Evaluation of Soil Oxide Mineralogy in Different Bedrock Lithologies in the Southern Guinea Savannah of Nigeria

Theophilus Olufemi Isimikalu, John Olajide Olaniyan, Bashiru Ademola Raji
Department of Agronomy, Faculty of Agriculture,
University of Ilorin, Ilorin, Kwara State, Nigeria
Corresponding Author: Theophilus Olufemi Isimikalu, e-mail: olufemith@gmail.com

Received: 13 June 2020 *Accepted: 5 October 2020*

Abstract

Agriculture has very important social and economic footprint in Africa. Its soil resource is however threatened by degradation resulting from mismanagement, due to lack of knowledge on important soil functional properties such as mineralogy, which impact many soil processes. This study was therefore conducted to access variations in soil oxide mineralogy in soils formed from differing bedrock lithologies. Soil sampling was carried out on soils from three different bedrock types; basement complex rocks, recent alluvium, and Nupe sandstone in Kwara state, southern Guinea Savannah of Nigeria. Data was subjected to analysis of variance to determine significant differences in treatment means ($p<0.05$), and correlation analysis was performed to determine relationships between measured variables.

Elemental oxide composition of soils from the different bedrock materials were found to be significantly different. Soils from all three bedrock types had very high amounts of silica by mass (>80 %). The highest mean percentage of 90.59 was recorded in recent alluvium-derived samples, while the least value of 80.75 % was recorded in basement complex-derived samples. Aluminum and iron oxides were the most saturating metal oxides in all the bedrock types, and significantly higher values of 5.65 % and 2.71 % for Al_2O_3 and Fe_2O_3 respectively were recorded in basement complex-derived soils. Dissimilar trends of mineral oxide relationships were observed in soils from the different lithologies, which are likely a result of bedrock characteristic, environmental and hydrologic factors. The relationships established between oxide minerals in this study could serve as a foundation for subsequent investigations into mineral interactions in the soils.

Keywords: soil management, oxide mineralogy, land, savannah

Introduction

Agriculture is the economic mainstay of more than 70 % of Africa's population, which impacts economic growth and social improvement, and forms a major trade component. This demonstrates the pivotal position of soil resources in the continent, both to keep up with food production for rapidly increasing populations, and for economic prosperity. Soils in this region however continue to be degraded due to poor management. According to the international fertilizer association (IFA, 2016), about 75 % of sub-Saharan

Africa (SSA) soils are already degraded. The soils have also been described as of limited resilience ability (Lal, 1995).

Rising populations in Africa implies more pressure on land resources for food production, which hangs majorly on soil fertility. Building soil fertility ordinarily implies increased use of nutrient inputs. Mineral fertilizers use in SSA soils is however constrained by high variability in responses to common standard fertilizers as a result of soil mineralogy variations, among other factors. For example, Ojanuga (1978) reported that most Nigerian soils are low in CEC and applied chemical fertilizer efficiency, due to the characteristic clay mineralogy of the soils. This leads to loss of mobile nutrients, nutrient deficiencies, and imbalance (Voortman, 2003).

High application of chemical fertilizers under this condition result in increased risk of nutrient elements and toxic chemicals contamination of surface and groundwater, and GHGs emissions which promote climate change. The situation is worsened when soil organic matter is depleted to critically levels (Vanlauwe et al., 2010). Optimum and sustainable soil management entails the generation of spatial information on soil functional properties such as nutrient capacity, toxic substances filtering, nutrient cycling and terrestrial gas fluxes, which are affected by factors such as texture and organic matter (OM) gradient, mineralogy, and elemental concentration.

Soil mineralogy is an important factor in crop selection and growth, and it has a direct effect on soil fertility, and the capacity of a soil to store and release nutrients for crop use (Ajiboye and Ogunwale, 2013). The extensive study of oxide and oxyhydroxide compounds in different soil types (Vandenberghe et al., 1986; Acebal et al., 2000; Stahr et al., 2010) highlights their importance in soil. According to Kinniburgh and Jackson (1981), soil adsorption is largely controlled by metal oxides and oxyhydroxides, and their level of coating on soil phyllosilicates. Iron oxides and other minerals whose structures are dominated by variable charge are major components in many acid soils such as those of the southern Guinea Savannah of Nigeria.

There is limited data on soil oxide mineralogical composition in Nigerian soils, which makes the study of their variation in different soils important. Knowledge of the mineralogical properties of the soils can help to better understand soil forming-factors and inherent functional properties, and inform the selection of management options that optimize yield, and conserve land resources for sustained agricultural productivity; an idea that is of utmost importance towards achieving food security in the SSA region. The foregoing formed the objective of conducting this study to improve the understanding of the relationships between soil bedrock type and oxide mineral composition in the studied soils.

Materials and Methods

This research was conducted in Kwara State, southern Guinea Savannah of Nigeria. Geographically, the state is located between latitudes 7^{o}55' and 10^o 05’ N, and longitudes 2^0 45' and 6^o 15' E. The region has a tropical wet and dry climate, with double rainfall maxima (two peaks in July and September) and a dry spell in August. The dry season begins in early November, ending in early March. Both dry and wet seasons last for about six months. The state has an annual rainfall range of 1000 to 1500 mm, and atmospheric temperature is uniformly high (between 25 ^{o}C and 30 ^{0}C) throughout the wet season except between July and August when clouding of the sky prevents direct insolation. In the dry season, temperature ranges between 33 °C to 34 °C (Olanrewaju, 2009). According to the federal department of agricultural land resources (FDALR) (1990), the geology of the state consists mainly of precambrian basement complex rocks (95 %), and recent alluvium and sedimentary (sandstone) rock materials (5 %). Olaniyan (2003) stated that the major metamorphic rocks found in the state are granitic gnesiss, biotite gnesiss, quartzite, augite gnesiss and banded gnesiss.

Free survey was carried out in three locations (Ilorin, Shonga and Patigi) within the state, informed by the FDALR (1990) soil map of Nigeria. According to the map, Ilorin falls within map unit 15g, with soils formed from basement complex rocks, Shonga falls on map unit 2a, having soils derived from recent alluvium, and Patigi is located on map unit 15e, with soils formed from Nupe sandstone. An area of 2 ha was marked out on fallow lands in each of these locations from which ten (10) surface (0-15 cm) soil samples were randomly taken. The soil sampling sites at Ilorin, Shonga and Patigi were located at approximately 8.450953° N, 4.658458° E; 9.012603° N, 5.172725° E; and 8.717586° N, 5.796669° E respectively (Figure 1). Soil samples were air-dried, <2 mm sieved, and subjected to physical and chemical analyses. Physical and chemical properties of soils were determined using routine laboratory procedures and presented in Table 1. Soils of the study location were classified according to USDA Soil Survey Staff guidelines (2014) as Anthraquic Ustorthent, Grossarenic Kandiustalf and Ustic Quartzipsamment for Ilorin, Shonga and Patigi locations respectively.

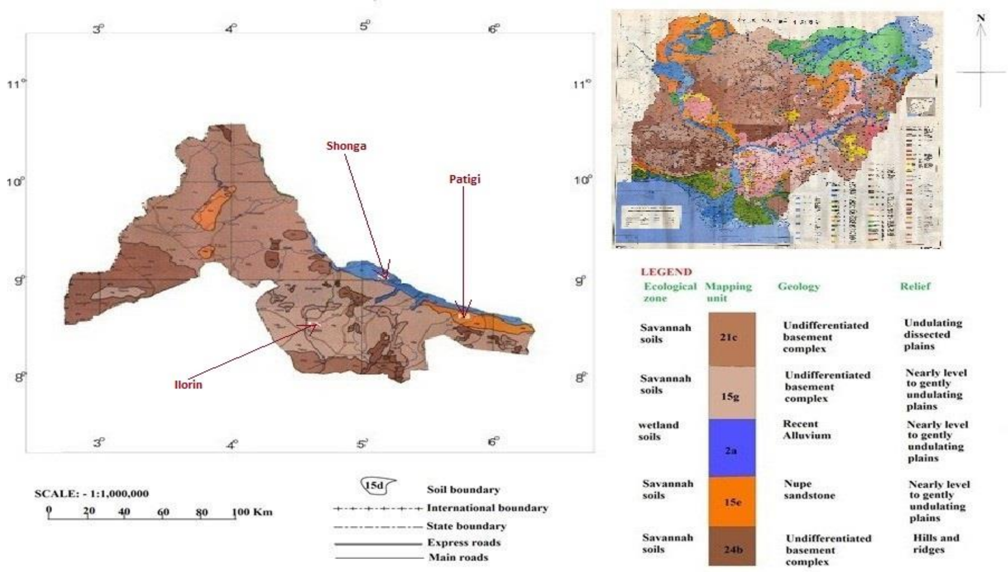

Figure 1. *Soil map of Kwara state (extract from soil map of Nigeria (FDALR, 1990) indicating survey locations.*

Quantitative determination of mineral element composition was done using X-Ray Fluorescence (XRF) spectroscopy analysis. Hundred grams (100 g) of soil samples were pulverized into a fine powder using a motorized agate mortar and passed through a 53 µm mesh screen. Two main analytical techniques were employed for the study; Energy Dispersive XRF (EDXRF) and atomic absorption spectroscopy (AAS). Loss on Ignition was determined by gravimetry using furnace method. Measured mineral oxide composition of the soils is presented in Table 2.

Table 1. *Physico-chemical properties and variations in the A_p horizon of soils formed from three bedrock types.*

Parameter	**15g**	**2a**	**15e**	**LSD**
Gravel (%)	3.92	5.22	4.85	1.681
Sand (%)	64.91	74.24	73.93	7.531*
Silt (%)	26.0	10.0	16.33	2.124**
Clay (%)	9.00	15.76	9.76	4.755*
pH	5.97	5.98	6.74	0.277**
Total N (%)	0.31	0.11	0.19	0.130*
P (mg/Kg)	1.46	3.10	2.43	0.43**
OC	0.21	0.47	0.54	0.088**
Ca^{2+} (cmol/kg)	0.80	1.0	3.11	0.414**
Mg^{2+} (cmol/kg)	0.33	0.28	1.17	0.310*
Na^{+} (cmol/kg)	0.40	0.09	0.20	0.157*
K^{+} (cmol/kg)	0.27	0.19	0.15	0.176
Exch. Acidity (cmol/kg)	0.10	0.13	0.1	0.042
ECEC (cmol/kg)	2.06	1.70	4.73	0.611**
BS (%)	94.83	91.98	97.88	1.408*

OC= organic carbon; ECEC= effective cation exchange capacity; BS= base saturation; LSD = Least significant difference; *= significant at $p<0.05$; **= significant at $p<0.01$

Table 2. *Oxide mineral composition and variation in the Ap horizon of soils on three bedrock types.*

	% composition			**LSD**
Oxide	**15g**	**2a**	**15e**	
SiO_2	80.75	90.59	89.86	0.0360**
TiO_2	2.07	1.57	1.2	0.004**
Al_2O_3	5.65	2.19	2.2	0.025**
Fe_2O_3	2.71	1.85	1.51	0.007**
Cl	1.0	-	-	0.047**
CaO	0.12	0.059	0.13	0.0003**
MgO	0.029	0.016	0.07	0.0005**
Na_2O	1.93	0.37	1.88	0.002**
K_2O	1.2	0.27	0.84	0.003**
MnO	0.077	0.049	0.059	0.0004**
V_2O_5	0.028	0.015	0.009	0.0003**
Cr_2O_3	0.016	0.012	<0.001	0.0005**
CuO	0.026	0.015	0.017	0.0005**
ZnO	0.003	-	-	0.0003**
Ga_2O_3	0.015	-	-	0.0008**
As_2O_3	0.007	-	0.01	0.0024**
Rb_2O	0.023	-	0.014	0.0017**
SrO	0.027	-	0.022	0.0009**
ZrO_2	0.621	0.297	0.271	0.0007**
BaO	0.28	-	-	0.0003**
PbO	0.010	-	0.007	0.00006**
LOI	3.4	2.7	1.9	
Σ	**99.992**	**100**	**99.999**	

LOI: loss on ignition; LSD = Least significant difference; **=significant at $p<0.01$

Soil properties data was subjected to analysis of variance, and significant means were separated using the least significant difference (LSD). The relationship between oxide minerals was tested using Pearson's Correlation analysis performed with SPSS V20. Graphs were plotted using Microsoft Excel 2016.

Results and Discussion

Variations in mineralogical properties of soils

As expected, there was wide variation in elemental concentration between soils from the different bedrock types (Table 2). Higher levels of metal oxides TiO_2, Al_2O_3, Fe_2O_3 and MnO were recorded in basement complex bedrock (15g)-derived samples, and many of the trace elements found in the 15g samples were absent in samples from the other bedrock types. An example of these is Cl which was present only in 15g at 1 % weight by mass (Table 2). The graphical plot of oxide elemental composition in the soils is presented in Figure 2. Alkaline earth and alkali metal oxides also varied widely between the soils. These variations can be attributed to differences in parent material properties, hydrological and pedological factors between the sampling sites. SiO_2 (as a primary mineral) constituted the greatest percentage of the oxide mineral assemblage in all the soils, and the loss on ignition (LOI) values suggests that the soils were higher in mineral matter contents with low amounts of carbonaceous matter.

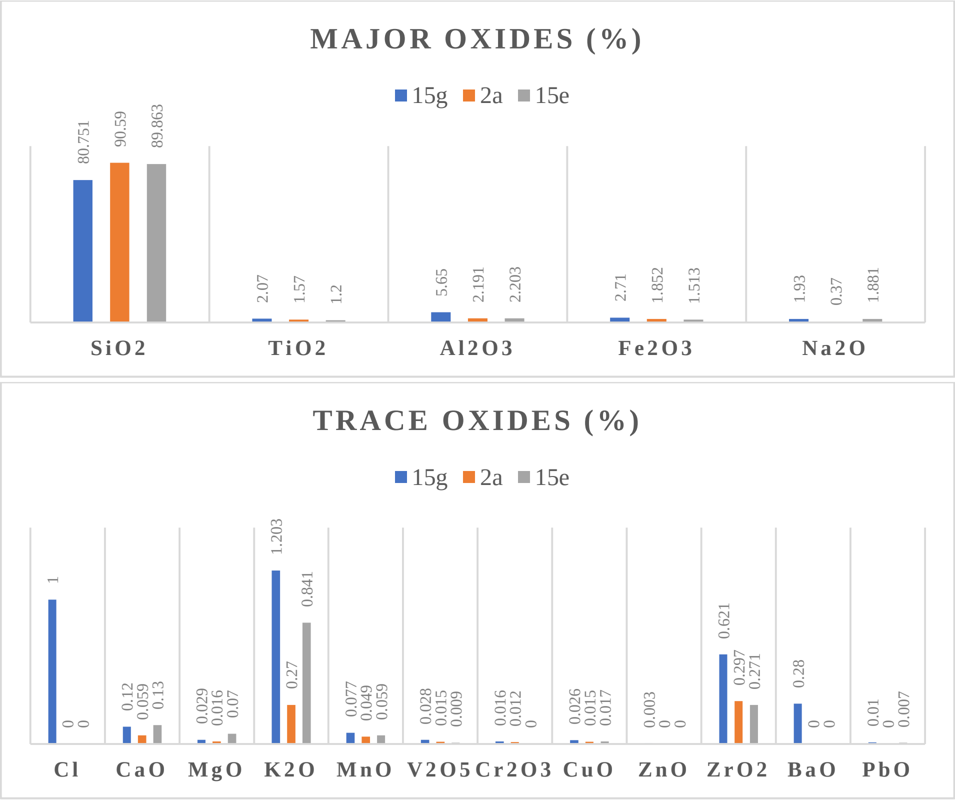

Figure 2. *Mean oxide mineral composition of soils*

The metal oxide composition trends in the soils in this study show that they have a high percentage of their primary rock minerals intact, signalling young weathering stages. According to Scheinost (2005), highly weathered soils that have lost a substantial amount of their Si, alkalis and alkaline earths are expected to contain high (up to 50 % by weight) amounts of metal oxides. Somehow, LOI which is expected to be positively correlated to soil organic matter was lowest in 15e whose samples had higher OC content than 15g in which the highest LOI was recorded. There are no direct relationships from studied parameters to explain this observation. Significantly lower amounts of alkali and alkaline earth metal oxides were recorded in 2a samples (Table 2). This may be an indication that the clay in samples derived from this bedrock type allow more rapid soil water movement, leading to higher loss of the mineral under leaching conditions. According to Loughan (1969), while Al, Si, Ti and Fe oxides largely stay at the weathering site in the form of clay minerals, alkaline earth metals such as Ca are readily lost in soil under leaching conditions.

Relationships between major mineral oxides in soils

Tables 3, 4 and 5 show the correlation relationships between major oxide mineral elements in soils from the three bedrock lithology types. Trends and relationships between mineral oxides differed in the different bedrock lithologies (Tables 3-5). While relationships between Si, Ti oxides and alkali and alkaline earths were mainly positive in 2a and 15e, negative correlation relationships were recorded in 15g (Tables 3-5). In 2a, TiO_2 had a positive significant ($p<0.01$) relationships with Na_2O (r (10) = .999) and K_2O (r (10) = 1.00). Na_2O and K_2O were also strongly positively correlated in this bedrock soils (r (10) = 1.000; $p<0.01$) (Table 3). In 15e, positive significant ($p<0.01$) relationships were recorded between TiO_2 and Al_2O_3 (r (10) = .998), Fe_2O_3 (r (10) = .997), CaO (r (10) = .998) and MgO (r (10) = .997).

Table 3. *Oxide minerals relationships in Recent Alluvium (2a)-derived soil samples.*

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	CuO	LOI
SiO_2											
TiO_2	.952										
Al_2O_3	.855	.655									
Fe_2O_3	.955	.817	.971								
CaO	.518	.756	.000	.240							
MgO	.877	.982	.500	.693	.866						
Na_2O	.952	.999**	.655	.817	.756	.982					
K_2O	.952	1.000**	.655	.817	.756	.982	1.000**				
MnO	.762	.924	.316	.535	.949	.980	.924	.924			
CuO	.952	.998**	.655	.817	.756	.982	.997**	.999**	.924		
LOI	.952	.997**	.655	.817	.756	.982	.997**	.998**	.924	1.000**	

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

Al_2O_3 and Fe_2O_3 were also strongly positively correlated with CaO and MgO, and Ca and Mg oxides had a positive significant correlation (r (10) = .998; $p<0.01$) (Table 4). In 15g, SiO_2 had a positive and significant relationship with TiO_2 (r (10) = .998; $p<0.05$) and K_2O (r (10) = .999; $p<0.05$) while negative significant relationships were recorded with CaO, MgO, MnO, CuO and ZnO. Strong ($p<0.01$) negative relationships were also recorded between TiO_2, CaO, MgO, MnO and ZnO. Cl which was detected only in 15g soil samples had a strong correlation with Fe_2O_3 (r (10) = 1.000; $p<0.01$).

These analyses show that Si, Ti, alkali and alkaline earth metal oxide relationships were majorly positive in 2a and 15e, while negative relationships were largely recorded in 15g. These geochemical characteristics and trends can be attributed to bedrock lithology imprint on the examined soils. Orescanin et al. (2009) reported similar oxide minerals relationships recorded in 15g, while the trends in 2a and 15e are not in consonance with the findings of their research.

Table 4. *Oxide minerals relationships in Nupe Sandstone (15e)-derived soil samples.*

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	CuO	PbO	LOI
SiO_2												
TiO_2	.682											
Al_2O_3	.682	.998**										
Fe_2O_3	.682	.997**	.998**									
CaO	.682	.998**	.999**	.997**								
MgO	.682	.997**	1.000**	.999**	.998**							
Na_2O	.956	.894	.866	.867	.885	.866						
K_2O	.974	.500	.566	.500	.511	.630	.866					
MnO	.929	.904	.911	.926	.903	.966	.997	.822				
CuO	-.731	0.000	.000	.000	.000	0.000	-.500	-.866	-.427			
PbO	-.468	.327	.387	.343	.327	.357	-.189	-.655	-.108	.945		
LOI	-.292	.500	.500	.500	.500	.500	0.000	-.500	.082	.866	.982	

Table 5. *Oxide minerals relationships in Basement complex (15g)-derived soil samples.*

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Cl	CaO	MgO	Na_2O	K_2O	MnO	CuO	ZnO	PbO	LOI
SiO_2														
TiO_2	.998*													
Al_2O_3	.984	.993												
Fe_2O_3	-.896	-.866	-.803											
Cl	-.896	-.867	-.803	1.000**										
CaO	-.998*	-1.000**	-.993	.866	.864									
MgO	-.998*	-1.000**	-.995	.861	.866	1.000**								
Na_2O	-.987	-.974	-.942	.956	.956	.974	.974							
K_2O	.999*	.998*	.990	-.879	-.879	-.998*	-.998*	-.980						
MnO	-.998*	-1.000**	-.993	.826	.863	.999**	.999**	.974	-.998*					
CuO	-.998*	.999**	-.992	.886	.856	1.000**	.999**	.972	-.999*	1.000**				
ZnO	-.998*	-.999**	-.993	.866	.866	.999**	.998*	.970	-.999*	.999**	.999**			
PbO	-.896	-.866	-.803	.999**	1.000**	.866	.887	.956	-.879	.866	.866	.866		
LOI	.554	.500	.397	-.866	-.866	-.500	-.570	-.682	.524	-.500	-.500	-.500	-.866	

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

*. Correlation is significant at the 0.05 level (2-tailed); **. Correlation is significant at the 0.01 level (2-tailed)

Generally, oxide minerals distribution and relationships in the soils point to the effect of bedrock materials on resulting soil mineralogical properties, and the likelihood of differing bedrock permeability and drainage type, which favours higher base saturation in 15g and 15e than in 2a (Table 1). The influence of differing weathering mechanisms on soil mineralogy in in different bedrock types have also been reported in previous research including Miko et al. (2001).

Conclusion

Results from this study highlighted marked differences in analytical values of oxide mineralogy in the soils examined, and suggests a likely impact of bedrock lithology on recorded geochemical properties. This is more so, as weather and climate characteristics are similar for all three locations examined. Soils formed from recent alluvium had higher quartz component and lower amounts of Al, Mn and Ti oxides which may be a result of depletion owing to the weathering mechanism in the bedrock material. The low Ca and Mg oxides and base saturation in soil samples derived from the recent alluvium bedrock material also suggests that the clay composition of this bedrock type is more prone to nutrient leaching losses than those of the other bedrock types. Further studies covering a wider land area and analytic approaches will be required to generalize the findings from this study.

Acknowledgements

This study was self-funded, and the contribution of all authors in its actualization are acknowledged. The authors declare that there are no conflicts of interest.

References

Acebal, S. G., A. Mijovilovich., E. H. Rueda, L. Maria., E. Agu1rre, C. Saragovi, 2000. Iron-Oxide Mineralogy of a Mollisol From Argentina: A Study by Selective-Dissolution Techniques, X-Ray Diffraction, And Mossbauer Spectroscopy. *Clays and Clay Minerals*, 48 (3), 322-330.

Ajiboye, G. A., J. A. Ogunwale, 2013. Forms and distribution of potassium in particle size fractions on talc overburden soils in Nigeria. *Archives of Agronomy and Soil Science*, 59 (2):247–58. https://doi.org/10.1080/03650340.2011.610031

FDALR (Federal Department of Agricultural Land Resources), 1990. Reconnaissance Soil Survey Report of Nigeria. Volumes 1-4. Jos: FDALR.

International Fertilizer Association (IFA), 2016. A presentation by Marrakech, Ms Charlotte Hebebrand, Director Gen. – International Fertilizer Association (IFA) on Climate-Smart Agriculture. What Role for Fertilizers? At the Science to Action Day at COP 22 http://www.motherchannel.com/cop-22-science-action-soil-management-charlotte-ebebrand-fertilisers/

Kinniburg, D.G., M. L. Jackson, 1981. Cation adsorption by hydrous metal oxides and clay. In *Adsorption of Inorganics at Solid--Liquid Interfaces*, M.A. Anderson and A.J. Rubin, eds., Ann Arbor Science Publishers, Ann Arbor, Michigan, 91-160.

Lal, R., 1995. S*ustainable management of soil resources in the humid tropics*. New York: United Nations University Press.

Miko, S., J. Halamic., Z. Peh, L. Galovic, 2001. Geochemical baseline mapping of soils developed on diverse bedrock from two regions in Croatia. *Geol Croat* 54(1), 53–118.

Ojanuga, A. G., 1978. Clay Mineralogy of Soils in the Nigerian Tropical Savanna Regions. *Soil Science Society of America Journal*, 43(6), 1237-1242. https://doi.org/10.2136/sssaj1979.03615995004300060038x.

Olaniyan J. O., 2003. *Evaluation of the soil map of Nigeria for Land Use Planning in Kwara State*. PhD Thesis, Ibadan: University of Ibadan.

Olanrewaju, R. M., 2009. Effect of climate on Yam Production in Kwara State, Nigeria. Environmental Issues, Department of Geography and Environmental Management, University of Ilorin, Ilorin; 3:1.

Orescanin, V., G. Medunic., N. Tomasic., V. Cosovic., I. L. Mikelic., S. Kampi, J. Urlic, 2009. The influence of aluminium industry and bedrock lithology on the oxide content in the urban soil of Sibenik, Croatia. *Environ Earth Sci.* 59*:* 695–701. DOI 10.1007/s12665-009-0066-9.

Scheinost, A. C., 2005. Metal Oxides. Swiss Federal Institute of Technology (ETH), Zurich, Switzerland. Elsevier Ltd. All Rights Reserved.

Stahr, K., U. Schuler., V. Häring., G. Clemens., L. Herrmann, M. Zarei, 2010. Clay and oxide mineralogy of different limestone soils in Southeast Asia. 19th World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August 2010, Brisbane, Australia.

United States Agency for International Development USDA. 2014. Soil Survey Field and Laboratory Methods Manual. Soil Survey Investigations Report No. 51 Version 2.

Vandenberghe, R. E., E. De Grave., G. De Geyter and C. Landuydt, 1986. Characterization of goethite and hematite in a Tunisian soil profile by Mrssbauer spectroscopy. *Clays and Clay Minerals*, 34, 275-280.

Vanlauwe, B., A. Bationo., J. Chianu., K. E. Giller., R. Merckx., U. Mokwunye., O. Ohiokpehai., P. Pypers., R. Tabo., K. D. Shepherd., E. M. A. Smaling., P. L. Woomer and N. Sanginga, 2010. Integrated soil fertility Management: Operational definition and consequences for implementation and dissemination Outlook on agriculture 39(1):17–19.

Voortman R. L., B. G. J. S. Sonneveld, M. A. Keyzer, 2003. African Land Ecology: Opportunities and Constraints for Agricultural Development CID Working Paper No. 37.