Preliminary Assessment of Heavy Metal Distribution in the Soils of the University of Cape Coast Nature Reserve, Ghana

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Abstract

Soil habitats are complex and heterogeneous, resulting in the formation of habitats that can support high microorganism abundance and diversity. A characteristic feature of soil habitats is their wide range of steep physicochemical gradients (e.g., of substrate concentrations, redox potential, pH, available water), which depend upon the size of the soil aggregate. Heavy metal contamination of soils could potentially counteract this steep gradient. The aim of the study was to determine the levels and distribution of heavy metals in the topsoil and subsoil of the University of Cape Coast Nature Reserve and also to assess the extent of anthropogenic impact using three indices-contamination factor (CF), geo-accumulation index (I_{geo}) and metal pollution index (MPI). The results indicate a wide variability in heavy metal concentrations. The concentrations of Pb, Zn, Fe, As and Cu in the top soil in mg/kg are as follows: 16.1 ± 12.42; 16.6± 1.21; 4650 ± 433.49; 17.9 ± 1.03; and 68.8± 1.37 respectively. The concentrations of Pb, Zn, Fe, As and Cu in the sub soil in mg/kg are as follows: 5.29 ± 0.59; 17.6 ± 1.80; 6780 ± 481.30; 6780 ± 481.30; and 10.3± 1.63 respectively. In the top soil, the order of magnitude of heavy metal concentration is as follows: As >Cu>Fe>Zn>Pb whereas in the subsoil the order is as follows: As > Fe > Cu >Zn>Pb. Heavy metal concentrations were found to be dependent on soil pH. The topsoil and subsoil are practically uncontaminated by Pb (I_{geo} = -0.76 and -1.88 respectively). Again, they are uncontaminated to moderately contaminated by Zn (I_{geo}=0.14 and 0.2 respectively). Also, the topsoil and subsoil are moderately contaminated by Fe (I_{geo}=1.13 and 1.5 respectively). Both the topsoil and subsoil are heavily contaminated by As (I_{geo}=3.53 and 3.75 respectively). The topsoil is moderately to heavily contaminated by Cu (I_{geo}=2.52) unlike the subsoil which is uncontaminated to moderately contaminated by Cu (I_{geo}=0.62). This study serves as the baseline for future monitoring of heavy metal deposition in the nature reserve.

Keywords: *geo-accumulation, contamination, soil depth, principal component, cluster analysis, forest*

1. Introduction

Tropical forests occur on a variety of soil types although most are found on fertile soils (Malhi *et al*. 2004). Soils are both an important reservoir of chemical elements and a living matrix (Hohl and Varma 2010). Soil pH is one of the most indicative measurements of the chemical properties of a soil. All (bio) chemical reactions in soils are influenced by proton (H^+) activity, which is measured by the soil pH (Wilke 2005). The pH values of most natural soils vary between <3.00 (extremely acidic) and 8.00 (weakly alkaline) (Solaimon 2008). The solubility of various compounds (e.g., heavy metals) in soils is controlled by soil pH, in addition to microbial action and the microbial degradation of pollutants (Hohl and Varma 2010). Optimum pH values for pollutant-degrading microorganisms range from 6.5 to 7.5. Soil pH is influenced by a plethora of factors including the nature and type of the inorganic and organic constituents that contribute to the soil's acidity, the soil/solution ratio, the salt or electrolyte content, and the CO_2 partial pressure (Hohl and Varma 2010).

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Soil pH has direct impact on heavy metal concentration, thus, at high soil pH, heavy metals are retained in soils if the buffering capacity is high enough to resist the acidic input solution and at low levels of soil pH, cation exchange capacity becomes the more dominant process in heavy metals retention (Sharma and Agrawal 2005). Fertilizers contain heavy metals such as lead and arsenic. Pesticides contain lead, arsenic and mercury. Sewage sludge contains cadmium, arsenic and lead. Irrigation water can transport dissolved metals to agricultural fields, where metals such as cadmium can be incorporated into plants. Copper occurs naturally in soil and plants. It occurs in rocks, soil, water, sediments, and air. Its average concentration in the soil is about 50 ppm (Jeewon and Hyde 2008). Lead is certainly the most common contaminant of and permanent resident in soils (Jeewon and Hyde 2008). Organic matter, can bind to heavy metals very effectively; for example, the number one source of lead contamination is lead-based paint, which chipped or scraped off building exteriors over periods of decades or centuries. Plant and soil microorganisms must cope with the resulting elevated levels of heavy metals in the soil. They have evolved complex systems for surviving and coexisting in such environments (Sharma and Agrawal 2005).

The purpose of the study was to

1. Investigate the effect of soil pH on heavy metals concentrations in the University of Cape Coast Nature Reserve,
2. Determine the variations in soil pH and heavy metal concentrations along a topographical gradient,
3. Determine the Contamination Factor of heavy metals in the soils of the reserve
4. Determine the Geo-accumulation Index of heavy metals in the soils of the reserve
5. Determine the Metal Pollution Index for the selected heavy metals in the soil

2. *Materials and Methods*

2.1 Study area

The sampling site is the University of Cape Coast Nature Reserve. It lies between latitudes 5° 05^1 N and longitudes 1° and 1° 07^1 W. The Reserve (approximately 17.6 hectares) stretches from flat to hilly grounds. The monthly mean temperature fluctuates between 28°C and 32°C. The climate follows the normal pattern of the coastal region of the country (Pappoe *et.al*, 2008). The highest temperatures are recorded between June and August. The relative humidity ranges between 68% and 90% (Pappoe *et.al*, 2008). The annual rainfall is between 750 mm and 1000 mm. It is a dry semi-deciduous and secondary forest with thicket vegetation which is reserved for research and academic purposes only. Consequently, poaching of animals is not allowed in the Reserve. Based on topography, the forest is divided into three (3) zones, thus, the Hill Bottom, Hill Slope and Hill Top (Pappoe *et.al*, 2008).

2.2 Data Collection and Laboratory Analyses

A total of at least 1–1.5 kg of soil was collected at each site. Each sample was deposited into a transparent 3.6-L plastic container with a sealed lid. A center point for each sampling location was identified using a handheld GPS unit (Garmin Etrex). From the center point, five sub-samples were collected; one at the center point and one each at 50 m north, south, east, and west of the center point. A 15 cm × 15 cm × 15 cm soil excavation was done to remove the top soil and the sub soil. Each sub-sample was collected about 0–15 cm in depth using a flat-bladed auger, and then combined at the center point and thoroughly mixed prior to storage. The soil samples were placed in the containers and kept intact at 5°C until ready for analysis. A total of 30 composite soil samples were generated and transported for laboratory analysis. Prior to the test, a pre-treatment was made from each sample. At first, soil intrusions (such as plant residual root, insect cadavers, and stone block, etc.) and new growth (such as ferromanganese nodules and lime nodules, etc.) were picked out from the samples, air-dried, and then sieved through 100µm mesh. The samples were digested using *aqua regia* (HCl/HNO_3, 3:1 solution)-$HClO_4$, and the concentrations of total As, Cu, Pb, Fe and Mn were measured by atomic absorption spectroscopy (Shimadzu model 6401F, Japan).

Duplicates were made for all samples and results accepted when the coefficients of variation was within 5%. Two blanks were included in each batch of analyses for quality control of heavy metal measurements. Using a spatula and an analytical balance, 2.0g of the soil samples was then weighed into a 50ml Erlenmeyer beaker and using de-ionised water the beaker was then filled to the 20ml mark, it was shaken and allowed to stand. A pH test probe was then inserted into the soil solution and allowing 60 seconds for equilibration, the result was read and recorded. This procedure was then repeated for subsequent samples.

The descriptive statistics for soil quality data was performed with SPSS version16.0 for windows (SPSS Inc., Chicago, IL, USA). The distribution of the data was tested for normality by Kolmogorov–Smirnov (K–S) test. The data was not severely skewed; consequently natural logarithmic transformations were not applied. Relationships between soil properties and metal concentrations were established by using correlation analysis. Principal component analysis (PCA) was employed to separate the element groupings inherent in the structure of the correlation matrix (Tao 1998) and to identify their common distribution patterns.

2.3 Calculation of Contamination Factor

The level of contamination of soil by metal is expressed in terms of a contamination factor (CF) calculated as: CF = C_m (sample)/C_m (Background) Where m= metal; the contamination factor CF < 1 refers to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination and CF > 6 indicates very high contamination.

2.4 Calculation of Index of Geo-accumulation

The geo-accumulation index (*I*geo) has been used for the past 40 years as an index of trace metal contamination in many soil types worldwide. Originally used for bottom sediments (Muller, 1969), it has been successfully applied to the measurement of soil contamination at different levels (Loska *et al*., 2003). The geo-accumulation index consists of 7 grades or classes (Ji et al 2008) (Table 1). Class 6 is an open class and comprises all values of the index higher than class 5. The elemental concentrations in class 6 may be hundredfold greater than the geochemical background value (Teng *et al*., 2002).

Mathematically,

$$I_{geo} = \text{In } \frac{Cm}{1.5Bm}$$

Where, *Cm* is the measured concentration of the element in soil, *Bm* is the geochemical background value. The constant 1.5 (background matrix correction factor) allows us to analyze natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences. The factor 1.5 is introduced to include possible differences in the background values due to lithological variations (Ji et al. 2008).

Table 1: Classes of geo-accumulation index

Class	Value	Soil quality
0	$I_{geo} \leq 0$	Practically uncontaminated
1	$0<I_{geo}<1$	Uncontaminated to moderately contaminated
2	$1<I_{geo}<2$	Moderately contaminated
3	$2<I_{geo}<3$	Moderately to heavily contaminated
4	$3<I_{geo}<4$	Heavily contaminated
5	$4<I_{geo}<5$	Heavily to extremely contaminated
6	$5<I_{geo}$	Extremely contaminated

2.5 Calculation of Metal Pollution Index

The overall metal contents along the three topographical gradients (Hill Top, Hill Slope and Hill Bottom) for both topsoil and subsoil were compared, using the metal pollution index (MPI). MPI was calculated using the following formula:

MPI = $(M_1 \times M_2 \times M_3 \times \cdot \cdot \cdot \times M_n)^{1/n}$, where *Mn* is the concentration of metal *n* expressed in mg kg^{-1}. In this case, number of metal (n) =5. When MPI > 1, the soil ecosystem is considered to be polluted and when MPI <1, it is regarded as unpolluted.

3. Results

The results of the analysis of the soils of the University of Cape Coast Nature Reserve for the heavy metal concentrations along topographical gradient have been presented in Table 1. The variations in Pb for both the top and sub soil samples along the topographical gradient were minor with the exception of the sub soils at Hill Slope. The levels of zinc in the soils were similar at the Hill Top unlike the Hill Slope. However, there were considerable variations in the concentrations of this heavy metal in the sub soil samples along the topographical gradient. The highest (26.51 ± 1.58) (from Table 1) concentration was recorded at Hill Slope while Hill Bottom recorded the least.

Iron was extremely high compared to the other parameters with the highest reading at the sub soils of the Hill Top. The value of Fe recorded for the sub soil sample at the Hill Top was 7922.7 ±956.68mg/kg. However, considering that the background value of Fe in the sampled soil is 1000 mg/kg, the Fe levels obtained in the study cannot be considered to be abnormal. The rest of the heavy metals varied slightly from another. The variations of copper in the soils were similar except for the top soil of the Hill Slope where the variations were slightly higher (13.01 ± 2.78 and 21.33 ± 1.90 mg/kg). pH readings experienced slight variations in each of the gradients. The highest pH reading was observed in the top soil of the Hill Top (10.61 ± 4.77) and the least reading was recorded for Hill Bottom, top soil samples with a reading of 6.04 ±0.11 mg/kg.

3.1 Levels, Distribution and Descriptive Statistics of Heavy metals in the Soils of the UCC Nature Reserve

In the top soil, the order of magnitude of heavy metal concentration is as follows: As >Cu>Fe>Zn>Pb whereas in the subsoil the order is as follows: As > Fe > Cu >Zn>Pb

Table 2: Effect of topography on heavy metal concentrations and pH of soils of the U.C.C. Nature Reserve

	Topography					
	Hill Top		Hill Slope		Hill Bottom	
Parameter	Top Soil x ± s.e	Sub Soil x ± s.e	Top Soil x ± s.e	Sub Soil x ± s.e	Top Soil x ± s.e	Sub Soil x ± s.e
Lead	4.11 ± 0.46	4.59 ± 0.32	3.47 ± 0.73	7.39 ± 1.39	3.65 ± 33.10	3.65 ± 0.40
Zinc	14.41 ± 1.44	14.81 ±4.84	20.71 ±2.39	26.51 ±1.58	13.98 ±1.52	10.56 ±1.41
Iron	5147.50 ±610.34	7922.7 ±956.68	3054.9 ±424.79	7014 ±667.57	5934.7 ±862.83	5788.2 ±864.04
Arsenic	19.82 ±0.77	23.41 ±1.42	16.34 ±2.26	2.38 ±2.02	1.73 ±1.44	2.00 ±1.06
Copper	2.23 ±0.39	4.84 ±1.96	13.01 ±2.78	21.33 ±1.90	3.84 ±1.28	3.01 ±0.75
pH	10.61 ±4.77	6.12 ±0.11	6.13 ±0.10	6.16 ±0.07	6.04 ±0.11	6.12 ±0.09

x = mean s.e = standard error

Analyses of heavy metals and pH of the soils of the University of Cape Coast Nature Reserve showed that with the exception of Cu, Pb and pH the values were lower in the top soil than the sub soil (Table 3). With the exception of the high values of Cu and Fe, the heavy metal concentrations were similar in the top soil. However, the values obtained for the subsoil were more varied.

Table 3: Concentration of heavy metals and pH of soils of the U.C.C Nature Reserve

Parameters	Top soil x ± s.e	Sub soil x ± s.e
Pb	16.1 ± 12.42	5.29 ± 0.59
Zn	16.6± 1.21	17.6 ± 1.80
Fe	4650 ± 433.49	6780 ± 481.30
As	17.9 ± 1.03	22.3 ± 0.95
Cu	68.8± 1.37	10.3± 1.63
pH	7.22 ± 1.19	6.13± .0.5

x = mean s.e = standard error

Comparisons of the heavy metal concentrations of the top and sub soils using the independent student t-Test showed significant differences among some of the mean values of the parameters (P>0.05) (Table 4). Arsenic, copper and iron showed significant differences between the top and sub soils unlike Pb and Zn which showed no significant differences.

Table 4: Independent student t-Test of the heavy metal concentrations and pH of the soils of University of Cape Coast Nature Reserve

Parameter	T-stat	T critical two tail	S/D
Pb_t - Pb_s	0.86	2.02	No
Zn_t - Zn_s	-0.59	2.02	No
Fe_t - Fe_s	-4.02	2.02	Yes
As_t - As_s	-3.54	2.02	Yes
Cu_t - Cu_s	-3.06	2.02	Yes
pH_t - pH_s	0.91	2.02	No

The linear model of the regression of Pb and soil pH showed no significant difference in the correlation between them at a confidence level of 5% and the regression equation was Pb = - 17 + 4.6 pH. The coefficient of determination (R-Sq) = 0.1% as referred from Table 5 and this is the percentage of the variations in the dependent variable that can be accounted for by the variations in the soil pH. Regression of zinc also showed no significant correlation between the element and the soil pH, with an equation of Zn = - 26.0 + 7.09 pH and an R^2 value of 0.07 (7%). There was no significant correlation with respect to the top and sub soils and the independent parameter having a constant of-25.96 (Table 5). Iron also showed no significant difference in the correlation with the soil pH. For iron, 0.1% of the variations in the iron could be accounted for the variations in the independent variable (soil pH). Again, correlation between the element arsenic and soil pH with respect to the top and sub soils also showed no significant difference among them. Copper followed the same trend as the other parameters and showed no significant difference in the correlation in relation to the top and sub soils. The coefficient of determination was 0.1% (Table 5).

Table 5: Results of stepwise linear multiple regression analysis

Element	Linear Regression Equation	R^2 (%)
Pb	Pb = - 17 + 4.6 pH	0.1
Zn	Zn = - 26.0 + 7.09 pH	7
Fe	Fe = 2448 + 683 pH	0.1
As	As = 19.8 + 0.04 pH	0.0
Cu	Cu = 2.6 + 0.99 pH	0.1

The simple linear regression for the top and sub soil samples along the topographical gradient has been presented in Tables 6 and 7. The coefficients of determination of Pb in all the 3 transect of the study area were not significantly correlated to the sub soils. Hill Slope recorded the highest of 6.6%. The stepwise equations have been presented in Tables 6 and 7 for top and sub soils respectively. Zinc recorded negative constants for the independent (predictor) parameters in the top soils with the Hill Slope recording the highest of the coefficient of determination of 11.6% among the top and sub soil samples. Iron recorded the least values in the coefficient of determination. Of all the R^2 values, arsenic recorded the highest of 34.4% in the sub soil samples of the Hill Top transect. Copper recorded 20.7% correlation of the sub soil samples and the soil pH at the Hill Top.

Table 6: Results of simple linear regression of top soil samples along topographical gradient in the University of Cape Coast Nature Reserve

Element (mg kg^{-1})	Topography	Simple regression equation	R^2 (%)
Pb	HB	Pb = 9.18- 0.826pH	5.4
	HS	Pb = -7.0 + 1.71pH	6.6
	HT	Pb = -93 + 21.4pH	0.5
Zn	HB	Zn = -2.8 + 1.75pH	2.4
	HS	Zn = -24.8 + 7.43pH	11.6
	HT	Zn = -1.7 + 2.59pH	3.6
Fe	HB	Fe = 5124-122pH	0.1
	HS	Fe = 4150 – 17pH	0.2
	HT	Fe = -5650 + 1916pH	6.2
As	HB	As = 37.4 – 2.99pH	17.4
	HS	As = 35.4 – 3.11pH	2.2
	HT	As = 56.1 – 6.43pH	25.1
Cu	HB	Cu = -2.53 + 0.819pH	5.6
	HS	Cu = 91.0 – 12.7pH	25
	HT	Cu = -4.4 + 1.36pH	1.4

Code: HT - Hill Top; HS – Hill Slope; HB – Hill Bottom

Table 7: Results of simple linear regression of sub soil samples along topographical gradient in the University of Cape Coast Nature Reserve

Element (mg kg^{-1})	Topography	Simple regression equation	R^2 (%)
Pb	HB	Pb = 4.91 + 0.015pH	0.0
	HS	Pb = 15.6 – 1.34pH	0.6
	HT	Pb = 71.5 – 1.27pH	5.8
Zn	HB	Zn = 12.7 + 0.47pH	0.0
	HS	Zn = -10.1 +5.95pH	8.8
	HT	Zn = -21.9 + 5.10pH	8.0
Fe	HB	Fe = 3780 + 761pH	1.5
	HS	Fe = 51841 - 6516pH	1.1
	HT	Fe = 6505 - 117pH	0.0
As	HB	As = 23.4 + 0.24pH	0.1
	HS	As = -13.4 + 6.06pH	5.5
	HT	As = -30.3 + 8.22pH	34.4
Cu	HB	Cu = -6.6 + 1.81pH	2.6
	HS	Cu = 45.9 – 3.99pH	2.7
	HT	Cu = -24.7 + 9.53pH	20.7

Analysis of variance of heavy metal concentrations in top and sub soil samples along the topographical gradient (Table 8) were carried out. The values showed significance ($\alpha = 0.05$), meaning, the concentrations of the heavy metals in the top soil samples of each transect is related to the corresponding concentration of its respective metal concentration in the sub soil samples.

Table 8: results for analysis of variance in the means of heavy metal concentrations of top and sub soils along topographical gradients

Soil Depth	Pb	Zn	Fe	As	Cu
Top Soil	F value: 0.97 Sig value: 0.38	F value: 5.68 Sig value: 0.01	F value: 1.34 Sig value: 0.28	F value: 1.38 Sig value: 0.26	F value: 10.61 Sig value: 0
Sub Soil	F value: 4.87 Sig value: 0.01	F value: 13.53 Sig value: 0.5	F value: 1.08 Sig value: 0.34	F value: 3.19 Sig value: 0.01	F value: 53.2 Sig value: 0

3.2 Contamination Factor

The results indicate that in the top soil, there is high contamination by As and Cu whereas there is low contamination by Pb. There is moderate contamination by Zn whereas there is considerable contamination by Fe. In the subsoil however, there is high contamination by As and Fe whereas there is moderate contamination by Zn and Cu. Like in the topsoil, there is low contamination by Pb in the subsoil.

3.3 Index of Geo-accumulation (I_{geo}) of Heavy metals in the Soils of the UCC Nature Reserve

The topsoil and subsoil are practically uncontaminated by Pb (I_{geo} = -0.76 and -1.88 respectively). Both are uncontaminated to moderately contaminated by Zn (I_{geo}=0.14 and 0.2 respectively). Also, the topsoil and subsoil are moderately contaminated by Fe (I_{geo}=1.13 and 1.5 respectively). Both the topsoil and subsoil are heavily contaminated by As (I_{geo}=3.53 and 3.75 respectively). The topsoil is moderately to heavily contaminated by Cu (I_{geo}=2.52) unlike the subsoil which is uncontaminated to moderately contaminated by Cu (I_{geo}=0.62)

3.4 Metal Pollution Index

The MPI calculated for topsoil and subsoil along the three topographical gradients exceeded the threshold of 1 indicating that they are all polluted. Calculated MPI values range from 16.8 to 34.1. The lowest and highest MPI values were obtained for Hill Bottom subsoil and Hill Slope subsoil respectively. Generally, Hill Slope recorded the highest MPI values indicating that it is more polluted than the Hill Bottom and Hill Top.

3.5 Principal Component and Cluster Analyses

From Table 9, the first three components explain approximately 78% of the variability in the data. The component matrix (Table 10) shows that the first component has strong positive factor loadings on all the heavy metals except Pb. Component two shows strong positive factor loadings on Pb and Fe, and strong negative factor loadings on Cu and Zn. Component three does not show strong factor loadings on any of the heavy metals except Pb. It can be inferred that Pb originates from a different compared to the others.

Table 9: Percentage of total variance explained by the principal components

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	1.956	39.127	39.127	1.956	39.127	39.127
2	1.027	20.538	59.666	1.027	20.538	59.666
3	.934	18.688	78.354	.934	18.688	78.354
4	.574	11.483	89.837	.574	11.483	89.837
5	.508	10.163	100.000	.508	10.163	100.000

Extraction Method: Principal Component Analysis.

Table 10: Component matrix of the selected heavy metals

Component Matrix[a]

	Component				
	1	2	3	4	5
As	.721	.182	-.381	.457	-.305
Pb	.313	.545	.766	.138	.015
Cu	.703	-.400	.249	-.386	-.368
Zn	.695	-.496	.110	.198	.469
Fe	.602	.539	-.359	-.398	.245

Extraction Method: Principal Component Analysis.

a. 5 components extracted.

The dendrogram (Figure 6) shows four spatially dissimilar groups. The first and second groups are evenly distributed with 6 and 7 members respectively whereas the last group has 14 members. The third group has 3 members. Dendrogram using Average Linkage (Between Groups)

Rescaled Distance Cluster Combine

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 C A S E    0         5        10        15        20        25
Label  Num  +---------+---------+---------+---------+---------+
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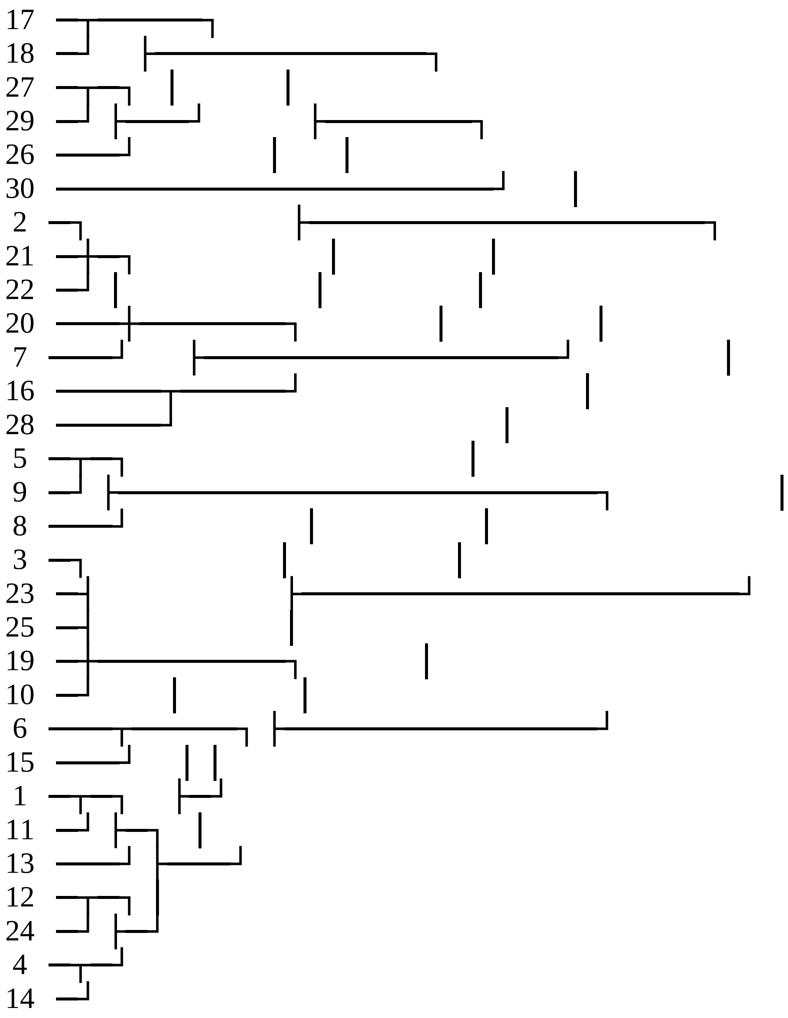

Figure 6: Dendrogram derived from hierarchical cluster analysis of heavy metal concentrations in analysed soil

4. Discussion

Abnormal concentrations of Lead are found in air, water, soil and vegetation, particularly near smelters and heavily played automobile freeways (Fuller, 1997). Significant levels of the lead in the forest confirm the assertion by Fergusson (1990) that lead concentrations found in the soil tend to be higher near motorways or freeways. Hill Slope and the Hill Top recorded 25.25 and 5.88 mg kg^{-1} Pb respectively. The former is high compared to the average concentration of Pb (13mg kg^{-1}) in the earth's crust (Brown *et. al*., 1999). Iron concentrations at the Hill Bottom was the highest for the entire study Agyarko et al. (2010) give background levels of heavy metals in soil (mg kg^{-1}) within the area as follows: Cu – 3.7; Fe – 1000.0; Zn - 9.6; Pb – 22.95 and As – 0.35. Higher levels of these heavy metals do not automatically constitute a health risk (Jankiewicz *et al*., 2002). The study area is a reserved forest consequently health risk to humans may probably be minimal. Copper recorded its highest reading in the Hill Slope of the sub soil (29.83mg kg^{-1}), whereas highest levels of arsenic (40.28mg kg^{-1}) were obtained at the Hill Slope. Arsenic combines with other elements to form organic and inorganic compounds (USEPA, 2000).

Arsenic in soil results from human activities including pesticide use, mining and ore processing operations, and waste disposal. Arsenic in the environment cannot be destroyed but can only change its form or become attached to or separated from other particles. Arsenic in soils may be transported by wind or in runoff or may leach into the sub surface soils. Although the above activities cannot be associated with the nature reserve, naturally, high soil pH could result in more dissolution of this metal. From the statistical analysis, all the measured heavy metals showed no significant correlation that could be accounted for by the variations in the soil pH. This implies that the soil pH is independent of the heavy metals but rather the heavy metals are dependent on the soil pH. Although the measured parameters showed some correlation (Pb – 0.1%, Zn – 7%, Fe – 0.1%, As – 0% and Cu – 0.1%) these values were not significant at the 5% confidence level. The soil pH readings were highest at the Hill Slope with a value of 6.69 and did not differ much at the other sites. Increase in concentrations of any of the heavy metals would affect the variation of soil pH but not at significant levels.

Rather, the decrease in soil pH causing higher acidity in the soil would increase the dissolution of the metals. Along the topography of the forest, Hill Bottom recorded relatively high values of metal concentrations compared to the Hill Slope and the Hill Bottom. The soil pH was low and this may be due to organic matter decomposition. There is a correlation between concentrations of heavy metals in the top soil and the sub soil along each topographical gradient. Yahaya *et al.* (2009) determined the levels of heavy metals and their relation with pH in the roadside of Yauri town, Nigeria. The iron content of the road side was high with a value of 6000 mg kg^{-1} with the prevalence of the heavy metals increasing towards the road side and decreasing as one draws away from the road side. This value compares fairly well with the values obtained in this study. As, Ni, Pb and Zn concentrations in Yahaya et al. (2009) were far above the background levels as in this study. Comparing the heavy metal concentrations in this study with the work of Agyarko *et al.* (2010), the former were generally higher.

5. Conclusion

A preliminary assessment of heavy metal contamination in the UCC Nature Reserve was carried out in this study. Using a variety of indices (contamination factor, geo-accumulation index, and metal pollution index) the level of anthropogenic impact on the Nature Reserve was evaluated. Principal component analysis and cluster analysis were applied to determine the distribution of the heavy metals in the soils of the reserve. In the top soil, the order of magnitude of heavy metal concentration is as follows: As >Cu>Fe>Zn>Pb whereas in the subsoil the order is as follows: As > Fe > Cu >Zn>Pb. It can be concluded that the soils are practically uncontaminated by Pb. The top soil and subsoil are uncontaminated to moderately-contaminated by Zn; moderately contaminated by Fe and heavily contaminated by Arsenic. The topsoil is moderately to heavily contaminated by Cu unlike the subsoil which is uncontaminated to moderately contaminated by Cu. This work is significant as it serves as a baseline for future work on heavy metal deposition in the nature reserve.

Acknowledgement

The authors wish to express their profound gratitude to David Ampoty for assisting the team in data collection and analysis. We are most grateful to you.

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