Asian Journal of Scientific Research

ISSN 1992-1454

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OPEN ACCESS **Asian Journal of Scientific Research**

ISSN 1992-1454
DOI: 10.3923/ajsr.2020.228.243

Research Article
Genesis and Classification of Soils over Limestone Formations in a Tropical Humid Region

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Abstract

Background and Objective: Soil development over limestone formations in the tropical humid region is unique and swayed by the environment. Its genesis gives an insight into the mode of origin and how the solum is formed from parent materials. Soils overlying Shale, Limestone and Sandstone (SLS) and Sandstone and Limestone (SL) geological formations in a tropical humid region were genetically investigated. **Materials and methods:** With the aid of google imageries, reconnaissance visits were carried out to areas underlain by SLS and SL formations. Slope maps were generated from the DEM (digital elevation model) obtained from USGS (United States Geological Survey) Explorer SRTM 1 (Shuttle Radar Topography Mission). Soil profile pits were sunk in each slope range, described and sampled. **Results:** The soils were characterized by Ap, transition B and Ckt horizons as well as low CCE (calcium carbonate equivalence). Ultisols, Alfisols and Inceptisols in the USDA (United States Department of Agriculture) System were correlated with Acrisols, Cambisols and Luvisols in the WRB (World Reference Base) for Soil Resources System. Iron and aluminum dominated the entire soils and were higher in SLS by ICP-OES (inductively coupled plasma optical emission spectrometry) procedure than XRF (X-ray florescence). Furthermore, Ca and K, as well as their oxides were low in the soils. **Conclusion:** The impact of the tropical humid climate on the soils' cation reserve was obvious; particularly the dominance of lateralization and decalcification over calcification. Relative to SL, indices of weathering presented more intense weathering in SLS.

Key words: Carbonate, pedogenesis, XRF, ICP-OES, weathering indices, DEM, classification

Citation: Ofem, K.I., C.L.A. Asadu, P.I. Ezeaku, J. Kingsley, M.O. Eyong, V. Katerina, T. Václav, N. Karel, D. Ondrej and P. Vít, 2020. Genesis and classification of soils over limestone formations in a Tropical Humid Region. Asian J. Sci. Res., 13: 228-243.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Most soils in the tropics are highly weathered as a result of high precipitation and temperatures. This disintegrates the crystal lattice of feldspars and alumino-silicates as well as the mica-like clays into kaolinite and sesquioxides that increase as the soil ages. During this process, some mobile elements are lost rendering them absent in the soil, while silica is removed and alumina accumulates[1]. Soil development and weathering are facilitated by environmental factors that govern weathering intensity in an area and leads to deep, weathered and highly leached soils; often deficient in weatherable minerals[2,3]. Many studies have been focussed on the origin and development of heterogenous soils[4-6]. Some of such studies have attributed soil heterogeneity to geomorphological processes[7] which has led to the heterogeneity in the parent material and geochemical properties[8] as well as the contribution of parent materials to soil development. Consequently, Turner[9] and Kowalska *et al.*[10] emphasized the relevance and influence of parent materials on soil properties.

Geology influences the overlying soils as much as soil type dictates vegetation type. There are possibilities that soils developed from a limestone region would have alkaline or near alkaline properties; perhaps due to the presence of carbonates that influence soil genesis, especially in young soils[11]. This assertion may, however, be contested when soils are influenced by weathering and highly leached; losing essential bases. Although limestone soils are common in arid and semi-arid regions or where rainfall is too low to leach soil minerals[12], they may not be very common in semi-humid and tropical rainforest areas. This is due to the influence of chemical weathering and rainfall on carbonate dissolution. This had prompted VandenBygaart and Protz[13] to attribute the lowering of soil pH as soil ages to the weathering of carbonate minerals, leaching of Ca^{2+} and Mg^{2+} and replacement by H^+. Limestone and perhaps, carbonate-rich soils have been studied at various scales in different parts of the world[14-16,10] and found to have diverse properties depending on the prevailing environmental condition.

In the past, several indices have been used to evaluate soil genesis. For instance, soil depth was used by Che *et al.*[17], Oliveira-Girao *et al.*[18] and VandenBygaart and Protz[13], sesquioxides (Fe and Al hydroxides) content by Yakubu and Ojanuga[2], Kurihara *et al.*[19] and Durn *et al.*[20] and element oxides and ratios by Li *et al.*[21], Wei *et al.*[22], Wei *et al.*[23] and Zhao and Zheng[24] to decipher the intensity of weathering of soils via indices of chemical weathering. There is, however, a dearth of information regarding pedogenesis *via* elemental oxides and pseudo metal elements in soils overlying limestone in Nigeria and resource inventory using a digital elevation model for the said soils.

Knowledge about soil genesis is required for the classification of soils[25]. This makes it possible for the properties of soils to be more easily remembered and predictions made about the behavior of soils. The USDA System of Soil Taxonomy and the World Reference Base for Soil Resources classification systems have been most widely used for this purpose[3]. Hence the present study.

An essential practice in field on-the-spot evaluation of soils is the qualitative observation of soil properties for soil survey, classification and evaluation. In an emerging technological sphere, quantitative evaluation of soil properties provides a more reliable research outcome. It is therefore not sufficient to inferentially adjudge a soil as highly weathered based on its morphology[26], hence the upsurge of controversies regarding the degree of maturity of specific soils. It is apt, therefore, to use indices that define weathering intensity as a guide to pedogenesis. This was the principal focus in combination with other soil properties Dokuchaev on which he established the concept of soil as a definite natural body with genetic horizons[27]. This has drifted the interests of researchers almost exclusively from the factors of soil formation[26] to an analysis of processes of soil formation[28] and now to the indices used to investigate soil genesis.

This study is timely and seeks to bridge the gap through a pedogenetic study. The study is focussed on evaluating the morpho-physicochemical properties as well as the classification of soils formed over two limestone formations in a humid tropical region. The availability, as well as soil genetic implication of pseudo total metal elements and element oxide content, were also evaluated in the study. Ruxton index, weathering index and molar ratio were used to identify the weathering trend of the soils.

MATERIALS AND METHODS

Location, geology and climate of the study area: The research was conducted in Cross River State (5°32' and 4°27' N, 7°50' and 9°28' E), Southeast Nigeria. The selected study sites were Ishibori in Ogoja (06°39'17'' N, 08°47'51'' E) and Agoi Ibami in Yakurr (05°43'27" N, 08°10'37.2" E). The Ogoja and Yakurr areas are characterized by southern guinea savannah (SGS) and tropical rainforest (TRF), respectively.

Limestone occurs throughout Nigeria in the Basement Complexes and Sedimentary Basins and is grouped into Cretaceous and Tertiary limestone based on geological age[29]. The Sedimentary limestone of Cretaceous and Tertiary ages is associated with shale, siltstone and fine-grained sandstone. The sedimentary limestone of Cretaceous and Tertiary ages in Cross River State is common in the Ikom depression (Mamfe Rift) and Calabar flank and is often intercalated with shale, siltstone and fine-grained sandstone[29].

Cross River State is characterized by a tropical humid climate with distinct wet and dry seasons which vary slightly in duration from the southern guinea savannah in the Ogoja area to the tropical rainforest of Yakurr. The Ogoja area is moist subhumid while Yakurr is moist humid to per humid. Rainfall varies between 1251.4 and 3347.8 mm/annum with a mean of 1983.02 mm/annum in the Ogoja area while a range of 1760.3-2683.8 mm/annum and mean of 2258.0 mm/annum are typical of the Yakurr area. Temperature varies between 22.96 and 33.75 °C with a mean of 27.85 °C in the Ogoja area and range of 22.56-31.89 °C with a mean of 26.96 °C in the Yakurr area[30].

Field and laboratory procedures: Google satellite imageries of the areas underlain by limestone were obtained and used as a base map and later, for the selection of sampling areas. Sample areas underlain by limestone were selected according to the criteria of Esu[3] for the selection of sampling areas. Such areas must be representative and include all soil units within the survey area, accessible and allow for very intensive observation. Selected Areas in the Ishibori location were underlain by shale, limestone and sandstone formation (SLS) in the SGS while some Agoi Ibami areas underlain by sandstone and limestone formation (SL) were in the TRF. Field reconnaissance visits were then carried out to the selected areas in the SGS and TRF areas that have been mapped by the Nigerian Geological Survey Agency and shown to be underlain by SLS and SL, respectively.

The digital elevation model of the study locations was obtained from USGS Explorer SRTM 1 arc-second Global[31] at a resolution of 30 m. Using ArcGIS (ESRI, US) software, the DEM was used to generate the slope maps of the study areas (Fig. 1a and b). The elevation ranges created in the slope maps were used to delineate slope transition from high to low elevations. This was in turn used to identify the soil mapping units which include IH1P1, IH2P2 (in the SLS), AI1P1, AI2P2 and AI3P1 (in the SL).

Guided by the elevation and slope ranges, one profile pit was randomly sited and dug in each of the 5 mapping units to represent the soils. The profiles were described according to Schoeneberger *et al.*[32] with emphasis on soil horizonation and depth, color (Munsell color chart), mottles and texture[17] as well as cutans, concretions and animal activities. The field study was carried out in Ishibori and Agoi Ibami areas of Cross River State, Nigeria between December, 2018 and February, 2019.

Soil samples were obtained from pedogenic horizons from bottom to top for the determination of bulk density (core method), particle size distribution (Bouyoucos hydrometer), organic carbon (Walkley-Black modified acid-dichromate) and cation exchange capacity by neutral NH_4OAc using standard procedures of Soil Survey Staff[33]. The soils were classified following the requirements of the USDA System of soil classification[34] and correlated with the WRB for Soil Resources System[35].

All soil samples were air-dried under laboratory conditions, ground and passed through a 2 mm mesh of sieves. However, samples meant for analysis by XRF and aqua regia extraction were pulverized and homogenized with an automatic mill into a fine powder (3-4 µm). Samples were then analyzed with XRF Delta Premium Spectrometer 2019 using the procedures of Tejnecky *et al.*[36]. Pseudo total elements were determined by aqua regia extraction using ICP-OES model iCAP 7000 by the procedures of Cools and De Vos[37]. Aqua regia treats a soil sample with a mixture of HCl and HNO_3 in the ratio of 3:1 and measures pseudo total concentration of elements. Soil samples were analyzed in the Departments of Soil Science, University of Nigeria, Nigeria and Soil Science and Soil Protection, Czech University of Life Sciences, Czech Republic from April to September, 2019.

Soil chemical indices of weathering: Ruxton index (R) represented by (SiO_2/Al_2O_3) was used to evaluate the chemical weathering of the soils[38]. Values of R increase up the profile and indicate an increase in profile weathering. Also, the weathering index (WI) represented by $\{(CaO+MgO+K_2O+Na_2O/CaO+MgO+K_2O+Na_2O+SiO_2+Al_2O_3+Fe_2O_3)*100\}$[39] and molar ratio (MR) ($SiO_2:R_2O_3$) by Bera *et al.*[40] were used as indices to evaluate the chemical weathering of the soils. Where R_2O_3 is either Al_2O_3 or Fe_2O_3.

Statistical analysis: Statistical analysis was done using the R software (version 3.6.1).

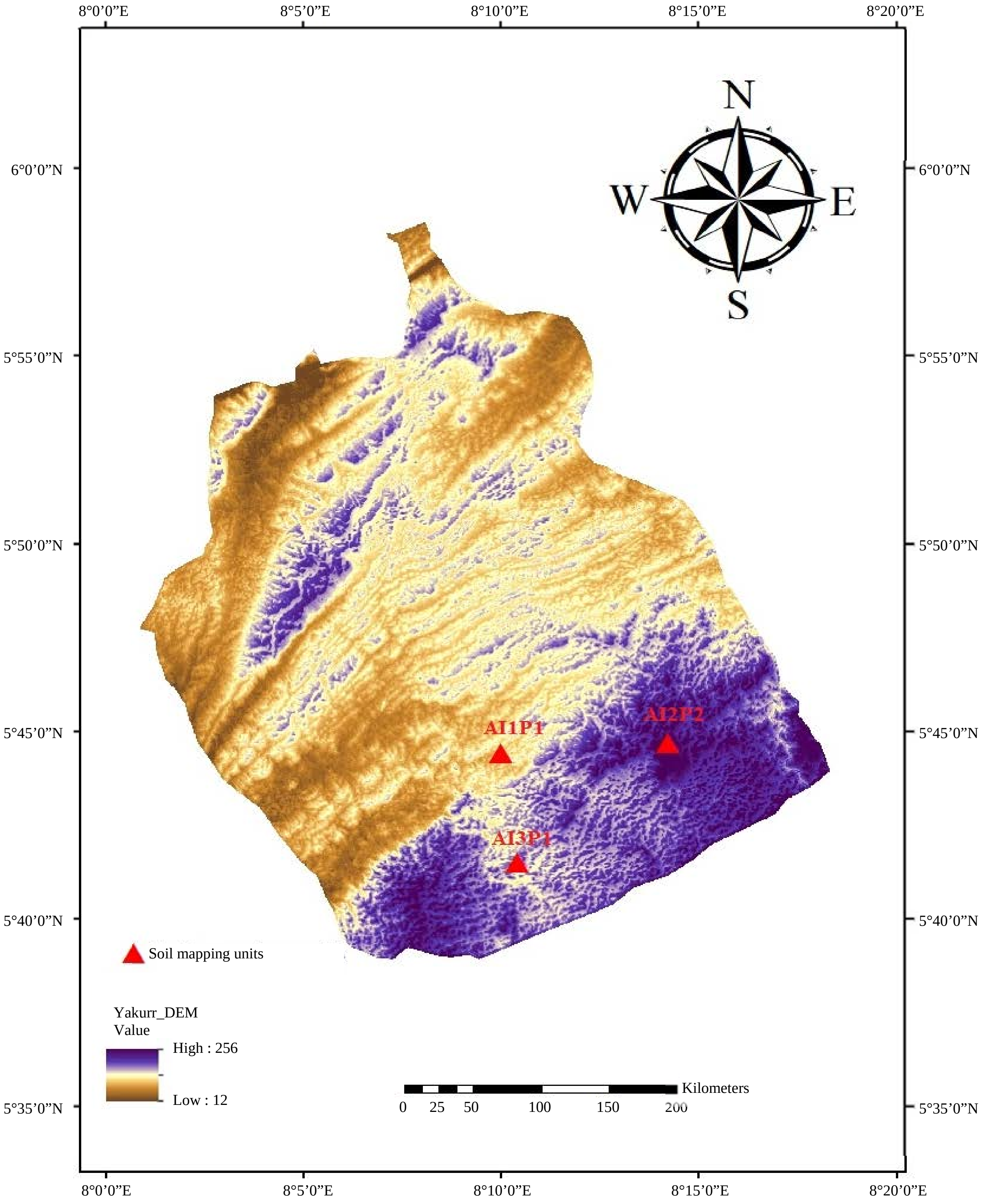

Fig. 1a: Slope map of Yakurr Area

Source: U.S. Geological Survey, 2017

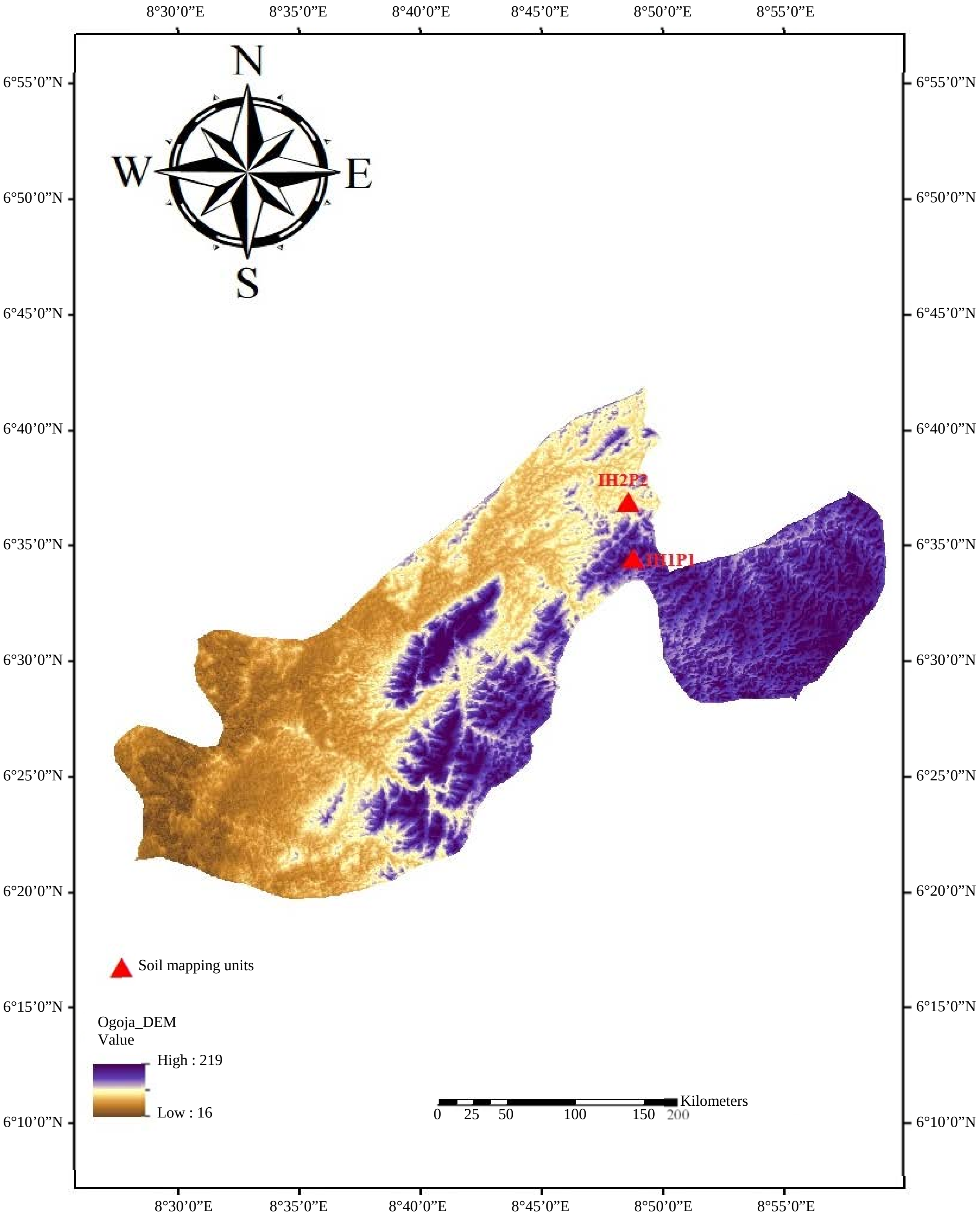

Fig. 1b: Slope of Ogoja Area

Source: U. S. Geological Survey, 2017

RESULTS

Morphological, physical and chemical properties of the soils are presented in Table 1a,b. The soils were characterized by Ap (mineral plough layer), transition B and Ckt (accumulation of carbonates <50% with illuvial clay) horizons. Except for poorly drained IH2P2 and AI3P2 in the low elevation ranges that were impeded by water at >80 cm, soil depth exceeded 120 cm in the entire soils. Surface soil color (moist) was dark reddish-brown (5YR 3/3) in the SLS and dark brown (7.5YR 3/2) to brown (7.5YR 4/2) in the SL. The B horizons appeared more brightly colored and depicted by either dark red in the SLS or yellowish red in the SL, except the limestone impeded layer in AI2P2 that was grayish brown (2.5Y 5/2). However, very dark greenish gray (Gley1 3/1) and dark reddish gray (5YR 4/2) dominated the subsurface soils of the poorly drained IH2P2 in the SLS and AI3P1 in the SL; both of the low elevation ranges. Soil mottles were common in all the subsurface horizons; common, fine to medium, distinct very pale brown (10YR 7/3), as well as gray (5Y 6/1), characterized SLS and few, medium and coarse, faint and prominent light yellowish brown (2.5Y 6/4) and yellowish red (5YR 5/6) mottles in the SL. However, mottles were in the form of distinct red streaks in the poorly drained soils found in the low elevation ranges (IH2P2 and AI3P1).

Sandy clay loam and sandy loam textural classes dominated the soils irrespective of limestone formation; however, soils on SLS were somewhat texturally finer than those on SL. The particle size distribution of the soils indicates sand dominance with clay ranges of 16-28 and 10-26% in the SLS and SL, respectively. Ranges of 10-14 and 4-14% were obtained for silt in the SLS and SL, respectively while values of sand exceeded 60% in the entire soil profiles (Table 1a). Bulk density had ranges of 1.45-1.66 g cm^{-3} and 1.19-1.59 g cm^{-3} in the SLS and SL, respectively with resultant lower values in the poorly drained low elevation ranges of IH2P2 (0.71-1.3 g cm^{-3}) and AI3P1 (0.98-1.52 g cm^{-3}) (Table 1a).

Cation exchange capacity by neutral NH_4OAc ranges of 15.2-54.4 and 6.0-19.6 cmol$_c$/kg were obtained in the SLS and SL, respectively, while organic carbon decreased regularly with soil depth from maxima of 7.55, 86.64, 8.92, 7.55 and 22.16 g kg^{-1} in IH1P1, IH2P2, AI1P1, AI2P2 and AI3P1, respectively (Table 1b). Correlation of bulk density with organic carbon foretells strong negative correlation (r = -0.88) while that of CEC with organic C resulted in a strong positive correlation (r = 0.67).

In the aqua regia extraction procedure using the ICP-OES technique, the soils in SLS and SL were prevalent in Fe and Al (Table 2); though comparatively higher in the SLS. The mean values of Fe and Al obtained in the poorly drained IH2P2 and AI3P1 in the low elevation ranges were lower than their well-drained counterparts in higher elevation ranges. Sequences of pseudo total elemental occurrence by soil profiles in terms of abundance are summarized as:

- IH1P1: Fe>Al>Mg>Mn>K>Na
- IH2P2: Fe>Al>Mg>Mn>K>Na
- AI1P1: Fe>Al>Mn>K>Mg>Na
- AI3P1: Fe>Al>K>Mn>Mg>Na

The total content of the element oxides identified and quantified by XRF are presented in Table 3. The entire soils were dominated by SiO_2, Al_2O_3 and Fe_2O_3; however, values of SiO_2 and Al_2O_3 were comparatively higher in SL relative to SLS, while those of Fe_2O_3 were higher in SLS.

Other immobile oxides such as ZrO_2, MnO_2 and TiO_2 had lower values with ranges of 0.021-0.099, 0.06-0.23 and 0.703-1.464%, respectively for the well-drained IH1P1 in the high elevation range. Their poorly drained counterpart (IH2P2) in the low elevation range had values with ranges of 0.023-0.055, 0.12-0.28 and 0.674-0.967 % (Table 3). CaO had a range of 0.203-0.407% in IH1P1 (SLS), while its values in SL were trace in all the soils studied.

Similarly, values of P_2O_5 in SL were either scanty or trace. In SL soils, the trend in values of SiO_2 was quite similar to those in the SLS; however, its mean values were slightly higher in SL compared to those in SLS. Means of TiO_2, MnO_2 and Fe_2O_3 were comparatively higher in the SLS than in SL; however, Al_2O_3 was higher in the SL than in SLS.

The coefficient of variability (CV) seemed to have shown some consistency as comparatively higher values were obtained in the SLS for ZrO_2, TiO_2 and SiO_2 while higher CVs of Al_2O_3, MnO_2 and Fe_2O_3 were obtained in the SL.

The positive correlation between Fe_2O_3 and Fe, Mg, Na and Al (r>0.68), and negatively so with K_2O and SiO_2 ($\alpha = 0.001$) was obtained, while Al_2O_3 correlated negatively with SiO_2 ($\alpha = 0.05$) and ZrO_2 ($\alpha = 0.001$) (Fig. 2). MnO_2 was correlated positively with Mg, Fe ($\alpha = 0.05$), Al ($\alpha = 0.01$) and Mn (α=0.001), while a negative correlation was obtained for SiO_2 with Al and Mg ($\alpha = 0.05$), as well as values that indicate a positive correlation with ZrO_2 ($\alpha = 0.05$).

Table 1a: Morphological, physical and chemical properties of the studied soils

Horizon	Depth (cm)	Munsell colour (moist)	Mottles	Texture	Particle size distribution (cm) Sand	Silt	Clay	Bulk density (g cm^{-3})	CEC NH$_4$OAc (cmol$_c$/kg)	Organic carbon (g kg^{-1})	Other features
IH1P1: N06°38.53', E008°48.75 ', 64 m; shale, limestone and sandstone formation (SLS)											
Ap	0-37	Dark reddish brown (5YR 3/3)		g-scl	60	12	28	1.45	28	7.55	Common ants and worms; many Fe and Mn concretions
AB	37-64	Dark red (10R 3/6)	C,f-m, d (Very pale brown) (10YR 7/3)	g-scl	62	10	28	1.48	35.6	4.66	Clay and Fe cutans on ped faces, few Fe
CB	64-130	Brown (7.5YR 5/3)	M, c, d (gray) (5Y 6/1)	scl	64	10	26	1.66	35.2	2.75	Thin clay cutans on ped faces; few Mn nodules
Cc	130-195	Very dark Grayish brown (10YR 3/2)	F, f-m, f' (gray) (5Y 6/1)	g-sl	68	12	20	1.61	23.6	6.18	Evidences of Fe^{3+} and Mn concretions
IH2P2: N06°38.836', E008°48.824 ', 51 m; shale, limestone and sandstone formation (SLS)											
Ap	0-13	Dark brown (7.5YR 3/2)		Sl	73	11	16	0.71	54.4	86.64	Many Ants and few earth Worms.
BC	13-46	Gray (2.5Y 5/1)	C, f-m, d (red) (2.5YR 4/8)	scl	66	12	22	0.91	40	52.39	Very few thin clay cutans in pores; few Earth worms
Cg	46-87	Very dark greenish gray (Gley1 3/1)	F, f-m, d (red) (2.5YR 4/8)	sl	68	14	18	1.3	15.2	28.21	
AI1P1: N06°38.836', E008°48.824 ', 51 m; sandstone and limestone formation (SL)											
Ap	0-9	Dark brown (7.5YR 3/2)		Ls	84	6	10	1.19	12	8.92	Many fine/medium roots; few fine and medium Ants
BA	9-54	Dark yellowish brown (10YR 4/6)		sl	78	8	14	1.46	17.6	3.43	Few Ants; cracks extending to the Bt horizon
Bt	54-122	Yellowish red (5YR 4/6)	F, m, f', light yellowish brown (2.5Y 6/4)	scl	68	6	26	1.59	17.6	1.72	Few thin clay cutans on ped faces; many medium Worm casts, some cracks
Ckt	122-200	Yellowish red (5YR 4/6)	M, m/c, p light yellowish brown (2.5Y 6/4)	g-scl	68	6	26	1.53	19.6	2.4	Few thin clay cutans on ped faces; many Mn-Fe concretions with quartz.
AI2P2: N05°44.386', E008°10.660 ', 63 m; sandstone and limestone formation (SL)											
Ap	0-13	Brown (7.5YR 4/2)		Sl	72	12	16	1.35	4.4	7.55	Many Ants
AB	13-60	Yellowish red (5YR 4/6)	C, m, d, red (2.5YR 4/6)	sl	74	10	16	1.59	5.2	4.12	Common moderate clay and Fe cutans; few quartz and Fe nodules
BC	60-82	Brown (7.5YR 5/4)	F, f, f, brownish yellow (10YR 6/6)	sl	76	10	14	1.45	6	1.72	Few thin clay cutans; few Fe nodules
Ckt	82-132	Grayish brown (2.5Y 5/2)	F, f/m, d, yellowish red (5YR 5/6)	g-scl	64	14	22	1.49	15.2	3.43	Few Fe-Mn concretions; many cracks between 1.0 and 1.7 cm wide
AI3P1: N05°43.725', E008°10.214', 52 m; sandstone and limestone formation (SL)											
Ap	0-21	Dark reddish brown (5YR 3/2)		Sl	78	10	12	0.98	10.8	22.16	Many Ants and few beetles
AB	21-80	Dark reddish gray (5YR 4/2)	F, f-m, d red (10R 4/8)	Sl	10	4	14	1.52	6	2.78	Very few Ants and Worm casts; few Fe nodules

Texture: gr: Gravel, L: Loam, S: Sand, C: Clay, CEC: Cation exchange capacity, Ap: Mineral plough layer, AB, BC, CB: Transition B horizons, Cc: C horizon with concretions, Cg: C horizon with strong gleying, Bt: Argillic B horizon, Mottles: F, C, M = few, common, many, f, m, c = fine, medium, coarse; f , d = faint, distinct, Source: Field and laboratory generated data

Table 1b: Chemical properties of the studied soils

		Exchangeable bases (cmol$_c$/kg)						
Horizon	Depth (cm)	Na	K	Mg	Ca	CEC (NH_4OAc)	BS (%)	CCE (g kg^{-1})
IH1P1: N06°38.53', E008°48.75 ', 64 m: Typic Rhodustult; Ferric Rhodic Acrisols (Ochric)								
Ap	0-37	0.04	0.07	3.4	3.4	28	24.68	28.6
AB	37-64	0.02	0.05	4	5.8	35.6	27.72	28.3
CB	64-130	0.02	0.05	1.4	7.2	35.2	24.63	29.2
Cc	130-195	0.03	0.07	1.8	3.8	23.6	24.15	22.1
IH2P2: N06°38.836', E008°48.824 ', 51 m: Humic Endoaquept; Stagnic Gleyic Cambisol (Humic)								
Ap	0-13	0.281	0.291	4.2	8.2	54.4	23.85	27
BC	13-46	0.11	0.15	2.4	5.2	40	19.68	30
Cg	46-87	0.05	0.09	4.2	5	15.2	61.45	17.7
AI1P1: N06°38.836', E008°48.824 ', 51 m: Rhodic Paleudults; Ferric Acrisols (Ochric)								
Ap	0-9	0.05	0.09	1	3.6	12	39.5	21.5
BA	9-54	0.02	0.05	1.2	2	17.6	18.58	16
Bt	54-122	0.02	0.05	0.2	1.8	17.6	11.76	21.3
Ckt	122-200	0.02	0.05	0.8	0.8	19.6	8.52	24
AI2P2: N05°44.386', E008°10.660 ', 63 m: Vertic Paleudalf; Vertic Ferric Luvisols (Differentic, Loamic, Ochric, Profondic)								
Ap	0-13	0.04	0.07	1.4	1.6	4.4	70.68	28.2
AB	13-60	0.02	0.06	0.8	1.6	5.2	47.69	15.8
BC	60-82	0.02	0.04	0.4	2.6	6	51	30
Ckt	82-132	0.02	0.05	2.2	5.6	15.2	51.78	30
AI3P1: N05°43.725', E008°10.214', 52 m: Humic Endoaquept; Dystric Gleyic Cambisols (Humic, Loamic)								
Ap	0-21	0.06	0.1	0.4	1.8	10.8	21.85	27.5
AB	21-80	0.01	0.04	0.6	0.6	6	20.83	20.7

CEC: Cation exchange capacity, BS: Base saturation, CCE: calcium carbonate equivalent, Source: Field and laboratory generated data

A negative correlation was obtained for K_2O with Fe, Mg, Na, Al ($\alpha = 0.001$) and Mn ($\alpha = 0.05$) and positive with K (0.05), just as TiO_2 correlated positively with Fe, Al ($\alpha = 0.001$), Mg and Na ($\alpha = 0.01$) ($r>0.55$) (Fig. 2). Similarly, ZrO_2 correlated positively with K ($r = 0.55$) at $\alpha = 0.05$.

Ruxton index (R), weathering index (WI) and molar ratio (MR) of SiO_2: R_2O_3 were used to evaluate the chemical weathering intensity of the soils. The results are presented in Table 4.

R increased in the SLS and decreased in the SL with increasing soil depth. WI had ranges of 0.62-3.79 and 1.62-1.76 in IH1P1 and IH2P2, respectively, for the SLS with values that were observed to have increased at the B horizons. In the SL, ranges of 5.98-7.49, 9.49-12.07 and 7.35-8.41 were obtained for AI1P1, AI2P2 and AI3P1, respectively, with a trend indicating a regular decrease in the B horizon; completely contradicting the trend in the SLS. The molar ratio of SiO_2: R_2O_3 had ranges of 1.14-2.21 and 1.20-1.83 in IH1P1 and IH2P2, respectively and in the SLS with values that increased with increase in soil depth. However, its trend in values contradicted those of AI1P1 (1.34-4.44), AI2P2 (1.53-3.44) and AI3P1 (2.10-3.87) in SL. Correlation of R with MR (SiO_2: R_2O_3) indicates a positive correlation ($r = 0.846$) while WI with MR resulted in a somewhat weak positive correlation ($r = 0.421$).

Soil classification: In the soils over SLS, IH1P1 had argillic horizons and low base saturation (<50% by NH_4OAc pH 7.0) at >125 cm depth below the soil surface and qualified as Ultisols. The soil was freely drained, in the southern guinea savannah with an ustic moisture regime and qualified as Ustults. Its epipedon had a color value of 3 (moist) and subhorizons within 100 cm of the argillic horizon had colors with the hue of 2.5YR or redder and value of 3 (moist) and met the requirements for Rhodustult and Typic Rhodustult at the subgroup category of the USDA Soil Taxonomy System. It correlated with Ferric Rhodic Acrisols (Ochric) in the WRBase for Soil Resources System. On the other hand, due to its sandy clay loam texture, weak indications of argillic horizons (higher clay in the subsurface soils) as well as higher color value and without inherent rock structure, IH2P2 had Ochric epipedon and cambic endopedon. The soils qualified as Inceptisols. Just beneath the epipedon and within 50 cm of the soil surface, the soil had chroma of 1 with redox concentrations and ferrous Fe. This qualified the soil as Aquept and by its endosaturated high ground water table fluctuating between 45 and 87 cm, the soil was classified as Endoaquept. A color value of 3 in the Ap horizon as well as low base saturation (<50% by NH_4OAc at pH 7.0) in most parts of the profile qualified it as Humic Endoaquept in the subgroup. It

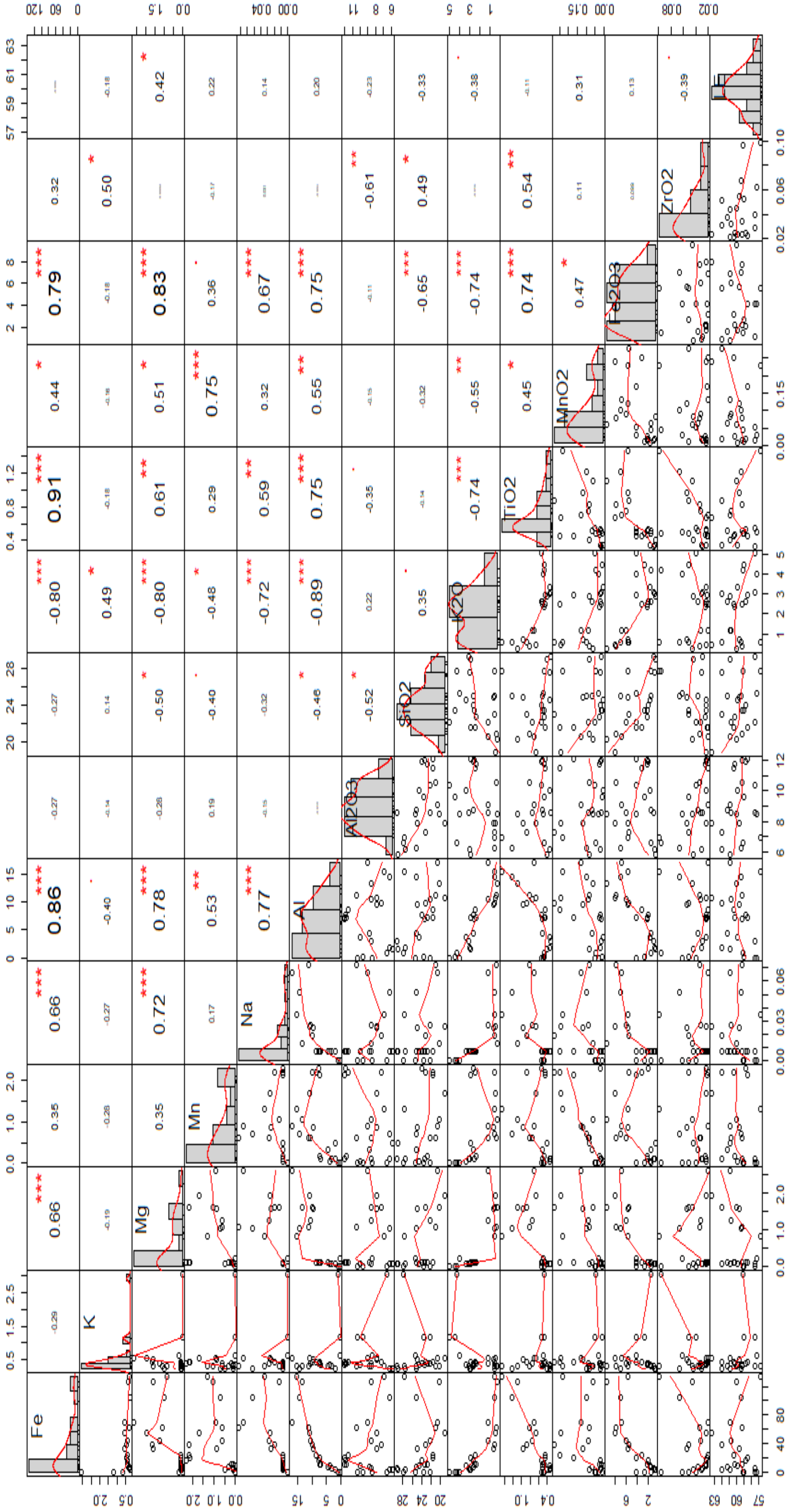

Fig. 2: Correlation matrix between elemental oxides (XRF) and pseudo total metal element (ICP-OES (significance levels were $\alpha = 0.05$, $\alpha = 0.01$ and $\alpha = 0.001$)

Table 2: Pseudo total metal elements extracted with aqua regia by ICP-OES technique in the studied soils (values in g kg^{-1})

	Fe	K	Mg	Mn	Na	Al
Soil depth	(g kg^{-1})					
IH1P1: N06°38.53', E008°48.75 ', 64 m; shale, limestone and sandstone formation (SLS)						
0-30	125.7	0.314	1.607	1.047	0.013	13.3
30-60	62.2	0.308	1.080	0.600	0.072	11.2
60-90	69.8	0.556	2.609	0.898	0.066	17.1
90-120	43.2	0.400	1.247	0.612	0.027	10.5
120-150	133.4	0.303	0.847	1.290	0.035	15.4
150-180	103.9	0.254	1.030	0.715	0.052	14.4
Mean	89.7	0.356	1.403	0.860	0.044	13.6
Range	43.2-133.4	0.254-0.556	0.847-2.609	0.600-1.29	0.013-0.072	10.5-17.1
CV	40.9	30.6	45.9	31.7	52.3	18.5
IH2P2: N06°38.836', E008°48.824 ', 51 m; shale, limestone and sandstone formation (SLS)						
0-30	55.6	0.543	1.943	1.674	0.026	10.8
30-60	33.3	0.528	1.595	0.867	0.025	9.5
60-87	37.5	0.439	1.629	2.163	0.019	9.9
Mean	42.1	0.503	1.722	1.568	0.023	10.0
Range	33.3-55.6	0.439-0.543	1.595-1.943	0.867-2.163	0.019-0.026	9.5-10.8
CV	28.1	11.2	11.1	41.7	16.7	6.8
AI1P1: AI1P1: N06°38.836', E008°48.824 ', 51 m; sandstone and limestone formation (SL)						
0-30	3.6	0.221	0.098	0.497	0.007	1.7
30-60	7.6	0.306	0.111	0.330	0.007	4.5
60-90	11.6	0.392	0.124	0.163	0.007	7.3
90-120	10.6	0.374	0.113	0.095	0.007	6.9
120-150	16.8	0.394	0.113	2.277	0.007	7.7
150-180	22.9	0.415	0.113	2.183	0.007	8.6
180-200	19.8	0.429	0.110	2.116	0.007	7.3
Mean	13.2	0.362	0.112	1.094	0.007	6.3
Range	3.6-22.9	0.221-0.429	0.098-0.124	0.095-2.277	-	1.7-8.6
CV	51.9	20.3	6.8	94.6	1.1	38.2
AI2P2: N05°44.386', E008°10.660 ', 63 m; sandstone and limestone formation (SL)						
0-30	0.154	3.05	0.028	0	0	0.9
30-60	0.04	0.64	0.223	0	0	0.0575
60-90	0.0154	1.182	0.0138	0	0	0.0682
90-120	0.0099	1.177	0.0129	0	0	0.0622
Mean	0.055	1.51	0.07	0	0	0.27
Range	0.0099-0.154	0.64-3.05	0.0129-0.223	0	0	0.0575-0.9
CV	8.3	73.8	15.2	0	0	64.4
AI3P1: N05°43.725', E008°10.214', 52 m; sandstone and limestone formation (SL)						
0-30	3.6	0.256	0.078	0.112	0.007	1.8
30-60	5.0	0.297	0.067	0.095	0.007	3.0
60-80	8.9	0.368	0.069	0.032	0.007	3.7
Mean	5.8	0.307	0.071	0.080	0.007	2.9
Range	3.6-8.9	0.256-0.368	0.067-0.078	0.032-0.112	-	1.8-3.7
CV	47.5	18.5	8.7	53.1	0.0	34.2

correlated with Stagnic Gleyic Cambisol (Humic) in the WRB for Soil Resources System.

In the soils over SL, AI1P1 had argillic B horizons, low base saturation (<50% by NH_4OAc at pH 7.0) with an ochric epipedon (Ap horizon <25 cm) and qualified as Ultisols. Less than 0.9% weighted average of organic carbon in the upper 15 cm above the argillic horizon with an udic soil moisture regime, well-drained and found in the tropical humid climate qualified it as Udults. With increasing depths, the soil had >20% of clay decrease from horizons of maximum accumulation and qualified as Paleudults. More than 50% colors with the hue of 2.5YR or redder and color value of 3 in the upper 75 cm of the argillic horizon qualified it as Rhodic Paleudults in the subgroup. This correlated with Ferric Acrisols (Ochric) in the WRB for Soil Resources System.

Table 3: Element oxide content (XRF technique) of the studied soils (values in per cent)

Horizon	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3	ZrO_2	LE
Cm				**Shale, limestone and sandstone formation (SLS)**						
IHP1 0-30	8.52	20.31	0.03	0.238	TR	1.104	0.06	9.561	0.045	60.067
IHP1 30-60	10.53	20.96	TR	0.411	TR	0.827	0.08	7.796	0.034	59.29
IHP1 60-90	9.08	20.65	0.02	1.179	0.265	0.703	0.13	6.93	0.021	60.907
IHP1 90-120	8.56	22.19	TR	1.199	0.23	0.743	0.09	6.105	0.032	60.757
IHP1 120-150	6.90	27.72	0.04	0.599	0.407	1.464	0.23	5.629	0.099	56.823
IHP1 150-180	6.22	25.06	TR	0.556	0.203	1.221	0.10	7.047	0.067	59.45
Mean	8.300	22.814	0.03	0.697	0.276	1.010	0.115	7.178	0.0496	59.549
Range	6.22-10.53	20.31-27.72	0.02-0.04	0.411-1.199	0.203-0.407	0.703-1.464	0.06-0.23	5.629-9.561	0.021-0.099	56.823-69.907
CV	18.6	13.0	33.3	57.6	32.6	30	53	19.4	57.9	2.5
IH2P2 0-30	7.88	18.97	0.10	0.426	0.191	0.674	0.24	7.994	0.023	63.42
IH2P2 30-60	7.89	24.85	0.06	0.687	TR	0.967	0.12	5.662	0.055	59.62
IH2P2 60-87	7.30	23.11	0.08	0.593	TR	0.88	0.28	5.546	0.051	62.077
Mean	7.69	22.309	0.08	0.569	0.191	0.840	0.213	6.401	0.043	61.706
Range	7.3-7.89	18.97-24.85	0.06-0.10	0.426-0.687	TR	0.674-0.967	0.12-0.28	5.546-7.994	0.023-0.055	59.62-63.42
CV	4.4	13.5	25	23.2	TR	17.9	39.0	21.6	40.5	3.1
				Sandstone and limestone formation (SL)						
AI1P10-30	5.78	29.08	0.027	2.886	TR	0.406	0.081	0.767	0.044	60.887
AI1P1 30-60	8.76	25.06	TR	2.623	TR	0.516	0.065	1.569	0.037	61.32
AI1P160-90	11.82	22.79	TR	2.339	TR	0.471	0.028	2.149	0.025	60.323
AI1P1 90-120	12.07	23.41	TR	2.516	TR	0.509	0.017	2.181	0.023	59.223
AI1P1 120-150	11.95	23.98	TR	2.618	TR	0.529	0.019	2.098	0.024	58.733
AI1P1 150-180	11.55	21.61	TR	2.505	TR	0.452	0.25	3.133	0.021	60.4
AI1P1 180-200	12.09	21.65	TR	2.934	TR	0.452	0.171	4.125	0.022	58.487
Mean	10.573	23.940	0.027	2.632		0.476	0.0901	2.289	0.028	59.910
Range	5.78-12.09	21.61-29.08	-	2.339-2.934	-	0.406-0.529	0.017-0.25	0.767-4.125	0.021-0.044	58.487-61.32
CV	22.9	10.8	-	8.1	-	9.2	98.3	47.1	31.7	1.8
AI2P2 0-30	6.57	27.78	0.045	4.243	TR	0.485	0.045	1.496	0.096	59.137
AI2P2 30-60	8.44	25.39	0.035	3.984	TR	0.503	0.031	4.158	0.062	57.297
AI2P2 60-90	9.62	23.53	TR	4.481	TR	0.48	0.01	2.707	0.052	59.003
AI2P2 90-120	10.36	22.19	TR	5.04	TR	0.549	0.052	4.156	0.039	57.493
Mean	8.74975	24.7225	0.04	4.437	-	0.50425	0.0345	3.12925	0.06225	58.2325
Range	6.57-6.57	22.19-27.78	0.035-0.045	3.984-5.04	-	0.48-0.549	0.01-0.052	1.496-4.158	0.039-0.096	57.297-59.137
CV	18.9	9.8	17.7	10.1	-	6.2	53.7	41.1	39.2	1.7
AI3P1 0-30	6.17	27.55	0.021	3.011	TR	0.351	0.02	0.843	0.031	61.977
AI3P1 30-60	8.57	29.32	TR	3.089	TR	0.335	0.016	1.036	0.029	57.547
AI3P1 60-80	10.06	24.59	TR	3.332	TR	0.346	0.007	1.64	0.023	59.957
Mean	8.267	27.154	0.021	3.144	-	0.344	0.0143	1.173	0.028	59.827
Range	6.17-10.06	24.59-29.32	-	3.011-3.332	-	0.335-0.351	0.007-0.02	0.843-1.64	0.023-0.031	57.547-61.977
CV	23.7	8.8	-	5.3	-	2.4	46.5	35.4	15.0	3.7

CV: Coefficient of variation; TR: Trace

The presence of ochric epipedon (13 cm thick), argillic endopedon and high base saturation (>50% by NH_4OAc at pH 7.0) qualified AI2P2 as Alfisol and Udalf by its udic soil moisture regime. Less than 20% clay decrease from the horizon of maximum accumulation with increased soil depth and redox concentrations having the hue of 5YR and 10YR, chroma of 6 in the endopedons qualified it as Paleudalf. Many wide cracks (1.0-1.7 cm) extending through a thickness of over 50 cm qualified the soil as Vertic Paleudalf at the subgroup, which correlated with Vertic Ferric Luvisols (Differentic, Loamic, Ochric, Profondic) in the WRB for Soil Resources System.

Poorly drained AI3P1 had ochric epipedons over cambic endopedons and qualified as Inceptisols. Aquic conditions within 50 cm of the mineral soil surface with chroma of 2 or less and distinct red mottles (10R 4/8) (redox concentrations) qualified it as Aquepts. It had a high endosaturated water table and qualified as Endoaquepts. Color value (moist) of 3 and low base saturation (<50% by NH_4OAc at pH 7.0) in all horizons within 100 cm of the soil surface qualified it as Humic Endoaquept in the subgroup which correlated with Dystric Gleyic Cambisols (Humic, Loamic) in the WRB for Soil Resources.

Table 4: Weathering indices of the studied soils

Horizon	Ruxton index	WI	Molar ratio
	Shale, limestone and sandstone formation (SLS)		
IHP1 0-30	2.38	0.62	1.12
IHP1 30-60	1.99	1.04	1.14
IHP1 60-90	2.27	3.79	1.29
IHP1 90-120	2.59	3.73	1.51
IHP1 120-150	4.02	2.44	2.21
IHP1 150-180	4.03	1.94	1.89
Mean	2.88	2.26	1.53
Range	1.99-4.03	0.62-3.79	1.12-2.21
CV	31.5	58.7	28.9
IH2P2 0-30	2.41	1.74	1.20
IH2P2 30-60	3.15	1.76	1.83
IH2P2 60-87	3.17	1.62	1.80
Mean	2.91	1.71	1.61
Range	2.41-3.17	1.62-1.76	1.20-1.83
CV	14.9	4.4	22.1
	Sandstone and limestone formation (SL)		
AI1P10-30	5.03	7.49	4.44
AI1P1 30-60	2.86	6.90	2.43
AI1P160-90	1.93	5.98	1.63
AI1P1 90-120	1.94	6.26	1.64
AI1P1 120-150	2.01	6.44	1.71
AI1P1 150-180	1.87	6.46	1.47
AI1P1 180-200	1.79	7.19	1.34
Mean	2.49	6.67	2.09
Range	1.79-5.03	5.98-7.49	1.34-4.44
CV	47.3	8.1	52.1
AI2P2 0-30	4.23	10.58	3.44
AI2P2 30-60	3.01	9.49	2.02
AI2P2 60-90	2.45	11.11	1.91
AI2P2 90-120	2.14	12.07	1.53
Mean	2.96	10.81	2.23
Range	2.14-4.23	9.49-12.07	1.53-3.44
CV	31.2	10.0	37.6
AI3P1 0-30	4.47	8.01	3.87
AI3P1 30-60	3.42	7.35	3.08
AI3P1 60-80	2.44	8.41	2.10
Mean	3.44	7.92	3.02
Range	2.44-4.47	7.35-8.41	2.10-3.87
CV	29.5	6.8	29.4

DISCUSSION

Clay cutans and accumulation of clay in the B horizons to the tune of over 1.2 relative to the overlying horizons indicates lessivation and soil maturity. An extension of the process to the Ckt horizons signify abridged pedogenesis and carbonate accumulation (Ck; as values of CCE were less than 50%)[32] in the SL. Emadi *et al.*[41] identified a similar process in the Iranian calcareous soils. Due to low CCE, the soils failed to meet the requirement for calcic horizon[35] which further infer youthfulness (particularly in the SL) and the dominance of decalcification over calcification. Bautista *et al.*[42] attributed carbonate dissolution and depletion to soil age and rainfall. Weakly formed Bk horizon is linked to carbonate leaching facilitated by the high precipitation associated with the tropical humid area. The pure SL formation[29] in the Calabar area may have limited soil development[3] and the rate at which it weathers and releases carbonates to the soils; hence the formation of transition AB, BA, BC and CB horizons which explains youthfulness.

The sand dominated soils was an indication of low weathering intensity in the soils over SL relative to SLS, as clay and silt may have been eroded[43] or sand may not have had sufficient time to weather into finer fractions. Root limiting layers were not observed since low bulk density values (<1.6 g m^{-3})[3,25] were obtained with indications, that the low values may be linked to the somewhat high organic C in the surface soils (Fig. 2).

Soil mottles in the high water table areas and Ckt horizons symbolize either inadequate aeration or the occurrence of redoximorphic process[3,32], while reddish streaks are indicative of pyrite. Furthermore, the grayish (hue of 2.5Y and chroma of 1 in the endopedons) and greenish (Gley1 3/1) colors are traced to prolonged wetting conditions, reduced Fe and seasonal fluctuation of water level. This qualifies IH2P2 for the gleization process. Similar colors were obtained by Irmak *et al.*[15] in the arid region of Turkey. Also, yellowish and reddish Munsell colors foretell the presence of goethite and hematite, respectively[44] or their precipitation in the soils. Brown to dark brown and reddish-brown colors bespeak organic matter accumulation as well as pigmentation by Fe-oxyhydroxides and their combined translocation[13].

Relative to soils over SL, CEC in soils over SLS was high* and had high capacity to sub cations such as Ca and Mg which dominated the exchange complex. Such property may be traced to the presence of weatherable minerals such as montmorillonite and ferromagnesian minerals. It is known that ligand exchange at silicate surfaces is reduced by H^+, Al^{3+}, Na^+ and organic matter[45]. Soils over SL are subjected to different conditions of weathering and dominated by kaolinite and quartz[46] or affected by Udic moisture regime. Also, the strong positive correlation of CEC with organic C suggests that organic matter and not clay may have been more responsible for the soil's capacity to retain cations. Similar findings were made by Gruba and Mulder[47] in acid forest soils while Wang *et al.*[48] obtained a positive correlation between CEC, clay and organic C in calcareous soils.

Furthermore, the accumulation of organic matter in the poorly drained soils (IH2P2 and AI3P1) is traced to littering. The

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*pH: extremely acid<4.0, strongly acid 4.1-5.2, acid 5.3-6.5, near neutral 6.6-7.4, alkaline 7.5-8.3 Organic: low<1.5, medium 1.5-4.5, high>4.5%, CEC: Very high>40, High 25-40, medium15-25, low 5-15, very low <5 $cmol_c$/kg process infers youthfulness, as soil organisms may not have had sufficient time to mineralize the organic soil materials. Accumulation exceeded decomposition in the poorly drained soils, while low values in high elevations was attributed to organic matter mineralization[41,49]. This aligns with studies by VandenBygaart and Protz[13] who opined that the organic matter enriched poorly drained soils were young compared to their counterparts in high elevations. Also, organic C in IH1P1, AI1P1 and AI2P2 increased at the deepest horizons (>82 cm) indicating that the environmental condition is sedimentary and cannot be solely attributed to limestone bedrock.

The dominance of Fe and Al obtained by aqua regia extraction procedure reveals that the soils may have been highly weathered, especially those at high elevation ranges in the SLS. According to Yakubu and Ojanuga[2], Zhao and Zheng[24] and Kefas *et al.*[50], the content of sesquioxides or immobile oxides increases as the soil ages due to intensive weathering. Consequently, soils over SLS were more intensely weathered, while the very low values in the poorly drained IH2P2 and AI3P1 indicate relative youthfulness. The low amount of Na and K in all the soils is attributed to high precipitation and aligns with the findings of Babechuk *et al.*[51] that K and Na are highly mobile during chemical weathering and are likely to be low in weathered humid tropical soils. Consequently, elemental abundance identified Na as the least abundant element and most leached while Fe and Al were the most abundant in the areas.

The dominance of SiO_2 and Al_2O_3 by the XRF technique indicates that their concentration reached solubility maxima in H_2O, such that the components precipitated as kaolinite releasing H^+ into the soil solution. Silica and alumina released during soil mineral weathering may react with CaO that would have been otherwise lost to form crystalline calcium silicate and aluminate. This process may render CaO unavailable. When SiO_2 and Al_2O_3 dominate in soils, the underlying silicate rocks may be responsible[10] or may be traced to soil acidity while Fe_2O_3 is attributed to aging[50]. Large amounts of primary minerals (quartz, feldspars, muscovite) may be responsible for high silica in coarse-textured soils while alumina is linked to clay minerals[52]. The predominance of alumina indicates a high degree of soil weathering[53]. Quartz (SiO_2), goethite (FeO(OH)), hematite (Fe_2O_3), kaolinite ($Al_2SiO_5(OH)_4$), gibbsite ($Al_2O_3{\cdot}3H_2O$) are commonly identified minerals of SiO_2, Fe_2O_3 and Al_2O_3 found in the humid tropics[54,55]. Relatively lower SiO_2 in SLS may be due to intense weathering in the area. Highly weathered soils contain less silica and more of Fe and Al oxyhydroxides which tend to accumulate[56]. The entire soils were low in Zr and Ti, however their irregular distribution throughout the profiles show discontinuous lithology and may be allochthonous in origin[10]. Oxides of Zr and Ti are resistant to weathering and persist in soils; consequently, the low amounts in the soils is indicative of relative youthfulness. However, authigenic anatase is commonly found in intensely weathered soils as products of the weathering of titanite and Ti bearing minerals[57,58].

Contrary to results obtained for immobile oxides, alkaline and alkaline earth (Mg) metals were very low (Na and K) or trace (K_2O, CaO) by the procedures of ICP-OES and XRF. There is the likelihood that the geology, sandy texture and high rainfall regime in the tropical rainforest area underlain by SL had encouraged the loss of the oxides. These oxides are labile[59]. When released during pedogenic mineral weathering, they may either be adsorbed by plants in the short term or lost to leaching. Also, values of the immobile element by the XRF technique were higher relative to their counterparts by ICP-OES. The technique of XRF allows deeper penetration of rays into sample bonds than the chemical extraction procedures of aqua regia which recovers elements present in the first layer of matter[60].

The relationship of Fe_2O_3 and MnO_2 with Fe, Mg and Al suggests increasing values of these components with soil age; however, MnO_2 correlated weakly as such, may only increase the elements slightly with age. MnO_2 has been found to concentrate on residual laterites in alkaline tropical soils[61]. Similarly, an increase in Al_2O_3 with soil maturity is likely to lead to the leaching of Na, Mg and K. Inverse relationship of SiO_2 with Fe, Mn and Al may suggest accumulation of SiO_2 as soil ages. Resistant TiO_2 and ZrO_2 are likely to increase Fe and Mg in the soils.

An increase in R with soil depth in the SLS against a decrease in the index in SL negates Ruxton's findings. Ruxton[38] had stated that an ideal trend for the index is the decrease in values up the profile which indicates an increase in weathering. Soils over SLS seem, therefore, to have been more weathered in the surface and less in the subsurface relative to those over SL. Low weathering intensity in the SL may be traced to the slightly lower mean annual temperature in the control section of the soils. This aligns with Van't Hoff's temperature rule of an increasing rate of a reaction with increased temperature. The Weathering Intensity (WI) was higher in the soils over SLS and was by far lower in SL. Lower values of WI explains more exposure to intense weathering condition. Depth wise, relatively higher subsurface values imply reduced weathering intensity with an increase in soil depth. This accords earlier findings by Evans and Cameron[39]. According to Che *et al.*[17], soil weathering with depth lacks uniformity, however, such irregularity may be attributed to the youthful stage of soil genesis. The SiO_2: R_2O_3 (MR) values were higher in SL than SLS and indicated lateralization (MR = 1.33-2.0) in the former[62]. Burt *et al.*[63] and Msanya *et al.*[64] observed that weathering is at a comparatively more advanced stage in soils over SLS where low values were obtained. During the early stages of pedogenesis, the MR ratio is low, as weathering proceeds and more resistant minerals are broken down, the ratio then rises.

CONCLUSION

In a limestone formation, soils in the higher elevation ranges were more mature; having well-developed B horizons as well as Fe-Mn concretions and clay cutans particularly in those over SLS. Pseudo total Fe and Al as well as their total oxides dominated the soils, especially those over SLS while SiO_2 appeared similar across the formations. Trace to low P_2O_5 and CaO were grossly influenced by the humid climate. The indices of R, WI and MR showed more advanced weathering in the soils over SLS with lessivation, decalcification, littering, gleization and lateralization as common soil-forming processes. The soils were variously classified as Acrisols, Cambisols and Luvisols with various principal and supplementary qualifiers.

SIGNIFICANCE STATEMENT

This study discovered the impact of tropical humid climate on soils formed from limestone formations (shale, limestone and sandstone and sandstone and limestone) as well as the variation in soil properties, weathering intensity and soil classification that can be beneficial to pedogenesis and land use planning in the humid tropics. This study will help the researcher to uncover the critical areas of the genesis of soils over limestone formations, as previous researchers emphasized high base status of the soils without due attention to the influence of climate on the soils. Thus a new theory on the pedogenesis of soils over limestone formations in the humid tropics may be arrived at.

ACKNOWLEDGMENT

This research is part of Ofem, Kokei Ikpi's Doctoral thesis at the University of Nigeria, Nsukka (UNN). The study was funded by Tertiary Education Trust Fund (TETFUND/DAST&D/UNIV/CALABAR/ASTD/2017/VOL.1). The contributions of Laboratory Staff of Soil Science and Soil Protection at the Czech University of Life Sciences, Czech Republic is acknowledged.

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