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Influence of forms of iron and manganese oxides on the physical and chemical properties of soils formed over mica-schist in a Northern Guinea Savanna, Nigeria

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ABSTRACT

Three forms of oxides of iron and manganese were evaluated on soils developed in mica-schist lithology within the basement complex formation of Taraba State, North-eastern Nigeria. The results from the three oxide forms namely; pyrophosphate extractable (Mn_p/Fe_p), oxalate extractable (Mn_{ox}/Fe_{ox}) and citrate-bicarbonate-dithionite extractable (Mn_d/Fe_d) examined were subjected to both descriptive and inferential statistics to analyse their trend and distribution in order to understand their influence on pedogenesis. Content of the three forms of manganese oxides were lower than those of the respective iron oxides (Mn_p : mean – 100.44 $mg\ kg^{-1}$, Mn_{ox} : mean – 128.72 $mg\ kg^{-1}$, Mn_d : mean – 144.96 $mg\ kg^{-1}$ and Fe_p : mean – 1212.30 $mg\ kg^{-1}$, Fe_{ox} : mean – 1305.20 $mg\ kg^{-1}$, Fe_d : mean – 2518.00 $mg\ kg^{-1}$) at their corresponding horizons; and was attributed to the mineralogical constitution of geology of the study area. Content of organic matter (mean, 0.632 %) and organic carbon (mean, 0.366 %) were low (but highly significant - $F = 2502$, $p = 216^{***}$) and was attributed to high mineralization rate caused by climate of study area (northern guinea savanna); thus, had proportional effect on the oxalate extractable Fe and Mn as they are organic bound. Also, a strong significant difference ($F = 187.6$, $p = 7.777^{***}$) between means of Mn_{ox} and Mn_p emphasized reciprocity in their pedogenic interaction. High content of Fe across the three oxide forms examined presupposes high plinthization on soils of the mica-schist.

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1.0 Introduction

The northern guinea savanna is one of the most intensively farmed areas in Nigeria. Nearly 80 % of West African land surface is covered by savanna vegetation (Sanford *et al.*, 1980). According to Jagtap (1995), FAO (1978) and Kassam *et al.* (1975), farmers' choice of the area may have been as a result of the favourable solar radiation during growing season, reliable and well distributed rainfall, and lower night temperatures that promote litter accumulation. Lithology has major influences on the properties of overlying soils and provides a starting material upon which other soil forming factors act to give rise to soil. It also influences the nature and properties of soil (Esu, 2010, Ibanga, 2006). Consequently, soils formed over a lithology have specific properties, support specific crops and result in a lithosequence of soils (Usul and Dengiz, 2010; Maniyunda, 2012). It is a major determinant of soils response to

management (Olaniyan *et al.*, 2011). Soils in the northern guinea savanna are mainly developed on the Basement Complex. The complex is made up of migmatite gneiss, schist, older granite and under formed acid dykes (Obaje, 2009) and mainly constitutes igneous and metamorphic rocks, and occupy 50 % of the Nigerian surface area (Ogezi, 1977).

Soils in the Nigerian guinea savanna are generally slightly acid, less leached, coarse textured and consist of sandy loam or loam over gravelly clay loam (Esu and Ojanuga, 1985) with lower clay content in the surface soil (Lawal *et al.* 2013) and are predominantly derived from crystalline Precambrian Basement Complex rocks. Soils of the savanna region are fragile (Salako, 2003) with large proportion of sand and low organic matter content (Adewale and Odoh, 2017) and are gravelly and shallow (Adeoye and Mohammed-Saleem, 1990., Salako *et al.*, 2002) in some

parts with low nitrogen content (Salako *et al.*, 2002). Esu (2010) attributed the low organic matter in the surface soils of the Nigerian Savanna to the rapid rate of mineralization of organic matter and the high degree of sheet erosion as well as the use of grasses in the region for roofing and grazing. Maniyunda *et al.* (2013) attributed the moderate and high variability in soil properties in a lithosequence in the area to land use, management and cultural practices.

Luvisols have been identified as the most common soils in Northern Guinea Savanna of Nigeria (Salako, 2003), while Ogungbile *et al.* (1999) classified similar soils as lithisols. However, Salami *et al.* (2011) described them as potentially fertile, while available P, organic matter, acidity and sand-silt components varied widely within the area. Similarly, textural and fertility variation were reported for the area by Okogun *et al.* (2004). Consequently, soil fertility decline among many factors was identified as the most remarkable for low yield among many factors (Salami *et al.*, 2011., Olaniyan, 2015). In a related study, Babalola *et al.* (2019) reported a significant difference in texture between parent materials, indicating the relevance of lithosequences and their influence on soil. Albeit, the fertility status of soils is bound to change when lithology changes and most likely to affect the type of crops supported by the soil.

The presence Fe-Mn concretions in the subsurface soils of the northern guinea savanna of Nigeria have been observed by Babalola *et al.* (2019). Oxides, hydroxides and oxy-hydroxides of Fe, Mn, Al and Ti are together referred to as sesquioxides (Maniyunda *et al.*, 2015). They are commonly present as amorphous, crystalline and organic complexes. Pedogenesis as well as soil physical and chemical properties are influenced by the nature, amount and occurrence of these oxides in soils (Schertmann and Taylor, 1989., Jelic *et al.*, 2011) and have been used to make predictions of the degree and stage of soil genesis (Durn *et al.*, 2001; Igwe *et al.*, 2001; Osodeke *et al.*, 2005; Kefas *et al.*, 2020). For instance, phosphorus is barely available in highly weathered tropical soils (Igwe, 2001) while high Ca availability may result in low solubility of manganese (Troeh and Thompson, 1993). The influence of the oxides and hydroxides of Fe-Mn on soil physical as well as chemical properties cannot be unattended in studies related to agricultural soils.

Agricultural production in the Nigerian northern guinea savanna is focused on crop and livestock production. Crop production in the area is dominated by cereals (millet, sorghum, maize and wheat) and legume (cowpea, groundnut

and soybean) production (Ajeigbe *et al.*, 2010; Foli, 2012). Though livestock is important in the farming system of the area (Smith *et al.*, 1997), it is often integrated with crops (Foli, 2012) as both have reciprocal benefits. Importantly, farmers in the region combine organic and inorganic inputs as well as intercrop cereal-legume mixtures to consciously manage and improve soil fertility status (Harris, 1998., Hoffmann and Gerling, 2001). The need for a robust soil data base has necessitated the present study. Earlier, Raji *et al.* (2000), Igwe (2001), and Ibia (2002) emphasized the forms of oxides in northwest Nigeria, flood plains of Niger, and southeast Nigeria, respectively. The present study goes beyond pedogenesis to assessing the influence of the forms of Fe and Mn on soil physical and chemical properties in the northern guinea savanna of Nigeria.

2.0 Materials and methods

2.1 Location, geology and climate of the study area

The study was conducted in Taraba State (6°30' and 9°30' N; 9°00' and 12°00' E), north eastern Nigeria. The State has a total land area of 60,291.8 km². Bauchi and Gombe states are located in the north, while Adamawa is in the east of Taraba state. To the south is the Republic of Cameroon, while Benue, Nasarawa and Plateau states are in the western axis. The geology of the study area is undifferentiated Basement Complex rocks with the occurrence of rocks identified as Precambrian granitic, migmatite gneisses and mica-schist with outcrops of the rocks occurring at intervals (Bawden, 1972).

The study area is characterized by tropical climate with distinct wet and dry seasons. The wet and dry seasons last for 5 and 7 months (Fig. 2), respectively with a mean annual rainfall which ranges from 800 mm in the northern part of the state to over 2000 mm in the southern part. Precipitation is lowest in January with an average of 0 mm, while in August, the most precipitation falls with an average of 217 mm. Mean annual temperature is 34 °C and varies in mean monthly values between 28.4 °C in the coolest month of December and 37 °C in the hottest month of March (NIMET, 2009).

Taraba State is characterized by three dominant vegetational zones. The guinea savanna (study area) is found in the northern part of the State. Sub-sudan vegetation is characterized by short grasses with a few short trees. The Mambila plateau area is uniquely marked by a semi-temperate climate with luxuriant pasture and short trees.

2.2 Field and laboratory studies

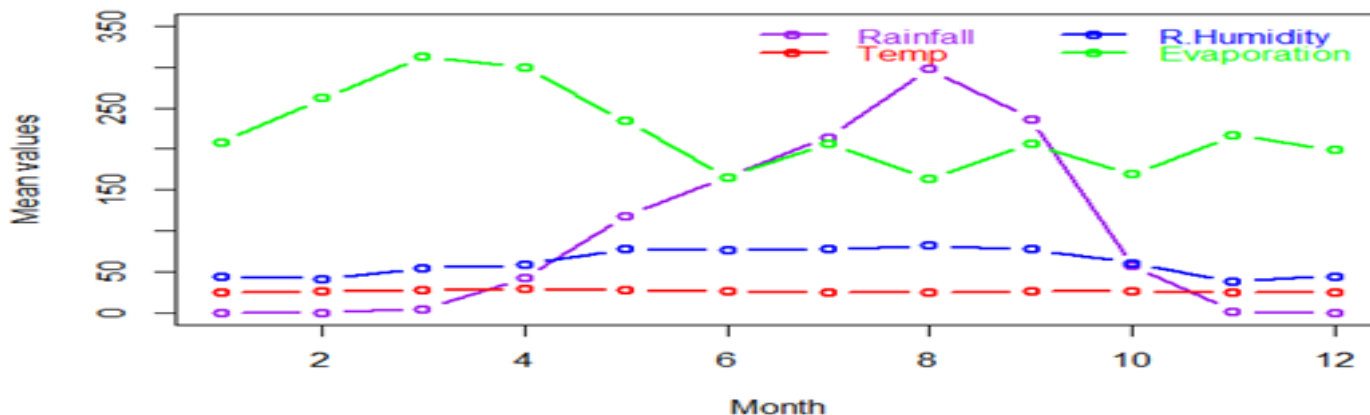


Fig. 1: Climatic data of the study area (1998-2017)
Source: Taraba State Water Board

The sites for the study were identified through reconnaissance visits using the geological map of Taraba State obtained from the Nigerian Geological Survey Agency. Soils on mica-schist were identified and selected because of their vastness and agricultural value. The contour map of the selected areas was produced to aid slope classification. Three soil profile pits were sited at crestal position of the lithology in order to obtain a true to type soil representative. It was dug, described and sampled for laboratory studies.

Particle size distribution was determined by the Bouyoucos hydrometer method with sodium hexametaphosphate acting as dispersing agent (Soil Survey Staff, 2014). Soil pH was determined using a ratio of 1:2.5 soil: liquid in 0.1 *N* KCl₂ solution with the aid of glass electrode pH meter (Udo *et al.*, 2009). Organic carbon was determined by the Walkley and Black wet oxidation method and total N by macro Kjeldahl digestion method as modified by Udo *et al.* (2009). Bray 1 method was used to determine available phosphorus while exchangeable bases (Ca, Mg, K, and Na) were determined by neutral NH₄OAc displacement method and read through by atomic absorption spectrophotometer as described by Udo *et al.* (2009). Cation exchange capacity was determined by 1 *N* NH₄OAc at pH 7 while base saturation was calculated by expressing the sum of exchangeable bases as a percentage of the CEC at pH 7. Dithionite and oxalate forms of iron and manganese were determined by the method of Mehra and Jackson (1960) as modified by Udo *et al.* (2009). Saturated hydraulic conductivity (K_{sat}) was determined by the constant head method using Eijkelkamp laboratory permeameter as described by Youngs (2001). Bulk density was determined by core method as described by Blake and Hartge, (1986) while total porosity (TP) was computed from bulk density (Bd) using the equation below (assumed particle density p_s

$$TP = \left(1 - \frac{Bd}{p_s}\right) \times 100$$

= 2.65 kg/m³).

Where TP = total porosity, Bd = bulk density, Ps = particle density.

2.3 Data analysis

Data generated from the laboratory analyses were subjected to statistical analysis using R statistical package.

3.0 Results and Discussion

The physical and chemical properties of the soils are presented in Tables 1-3.

The study area was characterized by deep (>100 cm) to very deep (>150 cm) soils (Table 1) indicating a soil of high volume that may provide ample root zone and support greater capacities to store plant nutrients and water. The low content of clay (Table 1) and OM (Table 3) however, will not facilitate the depth advantage for optimum agricultural use. The depth property also indicates a soil that had strong profile development and highly weathered as buttressed by the high content of free Fe - 2518 mgkg⁻¹ and free Mn - 144.96 mgkg⁻¹ (Table 6). The soil distribution cuts across crestal to lower slope positions. The soils had loamy sand surface soils underlain by sandy loam and loamy sand implying a light textured soil. The light-textured soil was associated to the granitic origin of the

lithology. The dominance of sand fraction in a basement complex soils have been reported by other researchers; Ande, 2010; Maniyunda *et al.*, 2014; Olatunji *et al.*, 2015; Shobayo *et al.* 2019.

The pyrophosphate extractable iron (Fe_p) and manganese (Mn_p) was the lowest fraction of the forms of iron (Fe_p: mean - 1191.90 mgkg⁻¹, Fe_{ox}: mean - 1267.30 mgkg⁻¹, Fe_d: mean - 2459.00 mgkg⁻¹) and manganese (Mn_p: mean - 56.17 mgkg⁻¹, Mn_{ox}: mean - 94.87 mgkg⁻¹, Mn_d: mean - 150.30 mgkg⁻¹) oxides examined (Table 7) in the surface soil on soils on mica-schist. Similarly, subsurface soils mean values of pyrophosphate extractable iron (Fe_p) (Fe_p: mean - 1221.10 mgkg⁻¹, Fe_{ox}: mean - 1321.50 mgkg⁻¹, Fe_d: mean - 2543.00 mgkg⁻¹) and pyrophosphate extractable manganese (Mn_p) (Mn_p: mean - 119.40 mgkg⁻¹, Mn_{ox}: mean - 143.23 mgkg⁻¹, Mn_d: mean - 142.67 mgkg⁻¹) obtained were lowest. Lowest nevertheless, they contributed more to the CEC of the soils as against the amorphous and free oxide forms.

The three forms of iron and manganese oxides contributed positively (though not statistically significant) to the improvement of the soils' bulk density (BD) which was rated moderate except for the Fe_p that recorded a negative correlation ($r = -0.3346$, $P < 0.5$) with BD implying that the organic bound iron oxide was so negligible and did not constitute a binding agent. This was further buttressed by its negative correlation ($r = -0.0620^{ns}$, $P < 0.5$) with OM. Contrarily, Mn_p, Mn_{ox}, Mn_d, Fe_{ox} and Fe_d did not contribute to the soil's total porosity (TP) except Fe_p. Total porosity of the soil was rated low and was attributed to the high level of free oxides in the soils which had crystallized. Generally, similar observation was noted for the soils' hydraulic conductivity (HC) and water holding capacity (WHC) (rated low). These observations were credited to the granitic origin of the lithology of the study area. Dominance of sand fraction (> 70 gkg⁻¹) in fine earth fraction which was associated to the basement complex coupled with the very high free oxides may render the soils agriculturally unproductive except proper soil management which include improving the physical conditions of the soils, addition of organic manure and incorporation of crop residues as well as serve as a source of N and K, which will raise the fertility of the soils. Soil and water conservation measures must be put in place such as to conserve water on the sandy soils along with other farm management practices that improves soil-water conservation.

The Fe_p and Mn_p distributed irregularly with pedal depth (Table 4) in the three profile pits sited on soils on mica-schist. Mean values of surface soils (1191.9 mgkg⁻¹ and 56.17 mgkg⁻¹ - Table 7) were higher than the mean values observed for subsurface soils (1221.1 mgkg⁻¹ and 119.4 mgkg⁻¹ respectively for Fe_p and Mn_p) (Table 8); a trend that was similar to the mean distribution of organic carbon (OC) and organic matter (OM) which contents were higher in the surface soils (Table 7). Similarly, Fe_p and Mn_p were positively correlated ($r = 0.031$ - Table 5) implying that they were mutually translocated with depth. This observation buttresses the assertion that they are organic bound. However, means (Table 6) of OM, Mn_p ($F = 0.088$, $p = 0.865$) and Fe_p ($F = 0.031$, $p = 0.774$) did not vary statistically when compared.

Furthermore, a non-coherence pattern was observed between the Fe_p and OM/OC and Mn_p and OM/OC as they were negatively correlated ($r = -0.062$, $r = -0.065$ and $r = -0.104$, $r = -0.103$ respectively) implying a reduced pedogenic internal transformational process within the surface horizons. Since the content of OM was low due to sparse

Table 1: Soil physical properties of the study area

Geology	Profile name	Horizon	Depth	Clay	Silt	Fine sand	Coarse sand	Textural class	Bulk density	Total porosity	Hydraulic C	WHC	
Soils on Mica-Schist	Profile pit 1							Lat. 08°46'41.2"N Long. 011°16'09"S					
	BDCP1	Ap	0–20	10	9	39	42	Loamy sand	1.82	31.32	6.83	23.1	
	BDCP1	Btv	20–81	18	7	37	38	Sandy loam	1.53	42.26	8.08	30.57	
	BDCP1	Bt	81–128	14	7	37	42	Sandy loam	1.85	29.81	5.05	23.5	
	BDCP1	CCv	128–175	12	7	30	51	Sandy loam	1.74	34.34	10.1	22.21	
	Profile pit 2								Lat. 08°46'14.2"N Long. 011°16'09"S				
	BDCP2	Ap	0–35	8	13	41	38		1.54	41.13	10.61	26.14	
	BDCP2	Btv	35–106	8	5	40	47		1.85	30.19	14.14	19.93	
	BDCP2	CBtv	106–173	8	19	44	29		1.84	30.57	8.92	15.1	
	Profile pit 3								Lat. 08°46'42.1"N Long. 011°16'02.5"S				
	BDUSP	Ap	0–12	12	7	37	44		1.47	44.53	3.54	24.43	
	BDUSP	CB	12–62	8	7	30	55		1.59	40	5.05	23.47	
	BDUSP	C	62–126	8	5	35	52		1.79	32.45	4.20	19.42	

Table 2: Soil chemical properties of the study area

Geology	Profile name	Horizon	Depth	pH _{H2O}	pH _{KCl}	EA	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	TEB	
Soils on Mica-Schist	Profile pit 1											
	BDCP1	Ap	0–20	6.2	5.6	1.4	0.02	0.05	1.8	0.6	2.47	
	BDCP1	Btv	20–81	5.8	4.7	2	0.02	0.05	2.2	1.0	3.27	
	BDCP1	Bt	81–128	6.6	5.3	1.4	0.02	0.05	2	0.8	2.87	
	BDCP1	CCv	128–175	6.7	5.4	1.2	0.01	0.005	1.8	0.8	2.615	
	Profile pit 2											
	BDCP2	Ap	0–35	6.1	5.1	2.2	0.04	0.09	1.6	1.2	2.93	
	BDCP2	Btv	35–106	6.9	5.7	1.2	0.006	0.01	1.6	1.8	3.416	
	BDCP2	CBtv	106–173	7.1	6.1	1.2	0.006	0.01	0.8	1.8	2.616	
	Profile pit 3											
	BDUSP1	Ap	0–12	6.9	6.2	1	0.05	0.09	4.6	0.8	5.54	
	BDUSP1	CB	12–62	6.5	5.3	1.4	0.008	0.01	2	1.4	3.418	
	BDUSP1	C	62–126	6.9	6.2	1.2	0.001	0.005	1.2	1.2	2.406	

vegetation that characterized the study area (guinea savanna), it can be surmised that pH (Table 2) cast an immobilization effect on Mn_p co-translocation with OM/OC as the organic bound sesquioxides were positively correlated with pH in water ($r = 0.130$, $p = 0.717$) and KCl ($r = 0.031$, $p = 0.931$) and also contributed to the soil's acidity. The soils varied in their chemical reaction from moderately acidic (5.8) to neutral (7.1) which possibly could account for the high content of Mg in the soils. Organic bound manganese (Mn_p) correlated positively (Table 5) with the amorphous (Mn_{ox}) and free (Mn_d) manganese oxides forms indicating an increase in any form will have a concomitant pedogenic effect on the other.

Mean values of Mn_{ox} (94.87 mgkg⁻¹) and Fe_{ox} (1267.30 mgkg⁻¹) at the surface soils shows that the sequence of their distribution is greater than Mn_p and Fe_p respectively (i.e., Mn_p < Mn_{ox} and Fe_p < Fe_{ox}). Generally, the contents of Fe were greater than those of Mn (Table 4) and was attributed to the parent material mineralogical composition which is richer in Fe; especially those contributed by mica. Therefore, it can be opined that Fe is the major contributor of the amorphous form. The Fe_{ox} correlated negatively ($r = -0.444$, $P < 0.5$) with Fe_p implying that there was a shift towards inorganic pedogenic phase, however, a positive correlation obtained between Mn_{ox} and Mn_p is an indication of reciprocal transformational process between the oxide forms at the surface horizons. Also, a strong significant difference ($F = 187.6$, $p = 7.777^{***}$) between their means (Table 6) (i.e., Mn_{ox} and Mn_p) buttressed their reciprocal interaction. The high content of Fe in the amorphous form might not have

translated to any beneficial pedogenic effect on cation exchange capacity and water holding capacity of the soils as it could not be unconnected to its inverse correlation with clay, water holding capacity and CEC (Table 5). But it perhaps had facilitated the adsorption/retention of N and P.

Contents of Mn_d and Fe_d were higher than those of Mn_{ox} and Fe_{ox} respectively in their corresponding horizons. Mean surface soil content of Fe_d (2459.00 mgkg⁻¹) was lower than the computed mean for Fe_d (2543.00 mgkg⁻¹) at the subsurface soils. The differential may be attributed to tillage that continually disturb the surface soils and subsequently retard the build up at the surface. This form of Fe is surmised not to be part of the silicate structure but present in soils as discrete bodies. Its distribution pattern shows increase with pedal depth suggesting an illuvial accumulation and at the subsoils, crystallinity might be improved. This phenomenon may not be best for agricultural land-use, because plinthization may be initiated. Again, the high value recorded may account for the soils being highly developed and approaching senility. High iron oxide values may indicate the presence of iron oxide either crystalline such as hematite or amorphous in an appreciable percentage (Sombroek and Zonneveld, 1971).

Thomas *et al.* (2019) submitted that free oxides in soils usually have distinct electrochemical properties that generate CEC as a consequence of the adsorption of proton and hydroxyl ions providing structural cementation in the soil. Only the free iron oxide was observed to contribute to the soils' CEC ($r = 0.1537$, $P < 0.5$) and was not significant ($F = 0.194$, $p = 0.672$); however, this study shows that the free manga-

Table 3 cont.: Soil chemical properties of the study area

Geology	Profile name	Horizon	Depth	CEC	ECEC	BS	OC	OM	N	P	
Soils on Mica-Schist	Profile pit 1				Lat. 08°46' 41.2" N			Long. 011° 16' 0.9" S			
	BDCP1	Ap	0 – 20	10	3.87	24.7	0.375	0.647	0.098	0.93	
	BDCP1	Btv	20 – 81	16.8	5.27	19.46	0.375	0.647	0.056	0.92	
	BDCP1	Bt	81 – 128	14	4.27	18.28	0.375	0.647	0.028	0.93	
	BDCP1	CCv	128 – 175	15.2	3.815	17.14	0.075	0.129	0.056	0.98	
	Profile pit 2					Lat. 08°46' 14.2" N			Long. 011° 16' 0.9" S		
	BDCP2	Ap	0 – 35	9.2	5.13	31.85	0.781	1.346	0.308	6.53	
	BDCP2	Btv	35 – 106	10	4.616	34.16	0.164	0.283	0.14	1.87	
	BDCP2	CBtv	106 – 173	7.2	3.816	36.33	0.164	0.283	0.224	1.87	
	Profile pit 3					Lat. 08°46' 42.1" N			Long. 011° 16' 02.5" S		
	BDUSP1	Ap	0 – 12	16.4	6.54	33.78	1.013	1.746	0.084	0.93	
	BDUSP1	CB	12 – 62	19.6	4.818	17.44	0.263	0.463	0.084	0.94	
	BDUSP1	C	62 – 126	9.6	3.606	25.06	0.075	0.129	0.07	0.93	

Table 4: Sesquioxide properties of the study area

Geology	Profile name	Horizon	Depth	Mn _d	Fe _d	Mn _{ox}	Fe _{ox}	Mn _p	Fe _p	Mn _o /Mn _d	Fe _o /Fe _d	
Soils on Mica-Schist	Profile pit 1					Lat. 08°46' 41.2" N			Long. 011° 16' 0.9" S			
	BDCP1	Ap	0 – 20	237.1	2063.55	131.1	773.6	106	1290	0.55	0.37	
	BDCP1	Btv	20 – 81	110.6	2793.65	66	1206.2	44.6	1587.5	0.6	0.43	
	BDCP1	Bt	81 – 128	95.15	2666.25	515	1384.7	419.8	1281.6	5.4	0.52	
	BDCP1	CCv	128 – 175	131.4	3047.7	70	1543.2	61.4	1504.5	0.53	0.51	
	Profile pit 2						Lat. 08°46' 14.2" N			Long. 011° 16' 0.9" S		
	BDCP2	Ap	0 – 35	82.4	2266.45	83.5	1485.2	1.1	781.3	1.01	0.66	
	BDCP2	Btv	35 – 106	131.1	3089.05	62.7	2312.7	68.4	776.4	0.48	0.75	
	BDCP2	CBtv	106 – 173	52.05	2977.2	29	1981.4	23.1	995.8	0.56	0.67	
	Profile pit 3						Lat. 08°46' 42.1" N			Long. 011° 16' 02.5" S		
	BDUSP1	Ap	0 – 12	151.65	2473.05	76	1201	75.7	1272.1	0.5	0.49	
	BDUSP1	CB	12 – 62	56.1	2377.1	22.1	683.2	34	1693.9	0.39	0.29	
	BDUSP1	C	62 – 126	402.05	1421.55	231.8	481.3	170.3	940.3	0.58	0.34	

nese oxide (Mn_d) did not contribute to the soils' CEC as increase in the Mn_d led to decreased CEC ($r = -0.2844$, $p = 0.4258$) but CEC was partly contributed by clay ($r = 0.5197$, $P < 0.5$) and OM ($r = 0.1863$, $P < 0.5$). The free oxides i.e. Mn_d and Fe_d also did not improve the soils' water holding capacity implying that they were not clay-sized except Fe_d that was somewhat clay-sized. It can also be surmised that the high content of the free oxides was crystallized and therefore inactive.

Contrastively, mean surface soil contents (150.30 mgkg⁻¹) of Mn_d was lower than the subsurface soils' average (142.67 mgkg⁻¹). This is an indication that Mn-oxide forms minimal fraction of the free forms in the soils formed on the mica-schist therefore, poses less crystallization threat that lowers pedogenesis. The correlation studies show that the fine earth fractions (clay, silt and fine sand) did not influence the formation and distribution of Mn_d. Even at lower presence, the Mn_d had resultant inhibitory effect on exchangeable bases i.e. Ca, Mg, K, Na and other macronutrients such as N and P (Table 5). It can be surmised that the content of Mn_d had contributed to the acidity (Table 2) of the soil which could temporarily heighten immobilization at the period field study was carried out (Figure 2). Ratios of oxalate extractable and dithionite extractable were measured to further determine the pedogenic development i.e. recrystallization in soils of the study area. The distribution with depth was irregular for both Mn_o/Mn_d and Fe_o/Fe_d (Table 4). The surface soils recorded mean ratios of 0.70 and 0.51 respectively for Mn_o/Mn_d and Fe_o/Fe_d (Table 7) and the corresponding subsurface mean ratios were 1.22 and 0.50 (Table 8). Increased mean ratio of Mn_o/Mn_d observed in the subsurface soils is suggestive of preponderant recrystallization at the surface soils. However, the similar Fe_o/Fe_d mean ratios observed for both surface and subsurface soils imply similarity in recryst-

tallization process taken place. Maniyunda *et al.* (2014) submitted that values ranging between 0.1 and 0.5 are of moderate pedogenic development. The mean ratios observed were between 0.5 and 1.06, therefore the soils have weathered appreciably. Sombroek and Zonneveld (1971) associated sesquioxides ratios to possible clay-sized minerals present in soils. They submitted that ratios between 2.0 and 3.0 suggest the presence of both montmorillonite/illite and kaolinite; 1.6 - 2.0 suggest the predominance of kaolinite. Values below 1.6 indicate the presence of considerable percentages of gibbsite or aluminium oxides. However, their analysis was subjected to the clay fraction solely.

4.0 Conclusion

It was concluded from the study that free iron oxide was the dominant form of oxide. The forms of oxide increased in the order Mn_p > Mn_{ox} > Mn_d > Fe_p > Fe_{ox} > Fe_d with percentage distribution of 1.86, 2.38, 2.68, 22.41, 24.13 and 46.56 respectively. Generally, the three forms of iron and manganese oxides did not significantly influence the soils' physical and chemical properties as the results revealed non statistically significant interactions between the oxide forms and other soil parameters. The dominant oxide forms (i.e. free form) were relatively inactive therefore, did not influence total porosity, hydraulic conductivity and water holding capacity except bulk density. Organic form influenced more to the cation exchange capacity more than the active form (amorphous form). Ratios of oxalate extractable and dithionite extractable indicated that the soils are highly weathered. Because they are highly weathered, the soils might lose much of its nutrients due to excessive leaching (low HD and WHC). Thus, corroborating the soils' general low (exchangeable bases, OC, OM, N and P) fertility status as presented in the study analytical data.

Table 5: Correlation results

	Clay	Silt	Fine sand	Coarse sand	Bulk density	Total porosity	Hydraulic C	WHC	pH_H2O	pH_KCl	OC	OM	TN	Na	K	Ca	Mg	CEC	TEB
ECEC	BS	EA	AvP	Mn_p	Mn_ox	Mn_d	Fe_p	Fe_ox	Fe_d	Mn-o	Mn-d								
Silt	-0.285																		
Fine sand	-0.175	0.636																	
Coarse sand	-0.179	-0.791	-0.847																
Bulk density	-0.294	0.076	0.219	-0.039															
Total porosity	0.300	-0.089	-0.234	0.052	-0.999														
Hydraulic C	-0.191	0.194	0.344	0.050	-0.705	-0.256													
WHC	0.685	-0.368	-0.254	0.050	-0.434	0.697	-0.123												
pH_H2O	-0.500	0.091	0.059	0.134	0.447	-0.434	-0.053	-0.856											
pH_KCl	-0.533	0.116	0.204	0.052	0.314	-0.299	-0.268	-0.760	0.854										
OC	0.168	0.090	0.242	-0.262	-0.711	0.696	-0.265	0.500	-0.251	-0.027									
OM	0.167	0.089	0.239	-0.259	-0.712	0.698	-0.267	0.501	-0.252	-0.028									
TN	-0.561	0.733	0.654	-0.534	-0.107	0.083	0.495	-0.208	-0.019	0.039	0.269	0.268							
Na	0.266	0.079	0.207	-0.278	-0.687	0.671	-0.210	0.551	-0.306	-0.098	0.980	0.980	0.230						
K	0.306	0.105	0.326	-0.378	-0.611	0.590	-0.202	0.610	-0.452	-0.205	0.946	0.946	0.263	0.962					
Ca	0.394	-0.361	-0.211	0.148	-0.648	0.657	-0.439	0.465	-0.024	0.106	0.758	0.759	-0.325	0.752	0.619				
Mg	-0.559	0.353	0.365	-0.159	0.227	-0.225	0.489	-0.549	0.428	0.219	-0.356	-0.355	0.503	-0.471	-0.479	-0.484			
CEC	0.520	-0.517	-0.758	0.493	-0.573	0.588	-0.406	0.586	-0.273	-0.406	0.183	0.186	-0.615	0.185	0.080	0.587	-0.363		
TEB	0.194	-0.231	-0.049	0.071	-0.646	0.657	-0.271	0.294	0.148	0.209	0.726	0.727	-0.114	0.668	0.517	0.919	-0.100	0.488	
ECEC	0.307	-0.152	0.032	-0.069	-0.833	0.833	-0.168	0.581	-0.211	-0.125	0.845	0.846	0.060	0.798	0.714	0.844	-0.133	0.492	0.912
BS	-0.487	0.491	0.786	-0.508	0.024	-0.028	0.318	-0.438	0.431	0.572	0.346	0.344	0.689	0.273	0.243	0.052	0.513	-0.643	0.307
EA	0.263	0.195	0.195	-0.334	-0.425	0.398	0.252	0.673	-0.856	-0.798	0.260	0.261	0.418	0.289	0.450	-0.204	-0.074	-0.006	-0.238
AvP	-0.364	0.458	0.446	-0.349	-0.266	0.230	0.453	0.135	-0.275	-0.247	0.399	0.398	0.879	0.399	0.458	-0.217	0.236	-0.431	-0.107
0.655																			
Mn_p	0.298	-0.337	-0.087	0.105	0.456	-0.467	-0.413	-0.033	0.131	0.031	-0.103	-0.104	-0.533	-0.077	0.018	0.019	-0.375	0.037	-0.152
0.370	-0.208	-0.345																	
Mn_ox	0.275	-0.268	-0.020	0.039	0.409	-0.427	-0.385	0.022	0.039	-0.029	-0.045	-0.046	-0.407	-0.012	0.110	-0.042	-0.390	-0.050	-0.222
0.342	-0.056	-0.177	0.979																
Mn_d	-0.151	-0.441	-0.131	0.385	0.245	-0.235	-0.337	-0.163	0.146	0.460	-0.212	-0.214	-0.315	-0.216	-0.168	-0.072	-0.270	-0.284	-0.213
0.036	-0.279	-0.274	0.214																
Fe_p	0.570	-0.285	-0.701	0.310	-0.335	0.355	-0.434	0.460	-0.353	-0.424	-0.065	-0.062	-0.656	-0.026	-0.089	0.327	-0.469	0.856	0.142
0.772	-0.015	-0.584	0.031	-0.060	-0.233	-0.276	0.786	-0.296	0.302	-0.001	-0.065	-0.067	0.417	-0.029	-0.075	-0.165	0.525	-0.353	0.056
Fe_ox	-0.060	0.351	0.511	-0.461	0.268	-0.276	0.786	-0.296	0.302	-0.001	-0.065	-0.067	0.417	-0.029	-0.075	-0.165	0.525	-0.353	0.056
0.514	-0.047	0.289	-0.156	-0.175	-0.552	-0.444	-0.079	0.593	-0.035	0.109	-0.270	-0.113	-0.114	0.045	-0.049	-0.139	0.026	0.282	0.154
0.062	-0.051	-0.152	-0.232	-0.758	0.145	0.823	-0.079	0.593	-0.035	0.109	-0.270	-0.113	-0.114	0.045	-0.049	-0.139	0.026	0.282	0.154
Mn-o	0.342	-0.088	0.047	-0.128	0.313	-0.336	-0.242	0.091	-0.022	-0.216	0.054	0.053	-0.274	0.090	0.194	-0.007	-0.289	0.054	-0.132
0.318	0.062	-0.035	0.902	0.917	-0.173	0.020	0.079	0.222	0.222	0.222	0.222	0.222	0.222	0.222	0.222	0.222	0.222	0.222	0.222
Fe-o	-0.197	0.426	0.659	-0.527	-0.240	-0.240	0.759	-0.296	0.278	0.069	0.092	0.089	0.616	0.117	0.102	-0.183	0.511	-0.540	0.038
0.668	0.067	0.529	-0.149	-0.113	-0.434	-0.678	0.943	0.612	0.078	0.078	0.078	0.078	0.078	0.078	0.078	0.078	0.078	0.078	0.078

Table 6: Summary of surface/subsurface soils on mica-schist

	Clay	Silt	Fine sand	CEC	ECEC
	Min. :8.0	Min. :5.0	Min. :30.00	Min. :7.2	Min. :3.606
	1st Qu.:8.0	1st Qu.:7.0	1st Qu.:35.50	1st Qu.:9.7	1st Qu.:3.829
	Median :9.0	Median :7.0	Median :37.00	Median :12.0	Median :4.443
	Mean :10.6	Mean :8.6	Mean :37.00	Mean :12.8	Mean :4.575
	3rd Qu.:12.0	3rd Qu.:8.5	3rd Qu.:39.75	3rd Qu.:16.1	3rd Qu.:5.052
	Max. :18.0	Max. :19.0	Max. :44.00	Max. :19.6	Max. :6.540
	Coarse sand	Bulk density	Total porosity	Hydraulic C	WHC
	Min. :29.0	Min. :1.470	Min. :29.81	Min. :3.540	Min. :15.10
	1st Qu.:39.0	1st Qu.:1.552	1st Qu.:30.76	1st Qu.:5.050	1st Qu.:20.50
	Median :43.0	Median :1.765	Median :33.40	Median :7.455	Median :23.29
	Mean :43.8	Mean :1.702	Mean :35.66	Mean :7.652	Mean :22.79
	3rd Qu.:50.0	3rd Qu.:1.835	3rd Qu.:40.85	3rd Qu.:9.805	3rd Qu.:24.20
	Max. :55.0	Max. :1.850	Max. :44.53	Max. :14.140	Max. :30.57
	pH_H2O	pH_KCl	OC	OM	TN
	Min. :5.800	Min. :4.70	Min. :0.075	Min. :0.129	Min. :0.0280
	1st Qu.:6.275	1st Qu.:5.30	1st Qu.:0.164	1st Qu.:0.283	1st Qu.:0.0595
	Median :6.650	Median :5.50	Median :0.319	Median :0.555	Median :0.0840
	Mean :6.570	Mean :5.56	Mean :0.366	Mean :0.632	Mean :0.1148
	3rd Qu.:6.900	3rd Qu.:6.00	3rd Qu.:0.375	3rd Qu.:0.647	3rd Qu.:0.1295
	Max. :7.100	Max. :6.20	Max. :1.013	Max. :1.746	Max. :0.3080
	Na	K	Ca	Mg	TEB
	Min. :0.0010	Min. :0.005	Min. :0.80	Min. :0.60	Min. :2.406
	1st Qu.:0.0065	1st Qu.:0.010	1st Qu.:1.60	1st Qu.:0.80	1st Qu.:2.615
	Median :0.0150	Median :0.030	Median :1.80	Median :1.10	Median :2.900
	Mean :0.0181	Mean :0.037	Mean :1.96	Mean :1.14	Mean :3.155
	3rd Qu.:0.0200	3rd Qu.:0.050	3rd Qu.:2.00	3rd Qu.:1.35	3rd Qu.:3.380
	Max. :0.0500	Max. :0.090	Max. :4.60	Max. :1.80	Max. :5.540
	BS	EA	AvP	Mn_p	Mn_ox
	Min. :17.14	Min. :1.00	Min. :0.920	Min. :1.10	Min. :22.10
	1st Qu.:18.57	1st Qu.:1.20	1st Qu.:0.930	1st Qu.:36.65	1st Qu.:63.52
	Median :24.88	Median :1.30	Median :0.935	Median :64.90	Median :73.00
	Mean :25.82	Mean :1.42	Mean :1.683	Mean :100.44	Mean :128.72
	3rd Qu.:33.30	3rd Qu.:1.40	3rd Qu.:1.647	3rd Qu.:98.42	3rd Qu.:119.20
	Max. :36.33	Max. :2.20	Max. :6.530	Max. :419.80	Max. :515.00
	Mn_d	Fe_p	Fe_ox	Fe_d	Mn-o_Mn-d
	Min. :52.05	Min. :776.4	Min. :481.3	Min. :1422	Min. :0.3900
	1st Qu.:85.59	1st Qu.:954.2	1st Qu.:880.5	1st Qu.:2294	1st Qu.:0.5075
	Median :120.85	Median :1276.8	Median :1295.5	Median :2570	Median :0.5550
	Mean :144.96	Mean :1212.3	Mean :1305.2	Mean :2518	Mean :1.0600
	3rd Qu.:146.59	3rd Qu.:1450.9	3rd Qu.:1528.7	3rd Qu.:2931	3rd Qu.:0.5950
	Max. :402.05	Max. :1693.9	Max. :2312.7	Max. :3089	Max. :5.4000
	Fe-o_Fe-d				
	Min. :0.290				
	1st Qu.:0.385				
	Median :0.500				
	Mean :0.503				
	3rd Qu.:0.625				
	Max. :0.750				

Table 7: Summary of surface soils on mica-schist

Clay	Silt	Fine sand	Coarse sand	Bulk density	Total porosity
Min. :8	Min. :7.000	Min. :30.00	Min. :38.00	Min. :1.54	Min. :31.32
1st Qu.:9	1st Qu.:8.000	1st Qu.:34.50	1st Qu.:40.00	1st Qu.:1.64	1st Qu.:32.83
Median :10	Median :9.000	Median :39.00	Median :42.00	Median :1.74	Median :34.34
Mean :10	Mean :9.667	Mean :36.67	Mean :43.67	Mean :1.70	Mean :35.60
3rd Qu.:11	3rd Qu.:11.000	3rd Qu.:40.00	3rd Qu.:46.50	3rd Qu.:1.78	3rd Qu.:37.73
Max. :12	Max. :13.000	Max. :41.00	Max. :51.00	Max. :1.82	Max. :41.13
Hydraulic C	WHC	pH_H2O	pH_KCl	OC	OM
Min. :6.830	Min. :22.21	Min. :6.100	Min. :5.100	Min. :0.0750	Min. :0.1290
1st Qu.:8.465	1st Qu.:22.66	1st Qu.:6.150	1st Qu.:5.250	1st Qu.:0.2250	1st Qu.:0.3880
Median :10.100	Median :23.10	Median :6.200	Median :5.400	Median :0.3750	Median :0.6470
Mean :9.180	Mean :23.82	Mean :6.333	Mean :5.367	Mean :0.4103	Mean :0.7073
3rd Qu.:10.355	3rd Qu.:24.62	3rd Qu.:6.450	3rd Qu.:5.500	3rd Qu.:0.5780	3rd Qu.:0.9965
Max. :10.610	Max. :26.14	Max. :6.700	Max. :5.600	Max. :0.7810	Max. :1.3460
TN	Na	K	Ca	Mg	CEC
Min. :0.056	Min. :0.01000	Min. :0.00500	Min. :1.600	Min. :0.6000	Min. :9.20
1st Qu.:0.077	1st Qu.:0.01500	1st Qu.:0.02750	1st Qu.:1.700	1st Qu.:0.7000	1st Qu.:9.60
Median :0.098	Median :0.02000	Median :0.05000	Median :1.800	Median :0.8000	Median :10.00
Mean :0.154	Mean :0.02333	Mean :0.04833	Mean :1.733	Mean :0.8667	Mean :11.47
3rd Qu.:0.203	3rd Qu.:0.03000	3rd Qu.:0.07000	3rd Qu.:1.800	3rd Qu.:1.0000	3rd Qu.:12.60
Max. :0.308	Max. :0.04000	Max. :0.09000	Max. :1.800	Max. :1.2000	Max. :15.20
TEB	ECEC	BS	EA	AvP	Mn_p
Min. :2.470	Min. :3.815	Min. :17.14	Min. :1.2	Min. :0.930	Min. :1.10
1st Qu.:2.542	1st Qu.:3.842	1st Qu.:20.92	1st Qu.:1.3	1st Qu.:0.955	1st Qu.:31.25
Median :2.615	Median :3.870	Median :24.70	Median :1.4	Median :0.980	Median :61.40
Mean :2.672	Mean :4.272	Mean :24.56	Mean :1.6	Mean :2.813	Mean :56.17
3rd Qu.:2.772	3rd Qu.:4.500	3rd Qu.:28.27	3rd Qu.:1.8	3rd Qu.:3.755	3rd Qu.:83.70
Max. :2.930	Max. :5.130	Max. :31.85	Max. :2.2	Max. :6.530	Max. :106.00
Mn_ox	Mn_d	Fe_p	Fe_ox	Fe_d	Mn-o_Mn-d
Min. :70.00	Min. :82.4	Min. :781.3	Min. :773.6	Min. :2064	Min. :0.5300
1st Qu.:76.75	1st Qu.:106.9	1st Qu.:1035.7	1st Qu.:1129.4	1st Qu.:2165	1st Qu.:0.5400
Median :83.50	Median :131.4	Median :1290.0	Median :1485.2	Median :2266	Median :0.5500
Mean :94.87	Mean :150.3	Mean :1191.9	Mean :1267.3	Mean :2459	Mean :0.6967
3rd Qu.:107.30	3rd Qu.:184.2	3rd Qu.:1397.2	3rd Qu.:1514.2	3rd Qu.:2657	3rd Qu.:0.7800
Max. :131.10	Max. :237.1	Max. :1504.5	Max. :1543.2	Max. :3048	Max. :1.0100
Fe-o_Fe-d					
Min. :0.3700					
1st Qu.:0.4400					
Median :0.5100					
Mean :0.5133					
3rd Qu.:0.5850					
Max. :0.6600					

Table 8: Summary of subsurface soils on mica-schist

Clay	Silt	Fine sand	Coarse sand	Bulk density	Total porosity
Min. :8.00 1st Qu.: 8.00 Median : 8.00 Mean :10.86 3rd Qu.:13.00 Max. :18.00	Min. :5.000 1st Qu.:6.000 Median :7.000 Mean :8.143 3rd Qu.:7.000 Max. :19.000	Min. :30.00 1st Qu.:36.00 Median :37.00 Mean :37.14 3rd Qu.:38.50 Max. :44.00	Min. :29.00 1st Qu.:40.00 Median :44.00 Mean :43.86 3rd Qu.:49.50 Max. :55.00	Min. :1.470 1st Qu.:1.560 Median :1.790 Mean :1.703 3rd Qu.:1.845 Max. :1.850	Min. :29.81 1st Qu.:30.38 Median :32.45 Mean :35.69 3rd Qu.:41.13 Max. :44.53
Hydraulic C Min. :3.540 1st Qu.:4.625 Median :5.050 Mean :6.997 3rd Qu.:8.500 Max. :14.140	WHC Min. :15.10 1st Qu.:19.68 Median :23.47 Mean :22.35 3rd Qu.:23.96 Max. :30.57	pH_H2O Min. :5.800 1st Qu.:6.550 Median :6.900 Mean :6.671 3rd Qu.:6.900 Max. :7.100	pH_KCl Min. :4.700 1st Qu.:5.300 Median :5.700 Mean :5.643 3rd Qu.:6.150 Max. :6.200	OC Min. :0.075 1st Qu.:0.164 Median :0.263 Mean :0.347 3rd Qu.:0.375 Max. :1.013	OM Min. :0.1290 1st Qu.:0.2830 Median :0.4630 Mean :0.5997 3rd Qu.:0.6470 Max. :1.7460
TN Min. :0.028 1st Qu.:0.063 Median :0.084 Mean :0.098 3rd Qu.:0.112 Max. :0.224	Na Min. :0.00100 1st Qu.:0.00600 Median :0.00800 Mean :0.01586 3rd Qu.:0.02000 Max. :0.05000	K Min. :0.00500 1st Qu.:0.01000 Median :0.01000 Mean :0.03214 3rd Qu.:0.05000 Max. :0.09000	Ca Min. :0.800 1st Qu.:1.400 Median :2.000 Mean :2.057 3rd Qu.:2.100 Max. :4.600	Mg Min. :0.800 1st Qu.:0.900 Median :1.200 Mean :1.257 3rd Qu.:1.600 Max. :1.800	CEC Min. :7.20 1st Qu.:9.80 Median :14.00 Mean :13.37 3rd Qu.:16.60 Max. :19.60
TEB Min. :2.406 1st Qu.:2.743 Median :3.270 Mean :3.362 3rd Qu.:3.417 Max. :5.540	ECEC Min. :3.606 1st Qu.:4.043 Median :4.616 Mean :4.705 3rd Qu.:5.044 Max. :6.540	BS Min. :17.44 1st Qu.:18.87 Median :25.06 Mean :26.36 3rd Qu.:33.97 Max. :36.33	AvP Min. :0.920 1st Qu.:0.930 Median :0.930 Mean :1.199 3rd Qu.:1.405 Max. :1.870	Mn_p Min. :23.1 1st Qu.:39.3 Median :68.4 Mean :119.4 3rd Qu.:123.0 Max. :419.8	
Mn_ox Min. :22.10 1st Qu.:45.85 Median :66.00 Mean :143.23 3rd Qu.:153.90 Max. :515.00	Mn_d Min. :52.05 1st Qu.:75.62 Median :110.60 Mean :142.67 3rd Qu.:141.38 Max. :402.05	Fe_p Min. :776.4 1st Qu.:968.0 Median :1272.1 Mean :1221.1 3rd Qu.:1434.5 Max. :1693.9	Fe_ox Min. :481.3 1st Qu.:942.1 Median :1206.2 Mean :1321.5 3rd Qu.:1683.0 Max. :2312.7	Mn-o_Mn-d Min. :0.390 1st Qu.:0.490 Median :0.560 Mean :1.216 3rd Qu.:0.590 Max. :5.400	
Fe-o_Fe-d Min. :0.2900 1st Qu.:0.3850 Median :0.4900 Mean :0.4986 3rd Qu.:0.5950 Max. :0.7500					

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