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EFFECTS OF OIL PALM BUNCH REFUSE ON HUMIC ACID CONTENT OF FIVE SOILS GROWN TO OIL PALM

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ABSTRACT

The effect of the addition of composted oil palm bunch refuse on five different soils supporting palms with respect to the acidic functional groups of the humic acids in the soils was investigated. The composts was added to the soils at different rates. The results showed that there was a highly significant (P =0.001) increase in the carboxylic (-C00H) groups as compared with the phenolic -OH groups.

Total acidity also increased with the E_4/E_6 ratio of the isolated humic acids. These changes were associated with the different types of soil and rates of applied composts. Carboxylic (-C00H) groups contributed more to total acidity of the humic acids. The study revealed that addition of composted oil palm bunch refuse to soil is a potential source of carboxylic (-C00H) groups in the humic acid fraction of the soil.

Key words. Oil palm bunch, humic acids, carboxylic groups, phenolic groups, E_4/E_6 ratio.

INTRODUCTION

Recently, there has been much interest in the subject of soil humus and humates, particularly humic and fulvic acids. However, there exist fundamental agreements on the benefits of humus and humic acids which include (i) humic acid is a source and sink for nutrient element which can form organic moieties with nitrogen, phosphorus sulphur, etc. (ii) they possess charge properties which make them a site for ion exchange (often the most important one in the low activity clay soil of the tropics (iii) they have physical and chemical properties which facilitate aggregation with mineral particles, particularly clays and in turn modify soil physical structure and influence soil water regimes (Tisdale et al., 1985; Chen and Avid, 1990, Swift and Woomer, 1993; Larson and Weber; 1994, Reintam et al., 2000), but controversies on the benefits of application of applied humates (the deposits containing the humic acids) are that (i) while addition of humates to soils, commonly increases the extractable form of an element, it may not necessarily increase its availability to plants (ii) the bond between the mineral particles of the soil and the functional groups of the humates may be of a physical or a chemical nature (iii) the available sources of humates are not standardized, hence its mechanism of reaction when applied to soil is not clearly understood (Mclaren and Skujins, 1971; Hoffman and Austin, 1993).

A basic component of the reactions involving humic acids in the soil plant water ecosystem is the presence of the carboxyl and phenolic hydroxyl group (Theng, 1979). Several workers have also investigated the reactions involving the distribution of oxygen containing functional groups in the macro molecular reactive sites of the humic substances. (Lobartini and Tan, 1988; Inskeep and Silvertooth, 1988; Chen et al., 1992; Baes and Bloom, 1989; Grossl and Inskeep, 1991). Their Studies showed that (i) almost all possible groups (carboxyls, phenolic, enolic and alcoholic hydroxyls, guinones, hydroxyquinones, other carboxyls, esters, lactones, ethers) can be found in humic acids (ii) total acidity of humic acids is generally calculated as the sum of the phenolic hydroxyl and carboxylic hydroxyl groups (iii) The adsorption of

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humic acids on solid phases is affected by the types of surface present and the pH of the medium. Despite these interesting findings there is scanty information regarding the contribution of humates or sources of humic acids to the availability or otherwise of these oxygen containing groups.

The present study aims at determining the effect of the application of composted oil palm bunch refuse on the concentration of the carboxylic and phenolic hydroxyl groups of some soils grown to oil palm.

MATERIALS AND METHOD

Four soils supporting palms at the Nigerian Institute for Oil Palm Research earlier classified using United States Department of Agriculture Soil Taxonomy (Soil Survey Staff, 1975) method of classification as Dystric Cambisol (Ahiara series) Dystric Nitosol (Alagba series) Dystric Nitosol, (Orlu series) and Dystric Cambisol (Kulfo series) as well as the transition soil between the sedimentary and basement complex soils at Ohosu in Edo State were

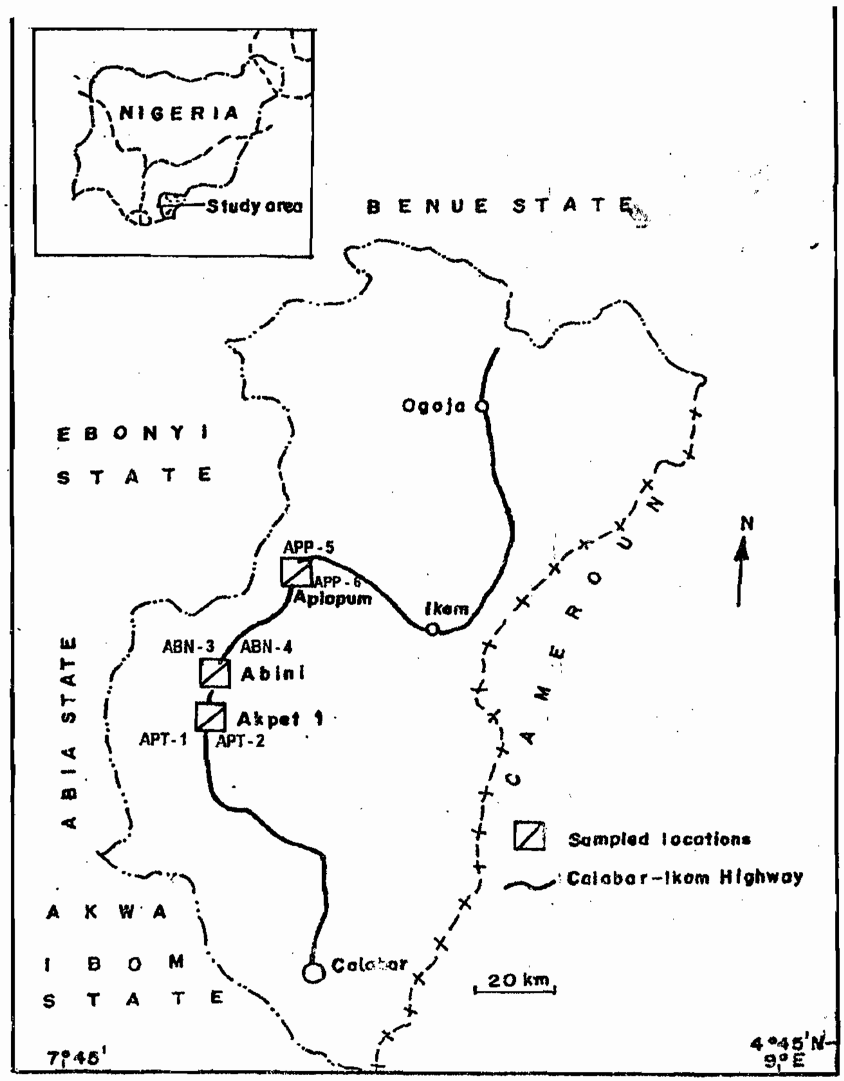

FIG.1: MAP OF CROSS RIVER STATE SHOWING SAMPLED LOCATIONS

TABLE 1: T al acidity, COOH, OH, E_4/E_6 ratio and **compost treatment** associated with the different soil types at 0 months.

Compost Treatmer (%)	Total Acidity	COOH	OH	E_4/E_6	Soil Type
	←	molkg^{-1}	→		Alagba Series
0	3.1	1.4	1.7	6.1	
1	3.1	1.4	1.7	6.0	
2	2.7	1.5	1.2	6.3	
3	2.5	1.7	0.8	6.4	
					Ahiara Series
0	2.2	0.9	1.3	5.8	
1	2.6	1.3	1.3	5.7	
2	2.7	1.5	1.2	5.9	
3	3.1	2.3	0.8	6.2	
					Orlu Series
0	3.2	0.5	2.7	6.5	
1	3.3	1.0	2.3	6.4	
2	2.7	1.5	1.2	5.9	
3	3.7	2.2	1.5	6.8	
					Kulfo Series
0	3.1	1.4	1.7	6.7	
1	3.0	1.5	1.5	6.4	
2	3.3	1.7	1.5	6.8	
3	3.7	1.8	1.9	6.9	
					Ohosu Series
0	3.4	1.4	2.0	6.1	
1	3.4	1.4	1.0	6.1	
2	3.5	1.0	2.5	6.2	
3	3.7	1.1	2.6	6.3	

sampled at 0-15cm depth. The soils were taken in 1.0kg lots in perforated plastic cups and amended with composted empty palm bunch refuse at the rate of 0, 1, 2 and 3%. The treatment were arranged in a completely randomized design and replicated three times and kept in the green house. Thereafter the compost amended soils were thoroughly mixed and moistened to field capacity with distilled/deionized water. Further moistening was done as and when necessary to maintain optimal moisture content throughout the period of incubation. The samples were taken for laboratory analysis at the beginning of incubation (O month) and at 6 Months of incubation.

LABORATORY ANALYSIS

Humic substances were extracted by a modification of the procedure described by Schnitzer and Preston (1986). Two hundred grammes (dry-weight basis) of the soil and soils applied with composts were put into 4L polyethylene container. Two litres of 0.5M NaOH solution was transfered into the container and shaken for 24hrs at room temperature (-27°C). The supernatant liquid containing the soluble humic substances was separated by centrifugation at 1600g for 45min. The residue was resuspendend in 0.5M NaOH solution and the procedure repeated 13 times. The combined solutions were filtered to remove solids, acidified with 6M HCl to pH 1, and allowed to stand at room temperature for 24hr. The supernatant containing the extracted fulvic acid was separated from the precipitated humic acids by centrifugation. The humic acids was purified by the HCl/HF method (Schnitzer and Preston, 1986) until the ash content [illegible].0% following this treatment, the humic acid was dialyzed against distilled water until the dialyzate was free of Cl and exhibited a neutral pH, at which point it was freeze dried.

Acidity: Total acidity and carboxyl groups were measured by methods described by Schnitzer and Gupta (1956). Phenolic hydroxyls were considered to be equal to the difference between total acidity and carboxyl groups.

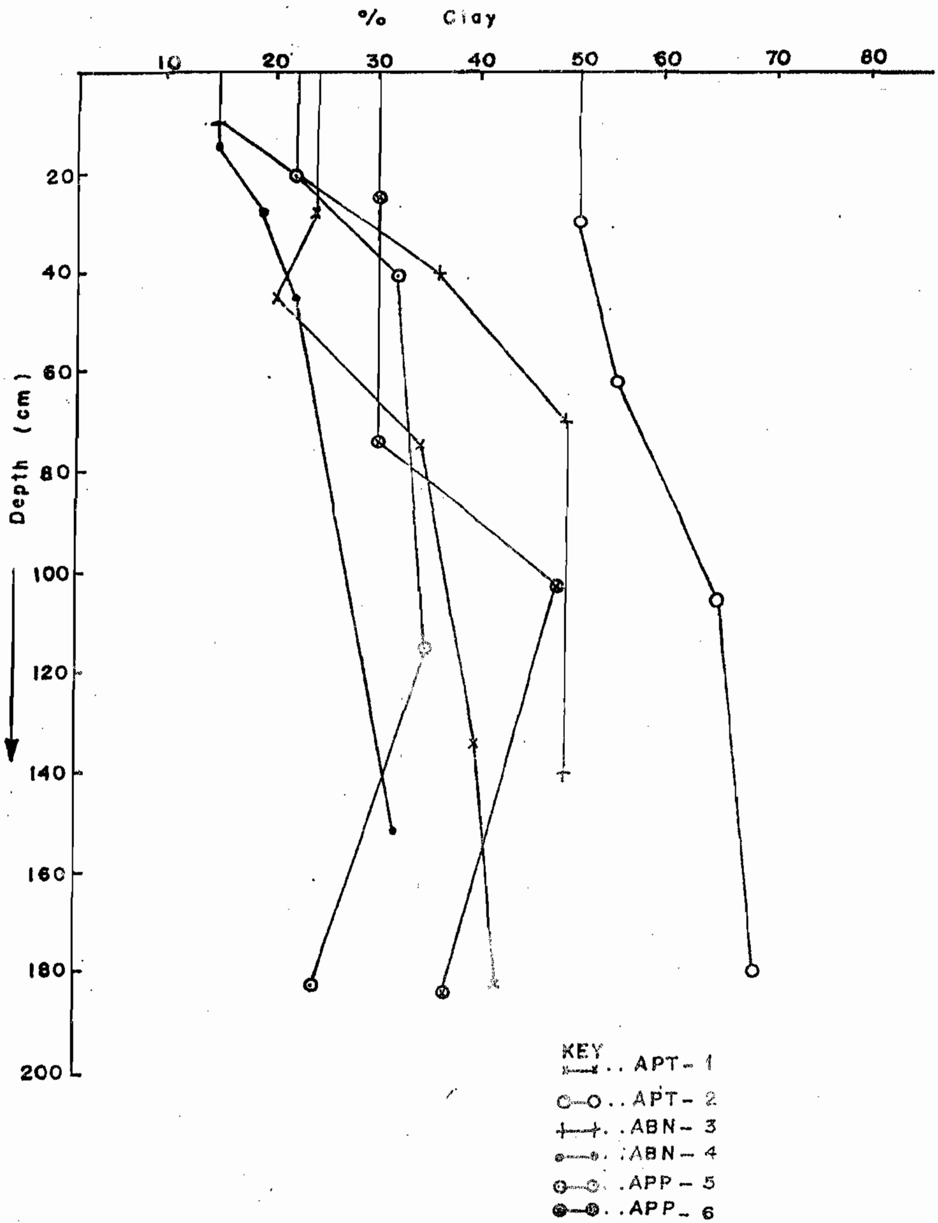

FIG 2: DEPTH DISTRIBUTION OF PERCENT CLAY OF THE SAMPLED PROFILES.

TABLE Total acidity, COOH, OH E_4/E_6 ratio and compost treatment associated with the different soil types at 6 months.

Compost Treatment (%)	Soil Type	Total Acidity	COOH	OH	E4/E6
		←	$molkg^{-1}$	→	
0	Alagba Series	3.22	1.6	1.6	6.1
1		3.2	1.8	1.4	6.2
2		3.1	1.8	1.3	6.4
3		3.4	2.1	1.1	6.4
0	Ahiara Series	2.2	1.0	1.2	5.9
1		2.8	1.5	1.3	5.8
2		2.8	1.4	1.4	6.0
3		3.0	2.1	0.9	6.7
0	Orlu Series	3.1	1.7	1.4	6.5
1		3.5	2.1	1.4	6.6
2		3.6	1.9	1.7	6.6
3		3.9	2.0	1.9	7.1
0	Kulfo Series	3.1	1.4	1.7	6.1
1		3.2	1.6	1.6	6.4
2		3.5	2.0	1.5	6.3
3		3.5	1.8	1.7	6.7
0	Ohosu Series	3.3	1.3	1.0	6.1
1		3.4	1.7	1.7	6.3
2		3.5	1.9	1.6	5.8
3		3.9	1.8	2.1	6.0

E_4/E_6 Ratio: The ratio of optical densities or absorbancies of dilute aqueous humic and fulvic acid solutions at 465nm and 665nm is known as the E_4/E_6 ratio and it is widely used by soil scientists for the characterisation of these materials (Kononova, 1966; Chen and Schnitzer, 1977). E_4/E_6 ratio was achieved by dissolving between 2-4mg of humic acids in 10ml of 0.05M $NaHCO_3$ solution of pH 8.0 and 0.05M $NaHCO_3$ solution was used in the reference cell of a UV-VIS spec[illegible] 21D Spectrophotometer. Absorbances were measured at 465nm and 665nm.

The data were subjected to analysis of variance (ANOVA) using the statistical analysis system (SAS, 1965).

RESULTS AND DISCUSSION

The application of composts at different treatments to the various soil types had different effects on the concentrations of the components of the humic acids studied (Tables 1 and 2). The composts applied had a highly significant effect on the carboxylic (-C00H) group of the humic acids (P = 0.001), (Table 3), while there was

TABLE 3: Mean effects of treatment on COOH and OH groups in the **five soil types.**

	Soil Types					
Treat. (%)	Alagba	Ahiara	Orlu	Kulfo	Ohosu	Mean
1.00 (0)	1.500	0.950	1.100	1.400	1.350	1.260
2.00 (1)	1.600	1.400	1.550	1.550	1.550	1.530
3.00 (2)	1.650	1.450	1.850	1.850	1.450	1.620
4.00 (3)	1.900	2.200	1.800	1.800	1.450	1.890
Mean	1.662	1.200	1.650	1.650	1.450	
Treat. (%)						
1.00 (0)	1.650	2.050	1.100	1.700	2.000	1.730
2.00 (1)	1.550	1.300	1.550	1.500	1.850	1.620
3.00 (2)	1.250	1.300	1.850	1.500	2.050	1.600
4.00 (3)	0.950	0.850	1.800	1.800	2.350	1.530
Mean	1.350	1.175	1.675	1.637	2.063	

Variate: COOH. Grand mean 1.575.

-COOH

LSD: Treat. = 0.2673***

Soil type = 0.2989 NS

Soil type = 0.5978 NS

***Highly significant at P = 0.001

NS = Not significant

Variate: OH. Grand Mean = 1.620.

-OH

LSD: Treat. = 0.2864 NS

Soil type = 0.3202***

Treat. x Soil type = 0.604 NS.

***Highly significant at P = 0.001

NS = Not significant

comparatively no significant interaction between the rates of applied composts on the soil type and equally no significant response was obtained from the applied composts and possible reactions with the different types of soil used (Table 3) on the concentration or availability of humic acids -COOH groups. Addition of composts at the various rates produced no significant effect on the changes in the amount of phenolic OH groups and applied compost showed no significant interaction with the various soil types resulting in steady concentration of phenolic OH groups. There was significant response (Table 3) by the various soil types on the amount of phenolic OH groups (P = 0.001) determined. In all, composts addition at the various rates, resulted in increased total acidity and pronounced effect of the different types of soil on the total acidity (P= 0.001), while there was equally significant interaction between the applied composts and the different types of soils (Table 4). A few reasons may be adduced for these observations.

It has been shown that carboxyl and phenolic hydroxyl groups are mainly responsible for the binding of the humic molecules in the clay minerals in soils (Theng, 1979). According to Baes and Bloom (1989), phenolic OH groups are less H^+ bonded in humic acids. Addition of composts may lead to increased availability of carboxyl (-COOH) group due to reduced bonding effect between phenolic OH groups and humic acids since there was an overall increase in the total acidity (summation of carboxylic and phenolic OH). Moreover, because the acidic groups will tend to be strongly hydrated in solution, a fewer number of such groups in this case phenolic OH, mean a decrease in the hydration energy. This implies that the heat energy available for breaking down the clay-humus bonds in the soil is consequently reduced (Nayak et al., 1990). The addition of composts may have suppressed the possible binding mechanism between the phenolic OH of the humic acids contained in the soil and that contributed by the composts, since there was a significant decrease in the concentration of phenolic OH as the composts was added to the various soils (Table 3). Organic matter (composts) addition to soil enhances greatly moisture retention capacity (Mbagwu and Piccolo, 1989), consequently increased water content in soil humate system may lead to higher concentrations of carboxylic groups. This perhaps supports the humic acid model proposed by Wershaw (1986) as resembling micelles or membranes where the inside is hydrophobic and the outside is hydrophilic.

The E_4/E_6 ratio significantly increased with the addition of composts with a high level of interaction ($P = 0.001$). Similarly, the various types of soils used had their responses on the E_4/E_6 ratio, while the compost interaction with the soils did not show any significant effect on the E_4/E_6 ratio (Table 4). Higher E_4/E_6 ratio associated with increased total acidity due to greater concentration of carboxylic groups has been reported indicating lower molecular weights of humic acids (Chen et. al., 1977). Chen et al., (1977) have also opined that the E_4/E_6 ratio is affected by the particle size (particle or molecular

TABLE 4: Mean effects of treatment on Total acidity and E_4/E_6 ratio in the five soil types.

	Soil Type					
Treat. (%)	**Alagba**	**Ahiara**	**Orlu**	**Kulfo**	**Ohosu**	**Mean**
1.00 (0)	3.150	2.200	3.150	3.100	3.350	2.990
2.00 (1)	3.150	2.700	3.400	3.100	3.400	3.150
3.00 (2)	2.900	2.900	3.600	3.400	3.500	3.230
4.00 (3)	2.950	3.050	3.800	3.600	3.800	3.440
Mean	3.037	2.675	3.487	3.300	3.512	
Treat. (%)						
1.00 (0)	6.100	8.850	6.500	6.400	6.100	6.190
2.00 (1)	6.100	5.750	5.500	6.400	6.200	6.190
3.00 (2)	6.350	5.950	6.600	6.550	6.000	6.290
4.00 (3)	6.400	6.450	6.450	6.800	6.150	6.550
Mean	6.237	6.000	6.000	6.637	6.112	

Variate: Total acidity. Grand Mean = 3.202. Variate: E_4/E_6 ratio. Grand Mean = 6.305

Total Acidity

LSD: Treat. = 0.1535***

Soil type = 0.1736***

Treat. x Soil type = 0.3472***

*** Significant at P = 0.001

*** Highly significant at P = 0.001

E_4/E_6 ratio

LSD: Treat. = 1.795***

Soil type = 0.2007***

Treat. x Soil type = 0.4010 NS.

***Highly Significant at P = 0.001

NS = Not significant

weight), pH, the free radical concentration, contents of 0, C, C00H and total acidity, and apparently independent on humic acid concentration.

CONCLUSION

Addition of organic matter, in this case composted oil palm bunch refuse to soil has effect on the concentrations of the carboxylic and phenolic OH groups of the humic acids. This effect depends on the rates of applied composts and the type of soil under investigation. The present study reveals that total acidity exhibited by the soils due to he summation of carboxylic and phenolic OH groups increased primarily due to increase in the carboxylic groups, while the E_4/E_6 ratio equally had higher values due to composts addition to the soil. Generally, application of composted oil palm bunch refuse to soil is a potential source of carboxylic (-C00H) group in the humic acids in the soil.

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