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PEDOLOGICAL DATA FOR THE STUDY OF SOILS DEVELOPED OVER A LIMESTONE BED IN A HUMID TROPICAL ENVIRONMENT

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Abstract

Lithological characteristics interact with other factors of soil formation to define soil genesis. This becomes more interesting as data on the mineral and elemental oxide components of soils developed from limestone are rarely available in the humid tropical environment. The present study investigated the elemental oxide content, forms of sesquioxides, and clay mineral species in some limestone soils. Soil samples were obtained from three (3) crestal soil profile pits and analyzed for elemental content by the use of an X-ray Fluorescence spectrometer, and sesquioxides forms by Inductively Coupled Plasma-Mass Spectrometer. Analyses were done in triplicates. The mineralogy of the clay fraction was determined on the A, B and C horizon samples using an X-ray diffraction Technique. The occurrence of SiO₂ (203-277 g/kg), Al₂O₃ (65-105 g/kg), and Fe₂O₃ (14-95 g/kg) in substantial amounts over MnO₂, ZrO₂, and TiO₂ with negligible quantities of CaO suggested comparatively more developed soils in the Agoi Ibami and Mfamosing tropical rainforests. Crystalline form of Fe was dominant over amorphous form, with indications of the co-migration of dithionite Fe with clay to the B horizons of the soils. Quartz, kaolinite, montmorillonite, and chlorite-vermiculite-montmorillonite interlayered minerals dominated the clay mineralogy of the studied soils. Mineral transformation places the soils at the transitory stage from the intermediate to the complete stage of soil development.

The expanding clay minerals are most likely to increase plant nutrient adsorption and soil fertility status to accommodate the cultivation of a wider range of crops.

Keywords Soil genesis, clay mineralogy, forms of Fe and Al, limestone

Introduction

Soil development in warm-humid climates corresponds with pedogenic kaolinite and acidic soils with moderate silica activity, depleted exchangeable basic cations, and the dominance of oxides and oxyhydroxides of Fe and Al. As a result, the soils are yellowish red, deep to consolidated parent rock, and have low organic matter content. These characterize soils in the humid tropics. In such soils, soluble and unstable CaCO_3 leaves the soils' exchange complex depleted of Ca^{2+} (Ofem *et al.*, 2020).

Deep soils are over 120 cm deep and promoted by the intensified weathering of unstable primary minerals like amphiboles, pyroxenes, and carbonates (Al-Khirbash, 2016), resulting in the loss of mobile soil components (H_2SiO_4 , Ca^{2+} , K^+ , Mg^{2+}) and the residual build-up of immobile components like Fe, Al, and Mn oxides. Such oxides have been used as a basis for the genesis of soils in the tropics (Ofem *et al.*, 2020), mainly for the quantification of soil-forming processes. The complete weathering and leaching of primary aluminosilicate minerals result in ferrallitic soils. Such soils are characterized by kaolinite, hermatite, and gibbsite, and perhaps quartz and magnetite as resistant products of weathering in humid tropical environments.

Clay mineralogy is of prime importance in soil functions. It plays a key role in soil processes such as erosion (Jafarzadeh *et al.*, 2013), leaching, and weathering (Kasanin-Grubin, 2013). It contributes to soil aggregate stability (Duiker *et al.*, 2003), surface area and charge density, and cation exchange capacity (Six *et al.*, 2000). Clay mineralogy also controls geochemical processes like element cycling, nutrient release, and availability (Kowalska *et al.*, 2020). The mineralogy of soils is influenced by parent rock (Omdi *et al.*, 2018), climate, relief, environment, and time and susceptibility of the soils or parent materials to weathering (Rozanov *et al.*, 2017).

The clay fraction of soils derived from limestone consists predominantly of kaolinite (Al-Farraj, 2011), and smectite/vermiculite interstratified minerals (Khresat and Taimeh, 1998). A common mineral in calcic soils is palygorskite (Owliaie *et al.*, 2006) which is also found in other soils with neutral to alkaline pH (Churchman and Lowe, 2012) and is often associated with B horizons but not detected in Btk and C horizons (Hameed *et al.*, 2018).

Clay minerals are unstable in the upper organic-rich horizons due to active biochemical, physical, and weathering processes.

Metal elements are mainly cycled during chemical weathering, soil formation, and other surface processes. Hence, soil and regolith developed on mineralized bedrock areas are often enriched in the elements (Négre *et al.*, 2019). Lithology has been identified as the main source of geochemical elements, while the abundance and spatial distribution of these elements have been linked to the process of mineralization (Fernández-Caliani *et al.*, 2020).

Data generated from X-ray diffraction (XRD) is marred by overlapping peaks (Bish, 1994), particle sizes and uniformity, sample preparation (Aparício and Ferrell Jr., 2001) and stratification in calcareous soils (Omdi *et al.*, 2018), and variable chemical and structural composition of soil minerals as well as series of chemical treatments. On the other hand, X-ray fluorescence (XRF) is a linear technique without chemical alterations of mineral structure. Hence, the adoption of XRF, oxalate, and dithionite Fe and Al extractions as complementary techniques to XRD. The combined analytical techniques will provide enhanced data for pedological studies.

Over the years, the mineralogy of limestone soils has received substantial attention (Hameed *et al.*, 2018., Irmak *et al.*, 2007), while the elemental oxide content of soils formed over limestone has been used as an index of pedogenesis (Irmak *et al.*, 2007, Girao *et al.*, 2014, Ofem *et al.*, 2020). Very limited information exists on the mineralogy, as well as oxalate and dithionite extractions of the soils developed from limestone in Cross River State. The inter-dependence of data obtained by XRD, XRF, Fe and Al extractions, and general soil characteristics for pedological studies in tropical environments is novel and deserves attention. The present study seeks to ascertain the total elemental oxides, oxalate and dithionite forms of Fe and Al, and mineral species in soils directly overlying limestone beds in a tropical environment of Nigeria.

Materials and methods

Location, climate and geology of the study

The study was conducted in Cross River State (5°32' and 4°27' N, 7°50' and 9°28' E), Southeastern Nigeria. Ishibori (IH), Agoi Ibami (AI) and Mfamosing (MF) are agricultural communities in Ogoja (06°39'17" N, 08°47'51" E), Yakurr (05°43'27" N, 08°10'37.2" E) and Akamkpa (05°04'41.8"N, 08° 27'49.8"E), and located at 196, 87 and 40 km, respectively away from Calabar, the capital city of Cross River State. The sampling sites were selected based on the underlying limestone formations. The Ogoja area is characterized by relatively drier and hotter climatic conditions, while Yakurr and Akamkpa areas are covered by tropical rainforests; both areas have a humid tropical climate. In the Koppen climate classification system, the areas qualify as a tropical moist climate with an average temperature that exceeds 18 °C in all months and precipitation of over 1500 mm/year. The Akamkpa and Yakurr areas have tropical wet climatic conditions with all year-round precipitation, high humidity and surface temperatures. Rainfall amounts vary from 1251–3348 mm/year in Ishibori, to 1760–3771 mm/year in the Agoi Ibami and Mfamosing areas. Temperature varies slightly from 23.0–34.0 °C in Ogoja to 22.6–32.0 °C in Yakurr and Akamkpa (Sambo *et al.*, 2016). Yakurr and Akamkpa vary slightly in temperature and have similar climate and vegetation conditions. Cretaceous and Tertiary limestone dominate limestone areas in Nigeria (Fatoye and Gideon, 2013). In Cross River State, limestone is associated with shale, siltstone, and often intercalated with fine-grained sandstone (Ofem *et al.*, 2020), with well-developed limestone beds and caves in the Agoi Ibami and Mfamosing areas.

Field study and soil sampling

The study areas have been mapped by the Nigerian Geologic Survey Agency and identified to be underlain by limestone. Ishibori, Agoi Ibami, and Mfamosing were selected in Ogoja, Yakurr, and Akamkpa, respectively. In the study areas, crestal positions were identified using the digital elevations of the locations. The study locations' digital elevation models (DEMs) were obtained from USGS Explorer SRTM 1 arc-second Global at a resolution of 30 m. 10 % HCl was used on rock outcrops, and an effervescence reaction was a confirmation of the presence of carbonate-rich rocks. One soil pit was randomly sited at the crestal positions of each of the three locations (IH: N06°38.53', E008°48.75', 64m; AI: N05°44.386', E008°10.660', 80m; MF: N05°04.714', E008°30.541'; 58m), such that limestone consolidated bedrocks were encountered before 200 cm depth. Soil samples were collected from pedogenic horizons from bottom to top of soil profiles, described by the procedures of Schoeneberger *et al.* (2012) and transferred in well-

labelled sampling bags to the laboratory. Clay mineral species were identified on only diagnostic A, B, C horizons. On the other hand, soil profile samples were analyzed in triplicates for total elemental oxides and forms of Fe and Al. The field study was carried out from December 2018 to February 2019. Soil samples were air-dried under laboratory conditions, ground, and passed through 2 mm sieves.

Laboratory studies

General soil characteristics: Particle size analysis was performed by the Bouyoucos hydrometer method using sodium hexametaphosphate as the dispersing agent. Soil pH (H₂O) was determined potentiometrically in a 1:2.5 soil:water suspension. Organic C was determined by the Walkley and Black wet oxidation method, while exchangeable Ca²⁺, Mg²⁺, K⁺ and Na⁺ were extracted using 1N NH₄OAc (pH 7.0) and read with atomic absorption spectrophotometry and flame photometry. Base saturation was determined by expressing the ratio of total exchangeable bases and cation exchange capacity as a percentage. The laboratory analyses were carried out as outlined by Soil Survey Staff (2014a)

Clay extraction and scanning: Hydrogen peroxide solution and deionized water were added to the < 2mm air-dry soil, and frothing was controlled by slow addition of octan-2-ol. After cold plate heating for 2h, the samples were made to 200 ml with distilled water and centrifuged at 4400 rpm and supernatant removed by careful suction. Sample dispersion was facilitated by sodium hexametaphosphate solution, polycarbonate and deionized water in an end-to-end shaker for 18hs. Upon sedimentation, clay flocculation was enhanced with 2 ml of MgCl₂ after each siphoning. The clear supernatant was disposed by siphoning and the clay suspension subjected to a 510 g of relative centrifugal force for 20 minutes in a 50 ml centrifuge tube. The clay residue was oven-dried at 60 °C.

The whole clay fraction was prepared for clay mineral identification and semi-quantification by XRD analysis using a back loading preparation method. Also, clay samples were exposed to ethylene glycol, scanned and heated to 500 °C for 1 hour. Diffractograms were obtained using a Siemens D5005 diffractometer configured in Bragg-Brentano geometry. The X-ray source is a Cu tube, Ni-filtered, Cu-K α radiation with an emission of 1.5 Å/ 8.05 keV and operates at a power of 1.6 Kw. It has a graphite monochromator and scintillator detector.

Total elemental oxide content: Whole soil samples meant for total elemental oxides analysis by XRF were further pulverized with an automatic mill into a fine powder of approximately 3-4 µm diameter and homogenized. Samples

were then analyzed with XRF Delta Premium Spectrometer 2019 by the procedures of Tejnecky *et al.* (2015). The total elemental abundances of Al_2O_3 , Fe_2O_3 , SiO_2 , MnO_2 , TiO , CaO , and ZrO were read and used for the study.

Dithionite and oxalate extractions: Dithionite-extractable Fe and Al were measured by the method of Mehra and Jackson (1960) and as modified in Soil Survey Staff (2014a) using the dithionite-citrate system buffered with sodium bicarbonate. Oxalate forms of Fe and Al were estimated by extraction with 0.2 *M* acid ammonium oxalate at pH 3.0 (McKeague and Day, 1966). Dithionite and oxalate Fe and Al in the extract were determined using Perkin Elmer NexION 450D inductively coupled plasma mass spectrometry (ICP-MS) model. The equipment has a detection limit of 0.01 g/kg.

Results

General soil characteristics

The general characteristics of the studied soils are summarized in Table 1. The particle size distribution shows that all the studied soils are dominated by sand, and are predominantly sandy loam, sandy clay and sandy clay loam in texture with a layer of clay accumulation at depths > 50 cm from the soil surface. All the soils are characterized by pH-values in the slightly acid to neutral range (5.5-7.1; Table 1). Consequently, limestone bedrocks and large boulders were encountered at 132 and 121 cm in AI and MF, respectively and none in IH. A considerably moderate organic carbon was measured in the surface soils of AI and MF (> 10 g/kg), but low values in IH (< 10 g/kg). Exchangeable Ca^{2+} and Mg^{2+} were moderate in the soils with values that are deeply and somewhat homogeneously distributed in all the profiles; however, exchangeable K^+ and Na^+ values were low in the soils. Cation exchange capacity by NH_4OAc was > 25 cmol/kg upto 60 cm depth in IH and < 25 cmol/kg in AI and MF at all depths, while base saturation seems to be < 50 % except in the Ap horizons and layers of deep clay accumulation. Fe and Mn concretions and nodules, as well as cracks (> 1.0 cm wide) characterized the endopedons.

Table 1: General characteristics of the soils

Horizon	Depth cm	Particle size distr. Clay Silt Sand g/kg			Texture	pH H ₂ O	Organic C g/kg	Exchangeable bases Na K Mg Cacmol _c /kg.....				CEC NH ₄ OA _c	BS %	Other properties
IH:														
Ap	0-37	280	120	600	ScI	5.5	7.55	0.04	0.07	4.4	5.4	28.0	35.4	Dark reddish-brown to dark red and brown, Fe and Mn nodules and concretions in the endopedons.
AB	37-64	240	100	660	ScI	6.4	4.66	0.02	0.05	5.0	5.8	35.6	30.5	
Bkt	64-130	400	100	500	Sc	6.2	2.75	0.02	0.05	4.4	7.2	21.2	55.1	
CB	130-195	200	120	680	ScI	6.9	6.18	0.03	0.07	2.8	3.8	18.6	36.0	
AI:														
Ap	0-13	160	120	720	SI	6.0	15.55	0.04	0.07	2.4	7.6	19.4	52.1	Brown to yellowish and grayish, Fe cutans in the B horizon, Fe-Mn concretions in the endopedons, 1.0-1.7 cm wide cracks at 82-132 cm depth.
AB	13-60	160	100	740	SI	6.2	6.12	0.02	0.06	2.8	2.6	20.2	27.1	
BC	60-82	140	100	760	SI	6.4	1.72	0.02	0.04	2.4	3.6	22.0	27.5	
Ckt	82-132	320	140	540	Sc	7.1	3.43	0.02	0.05	4.2	6.6	18.4	59.1	
MF:														
Ap	0-17	140	180	680	SI	6.3	13.73	0.06	0.11	2.6	6.0	17.2	51.0	Very dark gray to pale and pale brown, 2-3 cm wide cracks at 17-56 cm depth.
BC	17-56	160	130	710	SI	6.7	2.06	0.01	0.03	3.4	6.0	22.8	41.4	
Bt	56-121	260	130	610	ScI	6.8	0.69	Tr	0	2.4	6.6	14.6	61.6	

N/B: ScI: sandy clay loam, SI: Sandy loam, Sc: Sandy clay, BS: Base saturation

Total elemental oxides content

Total elemental oxides of the soils are presented in Table 2. The soils were dominated by Al₂O₃, Fe₂O₃, and SiO₂. Al₂O₃ had a range of 65.600-105.300 g/kg in the studied soils, with values increasing either in the B horizon or continuously with increasing soil depth. Fe₂O₃ had ranges of 63.39-95.61, 14.96-41.56, and 20.66-24.36 g/kg in IH, AI, and MF, respectively. Values decreased continuously with increasing soil depth in IH, while Fe₂O₃ in MF seemed to have been illuviated alongside clay in the horizons of clay accumulation (Bt and Ct) with a resultant bulge. MnO₂ and ZrO₂ were less than 2.0 g/kg, while TiO₂ varied from 3.3 to 13.4 g/kg, with values varying irregularly in all the studied soils. Values of TiO₂ decreased in the B horizons of IH. However, TiO₂ in IH was comparatively higher with values > 10 g/kg in the A and C horizons. SiO₂ had the highest values amongst the studied oxides with increasing values with soil depth in IH that contradicts decreasing values in AI and MF. CaO was very low in the studied soils and ranged from trace values in most Ap horizons to 3.02 g/kg with the highest values occurring in MF.

Table 2: Total elemental oxide analysis and ratios of the soils

Soil Profiles	Horizons	Depth cm	Al ₂ O ₃	Fe ₂ O ₃	MnO ₂	ZrO ₂	TiO ₂	SiO ₂	CaO
			g/kg						
IH	Ap	0-37	85.2	95.610	0.559	0.447	11.040	203.130	TR
IH	AB	37-64	105.3	78.000	0.800	0.340	8.270	209.600	2.400
IH	Bkt	64-130	88.200	65.170	1.090	0.265	7.230	214.190	2.300
IH	CB	130-195	65.600	63.390	1.666	0.832	13.430	263.870	2.000
		Minimum	65.600	63.390	0.559	0.265	7.230	203.130	-
		Maximum	105.300	95.610	1.666	0.832	13.430	263.870	2.400
AI	Ap	0-13	65.730	14.960	0.448	0.962	4.850	277.830	TR
AI	AB	13-60	75.080	28.270	0.380	0.790	4.940	265.830	TR
AI	BC	60-82	90.330	34.330	0.206	0.571	4.910	244.600	0.600
AI	Ckt	82-132	103.600	41.560	0.522	0.389	5.490	221.870	1.000
		Minimum	65.730	14.960	0.206	0.389	4.850	221.870	-
		Maximum	103.600	41.560	0.522	0.962	5.490	277.830	1.000
MF	Ap	0-17	79.030	20.700	0.282	0.466	3.451	269.030	1.330
MF	BC	17-56	80.730	24.360	0.228	0.346	3.702	244.630	2.300
MF	Bt	56-121	78.370	20.660	0.285	0.324	3.338	252.720	3.020
		Minimum	78.370	20.660	0.228	0.324	3.338	244.630	2.220
		Maximum	80.730	24.360	0.285	0.466	3.702	269.030	3.020

Note. TR: Trace, IH: Ishibori, AI: Agoi Ibami, MF: Mfamosing

Forms of Fe and Al

Dithionite Fe (Fe_d) and Al (Al_d) had ranges of 8.2-52.5 and 1.2-3.3 g/kg, respectively in the studied soils with values of Fe_d and Al_d decreasing continuously in IH and either bulging in the B horizons (MF) or increasing continuously with increase in soil depth (Table 3). Oxalate Fe (Fe_o) was less than 1.5 g/kg in the studied soils with profile mean values in IH (0.9 g/kg) exceeding the values in AI (0.3 g/kg) and MF (0.5 g/kg), while oxalate Al (Al_o) was less than 1.0 g/kg in the soils with 0.63, 0.28 and 0.57 g/kg obtained as the mean values in IH, AI, and MF, respectively.

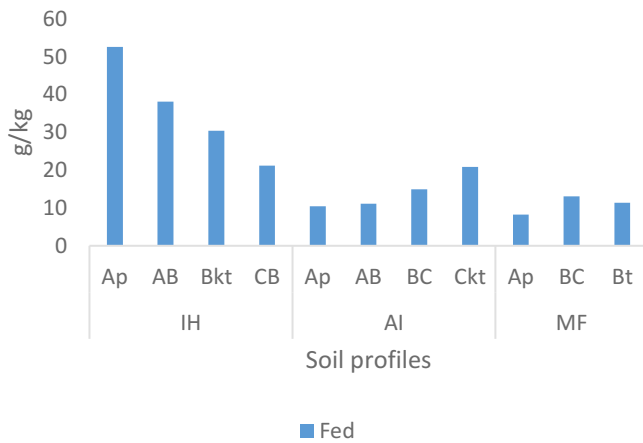
Overall, Fe_d and Al_d exceeded their oxalate counterpart, resulting in definite crystalline Fe (Fe_c= Fe_d-Fe_o) of 7.4 -51.8 g/kg, in the soils. The values of Fe_c regularly decreased with soil depth in IH but increased in AI and MF. Activity ratio of Fe (Fe_a) was less than 0.1 in the soils with comparatively higher values obtained in MF. There were indications of the co-migration of Fe (Fe_{co}) with clay to the endopedons as values of Fe_{co} increased in the B horizons (Table 3).

The distribution of the various forms of Fe the soil profiles is shown in Fig. 1.

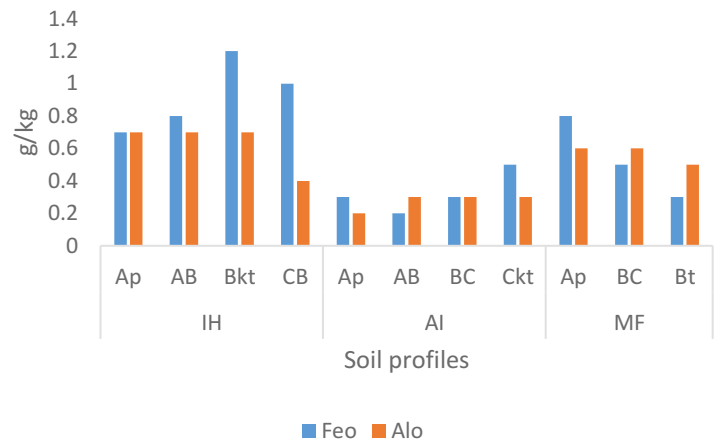
Table 3: Forms of Fe and Al in the studied soils

Soil Profile	Horizon	Depth Cm	Dithionite Form		Oxalate Form		Crystalline Fe (Fe _d -Fe _o)	Activity ratio of Fe (Fe _o /Fe _d)	Clay g/kg	Co-migration Fe _d /clay
			Fe _d	Al _d	Fe _o	Al _o				
-----g/kg-----										
IH	Ap	0-37	52.5	3.3	0.7	0.70	51.8	0.013	280	0.187
IH	AB	37-64	38.1	3.0	0.8	0.70	37.3	0.021	240	0.158
IH	Bkt	64-130	30.4	3.0	1.2	0.70	29.2	0.039	400	0.076
IH	CB	130-195	21.2	2.4	1.0	0.40	20.2	0.047	200	0.106
		Mean	35.6	2.9	0.9	0.63	34.6	0.030	280	0.131
		Minimum	21.2	2.4	0.7	0.40	20.2	0.013	200	0.076
		Maximum	52.5	3.3	1.2	0.70	51.8	0.047	400	0.187
AI	Ap	0-13	10.4	1.2	0.3	0.20	10.1	0.029	160	0.065
AI	AB	13-60	11.1	1.7	0.2	0.30	10.9	0.018	160	0.069
AI	BC	60-82	14.9	1.7	0.3	0.30	14.6	0.020	140	0.106
AI	Ckt	82-132	20.8	1.9	0.5	0.30	20.3	0.024	320	0.065
		Mean	14.3	1.6	0.3	0.28	14.0	0.023	195	0.076
		Minimum	10.4	1.2	0.2	0.20	10.1	0.018	140	0.065
		Maximum	20.8	1.9	0.5	0.30	20.3	0.029	320	0.106
MF	Ap	0-17	8.2	1.3	0.8	0.60	7.4	0.098	140	0.059
MF	BC	17-56	13.1	1.8	0.5	0.60	12.6	0.038	160	0.082
MF	Bt	56-121	11.4	1.5	0.3	0.50	11.1	0.026	260	0.044
		Mean	10.9	1.5	0.5	0.57	10.4	0.054	186.7	0.062
		Minimum	8.2	1.5	0.3	0.50	7.4	0.026	140	0.044
		Maximum	13.1	1.8	0.8	0.60	12.6	0.098	260	0.082

Distribution of dithionite form of Fe and Al in soil profiles



Distribution of oxalate form of Fe and Al in soil profiles



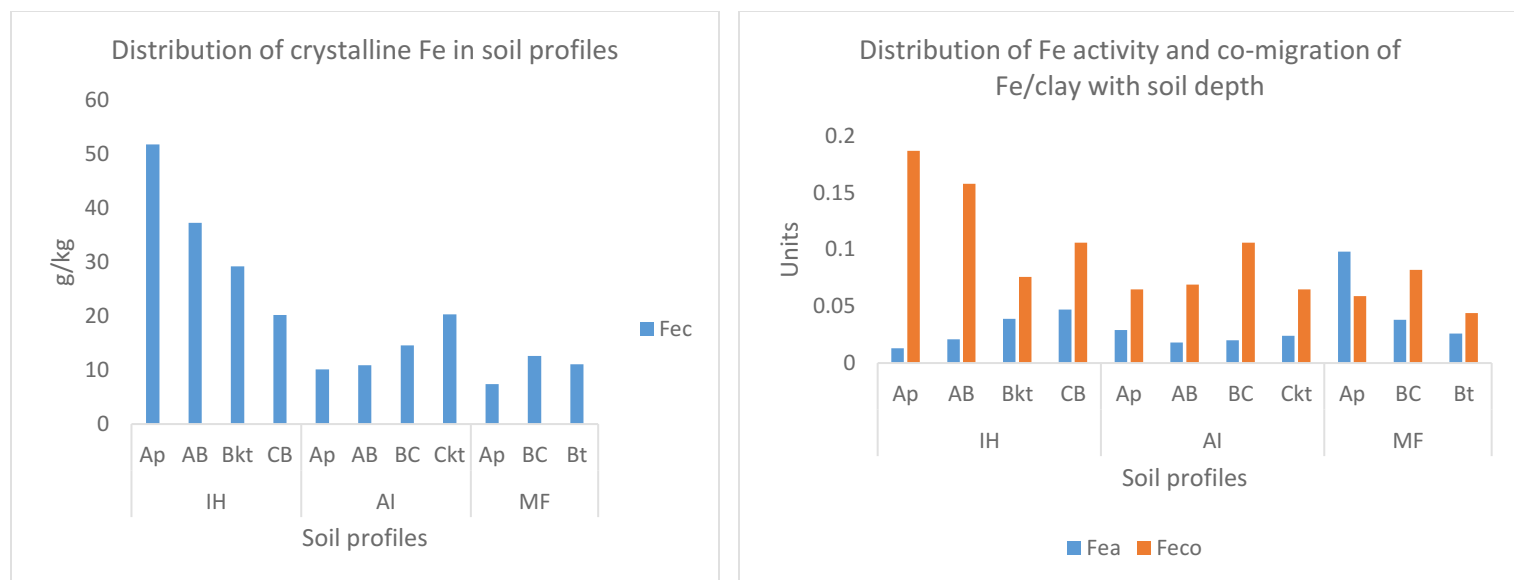


Fig. 1: Distribution of the forms of Fe and Al in the horizons of the studied soil profiles

Mineralogy of the clay fraction

The mineralogy of the clay fraction ($< 2 \mu\text{m}$) is presented in Table 4. The main clay mineral phases were quartz, kaolinite, montmorillonite and chlorite-vermiculite-montmorillonite mixed layered phases. Also, phyllosilicates were represented by a scanty occurrence of vermiculite, palygorskite, hematite, nacrite, mica, Na-Al-silicate, and Mg-Al-silicate in the represented and poorly represented ranges across the studied soils. X-ray diffractograms of the A, B, C horizons of the soils are presented in Fig. 2 (a - i).

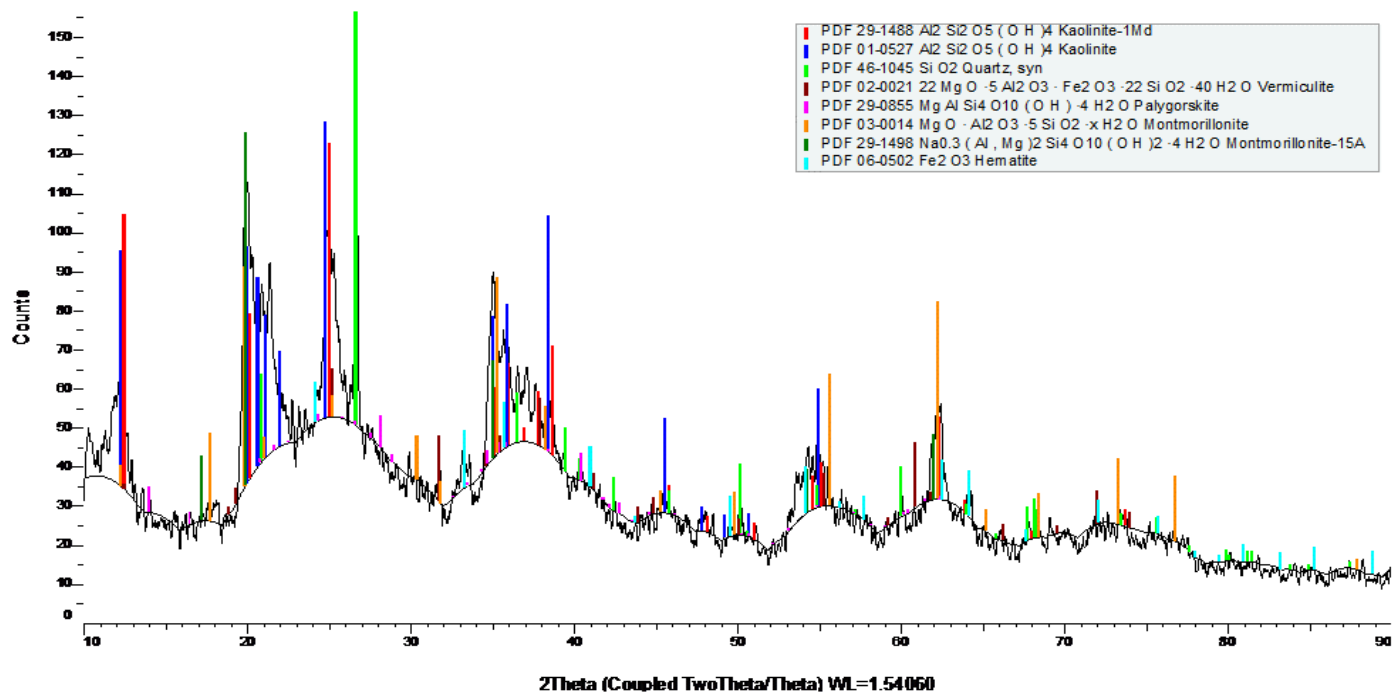
Quartz was the most dominant and well-distributed mineral in the soils, with very abundant ($>30\%$) and abundant ($15-30\%$) occurrences obtained in MF and IH, respectively while the endopedons of AI were only represented ($7-15\%$). Diffractograms indicate more prominent and sharp peaks in the second-order, except in the Ap horizon of IH (0-37 cm).

Montmorillonite was abundant ($15-30\%$) to very abundant ($> 30\%$) in the endopedons of the soils; however, values in the Ap horizons of the soils were either below the detection limit in MF, represented in IH or abundant in AI. Montmorillonite was not recorded in the Ap horizon of MF. Diffractograms indicate more prominent and sharp peaks for montmorillonite -15A in the second-order with a 2θ value of 20.0° ($d = 4.43 \text{ \AA}$). Kaolinite occurred in abundance

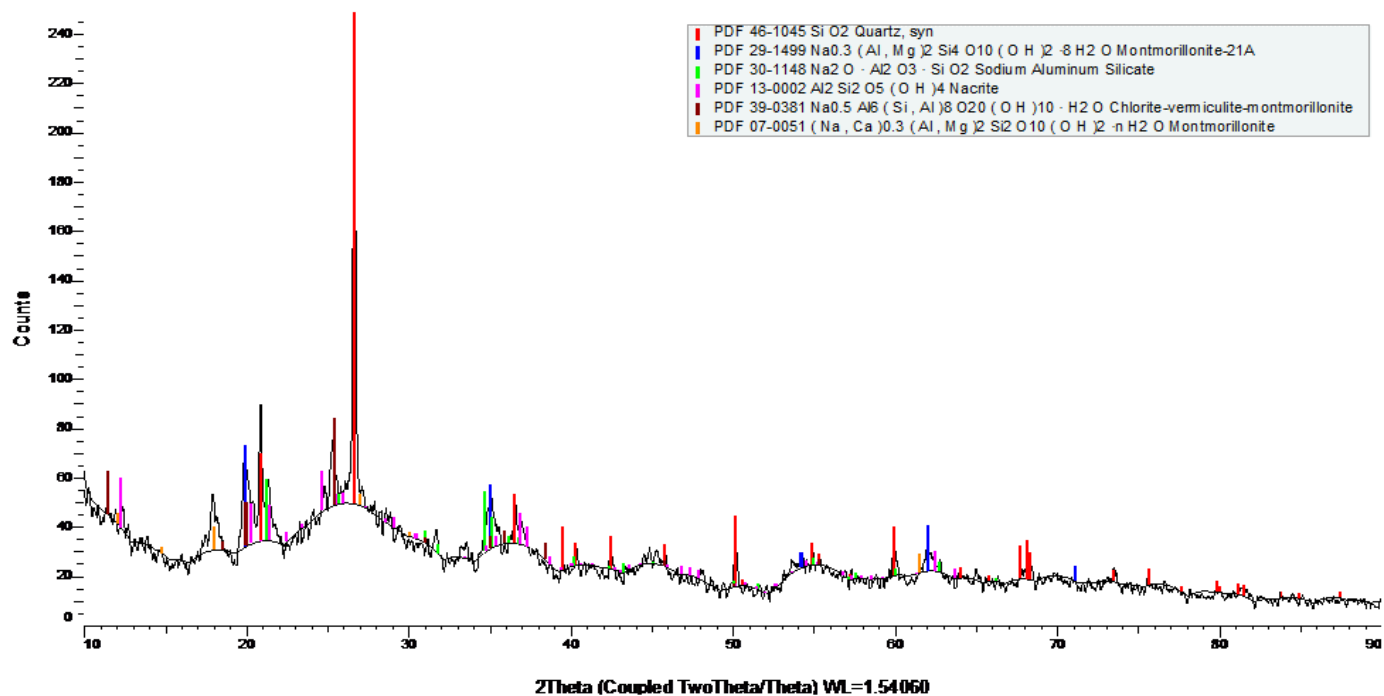
(15-30 %) in the Ap and C horizons of the studied soils except in IH where its abundance appeared represented (7-15 %) in the Ap horizon and not detected in the C horizon. Diffractograms of the soils indicate prominent and sharp peaks in the first-order for kaolinite-1Md with a 2θ value of 12.4° ($d = 7.13 \text{ \AA}$). On the other hand, kaolinite peaked on the diffractograms in the first-order ($d = 7.24 \text{ \AA}$).

Vermiculite was somewhat scarce with its abundance represented (7-15 %) in the Ap horizon of IH and abundant (15-30 %) in the Ckt horizon of AI. Similarly, palygorskite was obtained in represented (7-15 %) and poorly represented ($< 7 \%$) abundances in the Ap horizons of IH and AI, respectively, and abundant (15-30 %) in the BC horizon of AI. Chlorite-vermiculite-montmorillonite (C-V-M) interlayered structure was found in the abundant range (15-30 %) in the soils. However, C-V-M was not detected in the Ap horizons of IH and MF, and in the B horizons of IH and MF. Hematite was recorded in the Ap and B horizons of IH and AI, respectively, in represented (7-15 %) and abundant (15-30 %) amounts. Peak diffractograms were obtained in the first-order ($2\theta = 33.4^\circ$, $d = 2.68 \text{ \AA}$) in the B horizon of AI. Nacrite was recorded only in the CBk horizon of IH in represented amount (7-15 %).

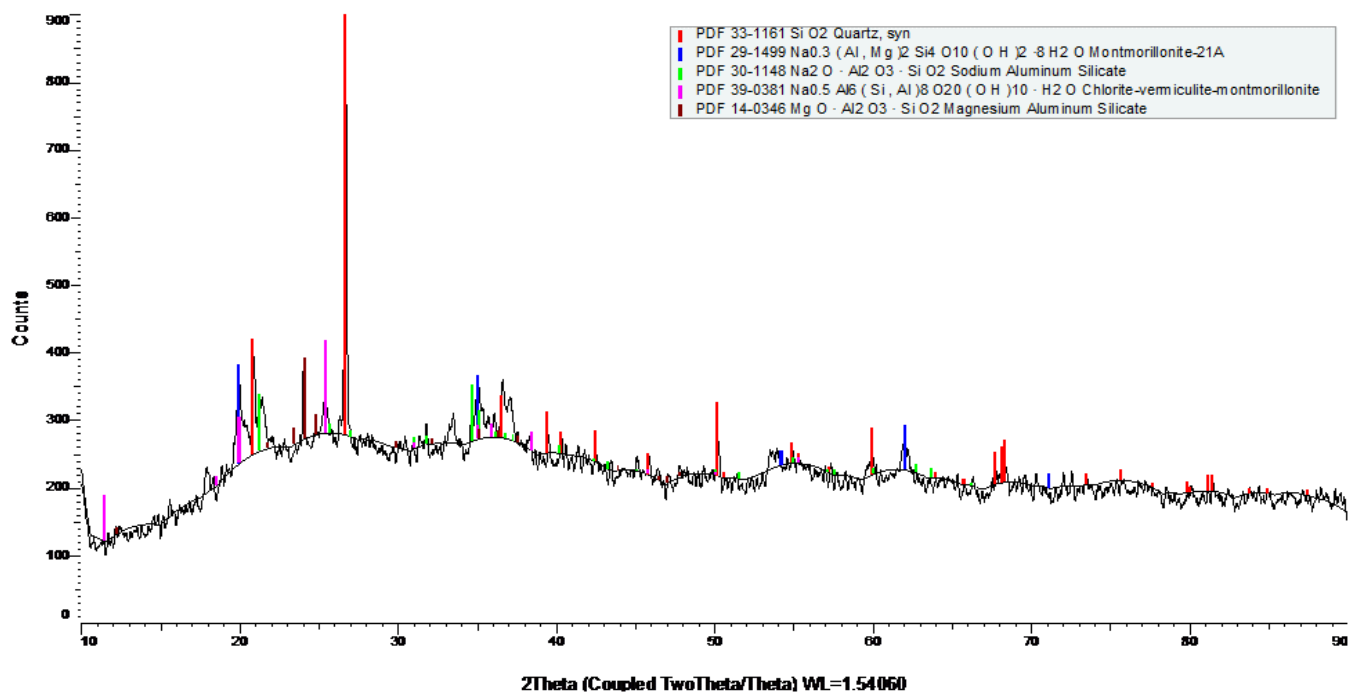
Na-Al and Mg-Al silicates were found in abundant (15-30 %) amounts in the C horizons of IH, while Na-Al silicate was represented and found in the range of 7-15 % in the B horizon. Diffractogram peaks were obtained at a 2θ value of 21.1° ($d = 4.20 \text{ \AA}$) in the first-order. However, Mg-Al-silicate recorded its peak value in the second-order at a 2θ value of 24.0° ($d = 3.70 \text{ \AA}$).



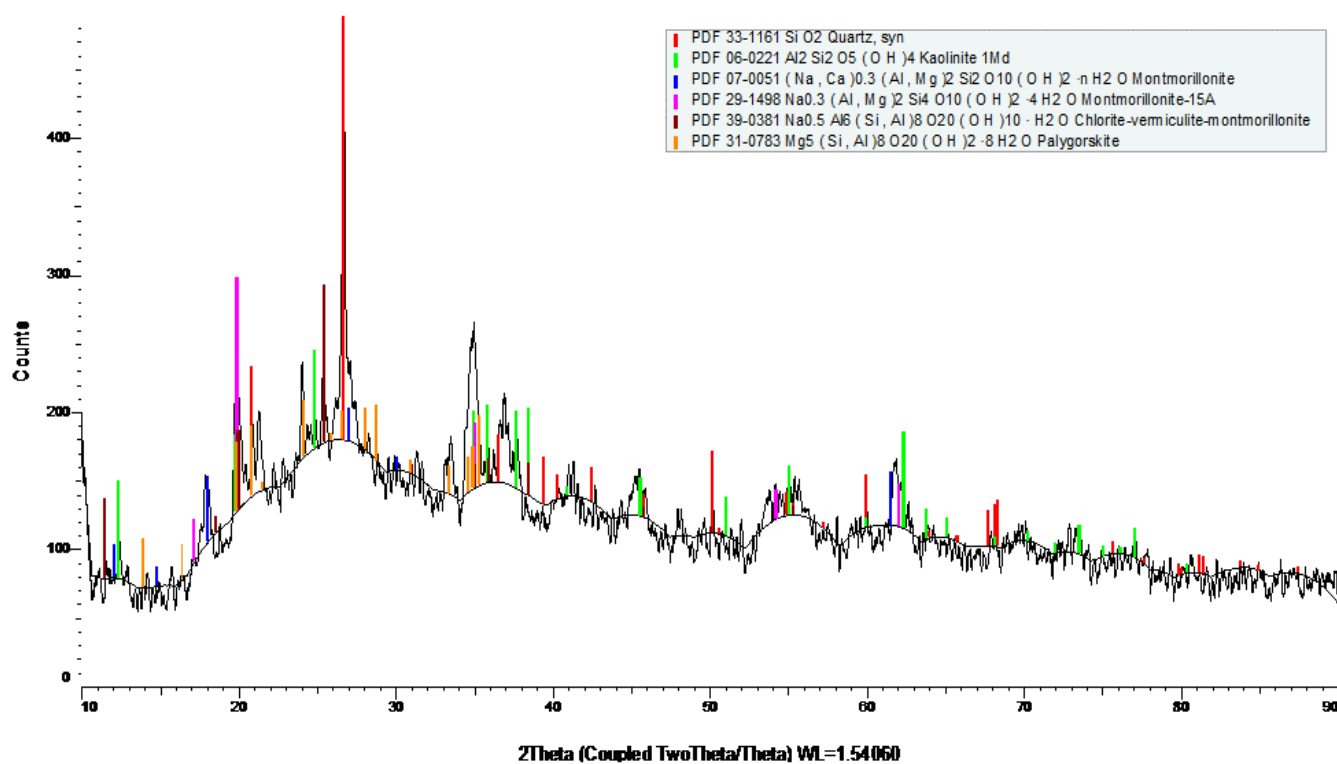
(a) IH: Ap horizon: 0 – 37 cm



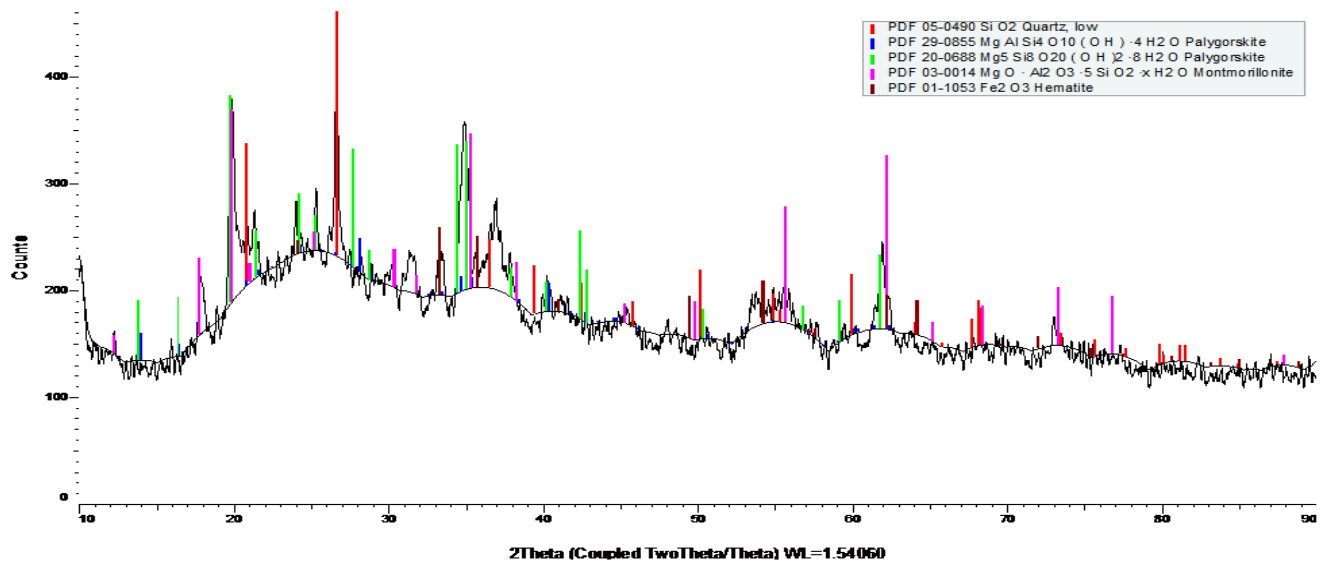
(b) IH: CBk horizon: 64 – 130 cm



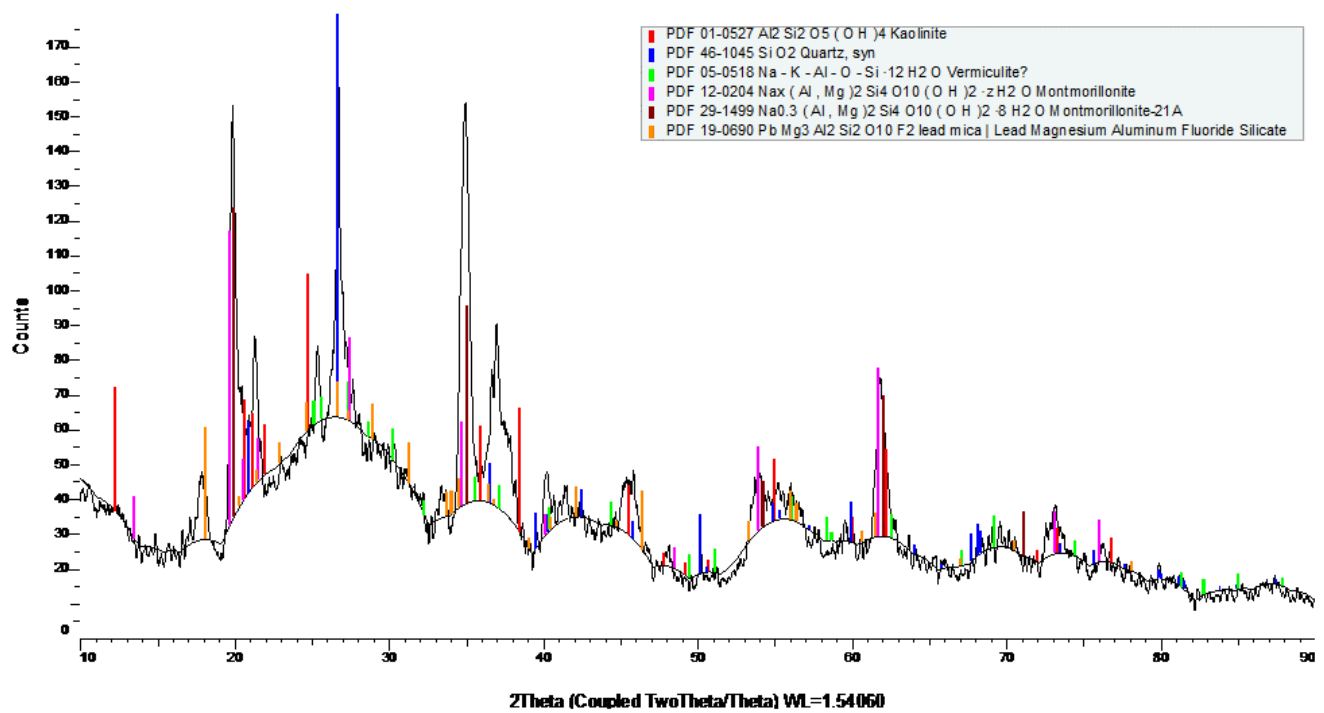
(c) IH: CB horizon: 130 – 195 cm



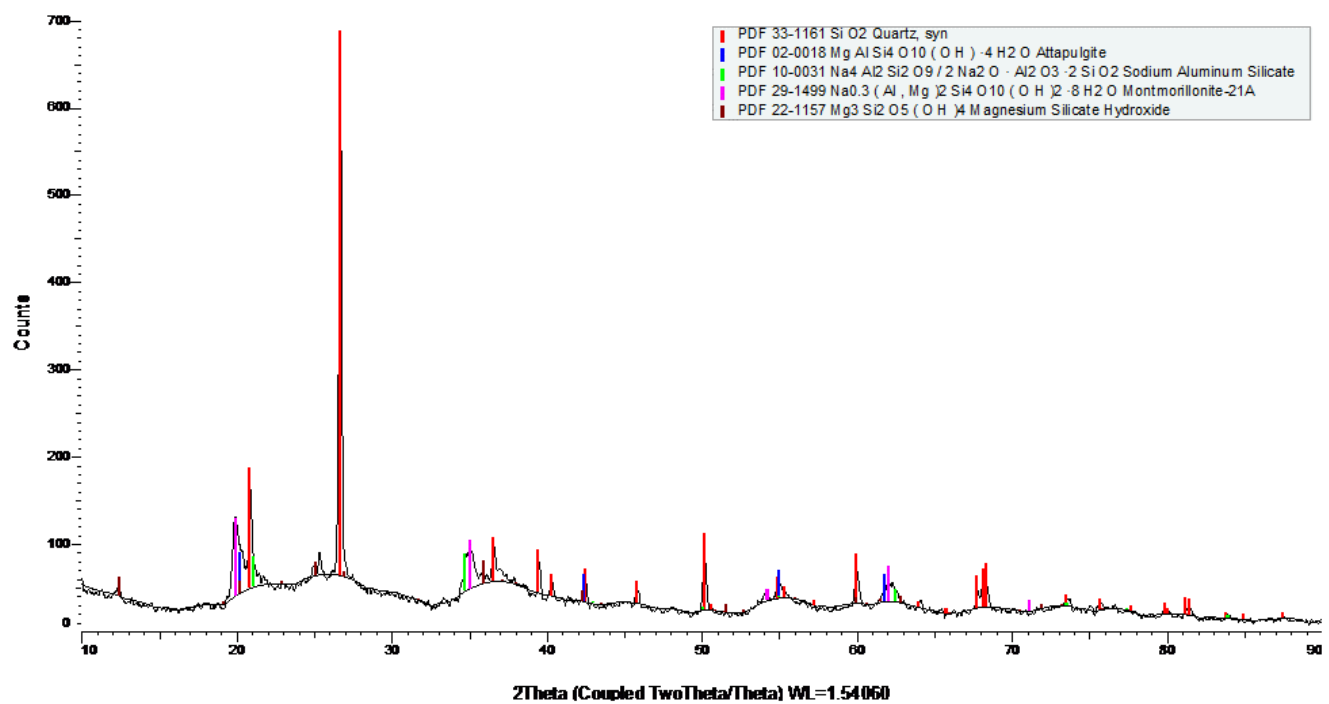
(d) AI: Ap horizon: 0 – 13 cm



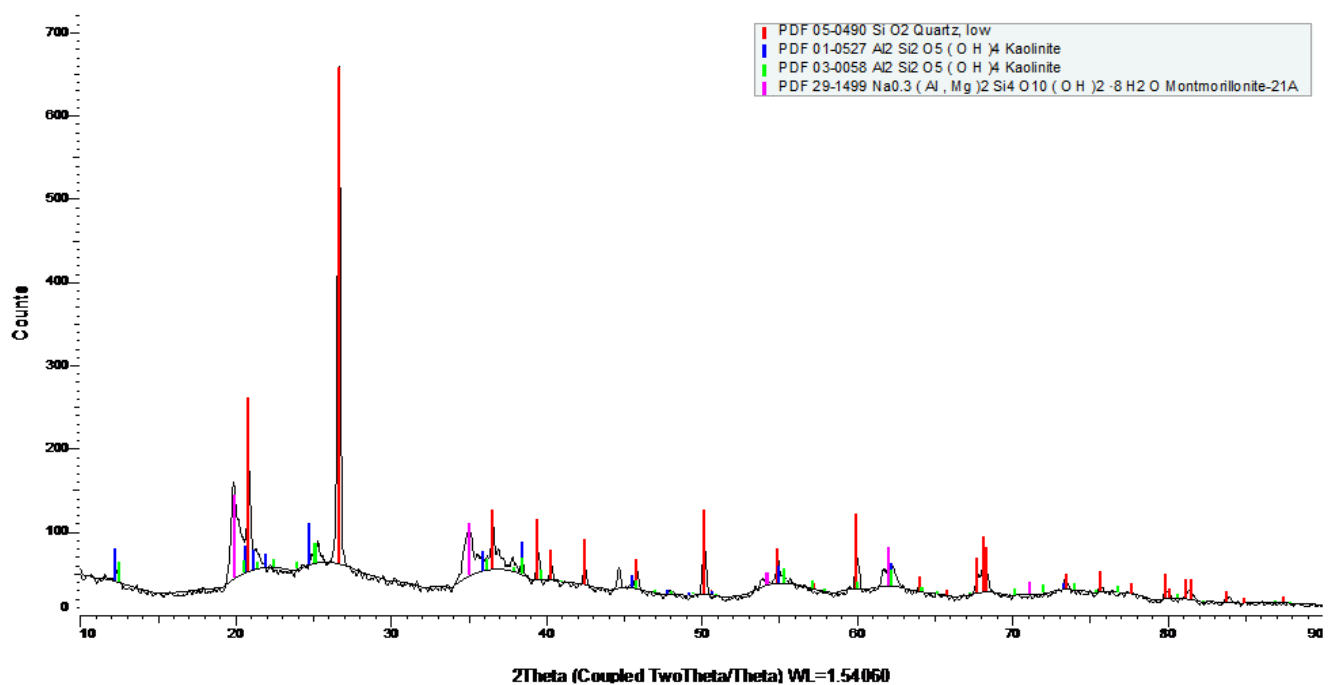
(e) AI: BC horizon: 60 – 82 cm



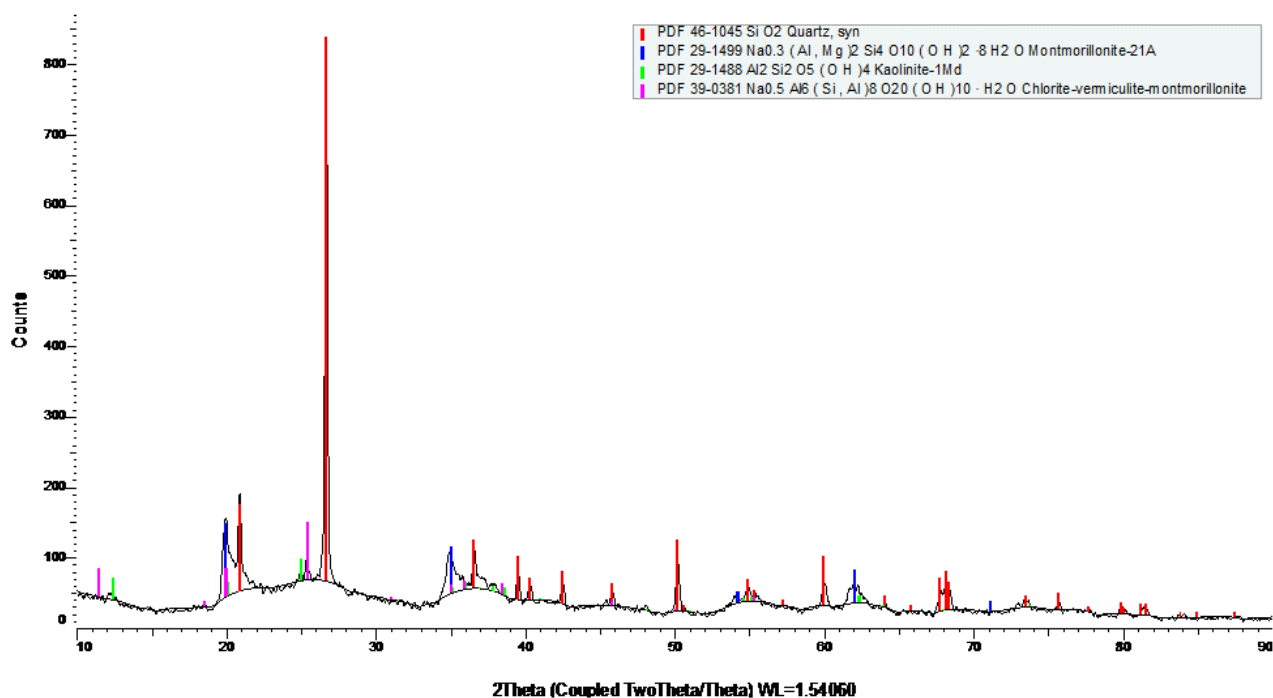
(f) AI: Ckt horizon: 82 – 132 cm



(g) MF: Ap horizon: 0 – 17 cm



(h) MF: Bt horizon: 17 – 56 cm



(i) MF: BC horizon: 56 – 121 cm

Fig. 2: X-ray diffractograms of the A, B, C horizons of the studied soils

Table 4: Distribution of clay minerals in the soil profiles

Soil Profile	Horizon	Depth	Q	K	M	V	P	C-V-M	H	N	m	Na-Al-Silicate	Mg-Al-Silicate
IH	Ap	0-37	xxx	Xx	xx	xx	xx		Xx				
IH	Bkt	64-130	xxx		xxx			xxx		xx		xx	
IH	CB	130-195	xxx		xxx			xxx				xxx	xxx
AI	Ap	0-13	xxx	xxx	xxx		x	xxx					
AI	BC	60-82	xx		xxxx		xxx		xxx				
AI	Ckt	82-132	xx	xxx	xxx	xxx					x(Pb)		
MF	Ap	0-17	xxxx										
MF	BC	17-56	xxxx	xxx	xxx								
MF	Bt	56-121	xxxx	xxx	xxx			xxx					

N/B: x: poorly represented (<7 %), xx: represented (7-15 %), xxx: abundant (15-30 %), xxxx: very abundant (> 30 %), M: montmorillonite, V: vermiculite, P: palygorskite, C-V-M: chlorite-vermiculite-montmorillonite interlayered structure, H: Hematite, Q: Quartz, K: Kaolinite, N: nacrite, m: mica

Discussion

General soil characteristics

The dominance of sand size particles over silt and clay can be traced to the intercalation of limestone with sandstone.

This implies an increase in infiltration rate, percolation and leaching of available nutrients away from plant roots zone,

and may cause nutrient enrichment of downslope water bodies, resulting in eutrophication. The deep accumulation of clay to a depth of >50 cm is attributed to prolonged pedogenesis. The process is slow and occurs over a long period (Krasilnikov et al., 2007) and is attributed to clay flocculation resulting from the accumulation of secondary carbonates (Ferreira et al. 2016). Comparatively higher values of organic carbon in AI and MF (tropical rainforests) compared to IH (southern guinea savannah) may be due to stalled mineralization against humification (Haynes, 2005). Similarly, Ferreira et al. (2016) attributed rapid mineralization to low organic carbon in limestone soils. Significant amounts of readily decomposed organic matter and enhanced nutrient release are greatly influenced by vegetations (Ofem et al., 2021). Though, exchangeable Ca^{2+} and Mg^{2+} dominated the soils' exchange complex, they were rated moderate in the studied soils mainly as a result of active dissolution and leaching processes facilitated by the impact of high rainfall in the area. Other researchers (Spalevic et al. 2017, Mukaetov et al. 2000) have reported the dominance of the adsorption complex of limestone soils by exchangeable Ca. High CEC by NH_4OAc in IH coincides and correlates with high clay, and not organic matter as in AI and MF. The implication is that, clay is responsible for high CEC in IH, while organic matter is responsible in AI and MF. Furthermore, base saturation in the endopedons of clay accumulation suggests that the soils are Alfisols.

Total elemental oxides content

a. Al_2O_3 : Comparatively higher values of Al_2O_3 in the endopedons of the studied soils were indicative of intensely weathered soil. This is because mobile Ca and Na released via weathering are easily leached in the tropical rainforests leading to the accumulation of Al_2O_3 . Consequently, soils in AI and MF were the most weathered as indicated by higher total mean and endopedons values. Its dominance is attributed to gibbsite-bearing minerals. Generally, the soils had Al_2O_3 accumulation in the endopedons because aluminum containing minerals would weather and be depleted in the epipedons resulting in its accumulated in the endopedons. Aluminum oxide depletion is favoured by $\text{pH} \leq 5$ (Chamayou and Legros, 1989) and goes on at a faster rate in the topsoil (Egli *et al.*, 2011) and becomes immobile at high pH (>5). As the intensity of weathering increase, Al_2O_3 accumulates (Duzgoren-Aydin *et al.*, 2002) in most tropical soils. Such accumulations may result in the formation of dominant crystalline form of Al_2O_3 (gibbsite) or aluminum toxicity in soils. This is a major constraint in crop production as it could result in reduced soil pH, heavy metal solubility and toxicity, as well as complexation with organic matter that inhibits crystallization (Hsu, 1989).

Girao *et al.* (2014) reported a 28.2-260.7 g/kg range for similar soils in Apodi plateau (Brazil) using a similar technique.

b. Fe₂O₃: The values of Fe₂O₃ were higher in the endopedons, especially in the tropical rainforest area (AI and MF), and indicate that the soils were more weathered and developed than those in IH. Weatherable minerals in the Ap horizons decompose and facilitate Fe-containing minerals' release and migration to the B horizons. Burt *et al.* (2003) attributed such Fe migration to cheluviation. As the soil advances in weathering, Ca, K and Si oxides are progressively leached, leaving behind TiO₂, Al₂O₃, and Fe₂O₃, which had comparatively remarkably higher values in all the studied soils. Values of Fe₂O₃ in the current study are within 10.1-99.6 g/kg range of values obtained by Girao *et al.* (2014) in the karstic soils of Apodi plateau, Brazil. Higher Al and Fe oxides and lower quartz in the epipedons of IH found in the southern guinea savannah than AI and MF in the tropical rainforest suggest relatively more active leaching of SiO₂ and accumulation of Fe₂O₃ and Al₂O₃ in IH.

c. MnO₂: The concentration of MnO₂ in the soils is less than 0.6 g/kg and closer to the lower limit of 0.05-7.75 g/kg recommended for calcareous soils. The somewhat low concentration may have been because of its presence in insoluble form. Moreover, most plants are affected by Mn concentrations of around 0.50 g/kg with toxicity experienced when soil pH < 5 in poorly drained conditions (Kabata-Pendias, 2011); however, when complexed with organic matter or under conditions of low pH, it may be soluble and present in available form (Lindsay, 1974). Most readily available Mn is present in acid and flooded soils with decreasing concentration when soil pH increases. When MnO₂ falls within the range of 1.6–50 g/kg, it rather exists as ferroxhyte instead of forming its minerals (Vodyanitskii *et al.*, 2004). Complexation reactions involving MnO₂ reduce the incidence of toxicity as the oxide is released in only quantities required for environmental tolerance (Tan and Binger, 1986). Values of MnO₂ in the studied soils were within 0.15-1.95 g/kg reported by Girao *et al.* (2014) for similar soils in Apodi, Brazil.

d. ZrO₂: The low concentration of ZrO₂ occurring in amounts less than 1.0 g/kg and decreasing in the endopedons indicate that zirconium minerals were resistant to weathering as to deplete the epipedons for subsequent movement to the endopedons. Regular or irregular decrease in the B horizons before a subsequent increase in values, mainly in the C horizons, indicates that time had not permitted the movement of ZrO₂ (due to the resistance of the mineral to weathering) to be illuviated in the endopedons. Even in small amounts, the presence of ZrO₂ in soils indicate its resistance to weathering. Zircon is resistant to weathering and provides a measure of chemical stability (Schaetzl and

Anderson, 2005), and often occurs mainly in highly weathered soils. Its content in the soils under study appears to be low and translates to poorly weathered soils.

e. TiO_2 : Decrease in the values of TiO_2 in the B horizons resulted in inward bulges (decrease in values in the B horizon) as soil depth increases. Translocation of soil materials including TiO_2 to other soil horizons is time bound. The inward bulges imply that TiO_2 has not had sufficient time to be illuviated in sufficient amounts in the endopedons. Values obtained in the tropical rainforest (AI and MF) were within 1.33 – 7.26 g/kg reported by Girao *et al.* (2014) in Apodi plateau, Brazil, while those in the southern guinea savannah (IH) were lower. According to the Soil Survey Staff (2014b), most tropical soils have the contents of TiO_2 to be less than 40 g/kg. The comparatively low values in the studied soils indicate that the soils have not attained the oxic state of soil development. Though with not so much variation with soil depth, probably due to its less mobile property (Curi and Franzmeier, 1987), the endopedons had comparatively higher values of TiO_2 than the epipedons, an indication that the endopedons were more intensively weathered than the surface soils. As weathering and pedogenic processes become intensified in tropical soils, TiO_2 increases or remains unchanged in soils (Duzgoren-Aydin *et al.*, 2002). TiO_2 is immobile in soils because it is poorly weathered or resistant during pedogenesis (Egli *et al.*, 2011), hence its low amount. However, it resides in rutile and other Ti-bearing minerals, and very small amounts in soil could imply intense weathering. The metal is recyclable and comparatively environmentally friendly, however, high concentrations of titanium dioxide in water bodies can be harmful to aquatics.

f. SiO_2 : The accumulation of SiO_2 in the endopedons suggests losses in the Ap horizons. Values seem to decrease with increasing soil depth in AI and MF as against IH, and show that the soils may not have had sufficient weathering time to warrant the loss of SiO_2 . The amount of pedogenic silica increases with increasing duration of weathering, and the depth of maximum silica accumulation coincides with the maximum expression of argillic horizon (Kendrick and Graham, 2004). SiO_2 may have been leached from the epipedons as it is a 'mobile soil component' and a major component of organic matter which often dominates organic-rich soils (Duzgoren-Aydin *et al.* 2002). Higher values of SiO_2 than Al_2O_3 as it was noticed in all the studied soils foretells poor silica solubilization and subsequent removal from the soils, with the resultant formation of kaolinite. High accumulation of SiO_2 in the soils may be due to high sand content which has quartz as a dominant mineral. It may reduce heavy metal toxicity in plants and increase crop yield in P deficient soils by decreasing the availability of Fe and Mn in plants (Ma, 2004). When silica content in soils

is higher than iron and aluminum oxides, it indicates that the soils are not highly weathered (Yakubu and Ojanuga, 2013). With increasing weathering intensity, silica is progressively leached and the contents in iron and aluminium oxides relatively increase. Similarly, Bohn *et al.* (2001) and Sharma *et al.* (1996) opined that highly weathered soils contain less silica and more Fe and Al oxyhydroxides which tend to accumulate. The dominance by SiO₂ indicates that the soils are not highly weathered.

g. CaO: High rainfall and temperature associated with the studied soils in the humid tropical area had encouraged chemical weathering, dissolution, and subsequent loss to leaching of the highly mobile CaO, resulting in trace values in the epipedons and low values in the endopedons. Weathering and translocation have been identified as key sources of losses of CaO in soils (Pavitch, 1989), while Petar *et al.* (2016) and Ofem *et al.* (2020) reported dissolution and leaching of alkaline earth carbonates as common pedogenic processes in the soils formed on limestone. Similarly, calcium is hosted by plagioclase (Nesbitt *et al.*, 1980, Babechuk *et al.*, 2014); a mineral whose refractive index increases with an increase in the proportion of calcium ((SSS, 2014a). Consequently, the low to trace content of CaO in most of the soils could also be as a result of low or absence of plagioclase even in the clay mineralogy. This may have a negative impact on the fertility status of the limestone soils and by extension on the crops in the humid tropics as it is involved in the creation of stable granular structures and insoluble Ca-humates complex.

Forms of Fe and Al

a. Dithionite Extracted Fe (Fed)

An increase in Fe_d in the B horizons of AI and MF (in the tropical rainforest) indicates intensified weathering compared to IH (in the southern guinea savannah), which had carbonate accumulation suggesting relatively more intensified weathering. Higher values in the endopedons align with the findings of Juo *et al.* (1974), that Fe_d in most Nigerian soils increases with soil depth. IH's comparatively higher profile mean value does not depict more intense weathering conditions or soil development. It is rather due to higher values in the epipedon arising from the low weathering of minerals in the horizon. In AI and MF, chemical weathering of ferromagnesian minerals in the epipedons may have given rise to free Fe which moved to the endopedons by eluviation. The eluviation-illuviation process occurs over

time and results in the depletion of the epipedons of Fe_d . Increasing soil development, weathering and age align with the increase in concentration of Fe_d as weathering intensifies (Schwertmann, 1993; Dolui and Bera, 2001).

The accumulation of Fe oxyhydroxides as weathering intensifies and soil development progress may not be true in all sense as the highest concentration of Fe_d in IH, had no indications of the migration or movement of Fe_d from the epipedons to the endopedons. However, the trend with increasing soil depth indicates accumulations in the endopedons of AI and MF. On this basis, AI and MF may be regarded as the most developed. The values of Fe_d exceeded Fe_o in all horizons in the soils studied and indicates that a considerable fraction of Fe is present in crystalline form (Dolui and Mondal, 2007).

b. Oxalate extracted Fe (Fe_o)

Relatively high values of Fe_o obtained in the B horizons may be due to the presence of amorphous forms of Fe oxides, or the Fe may have been complexed with organic matter and moved to the endopedon. Also, high concentrations of Fe_o in the endopedons may be due to the expressive occurrence of low crystalline hydroxides in the illuvial horizons resulting from the dissolution of minerals in the epipedons by ferrolysis. Such minerals are dissolved in the epipedons and accumulated in the endopedons (da Silva *et al.*, 2019). According to Osayande *et al.* (2013) and Obi *et al.* (2009), non-crystalline or amorphous forms of Fe are associated with soil organic matter. In the findings of Juo *et al.* (1974), Fe_o either decreases or increases with soil depth in Nigerian soils. Fe_o was low as values were less than 2.0 g/kg, as reported by Wilson *et al.* (2017). The low values may also be due to high temperatures (> 22 °C) responsible for low contents of amorphous Fe (Juo *et al.* 1974). Raised temperatures enhance dehydration of Fe oxides and cause a shift to a system of lower crystallinity (Sherman *et al.*, 1964). According to Seal *et al.* (2006), Fe_o is more in the illuvial horizons of soils, while a range of 0.39-4.35 g/kg was reported for soils over limestone in the Apodi plateau (Girao *et al.* 2014).

c. Crystalline form of Fe (Fe_c)

IH had the highest mean values of Fe_c and is expected to be more developed and weathered. However, there was no obvious movement of the crystalline form of Fe down the profile. On the other hand, in AI and MF both found in the tropical rainforest, mean values of Fe_c were comparatively lower but with clear indications of an increase in the B horizons (the formation of bulges in the B horizons) indicating the accumulation of Fe_c . With increasing soil age, the

crystalline iron oxides increase at the expense of poorly crystalline forms (Seal *et al.*, 2006). Regions with higher temperatures and prolonged dry season (4-5 months) often facilitate the formation of Fe_c (Seal *et al.*, 2006). This is a probable reason for the comparatively higher values in IH.

d. Activity ratio of Fe (Fe_a)

Higher values of Fe_a in IH and MF relative to AI may be described as more active and coincide with higher clay amounts, particularly in IH. Clay amount and type may be responsible for a higher activity ratio. The highest values of Fe_a were recorded in the B horizons of soils over IH, while in soils over AI and MF, the highest values were obtained in the epipedons. Similar findings were reported by Jonczak *et al.* (2015) in humus-rich and slightly acid topsoils, while Cornell and Schwertmann (1979) posited that acid soil reactions and humic substances do not favour free Fe oxides crystallization. Furthermore, Wilson *et al.* (2017) reported Fe_a with values of less than 0.18 as low, while Seal *et al.* (2006) reported low values when Fe_a is less than 1. Low values indicate that free Fe oxides in the soils are at an advanced stage of crystallinity or aging (Mahaney *et al.*, 1991). The authors further implied the dominance of crystalline Fe oxides in the pedogenic Fe fraction of the soils. In the present study, the soils had values of Fe_a less than 0.18, and reflect high crystallinity. Also, when the values of Fe_a are within 0.09-0.33, a high degree of free Fe oxide crystallization is inferred (Jonczak *et al.*, 2015). Fe_a in the solum is low when values are < 1 (Seal *et al.*, 2006), and indicates that the Fe_a of the studied soils was low. Such low values indicate that free iron oxides in the soils are at an advanced stage of crystallinity or aging (Mahaney *et al.*, 1991). This implies that AI was more intensely weathered or developed as they had the least mean values. It further suggests that weathering had progressed to an advanced stage or the soils were older (Seal *et al.*, 2006).

e. Co-migration of clay with Fe (Fe_{co})

Fe_{co} increased in the B horizons resulting in the formation of bulges. An increase in Fe_{co} with soil depth suggests that the soils had sufficient time to warrant the movement of clay in the company of Fe down the profiles. In soil profiles with distinct soil horizons, the Fe_{co} increases with soil depth (Dolui and Bera, 2001). Most of the weathered Fe-bearing minerals in the epipedons may have released Fe that had moved in the clay company to the endopedons. However, mineral weathering in IH was low with less pronounced bulge and reduced rate of migration of Fe down the profiles, hence, the co-migration of clay with Fe_d was not sufficient to be identified. When Fe_{co} decreases with soil depth, the implication is that Fe movement is partially independent of the movement of clay (Juo *et al.*, 1974). According to Juo

et al. (1974), the trends of Fe_d and clay are similar in most Nigerian soil profiles. Aubert and Segalen (1966) reported the combined movement of clay and Fe from epipedons with the resultant formation of distinct argillic horizons.

f. Dithionite extracted Al (Al_d)

The values of Al_d in IH portrayed a decrease in values with soil depth and indicates that Al-containing minerals in the epipedon have not had sufficient time to weather and release the oxides to the endopedons and further translates to poorly weathered soils. Conversely, in AI and MF, values of Al_d increased with increasing soil depth, bulging in the B horizons. This suggests more exposure to pedogenetic processes, weathering, and migration of Al compounds to the B horizon. The value reported for Al_d is far less than those obtained for Fe_d and negates findings by Jonczak *et al.* (2015). They observed that Al_d was twice as high as Fe concentration. This implies the dominance of Fe-bearing weatherable minerals over aluminosilicate minerals.

Higher values of Fe_d and Al_d in the epipedons may also imply the ease of the fraction to chelate with organic ligands (Wagai *et al.*, 2020). When the oxides of Al and Fe are released *via* weathering, they react with organic ligands and are rarely lost to leaching. Tsozue *et al.* (2009) reported the highest values of Al_d in the humic horizon.

g. Oxalate extracted Al (Al_o)

Comparatively high Al_o in the Bt horizons is attributed to the expressive presence of low crystalline hydroxides due to illuviation. In this case, soil minerals are dissolved by ferrolysis in the epipedons and get accumulated in the endopedons. The values of Al_o in the current study are low and seem to have been influenced by the high temperatures in the tropics. According to Juo *et al.* (1974), high temperatures may be responsible for the low content of amorphous Al. High temperatures cause amorphous Al oxides to dehydrate and shift to a system of greater crystallinity (Sherman *et al.*, 1964). Dehydration and crystallization are important factors controlling the presence of amorphous materials in tropical soils (Juo *et al.*, 1974).

Mineralogy of the clay fraction

a. Quartz

Quartz was the most abundant and distributed minerals in the studied soils, with dominance in the Ap and C horizons. The high quartz content may have been inherited from sandstone which commonly intercalates with limestone in the study areas since most minerals in parent materials are transferred to the overlying soils upon weathering. This might be a probable reason why the quartz was higher in the C relative to the B horizons. Its presence in the B horizons may be due to translocation during soil formation.

The small to no CEC of most quartz dominated soils is attributed to the Si-O broken bonds and Si-OH groups on particle edges, as well as its small surface area. Soil water retention, CEC, pesticide adsorption, and some biological processes are reliant on the specific surface area of soils minerals. The preponderance of quartz and its relative accumulation have an adverse effect on the overall fertility condition of the soils, and may require the application of fertilizers for agronomic crop growth. Such silication and raised values of quartz may imply slow weathering potential of the soil. This is consistent with results obtained by XRF, which indicated the dominance of SiO₂ over other soil oxides.

Quartz was obtained by Kowalska *et al.* (2017) in the carbonate-rich soils of South Poland as the main mineral phase. Mota *et al.* (2007), and Moreira *et al.* (2000) also reported quartz in soils formed from calcareous materials in the Apodi plateau, Brazil. However, Ferreira *et al.* (2016), described its occurrence in soils over limestone as 'accessory' and further stated that its abundance depends on the purity of the rock. This further explains its non-uniformity in abundance across the three soils studied.

b. kaolinite

Higher values of kaolinite in the horizons of clay accumulation (Bt and Ckt) relative to the transition, Cr, and Ap horizons indicate intense soil weathering. The dominance of kaolinite in the studied soils, especially in the tropical rainforest (AI and MF) indicates the effect of vegetation and rainfall on clay mineral distribution and fortells, that most of the weatherable minerals with significant negative charges have been removed through hydrolytic weathering, leaving very low negatively charged kaolinite as the dominant crystalline mineral. This has led to prolonged and advanced weathering in the tropical rainforest soils (AI and MF), giving rise to kaolinite and sesquioxidic minerals. Kaolinite is the end product of clay weathering in limestone soils (Ross and Hendricks, 1945) and may have originated from the transformation of the micas, and other secondary minerals or by neoformation through recombination of Si in solution. Furthermore, illite may have been altered, resulting in the formation of kaolinite (Tan, 2011). Tropical

soils are known to be dominated by kaolinite (Ofem *et al.*, 2020., Ofem and Esu, 2015) which has low CEC and contributes little to the activity of soils and by extension the chemical fertility of the soils. Compared to smectite ($810 \text{ m}^2 \text{ g}^{-1}$), kaolinite ($20 \text{ to } 40 \text{ m}^2 \text{ g}^{-1}$) has a smaller specific surface (SSS, 2014a) for the adsorption of nutrients with a less capacity to “fix” significant amounts of N compared to soils dominated by vermiculites and illites (Young and Aldag, 1982). Durn (2003) in the Mediterranean region, Irmak *et al.* (2007) in the karst environment of Apordi plateau, Brazil, and Petar *et al.* (2016) in Pivska Planina have variously reported the occurrence of kaolinite in limestone or carbonate soils.

Nacrite was found in a represented amount in the CBk horizon of IH. The transition from kaolinite to dickite and then nacrite at raised temperatures has been documented (Katsumi, 1989). The presence of nacrite in the Flood plain soils of Onwu River was reported by Akpan-Idiok and Ogbaji (2013). Nacrite, together with kaolinite and dickite have similar chemical compositions: 46.5 % SiO_2 , 39.5 % Al_2O_3 , and 13.9 % H_2O , leading to the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. However, nacrite has a different stacking sequence and was earlier interpreted as a 6-layered structure and later as a 2-layer structure in which the X and Y axes interchange (Brindley and Brown, 1980).

c. montmorillonite

Montmorillonite was more abundant in the endopedons relative to the epipedons. The wide distribution of montmorillonite in the soils implies that it is the original mineral in the limestone soils and it is transformed during soil development under the influence of leaching to kaolinite and chlorite. However, findings in the current study negate those of Deepthy and Balakrishnan (2005), who posited that minerals in the smectite group are scarce in soils formed from karst in older landscapes with good drainage. Montmorillonite is high activity and expanding clay mineral that is most likely to impart high-base status and natural fertility to the soils. Montmorillonite had earlier been obtained at various abundances in similar soils by Irmak *et al.* (2007) and Yilmaz (1990). Montmorillonite is active in the elimination of contaminants from solutions. It has performed well towards wastewater, dyes, pharmaceuticals, heavy metals, and other organic and inorganic contaminants remediation (Zango et al. 2022).

d. Palygorskite/attapulgit

In the southern guinea savannah (IH), the abundance of palygorskite indicates that it was only represented in the Ap horizons with occurrences in the Ap and BC horizons of AI in the tropical rainforest, while attapulgit was identified

in the Ap horizon of MF (in the tropical rainforest). It is important to consider such clay mineral variation with vegetation type and rainfall amount during land use planning. Both minerals are synonymous terms for the same hydrated magnesium aluminum phyllosilicate and have a 2:1 structure. One may state that palygorskite and attapulgite are most likely obtained in the epipedons of limestone soils where clay is poorly accumulated. Palygorskite was reported in some limestone-derived soils of southern Iran (Emadi *et al.*, 2008) and has been identified as the second most abundant mineral in the karstic soils of Apodi plateau, Brazil (Irmak *et al.*, 2007). Emadi *et al.* (2008) traced its origin in limestone soils to inheritance, neoformation, and transformation from other minerals in limestone areas. However, Bautista *et al.* (2011) obtained a trace of the mineral in the tropical karst of Yucatan, Mexico, while Krekeler *et al.* (2010) obtained it in good measures in similar soils. Palygorskite in the studied soils seems unstable and easily weathered to more stable minerals like kaolinite and quartz. It has been found to exist naturally in other parts of the world and has been explored for environmental remediation applications (Lazaratou, 2020).

e. Pb-mica

Micas were quite scanty and unevenly distributed in the studied soils and poorly represented in the Ckt horizon of AI, found in the tropical rainforest area. Micas in the Ap horizons of the studied soils have been weathered as the high rainfall in the area encourages intense weathering. Micaceous minerals are common in calcareous materials and soils. In the Apodi plateau, Brazil Ferreira *et al.* (2016) obtained small amounts of mica as interstratified illite-smectite in the carbonate-rich soils' clay fraction.

f. Vermiculite

The low and scanty amounts of vermiculite in the studied soils may be attributed to relatively high soil pH and low activity of Al^{3+} in the soils. At advanced soil age, illite weathers to vermiculite. This may have been a probable reason for the poor identification of illite in the soils. Vermiculite is a 2:1 expanding clay mineral with high CEC and the potential to adsorb soil nutrients for enhanced plant nutrition. Its availability in the soil, even in small quantities, will improve the fertility status of the soils. Fe-coated vermiculite composite has been reported to effectively contribute to the passivation of As/Cd at different pollution levels in soils (Yingbo *et al.* 2020). In the soils formed over massive limestone in Pivska Planina, the clay fraction was dominated by vermiculite (Petar *et al.*, 2016). Similarly, Cabadas-Baez *et al.* (2010) in Northeast Yucatan, Mexico and Sedov *et al.* (2008) in the Phaeozems from tectonic karstic plains

had reported vermiculites in limestone soils, while in southern Iran, Emadi *et al.* (2008) reported very low vermiculite within the range of 1-6 % in soils of calcareous origin.

g. Interstratified chlorite-vermiculite-montmorillonite (C-V-M)

The interlayered structure (C-V-M) increased in the endopedons of the soils. The abundance of the mineral decreased as rainfall amount increases from the southern guinea savannah (IH) to the tropical rainforest (AI and MF), and indicates the effects of vegetation and rainfall on the mineral distribution. The interstratification of the minerals is such that, chlorite, vermiculite, and montmorillonite are stacked in various ways to result in C-V-M, which is different from the individual components. The combinations are made possible due to the similarity in structure between the components which are all made of tetrahedral and octahedral sheets, and are ferromagnesian minerals. Distinctions among smectite, vermiculite and chlorite in thin sections are seldom possible (SSS, 2014a). They are usually mixed in the soil, seldom occur in pure form, and mixed with ferrous compounds and humus as complexes. Amongst the available literature, no such combination of C-V-M was reported in soils developed from limestone. However, the addition of modified vermiculite-montmorillonite can achieve remediation of coal gangue-containing soil (Li *et al.* 2022). Coal gangue is a solid waste produced during coal mining, and includes hazardous substances that contain potentially toxic trace elements (Li *et al.* 2021). chlorite was reported in limestone soils by Intamo *et al.* (2014) in Western Thailand, Petar *et al.* (2016) in Pivska Planina and Emadi *et al.* (2008) in southern Iran.

h. Hematite

Hematite was scanty in the studied soils, however, it was found in represented and abundant ranges in the Ap and BC horizons of IH and AI, respectively. The presence of hematite in tropical soils, irrespective of the lithology is common and signifies advanced soil development, prolonged and intense weathering. High temperatures favour the formation of hematite (Kampf and Curi, 2012), while high pH in carbonate-rich soils facilitates its precipitation (SilvaNeto, 2008; Tardi and Nahon, 1985). It has been reported in the karstic plains of Yucatan (Bautista *et al.*, 2011) and the karstic landscapes of Brazil (Mota *et al.* 2007; Moreira *et al.* (2000).

Conclusions

The soils under study are formed *in situ* from the underlying limestone bedrock. The differences in mineral species between the studied soil profiles suggest that the soils were affected by the differences in vegetation and rainfall regimes resulting in more developed soils in the tropical rainforest (AI and MF). The predominance of quartz and kaolinite in the soils reflects the influence of the intercalated sandstone. However, the wide distribution of montmorillonite implies that it is the original mineral in the limestone soils and it has immediate agronomic effects on the CEC of the soils. The sequence and concentration of elemental oxides as well as the abundance of clay mineral type change when vegetations change. For instance, the amounts of Fe_2O_3 and Al_2O_3 are more in the epipedon of IH (in the southern guinea savannah) with higher profile means but do not show that movements of materials have been made to the endopedons, a condition that has been met by soils in the tropical rainforest (AI and MF). Furthermore, CaO which we anticipated high values for, was grossly affected by dissolution and leaching, resulting in trace to low values. We can conclude that AI and MF occurring in the same tropical rainforest have similar characteristics and are different from IH (found in the southern guinea savannah). This, in turn, qualifies AI and MF as more intensely weathered. Therefore, There is there need to keep a periodic check on the elemental oxides and other pedological properties to ensure that, the tolerable limits for crop production and soil organisms' acceptability are not exceeded as the studied soils transit the intermediate to complete stage of weathering.

Though XRF technique allows deeper penetration of x-rays into sample bonds than the chemical extraction procedures, it neither identifies nor reports the abundance of clay mineral species. On the other hand, XRD identifies mineral species, but is more expensive, procedural and may not provide the basic details that chemical extraction provides for recommendation on fertilizer application and land use planning. Therefore, combining the techniques in pedological studies provide a more reliable set of data.

Author contribution statement

Kokei Ikpi Ofem and Mark Pawlett designed and wrote the initial paper. Kingsley John and Victoria Francis Ediene analysed the soil samples and did initial grammer check, while Victor Ikemefuna Ezeaku and Alungbe Moses Ede organized the data, references and prepared Fig. 1. Patrick K. Kefas and Kokei Ikpi Ofem were involved in field study and processing of soil samples. All authors reviewed the manuscript.

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Data availability statement

The data used in the current study are available on reasonable request from the corresponding author.

Declaration statement

All Authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities” as found in the instructions for Authors.

Competing interest statement

The authors declare that there are no competing interests.

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Pedological data for the study of soils developed over a limestone bed in a humid tropical environment

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