

*Full Length Research Paper*

# Multivariate cluster analysis of some major and trace elements distribution in an unsaturated zone profile, Densu river basin, Ghana

Edward Komla P. Bam<sup>1,2\*</sup>, Thomas T. Akiti<sup>2</sup>, Shiloh D. Osae<sup>1,2</sup>, Samuel Y. Ganyaglo<sup>1,2</sup>, and Abass Gibrilla<sup>1</sup>

<sup>1</sup>Chemistry Department, National Nuclear Research Institute, Ghana Atomic Energy Commission, P. O. Box LG80, Legon –Accra, Ghana.

<sup>2</sup>Department of Nuclear Science and Applications, Graduate School of Nuclear and Allied Sciences, University of Ghana, P. O. Box AE1, Kwabenya-Accra, Ghana.

Accepted 14 February, 2011

**This study comprises soils formed on Paleoproterozoic Birimian Basement rocks (poorly graded silty sand, gravely sand and silty clays) from the unsaturated zone of the Densu River Basin, taken from a five meter depth. Elemental analysis of the soils samples were carried out by Energy Dispersive X-ray Fluorescence (EDXRF) to ascertain the levels of major and trace elements (K, Ca, Ti, Fe, Mn, Zn, Cu, Zr, Sr, Y, Pb, V, Cr, Ga, Ni and Rb) and to determine by statistical analysis the soil components which control the vertical distribution and the geochemical processes associated with the migration of the elements. The results indicated that there was general leaching of the base cations (K and Ca) near the surface 25 to 75cm depth while Fe and Ti concentrations remained fairly constant. Iron was the most abundant element found in the soil with concentrations ranging from 23.84g/kg to 143.70g/kg. The physicochemical analysis on soils shows moderately acidic to alkaline (pH<sub>H2O</sub> range 5.6 to 8.3) and reducing properties, Eh (mV) ranged from -107.1 to +50.2. Enrichment factor calculations show the metals were depleted or of minimal enrichment (EF values between 0 to 12.14) due to human activities. Cluster analysis of the samples shows only one sample is needed from depths characterised by similar physical properties of texture and colour.**

**Key words:** Unsaturated zone, energy dispersive x-ray fluorescence, vertical distribution, enrichment factor, cluster analysis.

## INTRODUCTION

In areas with relatively well developed soils and a relatively thick unsaturated zone (UZ), the chemistry of underlying shallow groundwater is often determined more by processes which take place in the unsaturated zone and less by processes in the phreatic zone (Malecki and Matyjasik, 2002). The chemical composition of water infiltrating unsaturated zones evolves with depth and is influenced by the properties of the precipitation and mineralogical composition of the sediments. Major and trace metals determined in soil and water from a

particular unsaturated zone could serve as a tool in understanding the source as well as the flow and incorporation of these elements into the groundwater system. The major and trace metal composition in the soils provides necessary information on mineralogical composition and the soil solution gives valuable information on mobility and availability of the metals (Litaor, 1988). With the growing concerns of trace metal pollution of soils and groundwater, it has become important to evaluate the levels of the metals measured in soils with no previous records. In estimating the levels of the major and trace metals to ascertain whether the selected soils were depleted, enriched, or contaminated as a result of human activities, the enrichment factor (EF) approach is used (Blaser et al., 2000; Hernandez et al., 2003). This

\*Corresponding author. E-mail: [evangelbam@yahoo.com](mailto:evangelbam@yahoo.com). Tel: 00233-244-096-565.

approach has been employed as it takes into consideration, the abundance of the metal of interest, relative to the abundance of a conservative, lithogenic element with no significant anthropogenic source (Bowen, 1979). The ratio is then normalized to the corresponding ratio in crustal rocks or the deeper soil horizon (Golchert et al., 1991; Blaser et al., 2000; Hernandez et al., 2003).

Data analysis in geochemical studies is easier with statistical tools such as factor analysis and hierarchical classification which are explanatory techniques. Cluster analysis and Pearson's correlation matrix have proven to be useful in offering reliable classification of the metals and physicochemical properties of soils. This approach has been used widely in the classification of sites under investigation in geochemical and water quality analysis (Wu et al., 2009; Venugopal et al., 2009; Bhuiyan et al., 2010). The objectives of this study were; to investigate the concentration of major elements such as Ti, Fe K and Ca and trace elements Mn, Zn, Cu, Zr, Sr, Y, Pb, V, Cr, Ga, Ni and Rb in the unsaturated zone profile on the Birimian geology, to determine by statistical analysis the soil components which control the vertical distribution and the geochemical processes associated with the migration of the elements.

## MATERIALS AND METHODS

### Study area

The Densu River Basin lies between latitude 5°30' to 6°20'N and longitude 0°10' to 0°35'W in the southern part of Ghana. The Basin has an area of 2,490 km<sup>2</sup> and spans 10 administrative districts. There are about 200 settlements in the basin and the total population is approaching 600,000, equivalent to 240 persons per km<sup>2</sup> compared to a national average of 140 (WRC, 2003). The area is underlain by the rocks of the "upper and lower" Birimian Precambrian crystalline basement rock types. The main soil type in the basin is the forest and savannah ochrosols. The extent, thickness and physical character of the weathered layer vary from one area to another. The forest ochrosols developed over a wide range of weathered parent including granites and the birimian rocks. They are not highly leached soils as a result, containing greater quantities of nutrients as compared to the forest ochrosols and are generally alkaline. The savannah ochrosols are well drained porous and loamy soils developed over granites, birimian and sandstones, whereas the lithosols are found on steep slopes made up of hard resistant rocks. The soils are immature, shallow and generally poor in nutrients (Bekoe, 2005). In the lower lands, the soils are generally deep, well supplied with moisture and sometimes waterlogged near the rivers.

The main socio-economic activities in the basin are agriculture, which engages about 38.9% of the economically active population (Bekoe, 2005). Cocoa, cassava, maize, cocoyam, plantain and vegetables are the major crops cultivated. Other economic activities in the basin include industrial activities of manufacturing, trading, carpentry, and blacksmithing (Figure 1).

### Sample collection and preparation

Soil sampling was carried out during the wet season in June 2008 using an auger drill-rig. At least 500.0 g of single fresh soil sample

was collected at every 25.0 cm depths interval. The soil samples were collected using plastic trowel into clean polyethylene bags. The bags were immediately sealed with thread at the mouth. A total of 20 fresh single soil samples (between 0.25 to 5.0 m) were collected for the entire profile. Soil colour was determined using Munsell soil colour chart and texture and wetness determined after Faniran and Areala (1978). The soil classification was based on the unified soil classification system of the United States Department of Agriculture. The soil samples were air-dried at 29°C in a dust-free place for 7 days and disaggregated using agate mortar and pestle. The samples were then passed through 180 µm sieve (for fine sand fraction) and were homogenized by pulverizing using a Retsch MM200 ball mill with sample compartment and balls made of agate.

### Soil pH and Eh

Soil pH and Eh were measured following the method described by Blakemore et al. (1987). A soil paste (1:5) was prepared by taking 5.0 g of each of the homogenized soil samples and adding 25.0ml of de-ionized distilled water. pH and Eh readings were taken using an Ion Selective Electrode, Ion 6 (Eutech Instruments Pte Ltd/Oakton Instruments). The meter was calibrated using pH buffers of pH 7.00 and 4.00 from National Institute of Standards and Technology (NIST).

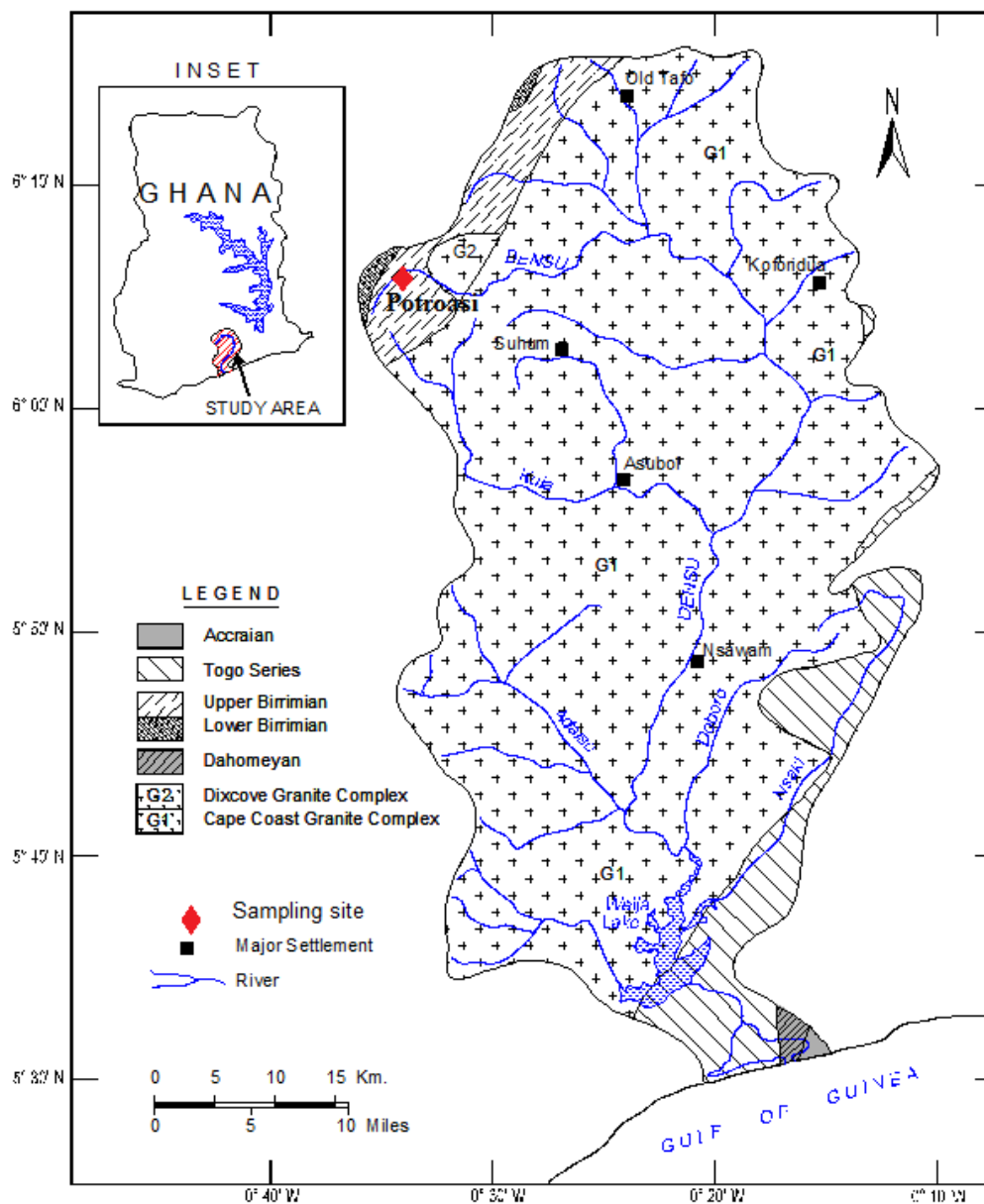
### Energy dispersive-x-ray fluorescence (ED-XRF) analysis

The total elemental concentrations of the soils were determined by weighing 5.0 g each of the pulverized, homogenized powdered samples (<100 µm fraction) into a die and pressed with a manual press (at a pressure of 15 tons) into 32 mm diameter pellet. Using the X-ray fluorescence technique, the sample pellets were transferred onto the sample holder and placed on the excitation source for irradiation for 10 min. A low power X-ray generator tube, compact 3K5 X-ray generator (Ital IS Structures, Italy) was used for the production of the X-rays. The energy dispersive X-ray fluorescence has a maximum power of 3.0 kW (60 kV and 50 mA). The samples were irradiated at 0.8 kW (40 kV and 20 mA) with Mo secondary target as the anode. A Canberra Si (Li) detector, model SL30165 (Canada) with energy resolution of 160 eV for Mn K $\alpha$  energy peak at 5.895 keV, coupled to a preamplifier and amplifier operating at -500 V, was used to detect the resulting fluorescent X-ray lines. The resulting fluorescent X-ray lines were stored in a computer after being analysed in Accuspec multichannel analyser card. The analyses of complex spectra were performed by AXIL software, which is based on iterative nonlinear least square fit of the spectra by the Gaussian shaped spectral lines.

The resulting intensities of pure K $\alpha$  and L $\alpha$  lines of measured elements were then utilized in the quantitative analyses, employing the quantification software QAES (quantitative analysis of environmental samples) designed by Kump (1988). Internal standards and standard reference material 1646a: Estuarine sediment (NIST) and reference material, IAEA SOIL-7(Austria) were analyzed intermittently during sample irradiation to ascertain analytical precision and accuracy of the instrument.

### Statistical procedures and graphical representations

Statistical analysis was performed with Statistical Programme for Social Sciences (SPSS) version 16.0 software for the computation of Pearson's correlation matrix and the hierarchical cluster analysis (CA) which represents a quantitative independent approach of samples and variables classification in environmental studies. CA was performed to identify analogous behaviour among the different parameters (metal contents and the physico-chemical



**Figure 1.** An area map of the sampling site and the Densu River basin.

characteristics of soil), and also among the samples. It was performed on the normalized data set by means of Ward's method using squared Euclidean distances as a measure of similarity between metal concentrations, pH and Eh and also samples. The profile log and graphs were obtained by Hydrogeoanalyst software and Microsoft office excel 2007 for windows.

## RESULTS AND DISCUSSIONS

### Physicochemical characteristics of soils from the profile

The vertical section of the core obtained and the lithologic

compositions are shown in Figure 2. The soil pH ranged from 5.6 to 8.3 pH units and was generally uniform. The soils were classified as moderately acidic to alkaline. The soil depth of 25 cm to 100 cm registered the highest pH values (Figure 3). The redox potentials Eh (mV) recorded for the entire profile ranged between -107.1 (pe = -1.6) to +50.2 (pe = 0.8). The soils can be classified as anaerobic soils, since anaerobic soils have values from +118 to -414 mV (pe +2 to -7) (Rowell, 1981; Alloway, 1995). The highest reducing Eh (mV) of -107.1 (pe = -1.6) to -64.4 (pe = -1.1) were observed from 25 to 100 cm depth. The anaerobic nature and the pH rise in the soils at these depths are due to the stagnation of water on the soil

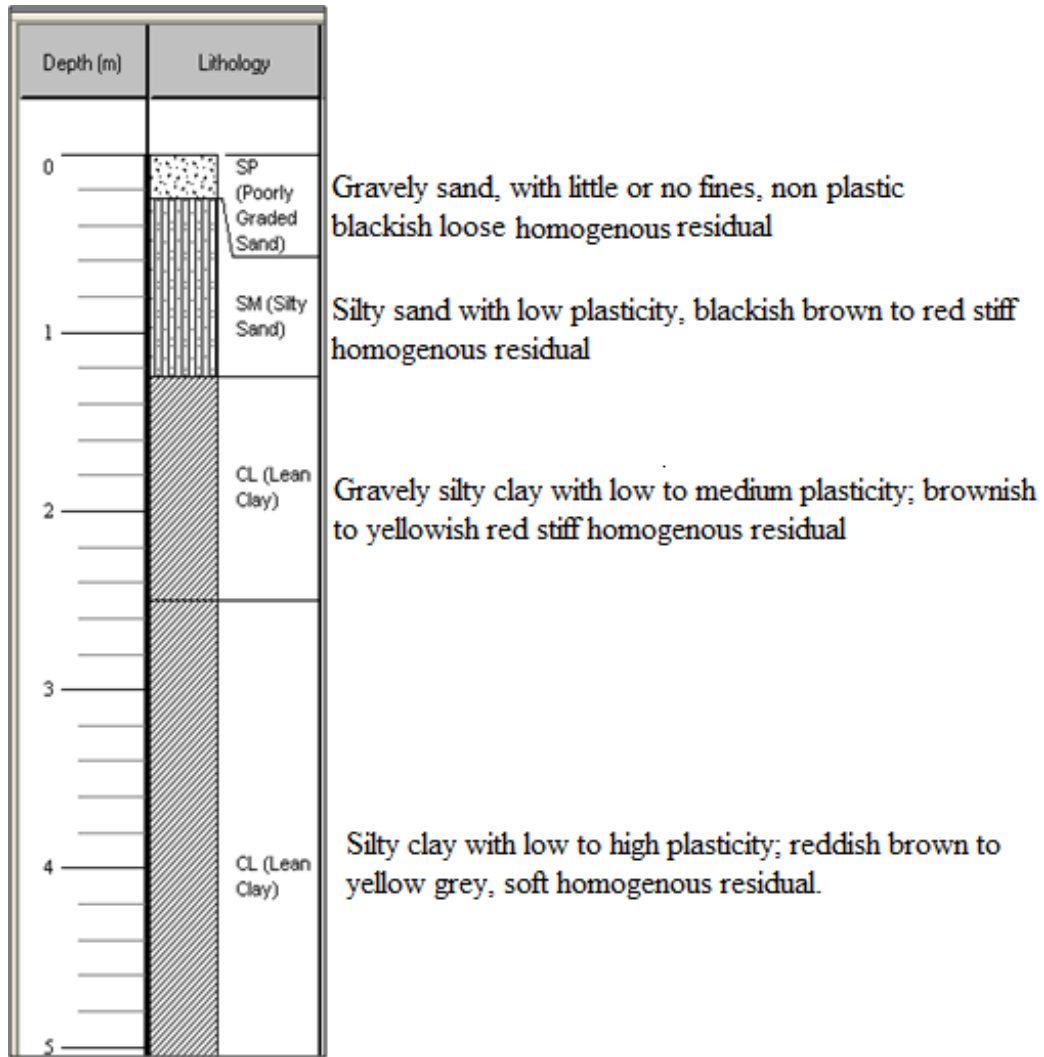


Figure 2. The vertical section of the core obtained and the lithologic compositions.

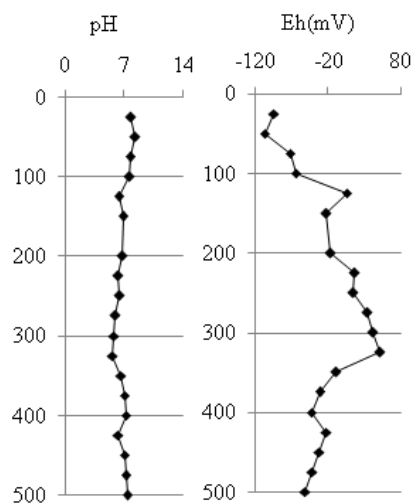
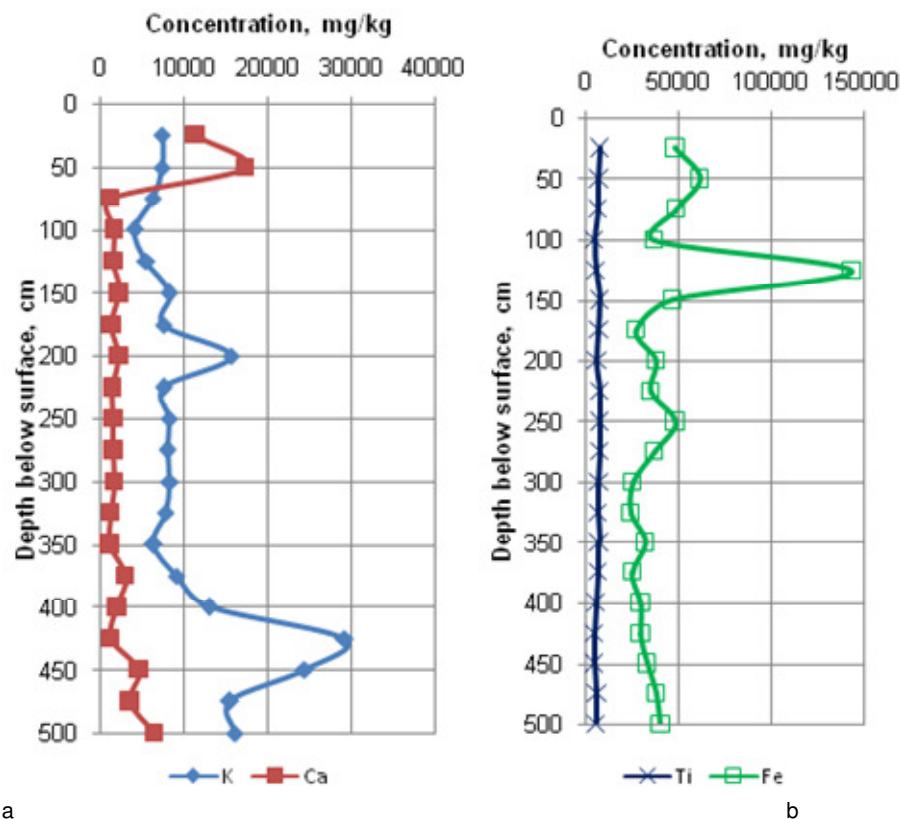


Figure 3. The vertical distribution of the physical parameters of the soil with depth.



**Figure 4.** Vertical distribution of the concentration of major elements in the profile: a) K, Ca b) Ti, Fe.

surfaces. Generally, low pH below 5 and strong reducing conditions favours the dissolution and mobility of most trace metals.

### The vertical distribution of the major elements in the profile

#### Potassium (K) and Calcium (Ca)

For the entire core, Potassium concentrations averaged 10.74 g/kg. The minimum concentration of the entire core is 4.04 g/kg at 100 cm and a maximum of 29.18 g/kg at 425 cm depth and decreases to 16.00 mg/kg at 500 cm. Ca concentration averaged 3.40 g/kg, a maximum of 17.31 g/kg at 475 cm and a minimum of 1.12 g/kg at 350 cm were observed. Ca concentration decreased from 25 to 75cm depth and maintained an almost uniform concentration from 100 to 350 cm depth as shown in Figure 4a.

#### Titanium (Ti) and Iron (Fe)

Titanium concentrations vary from a maximum of 7.39g/g at 150cm to a minimum of 4.39 g/kg at 450 cm depth. A

mean of 6.13g/g is recorded for the entire profile. Ti showed an almost even distribution throughout the entire profile. Iron is the most abundant element observed throughout the entire profile (Figure 4b). An average of 42.28g/kg was observed for Fe in the entire profile. A maximum of 143.70g/kg at 125cm to a minimum of 23.84g/kg at 325cm depth was also observed. Generally, strongly weathered soils are enriched with minerals such as Al, Fe and Ti, which readily forms insoluble oxides and consequently depleted in elements such as Na, Mg, K and Ca which form easily soluble compounds (Agbenin and Felix-Henningsen, 2002; Borggaard and Elberling, 2004) due to leaching out of the soil by downward percolating water under heavy rainfall.

Also considering the poorly graded sand soil found near the surface, it would be easier for compounds of K and Ca to be leached by percolating rainfall.

### The vertical distribution of trace elements in the profile

For ease of discussion, the trace metals were put into three groups. The first group consists of trace elements whose individual concentrations in the soil(s) at any

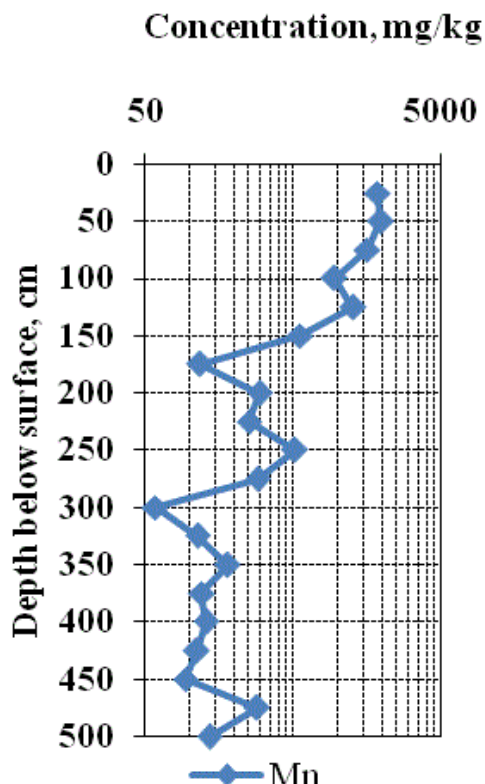


Figure 5. Vertical distribution of Mn in the profile.

depth exceeded 1000 mg/kg (0.1%wt) and the average concentration in the entire profile exceeds 100 mg/kg. These elements were considered to be enriched, and could constitute a main commercial source of those minerals (Alloway, 1995). This group comprised Mn, whose maximum concentration was 1940.50 mg/kg at 50cm with an average of 541.30 mg/kg. Mn concentration decreased down uniformly through the entire profile (Figure 5). Mn forms heavily insoluble oxides which can not be easily leached out by water under conditions of heavy rainfall and the moderately acidic to alkaline (5.60 to 8.31) pH conditions of the soils. The second group comprises trace elements whose individual concentrations and averages throughout the entire profile were less than 1000mg/kg and 100mg/kg respectively. These metals are considered to be in trace metals.

Trace metals depleted or enriched due to natural variability in soils usually individual concentrations less than 1000 mg/kg (0.1%wt.) and average concentrations rarely exceeding 100 mg/kg (Alloway, 1995). The concentrations of these elements are considered to be normal levels as expected of uncontaminated soil. They consist metals typical of those found in soils: Ni, Cu, Zn, Ga, Sr, Y and Pb.

There was no clear distribution pattern for the entire group (Figure 6). Rb concentration increased from 19.78

(100) to 46.79 mg/kg (450 cm). The third group can be called the 'complicated group'. This group comprises trace elements whose individual concentrations in the soil at a particular depth throughout the profile do not exceed 1000 mg/kg (0.1%w) but the average concentration for the profile exceeds 100 mg/kg. It comprised, Cr, V and Zr. Zirconium concentration, increased from 105.37 mg/kg at 100cm to 192.47 mg/kg at 475 cm. However, low concentrations of these elements were recorded at the 25cm depth near the surface. The fairly uniform distributions of Cr, V and Zr in the profile (Figure 7) suggest that they are present in soil mineral fractions or skeletons (Xing and Dudas, 1993; Agbenin and Felix-Henningsen, 2002).

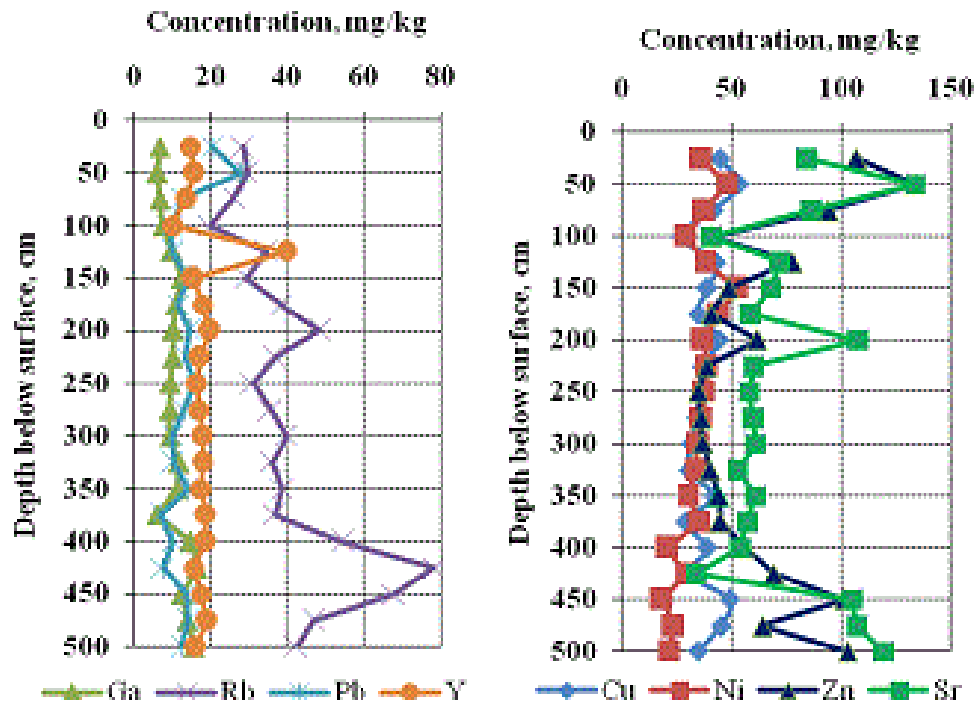
### Correlation and cluster analysis

In order to deduce the inter-relationships between the depths, elemental concentrations and physicochemical characteristics of the soils, cluster analysis and Pearson's correlation matrix was run on the experimental data.

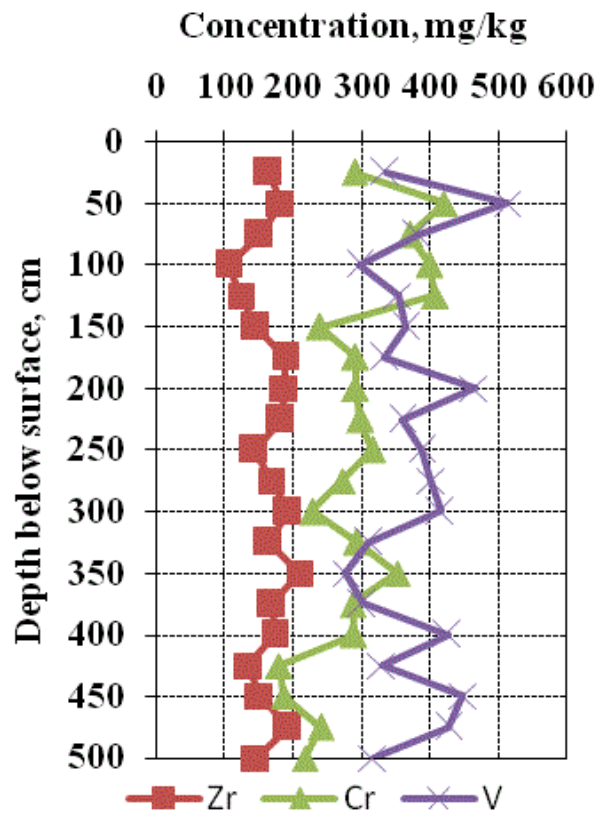
### Cluster analysis and measured experimental data

Cluster analysis was run to identify geochemical groups, clustering the metals that occur and may sometime be moving together on the soil. The result of this analysis is shown as a dendrogram (Figure 8). Cluster 1, includes metals K, Rb and Ga. K and Rb are alkali metals (have similar chemical properties) and occur mostly as lithophiles according to Goldschmidt's classification of geochemical elements (Mason and Moore, 1982). Gallium occurs in soils as sesquioxides and hydroxides or in association with sulphate, nitrate and chloride, and can be adsorbed on clay surfaces (Goering and Fowler, 1991; Agbenin and Felix-Henningsen, 2002). The commonest minerals present in the rocks of the geological terrain are the plagioclase feldspars, ranging in composition from albite ( $\text{NaAlSi}_3\text{O}_8$ ) to anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), and K-feldspars with hornblende and micas occurring as accessories. Cluster 2 includes pH, Ca, Pb, Cu, Sr, Zn and V. Though these parameters grouped in one cluster, the physico-chemical parameter pH clustered separately on minor scale indicates that these factors may not be impacting directly on other members. However, pH affects the dissolution, precipitation and adsorption of trace metals in soils.

Ca, Sr and V are associated with weathering of silicate bearing minerals for example, calcium-rich component of the plagioclase feldspars, pyroxenes, anorthite and amphiboles found in the study area (Alloway, 1995; Ganyaglo et al., 2010). Cu, Zn and Pb may be the result of weathering of sulfide minerals as galena and sphalerite. Ca and Sr have similar chemical properties, while V is found normally co-precipitated on calcium carbonate minerals (Dinescu et al., 1998; Alloway, 1995). Cluster 3 includes Ti, Ni, Zr and Eh. Ti and Zr have



**Figure 6.** Vertical distribution of trace elements Sr, Pb, Rb, Zn, Y, Ga, Ni and Cu in soils of the profile.



**Figure 7.** Vertical distribution of trace elements Zr, V and Cr in soils of the profile.



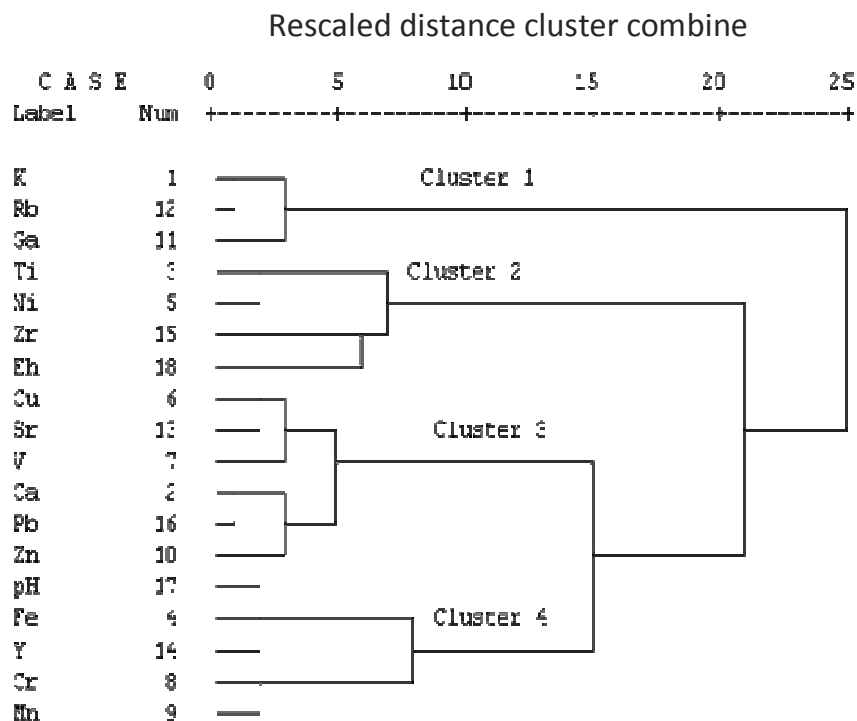


Figure 8. Dendrogram of 16 metals measured, pH and Eh using Ward method.

similar chemical properties and occur in silicate bearing minerals which are resistant to weathering, while Ni occurs with native iron rich minerals (siderophile) and can exhibit the same properties of transition metals as Ti and Zr. Cluster 4 includes Fe, Mn, Cr and Y. These metals are associated with silicate minerals.

The Cluster analysis organised the metals and physico-chemical parameters into groups such that within-group similarity is maximized and among-group similarity is minimized. The cluster analysis points to weathering of rocks in the study area as the source of the metals in the soils. The data on major and trace elements in the parent rock can be used as an indication of the background composition of the soil.

### Correlation analysis

The results of the Pearson's correlation matrix have been presented in Table 1, with significant correlation at  $p < 0.01$  in black bold. The correlation matrix identified the relationship among metals and supported the results obtained by multivariate analysis (CA). Correlation coefficient values exhibiting +1 or -1 between the variables reveal that there exists a strong correlation and a value of zero indicates no relationship between the variables. In general, a correlation coefficient  $> 0.7$  is interpreted as a strong relationship between two parameters, whereas values between 0.5 and 0.7 represent

a moderate relationship.

### Cluster analysis and samples grouping

Cluster analysis was applied to detect spatial similarity for grouping of the samples under investigation in relation to the measured metal and physico-chemical characteristics of the soil. The clustering procedure generated three groups of samples in a convincing way, indicating relatively high independency for each cluster (Figure 9). The cluster 1 includes samples POT07, POT09, POT10, POT11, POT12, POT13, POT14 and POT 15, all located 2.25 to 3.75m except, POT07. Also, these lay within the lean clay classification of the profile (middle) and characterised mostly by soils described as silty clay with low to high plasticity; reddish brown to yellow, soft residual. The soils at POT07 and POT09 are described as gravely silty clay with low to medium plasticity, brownish to yellow red stiff homogenous residual and occur at interboundary of the silty clay and gravely silty clay. Except for texture differences, all the soils are clay. Cluster 2 includes samples POT08, POT16, POT17, POT18, POT19 and POT20. All these samples lay at the bottom 4.0 to 5.0m, except POT08. These are purely lean clays with properties described as silty clay with low to high plasticity, reddish brown to yellow grey, soft homogenous residual. POT08 is described as gravely silty clay with low to medium plasticity, brownish to yellow red



**Table 1.** Pearson correlation coefficient matrix of the 16 elements and the physiochemical characteristics measured for the soils in the profile.

	K	Ca	Ti	Fe	Ni	Cu	V	Cr	Mn	Zn	Ga	Rb	Sr	Y	Zr	Pb	pH
Ca	-0.026																
Ti	<b>-0.606</b>	0.148															
Fe	-0.262	0.149	-0.116														
Ni	-0.552	0.168	<b>0.708</b>	0.251													
Cu	0.104	<b>0.591</b>	0.089	0.373	0.073												
V	0.217	0.403	0.035	0.089	0.069	<b>0.653</b>											
Cr	<b>-0.736</b>	0.212	0.183	0.514	0.395	0.189	-0.022										
Mn	-0.420	<b>0.632</b>	0.195	0.551	0.413	0.486	0.190	<b>0.660</b>									
Zn	0.262	<b>0.791</b>	-0.241	0.333	-0.095	<b>0.695</b>	0.379	0.106	<b>0.628</b>								
Ga	<b>0.860</b>	-0.305	-0.432	-0.178	-0.524	-0.088	-0.057	<b>-0.656</b>	<b>-0.617</b>	-0.069							
Rb	<b>0.935</b>	-0.160	<b>-0.566</b>	-0.251	<b>-0.565</b>	0.073	0.198	-0.694	-0.545	0.105	<b>0.715</b>						
Sr	0.151	<b>0.673</b>	-0.028	0.202	-0.044	<b>0.771</b>	<b>0.594</b>	0.037	0.352	<b>0.761</b>	-0.048	-0.008					
Y	-0.073	-0.162	-0.172	<b>0.781</b>	0.044	0.213	0.056	0.201	0.020	0.014	0.076	0.091	0.047				
Zr	-0.083	0.107	0.509	-0.403	0.083	0.287	0.270	-0.112	-0.264	-0.126	-0.025	0.084	0.229	-0.056			
Pb	-0.196	<b>0.831</b>	0.462	0.165	0.366	<b>0.747</b>	0.534	0.332	<b>0.640</b>	<b>0.596</b>	-0.351	-0.305	<b>0.661</b>	-0.186	0.270		
pH	0.085	0.394	-0.196	0.169	-0.247	0.322	0.222	0.155	0.414	0.465	-0.133	-0.071	0.358	-0.131	-0.254	0.306	
Eh	-0.072	<b>-0.687</b>	0.215	-0.096	0.066	-0.480	-0.185	-0.261	<b>-0.653</b>	<b>-0.756</b>	0.219	0.115	-0.512	0.322	0.171	-0.502	-0.522

Correlation is significant at the 0.01 level (2-tailed) in bold.

stiff homogenous residual. The grouping of POT08 in cluster 2 cannot be explained even though all the members in this group are lean clay soil types, a difference occurs whereas POT08 is a gravely clay; the remaining members are silty clays.

Cluster 3 includes POT01, POT02, POT03, POT04, POT05 and POT06. These lay between 0.25 to 1.25m depth at the top of the profile. Soils are described as silty sand with low plasticity, blackish brown to red stiff homogenous residual, except for POT01. POT01 is a gravely sand, with little or no fines, non plastic blackish loose homogenous residual in direct contact with silty sand fraction.

The results of cluster analysis consider the sampled depths in one group have similar

characteristic features and natural background source type. Thus this could be employed to design a future spatial sampling strategy in an optimal manner by reducing the number of sample taken a given profile considering all factors discussed without losing the significance of the outcome. The results of cluster analysis in this study reveal that for an unbiased study of the unsaturated zone, only one sample is needed from sampling depths which are characterised by similar physical properties of texture and colour, and this may serve as good in spatial assessment of the layer as a whole in the profile.

#### Enrichment factor analysis

In order to evaluate if the present-day metal

content in the soil derives from natural or anthropogenic sources, enrichment factor was calculated for all studied soils using zirconium as a reference element. The enrichment factor is the relative abundance of a chemical element in a soil compared to the bedrock. Zirconium is generally considered as mainly originated from natural lithogenic sources (rock weathering of mineral zircon) and has no significant anthropogenic source. It has widely been used in geochemical studies of mineral weathering as a 'conservative' lithogenic element, against which relative enrichments has been compared (Shotyk, 1996; Blaser et al., 2000). The enrichment factors (EF) calculated here using Zr thus, emphasize the extent of changes in the elemental concentrations of the individual soils relative to the concentration of the

Rescaled Distance Cluster Combine

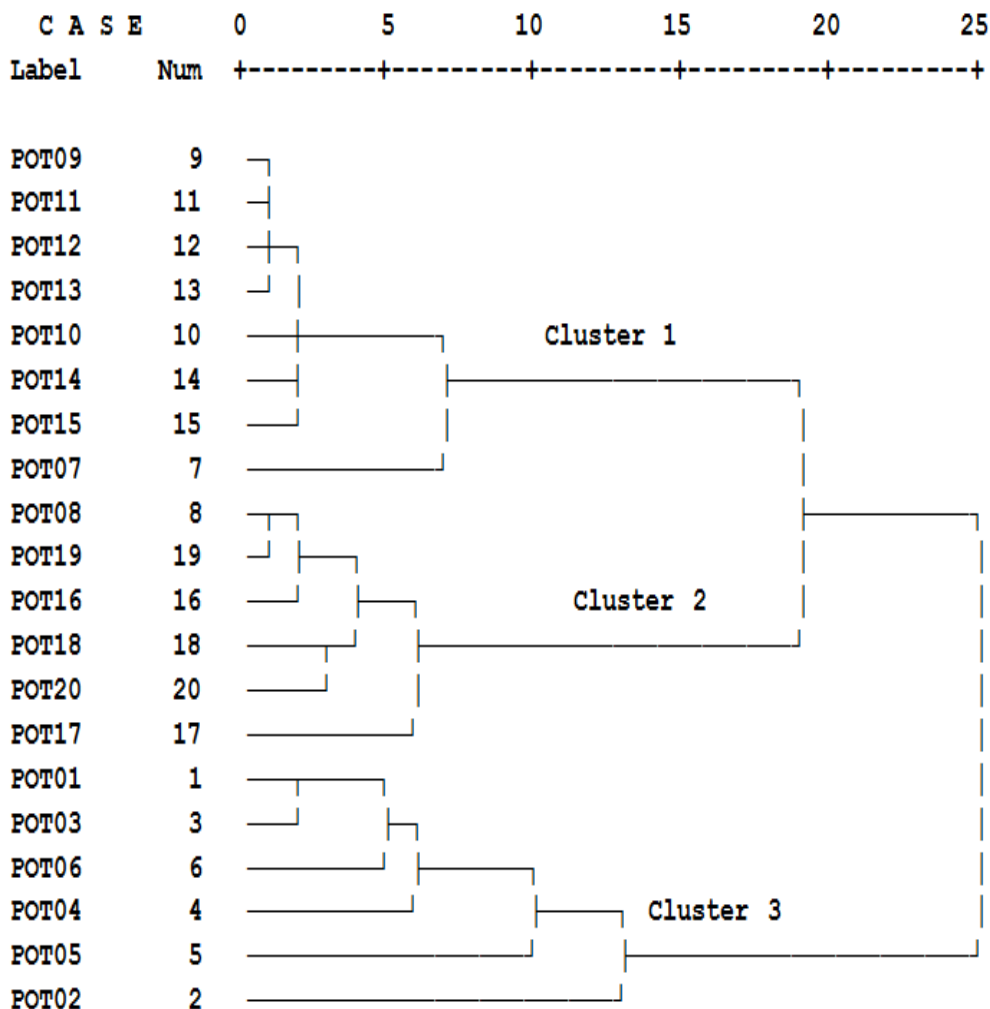


Figure 9. Dendrogram of sampled depths using Ward method.

samples obtained from the average earth's crust since rock values were not available. The reference values were taken for some metals from the earth's crust (Equation 1):

K = 25900 mgkg<sup>-1</sup>, Ca = 36300 mgkg<sup>-1</sup>, Ti = 4400 mgkg<sup>-1</sup>, Fe = 50000 mgkg<sup>-1</sup>, Ni = 75 mgkg<sup>-1</sup>, Cu = 55 mgkg<sup>-1</sup>, V = 135 mgkg<sup>-1</sup>, Cr = 100 mgkg<sup>-1</sup>, Mn = 950 mgkg<sup>-1</sup>, Zn = 70 mgkg<sup>-1</sup>, Ga = 15 mgkg<sup>-1</sup>, As = 1.8 mgkg<sup>-1</sup>, Br = 2.5 mgkg<sup>-1</sup>, Rb = 90 mgkg<sup>-1</sup>, Sr = 375 mgkg<sup>-1</sup>, Y = 33 mgkg<sup>-1</sup>, Zr = 165 mgkg<sup>-1</sup>, Pb = 55 mgkg<sup>-1</sup>, (Krauskopf and Bird, 1995). On the other hand, for all the considered metals from the concentrations in each deepest soil horizon (Equation 2); this is to determine a relative range of enrichment factors.

$$EF1 = [(M / Zr)_{soil} / (M / Zr)_{Earth's\ crust}] \quad (1)$$

$$EF2 = [(M / Zr)_{soil} / (M / Zr)_{deeper\ horizon\ soil}] \quad (2)$$

Where (M) is total elemental concentration (mg/kg) and (Zr) is total concentration of Zr (mg/kg) measured in soil sample/earth's crust, respectively.

EF values ranging between 0.5 and 2 can be considered in the range of natural variability, whereas ratios between 2 and 10 indicate some enrichment caused by the presence of humans and a clear indication of substantially increased values caused by human influence (anthropogenic inputs) EF ≥ 10 (Golchert, 1991; Hernandez et al., 2003). EF 20 to 40 is very high enrichment and EF > 40 is extremely high enrichment (Fong et al., 2008). The result of EF calculations are shown in Table 2.

**Table 2.** Enrichment factors calculated with Equation (2) and (3).

Sample ID	Depth/cm	K		Ca		Ti		Fe		Ni		Cu		V		Cr		Mn	
		EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2
POT01	25	0.29	0.41	0.31	1.57	1.67	1.29	0.97	1.06	0.49	1.53	0.82	1.14	2.50	0.94	2.92	1.19	1.96	12.14
POT02	50	0.25	0.36	0.43	2.17	1.42	1.10	1.12	1.22	0.58	1.81	0.88	1.23	3.44	1.30	3.82	1.56	1.85	11.45
POT03	75	0.26	0.38	0.04	0.19	1.56	1.21	1.07	1.17	0.55	1.73	0.83	1.16	3.10	1.17	4.06	1.65	1.82	11.28
POT04	100	0.24	0.35	0.07	0.37	1.65	1.28	1.15	1.26	0.61	1.91	0.76	1.06	3.45	1.30	6.26	2.55	1.56	9.64
POT05	125	0.28	0.40	0.06	0.29	1.55	1.20	3.85	4.22	0.68	2.13	1.05	1.46	3.51	1.32	5.46	2.22	1.79	11.03
POT06	150	0.36	0.52	0.07	0.35	1.91	1.48	1.07	1.17	0.79	2.48	0.81	1.13	3.07	1.16	2.72	1.11	0.66	4.10
POT07	175	0.25	0.36	0.03	0.16	1.34	1.04	0.47	0.52	0.52	1.61	0.55	0.77	2.17	0.82	2.54	1.04	0.11	0.66
POT08	200	0.53	0.76	0.05	0.27	1.19	0.92	0.66	0.73	0.44	1.36	0.71	0.99	3.03	1.14	2.57	1.05	0.27	1.69
POT09	225	0.27	0.38	0.04	0.18	1.44	1.11	0.64	0.70	0.47	1.47	0.60	0.84	2.42	0.91	2.71	1.10	0.24	1.48
POT10	250	0.36	0.52	0.05	0.24	1.88	1.46	1.11	1.22	0.58	1.81	0.76	1.06	3.32	1.25	3.64	1.48	0.62	3.85
POT11	275	0.30	0.43	0.04	0.21	1.56	1.21	0.72	0.79	0.48	1.49	0.61	0.85	2.92	1.10	2.66	1.08	0.30	1.83
POT12	300	0.27	0.39	0.04	0.19	1.32	1.03	0.43	0.47	0.40	1.25	0.49	0.69	2.63	0.99	1.94	0.79	0.05	0.33
POT13	325	0.30	0.43	0.03	0.17	1.51	1.17	0.48	0.53	0.45	1.41	0.56	0.77	2.32	0.87	2.96	1.20	0.12	0.74
POT14	350	0.19	0.28	0.02	0.12	1.24	0.96	0.50	0.55	0.32	1.00	0.60	0.84	1.62	0.61	2.78	1.13	0.15	0.92
POT15	375	0.34	0.49	0.08	0.40	1.33	1.03	0.49	0.53	0.46	1.45	0.52	0.73	2.19	0.82	2.81	1.14	0.12	0.76
POT16	400	0.48	0.68	0.05	0.26	1.13	0.88	0.56	0.62	0.26	0.82	0.67	0.94	3.02	1.14	2.75	1.12	0.13	0.80
POT17	425	1.38	1.98	0.04	0.22	1.26	0.98	0.72	0.79	0.47	1.47	0.69	0.96	3.00	1.13	2.19	0.89	0.14	0.89
POT18	450	1.03	1.48	0.14	0.69	1.09	0.85	0.71	0.78	0.27	0.84	0.97	1.36	3.64	1.37	2.03	0.83	0.11	0.66
POT19	475	0.51	0.73	0.08	0.41	1.13	0.87	0.65	0.71	0.27	0.84	0.71	0.98	2.72	1.02	2.06	0.84	0.26	1.59
POT20	500	0.70	1.00	0.20	1.00	1.29	1.00	0.91	1.00	0.32	1.00	0.72	1.00	2.66	1.00	2.46	1.00	0.16	1.00

Table 2. Continued

Sample ID	Depth/cm	Zn		Ga		Rb		Sr		Y		Pb	
		EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2	EF1	EF2
POT01	25	1.54	0.92	0.44	0.37	0.32	0.59	0.23	0.63	0.44	0.80	0.37	1.48
POT02	50	1.73	1.04	0.36	0.30	0.30	0.56	0.32	0.90	0.43	0.78	0.46	1.82
POT03	75	1.47	0.88	0.47	0.40	0.32	0.59	0.25	0.70	0.44	0.81	0.25	1.01
POT04	100	0.91	0.55	0.75	0.63	0.34	0.64	0.17	0.47	0.47	0.86	0.27	1.07
POT05	125	1.49	0.89	0.86	0.73	0.51	0.95	0.26	0.72	1.61	2.94	0.24	0.96
POT06	150	0.78	0.47	0.93	0.79	0.37	0.69	0.21	0.57	0.53	0.96	0.29	1.14
POT07	175	0.51	0.30	0.62	0.52	0.37	0.69	0.14	0.38	0.47	0.86	0.18	0.72
POT08	200	0.78	0.47	0.59	0.50	0.47	0.88	0.25	0.70	0.53	0.96	0.23	0.92
POT09	225	0.50	0.30	0.60	0.50	0.37	0.69	0.15	0.40	0.47	0.87	0.22	0.87
POT10	250	0.57	0.34	0.72	0.61	0.40	0.74	0.18	0.49	0.57	1.04	0.33	1.33
POT11	275	0.50	0.30	0.60	0.51	0.39	0.72	0.16	0.43	0.51	0.93	0.23	0.92
POT12	300	0.45	0.27	0.52	0.44	0.38	0.71	0.14	0.39	0.46	0.84	0.15	0.62
POT13	325	0.58	0.35	0.77	0.65	0.40	0.75	0.14	0.39	0.54	0.99	0.18	0.74
POT14	350	0.50	0.30	0.59	0.49	0.34	0.63	0.13	0.36	0.42	0.76	0.20	0.80
POT15	375	0.63	0.38	0.37	0.32	0.40	0.74	0.15	0.41	0.55	1.01	0.12	0.49
POT16	400	0.77	0.46	0.93	0.78	0.58	1.08	0.14	0.38	0.54	0.98	0.17	0.69
POT17	425	1.22	0.73	1.34	1.13	1.06	1.99	0.11	0.31	0.57	1.05	0.17	0.66
POT18	450	1.58	0.95	0.90	0.76	0.83	1.54	0.31	0.85	0.58	1.05	0.27	1.07
POT19	475	0.79	0.47	0.78	0.66	0.45	0.83	0.25	0.68	0.50	0.91	0.22	0.88
POT20	500	1.66	1.00	1.19	1.00	0.54	1.00	0.36	1.00	0.55	1.00	0.25	1.00

The enrichment calculations using the earth's crust (EF1) and deeper horizon soil (EF2) for K, Ca, Ti, Fe, Ni, Cu, V, Cr, Zn, Ga, Sr, Y and Pb registered EF values between 0 and 7.0. This implies the metals are depleted (< 2) or have minimal enrichment (2 to 5) as in the cases of V, Cr and Fe. The relatively high EF values for these metals could be result of natural variability of metals in soil and human influence from agricultural and vehicular activities associated with the

area. EF2 value for Mn shows general enrichment as values decrease from the top to the bottom of the profile. This is a sign of pollution, and could be attributed to fertilizer use in farms. The differences between EF1 and EF2 can be attributed to the disparity between the earth's crust and the deep soil horizon concentrations. Consequently, without bedrock data reference for the studied soils; the accurate value for the enrichment factor is in between the values given in Table 2.

## Conclusion

The physico-chemical analysis of the soils shows that the soils are moderately acidic to alkaline in nature with pH values ranging 5.6 to 8.3 in 1:5 soil: water analysis. A redox potential value of -107.1 to +50.2 suggests anaerobic soils with reducing properties. Soil moisture content shows the soils were slightly moist with volumetric moisture content average of 17.4%. The soil pH

and moisture content were moderately correlated suggesting their interdependence on each other. The order for elemental abundance of major elements measured is Fe > K > Ti > Ca. Base cations K and Ca showed a decrease in the profile at the topmost layer while, Fe and Ti were relatively distributed uniformly within the entire profile. Enrichment factor calculations using Zr as normalizing element, show 16 elements measured; K, Ca, Ti, Fe, Mn, V, Cr, Pb, Cu, Zn, Sr, Y, Ga, Rb and Ni were depleted or minimal enrichment due to human influences from agriculture and vehicular activities. Differences exist between EF1 and EF2 attributed to the disparity between the earth's crust and the deep soil horizon concentrations consequently, calls for bedrock data reference for the studied soils in future.

The results of cluster analysis in this study reveal that for an unbiased study of the unsaturated zone, only one sample is needed from sampling depths which are characterised by similar physical properties of texture and colour, and this may serve as good in spatial assessment of the layer as a whole in the profile.

## ACKNOWLEDGEMENT

We are indebted to the technologists and the National Nuclear Research Institute, Ghana Atomic Energy Commission for allowing us use their laboratory facilities and Water Resources Commission for providing funds to support the sampling.

## REFERENCES

- Agbenin JO, Felix-Henningsen P (2002). The Status and Dynamics of Some Trace Elements in a Savannah Soil under Long-Term Cultivation. *Sci. Total Environ.* 277: 57-68.
- Bekoe EO (2005). Application of a Hydrological Model in a Data-Poor Tropical West African Catchment, A Case Study of the Densu Basin of Ghana, PhD. Thesis, Institute of Water and Environment, Cranfield University, Silsoe, 223 p.
- Bhuiyan MAH, Parvez L, Islam MA, Dampare SB, Suzuki S (2010). Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. *J. Hazard. Mater.* 173: 384-392.
- Blakemore LC, Searle PL, Daly BK (1987). *Methods for the Chemical Analysis of Soils*, New Zealand, Soil Bureau Scientific Report, 80 p.
- Blaser P, Zimmermann S, Luster J, Shotyk W (2000). Critical Examination of Trace Element Enrichment and Depletion in Soils, As, Cr, Cu, Ni, Pb, and Zn in Swiss Forest Soils. *Sci. Total Environ.* 249: 257-280.
- Borggaard OK, Elberling BO (2004). *Pedological Biogeochemistry*, Institute of Geography, University of Copenhagen, Denmark, 488 p.
- Bowen HJM (1979). *Environmental Chemistry of the Elements*, New York, Academic Press, 333 p.
- Dinescu LC, Dului OG, Mihailscu NG, Vanghelie IM (1998). Investigation of the Vertical Distribution of Major and Trace Elements in Matita Lake (Danube Delta) Sediment by Activation Analysis. *J. Radioanal. Nucl. Chem.* 238(1-2): 75-81.
- Fong FT, Chee PS, Mahmood AA, Tahir NM (2008). Possible Source and Pattern Distribution of Heavy Metals content in urban soil at Terengganu town center. *Malay. J. Anal. Sci.* 12:458-467.
- Goering PL, Fowler BA (1991). Gallium. In: Merian E, editor. *Metals and their compounds in the environment: occurrence, analysis and biological relevance*. Weinheim: VCH, pp. 1127-1133.
- Golchert B, Landsberge S, Hopke PK (1991). Determination of Heavy Metals in the Rock River (Illinois) through the Analysis of Sediment. *J. Radioanal. Nucl. Chem. Articles*, 148(2): 319-337.
- Hernandez L, Probst JL, Ulrich E (2003). Heavy Metal Distribution in some French Forest Soils, Evidence for Atmospheric Contamination, *Sci, Total Environ.* 312(1-3): 195-219.
- Krauskopf KB, Bird DK (1995). *Introduction to Geochemistry*, 3rd Edition, McGraw-Hill Inc., USA, 647p.
- Litao MI (1988). Review of Soil Solution Samplers. *Water Resour. Res.* 24 (5): 727-733.
- Malecki J, Matyjasik M (2002). Vadose zone – challenges in hydrochemistry. *Acta Geol. Polonica* 52(4): 449-458.
- Mason B, Moore CB (1982). *Principle of Geochemistry*, 4th Edition, Wiley, New York, pp.46-177.
- Venugopal T, Giridharan L, Jayaprakash M (2009). Application of chemometric analysis for identifying pollution sources: a case study on the River Adyar, India. *Marine Freshwater Res.* 60: 1254 -1264.
- WRC ( 2003). *Water Resources Commission of Ghana Annual report 2003*, Accra
- Wu B, Zhao D, Zhang Y, Zhang X, Cheng S (2009). Multivariate statistical study of organic pollutant in Nanjing reach of Yangtze River. *J. Hazard. Mater.* 169: 1093- 1098.
- Xing B, Dudas MJ (1993). Trace and rare-earth element content of white clay soils of the Three River Plain Heilongjiang Province, PR China. *Geoderma*, 58: 181-199.