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# **A Geochemical assessment of Soils within Oke-Ogun Area, Southwestern Nigeria.**

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#### **Abstract**

Soil samples within Oke-Ogun area, Southwestern Nigeria, have been analysed for major elements and trace metals with a view to investigate the lithogenic concentrations and distribution, assess the relative mobility of elements during weathering and understand the heavy metals association using multivariate statistical analytical methods. Inductively coupled plasma-mass spectrometry (ICP-MS) analytical results of trace metals in the residual soils indicate elevated values (ppm) for Pb(66.78), Ni(10.64), Cr(35.17), Se(0.73), V(19.36), Mn(665.41) and depletion for Cu(16.59), Zn(52.85), As(1.18), Sn(1.41), Sb(0.18) when compared with those of underlying rocks. Also Pb, Cr and Cd recorded greater values than the maximum limits repoted for Poland, Russia, U.S.A. and UK. Multivariate analysis shows good to strong correlation between Cu-Pb-Cd-Ni-Co; Zn-V and Mn-Cr associations. Hierarchical cluster analysis on the other hand revealed early cluster associations between Cu-V-Cd-Zn and Ni-Co while Pb and Mn formed subsequently later as two additional clusters. The Principal Component Analysis (PCA) revealed a three-factor association with the first having a loading of Cu-Pb-Cd-Ni-Co-Se at a loading factor > 0.6. The ambiguity presence of Cu in Factors 1 and 2 was resolved using orthogonal rotation (varimax) revealing differing sources for the trace metals. Soil matrix inclusion in the plot revealed that the metal loadings of Factor 1 were associated with the Fe-leachate phase. Weathering indices and metal ratio showed that the freshly weathered soils have marked enrichment in Pb, V, Cr and Co which can be linked to the weathering of amphibolites within the area.

**Keywords:** Principal Component Analysis (PCA), Weathering, Metal mobility, Soil Geochemistry

#### **1. Introduction**

Soil, a product of weathering, is the portion of the regolith that is capable of supporting organic part of the ecosystem. Generally this can be grouped as either residual-soils formed on bedrock; or transported-soils formed from materials that have been moved to its current location. The insoluble residues that result from intense weathering of surface rocks in tropical climates where rainfall is high and intermittent, with good drainage, minimal erosion and soils dry out regularly are known as residual deposits of Lateritic type (Brevik., 2002 ). Lateritic soils rich in insoluble oxides of iron and aluminium are a common form of residual deposit and can develop where soluble substances are removed, leaving behind more valuable mineral resources by residual concentration. Release of trace metals may be a potential threat to plants, and consequently animals and humans that may feed on these plants. The trace metals are adsorbed unto surfaces of weathered products such as sediment and soils. These metals posses the ability to remain on the surfaces of these weathered particles for long periods unless they are mobilized by decomposition processes such as redox conditions (Filgueiras *et al*., 2004). Generally, over 99% of trace metals serving as contaminants within water bodies may be trapped on the surfaces of sediments and soils during percolation of water and runoffs. Bowen (1979) put forward residence time in years, for trace elements in temperate soils as 740-5900yrs for Pb, 70-510yrs for Zn, 13-1100yrs for Cd and 310-1500yrs for Cu while residence time in tropical soils is 40 years due to shorter rate of leaching.

The reduced influence of the variety of anthropogenic activities in rural areas may well presuppose that contamination effects are more dominant than pollution. Knox et al. (1999) refers to soil contamination as soil whose chemical state deviates from the normal composition but does not have a detrimental effect to organisms. Trace elements originating from various sources may finally reach the surface soil, and their further fate depends on soil chemical and physical properties and especially on their speciation. Chemical alteration and mechanical breakdown of bedrocks, followed by sorting of particles during transport and deposition, lead to preferential enrichment of specific metals in certain grain-size fractions, and hence, soil and sediment composition tends to be a function of grain size (Weltje and Eynatten, 2004). Hence, an assessment of trace metal concentrations and mobility within the soil medium is germane in environmental monitoring. Metals such as Ca, Na, P, K, Si, Sr, Ba, Rb, Mg, Pb, Ni, Zn, Cr and Co have been described as mobile metals (Taylor and Eggleton, 2001). Soil contaminated with heavy metals can produce apparently normal crops that may be unsafe for human or animal consumption. Therefore, the aim of the study is to present the concentration of some of these metallic ions in residual soils within Oke-Ogun area, southwestern Nigeria, so as to investigation the extent of weathering and assess the mobility of metals released during weathering processes.

#### **2. Description of the study area**

Oke-Ogun is located within the southwestern part of Nigeria. It is a geographic region that covers Iwere-Ile, Itasa, Ijio, Iganna, Oke-Iho and environs. The study area lies between latitude  $07^055^14^{11}N$ , and  $08^007^148^{11}N$  and  $002^058^1$   $12^{11}$ E and  $003^000^1$   $00^{11}$ E longitudes and covers Ijio, Itasa and Iwere-Ile (Fig. 1). The relief is generally low and the area is adequately drained. The area is underlain by granite complex associated with undifferentiated schist supracrustal. Petrographic study of the granite shows abundance of plagioclase feldspars, orthoclase feldspars quartz and others. There is a thick lateritic cover over these rocks believed to be the result of intense weathering of the underlying rocks that are rich in feldspars and quartz among other minerals.

#### **3. Materials and Methods**

Two hundred and twenty (220) soils and twelve rock samples were collected to determine the level of enrichment in the soil of Oke-Ogun area. Each of the soil samples was packed in sack sample clothes using plastic hand trowels. The samples were air-dried for about 21 days, crushed and pulverized in a pestle and mortar. Composite samples of soils were selected and sieved to a mesh size of 63μm.. All samples were analyzed for their major and trace elemental compositions by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at ACME lab, Vancouver, Canada. All statistical analyses performed were done using Statsoft®.

#### **4. Results and Discussion**

## **4.1. Lithogenic Concentrations**

The concentrations of major oxides (Na<sub>2</sub>O, K<sub>2</sub>O, CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO and Al<sub>2</sub>O<sub>3</sub> in weight %), trace elements (Cu, Pb, Zn, Cd, Ni, Cr, Co, Mn, V, Se, As, Sn and Sb in ppm) and statistical parameters of the data (arithmetic mean, standard deviation and range) are presented in Table 1. For the rock samples, average values for the elements were calculated to represent the underlying geology. Mean values of major elements show slightly lower values (wgt%) of Al<sub>2</sub>O<sub>3</sub> (11.25) and K<sub>2</sub>O (4.10) in soils as compared with that of the rock having Al<sub>2</sub>O<sub>3</sub> (12.54) and K<sub>2</sub>O (4.50). The soil samples within the study area revealed a markedly lower value in Na<sub>2</sub>O, 1.55wgt%, against 2.81wgt% recorded for the rock samples. However, MgO, CaO and  $Fe<sub>2</sub>O<sub>3</sub>$  were observed as higher values. The trace element concentrations obtained reveal mean concentrations (ppm) as follows: Pb (66.78), Zn (52.85), V (19.36), Ni (10.64), Cr (35.17), As (1.18), Se (0.73), Cu (16.59) (Table 1). When compared with the bedrock compositions, it was observed that the soil shows enrichment in the following metals Pb, Cr, Co, and V while revealing depletion in Cu, Zn, Ni, Se, As, Sb and Sn. Also, when compared with limits from elsewhere such as Poland, Russia, UK; and U.S.A; result shows that the soil within the study area contains trace metals that are within the allowable limits (Table 2). This presupposes very negligible effect of contamination. However, it was observed that some metals concentrations fall slightly beyond Maximum Allowable Concentrations (MAC) when compared with data from some countries. For example, Pb concentration of 66.78 ppm shows some elevation over the limit proposed by Russia (20 ppm) and U.S.A. (60 ppm). Also, Cr (35.17 ppm) is observed to be above the limit proposed by Russia (0.05 ppm). These metals are described forthwith as lithogenic metals as there was no evidence of contamination from anthropogenic sources suggesting that the negligible values observed may be of geogenic origin. Observation shows that the concentration values of  $Al_2O_3$  and Fe $_2O_3$  in the study area increases away from the rock. Differential leaching of bedrock may be largely responsible for the variation in major oxide concentration in relation to soil geochemistry. Oxides suspected to have been leached with Fe<sub>2</sub>O<sub>3</sub> include MgO, CaO and K<sub>2</sub>O. This trend may not be unconnected to mineralogy.

## **4.2. Multivariate analysis**

The lithogenic metals were subjected to statistical analysis (multivariate analysis) with a view of finding relationships and attempting a definition for their mobility and origin.

#### **4.2.1. Correlation**

Good to very strong relationships exist among lithogenic metals of the Oke-Ogun study area (Table 3). The correlation ratings for this study is put at 0.5 for good correlation (group 1),  $0.6 - 0.7$  for strong (group 2) and 0.8 – 1.0 for very strong (group 3). It is observed that good relationships exist for Ni-Pb-Cd-Co, As-Sn and Zn-V associations. Strong relationship is noticed for Cu-Pb-Cd-Ni-Co and Mn-Cr associations while the relationship between Pb-Cd represents the only very strong relationship that exists for this environment. It is observed that two classes exist for both the good and the strong correlation groups while the very strong group presents only one class. Three mutual relationships are seen between Zn-V, Mn-Cr and Pb-Cd.

#### **4.2.2. Hierarchical Cluster Analysis**

Multivariate statistical approach is used to identify the sources of heavy metals and other elements in soil samples (Yalcin, et al. 2009). Hierarchical cluster analysis was applied to quantify spatial similarity for metal associations of the samples under investigation in relation to the measured metal and physico-chemical characteristics of the soils (Bam et al., 2011). One main primary and two secondary clusters are observed from the dendrogram (Fig. 2a) for the trace metals in soils with significant linkage distance, indicating relatively high independency for each cluster. The dendogram of single linkage Euclidean distances revealed early primary clusters of Cu, Ni, Co, V, Cd, Se, Sb, As, Sn and Zn forming the first cluster. Secondary clusters were formed with late addition of Pb and Mn together with the first cluster to form the second and third clusters respectively.

The first cluster is very well correlated with each other and forms cluster associations with the secondary clusters of Pb and Mn. Chromium (Cr) appears to be associated very closely to the first cluster as well as Pb and Mn. However, the dendogram diagram of weighted pair-group centroid (median) Euclidean distances lends great clarity on the sequence of clustering and the pattern (Fig. 2b). It is observed that an initial cluster, consisting of As, Sn, Se and Sb formed early as **cluster 1**. Nickel (Ni) and Cobalt (Co) formed as a sub-cluster shortly afterwards which later joined with cluster 1 to form **cluster 2**. Much later another cluster is seen to form comprising of Cu and V. Cluster 2 is seen to be joined with this second sub-cluster to form **cluster 3.** Subsequent clusters that formed did not reveal any other sub-class. It is observed that the third cluster joined as a mega cluster with metals Cd, Cr, Zn, Pb, and Mn to form **cluster 4** in a sequence. The presence of Sn, As and Ni in **clusters 1 and 2** is an indication of a mineralised terrain. The proximity matrix (Table 3), a measure of similarity, suggests similarity of metals as follows (i) Cu, Pb, Zn and Mn, (ii) Zn and Mn (iii) Cd, Cr and Mn, (iv) Ni, Cr and Mn. It is inferred that these metals are linked as they are observed to have formed sub-clusters within the major clusters designated as Clusters 1, 2, 3 and 4. Cu, Cd, Zn and very closely Pb show strong similarities in the proximity matrix when compared with the dendogram (Fig. 2b).

The amalgamation schedule, unlike the proximity matrix, reveals the order of similarity with distance (Table 4). This is consistent with other indicators, with the show of an early relationship between As, Sn, Se, Sb, Ni and Co while Cu and V revealed a later relationship. Cd, Cr, Zn, Pb and Mn are shown to be joined to the association much later.

## **4.2.3. Principal Component Analysis (PCA)**

The PCA analysis was employed as the data reduction technique with the result indicated in Table 5. Initial Eigenvalues for all the metals investigated, revealed four principal components with values greater than 1.0 at a total variance of 84%. The factor loadings of 84% total variance did not post loadings for factor 4. However from the factor loadings with a total variance of 76% only three components were loaded (Table 7). For a better understanding, an un-rotated loading factor of greater than 0.6 was chosen. The first factor (Factor 1) is seen to be loaded with Cu, Pb, Cd, Ni, Co, V, Se and Sb and accounts for 41.82% of the common variance (Table 7. This association suggests a common source as all elements have negative values.

Factor 2 shows an interesting pattern as it is seen to be loaded with Cu, As and Sn accounting for 19.74% of the common variance. The Cu is observed here to have a positive loading value that suggest a different source when compared with other loadings of As and Sn in this factor. The source of Cu and its associates (i.e. Pb, Cd, Ni etc.) appears to be different from the metal loadings of As, Sn and Sb, in factor 2. This is an indication of a mineralized soil. Also, the presence of positive loading factor >0.6 for Cu against the source of the same metal in factor-1 suggest a different source. Factor 3 is observed to be loaded with Cr and Mn. Rotation of the factor solution is proposed for clarity (Filgueiras, et al. 2004).

An orthogonal rotation was done using normalized varimax (Table 8) to the rid result of Cu ambiguity. The loadings for factor 1 include Cu, Pb Cd, Ni, Co and Se while that of factor 2 is seen loaded with Zn, V, As, Sn and Sb. Factor 3 remained unaltered. It is also observed that the loading of factor 3 showed a different source from the other metals as they are of negative values (Table 8). The plot of the factor loadings using varimax rotation revealed that As, Sn, Cr, Cu and Co formed an association. Also, As and Sn are revealed to have a differing source from Cr, Cu and Co. The other association involves Mn forming with Pb, Cd, Zn, V, Se, Sb and Ni. Manganese is seen in this other association to be of a different source (Fig. 3a). A varimax factor plot was also performed for the soil matrix and the incorporated trace metals (Fig. 3b) and it is observed that factor 1 are loaded with all the oxides within the soil except Na<sub>2</sub>O that is seen associated with loadings of factors 2 and 3. Also observed is that the trace metals in factor 1 (Pb, Cu, Ni, Co, Cd) appear to have a different source from the leached oxide phase of Fe<sub>2</sub>O<sub>3</sub>, MgO although they show a close association (Fig 3b).

## **4.2.4. Weathering Indices**

The degree of weathering of the bedrock was compared to that of the regolith. The Chemical Index of Alteration,  $(CIA)$ ,  $(100)[A]_2O_3/(A]_2O_3 + CaO + Na_2O + K_2O$ ], (Nesbitt and Young, 1982), reveals an average CIA value of 57.32 for the bedrock within the study area. This value suggests a moderately weathered underlying rock. The Weathering Index of Parker, (WIP),  $(100)[(2Na_2O/0.35) + (MgO/0.9 + (2K_2O/0.25) + (CaO/0.7)]$ , (Parker, 1970; Eswaran, et al., 1973) was used to evaluate the degree of weathering for the soil. This index reveals that the soil is recently weathered with an average value of 8029.26. The intensity of weathering within the study area can be described as mild; as CIA and WIP values infer fresh weathering.

## **4.2.5. Metal Ratio**

The degree of mobility of trace metals from bedrock to soil was examined using metal ratio. The result shows that Pb, Cr, Co and V are mobilized (Fig. 4,) but Pb seems to be the least mobile of the four. Mafic minerals are unstable to meta-stable upon weathering and appear to degrade quite quickly upon exposure which may be responsible for the formation of soils. These minerals serve as source for Cr, Co and V. Vanadium is identified to have preference for organic matter while Cr and Co has affinity for Fe-Mn phase (Pendias and Pendias-kabata, 2001).

#### **5.0 Conclusion**

The assessment of the lithogenic metals within the study area shows that the soil is freshly weathered and that, the mafic minerals are the likely sources of the observed enrichment. From the multivariate analysis, cluster analysis reveals four associations which are (i) As, Sn, Se and Sb; (ii) Ni and Co; (iii) Cu and V and (iv) Cd, Cr, Zn, Pb and Mn while PCA analysis identified three factors with Cu, Pb, Cd, Ni, Co and Se loadings forming the first factor. Factors 2 and 3 are loaded with Zn-V-As-Sn-Sb, and Cr-Mn respectively. This observation is similar to that obtained from the correlation matrix. Examining this relationship under a factor plot (varimax rotation) the following were revealed:

- i) Three associations exist based on source.
- ii) An association exists between Pb, Cd, Ni, Co, Cu which is markedly different from the other two associations.
- iii) The other two association are Zn-V-Se-Sn-Sb-As and Mn-Cr. The former is interpreted to have a source different from the latter. This view is confirmed from the factor loadings after rotation.

The mobility ratio, when considered in the light of the information presented in the amalgamation schedule, infers that enrichment of Pb, V, Cr and Co is localized as transport progresses. The elevated values of Cr and V suggest the presence of Fe-Mn oxide and Organic matter phases. The association of Sn, As and Ni in all the statistical methods employed may be re-investigated for possible mineralization.

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## Table 1:Major oxide (%) and Trace element (ppm) values for rock and soil samples for the study area.

RF - Iwere Ile; IJ - Ijio

Table 2: Maximum allowable concentrations of trace elements in Agricultural soils proposed in the directives of the various countries and different



years (ppm DW) (Kabata-Pendias, A. and Pendias, H., copy right CLC press LLC, 2001).

Table 3: Correlation matrix of trace metals for the Oke-Ogun area.



Table 4: Proximity Matrix of Trace metals within the Oke-Ogun Soils unit.







Table 6: Total Variance explained.







Table 8: Matrix of factor loadings for the trace metals.

	Factor Loadings (Varimax normalized) <b>Extraction: Principal components</b> (Marked loadings are >.600000)		
	Factor	Factor	Factor
Variable		2	3
Cu	0.897	$-0.101$	$-0.211$
Pb	0.854	0.294	0.080
Zn	0.310	0.628	$-0.342$
Cd	0.845	0.288	0.073
Ni	0.792	0.156	0.116
Cr	0.008	0.066	$-0.879$
Co	0.812	$-0.114$	0.119
Mn	$-0.181$	$-0.147$	$-0.849$
V	0.380	0.636	0.225
Se	0.682	0.566	0.076
As	$-0.196$	0.802	$-0.203$
Sn	$-0.086$	0.816	0.498
Sb	0.314	0.873	0.144
Expl.Var	4.416	3.433	2.061
Prp. Totl	0.340	0.264	0.159



Figure 1: Geological map of the study area. (Courtesy Nigerian Geological Survey Agency, NGSA, 2008).







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Figure 3: Factor plots using orthogonal varimax rotation.



Figure 4: Mobility pattern for the trace metals from bedrock to soil for the Oke-Ogun study area.