HEAVY METALS DISTRIBUTION AND MINERALOGY OF SAPROLITE OF SOILS DEVELOPED ON COASTAL PLAIN SANDS IN SOUTHEASTERN NIGERIA

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ABSTRACT

The distribution of heavy metals as well as minerals in the fine sand andclay fractions in saprolite derived from coastal plain sands in Southeastern Nigeria were investigated.Heavy metal levels were generally low,when compared to existing permissible standard limits.Ranges for Iron, Manganese, Copper and Zinc were 400-1750 mgkg^{-1},51.75-223.75mgkg^{-1}, 12.01-92.75 mgkg^{-1}and 55-122.1mgkg^{-1} respectively. Chromium rangedfrom 1.15-2.53mgkg^{-1},Nickel and lead ranged from 0.02-0.08mgkg^{-1}and0.02-0.25 mgkg^{-1}respectively. Mineralogical results from the XRD revealed the dominance of quartz, followed by kaolinite with occasional occurrence of illite andwiserite.Trace amountsof Al-Si-Oxide(0.8%) was also found in the fine sand fraction at 18.2-18.9m depth at Uyoafaha. Infrared spectroscopy of the clay fraction also revealed the presence of quartz, kaolinite and Illite as well as gibbsite and halloysite.

KEYWORDS: Heavy Metals; Mineralogy; Saprolite; Coastal Plain Sands.

INTRODUCTION

Heavy metals are elements having densities greater than 5g/cm^3 which are basically, transition metals and higher atomic weight metals of groups 3 to 5 of the periodic table.Under natural conditions, the main sources of metals in soils is parent materials (Silveira*et al*, 2003), however; anthropogenic activities such as industrial emissions and effluents, biosolids, fertilizer applications, soil ameliorants and pesticides as well as transportation fuel can increase the amount of metals in the soil (Lund, 1990, Silveira*et al*, 2003).The soluble and exchangeable forms of heavy metals have been identified as the most important fractions associated with ground water pollution and plant nutrition (Sastre*et al*, 2001). Heavy metals can pollute the drinking water system when they seep through soils into ground water, and, can also contaminate the food chain causing a reduction in crop yield (Wang *et al*, 2003).However, a goodknowledge of the composition of the soil mineral fraction by identification and characterization of clay minerals is important for understanding the genesis, properties and behavior of soils as well as aid in their classification (Islam and Hussein, 2008).Soil physical properties like plasticity, water retention, hydraulic conductivity, swelling and shrinking as well as cation exchange in most soils, are largely controlled by the mineralogical composition of the clay fraction (Islam and Hussain, 2008; Esu,2010).Islam and Hussien(2008) also opined that agronomic practices to a large extent depend on the clay mineralogy which according to them is a reflection of the inherent fertility status of such soils. Coastal plain sands derived soilsare usually dominated by low activity clays such as kaolinite (Enwezor*et al*, 1981); hence they are often low in cationexchange capacity, due to absence of isomorphous substitution on the mineral crystal surface (Fitzpatrick, 1983).

Information on heavy metals content and mineralogy of saprolites derived from coastal plain sands is scanty, especially in Nigeria due in part to, the paucity of relevant laboratory equipments used in their determination as well as the great depth at which they occur.Considering the extensive occurrence and the great economic importance attached to the soils developed on this parent material in southeastern Nigeria,this study was designed to investigate the heavy metals content with their potential effect on ground water quality ,as well as the mineralogical composition ofsaprolite derived from coastal plain sands in southeastern Nigeria.

MATERIALS AND METHODS

Study Area

The study was conducted in five selected locations within Southeastern Nigeria (Fig.1).These areas include Ayaedeghe (5°10'N; 8°2'E), Mbak-Atai(5°10'N ; 8°E) and Uyoafaha (5°10'N; 49'E), in Akwalbom State; Okaiuga-Nkwoegbu (5°33'N; 7°E), in Abia State as well asEmekuku (5° 28'N; 7° 8'E) in Imo State. Southeastern Nigeria is located on latitude 4°15'-7°0'N, and longitude 5°50' - 9° E. The area lies within the rainforest agro-ecological zone of Nigeria. The climate is humid tropical and is characterized by prolonged rainy season (March to October) and a relatively shorter dry season (November to March), though this appears to be inconsistent for the past eleven years due perhaps, to global climate change. Annual rainfall ranges from 2000mm to 3500mm while average air temperature ranges between 26 and 28°C.Relative humidity is usually high in the rainy season ranging from 75 to 85% but can be as low as 25% in the dry season.

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Field Study

Reconnaissance visits were carried out to various deep profile locations within Southeastern Nigeria. From these visits, five deep profiles were selected and their respective coordinates and elevations taken with the aid of the Global Positioning System (GPS).Profile description and sampling was restricted to the C- horizon and was done according to Soil Survey Staff (2002).Saprolite samples were also collected for laboratory analysis.

Laboratory Analysis

Heavy metals content in saprolites were determined by the wet digestion method according to the procedures of Stewart (1973). Accordingly, 1gof fine earth sample ofsaprolite was digested with acid mixture of concentrated HNO_3 ($15cm^3$) and HCl ($5cm^3$). The digest was analyzed for Fe, Mn, Cu, Zn, Cr, Ni, Pb, Cd and Co using a Buck Scientific 210/211/VgP Atomic Absorption Spectrophotometer. The concentration of each element was obtained by reference to standard calibration curves for atomic absorption spectrophotometry sigma.

Mineralogical analyses involved the X-ray diffraction and the Infrared spectroscopic methods. For the X-ray method,ten grams of air dried soilwas treated with 30% H_2O_2 and heated for about 2 hours to decompose organic matter. Excess H_2O_2 present in the sample was removed through centrifugation by washing 3 times with water and 3mgof NaCl added each time, to prevent de-flocculation of clay particles, and the supernatant solution discarded by decantation. The pH of the soil suspension was adjusted to 10 by addition of NaOH. Clay fraction (<0.002mm) was separated by repeated sedimentation-siphoning method .The XRD pattern was obtained using a Bruker AXS diffractometer (Model D8,Karlsruhe,German) with Ni-filtered Cu k-α-radiation at 40kV and 30mA at a scanning speed of $2.0°/min$ over a range of $3-35°2\theta$. Approximate clay mineral content in samples was estimated on the basis of the relative peak intensities in the XRD pattern as described by Islam and Lotse (1986).

The infrared(IR) spectra was obtained by preparing compressed pellets through grinding a mixture of 2mg sample with 100mg KBr and mounting on a disc, and kept under vacuum, free of humidity(Russel,1987). A pressure of 10 Mpawas applied for 2 minutes for the powdered sample to form a disc sheet with a thickness of 1mm prior to analysis. A Thermo Scientific Nicolet Magna 6700 Infrared Spectrophotometer in the absorbance mode with $4cm^{-1}$ resolution was used for the analysis. For the region of wave number between $4000cm^{-1}$ to $400cm^{-1}$, a CsI detector and a CsI beam-splitter was used and 64 scans performed on each sample so that an average spectrum was recorded. The OMNIC NICOLET FT-IR software was used to obtain the spectra as well as eliminate any possible interference from H_2O and CO_2 on the analyses.

RESULTS AND DISCUSSIONS
Heavy Metals Content of Saprolites

Table 1 presents a summary of data for heavy metals content in the saprolitic horizons as well as the globally acceptable limits of concentration in soils.

Results showed that iron ranged from 400 to 1750 $mgkg^{-1}$ in all the samples with higher means of 1635 $mgkg^{-1}$ and1232.5$mgkg^{-1}$obtained at Okauiga-Nkoegbu and Uyoafaha, respectively, when compared to other locations.Manganese (Mn) was detected in all the selected samples with means that ranged from 52.88 to 219.53$mgkg^{-1}$.The high Fe and Mn concentrations in all the samples may be due, perhaps to the acidic nature of the saprolites (pH 3.6-5.1).The concentration of Cu in MbakAtai, Ayaedeghe and UyoAfaha were below the permissible limits (Alloway, 1990; Kabata-Pendias and Pendias, 1992).However, relatively higher concentrations of Cu was recorded atEmekuku (mean 63.47 $mgkg^{-1}$) and OkaigaNkoegbu (mean, 91.38$mgkg^{-1}$), due perhaps to industrialactivitiesin these areas. It could also possibly be inherited from the parent rock of the saprolite.Zinc content as recorded at Uyoafahahad a mean value of 120.1$mgkg^{-1}$ andexceeds the benchmark of 72.5-78.2$mgkg^{-1}$ allowed for industrialized nations(Alloway, 1990). The relatively high zinc concentration (mean, 120.1$mgkg^{-1}$) in Uyoafaha may be attributed to the mobility of zinc containing waste possibly disposed on the soils at the location. Chromium was present at low concentrations with means that ranged from 1.33 - 2.45$mgkg^{-1}$in all the saprolitic horizons. Nickel was also present at lower concentrations,and ranged from 0.02-0.08 $mgkg^{-1}$ in all the saprolitic horizons studied.Mean lead values were very low,possibly due to less influence from highway traffic because of its great distance for the highway.Cadmium, a very toxic heavy metal with no beneficial function in the human body, occurred at very safe levels, with means that rangedfrom 0.45-0.6$mgkg^{-1}$.These values arebelow the maximum permissible range of 0.07-1.1$mgkg^{-1}$ for non-polluted soils (Kabata-Pendias and Pendias, 1992). Cobalt was also low.The generally low concentration of heavy metals in the study area can be attributed to the predominance of the sand fraction in the coastal plain sands saprolite and low clay and organic matter contents. This result agrees with the views ofSilvieraet al, (2006) that, high clay and organic matter contents favours the bioavailability of heavy metals in soils. From this study one can postulate that ground water underlying the coastal plain sands would require very little or no treatment to make them potable.

Mineralogical Properties of Saprolitic Horizons

Result of the X-ray diffraction analysis of saproliteis summarized in Table 2 and, the peaks shown in Figures 2-5. Quartz was the most dominant mineral in both the fine sand and clay samples and ranged from 71.9-99.2% and 61.1-89.1%, respectively. Onyeagocha (1980) obtained similar results from the fine sand fraction of coastal plain sands derived soils in Owerri. The quartz content was relatively higher in the fine sand than clay samples with exception to MbakAtai where the result was different. Clay minerals were present in the following order of abundance: kaolinite >illite>wiserite and trace amounts of aluminium silicon oxide (0.8%) occurred at 18.2-18.9m depth at Uyoafaha in place of kaolinte. This amorphous aluminosilicate is said to vary in composition, depending on the nature of the weathering material, environment and age, and is found to slowly weather to halloysite and then to kaolinite (Fitzpatrick, 1983).Thisresult agrees with the

findings of Parham (1969),that amorphous aluminosilicates usually form as intermediate stage to halloysite and kaolinite formation. Perhaps, this may suggest that the saprolite at MbakAtai was relatively less weathered when compared with saprolites in the other locations. However, the dominance of quartz in all the samples analyzed could be attributed to the sandy nature of coastal plain sands (Akamigbo and Asadu, 1983) as well as it being the major constituent of sandstone,while its constancy in all the locations, suggests, lithological uniformity. The dominance of low

activity clay mineral (kaolinite) is characteristic of coastal plain sands (Enwezor et al, 1981; Chikezie et al, 2010).

The infrared spectra obtained were similar for all the selected samples and are represented by Figure 6.The result reveals the presence of quartz, kaolinite, gibbsite, illite as well as halloysite and they all occur around the adsorbance wave band range of 410-820cm^{-1}. This method, apart from corroborating the result obtained through the x-ray diffraction method, has also assisted in elucidating the presence of other minerals that were not represented by the XRD method.
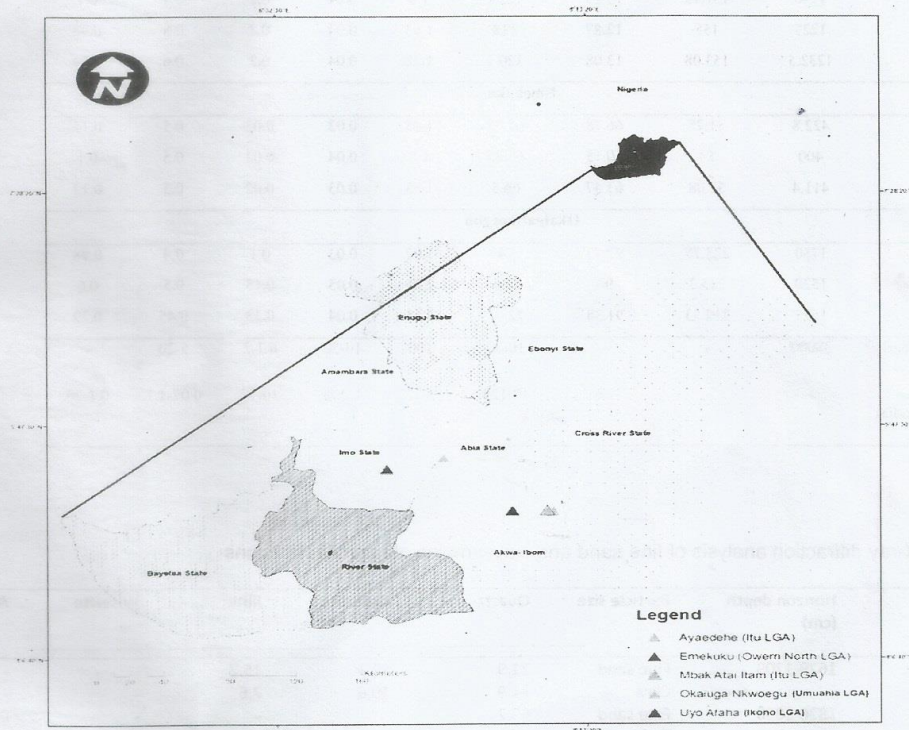

FIG. 1: Map of South Eastern Nigeria Showing Locations of Sampling Areas

Table 1: Concentration of heavy metals in selected saprolite horizons

Depth (m)	Fe	Mn	Cu	Zn	Cr	Ni	Pb	Cd	Co
				mgkg^{-1}					
13.0-13.6	572.4	94.15	16.2	61.5	2.4	0.08	0.15	0.52	0.55
16.3-17.1	568.8	92	13.66	55	2.5	0.05	0.25	0.5	0.5
Mean	570.6	93.08	14.93	58.3	2.45	0.07	0.2	0.51	0.53
Ayaedeghe									
8.0-9.6	612.5	62.25	12.33	65	2.55	0.03	0.1	0.7	0.63
10.5-11.6	589.2	60	12.01	62.3	2.2	0.03	0.15	0.5	0.58
Mean	600.9	61.13	12.17	63.7	2.38	0.03	0.13	0.6	0.61
UyoAfaha									
15.1-15.7	1240	151.15	13.28	122.1	1.8	0.04	0.2	0.4	0.1
17.6-18.2	1225	155	12.87	118	1.63	0.04	0.2	0.8	0.98
Mean	1232.5	153.08	13.08	120.1	1.72	0.04	0.2	0.6	0.54
Emekuku									
12.4-17.8	422.8	51.75	66.78	67.75	1.15	0.02	0.02	0.5	0.15
18.9-19.8	400	54	60.15	65.25	1.5	0.04	0.02	0.5	0.1
Mean	411.4	52.88	63.47	66.5	1.33	0.03	0.02	0.5	0.13
OkaigaNkoegbu									
7.5-8.7	1750	223.75	92.75	74	1.97	0.03	0.1	0.4	0.98
10.6-12.2	1520	215.3	90	71.5	2.25	0.05	0.15	0.5	0.6
Mean	1635	219.53	91.38	72.75	2.11	0.04	0.13	0.45	0.79
UNEP Standard	38000	-	-	10-50	100	10-50	0.1-2	5-20	-
Kabata-pendias&Pendias 1992	-	-	5-6	17-125	5-12	1-200	10-70	0.07-1.1	0.1-20

Table 2: X-ray diffraction analysis of fine sand and claysamples of saprolite horizons

Location	Horizon depth (cm)	Particle size	Quartz	Kaolinite	Illite	Wiserite	Al-Si-oxide
%							
MbakAtai	1629-1709	Fine sand	71.9	12.9	15.2	-	-
		Clay	81.9	10.6	7.6	-	-
Uyoafaha	1820-1890	Fine sand	99.2	-	-	-	0.8
		Clay	89.1	5.4	-	5.5	-
OkaigaNkoegbu	748-866	Fine sand	91.6	8.4	-	-	-
		Clay	61.6	14.3	13.9	10.3	-
Emekuku	530-1240	Fine sand	90.7	6.0	-	3.3	-
		Clay	72.8	19.2	-	8.0	-

File: 2.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 70.014 ° - Generator kV: n.a. - Generator mA: n.a. - Step: 0.021 °
Operations: Import
01-070-3755 (*) - Quartz - SiO2 - WL: 1.5406 - S-Q 81.9 %
00-058-2028 (I) - Kaolinite-1A - Al2S2O5(OH)4 - WL: 1.5406 - S-Q 10.6 %
00-026-0911 (I) - Illite-2M1 (NR) - (KH3O)Al2S3AlO10(OH)2 - WL: 1.5406 - S-Q 7.6 %
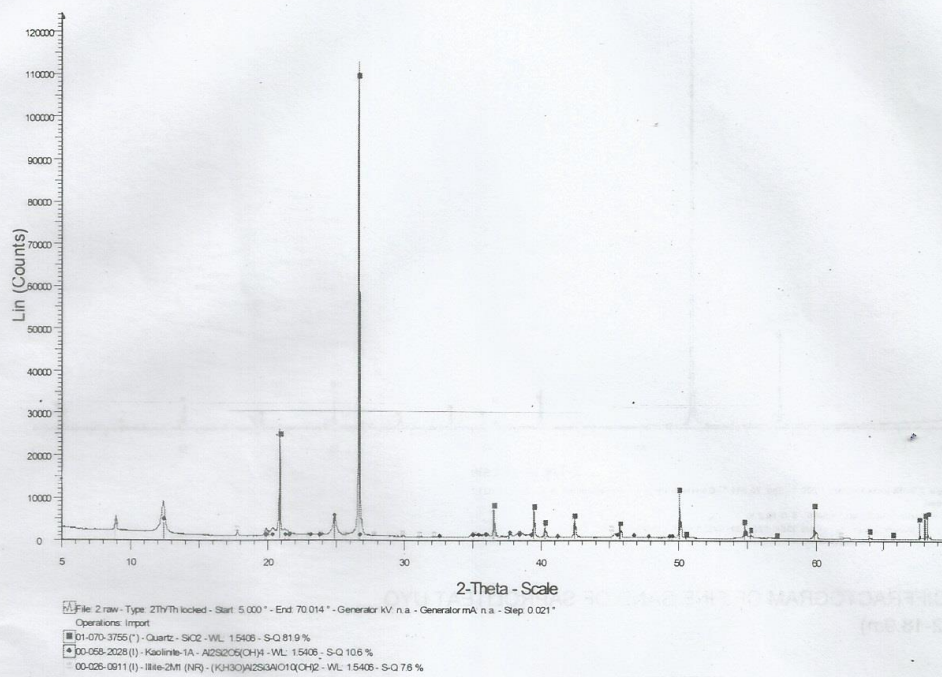
FIG 2: X-RAY DIFFRACTOGRAM OF CLAY OF SAPROLITE HORIZON AT MBAK ATAI
(CR4:16.3-17.1 m)
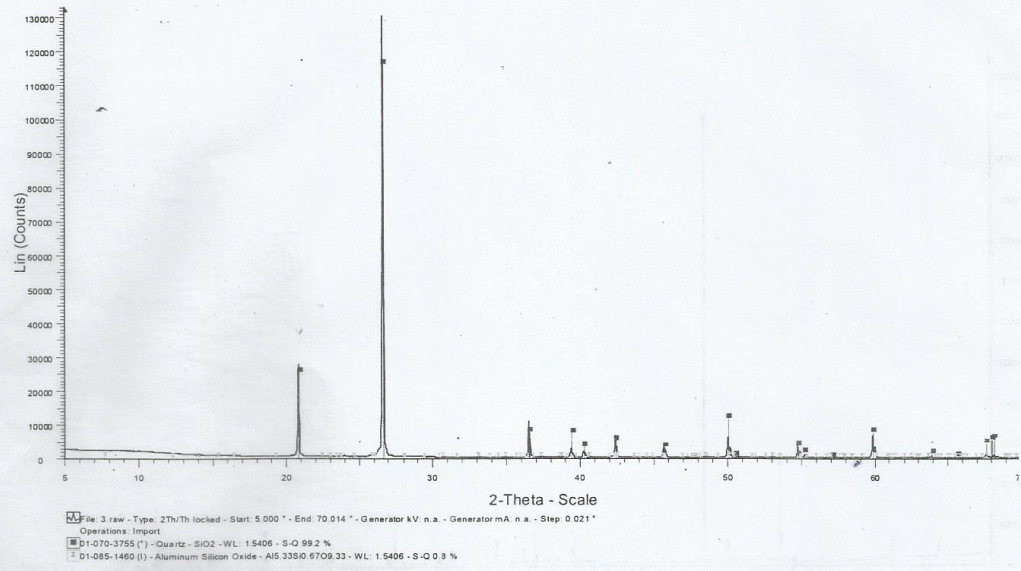
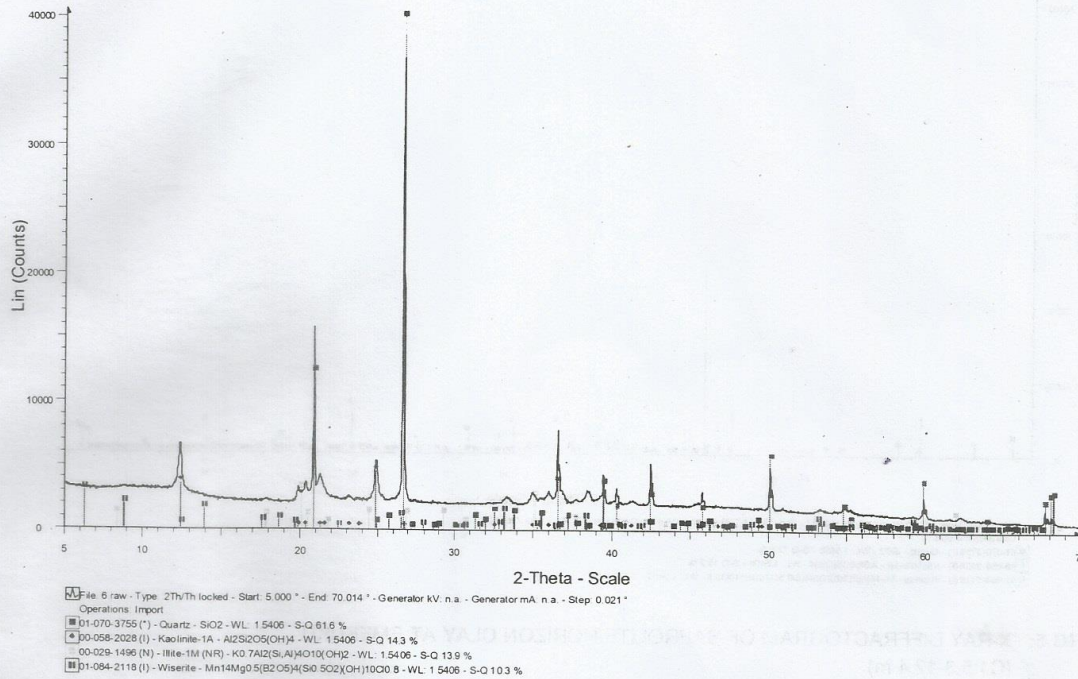FIG 3: X-RAY DIFFRACTOGRAM OF FINE SAND OF SAPROLITEAT UYO AFAHA(C5:18.2-18.9m)

File: 6 raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 70.014 ° - Generator kV: n.a. - Generator mA: n.a. - Step: 0.021 °
Operations: Import
01-070-3755 (*) - Quartz - SiO2 - WL: 1.5406 - S-Q 61.6 %
00-058-2028 (I) - Kaolinite-1A - Al2Si2O5(OH)4 - WL: 1.5406 - S-Q 14.3 %
00-029-1496 (N) - Illite-1M (NR) - K0.7Al2(Si,Al)4O10(OH)2 - WL: 1.5406 - S-Q 13.9 %
01-084-2118 (I) - Wiserite - Mn14Mg0.5(B2O5)4(Si0.5O2)(OH)10Cl0.8 - WL: 1.5406 - S-Q 10.3 %

FIG 4: X-RAY DIFFRACTOGRAM OF CLAY FRACTION OF SAPROLITE HORIZON AT OKAIGA-NKOEGBU(C1:7.5-8.7m)

File: 8 raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 70.014 ° - Generator kV: n.a. - Generator mA: n.a. - Step: 0.021 °
Operations: Import
■ 01-070-3755 (*) - Quartz - SiO2 - WL: 1.5406 - S-Q 72.8 %
◆ 00-058-2028 (I) - Kaolinite-1A - Al2Si2O5(OH)4 - WL: 1.5406 - S-Q 19.2 %
■ 01-084-2118 (I) - Wiserite - Mn14Mg0.5(B2O5)4(Si0.5O2)(OH)10Cl0.8 - WL: 1.5406 - S-Q 8.0 %
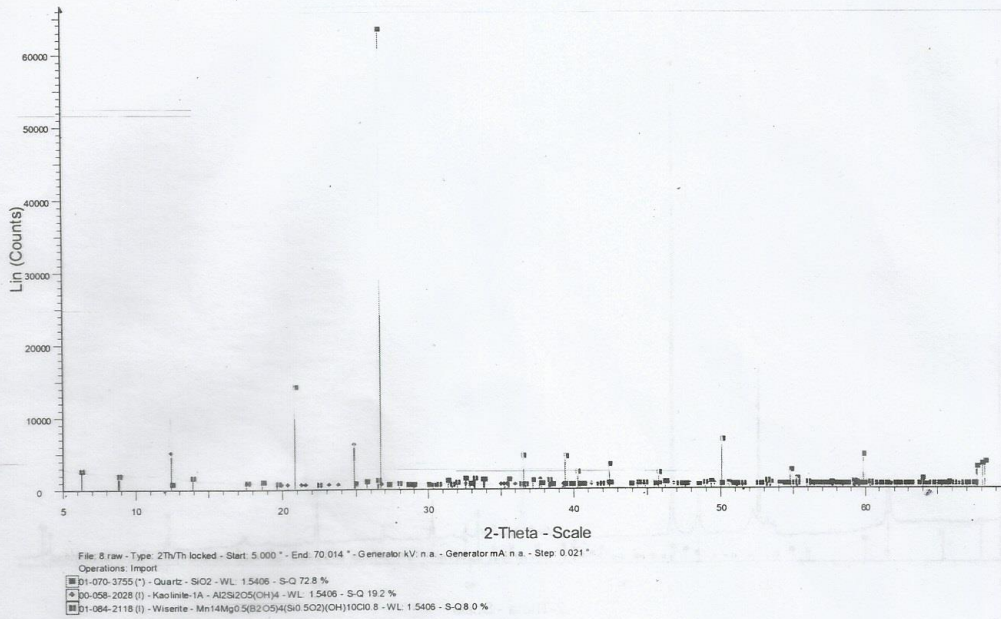
FIG 5: X-RAY DIFFRACTOGRAM OF SAPROLITE HORIZON CLAY AT EMEKUKU
(C1:5.3-12.4 m)
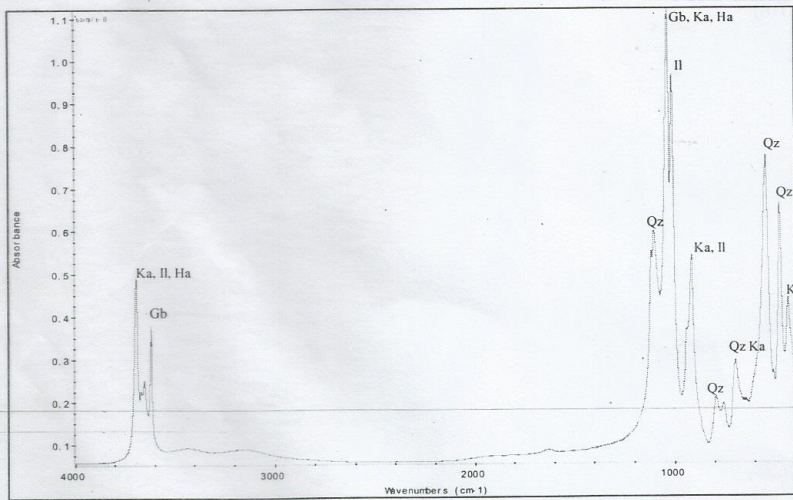
Ka=kaolinite,Il=ilite,Gb=gibbsite,Qz=quartz,Ha=halloysite

FIG.6: INFRARED SPECTRUM OF CLAY OF SAPROLITE HORIZON AT MBAK ATAI

CONCLUSION

The general low content of heavy metals in the saprolites suggests a no threat of ground water contamination while the similarity of the result of the mineralogical properties to that of soils around the area of study ,implies that these saprolitic materials are largely responsible for the properties exhibited by soils within this area.

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