Trace elements characterization of soils and rocks in Agricultural areas of Labunwa, Near Idanre, Southwestern Nigeria

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Abstract

Trace elements (TE) concentrations of subsoil and the underlying parent rocks of Labunwa – Odele area were determined in order to ascertain the enrichment level, distribution and sources of these TEs in the subsoil in the study area. Twenty-one (21) subsoil (at depth of 30 -100 cm) and thirteen (13) rock samples were collected, pulverised and digested using aqua regia for soil samples and near total digestion of HClO$_4$, HF, HCl and HNO$_3$ of different proportions for the rocks. The samples were analysed using Inductively Coupled Plasma-Mass Spectrometry, (ICP-MS). The mean TE concentrations in ppm for 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) with Cu (22.9), Pb (61.4), Zn (64.6), As (1.0), U (2.6) and Pegmatite, (PGM) 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 PGM in the area. Pollution status indices, I-geo, Contamination factor and PLI showed that the study area is practically unpolluted. This suggests that locations with relatively higher concentrations of some TEs are probably due to mineralisation and since most of the subsoil TEs are significantly lower in concentrations compared to the underlying bedrock, the area is safe for agricultural activities.

Introduction

Soils are heterogeneous mixture of organic and inorganic materials that have been formed as a result of the breakdown of biological, chemical and physical materials, which are mobilised by various means of transportation and deposition. According to Abou El-Anwar et al., (2019), 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 makes up the remaining. However, the chemistry of the local soils are essentially influenced by factors such as the underlying rocks (podogenic and lithogenic weathering effects) (Salman 2013), regional and local climatic conditions, 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 significant amount of water as well as other biological materials. These phenomena, also add to the physical characteristics that the soils exhibits, such as acidity and alkalinity, texture, colour, moisture content, organic matters, structures and shapes, among other physical attributes. These attributes make soil very important component of the ecosystem for agricultural activities as well as other economic benefits. Owning to these strategic relevance of soil to mankind, interest in the understanding of trace element enrichment, distribution and the source apportionment, whether anthropogenic or geogenic, becomes very important for environmental and health wellbeing of end users.

Soils are 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 that underlay crystalline environment mostly, undergo weathering to form the overlying soils in such area, often than not, the chemistry of the overlying soil shows close resemblance to the chemistry of the rocks, except in cases where there are enrichment resulting from anthropogenic inputs. Hence, Soils can serve as sink for trace element accumulation, which can have records of past anthropogenic events. In the same vein, soils can serve as habitant for diverse organisms and plants.

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

The use of Agrochemicals such as herbicides for weeding, pesticides as well as plants fertilizers has been reported to influence the enrichment of trace elements in agricultural landuse (Larrios et al. 2012, Shi et. al., 2015; Gall et. al, 2015; Quitero et. al.,
And such relative enrichment of these trace elements that are present in the agricultural input might be of hazardous status when they exceed permissible limit in the geomedia.

Agricultural soil are critical assets that need to be monitored, particularly with respect to the chemical status, because there is the possibility of mobility of such trace elements into the plant and other living things that interact 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 from geochemical characteristics of sediments and soils. This 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, with the exception of samples from Owode Onirin stream catchment, which fell within very high to extremely high risk. Several published works have similarly used inference statistical methods in assessing soils and sediments’ elemental enrichment status, whether the geomedia are from geogenic or otherwise(Grba et 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 forgoing, it becomes very important that such an agricultural soil needed to be continuously monitored.

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

**Study Area**

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 temperature varying between 21.1 to 22.3°C during the raining season, while it ranges from 31 to 32.1°C during the dry season and with mean temperature between 26.0 to 28.1 °C (Nicholson, 1981, Abuloye et al., 2017; Omogbai 2010). The rainy (wet) season extents from April to November every year, while the dry season starts from late November to end of March every year. Because of the relative abundant rainfall recorded every year, the area is characterized by moderate to dense vegetation. The vegetation ranges from shrubs to tall trees, hence plants like cocoa, yam tubers, cassava, and maize among others are cultivated in this area. Isolated floodplains of little 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 as a result of tectono-stratigraphic 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 (Ajbade et al., 1987, Ajibade et al., 2008, Adekoya 1991). In the study area, two rock types were mapped in the course of the field exercise. The two rock types are Granite Gneiss, which dominate over 90% of the study area as well as the pegmatite. The pegmatite are mainly exposed along the stream channels (Figure 2). The dominate felsic minerals include quartz, alkaline (K) feldspar and plagioclase feldspar, while the mafic minerals include biotite, hornblend and muscovite mica. Accessory mineral include rutile, nepheline and opaque minerals.
Methodology

Twenty – one (21) composite subsoils samples were collected from the B – horizon at depth that ranged between 30cm – 100cm. To obtained the composite samples, three (3) sub samples were collected from each of the grids that had been drawn of the topographic sheet prior to sample collection. The three sub-samples were then mixed together to obtained the composite sample (Figure 1). The soil sampling exercise was conducted at the peak of dry season, precisely in February, 2019. Collection was done with the aid of hand auger and care was taken to ensure that samples were not contaminated. This was achieved by carefully washing the hand auger with detergent, properly rinsed and drying it after each samples collection. The collected samples are, thereafter, carefully put in a well-labelled sample bag, the coordinates of the location and other necessary observations recorded in the field notebook. Similarly, at every sample point, a larger diameter cutting head was employed in order to first 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. Both the soil and rock samples were properly labelled upon sampling, in a bag and transported to the laboratory for sample preparation.

The soil samples were air dried at room temperature for a period of eight (8) days. The dried samples were, subsequently, pulverized and sieved using 053um mesh fraction. Furthermore, the sieved samples were digested using modified partial digestion method, (Aqua regia). The digestion process involves gradual input of 5ml nitric acid (mesh Suprapur of 65%), with the addition of 2ml hydrochloric acid (HCL) (merch supapur 36°C) and 10ml of pure water of 18mΩ/cm specific resistivity) in ultraclean tube. The samples were heated at temperature of 95°C for two (2) hours, using microwave oven. At the end of heating, the samples were decanted in volumetric flask of 50ml size. Then, the solution were extracted using disposable syringe filtered through a 0.45 filter membrane. The digested samples were analysed using Inductive Coupled Plasma – Mass Spectrometry (ICP-MS), using AVIO200, PerkinElmer, MA USA model. Similarly, for the rock samples, thirteen (13) representative samples were further selected from the thirty – one (31) field samples for geochemical analysis. Prior to ICP-MS analysis, near total digestion method, using HClO₄, HF. HCl and HNO₃ 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 shaking in clean bath for a period of 35 minutes. The digestion procedures followed the established protocol of 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 (HClO₄) of 60 w% and 0.3 ml of concentrated hydrofluoric HF acid of 60 wt, were gradually added to 0.5g 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 hours in other to properly mix up and dissolve the samples. Thereafter, the bottles were opened, using hot plate that was made of ceramic materials, the samples were gradually dried from increased temperature of 120°C through 140°C to a maximum temperature of 200 °C for a period of six (6) hours. Thereafter, the degraded samples were again gradually introduced with 0.2 ml of 35 wt % of Hydrochloric acid (HCl) in other to dissolve the samples completely. Then, the dissolved samples were dried under a temperature of 120°C for another 6 hours and then nitric acid (HNO₃) where added to the dried samples to round up the dissolution process before about 25 ml of 0.5 M of HNO₃ was added to 50 ml bottles before the analysis of trace elements. Subsequently, the analysis of the digested samples were carried out using ultra-trace Inductively Coupled Plasma Mass Spectrometry method (ICP-MS)(AVIO 200, PerkinElmer, MA, USA) at ACME Laboratory, Canada.

Procedures for quality control and assurances were carried out before and in between the analysis of the samples. These were done using certified reference materials, duplicate samples as well as 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 showed in Table 1, indicated significantly high sensitivity values which suggest that the equipment was highly sensitive and was satisfactory for the determination of 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 | 327      | 164          | <1 |
| 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

In order 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 in evaluation of 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 below;

\[
I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right)
\]

From the equation, \( C_n \) means the concentration of trace element in the subsoil in ppm, \( B_n \) 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, which is used as a factor to minimize variation in the litho materials. Under this evaluation, classification that ranges from 0 to 5, as stated below, have been adopted to represent the relative pollution status of each element in every location.

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

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

$$CF = \frac{C_{metal}}{C_{background}}$$

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 have been adopted in this study. The classification is given below.

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

Similarly, for the Pollution Load Index (PLI), the equation below was also used to complimentarily assess the pollution index of each sample location.

$$PLI = \left( CF_1 \times CF_2 \times CF_3 \times CF_4 \times CF_5 \right)^{1/n}$$

Where,

- $CF$ = Contamination Factor
- $C_{metal}$ = Metal concentration in the subsoil
- $C_{background}$ = Natural background value of the metal
- $n$ = Number of metals $(n= 14)$

PLI is an index for evaluation of contamination status of sediment and soil sample to trace elements. It represents the number of times by which 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 according to Priju and Narayana, 2006.

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

### Results And Discussions

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 9.26ppm, as found in location IDS16, to 76.28ppm 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 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 lowest concentration (19.5) recorded in location IDS19, while the highest concentration (134.1) was found in location IDS18. The mean concentration was found to be 56.3 ± 25.8 as the standard deviation. Other locations with relatively low concentration 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 found to be 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 following order: Mn > Ba > La > Zn > V > Cr > Cu > Pb > Co > Sr > Th > Ni > Sc > U > Se > As > Cd.

The mean value of As in the subsoil was 0.9 ppm, which is slightly higher than that in the granite gneiss 1.0 ppm and pegmatite 1.1 ppm (Table 2). Sr in the subsoil also recorded much more lower average value 21.1 ppm, as against 255.1 ppm 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 was found in both the pegmatite and the granite gneiss compare to that in the subsoil. Similar trend 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, the concentrations in pegmatite were relatively higher compared to 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
Summary Results of Trace Elements (ppm) in the Subsoils, Granite Gneiss and Pegmatite Rocks

| Elements | Subsoil \(n = 21\) | Pgm \(n = 5\) | GGN \(n = 8\) |
|----------|---------------------|----------------|----------------|
|          | Max     | Min     | Mean  | STDV | Max     | Mean  | Stdv | Max     | Min     | Mean  | Stdv | Max     | Min     | Mean  | Stdv |
| Cu       | 76.28   | 9.26    | 40.0  | 20.5 | 4.6     | 128.4 | 91.7 | 3.8     | 22.9    | 28.4   |
| Pb       | 36.6    | 16.4    | 24.7  | 5.5  | 8.4     | 17.0  | 9.8  | 126.6   | 25.5    | 61.4   | 37.5 |
| Zn       | 134.1   | 19.5    | 56.3  | 25.8 | 68.0    | 108.8 | 35.3 | 115.1   | 7.8     | 64.6   | 31.2 |
| Ni       | 15.2    | 4.9     | 9.9   | 3.1  | 3.4     | 130.5 | 81.4 | 16.3    | 7.3     | 4.4    |
| Co       | 38.6    | 4.5     | 21.8  | 8.7  | 10.6    | 56.2  | 25.7 | 17.3    | 7.2     | 4.5    |
| Mn       | 2267    | 79      | 1099.3| 541.7| 1923.0  | 1683.0| 243.9| 992.0   | 123.0   | 468.1  | 304.4|
| As       | 2.3     | 0.1     | 0.9   | 0.5  | 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  |
| Th       | 30.9    | 10.6    | 19.0  | 5.9  | 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   | 161.0   | 257.4  | 107.8|
| Cd       | 0.19    | 0.01    | 0.1   | 0.0  | 0.4     | 0.2   | 0.3  | 0.1     | 0.2     | 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 |
| La       | 207     | 36.6    | 78.5  | 37.3 | 110.1   | 27.4  | 51.8 | 35.1    | 29.3    | 3.0    | 127.7|
| Cr       | 124.2   | 13.7    | 36.9  | 29.9 | 361.0   | 13.0  | 266.2| 144.2   | 44.0    | 5.0    | 18.0 |
| Ba       | 365.2   | 72.7    | 197.6 | 74.2 | 2496.0  | 341.0 | 788.4| 954.8   | 2485.0  | 443.0  | 1338.0|
| Sc       | 15.2    | 3.5     | 8.9   | 2.8  | 47.3    | 16.6  | 36.6 | 12.0    | 17.7    | 0.5    | 6.9  |
| Se       | 1.7     | 0.1     | 1.0   | 0.4  | 0.8     | 0.3   | 0.6  | 0.2     | 0.6     | 0.3    | 0.5  |

**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), while coefficient of determination, principal component analysis and cluster (Dendrogram) analysis were carried out on the subsoil trace elements.

For the Pearson correlation analysis \(R^2\), the correlation between Cr and Zn showed 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 fair correlation of 0.511 for subsoil, strong correlation of 0.618 and 0.771 for GGN and PGM respectively. The \(R^2\) of Th and U had 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 relatively fair association of 0.403 and 0.540 for subsoil and GGN respectively, but weak correlation of 0.011 for PGM. 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. In the same vein, the correlation of La and Th was such that the subsoil showed very strong \(R^2\) value of 0.929, while very weak correlation of 0.124 and 0.013 for both GGN and PGM. V and Cu also showed very strong correlation of 0.994 for GGN but very weak to 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 degree of correlation (Table 3). From the correlation coefficient \(r\), it was observed that it ranges from negative correlation of \(-0.4\), between Th and Cu, to 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 possibly 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 Analysis (PCA) with varimax rotation. From the results, a total of five factors with 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 suggest 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 suggests 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 as a result of the substitution of Co with Mn oxides as well as the adsorption of Co on the surface of Mn oxides. This metal association could be interpreted as environmental factor. Elemental affinity may have been associated with lithologic association with pegmate veins that are present in the study area. And since Mn-Oxide can effectively associate with large number of 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 as well as 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 association 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 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 possibly suggest the presence of 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 eigen 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. A similar trend was exhibited by the Bi-plot (Figure 5) which showed a strong correlation between La, Ba and Mn; U and Th; Cu and Se and 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 are two main clusters: Cluster I contains only Mn, while Cluster II contains all the other elements. This analysis is in agreement with the results of the Factor analysis. One of the dominant processes in the secondary geochemical environment is the scavenging action of Mn oxides on other metals (Figure 6).
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 |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Cu  | 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|
| Pb  | 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 |    |
| Zn  | 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|    |    |
| Ni  | 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|    |    |    |
| Co  | 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|    |    |    |    |
| Mn  | 1  | 0.2| 0  | -0.1| 0.3| 0.9| -0.1| 0.5 | 0.1 | 0.5| 0.1| 0.5 |    |    |    |    |    |
| As  | 1  | 0.4| 0.5| 0.1| 0.1| 0.6| 0.1 | 0.4 | 0.1 | 0.3| 0.2|    |    |    |    |    |    |
| U   | 1  | 0.8| -0.1| -0.1| 0.6| 0.1 | 0.2 | 0.1 | 0.5 | -0.2|    |    |    |    |    |    |    |
| Th  | 1  | -0.2| -0.3| 0.5| 0.4 | 0.1 | 0.1 | 0.7 | -0.1|    |    |    |    |    |    |    |    |
| Sr  | 1  | 0.3| 0.1 | 0.1 | -0.1| 0.5 | 0.1 | 0.1 |    |    |    |    |    |    |    |    |    |
| Cd  | 1  | -0.2| 0.4 | 0.1 | 0.6 | -0.2| 0.5 |    |    |    |    |    |    |    |    |    |    |
| V   | 1  | -0.3| 0.8 | -0.2| 0.1 | -0.4|    |    |    |    |    |    |    |    |    |    |    |
| La  | 1  | -0.3| 0.6 | 0.4 | 0.5 |    |    |    |    |    |    |    |    |    |    |    |    |
| Cr  | 1  | -0.3| -0.2| -0.3|    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ba  | 1  | 0.4| 0.6 |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sc  | 1  | 0.4|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Se  | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
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 |

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 are presented in Table 5. Also included in the table are concentrations of trace elements from other parts of the world as well as average world shale concentration. From the results, mean concentration of Cu in the study area subsoil is found to be higher that the Cu concentration in Agricultural soils, Assiut governorate, Egypt (Abou El-Anwar et al., 2019), soil of Agricultural Sites in Sri Lanka (Jayawardana et al., 2013), Cerrado Soils, Brazil (Marques, et al., 2004), Agricultural Soil in Dinxing 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) as well as top and sub soil of Ile · Ife area (Asowata and Akinwumiju, 2020). The mean concentration of Pb in the subsoil in this study is found to be slightly higher compared to soil of Agricultural Sites in Sri Lanka (Jayawardana et al., 2013). And the mean Pb concentration, from this study, is significantly lower compared to the data from other soils in Egypt, Sri Lanka, among other areas of comparison (Table 5). Similarly, the mean Zn concentration, in subsoil of this study, 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 that the sources of these elements are essentially geogenic rather than anthropogenic.
Table 5
Comparison of The Studied Subsoil, Granite Gneiss, Pegmatite (ppm) with other Soil studied in other areas

| Elements | Soil | Pgm | GGN | A | B | C | D | E | F | G | H | I  |
|----------|------|-----|-----|---|---|---|---|---|---|---|---|----|
| 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 | 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 5. These elements include Cu, Pb, Zn, Ni, Co, Mn, As, Th, Sr, Cd, V, U, La and Cr. From the results, it was observed that elements such as Pb, Th, Sr, Cd, As U and La, practically showed negative Igeo values which suggests that the subsoil are practically unpolluted with respect to these elements. Cu Igeo values fall within the range of “unpolluted” in more than 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, locations that were uncontaminated are found to be significantly (about 60%) higher than the sample locations (about 40%) that were moderately contaminated. Similar trend were 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 results for the Contamination Factor (CF), are presented in Table 6. 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, (PLI), as presented in Table 6, showed most of the sampled locations are not polluted except in locations 15, 18, 19 and 21 where their PLI is higher than 1. This may probably be attributed to mineralisation rather than pollution.

Table 5
Geo Accumulation Index results of trace elements in the subsoil in the study area

| Sample | Ig Cu | Ig Pb | Ig Zn | Ig Ni | Ig Co | Ig Mn | Ig As | 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 |
| 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 |
| 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 |
| 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  |
| 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  |
| 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 |
| 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 |
| 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 |
| 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  |
| 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 |
| 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 |
| 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 |
| 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 |
| 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 |
| 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  |
| 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 |
| 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 |
| 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  |
| 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 |
| 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 |
| 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  |

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Table 6
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   | PLI |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-----|
| 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 | 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, with a view to ascertaining the relative concentration, distribution and sources of the metals in the study area since the area is economically an agrarian terrain. The concentrations of these elements decreased in the following order: Mn>La>Zn>V>Cu>Cr>Pb>Co>Sr>Th>Ni>Sc>U>Se>As>Cd. The trace elements were found to be relatively low in concentration. The average concentration of the trace elements in the subsoil were found to be lower than the average shale (earth crust) concentration except for Pb, Co, Mn, Th and Se, which showed slightly higher concentrations. Similar lower concentrations were observed when compared with the results from other authors. Furthermore, it was 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 were influenced by the weathering of the rocks in the study area. Locations with relatively higher concentrations of these trace elements suggest possible mineralisation.

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.

**Declarations**

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Figures
Figure 1

Samples location map of the study area.
Figure 2

the geologic map of the study area
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 Max. and Min. values of the distribution. Also, S represent Subsoil, GGN, Granite Gneiss and PG represent Pegmatite.
Figure 4

(a-g). Bivariant plots of some selected trace elements in the Subsoil, GGN and PG.
Figure 5

Bi-Polar plot for the selected trace elements.

| CASE | Label | Num |
|------|-------|-----|
| As   |       | 7   |
| Se   |       | 17  |
| Cd   |       | 11  |
| U    |       | 8   |
| Ni   |       | 4   |
| Sc   |       | 16  |
| Pb   |       | 2   |
| Th   |       | 9   |
| Co   |       | 5   |
| Sr   |       | 10  |
| V    |       | 12  |
| Cr   |       | 14  |
| Cu   |       | 1   |
| Zn   |       | 3   |
| La   |       | 13  |
| Ba   |       | 15  |
| Mn   |       | 6   |

Figure 6

Dendogram plot the analysed trace elements and sample location, using Average Linkage (Between Groups)