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Distribution of Minerals and Elemental Contents of Soils from *Termiteria* (Ant Mounds) and 10 Meter (10 M) Adjacent Soilsin Yola South,Adamawa,Nigeria

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ABSTRACT:

Geozoological method of prospecting for minerals is one of the easier, cheaper and indirect ways of assessing mineral deposit. The current work assessed the distribution of minerals and elemental contents of termiteria and 10 M adjacent soils in Yola south local government areas of Adamawa state, Nigeria during rainy and dry season. X- ray diffraction (XRD) method of analysis was used for identification of the minerals present in the samples while the elemental contents of the samples were determined by the used of X-ray fluorescence (XRF) method. Eight minerals were identified in the study area and in terms of abundance can be arranged thus: quartz > rutile >(corundrum and ulvospinel) > (almandine, montmorillonite, microcline and wulfenite). Quartz and rutile were the most abundant minerals identified in the study area. XRF analysis of the samples determined nine major elements which include: Al, Si, K, Na, Ca, Mg, Fe, Mn and Ti, while seventeen trace elementswere determined namely; Ni, Cr, V, Cu, Ba, Zn, Sr, As, Ir, Pb, Ga, Rb, Zr, Yb, Eu, Re, and Ag. The results are presented as mean of three replicate measurements and their standard deviations. Si has the highest value ranging from (52.90 ± 0.27 – 51.60 ± 0.08)% in termiteria soil,(60.0 ± 0.60 -51.20 ± 0.16)% in 10 M soil. Kis second with range of values,(11.20 ± 0.08 – 4.53 ± 0.15)% in termiteria soil,(14.70 ± 0.23 –4.64 ± 0 .07)%in 10 M soil. Followed by Al with range (11.50 ± 0.35 – 10.0 ± 1.00)% in termiteria soil, in 10 M soil the range is(12.04 ± 0.01 – 8.33 ± 0.75)%, Others are Fe, Ca and Ti. Among the trace element,Zr was the most abundant with range (2.2 ± 0.10 -1.40 ± 0.23) PPMin termiteria and (2.50 ± 0.14 – 1.90 ± 0.06) PPM in 10 M soil. Ba highest value of 0.87 ± 0.025 PPM in $10M^{r}$inYola South South, lowest value (0.071 ± 0.017) was in termiteria, Ba was not detected in Yola South North. Pb was not detected in temiteria but in two sampling sites only ($10M^{d}$ and $10M^{r}$). Cr, V and Cu were detected in all the sampling sites in the study area.Single factor analysis of variance (ANOVA) was used to test for variation between the elemental composition of the termiteria soils and those of 10 M surrounding soils. Generally, statistically there is no significant difference between the elemental composition of the termiteria soils and those obtained from 10 M adjacent soils in the study area (P< 0.05). This indicated that the elements were distributed around the termiteria as far as 10 M away. In nutshell, termiteria can serve as a tool for exploring underground minerals deposit.

Key words: Analysis; elemental composition; geozoological method; termiteria; trace element

Introduction

Minerals have occupied important place in the lives of modern man that the more available they are in a useful form the higher the living standard of the users as they determined the status of a country politically, economically, technologically and are keys to the overall total development of our modern societies (Botkins & Keller, 1998). Several authors have shown that there is positive relationship between the economic status of a society and availability of its mineral resources once exploited. Furthermore, a physical need of man is met by agriculture and mining activities (Abaa & Najime,2006). Mineral constitutes 96% of soil ((Singh, 2009), about 30,000 mineral species are known most of which are characterized by definite chemical compositions, crystalline structures and physical properties, primarily they are classified by chemical compositions, crystal class, hardness and appearance (color, luster and opacity) and as a rule are restricted to solids with the exception of mercury and water and hence all the metalliferous minerals of economic value which are mined for their metals are described as solid minerals. The fact that solid minerals are not evenly distributed over the earth implies that they are not easily obtainable. It takes time, money and expertise to explore, extract and put them into useful forms. Developing countries especially, Nigeria derives numerous benefits from small scale mineral and material producing operations (Woakes, 1982). Though mineral exploration and extraction is not new in Nigeria for instance, before the advent of the British several communities have been mining mineral resources such as gold, galena, lead, zinc etc and used as cosmetics locally, in fact the recorded production of lead/zinc ore from Enyigba mine was as early as 1925. (Orazulike, 1994). Despite such a long history, statistics shows that solid mineral in Nigeria has been under developed (contributing less than 1% of the GDP) while its counterparts, the fuel mineral resources were developed. Currently, the federal government has acknowledged solid mineral as a potential alternative to the petro-industry for foreign exchange earnings and has set to revitalizing the sector. This is because mineral resources are the foundation upon which an industrialized economy is built, furthermore petroleum industry provides only 6% of Nigeria labour force and over dependence on petroleum industry leaves the economy vulnerable to both international politics and fluctuation in oil prices (Gill, 2011).

Solid mineral exploration expenses have to be optimized to minimize the risks of mining investment (Fodor & Bardossy, 2005).This is because the uncertainty associated with exploration of solid mineral deposit is usually high and is discouraging to the mining entrepreneurs, more especially when after spending time, energy and fund the result proves abortive. According to Orazulike (2002), discovery of mineral deposits is achieved through exploration by geochemical, geological and geophysical methods. In addition, novel methods of mineral exploration have been successfully used to locate prospective mineral deposits, these help to reduce demands associated with the exploration stage of mining. The methods indirectly assess the presence or absence of underground solid mineral deposits, through analyzing plants to determine mineral deposit in the soil of a particular area, this method is known as biogeochemical exploration (Dunn, 1995), use of animals and insects, termiteria inclusive (Spore,1996;). The latter unique method is termed geozoological method of prospecting for solid minerals. Termiteria soils have been analyzed to serve as bio-indicator of mineral deposit (Reddy,2014).

Termites are small soft–bodied social insects classified at the taxonomic rank order of Isoptera (Adeyeye, 2005).Termites live in nests built from underground soil, the types of nests are associated with the species of termites that built them. Nests are classified as ground mound, subterranean, pole and tree nests (Adekayode & Ogunkoya, 2009). Anthills, ant mounds, and ant nests are used interchangeably to refer to “termitarium”, which is the scientific name (Spore, 1996 ; Folgariat et al., 2003).Ecologists view anthills as natural disruptions that maintain heterogeneity in an ecosystem (Bode, et al., 2013). Termites are categorized according to the shapes of their termiteria and methods of feeding for instance; the forager termites Trinervitermes build dome-shaped mounds usually less than a metre in height, mushroom-shaped mounds are built by decomposers, Cubitermes, (Spore, 1996) and the most prominent in Africa the fungus termites, macrotermes which live in cathedral mound as high as 20 meters dotting many landscape of tropical grassland (Retallack, 1990). The processes involved in building these large epigeal mounds lead to concentration of minerals in the termiteria since soils as deep as 50 M below the earth surface are brought up to the surface (Daniel& Emana, 2014).

Biogeochemical studies have demonstrated that in tropical part of India these termite mounds have been used as important tool in explorations for copper,chromium tin and barite (Reddy,2015), in Mali for gold (Spore, 1996).

The aim of this research work was to assess the mineral and the distribution of the elemental contents of soils from termiteria and 10 M adjacent soils sampled inYola South local government area of Adamawa state, Nigeria during rainy and dry seasons. The objectives are: to identify minerals in the study area, to quantitatively determine both themajor and the trace elements and compare them with those obtained from 10 meter adjacent soils and to determine the distribution of the elements 10 M way from the termiteria.

MATERIALS AND METHODS

Materials -The following instruments, equipment and apparatus were used during this work: X-ray Fluorescence Spectrophotometer (XRF), X-ray diffractometer (XRD), core scoop, hammer, polythene bags, sieve, Pestle and mortar, spade, crucibles, analytical balance.

Sampling and SamplePreparation

Sampling Technique- geozoological method of prospecting for solid minerals sampling technique was utilized In this method, soils from termiteria were sampled and analyzed for presence of solid minerals which in turn served as an indicator of underground mineral deposits (Pray, 2013).

Sampling area, locations and sites

Yola south local government areas of Adamawa state, Nigeria, the sampling area, was stratifically divided into two locations (south and north) from where a termiterium and its 10 M adjacent soil were chosen as sampling sites.

Sample collection

Method of Bode, et al, (2013) was adoptedwith some modifications,where termiteria were surveyed in the sampling location with the help of the local residents. Termiteria of various sizes were randomly chosen for sampling. Three samples were taken with core scoop to form a composite sample of each sampling site. Control samples were taken from the depth of 0 – 50cm located at 10 M away from each termiteria in the four cardinal directions which were mixed to form composite control sample as in figure 1. Samples collected were stored in properly labeled polythene bags and conveyed to the laboratory

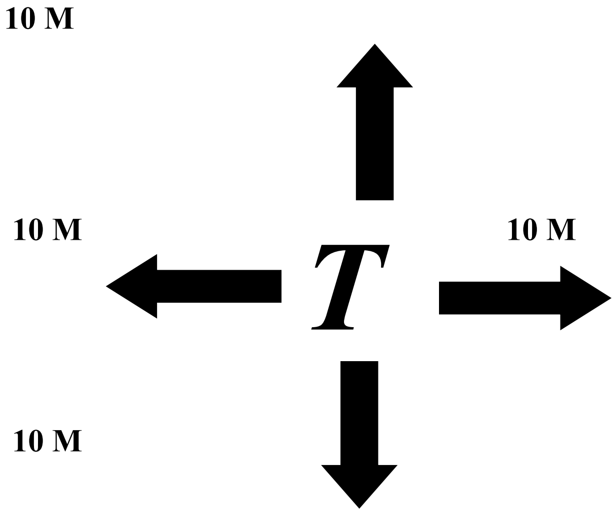


Figure 1: Outline of sampling plan

T = termiteria sampling site

10 M = 10 meter away soil sampling site

Sample Preparation

Soil samples were dried by spreading them on clean polythene sheet in the laboratory for seven days. The dried soil samples were ground using mortar and pestle and sieved to obtain powder form. Gross samples were reduced to test sample sizes through the process of cone and quartering (Okunola et al., 2008). The method involved forming cone shape with the sample and dividing it into four equal portions and taking the two opposite sides of the quarter while the other two quarters were discarded. The retained two quarters were recombined and the process was repeated until about 100g of the sample was obtained.

Analytical Studies of the Samples

X-ray diffraction analysis of the samples were carried out at National Geoscience Research Laboratory Centre, Kaduna (Nigerian Geological Survey Agency) following a modified method outlined by Adesaki & Olunlade (2011). Ground soil sample weighing 0.35g was placed into a sample holder of the computer interfaced XRD instrument and then smeared uniformly on a glass slide to ensure upper surface was flat so as to achieve random distribution of lattice orientation. This was then packed into a sample container and sprinkle on double sticky tape. X-ray of CuKa with wavelength of 1.5418 was used to scan between 2Θ 0f 10o and 2Θ of 45o at increments of 0.04o with count time of four seconds for each step. Count time of four seconds gave good signal to noise ratio and enabled the analysis to occur at appropriate period. Intensity of the diffracted rays was recorded continuously as the sample and the detector rotated through their respective angles. Peak intensity occurred when mineral containing lattice with d-spacing diffract x-ray at that value of Θ. Each peak was made up of two separate reflections _k1 and k2, at small values of 2Θ the peak locations overlapped with k2 and appeared as a hump on the side of k1, these combined peaks were considered as one. Higher values of Θ yield greater separation of peak where the 2λ position of the diffraction peak was measured at the center of the peak at 80% peak height. Presentation of result of x-ray analysis was at peak positions at 2Θ and x-ray counts (intensity) in the form of x-ray plot. Intensity was reported as peak height intensity. Relative intensity was recorded as the ratio of the peak to that of the most intense peak. Thus;

Relative intensity = I x 100 / Ii. Where I = peak intensity, Ii = most intense peak.

The d-spacing of each peak was obtained by solution of the Bragg equation for appropriate value of λ, that is; $n\lambda = 2d\sin\Theta$. When d-spacing was determined, automated/match routines compared the d- spacing of the unknown to the known substance.

X-ray fluorescence procedure for determination of minerals in soil as described by Baranowska, et al., (2002) was adopted. 20g of each of the ground soil samples was fused with 0.40g stearic acid in a 20ml platinum crucible and pressed with hydraulic press. The fused button was then x-rayed and counted to determine the elements, the excitation source emitted Ag-k x-ray (22.1 KeV) hence all elements with lower characteristics excitation energy were detected in the samples.

RESULTS AND DISCUSSION

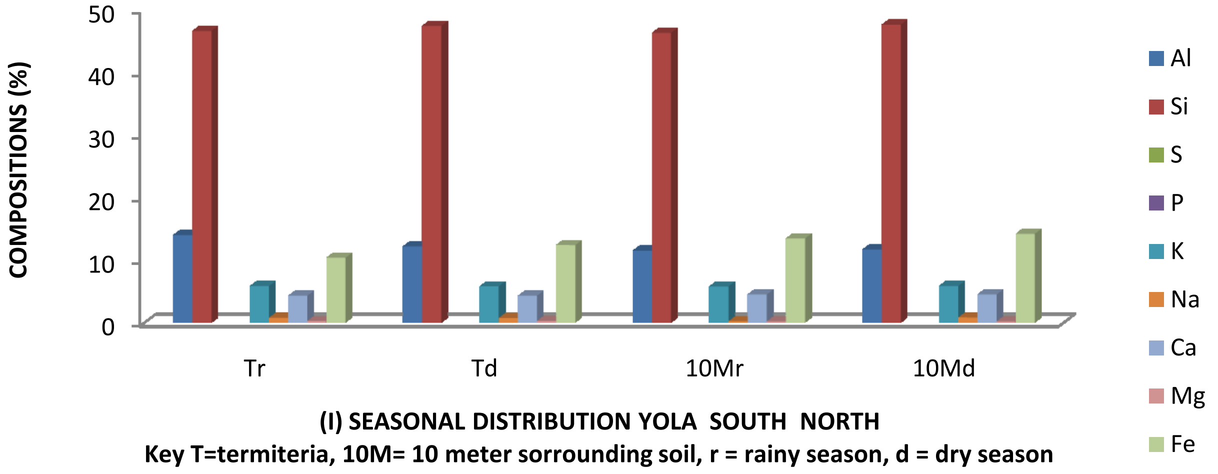
Results of analysis from this research work are presented below. Minerals identified by XRD analysis of the samples from Yola South local government areas of Adamawa State, Nigeria are presented in Table 1. Results obtained from XRF elemental analysis of the samples are presented as figures 2 and 3 and discussed below:

Eight minerals were identified in the study area, these can be arranged in terms of abundancethus: quartz > rutile >(corundrum and ulvospinel) > (almandine, montmorillonite, microcline and wulfenite). Quartz and rutile were the most abundant minerals identified in the study area, corundumand ulvospinel were detected in only two sampled sites. This agrees with the result of a similar work reported by Ptacek etal. (2013). Rutile was detected in all the sites but two (T^d in Yola South South and T^d in Yola South North). The most abundant form of TiO_2 is rutile because it is the most stablecompared to the other polymorphs, example, anatase. Both anatase and rutile are oxides of titanium, rutile (TiO_2) occupies important place in paint industries because it has high refractive index, strong absorption of UV region of light spectrum and strong reflectance in the visible spectrum which gives it a light scattering properties in addition to particle size which makes it effective pigment for brightness and opacity (Alabi & Omojala,2013). Three different minerals were detected in each of the sampling sites with the exception of two sampling sites in Yola South North location (10mr and 10md) which showed presence of only two minerals each. The minerals; almandine, montmorillonite and microcline are alumino-silicate minerals, they are major rock –forming minerals. Most of the minerals detected in the study area are among the 34 minerals ear-marked for development in Nigeria.

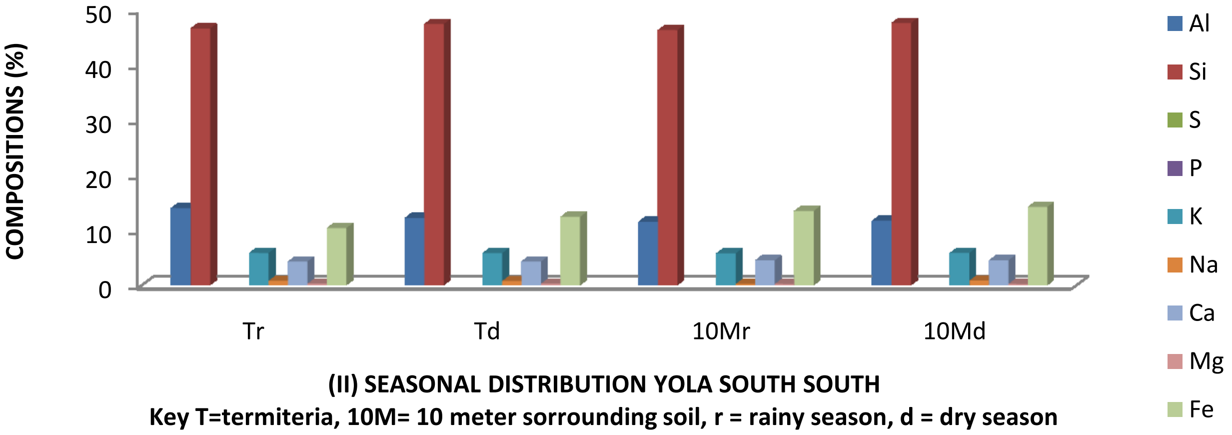
Table 1: Minerals identified in termitera (T) and 10 meter surrounding (10 M) soils in Yola South Local Government Area

Minerals	Compound name	Chemical formula	Crystal system	Yola South South				Yola South North			
				Tr	Td	10mr	10md	Tr	Td	10mr	10md
Almandine	Iron aluminum silicate	$Fe_3(Al_2Si_3O_{12})$	Cubic	-	-	-	-	*	-	-	-
Corundum	Aluminum oxide	Al_2O_3	Rhombohedral	*	-	-	*	-	-	-	-
Montmorillonite - 22A	Sodium magnesium Aluminum Silicate Hydroxide Hydrate	$Na_{0.3}(Al,Mg)_2 Si_4O_{10}(OH)_{2.8}H_2O$	Hexagonal	-	-	-	-	-	*	-	-
Microcline	Potassium Aluminum Silicate Hydrate	$K(Si_{0.75}Al_{0.25})_4O_8$	Anorthic	-	-	*	-	-	-	-	-
Quartz	Silicon oxide	SiO_2	Hexagonal	*	*	*	*	*	*	*	*
Rutile	Titanium oxide	TiO_2	Tetragonal	*	-	*	*	*	*	*	-
Ulvospinel	Iron titanium oxide	Fe_2TiO_4	Cubic	-	*	-	-	-	-	-	*
Wulfenite	Lead molybdenum	PbMoO4	Tetragonal	-	*	-	-	-	-	-	-

Key: r = Rainy Season, d = Dry Season, __ = Absents, * = Present

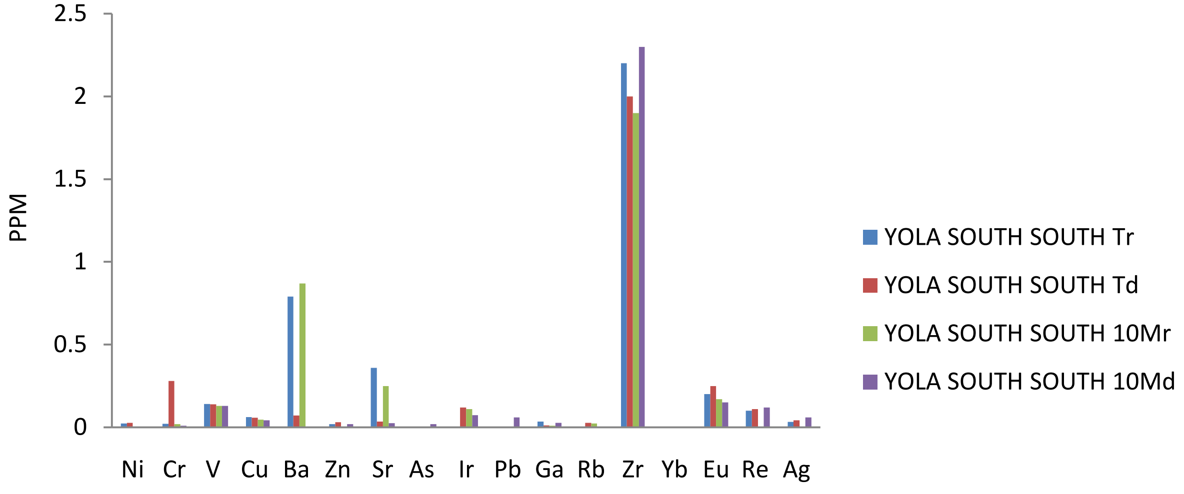


(I) SEASONAL DISTRIBUTION YOLA SOUTH NORTH
Key T=termiteria, 10M= 10 meter sorrounding soil, r = rainy season, d = dry season

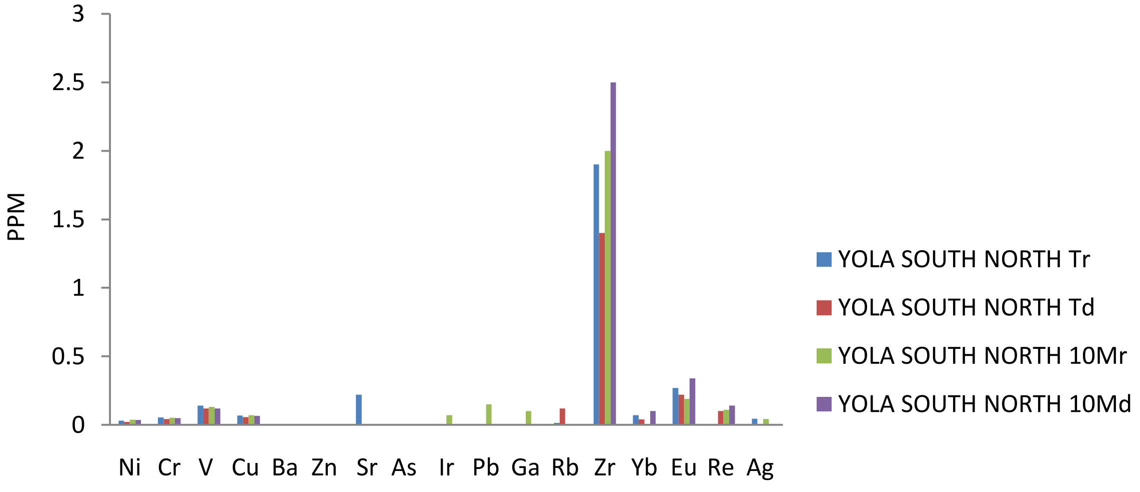


(II) SEASONAL DISTRIBUTION YOLA SOUTH SOUTH
Key T=termiteria, 10M= 10 meter sorrounding soil, r = rainy season, d = dry season

Figure 2: (i) & (ii), Comparisons of Major Elemental composition of termiteria (T) and 10 M surrounding soils in Yola South local government area for the two seasons.



(1) Trace Element Contents of *Termitria* (T) and 10 M Surrounding Soils in Yola South South



(11) Trace Element Contents of *Termitria* (T) and 10 M Surrounding Soils in Yola South North

Figure 3: Trace Element Contents of Termiteria (T) and 10 M Surrounding Soils in Yola South.

Detection of corundrum and abundance of quartz may be associated with the kaolinite thermal transformation.

Among the eight minerals detected in Yola South three were the aluminosilicate minerals (almandine, montmorillonite, microcline) while, corundum and quartz which were detected in severalsampling sites are closely related to thealuminosilicates as products of thermal transformation of termiteria clay (kaolinite)(refer to appendix). The wide spread the aluminosilicates may be attributed to the fact that about 95% of the earth's crust is made up of Silicate minerals-aluminosilicate clays or Silica, they constitute the bulk of all rocks, sands and their breakdown products, clay and soil (Lee, 2007). Generally, the distribution of the elements in terms of quantity as indicated by figures 2 and 3 agrees with the theory that eight elements accounted for 99% of the earth's crust by weight, these elements also known as rock forming elements are: O_2 46.6%, Si = 28.2%. Al = 8.2%, Fe = 5.6%, Ca = 4.2%, Na = 2.4%, K = 2.1 and Ti= 0.6% (Botkin& Keller, 1998).

Al contents of the study area has range of, (11.50 ±0.35 – 10 ± 1.00)% for termiteria while that of adjacent soil was (12 .04 ± 0.01– 8.33 ± 0.75)%. (52.90 ± 1.50– 52.60 ±08)% and (60 ±0.60– 51.20 ± 0.16)% were the ranges of Siin termiteria and its10 M adjacent soilrespectively. Sicontents of termiteria soil was slightly low compare to its adjacent soil this may be due to high clay contents of termiteria. Fe has values ranging from (12.00 ± 0.04 – 2.87 ± 0.13) %, Fe contents of termiteria sample sites in Yola South South sampling location were twice those of their 10 Madjacent soils and in Yola South North, values of Fe in termiteria were either slightly more thanor equal to their 10M adjacent soils. Higher values of Fe in territorial and its adjacent soils in the study area more than 5.6%, its natural abundance in soils may be explained in terms of its mineralization in the territorial, in addition, higher quantities of; Al, Fe, and Si in the study area are associated with the presence of mineral compounds detected containing them (Table 1).K ranged from (11.20 ± 0.08– 4.53 ± 0.15) % and (14.70 ± 0.23 –4.64 ± 0.074)% in termiteria and adjacent soils respectively. Quantity of K inYola South South sampling locationwas at least twice those of Yola South North. This may be attributed to the presence of itsore deposit in Yola South South sampling location which may be absent in Yola South North sampling location, since minerals are not evenly distributed in the earth's crust (Botkin & Keller, 1998). High content of Ti in the samples compare to its natural content of 0.6% in the earth's crust (Botkin & Keller, 1998), can be attributed to its mineralization in the study area as oxides of titanium(table I). Generally, Mg and Ca contents of territorial are slightly higher than the ones in the adjacent soils. This trend is usual because Ca, Mg,and K contents of termiteria have been reported to be higher than for surrounding soil, furthermore, most of the elements fall within the reported values for termiteria as; (Si = 46.5, Al = 18.6, Mg = 1.6, Fe = 6.7, Ti = 1.4, Ca = 6.3, K = 2.0 and Na = 1.6) % (Ptacek, 2013). Among the trace elements determined, Cr, V, Cu, Zr and Eu were detected in all the sampling sites, Zr has the highest value with range of (2.50 ± 0.10 – 1.90 ± 0.06) PPM and (2.20 ± 0.10 – 1.40 ± 0.02) in 10 M adjacent soils and termiteria soils respectively.This was followed by Ba detected in Yola South South location only. Pb and As were not detected in termiteria samples but in 10 M adjacent soils, this may be due to pollution by flood. Almost all the trace elements detected were very low in concentration (Figure 3) compare to the result of trace element contents of soil in three locations reported by Ananfi, et al., (2011); (Pb = 103.15, 621.60 and 6.20; Zn = 963.90,1269.90 and 1180.65)Mg/L, this entails lesser environmental pollution in the study area.

Though there are slight variations between the values obtain for elemental contents of territorial soils and those of the adjacent soils, statistically there is no significant difference $p< 0.05$.This indicates that the elements from the termiteria have distributed to the surrounding soils as far 10 M away. This further explains reason for exceptionally good growth of plants around termiteria environment.

CONCLUSION AND RECOMMENDATION

The result of this preliminary work on using termiteria as a tool for easier and cheaper method of mineral exploration has shown that termiteria can be a prospective tool if properly handled for this purpose since the result indicated mineralization of several minerals in the study area. Detection of trace elements in the vicinity of termiteria from the study area indicates that the practice of eating termiteria soils (geophagia) should be done with caution.

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APPENDIX

The stages involved in the thermal transformation of kaolinite are:

Dehydroxylation of Kaolinite into Metakaolinite;

$Al_2O_3{}_{.}2SiO_2.2H_2O \xrightarrow{400 - 700^{0}C} Al_2O_3{}_{.}2SiO_2 + H_2O$

Formation of the Al- Si spinel phase;

$2\ (Al_2O_3{}_{.}\ 2SiO_2) \xrightarrow{925\ \_\ 1050^{o}C} 2Al_2O_3 + 3SiO_2 + SiO_2$ (amorphous)

Formation of the Mullite:

$3(2Al_2O_3\ .\ 3SiO_2) \geq \xrightarrow{10500C} 2(3Al\ {}_2O_3\ .\ 2SiO_2) + 5\ SiO_2$ (amorphous)

Formation of Cristoballite;

SiO_2 (amorphous) $\geq \xrightarrow{12000C}$ SiO_2 (cristoballite tetragonal)

(Source: Ptacek et al., 2013)