju, 2020). The mean concentration of Pb in the subsoil in this study is slightly higher than soil of Agricultural Sites in Sri Lanka (Jayawardana *et al.*, 2013). And the mean Pb concentration from this study is significantly lower than the data from other soils in Egypt, Sri Lanka, among other areas of comparison (Table 5). Similarly, in the subsoil of this study, the mean Zn concentration is found to be significantly lower compared to the data from most of the areas of comparison except in Cerrado soils, Brazil (Marques *et al.*, 2004).

The mean concentrations of the other elements in the subsoil, from this study are comparatively lower than the concentrations from most of the selected areas of comparison (Table 5). This suggests that these elements' sources are essentially geogenic rather than anthropogenic.

Table 5: Comparison of the studied subsoil, Granite Gneiss, Pegmatite (ppm) with other soil studied in other areas.

	Soil	PG	GGN	A	B	C	D	E	F	G	H	I
Elements	Mean	Mean	Mean									
Cu	40.0	128.4	22.9	31.6	47.2	25.0	33.0	33.0	71.1	76.6	28.7	50
Pb	24.7	17.0	61.4	38.4	31.69	21.0	26.0	39.0	93.5	77.9	23.9	20
Zn	56.3	108.8	64.6	119.3	1390	75.0	38.0	81.0	826	622.3	149.0	95
Ni	9.9	130.5	7.3	84.2	58.19	40.0	14.0		25.3	27.2	57.0	50
Co	21.8	56.2	7.2	35.4	38.17		5.0		24.6	28.7	14.9	19
Mn	1099.3	1683.0	468.1	1180.6	858.1		455.0	275.0	1323	1190	646.0	850
As	0.9	1.1	1.0	15.4		3.0		10.0	3.1	3.4	3.5	13
U	2.7	1.3	2.6				3.0				4.7	-
Th	19.0	9.8	72.7				15.0		4,3	4.5	15.7	12
Sr	21.1	255.2	257.4		206.9				32.9	30.6	128.0	170
Cd	0.1	0.3	0.1	1.4	19.69			0.2	1.42	1.28	0.36	0.3
V	55.9	214.8	29.4				257.0		142.6	161.7	112.0	130
La	78.5	51.8	127.7				83.0		32.2	34.0	20.3	43
Cr	36.9	266.2	18.0	116.7	133.1	123.0	112.0		108.8	128.5	122.0	90
Ba	197.6	788.4	1338.0				67.0				461.0	580
Sc	8.9	36.6	6.9		15.15		21				9.5	13
Se	1.0	0.6	0.5								0.06	0.89

A: Agricultural Soils, Assiut governorate, Egypt (Abou El-Anwar *et al.*, 2019)
B: Agricultural Soil of Aswan area, South Egypt (Darwish and Pollmann, 2015)
C: Soil of Agricultural Sites in Sri Lanka (Jayawardana *et al.*, 2013)
D: Cerrado Soils, Brazil (Marques, *et al.*, 2004)
E: Agricultural Soil in Dexing area (Teng *et al.* 2010)
F: Urban Topsoil in Ile-Ife, Nigeria (Asowata and Akinwumiju, 2020)
G: Urban Subsoil in Ile-Ife, Nigeria (Asowata and Akinwumiju, 2020)
H: Background Concentrations of Trace and Major Elements in California Soils: (Bradford *et al.*, 1996)

I: Average Earth Crust metal Concentration (Turekian and Wedepohl, 1961)

Assessment of the subsoil trace elements based on Geoaccumulation Index (I-geo) and Pollution Load Index

The results of the Igeo index for some selected high priority trace elements are presented in Table 6. These elements include Cu, Pb, Zn, Ni, Co, Mn, As, Th, Sr, Cd, V, U, La and Cr. The results showed that elements such as Pb, Th, Sr, Cd, As U and La, practically showed negative Igeo values, which suggest that the subsoil is unpolluted concerning these elements. Cu Igeo values fall within the range of "unpolluted" in > 60% of the studied locations, while about 30% of the locations are uncontaminated to moderately contaminated. The remaining 10% of the sample locations are moderately contaminated. Mn Igeo values were found to range from uncontaminated to moderately contaminated. However, uncontaminated locations are found to be significantly (about 60%) higher than the sample locations (about 40%) that were moderately contaminated. A similar trend was observed for V and Cr, with much of the sample locations exhibiting uncontaminated to moderately uncontaminated. Generally, it was observed that the Igeo index values of the selected trace elements in the subsoil samples were essentially uncontaminated.

Similarly, the Contamination Factor (CF) results are presented in Table 7. From the result, as earlier explained in the methodology, it was observed that Cu in the subsoil recorded low to moderate contamination, which ranged from 0 to < 3. Pb, Zn, Ni, U, Th, La and Sr showed essentially low contamination of (CF <1). However, Co, Mn and Cr showed relatively higher CF values of >3 but < 6, suggesting considerable contamination in many of the locations sampled. The high CF values of Mn, Co and Cr may not be unconnected with the Mn-Oxides presence in the in-situ weathered lateritic soils from the granite gneiss that essentially underlain the study area. It could also be due to the scavenging action of Mn-oxides on these elements in the secondary environment. The result of the calculated Pollution Load Index, (PI$_N$), as presented in Table 6, showed most of the sampled locations are unpolluted except in locations 15, 18, 19 and 21 where their PI$_N$ is higher than 1. This may probably be attributed to mineralisation rather than pollution.

Table 6: Geo accumulation index results of trace elements in the subsoil in the study area.

Sample	Ig Cu	IgPb	Ig Zn	Ig Ni	IgCo	IgMn	Ig As	IgU	Ig Th	Ig Sr	Ig Cd	Ig V	Ig La	Ig Cr
IDS001	0.6	-1.1	0.1	0.5	1.2	1.0	0.3	0.5	-1.9	-3.5	-0.2	0.9	-0.4	0.6
IDS002	0.3	-0.2	0.3	0.9	2.1	1.1	1.8	1.1	-0.8	-3.3	-0.2	2.4	-0.7	1.6
IDS003	1.6	-0.8	-0.4	0.5	2.5	1.7	1.1	0.5	-1.3	-3.7	0.1	2.4	-1.2	3.4
IDS004	2.1	-0.4	0.0	1.0	2.4	2.2	0.3	0.2	-1.5	-3.0	-0.2	1.1	0.3	1.3
IDS005	1.2	-0.5	1.1	0.9	1.8	2.0	0.8	0.7	-1.0	-3.2	-0.2	1.1	0.4	0.7
IDS006	1.6	-0.3	-0.1	1.2	2.7	2.3	0.6	0.5	-1.4	-3.3	0.3	1.1	-0.1	1.1
IDS007	0.0	-0.9	0.3	1.6	2.5	1.4	0.3	1.2	-0.6	-2.8	-2.7	2.2	-0.3	1.3
IDS008	1.7	-0.9	-0.3	1.2	3.0	2.6	-0.4	0.6	-2.0	-3.2	0.7	1.6	-0.7	1.8
IDS009	0.9	-0.9	0.8	0.9	1.7	1.4	-0.2	0.7	-1.2	-3.5	-0.2	1.0	0.1	0.8
IDS010	1.8	-0.7	0.6	1.2	2.2	1.9	1.1	0.1	-2.0	-2.1	0.1	1.8	-0.2	1.7
IDS011	2.0	-0.8	-0.2	0.5	0.8	0.9	0.1	0.6	-1.4	-3.6	-1.2	0.9	-0.6	0.9
IDS012	2.3	-0.8	1.0	0.7	2.0	2.5	0.3	0.2	-2.0	-2.9	1.0	0.7	-0.1	0.6
IDS013	0.0	-1.0	0.2	1.6	2.6	1.9	0.6	1.0	-1.3	-3.2	0.1	1.8	-0.3	1.6
IDS014	0.4	-1.2	0.0	1.6	1.7	0.3	0.1	1.0	-1.1	-2.8	-1.7	2.2	-0.2	2.5
IDS015	1.5	-0.6	0.1	0.5	2.0	1.8	0.6	0.2	-1.3	-3.5	-0.7	1.0	0.4	1.4
IDS016	-0.7	-1.3	-0.3	0.1	-0.1	-2.0	-2.7	-0.4	-1.9	-3.8	-2.7	1.0	-0.7	0.7
IDS017	2.0	-0.9	0.3	1.1	2.4	2.2	0.1	0.2	-2.2	-1.9	1.0	0.8	-0.6	0.6
IDS018	1.9	-0.8	1.6	1.3	2.6	2.9	0.4	0.9	-1.0	-2.9	1.5	0.9	1.3	0.7
IDS019	0.2	-1.2	-1.1	0.0	1.8	1.0	-1.2	0.5	-1.8	-3.2	-0.4	0.7	-1.1	0.2
IDS020	2.2	-0.4	0.8	1.5	2.9	2.5	1.0	0.9	-1.3	-3.1	0.7	2.3	-0.7	3.3
IDS021	1.0	-0.5	0.8	1.3	1.9	1.5	0.8	0.8	-0.8	-2.9	-0.7	1.4	0.2	1.1

Table 7: Contamination factor and pollution load index results of trace elements in the study area.

Sample	Cu	Pb	Zn	Ni	Co	Mn	As	U	Th	Sr	Cd	V	La	Cr	PI$_N$
IDS001	1.00	0.32	0.72	0.95	1.57	1.31	1.31	0.96	0.18	0.06	0.6	1.22	0.51	1.01	**0.01**
IDS002	0.84	0.60	0.81	1.26	2.86	1.46	1.46	1.46	0.39	0.07	0.6	3.40	0.42	2.01	**0.08**
IDS003	2.02	0.40	0.50	0.93	3.81	2.13	2.13	0.92	0.26	0.05	0.7	3.54	0.29	6.90	**0.03**
IDS004	2.78	0.51	0.65	1.34	3.61	3.08	3.08	0.77	0.24	0.08	0.6	1.46	0.83	1.67	**0.09**
IDS005	1.52	0.46	1.41	1.22	2.29	2.65	2.65	1.08	0.34	0.07	0.6	1.39	0.90	1.06	**0.45**
IDS006	1.96	0.56	0.60	1.53	4.24	3.17	3.17	0.92	0.25	0.07	0.8	1.39	0.64	1.47	**0.09**
IDS007	0.66	0.36	0.80	2.00	3.81	1.79	1.79	1.58	0.43	0.10	0.1	2.99	0.56	1.68	**0.06**
IDS008	2.17	0.36	0.55	1.49	5.36	3.93	3.93	1.00	0.17	0.07	1.1	2.04	0.40	2.27	**0.04**
IDS009	1.22	0.36	1.19	1.27	2.18	1.79	1.79	1.08	0.28	0.06	0.6	1.36	0.71	1.17	**0.19**
IDS010	2.25	0.41	0.99	1.55	3.03	2.47	2.47	0.73	0.17	0.16	0.7	2.28	0.60	2.24	**0.01**
IDS011	2.59	0.37	0.60	0.92	1.19	1.24	1.24	1.00	0.25	0.06	0.3	1.26	0.45	1.23	**0.15**
IDS012	3.33	0.38	1.29	1.07	2.74	3.76	3.76	0.77	0.16	0.09	1.3	1.05	0.63	1.02	**0.17**
IDS013	0.65	0.34	0.77	2.01	4.15	2.48	2.48	1.31	0.28	0.07	0.7	2.28	0.55	2.06	**0.01**
IDS014	0.89	0.29	0.69	2.08	2.18	0.81	0.81	1.31	0.31	0.09	0.2	3.03	0.59	3.73	**0.09**
IDS015	1.95	0.45	0.71	0.93	2.61	2.28	2.28	0.77	0.27	0.06	0.4	1.33	0.89	1.72	**1.20**
IDS016	0.40	0.27	0.52	0.71	0.63	0.17	0.17	0.50	0.18	0.05	0.1	1.29	0.40	1.11	**0.01**
IDS017	2.71	0.35	0.81	1.38	3.44	2.97	2.97	0.77	0.15	0.18	1.3	1.19	0.43	1.02	**0.12**
IDS018	2.42	0.39	2.08	1.62	4.03	4.84	4.84	1.23	0.34	0.09	1.9	1.26	1.62	1.11	**1.30**
IDS019	0.77	0.30	0.30	0.67	2.39	1.29	1.29	0.92	0.19	0.07	0.5	1.05	0.31	0.76	**3.49**
IDS020	3.17	0.52	1.17	1.84	5.03	3.80	3.80	1.23	0.27	0.08	1.1	3.30	0.40	6.36	**0.10**
IDS021	1.38	0.48	1.15	1.62	2.54	1.90	1.90	1.19	0.38	0.09	0.4	1.77	0.78	1.44	**0.18**

PLI = Pollution load Index.

CONCLUSION

Trace element concentrations of subsoil and rocks (Granite Gneiss and Pegmatite) that underlain Labunwa-Odole and environs have been determined to ascertain the relative concentration, distribution and sources of the trace elements in the study area since the area is economically an agrarian terrain. The concentrations of these elements decreased in the following order: Mn > Ba > La > Zn > V > Cu > Cr > Pb > Co > Sr > Th > Ni > Sc > U > Se > As > Cd. The trace element concentrations were relatively low. The average concentration of the trace elements in the subsoil was lower than the average shale (earth crust) concentration except for Pb, Co, Mn, Th and Se, which showed slightly higher concentrations. Similarly, lower concentrations of trace elements were observed when compared with the results from other cited published works. Furthermore, we observed that the trace element concentrations in the subsoil were largely lower than the concentrations in the underlying crystalline rock, suggesting that the enrichment of these trace elements in the subsoil was influenced by the weathering of the rocks in the study area. Locations with relatively higher concentrations of these trace elements suggest possible geogenic source.

Results of the pollution status quantifications such as the Igeo, Contamination Factors and Pollution Load Index showed that the trace elements ranged from uncontaminated to moderately contaminated. Correlation and clustering analyses point to a geogenic rather than anthropogenic source for the trace elements.

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Compliance with ethical standards

Conflict of interest: The authors declare no conflict of interest whatsoever.

Data Availability Statement

The authors hereby declare that the data of this manuscript with expressly be provided when it is requested for.

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