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HUMIC SUBSTANCES IN SOILS OF DIVERSE PARENT MATERIALS IN HUMID TROPICAL ENVIRONMENT OF SOUTH EAST NIGERIA.

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ABSTRACT

The knowledge of humic substances of soil is essential for soil fertility management and productivity. The study evaluated the humic substances (HS) and physicochemical properties of soils of different lithologies. Twenty composite soil samples were collected at the depths of 0-15 and 15-30 cm in both upland and inland of sandstone (SS), limestone (LS), mudstone (MS), basement complex (BC) and shale (SH) and analyzed for HS and physicochemical properties. HS were higher in surface than subsurface soils and in SH, SS and MS than other parent materials. Humic acid had mean values of 0.649 and 0.683 g/kg, 0.327 and 0.055 g/kg, 0.736 and 1.167 g/kg, 0.976 and 0.839 g/kg and 0.449 and 0.411 g/kg in surface soils of upland and inland in BC, MS, SS, SH and LS. In subsurface soils, average values of humic acid were 0.322 and 0.426 g/kg, 0.055 and 0.012 g/kg, 0.499 and 0.713 g/kg, 0.656 and 0.908 g/kg and 0.276 and 0.047 g/kg in the upland and inland of BC, MS, SS, SH and LS correspondingly. Fulvic acid had averages of 0.237 and 0.3125 g/kg, 0.533 and 0.751 g/kg, 0.297 and 0.707 mg/kg, 0.6524 and 0.568 g/kg and 0.220 and 0.007 g/kg in the surface soils of upland and inland of BC, MS, SS, SH and LS. In subsurface, fulvic acid had means of 0.244 and 0.363 g/kg, 0.227 and 0.328 g/kg, 0.056 and 0.128 g/kg, 0.040 and 0.402 g/kg and 0.001 and 0.415 g/kg in upland and inland of BC, MS, SS, SH and LS respectively. BC was higher in clay content than other parent materials. ECEC correlated significantly and positively with BS, Ca, Na, pH, silt, K and Mg while fulvic and humic acids correlated positively with TN and OM. pH was strongly acidic in soils of upland and varied from medium acid to slightly acid in inland. OC was high in inland and varied from high in MS, SH and SS to low in BC and LS in upland. Available P, TN, exchangeable bases, ECEC varied from low to high while BS was high in soils of both upland and inland.

KEYWORDS: humic substances, soil fertility, inland soil, upland soil, ECEC

INTRODUCTION

Improved management of soil organic matter (SOM) in arable soils is essential to sustain agricultural lands and natural ecosystems with which they interact (Wander, 2004). Consequently, the knowledge of distribution of SOM fractions is important in managing soils towards a sustainable agricultural system in a tropical environment (Valladares *et al*., 2007) and have been used as indicators of soil quality in some studies (Pulido-Moncada *et al*., 2018; Jensen *et al*., 2019; Murindangabo *et al*., 2023).

The loss of soil organic matter with consequent reduction in soil organic matter fraction formation leads to overall decline in soil chemical, physical and biological functions. Organic matter fractions or humic substances (HS) are the largest part of SOM, which can be operationally divided into three fractions according to their solubility in water at various pH, e.g., fulvic acids (soluble at all pH values), humic acids (soluble in alkaline media) and humins (insoluble at all pH values) (Ukalska-Jaruga *et al*., 2021; Nguyen *et al*., 2021). The chemical composition of each fraction is believed to determine its stability and turnover time

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(Poeplau *et al*., 2013) and plays an important role in the formation and stabilization of soil aggregates (Six *et al*., 2000), nutrient retention and release and overall plant growth and development. Different reactivity of humic substances may be primarily caused by the content of functional groups and charges (Ukalska-Jaruga *et al*., 2021). The chemical behavior of humic matter is controlled by carboxyl and phenolic functional groups, whereas the contribution of the alcoholic -OH functional group is yet to be established (Tan, 2011).

Humic acid is generally characterized by a lower carboxyl group content than fulvic acid. The total acidity or exchange capacity of humic compounds is attributed to the presence of dissociable protons or H^+ ions in the aromatic, aliphatic, carboxyl and phenolic hydroxyl groups. The total acidity of humic acid amounts generally to 5-6 cmol/kg. In contrast to humic acid, fulvic acid has total acidity of 10-12 cmol/kg which is approximately two times that of humic acid, but the phenolic hydroxyl group concentration according to Tan (2011) does not seem to differ significantly from that of humic acid. The major components of humin are the aliphatic hydrocarbon functionalities especially those found in lipid and they are resistant to decomposition. The dominance of fulvic acid in soil has a greater influence on its fertility than humic acid even as both increase soil potential to hold and release nutrients to soil for plant uptake. This is particularly important since humic substances are principally responsible for cation exchange capacity reaction of soils aside clay minerals.

Provision of adequate food to satisfy the needs of populace is among the major goals of any country's government worldwide (FAO,2001). In Nigeria, one of the major factors responsible for poor yields of agricultural crops is farmers lack of knowledge of critical properties of their soils including HS. Mostly in southern part of Nigeria, farmers are faced with declining yield even with increase in the use of inorganic fertilizers because of poor adsorptive or nutrient retention capacity of their soils. This imbalance between fertilizer/inputs usage and overall yield of their crops/productivity of their soils has remained an imagination to the farmers. A detailed evaluation of HS of soils is therefore needed for optimal and profitable soil productivity in this region since the knowledge of organic matter fractions of soil can serve as a guide in fertilizer use and economy for optimal and enhanced crop fertilizer use efficiency.

This is because among the soil colloids, organic colloids particularly fulvic acid has the highest cation exchange capacity (Tan, 2011). The type and amount of humic substances present in soil can provide an insight for decision making on how soils can be best managed for sustainable productivity.

Studies have shown that changes in the climate of soil environment and fertilizer application (Machado *et al*., 2020; Sootahar *et al*., 2020) and land use (Banach-Szott *et al*., 2021; Reddy *et al*., 2012; Afu *et al*., 2016) can affect HS but little or no studies have been done on parent materials and landscape positions on SOM fractions or HS. Evaluation of HS of soils of diverse parent materials therefore requires special attention. This is on the account that SOM fractions principally play active roles in enhancing a soil's physicochemical characteristics by increasing soil aggregation, water holding capacity, aeration, permeability and buffering capacities of soils (Vikram *et al*., 2022; Ukalska-Jaruga *et al*., 2021) because of their reactivity in soil (Ukalska-Jaruga *et al*., 2021). HS stimulates organic component of manure in improving soil K cycling and have also shown to enhance iron (Fe) uptake by plants in solution culture and field conditions (Olk *et al*., 2019b). An understanding of humic substance properties can be key to understanding issues including environmental pollution due to toxic metals, pesticides or persistent organic pollutants and the effects on soil performance of organic amendments and other land management practices (Olk *et al*., 2019a). Cassman *et al*. (1992) reported that two years of application of poultry manure maintained cotton lint yield and prevented fixation of residual soil K than did amendment with K fertilizer equivalent to the K content of the manure.

Even with the contribution of HS in enhancing soils' capacity to perform ecosystem services, growth and development of crops, it is still being relatively understudied in developing countries. This, according to many scientific views is because of the complex chemistry of HS and to some extent lack of equipment for their isolation/determination in most developing countries. According to Ziechmann (1994), the main obstacle in the study of HS or SOM fractions is due to repetitive sequences and the variety of chemical and biological reactions involved in their genesis. These make HS very complex and multifaceted molecules able to exert important signaling and nutritional functions in soil-plant system (Trevisan *et al*., 2010).

Nevertheless, it is necessary to quantify the SOM fractions to guide in selecting sustainable application of agrochemicals such as fertilizers and other soil management practices that bring about increase in soil fertility and productivity. In this study, we aim to quantify the organic matter fractions of soils, find out the correlation between organic matter fractions and selected soil properties and relate same to management of agricultural soils.

MATERIALS AND METHODS

Location of the study area and soil sample collection

The study was carried out in Adagom, Nkpagna, Nwang, Eshinjock and Ngbagidi communities in Ogoja Local Government Area of Cross River State. The area (Fig. 1) lies between latitudes 6^0 20'E and 6^0 43' N and longitudes 8^0 00' and 9^0 10'E and bounded in the north by Benue State, south by Ikom and Boki Local Government Areas and west by Ebonyi State (Bulktrade, 1989). Geologically, the Ogoja is dominated by Holocene cretaceous and tertiary sediments which make up the lower Benue Trough lying unconformably on rocks of the crystalline basement (Oban – Obudu Massif) which are Precambrian in age. The vegetation of the area is transition between tropical rainforest and guinea savanna characterized largely by woody trees, grasses and herbaceous growths (Afu *et al.*, 2016a). The study area has humid tropical climate with annual rainfall, temperature and relative humidity ranges of 1750 to 2000 mm, 27^0C to 29 ^{0}C and 50 to 70 % accordingly (Akpan-Idiok, 2010).

The geological map of the study area (Fig. 1) was used to delineate the parent materials in the study corresponding to the names of the communities where they are located. Five parent materials delineated include sandstone (SS), limestone (LS), mudstone (MS), basement complex (BC) and shale stone (SH). In each parent material or community, four composite samples were collected with aid of an auger at the depths of 0-15 and 15-30 cm in both upland and inland making a total of twenty composite soil samples used in this study. The soil samples were properly bagged, labelled and transported to laboratory where they were processed using standard procedures and used for organic matter fraction analysis.

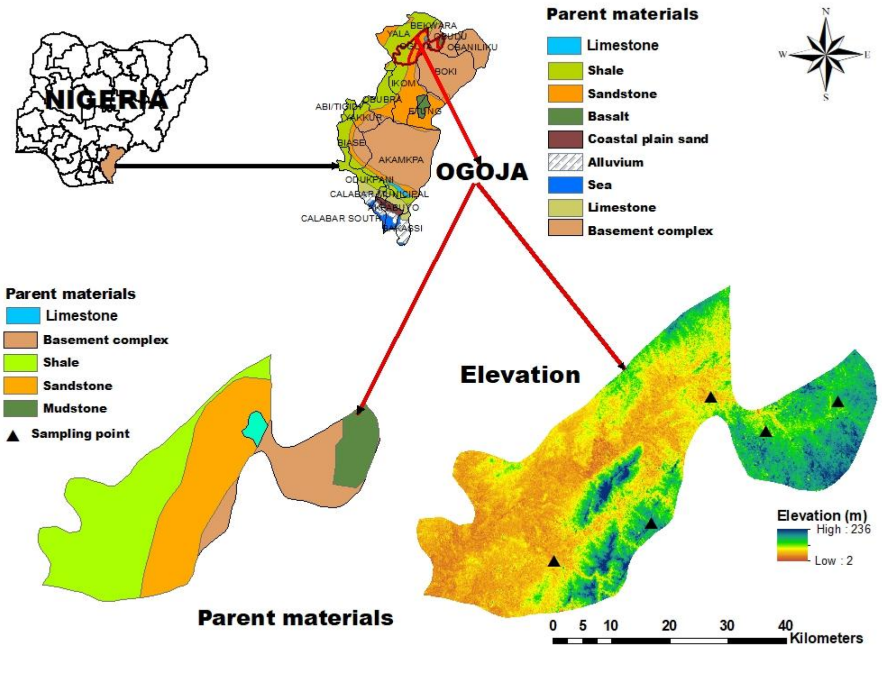


Fig. 1: Map of Ogoja L. G. A. in Cross River State showing locations of the study area.

Laboratory analysis

Humic substances: Determination of organic matter fractions was done by first determining total organic matter content of the soils. Humin and humic acid were determined by extraction with 0.1 N NaOH and 0.1 M pyrophosphate. An aliquot of the extract with 0.1 N NaOH and 0.1 M pyrophosphate was centrifuged and acidified to pH 2.0 with H_2SO_4 – 0.1 N. After 24 hour shaking the precipitate was filtered, washed several times with 0.05 N HCl, and dissolved again in NaOH 0.05 N to yield humic acid. Further washing with HCI and shaking yielded humin. Fulvic acid was calculated as humic acid minus humin (Black, 1965).

Physicochemical properties: Particle size analysis was done using Bouyocous hydrometer method (Gee and Or 2002). pH was obtained potentiometrically in soil: water suspension (1:2.5) as reported by Udo *et al*. (2009) while organic carbon was determined by Walkley-Black wet oxidation method using acid dichromate($K_2Cr_20_7$) method (Nelson and Sommers 1996). Total nitrogen was analyzed with modified micro-kjeldhal method (Udo *et al*., 2009) while available phosphorus was obtained using Bray P-1 method according to the procedures of Kuo (1996). Exchangeable cations were determined using the extract obtained after leaching samples with one normal neutral ammonium acetate (1 *N*, NH_4OAC, pH 7.0) solution. Calcium and magnesium were analyzed using the EDTA titration method while potassium and sodium were estimated by Flame photometer. Aluminum and hydrogen determined by titration using 0.1*N* Na0H solution (Udo *et al.*, 2009). ECEC and base saturation were obtained by computation method. ECEC was gotten by summing up all the exchangeable bases and exchangeable acidity while base saturation was computed by dividing the sum of all the exchangeable basic cations (Ca, Mg, K and Na) by the effective cation exchange capacity (ECEC) and then the quotient was multiplied by 100.

Data Analysis

The data collected were subjected to descriptive statistics such as minimum, maximum, mean, coefficient of variability and correlation.

Results and discussion

Organic matter fractions

The results of humic substances of the soils are presented in Table 1. All the fractions of organic matter were observed to be higher in organic matter rich surface soils than subsurface soils, however, humic acid and humin were relatively more concentrated than fulvic acid in the soils. Highest mean values of humic acid were obtained in the surface soil developed from SS in the inland (1.167 g/kg), followed by 0.908 g/kg in the subsurface soils of SH in the inland, while the least value (0.012 g/kg) was recorded in subsurface soil of MS in the inland. Humic acid had mean values of 0.649 and 0.683 g/kg, 0.327 and 0.055 g/kg, 0.736 and 1.167 g/kg, 0.976 and 0.839 g/kg and 0.449 and 0.411 g/kg in surface soils of upland and inland in BC, MS, SS, SH and LS accordingly. Similarly, in the subsurface soils, average values of humic acid obtained were 0.322 and 0.426 g/kg, 0.055 and 0.012 g/kg, 0.499 and 0.713 g/kg, 0.656 and 0.908 g/kg and 0.276 and 0.047 g/kg in the upland and inland of BC, MS, SS, SH and LS correspondingly. These values are slightly lower than the mean values of humic acid in a related study on land uses reported by Afu *et al.* (2016a), however similar finding have been reported by Asadu and Akamigbo (1990) and Asadu *et al.* (1997)

Fulvic acid was discovered to be consistently higher at surface than subsurface in both upland and inland soils of all the parent materials and the highest mean value (0.751 g/kg) was obtained in the inland soil of MS. Fulvic acid had averages of 0.237 and 0.313 g/kg, 0.533 and 0.751 g/kg, 0.297 and 0.707 mg/kg, 0.652 and 0.568 g/kg and 0.220 and 0.007 g/kg in the surface soils of upland and inland of BC, MS, SS, SH and LS correspondingly. In subsurface, fulvic acid had means of 0.244 and 0.363 g/kg, 0.227 and 0.328 g/kg, 0.056 and 0.128 g/kg, 0.040 and 0.402 g/kg and 0.001 and 0.415 g/kg in upland and inland of BC, MS, SS, SH and LS respectively (Table 1). Humin also had higher concentration in surface soils than in subsurface soils with the highest value of 1.039 g/kg obtained in the surface soil of SH (Table 1).

The values of humic and fulvic acids obtained in this study are in agreement with the values obtained in different land uses in Western Ghats, Karnataka State by Reddy *et al*. (2012) and Afu *et al.* (2016) in northern Cross River State, Nigeria. Highest values of fulvic acid and humic acid recorded in SH, SS and to some extend MS soils have positive implications on their physical and fertility properties. This means that SH, SS and MS are more fertile and also, that lower doses of fertilizers should be applied since the soils will tend to have higher CEC to retain the fertilizer nutrients and gradually release them to crops against leaching and other processes responsible for nutrient loss in soils. This is so because fulvic and humic acids contribute or have greater effects on soil CEC among the soil colloids. Fertilizers derived from humic substances have been reported to increase soil fertility properties and crop yield in several studies (Li *et al*., 2019). The importance of fulvic and humic acids in improvement of soil physical and fertility properties have been reported by several authors including Swift (1991), Khaled and Fawy (2011), Tan (2011), Moody and Aitken (1997), Nguyen *et al*. (2021), Ampong *et al*. (2022). According to Stevenson (1994), flocculation of clay-humic complexes is a major requirement for the aggregation process. Studies by Sootahar *et al.* (2019) and Sootahar *et al*. (2020) revealed that application of fulvic acid significantly increased soil buffering capacity, biological and chemical properties. Similar findings have been reported for fulvic and humic acids by Alsudays *et al*. (2024) and Ampong *et al*. (2022). Fulvic and humic acids in soils control

Table 1: Concentration of humic substances in the soil (g/kg)

		RANGE			MEAN		
Parent material	**Depth**	**HA**	**FA**	**H**	**HA**	**FA**	**H**
BC Upland	0 – 15	0.643 – 0.655	0.000 – 0.475	0.191 – 0.643	0.649	0.237	0.417
	15-30	0.000 – 0.643	0.161 - 0.328	0.328 - 0.726	0.322	0.244	0.527
Inland	0 – 15	0.000 – 1.367	0.161 - 0.464	0.464 – 1.206	0.683	0.313	0.835
	15-30	0.027 – 0.825	0.000 – 0.726	0.016 - 0.726	0.426	0.363	0.371
MS Upland	0 – 15	0.000 – 0.656	0.410 – 0.655	0.000 – 0.655	0.327	0.533	0.328
	15-30	0.055 – 0.055	0.045 – 0.409	0.045– 0.464	0.055	0.227	0.254
Inland	0 – 15	0.000– 0.109	0.273 – 1.229	0.164 – 1.229	0.055	0.751	0.696
	15-30	0.000 – 0.024	0.000 – 0.655	0.042 - 0.655	0.012	0.328	0.349
SS Upland	0 – 15	0.109 – 1.367	0.273 – 0.322	0.382 – 1.045	0.736	0.297	0.714
	15-30	0.276 – 0.724	0.000 – 0.112	0.246 - 0.884	0.499	0.056	0.564
Inland	0 – 15	0.967 – 1.367	0.321 – 1.092	0.126 - 1.045	1.167	0.707	0.585
	15-30	0.622 – 0.804	0.000 – 0.257	0.273– 0.965	0.713	0.128	0.619
SH Upland	0 – 15	0.827 – 1.126	0.322 – 0.983	0.154– 1.045	0.976	0.652	0.600
	15-30	0.482 – 0.829	0.000 – 0.080	0.082 – 0.402	0.656	0.040	0.242
Inland	0 – 15	0.069 – 1.608	0.170 – 0.965	0.792– 1.286	0.839	0.568	1.039
	15-30	0.691– 1.126	0.000 – 0.804	0.055 – 0.322	0.908	0.402	0.188
LS Upland	0 – 15	0.069– 0.829	0.013– 0.428	0.082 – 1.256	0.449	0.220	0.669
	15-30	0.000 – 0.553	0.000 – 0.002	0.000 – 0.546	0.276	0.001	0.273
Inland	0 – 15	0.062 – 0.759	0.000 – 0.013	0.082 – 0.792	0.411	0.007	0.437
	15–30	0.025 – 0.069	0.011 – 0.819	0.000 – 0.021	0.047	0.415	0.010

BC=basement complex, MS=mudstone, SS=sandstone, SH=shale, LS=limestone, HA=humic acid, FA=fulvic acid, H=humin

many environmental processes such as carbon sequestration, nutrient cycling and pollutant retention (Rice, 2001). Fulvic and humic acids can improve plant growth directly by accelerating respiration through their effects on photosynthesis and by increasing water and nutrients uptake and yields of plants (Raiesi *et al*., 2021). They are also assumed to increase the chlorophyll content of green plants and hence can be used to control chlorosis and improve photosynthesis. The implication of having high contents of humic substances in these soils formed from diverse parent materials ranges from contributing to high CEC of the soils to increased fertility. From environmental standpoint, complexing of heavy metal ions by humic substances may temporarily reduce toxic hazard for humans, plants and animals. Of considerable interest in environmental pollution are also the interactions of pesticides and other agrochemicals and their degradation products with soil organic matter. Stevenson (1994) believes that pesticide residues can form stable complexes with soil organic compounds greatly increasing their persistence in soils

Physico-chemical properties

The results of physicochemical properties of the soils studied are presented in Tables 2 and 3. The values of soil properties therein show that inland soils are relatively higher in fertility indices (ECEC and base saturation) compared to upland soils with SH and LS soils being higher in these indices in both upland and inland than other parent materials. The texture of the soils varied across parent materials with sand as the most dominant among the soil separates varying from 380 in BC to 810 % in LS and 300 in BC to 540 % LS in the surface and subsurface soils of the upland. In the inland sand varied from 380 % in BC to 680 % in MS with mean of 500 % and 260 % in SS to 600 % in MS with mean of 412 % in surface and subsurface soils respectively. In both inland and upland soils, BC had higher percentages of clay than other parent materials. Higher content of clay fraction in soil has positive implication in the soil fertility. This is confirmed in the studies of Thabit *et al*. (2023) who obtained average CEC of clay fraction of soil as 57.6 % compared to 30.66 % in silt fraction.

This means that contribution of clay to CEC or buffering capacity of soils will be higher in BC than soils of other parent materials. Also, higher fertility indices obtained in inland soils than upland may be due to transportation and deposition of organic matter and soil nutrients in inland by flooding and surface runoff. The implications of higher fertility parameters in inland soils and in SH and LS is that productivity can be optimized and sustained in these soils with low input while the reverse is the case for other parent materials.

In upland, the results obtained showed that pH was strongly acidic in all parent materials except LS that was slightly acid (pH 6.1) in both surface and subsurface soils. However, inland soils pH was slightly higher varying from medium acid in BC, MS, SS to slightly acidic in SH and LS (Foth, 2006). Higher pH values gotten in LS and SH may be due to higher level or values of Ca obtained in the soils. Limestone is basic in nature and has been used in several soil studies to correct pH (Arobas *et al*., 2023; Kowalenko and Ihnat, 2010). The results of this study further revealed that in the upland, OC was high (> 2%) in MS, SH and SS and low (<1.5) in BC and LS at both soil depths while in the inland soil OC was only high in SH and low in the remaining parent materials using the soil fertility rating of Landon (1991).

In the upland, TN was low (0.1-0.2%) except in SS and surface soil of SH where it was moderate (0.2 – 0.5 %) whereas in the inland it was low in all parent materials except in the subsurface soil of SH (0.23 %). Available P was low (< 8 mg/kg) across the parent materials in upland and inland except subsurface of LS having high value of 70.75 mg/kg in upland and SH that had 24.62 mg/kg in the inland. Similarly, Ca was low across soil depths and parent materials in the upland but moderate (5.0 – 10 cmol/kg) in LS in the upland, MS and LS in the inland and high (> 10 cmol/kg) in SH in the inland. Furthermore, in both the upland and inland Mg was generally moderate (1.5 – 3.0 cmol/kg) except in surface soils of LS and SH where it was high (> 3.0 cmol/kg). Unlike other fertility indices, K was generally low across the studied parent materials in both inland and upland. Low soil K is a common problem in tropical soils (Rosolem and Steiner, 2017; Benites *et al*., 2010) due to its fixation by minerals, leaching and low levels of K minerals like feldspar and mica in tropical soils. Sodium was generally low. Also, K is very sensitive to changes in soil environment in high temperature and precipitation areas (Shao *et al*., 2022) and as a result, it is a limiting factor for plant growth mostly in regions with acid soils. These, among other factors including the essential role K plays in plants are the reasons why K is an integral component of fertilizer program for tropical soils in order to obviate the problems that emanate from K deficiency in plants.
In the upland Al and H contributed to the acidity of the soil with highest values of Al (1.68 and 1.69 cmol/kg in surface and subsurface) recorded in BC while in LS Al was not detected.

Table 2: Physico-chemical properties of upland soil

PM	Soil depth (cm)	Particle size			Texture	pH (H_2O)	OC	TN	AV. P (mg/kg)	Exch. Cations				Exch. Acidity		ECEC	BS(%)
		Sand	Silt	Clay						Ca	Mg	K	Na	Al^{+3}	H^+		
		→ g/kg ←					← g/kg →			→ cmol/kg ←							
BC	0-15	380	220	400	Clay loam	4.8	1.3	0.11	2.75	1.4	2	0.09	0.08	1.68	0.96	6.21	57
	15-30	300	200	500	Clay	5.2	1.32	0.11	2.74	1.42	2.2	0.1	0.08	1.69	0.97	6.24	62
MS	0-15	400	380	220	Loam	4.8	2.39	0.21	3.27	2.6	1.6	0.09	0.07	1.48	0.96	6.8	64
	15-30	500	250	250	SCL	5.2	2.32	0.22	6.12	1.6	1.7	0.08	0.11	1.52	0.96	6.82	65
SS	0-15	380	360	260	Loam	4.9	3.15	0.27	2	2.6	1.8	0.1	0.08	1.0	0.4	5.98	77
	15-30	380	350	270	Clay loam	5.2	3.2	0.3	2.3	2.8	1.9	0.11	0.11	1.2	0.42	5.99	78
SH	0-15	550	400	50	Sandy loam	5.6	2.77	0.24	13	4.4	2.2	0.1	0.08	0.52	1.56	8.86	77
	15-30	490	320	190	Loam	5.2	0.82	0.07	6.87	2.4	1.4	0.11	0.09	0.52	1.82	5.6	71
LS	0-15	810	140	50	Loamy sand	6.1	0.28	0.01	4.12	5.8	3.6	0.13	0.11	0	0.4	10.32	93
	15-30	540	140	320	SCL	6.1	0.66	0.05	70.75	7.2	3	0.11	0.09	0	0.68	11.22	93
Surface sample																	
Min		380	140	50		4.800	0.280	0.010	2.000	1.400	1.600	0.090	0.070	0.000	0.40	5.980	57
Max		810	400	400		6.100	3.150	0.270	13.000	5.800	3.600	0.130	0.110	1.680	1.56	10.320	93
Mean		504	300	196		5.240	1.978	0.168	5.028	3.360	2.240	0.102	0.084	0.936	0.85	7.634	73.6
SD		185.28	114.01	149.1		0.586	1.174	0.107	4.523	1.734	0.792	0.016	0.015	0.690	0.48	1.883	13.85
CV (%)		36.8	38.0	76.1		11.2	59.4	63.6	90.0	51.6	35.4	16.1	18.1	73.7	56	24.7	18.8
Sub-surface sample																	
Min		300	140	190		5.20	0.660	0.05	2.300	1.420	1.400	0.080	0.080	0.000	0.42	5.600	62
Max		540	350	500		6.10	3.200	0.30	70.750	7.200	3.000	0.110	0.110	1.690	1.82	11.220	93
Mean		442	252	306		5.38	1.664	0.15	17.756	3.084	2.040	0.102	0.096	0.986	0.97	7.174	73.8
SD		99.096	85.849	118.025		0.402	1.076	0.11	29.693	2.370	0.611	0.013	0.013	0.710	0.527	2.305	12.36
CV (%)		22.4	34.1	38.6		7.5	64.6	71.0	167.2	76.8	29.9	12.8	14.0	72.0	54.3	32.1	16.7
Overall mean		473	276	251		5.31	1.82	0.16	11.39	3.22	2.14	0.10	0.09	0.96	0.91	7.40	73.7

OC = organic carbon; OM = organic matter; TN = Total nitrogen; AV. P = available phosphorus; BS = base saturation; ECEC effective cation exchange capacity; BC = basement complex, MS = mudstone, SS = sandstone, SS= shale stone, LM = limestone; SCL = sandy clay loam

Table 3: Physico-chemical properties of inland soil

	Soil depth (cm)	Particle size Sand	Silt	Clay	Texture	pH (H_2O)	OC	TN	AV. P (mg/kg)	Exch. Cations Ca	Mg	K	Na	Exch. Acidity Al^+	H^+	ECEC	BS (%)
		→ % ←					← g/kg	→	→	cmol/kg ←							
BC	0-15	380	220	400	Clay loam	5.4	1.4	0.12	2.8	1.5	2.4	0.1	0.09	1.56	0.57	6.8	60
	15-30	380	200	420	Clay	5.5	1.3	0.11	2.7	1.41	2.6	0.11	0.07	1.68	0.68	0.21	62
MS	0-15	680	250	70	Sandy loam	5.6	1.44	0.12	6.12	6.6	1.8	0.13	0.11	0.52	0.2	9.36	92
	15-30	600	300	100	Sandy loam	5.8	1.45	0.13	6.22	6.7	1.9	0.14	0.08	0.56	0.26	9.46	93
SS	0-15	550	20	250	SCL	5.5	1.6	0.14	2.75	4.6	1.6	0.11	0.09	0.24	0.84	9.25	87
	15-30	260	350	90	Clay loam	5.3	0.94	0.08	4.62	3.4	2.6	0.09	0.07	0.96	1	8.12	76
SH	0-15	450	420	130	Loam	6.8	2.15	0.18	6.25	10.4	4.2	0.13	0.11	0	0.4	15.84	97
	15-30	560	270	160	Sandy loam	6.9	2.71	0.23	24.62	12.8	2.4	0.13	0.1	0	0.68	10.32	93
LS	0-15	440	400	160	Loam	6.3	0.86	0.07	3.25	8.6	2.4	0.12	0.1	0	0.6	11.82	95
	15-30	260	400	340	Clay loam	6.4	0.87	0.08	3.27	8.7	2.6	0.11	0.09	0	0.62	11.22	90
Surface sample																	
Min		380	20	70		5.400	0.860	0.070	2.750	1.500	1.600	0.100	0.090	0.000	0.200	6.800	60
Max		680	420	400		6.800	2.150	0.180	6.250	10.400	4.200	0.130	0.110	1.560	0.840	15.840	97
Mean		500	262	202		5.920	1.490	0.126	4.234	6.340	2.480	0.118	0.100	0.464	0.522	10.614	86.2
SD		117.69	161.617	128.335		0.606	0.462	0.040	1.792	3.468	1.026	0.013	0.010	0.649	0.239	3.419	15.12
CV (%)		0.235	0.617	0.635		10.2	31.0	31.5	42.3	54.7	41.4	110	100	139.9	45.7	32.2	17.5
Sub-surface sample																	
Min		260.0	200	100		5.300	0.870	0.080	2.700	1.410	1.900	0.090	0.070	0.000	0.260	0.210	62
Max		600.0	400	420		6.90	2.710	0.230	24.620	12.800	2.600	0.140	0.100	1.680	1.000	11.220	93
Mean		412.0	306	282		5.98	1.454	0.126	8.286	6.602	2.420	0.116	0.082	0.640	0.648	7.866	82.8
SD		161.62	75.37	143.248		0.661	0.743	0.062	9.231	4.473	0.303	0.019	0.013	0.709	0.263	4.430	13.59
CV (%)		39.2	24.6	50.8		11.1	51.1	49.1	111.4	67.8	12.5	16.8	15.9	110.8	40.6	56.3	16.4
Overall mean		442	252	306		5.380	1.664	0.150	17.756	3.084	2.040	0.102	0.096	0.986	0.970	7.174	73.8

OC = organic carbon; TN = Total nitrogen; AV. P = available phosphorus; BS = base saturation; ECEC effective cation exchange capacity; BC = basement complex, MS = mudstone, SS = sandstone, SH= shale stone, LM = limestone; SCL =sandy clay loam

Also, in the inland highest values of Al of 1.56 cmol/kg and 1.68 cmol/kg for surface and subsoil were recorded in BC while Al was not detected in SH and LS. Additionally, ECEC was moderate (10 – 20 cmol/kg) in LS, SH in the inland, LS in the upland and low in (< 10 cmol/kg) in the remaining parent materials in both upland and inland. BS was high across the soils, however, higher values were obtained in the inland than the upland (Tables 2 and 3). The findings of this study are in agreement with similar works by Afu *et al*. (2022) and Abam and Orji (2019) on soils of different parent materials within Cross River State. However, contrary findings to the physicochemical properties obtained in this study have been made in similar studies in the area by Afu *et al*. (2015) and Afu *et al.* (2016b)

Correlation between organic matter fractions and ECEC with soil properties

The relationship between organic matter fractions and ECEC with soil properties are shown in figures 2 and 3. In the upland soils, the results showed that fulvic acid correlated negatively and non-significantly with most soil properties except for its significant and positive correlation with silt and non-significant relationship with OM, Al and TN (Fig 2a). This implies that an increase in fulvic acid will result to a decrease in these soil properties. Furthermore, in inland soil, fulvic acid was negatively correlated with silt, H^+, Al^{+++} and Mg^{2+} while positive association were recorded between fulvic acid and sand, TN, Na, OM, K, ECEC and Ca (Fig. 3a). The implication of this is that in inland soils, increase in level of fulvic acid causes increase in TN, Na, OM, K, ECEC and Ca and reduction in the levels of H^+, Al^{+++} and Mg^{2+}. This positive association is in agreement with the study of Vikram *et al*. (2022) who reported increased phosphorous, potassium, nitrogen and organic matter with increase in humic substances. However, the correlation between fulvic acid and all soil properties were not significant in the inland (fig. 3a).

Also, humic acid had positive association with H^+, OM and TN in both upland and inland soils, had negative association with H^+ and clay in both upland and inland soils, negative association with ECEC, Al, Mg, Na and available P in the upland while it had positive association with Mg and OM in the inland soils (Figures 2b and 3b). The association between humic acid and soil properties is somewhat similar to the study of Ren *et al*. (2022) who in their study observed that application of fulvic acid led to 7.74 %, 174.82 %, 231.91 %, 335.93 % and 316.10 % increase in pH, OM, nitrogen, exchangeable Ca, and Mg content of soil. Only silt had significant correlation with humic acid in the upland while in the inland humic acid had significant relationship with H, OM, and TN. The relationship between humin and soil properties in upland was all positive and non-significant except for the negative and non-significant relationship it had with H, AP, clay and Al while contrary observation was made in the inland were most soil properties correlated negatively with humin. ECEC had higher and significant relationship with soil properties when compared to humin, fulvic and humic acids. ECEC correlated significantly and positively with BS, Ca, Na, pH, silt, K and Mg, negatively and significantly with Al, clay, H and OM in both the inland and upland soils.

The results of positive correlation between humic substances and ECEC obtained in this research are in agreement with study of Afu *et al.* (2016a) who reported that organic matter fractions along with inorganic soil components (clay and silt) contributed to the CEC of soils. This further confirms the importance of contribution of humic substances to CEC of soils which is a critical parameter in soil fertility consideration.

Fig 2: Correlation between organic matter fractions and ECEC with soil properties in upland soil

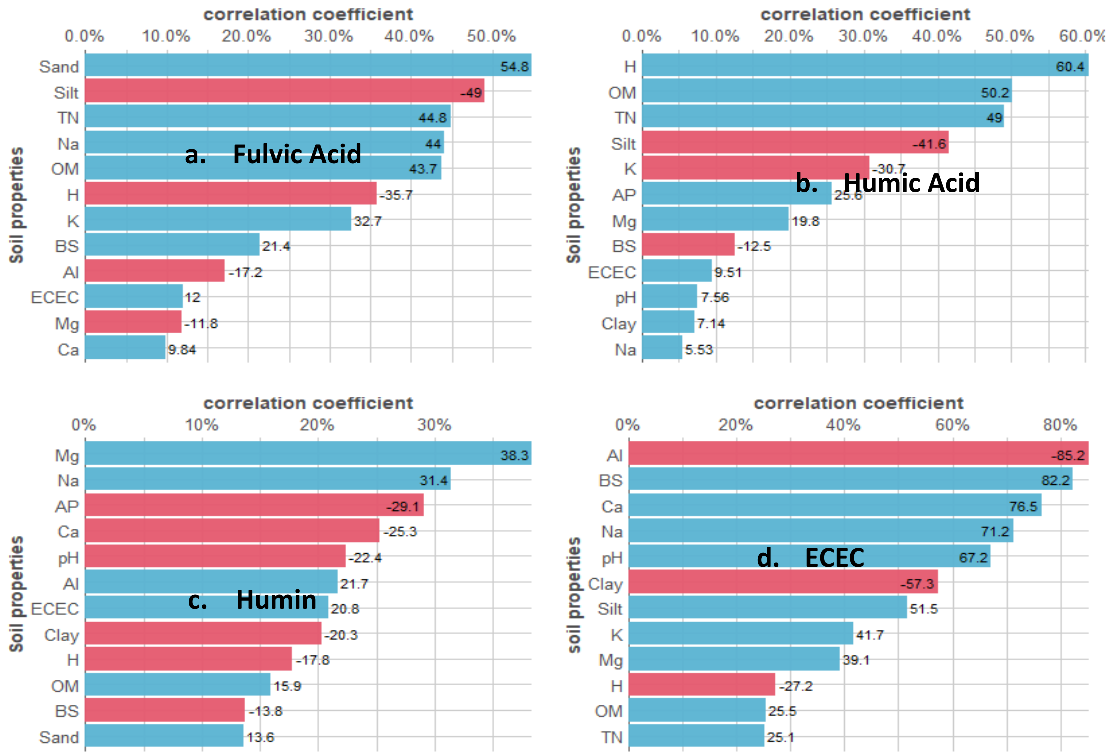
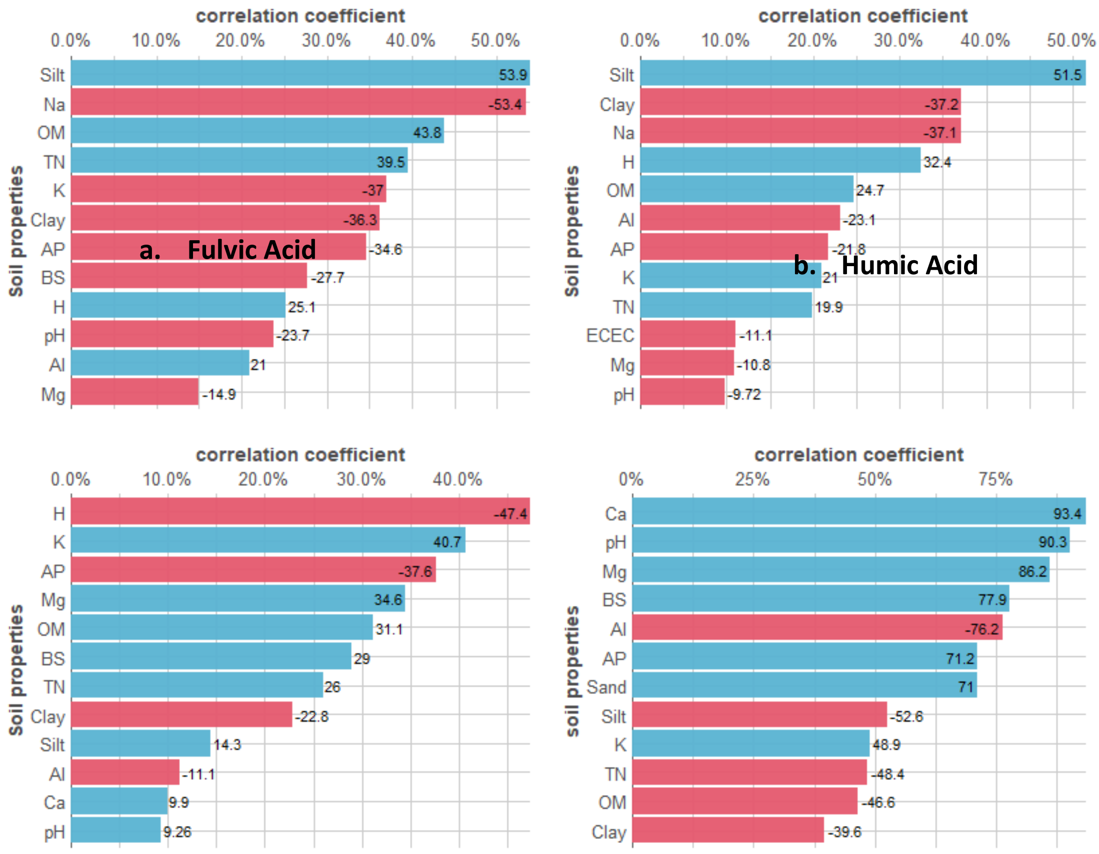


Fig. 3: Correlation between organic matter fractions and ECEC with soil properties in inland soil

SUMMARY AND CONCLUSION

The importance of organic matter in soil fertility is in the processes of mineralization releasing nutrients for plant uptake and humification producing humic substances that contribute to the soil's CEC and also playing other functions in the soil. From this study it was revealed that SH, SS and MS had higher contents of humic substances in both upland and inland and as such will tend to be fertile than other soils with greater content of humin that contributes to soil structural stability and resistance to erosion due to its inert nature. The study also showed that humic substances were more concentrated in the surface than subsurface soils. ECEC correlated positively and significantly with BS, Ca, Na, pH, silt, K and Mg, fulvic and humic acids correlated positively with TN and OM while other correlation relationship between HS and soil properties varied between negative/positive non-significant relationship to negative/positive significant relationship in all parent materials of both upland and inland. The result of physicochemical analysis indicated that inland soils were relatively higher in fertility indices (ECEC and base saturation) compared to upland soils with SH and LS soils being higher in fertility parameters in both upland and inland than other parent materials.



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