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Analysis of Savannah and Rainforest Soils of Nigeria using Thermal Neutron Activation Analysis Technique

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ABSTRACT

In Nigeria, large percentages of the populations are engaged in farming on the arable land. Elements play very important role in the fertility of these arable soils. To determine the essential elemental composition of soils obtained from Savannah and Rainforest parts of Nigeria, thermal neutrons activation analysis technique (TNAA) was used and the outer irradiation channel of Nigeria Research Reactor -1 (NIRR-1). This research reactor was operated at full power of 31kW and a neuron setting of 2.50 x 10^{11} $cm^{-2}s^{-1}$. Nine elements were determined in all the samples and identified in two groups. Group I elements identified as nutritionally-essential macronutrients to plants includes; Mg, K, Ca Na, Mn, and V. Group II elements identified to be non metabolic nutrients to plant includes Al Ti and Dy. However, Mg, K, Ca were present in large concentration and Na, Mn, V present in minor concentration in all the samples. Also, Al and Ti were present in minor concentration and Dy present in relatively low concentration in all the samples.

Keywords: *Savannah soils, rainforest areas, TNAA Technique, NIRR-1*

1. INTRODUCTION

Over the years a number of soil analyses have been carried to determine soil fertility, proper fertilizer applications, geochemical mapping and mineral exploration. In past few decades, heavy metals in soils have been the base of focused since they do not decay with time. Like many organics matter, radionuclides are always present at a background level of non-entropic region such that their inputs in soils are related to weathering of parent rocks and pathogenesis. They may be present in inert non harmful forms and become mobile as a result of changing environmental conditions (land use, agricultural input, and climatic change) or by saturation beyond the buffering capacity of the soil. This situation is referred to as a "chemical time bomb" (Stigliani et al., 1993).

Trace elements are introduced into soil from both natural and anthropogenic sources. Major and minor trace elements in parent rocks are eventually included in the formed soil fractions. Atmospheric deposition of particles emitted from natural sources such as forest fires, volcanic activity, bubble bursting over the ocean and biogenic emissions are also natural sources of elements found in soils (Nriagu, 1989). Such natural metal sources in soil can be detected only in pristine regions. In regions where anthropogenic activities are abundant, such as urban areas or areas with excessive industrial activity, elemental composition of soil is modified by deposition of pollution-derived particles from the atmosphere. The primary anthropogenic source of trace metals in soil is agricultural activities, pesticides and fertilizers that are directly applied to soil results to heavy elements such as As, Pb and Cd (Bloemen et al., 1995; Fergusson, 1990). Human activities other than agriculture such as irrigation water taken from streams and lakes contaminate the soils with industrial and domestic discharges.

Chemical fertility and physical stability of sandy soils in West Africa are low (Sanchez and Logan, 1992). Coarse texture, low activity clays, and harsh climatic conditions are the main reasons for nutrient leaching, erosion and low organic status of soils. Consequently, biota plays a crucial role in the fertility of these soils (Lavelle, 1997). Mechanisms commonly put forward for the beneficial impact of biota on soil properties are the improvement of physical properties (aggregate stability and porosity) due to root dynamics, macro faunal activity, and the conservation of nutrients in the plant biomass (Abbadie et al., 1992).

In the West African Savannah (WAS) zone, the sustainability of farming systems relies very much on practices meant to promote biological activity and diversity in soils. Fallowing and manure amendment are thought to be the most popular means (Feller and Beare, 1997).

The hypothesized that the sustainability of ecosystems of West African Savannah relies largely on the relationships between the status of soil biota (fauna, mesofauna, micro-organisms) and soil carbon quantity (Menaut et al., 1985; Lavelle, 1997).

However, the correlation between plant yield and elements or nutrients available is important in determining the effectiveness of the soil to support healthy and less cost expensive crop production. Adequate information about the composition of soil must be available before it can be adequately utilized for agricultural purposes including fertilization when the soil is found to be deficient in the elements of interest.

The complex nature of soil requires the choice of thermal neutron activation analysis (TNAA), available in Nigeria Research Reactor (NIRR-1), CERT, Zaria. In environmental analyses, samples are usually collect for one or several reasons: to establish hazardous levels in the environment, to understand the chemistry of the environment, to evaluate the efficiency of environmental control measures,

or to determine the source of pollutant. Hence, the mode of sampling is important.

This work basically determined the concentrations of available nutrients in the soil which are vital to plant intake, and to guide farmers in terms of fertilizer application in areas where some elements are observed to be deficient. Agricultural activities are the commonest activities among Nigeria populace especially farming. In Nigeria, farming is done in crude or traditional method where the farmers do not have the means to check the integrity of the soil they cultivate on this result in poor yield.

2. MATERIALS AND METHODS

2.1 Sample Collection

A comprehensive representative soils from savannah and rainforest areas of Nigeria covering four States; Niger State (Cece 1& 2), Kogi State (Kaba 1 & 2), Ekiti State (Ado-Ekiti, Ipoti-Ekiti 1 & 2, and Ekiti 1 & 2) and Osun State (Jesa 1 & 2) were obtained. The soil samples were obtained at certain specified depths using some physically observable soil layers or horizon properties such as colour changes. These different colour regions were referred to as different horizons and were considered to be subsamples of a sampling site. The following steps were taken to sample the soils; scrapping away of soil surface containing humus and other organic waste, digging into the earth to obtain a loose soil structure with an auger or spade, collecting the loose structure with a plastic spoon, and using a measuring tape to measure the boundaries between layers were colour changes were observed (horizons) and the soils were sampled as shown in Table 1.

Table 1: Sampling Sites with their Locations and their Horizons

S/N	States in Nigeria	Sampling sites	Horizon depth (cm)
1	Niger	Cece 1	0 - 20
		Cece 2	21 - 33
2	Kogi	Kaba 1	0 - 15
		Kaba 2	15-29
		Lokoja 1	0 - 15
		Lokoja 2	15 - 29
		Lokoja 3	29 downward
3	Osun	Jesa 1	0 – 15
		Jesa 2	15 – 30
4	Ekiti	Ekiti 1	0 – 15
		Ekiti 2	15 – 30
		Ado-Ekiti	0 - 33
		Ipoti-Ekiti 1	0 -18
		Ipoti-Ekiti 2	18 downward

2.2 Sample Preparation

After sampling on the field, the next step was to obtain a laboratory representation of the sample from the field. To achieve this, the following steps were followed; washing of glassware and plastic ware with detergent and rinsed thoroughly with tap water, fetched an appropriate quantity of the samples and added some reasonable volume of water to the sample in the beaker, stirred continuously using a plastic spoon (to homogenize the soil water mixture), smeared to remove organic matter from the soils (organic matter like roots), decanted the soils solution in a beaker to separate the coarse soils from the fine soil solution, allowed the soil solutions to stand for 48 hours to settle (water phase to separate from the slurry soil phase), water is then decanted off the soils to leave a fine slurry soil (process repeated several times to reduce the amount of water in the soil as possible), and the soils in its slurry form was then poured into an envelope and expose to natural atmosphere for 7 days to dry via a natural drying process.

The solidified dried soils were crushed with agate mortar to obtain a fine soil grain. The crushed soils were then transferred into an evaporating dish and oven dried at temperature of 100^{o} C for 5 hours to allow the residual water in the soil to evaporate.

3. EXPERIMENT

3.1 Measurement of pH

From the soil samples, 20 g plus 40 ml of water were mixed together to form a solution. The solution was stirred for about 30 minutes to homogenize the mixture. The pH meter was calibrated using a set of standard solutions with known pH value. The electrode of the pH meter and the thermometer were immersed in the solution. The pH and the temperature of the solution were measured simultaneously and the results shown in Table 2.

3.2 Sample Preparation for NAA

The soil samples were weighed with a four-digit Melter model weighing balance in the range of 150 mg to 250 mg, encapsulated, heat sealed in a polyethylene material and package finally into a polyethylene vial. After encapsulation, the samples were finally labeled and ready to be injected into the reactor. The scheme for sample irradiation was performed in two stages (Oladipo et al., 2012). The first irradiation was designed to capture short half-lives radionuclide, the second irradiation was designed to capture long half-life radionuclide in the inner channel of the Miniature Neutron Source Reactor (MNSR) operating at full power of 30 kW thermal with a neutron flux of 2.50×10^{11} $ncm^{-2}s^{-1}$.

The counting of activated soil samples were done using the High Purity Germanium (HPGe) detector calibrated using ^{137}Cs (661.6 keV) and ^{60}Co (1173 keV and 1332.5 keV)

sealed standard radioactive sources. This was done by acquiring sufficient activity from both sources and using the channel numbers i.e the positions on the energy/channel axis of the spectrum versus the intensity of the following gamma energies 661.6 keV and 1332.5 keV. Both sources were placed on the HPGe detector and the gammas were acquired (or measured) for some time. The expected three gamma rays were seen appearing in the spectrum. A straight line was drawn through the points. The second peak of ^{60}Co at 1173 keV was used in confirming the accuracy of the calibration procedure. The efficiency curves of the detector system near and far geometries have been determined by Njinga et al., 2011 and Jonah et al, 2006. For the data processing we used the gamma ray spectrum analysis software WINSPAN 2004 (Liyu, 2004), a software developed at CIAE, Beijing, China. On the basis of the well known activation equation, using a multi-element standard reference material for elements of interest, the calibration factors were pre-determined using adopted irradiation and counting regimes (Oladipo et al., 2012).

For the short irradiation regimes, the first round of counting was performed for 10 minutes (S1) after decay time of 2 minutes. The second round of counting was performed for 10 minutes, following the short irradiation regime (S2) after decay time of 3 to 4 hrs. With respect to the long irradiation regime, the first round of counting was carried out for 30 minutes (L1) after decay time of 4 to 5 days. The second round of long irradiation regime (L2) of counting was performed for 60 minutes after cooling time of 10 to 15 days. The choice of the cooling time and sample-detector geometry is such that the detector's dead time is less than 6% with peak statistic of 5%.

4. RESULTS AND DISCUSSION

The pH of soils affect the availability of nutrients for plant uptake, therefore, pH is an important parameter to be determined in a soil analysis. The results of the pH readings of the savannah and rainforest regions of Nigeria are shown in Table 2 below.

Table 2: Results of the pH and Temperature of the Soil Samples

S/N	Sample sites	Horizons (cm)	pH	Temperature ^{0}C
1	Cece 1	0 - 21	6.78	29.00
2	Cece 2	21 – 33	7.15	28.70
3	Kaba 1	0 - 15	6.30	28.80
4	Kaba 2	15 – 29	6.37	28.60
5	Lokoja 1	0 - 15	6.73	28.40
6	Lokoja 2	15 - 29	6.41	28.30
7	Lokoja 3	29 downward	6.49	28.50
8	Jesa 1	0 - 15	6.16	28.70
9	Jesa 2	15 – 30	6.45	29.30
10	Ekiti 1	0 - 15	6.24	28.80
11	Ekiti 2	15 – 30	5.51	28.80
12	Ado-Ekiti	0 - 33	7.34	28.70
13	Ipoti-Ekiti 1	0 - 18	6.41	29.10
14	Ipoti-Ekiti 2	18 downward	6.49	29.20
15	Distilled water	-	6.98	28.60

From these results, the samples showed a significant similarity in the pH and temperature range. The pH values were observed to be increasing with soil depth and could be seen to be fairly neutral. However, pH optimal for most plant nutrients ranged from 5.5 to 7.0. The higher the pH values, the increase the alkalinity and the lower the pH values, the increase the acidity (Doerr, 2007).

3.1 Quality Control and Assessment of Data

The analysis of reference materials which has the same matrix and comparable in concentrations with the unknown samples is one of the means by which the accuracy of analytical results can be assessed (Oladipo, 2003). Assessment of the results obtained from the analysis of the reference material(s) using the same technique as used for the unknown samples (being investigated) provide a means of accepting or rejecting the result on element to element basis. In other words, it will give one the opportunity to know which element to accept and which are to reject. This process helps the laboratory to identify specific errors affecting data suites being generated. The accuracy of the method employed in this project was assessed by analyzing two reference standards, namely- IAEA soil 7 and Coal Fly Ash SRM 1633b. The results of the analysis are displayed in Table 3.

Table 3: Results of Coal Fly ash 1633b and IAEA Soil 7 standard reference materials

Element	Coal Fly Ash SRM 1633b		IAEA-Soil-7	
	This work	Certified values	This work	Certified values
Na [a]	0.185	0.201	0.277	0.240
Mg [a]	*0.997	0.492	0.583	1.130
Al [a]	14.600	15.050	4.840	4.700
Ti [a]	0.742	0.791	16.100	16.300
Ca [b]	1.410	1.510	0.340	0.300
V [b]	260.000	295.600	79.400	66.000
Mn [b]	158.700	131.800	647.000	631.000
K [b]	2.019	1.950	1.205	1.210
Dy [b]	20.100	17.000	-	-

[a] = measurements in percentage (%), [b]= measurement in ppm (µg/g) * = large deviation

These results displayed in Table 3 showed the concentrations obtained for the elements of interest analyzed in this work compared favorably with the certified or literature values. However, the value displayed for Mg appears to be twice the expected certified value. This may arise from (n, p) reaction on Al as explained by the nuclear

reaction; 27Al (n, p) 27Mg on 26Mg (n, γ) 27Mg. Therefore the product of interest is obtained from 26Mg (n, γ) 27Mg reaction and 27Al (n, p) 27Mg reactions. This error was corrected by measuring the contribution arising from the (n, p) reaction on Al and subtracting same from the Mg counts.
The elemental concentration of soils collected from Niger, Kogi, Ekiti and Osun States are shown in Table 4. These elements were obtained using neutron activation analysis and nine elements were analyzed showing appreciable concentrations. Samples with the same name but differentiated by number 1 or 2 are from the same sampling site; only sampling depths differ.

Table 4: Elemental concentration of Soils collected from Niger, Kogi, Ekiti and Osun States

Sample	Na	Mg	Al	Ca	Ti	V	Mn	K	Dy
Cece 1	122	3170	9920	2430	2750	12.4	205	996	317
Cece 2	152	4220	20200	2000	3520	20.5	215.4	3080	599
Ekiti 1	1306	7780	97900	3360	5180	64.9	347.1	12100	1390
Ekiti 2	738.8	8260	128000	2990	5170	73.1	217.8	**	**
Jesa 1	271	10020	60100	3660	7920	81	635.8	2460	1180
Jesa 2	218.8	6270	65800	3170	11700	100.7	545.5	1570	1720
Kaba 1	4390	5130	45200	3720	1520	35.5	415	20700	1.61
Kaba 2	4300	3580	50700	1940	1920	16.5	374	19400	1.2
Lokoja 1	6270	NA	29600	1750	4410	24.8	394	8460	28.4
Lokoja 2	7240	2080	30800	2400	1140	15.8	354	10400	29.9
Lokoja 3	7040	6900	34600	4700	3770	29.5	344	92800	87.8
Ado-Ekiti	598	7080	79400	4060	7210	116	1256	3570	5.17
Ipoti-Ekiti 1	313	6960	51200	3850	4280	80.1	5661	NA	53.8
Ipoti-Ekiti 2	513	2590	58900	3130	4400	92.9	1040	2920	6.21

All units are in ppm (ugg^{-1}) , ** = Below detection limit, NA= Not analyze

A cluster analysis of the data sets Table 4 was evaluated and the similarities among the samples based on the concentrations of the nine elements determined was carried out using cluster package contained in Minitab 14 on Windows. The product of the cluster analysis of the data resulted in a two dimensional tree diagram referred to as dendrogram. The dendrogram is a multivariate diagram usually represented in two dimensions, namely similarity and the samples/clusters. The dendrogram or tree diagram highlights the similarity existing between various soil samples and clusters observed is shown in Figure 1 below.

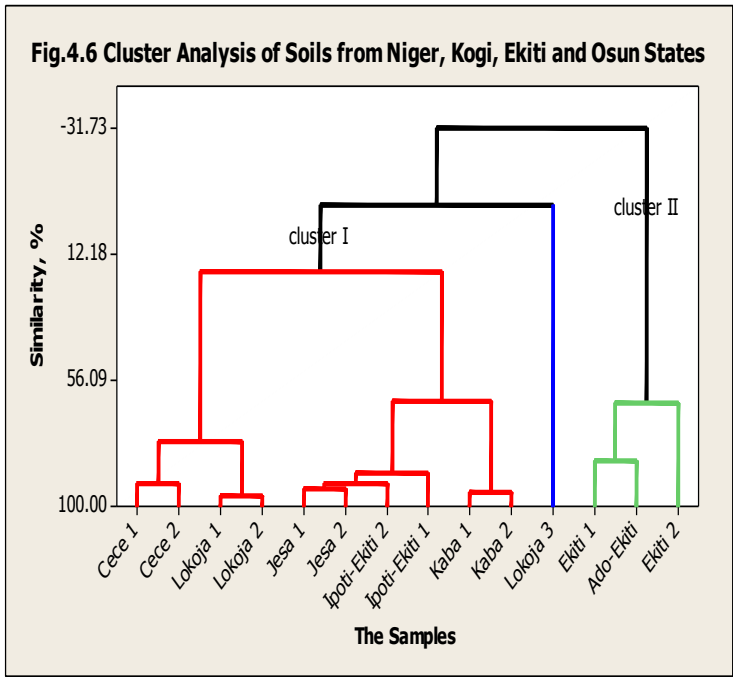

Figure 1: Cluster Analysis of Soils from Niger, Kogi, Ekiti And Osun State

From Fig, 1, the elemental data suits obtained for the soil samples were subjected to cluster analysis treatment. The dendogram resulting from cluster treatment showed Cece 1 and 2 samples clustering together based on the similarity of their elemental concentrations. Ekiti 1, Ekiti 2, Jesa 1 and Jesa 2 clustered together. No outlier was observed affirming the fact that all samples elemental concentrations are similar.

The probable variation in the soil samples analyzed may be due the types of crops cultivated and farming system practiced in the regions where the samples were collected. Cece (Niger State) is a Savannah region where crops are grown with their root within 10 to 30 cm in depth for the plant nutrients. Another factor is the excessive use of land for cultivation of crops without allowing the land to fallow for some time to replenish its nutrients. Ekiti and Jesa (Osun State) are in the Rainforest area of Nigeria where cash crops like cocoa are mainly cultivated. Large concentration of elements observed may be due to the fact that the crops cultivated there goes deep in the ground to extract its nutrient. Another reason may be that land fallow system is practiced there allowing the soil to replenish its nutrients after some fallow time. The result of this analysis shows that the concentrations of these nine elements except K are within the expected range for soils (Tisdale et al, 2003). The K deficiency can be remedied by using inorganic fertilizer in adequate proportion.

The nine elements analyzed in Table 4 were categorized according to concentrations. The elements Magnesium, Aluminum, Calcium, Titanium and Potassium are major, measured in percentage. Sodium and Manganese are in minor level and Dysprosium in trace level.

Sodium

Sodium (Na) was observed to be of the concentration range 122 to 7240 ppm across the samples with Lokoja 2 having the highest concentration. The erratic trend shown by Na is because the element is essential for halophytic plant growing in salty soils. Cece (Niger State) shows decrease in Na concentration due to crops cultivation like spinach which reduces the concentration in the first horizon (Cece 1) by intake of Na through its root which is just about 5 to 10cm in depth (Tisdale et al., 2003). The concentrations of Na in Jesa (Osun State) and Kaba 1 & 2 (Kogi State), Ekiti 1 & 2 (Ekiti State) are high because the cash crops cultivated there have their roots relatively deep inside the soil (~60 cm downward) which includes crops like; cocoa, kolanuts, bitter kola and so on. Na is necessary for osmotic pressure and acid-base balance with Cl (Romheld and Marscher, 1991).

Magnesium

Magnesium (Mg) concentration ranges from 0.317 to 1.1002 %. Highest concentration of Mg was observed in Jesa 1 (Osun State). Mg concentration increases as depth increases because of the solubility in the soil. Therefore, Mg intake by some crops especially those of oil seeds like groundnut, soya bean, melon etc which are commonly cultivated in the savannah region of Nigeria may not be difficult. Hence, Cece has low concentration of Mg compared to Jesa and Ekiti where such crops are not cultivated. Mg concentration required by most plants is between 0.1 to 0.4% (Tisdale et al., 2003).

Aluminum

Concentration of aluminum (Al) ranges from 0.992 to 12.8 % with concentration increasing as depth increases. Factors such as leaching, erosion and other plant intake may be responsible for low concentration in topsoil. Other factors such as bush burning, excessive clearing of field may have contributed to the overall concentration of Al in the soil matrix. The physiological function of Al in plants is not clear, although it is evidence that low levels of Al can have a beneficial effect on plant growth, especially in Al-tolerant plant species like wheat (Clark, 1977 and Foy, 1979).

Calcium

Concentration of calcium (Ca) ranges from 0.200 to 0.366 % in the samples. The Ca concentration range required by plants is between 0.1 to 0.2 % (Tisdale et al., 2003; Steven, 1995). Ca shows a decreasing trend in concentration as depth increases thus contradicting what was observed for Mg in the samples (Mg concentration of increases with depth). This is because enrichment factor such as dead animals' bones may decay or be burnt during bush burning exercise which may invariably lead to increase in the Ca content of the soil. However, weathering of calcareous rocks increases Ca concentration.

Vanadium

The concentration of vanadium (V) obtained in this work ranges from 12.4 to 100.7 ppm. Low concentration of V is beneficial to microorganisms, animals and higher plants (Tisdale et al., 2003). Increases in plant growth attributable to V have been observed in rice and corn (Steven, 1995). Normal concentration of V required for plant growth is 2 parts per billion (ppb) whereas normal V concentration in plant material averages about 1 ppm (Esptein, 1972).

Manganese

Manganese (Mn) is a micronutrient whose concentration in plants ranges typically from (20 to 500) ppm (Epstein 1972). Concentration range of 205 to 635.8 ppm was noted in the samples. This mineral is required by plants such as soya bean, ground nut, which are mostly cultivated in the savannah region of Nigeria. Deficiency of Mn in soya bean causes marsh spot of peas (Tisdale et al., 2003).

Potassium

Concentration of potassium (K) ranges from 0.0996 to 1.21 %. Concentration of K required by plant usually ranges from 1 to 4 % (Tisdale et al., 2003). K is necessary in many plants functions, including carbohydrate metabolism, enzyme activation, osmotic regulation and efficient use of water (Epstein, 1972). All the samples except Ekiti 1 are deficient in K. This deficiency can be remedied by using inorganic fertilizer in appropriate amount.

Titanium

Concentration of titanium (Ti) obtained in this work ranges from 0.275 to 1.17 %. No clear evidence of a biochemical role of Ti has been reported, although Chapman (1972) and Shkolnik (1974) described its possible catalytic function in N fixation by symbiotic microorganisms and in photooxidation of N compounds by higher plants, as well as in some processes of photosynthesis Ti is not an essential element for plant nutrition. Pais et al., (1977) observed an increase of chlorophyll in tomato plants grown in culture solution after spraying with a Ti-chelate solution and this observation is an evidence for the biochemical role of Ti in plant.

Dysprosium

Concentration of Dy obtained in this work ranges from 317 to 1720 ppb. Ure and Bacon (1972) stated that average concentration of Dy in soil is 3.8 ppm. Ahrichs (1972) reported that the average concentration of Dy 5 ppm. Dysprosium (Dy) can therefore be described to be present in trace level. Dy is a member of the group of elements referred to as rare elements. From this information, it could be that this mineral may not be required for plant nutrition, though it may be of other uses to plant. Jesa and Ekiti have more concentration of Dy than Cece. This trend may be best explained as this element shows a special characteristics that may be used to characterize soils from one place to another. Such distributions sometimes show anomaly in Dy or Eu (Oladipo, 1989).

5. CONCLUSION

TNAA was employed to analyzed soil samples and the results were confirmed to be of high integrity as shown by the product of the cluster analysis of the data. The soils obtained from the same area showed similarity in composition. However, nine elements have been determined in soil samples from the four (savannah and rainforest) states and the data suits will add to the chemical database for soil fertility of savannah and rainforest belt of Nigeria. The variations of the elements in the samples have been established as well as the similarity among the samples using the appropriate statistical techniques.

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