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SULPHATE SORPTIVITY IN RELATION TO LAND USE TYPES OF SOILS OF THE HUMID TROPICAL RAINFOREST, SOUTHEASTERN NIGERIA

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ABSTRACT: *Sorption phenomenon plays relevant role in the estimation of the solubility, availability, mobility and tendency of ion pollution of the environment. Sulphate sorptivity in relation to selected land use types of soils of the humid tropical rainforest, southeastern Nigeria was evaluated by equilibrating 2 g fine earth soil samples with 20 ml of 0.2 N* $ZnS0_4$ *containing graded (0, 5, 10, 15 and 20 mg* kg^{-1}*) concentrations of S in a 50 ml centrifuge tubes at* 25^oC *for 2hrs. Sorption data was fitted and sorption parameters especially sorption maximum (b), affinity constant (k), maximum buffering capacity (MBC), distribution coefficient (*k_f*), sorption intensity (n), native S (So), native sorbed S (*k_d*) and equilibrium solution concentration (*EPC_o*) calculated. Also thermodynamic parameters particularly the separation coefficient (*K_R*), Gibbs free energy (*ΔG^0*), enthalpy (*ΔH^0*) and entropy (*ΔS^0*) were determined. Equally the relationship between sorption parameters and soil properties were determined. The b, k, MBC,* k_f*, n,* S_o*,* k_d *and* EPC_o *ranged from 10.64-20.75 and 11.49-17.04 mg* kg^{-1}*, 1.11-5.07 and 0.33-6.46 L* mg^{-1}*, 5.62-87.41 and 10.80-83.66 mg* kg^{-1}*, 1.14-6.81 and 1.02-3.53 mg* g^{-1}*, 0.28-4.51 and 0.38-1.20 mg* g^{-1}*, 0.28-2.86 and 0.76-3.71L* mg^{-1}*, 1.94-15.06 and 2.00-5.29 mg* g^{-1} *and 0.02-0.68 and 0.24-1.86 L* mg^{-1}*in the top and sub soils respectively, with the former better than the later for all parameters except So and EPCo. Sulphate sorption capacity using the b decreased in the order fallow > cassava > rice > oil palm in the top and rice > fallow > cassava > oil palm in the sub soils. The* $K_{R,}$ ΔG^0*,* ΔH^0 *and* ΔS^0 *ranged from 0.216-0.267 and 0.212-0.373, -4752.92- -324.63 and -3124- -49.06 J* $mol^{-1}k^{-1}$*, -68.76- -4.70 and -45.21- -0.71 J* $mol^{-1}k^{-1}$ *and 1.07-15.72 and 0.16-10.33 J*mol^{-1} k^{-1}*in the top and sub soils respectively. Sorption parameters correlated with selected soil properties especially sand, silt, clay, OM, pH, ECEC, N and P. In general, sulphate sorption process was favourable, spontaneous, exothermic and controlled by dissociative mechanism.*

KEYWORDS: Sulphate, Sorptivity, Land Use, Humid Tropics and Rainforest

INTRODUCTION

Sulphur deficiency has been widely reported in most highly weathered and variable charged soils of the humid tropics (Fox, 1980). Under acid conditions, surface charges of the soils become highly positive thereby depressing sulphur availability and mobility due to sorption reaction by the soil constituents (Fox and Blair, 1986; Alves and Lavorenti, 2004). High sorptivity of the soils has been ascribed to the nature of the dominant clay minerals particularly kaolinite, goethite, lepidocricite, gypsite and sesquioxides known to have high surface area and sorption capacity (Adetunji and Adepetu, 1987).

Mechanisms of sulphate sorption include ligand exchange in which SO_4^- enters into direct coordination with Fe or Al ions of the oxide surfaces as OH^- groups are displaced, thus causing an alteration of the point of zero charge (PZC) of the oxide minerals (Marcono-Martinez and McBride

1989; Zhang and Sparks, 1990). The OH^- so displaced during SO_4^- sorption is released into soil solution, causing an increase in soil pH and the CEC (Johnson, 1980; Dolui and Mustaffi, 1997). Another mechanism could be electrostatic in which $S0_4^{2-}$ is held as a counter ion in the diffuse double layer next to a positively charged colloid surface (Mash et al., 1987; Ghosh and Dash, 2012). Sorption isotherms particularly Temkin, Freundlich and Langmuir isotherms amongst others yield parameters useful for description of ion sorption in soils (Hinz, 2001). For instance the sorption maximum (b) explains the maximum amount of sorbate that can be sorbed by a sorbent, factor related to the bonding energy (k) describes the tenacity with which sorbates are sorbed to the sorbents, bonding energy (k_f) determines the magnitude of the energy with which sorbates are bonded to the sorbent and equilibrium solution concentration (EPCo) determines the concentration of the sorbate in equilibrium solution concentration at which the amount sorbed is equal to that desorbed (Litaor et al., 2005; Brand-Klibanski et al., 2007).

Ion and in particular sulphate sorption reaction is driven by certain forces, the extent and spontaneity of which can be measured using thermodynamic principles (Casagrande et al., 2008; Uzoho et al., 2014a). For instance the Gibbs free energy measures the extension or force that guides sorption reaction (Casagrande et al., 2008) or corresponds to the transfer of ions from bulk solution into appropriate site of the double layer or clay mineral lattice (Dandanmozd and Hosseinpur, 2010).

Sulphate sorption may be influenced by land use types and soil management practices (Johnson, 1980; Coughenour et al., 1980; Stanko-Golden et al., 1994). Effects of land use on ion sorption have been reported by others and attributed to alteration in the soil physicochemical properties (Pant and Reddy, 2001; Litaor et al., 2005; Uzoho et al., 2014a). According to Uzoho et al. (2007), soil properties vary seriously with changes in land use types.

Common soil properties affecting sulphate sorption include pH, organic matter, CEC, texture and presence of other ions (Mash et al., 1987; Zhang et al., 1987; Patil et al., 1989 Osodeke and Ubah, 2006; Ghosh and Dash, 2012). Influence of pH includes an increase in sulphate sorption with pH decrease due to increased positive surface charge (Mash et al., 1987; Patil et al., 1989; Zhang and Yu, 1997). Effect of OM has been reported to be an increased sulphate sorption due to formation of Al- and Fe- humus complexes (Patil et al., 1989: Stanko-Golden and Fitzgerald, 1991; Stanko-Golden et al., 1994) and the inhibition of the crystallization of Fe and Al oxide by organic matter (Huang and Violante, 1986) or a decrease due to competition between sulphate and organic anions for sorption sites (Johnson and Todd, 1983; Martinez et al., 1998; Liu et al., 1999). Sulphate sorption has been noted to increase with Ca sorption (Bolan et al., 1993; Marcano-Martinez and Mcbride, 1989) but depressed with P sorption (Bolan et al., 1988).

In Nigeria and indeed the humid tropical rainforest, limited information exists on soil sulphate sorption capacity and where available has been restricted to its relationship with soil parent materials (Adetunji and Adepetu, 1987; Osodeke and Ukah, 2006). There appears a dearth of information on the influence of land use on sulphate sorption. The objectives of the present study were therefore to determine the sulphate sorptivity of soils of selected land use types and to correlate it with selected soil properties of Nando, in the humid tropical rainforest, Southeastern Nigeria.

MATERIALS AND METHODS

Site Description and Sample Collection

The study site was Nando, Anambra state, situated between Latitudes 6°15^1 and 6°25^{1}N and Longitudes 6° 48^1 and 7^{0}12^1 E in the humid rainforest zone of Southeastern, Nigeria. Mean annual rainfall ranged from 2250-2500 mm, mean daily temperature (26-29°C) and mean relative humidity (78-86%). Four land use types; fallow, cassava, rice and oil palm were selected from the study site. The soil types included Typic Kanhaplohumults for fallow and Typic Dystropepts for oil palm, cassava and rice land use types (Soil Survey Staff, 1999). Parent geology of the soils included Coastal Plain Sands for fallow and recent alluvium for rice, cassava and oil palm land uses (Orajiaka, 1975). Fallow land use consisted of a 1$^{1/2}$ yr old fallow with outcrops of different plant species. Cassava land use consisted of a 2yr old cassava farm that has received NPK: Mg 15:15:17:12 fertilization. Rice land use included an annually cultivated rice paddy while the oil palm land use was a more than 15yr old oil palm plantation that has received doses of Urea and Muriate of Potash (MOP) at different periods.

Triplicate soil samples were collected from the 0-15 cm (top soil) and 15-30 cm (subsoil) depths of each land use and making a total of 24 soil samples. The soil samples were air dried, sieved using a 2 mm diameter mesh and the fine earth soil fractions subjected to laboratory analyses. Routine analyses were conducted for soil texture (Gee and Or, 2002), pH in 1:2.5 solute/suspension ratio using the glass electrode of a pH meter, CEC (Thomas, 1996), OM (Nelson and Sommers, 1996), N (Bremner, 1996) and P (Olsons and Sommers, 1982).

Sulphate Sorption Study

Sulphate sorption was conducted by equilibrating 2 g fine earth soil samples at 25°C with 20 ml of 0.2 N $ZnS0_4$ containing graded (0, 5, 10, 15 and 20 mg kg^{-1}) concentrations of S in a 50 ml centrifuge tubes for 2hrs (Chesin and Yien, 1951). At the end of the equilibration period, the tubes were centrifuged at 2000 x g for 20mins and the clear supernatant decanted. The S in solution of the clear supernatant was then determined turbimetrically (Bhogal et al., 1996) on a B and L Spectronic 70 Electrocolourimeter Model. All determinations were in duplicates. The difference between the S added and that in equilibrium solution was taken as the amount sorbed.

Calculations

Sorption Isotherms

Sorption data was fitted to the Langmuir, Freundlich and Temkin isotherms and sorption parameters obtained using the following equations.

Langmuir Equation

This was obtained as $C/X = 1/kb + C/b$ -- (1)

Where:
C = Concentration of the equilibrium solution (mg L^{-1})
X = Amount of S sorbed (mg kg^{-1})
b = Sorption maximum (mg kg^{-1})
k = Factor related to the bonding energy or affinity constant (L mg^{-1})

A plot of C/X vs. C gives a straight line equation with slope as 1/b and an intercept as 1/kb.

Maximum buffering capacity (MBC) was calculated as a product of b x k according to Karimian and Moafpourian (1999) and Reyhanitabar et al. (2007) ie. MBC = k x b ----------- (2)

Freundlich Equation

This is given as $X = K_f C^{1/n}$ --- (3)

Where:

K_f and n are empirical constants. K_f = Energy of sorption or Partition coefficient or distribution coefficient (L kg^{-1}), n = dimensionless constant or correction factor. By plotting the linear form of the equation ie Log S vs. Log C, the slope is equal to 1/n and the intercept equal to Log K_f.

Temkin Equation

This is given as S = kd x C –So -- (4)

Where:

S is the total amount of sulphur sorbed by the solid phase (mg kg-1), k_d is the sulphur sorption coefficient (Lkg^{-1}) and S_o is initial or native sorbed S (mg kg^{-1}). By plotting S vs. C, the intercept is equal to S_o and the slope is equal to k_d. The EPCo (mg L^{-1}) is the concentration of sulphur in solution where no net adsorption or desorption of sulphur occurs ie S = 0. By substituting the values of S and C in eqn. 4, EPCo can be obtained as follows:

EPCo = So/kd --- **(**5)

Thermodynamic Parameters

Thermodynamic parameters included:

Separation Factor (K_R):

Obtained using the equation: $K_R = 1/ (1 + kC_0)$ ------------------------------------- (6)

Where:

K_R = Separation factor, a dimensionless constant that indicates whether sorption was favourable or not. k = the affinity constant, estimated by the Langmuir equation (Ho et al., 2002; Singh & Pant, 2004).

Gibbs free energy (ΔG): A force that determines the spontaneity of adsorption reactions was obtained using the equation:

$\Delta G^o = -RT\ln k_f$--- (7)

Where:

ΔG^o = Variation in free energy (J mol^{-1}), R = the universal gas constant (8.314 J mol^{-1} K^{-1}), T = the absolute temperature (K) (Casagrande et al., 2008). K_f = Distribution coefficient

Enthalpy(ΔH^o):This is obtained using the van't Hoff Equation as:

$$\frac{\ln k_{d2}}{\ln k_{d1}} = \frac{\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ ---} \quad (8)$$

Entropy (ΔS^o): Obtained as:

$$\Delta S^o = \frac{(\Delta H^o - \Delta G^o)}{T} \text{ ---} \quad (9)$$

Statistical Analysis

Correlation between sorption parameters and soil properties was conducted using Genstat Statistical package (Buyse et al., 2004).

RESULTS AND DISCUSSION

Soil Characterization

Sand, silt and clay contents ranged from 432.40-762.40, 132.80-442.80 and 34.80-364.80 g kg^{-1} respectively (Table 1). Concentrations of sand and silt were higher in the top soil while the reverse was the case for clay in the various land uses

Table 1.

Land use	Soil Depth	Sand	Silt	Clay	OM	N	p	ECEC	pH
	cm	g kg^{-1}					mg kg^{-1}	cmol kg^{-1}	
Cassava	0-15	562.40	222.80	214.80	15.40	0.30	21.56	2.56	5.66
	15-30	502.40	132.80	364.80	12.40	0.20	28.04	2.13	5.15
Fallow	0-15	762.40	202.80	34.80	15.50	0.30	35.27	2.18	6.63
	15-30	612.40	182.80	204.80	12.80	0.10	35.03	1.56	5.65
Rice	0-15	462.40	392.80	144.80	15.00	0.20	28.54	2.70	5.52
	15-30	442.40	382.40	175.20	9.10	0.10	28.04	2.60	4.82
Oil Palm	0-15	462.30	442.80	94.90	13.40	0.20	28.13	3.19	6.52
	15-30	432.40	432.80	134.80	10.70	0.20	35.02	3.10	6.36

Selected Physicochemical Properties of the Soils

Fallow was sandier than the other land uses attributable to differences in their parent materials. Whereas soils under fallow land use were derived from Coastal Plain Sands, others were from alluvial deposit (Orajiaka, 1975). Soil pH (4.82-6.63) were acidic and characteristic of the humid rainforest soils of southeastern, Nigeria (Enwezor et al., 1990). Least pH was under rice (4.82-5.52) while the highest was under oil palm (6.36-6.52) land uses. The OM, N and ECEC were low and below critical limits for soils of southeastern Nigeria (Enwezor et al., 1990). Values of soil P were high and could be due to impact of fertilization probably with inorganic fertilizers.

Sulphate Sorption Characteristics

Sorbed and equilibrium S solution concentrations increased with added sulphur (Table 2). Similar observations have been reported for S (Osodeke and Ubah, 2006; Ghosh and Dash, 2012) and other ions especially P, Cu and Zn (Uzoho et al., 2005; Cassagrande et al., 2008; Uzoho et al., 2014a; 2014b). Sorption data was fitted and sorption parameters obtained (Table 3) were used to describe S sorption characteristics of the soils. For instance, sorption maximum (b) ranged from 10.64-20.75 mg kg^{-1}. Variation amongst land uses included 17.24, 20.75, 12.49 and 10.64 mg kg^{-1} in the top and 12.95, 15.33, 17.04 and 11.49 mg kg^{-1} in the sub soil depths of cassava, fallow, rice and oil palm land uses respectively. This showed a decreased trend of fallow > cassava > rice > oil palm in the top and rice > fallow > cassava > oil palm in the sub soils. Oil palm had the least b in both top and subsoil depths, ascribable to the high pH values (6.36-6.52) of the land use. It has been indicated that Sulphate sorption decreases with increased soil pH (Fox and Blair, 1986; Alves and Lavorenti, 2004). Amongst land uses, b was better in the topsoil for cassava and fallow and subsoil for rice and oil palm. Mean top and subsoil b ranged from 11.07-18.14 mg kg^{-1} and low compared to values obtained for soils of Abia state, Nigeria (Osodeke and Ubah, 2006) but high relative to those of red and lateritic soils of Birbhum district of West Bengal, India (Ghosh and Dash, 2012).

Affinity constant or factor related to the bonding energy (k) ranged from 1.11-5.07 and 0.33-6.46 L mg^{-1} in the top and sub soils respectively with a mean range of 0.85-5.77 L mg^{-1}. Distribution amongst land uses included 5.07, 1.65, 1.36 and 1.11 L mg^{-1} and 6.46, 0.44, 0.33 and 0.94 L mg^{-1} in the top and sub soil depths for cassava, fallow, rice and oil palm land use types respectively. This gave a decreased trend of cassava > fallow > rice > oil palm and cassava > oil palm > fallow > rice in the top and sub soils respectively, with cassava better in both soil depths. Sorbed S was held with greater tenacity in the top soil of the various land uses exception being cassava where the subsoil was superior.

Maximum buffering capacity (MBC) referred to the resistance to changes in soil solution ion concentration (Uzoho et al., 2014a) ranged from 5.62-87.41mg kg^{-1} in the topsoil and 10.80-83.66 mg kg^{-1}in the subsoil with best values for both soil depths being in cassava land use and the least in the top and subsoil of oil palm and rice land uses respectively. The MBC is related to the b (Pant and Reddy, 2001) as indicated by the high values of both in the top soil of most land uses. Distribution coefficient or partition factor (k_f) was higher in the top than subsoils of most land uses as was the b and MBC and thus indicating some close relationships amongst the factors (Uzoho et al., 2014a). The k_f estimates ion mobility and retention in soils, with high values indicating greater retention and low mobility (Casagrande et al., 2008; Nystrom, 2012; Kumar et al., 2013; Uzoho et al., 2014a). Best k_f in the top and sub soils were in fallow and cassava land uses respectively while the least were in cassava and oil palm land uses respectively. Thus S mobility will be greater in the top and sub soils of cassava and oil palm land uses respectively whereas the retention will be greater in the top and sub soils of fallow and cassava land uses respectively.

Freundlich constant n referred to as sorption intensity (Nystrom, 2012) ranged from 0.28-4.51 and 0.38-1.20 mg g^{-1} in the top and sub soils respectively, with mean range of 0.37-2.56 mg g^{-1}. Besides cassava with higher n value in the sub soil, concentrations were higher in the top as was the Langmuir k. Similarity in n and k distribution indicates a close relationship between the factors. High n values in the topsoil of most land uses indicate that the intensity of S sorption will be great at this depth. Whereas, native soil sulphur (S_o) was higher in the sub soil, distribution of native sorbed S (k_d) was in the top than subsoil. This showed that S_o and k_d are inversely related as have been reported by others (Pant and Reddy, 2001; Litaor et al., 2005; Uzoho et al., 2014b).Equilibrium S solution concentration (EPCo) ranged from 0.02-0.68 and 0.24-1.86 L mg^{-1} in the top and sub soils respectively. High values in the subsoil indicate greater S availability at this depth than the topsoil probably due to low sorption from the poor OM contents. Soil EPC_o influences ion availability and mobility (Litaor et al., 2005; Brand-Klibanski et al., 2007). This showed that S mobility and availability will be minimal in the top soil of fallow land use with the least EPCo (0.02 L mg^{-1}) and highest in the subsoil of cassava land use with the highest EPCo value (1.86 L mg^{-1}).

Table 2.

Land use	Added S	C	X	C/X	Log C	Log X	K_R	C	X	C/X	Log C	Log X	K_R
		0-15cm						15-30 cm					
Cassava	0	0.00	0.00	0.00	0.00	0.00	1.000	0.00	0.00	0.00	0.00	0.00	1.000
	5	2.60	2.40	1.10	0.40	0.40	0.038	0.00	5.00	0.00	0.00	0.70	0.030
	10	3.50	6.50	0.50	0.50	0.80	0.019	1.00	9.00	0.10	0.00	1.00	0.015
	15	4.10	9.90	0.40	0.60	1.00	0.013	4.50	10.50	0.40	0.70	1.00	0.010
	20	5.00	15.00	0.30	0.70	1.20	0.010	5.00	15.00	0.30	0.70	1.20	0.008
Fallow	0	0.00	0.00	0.00	0.00	0.00	1.000	0.00	0.00	0.00	0.00	0.00	1.000
	5	0.50	4.50	0.10	-0.30	0.70	0.108	1.50	3.50	0.40	0.20	0.50	0.313
	10	0.50	9.50	0.10	-0.30	1.00	0.057	3.10	6.90	0.50	0.50	0.80	0.185
	15	1.10	13.90	0.10	0.00	1.10	0.039	4.10	9.90	0.40	0.60	1.00	0.132
	20	1.10	18.90	0.10	0.00	1.30	0.029	4.10	15.90	0.30	0.60	1.20	0.102
Rice	0	0.00	0.00	0.00	0.00	0.00	1.000	0.00	0.00	0.00	0.00	0.00	1.000
	5	1.60	3.40	0.50	0.20	0.50	0.129	2.00	3.00	0.70	0.30	0.50	0.377
	10	2.00	8.00	0.30	0.30	0.90	0.068	3.00	7.00	0.40	0.50	0.80	0.189
	15	2.10	12.90	0.20	0.30	1.10	0.047	3.00	12.00	0.30	0.50	1.10	0.168
	20	2.10	17.90	0.10	0.30	1.30	0.036	4.00	16.00	0.30	0.60	1.20	0.132
Oil Palm	0	0.00	0.00	0.00	0.00	0.00	1.000	0.00	0.00	0.00	0.00	0.00	1.000
	5	2.00	3.00	0.70	0.30	0.50	0.153	2.00	3.00	0.70	0.30	0.50	0.175
	10	2.10	7.90	0.30	0.30	0.90	0.083	2.00	8.00	0.30	0.30	0.90	0.096
	15	2.50	12.50	0.20	0.40	1.10	0.057	2.10	12.90	0.20	0.30	1.10	0.066
	20	2.60	17.40	0.20	0.40	1.20	0.043	3.00	17.00	0.20	0.50	1.20	0.051

Sorbed, Equilibrium concentration and Separation Coefficient of S with Added S

Table 3.

Land use	Soil Depth cm	b mg kg^{-1}	k L mg^{-1}	MBC mg kg^{-1}	K_f ml g^{-1}	n ml g^{-1}	S_o L mg^{-1}	K_d mg g^{-1}	EPC_o L mg^{-1}
Cassava	0-15	17.24	5.07	87.41	1.22	0.59	2.86	1.94	0.68
	15-30	12.95	6.46	83.66	3.53	1.20	3.71	2.00	1.86
Mean		15.10	5.77	85.55	2.38	0.90	3.29	1.97	1.27
Fallow	0-15	20.75	1.65	34.24	6.81	4.51	0.28	15.06	0.02
	15-30	15.53	0.44	6.83	1.23	0.61	0.76	3.13	0.24
Mean		18.14	1.05	20.54	4.02	2.56	0.52	9.10	0.13
Rice	0-15	12.49	1.36	15.63	1.14	0.28	1.41	6.32	0.23
	15-30	17.04	0.33	5.62	1.09	0.49	1.74	3.89	0.45
Mean		14.77	0.85	11.63	1.12	0.39	1.58	5.11	0.34
Oil Palm	0-15	10.64	1.11	11.81	1.17	0.35	1.67	5.34	0.31
	15-30	11.49	0.94	10.80	1.02	0.38	1.45	5.29	0.27
Mean		11.07	1.03	11.31	1.10	0.37	1.56	5.32	0.29

Sorption Parameters of the Soils Studied

Lowest EPCo of the topsoil of fallow land use occurred at values equivalent to highest b, MBC k_f and k_d indicating an inverse relationship between the parameters as have been reported by others (Pant and Reddy, 2001; Litaor et al., 2005;Brand-Klibanski et al., 2007; Uzoho et al., 2014a). Sulphate sorption parameters were affected by some soil properties (Table 4). For instance sorption maximum (b) was significantly ($P \leq 0.05$) correlated with clay (r = 0.56), sand (r = 0.78), silt (r = -0.53), ECEC (r = -0.53) but not with N (r= 0.30), OM (r = 0.26), pH (r = -0.04) and P (r= 0.07). Other workers have reported significant relationship between b and silt content, OM and ECEC but not pH, sand, clay, P and N (Osodeke and Ubah, 2006), pH, OM, clay, Ca and P (Alves and Lavorenti, 2004; Pigna et al., 2007), OC, K, Na and P (Murthy, 2004). Apart from sand content (r^2 =0.61), b was poorly estimated by other soil properties especially clay content, ECEC, pH, N, P, OM and silt as indicated by their coefficient of determination (r^2) of less than 0.32. Soil EPCo was significantly correlated ($P \leq 0.05$) with clay (r = 0.51), pH (r = -0.53), P (r = -0.43) and silt (r = -0.49). Others have reported distinct relationship between EPCo and soil pH, clay content, P, OM and ECEC for anions such as P sorption (Litaor et al., 2005; Uzoho et al., 2014b). Soil EPCo was weekly predicted by all the soil properties studied (clay, ECEC, pH, N, OM, P, sand and silt) as indicated by the r^2 values of less than 0.30. There was serious ($P \leq 0.05$) correlation between MBC with clay (r = 0.62), N (r = 0.60), OM (r = 0.74), P (r = -0.59) and silt (r = -0.65) and with only OM able to account for more than 50% of the soil MBC. Serious relationship between MBC and pH, ECEC, OC and silt content has been reported (Osodeke and Ubah, 2006). Besides OM and silt content, all the other soil properties were poor estimators of MBC. Apart from pH (r = 0.63), N (r = 0.45), P (r = 0.54) and sand (r = 0.64), there was no distinct correlation between k_d and the other soil properties (clay, ECEC, OM and silt). Only pH and sand content accounted for more than 40% of the soil k_d. Freunlich k_f and n were similarly affected by soil properties being significantly correlated ($P \leq 0.05$) with clay (r = 0.82 and 0.72), N (r = 0.52 and 0.53), OM (0.41 and 0.41), sand (r = 0.79 and 0.86) and silt (-0.54 and -0.46 respectively). Both k_f and n can be predicted by more than 50% of clay and 60% of sand respectively. Affinity constant (k) correlated seriously with clay (r = 0.60), N (r = 0.49), P (r = -0.56) and silt (-0.61) and was poorly predicted by all the soil properties (clay, sand, silt, pH, N, OM, P and ECEC). Osodeke and Ubah (2006) have noted significant correlation between soil k and pH, OM, ECEC and sily content. Apart from pH (r = -0.52), P (r = -0.72) and sand (r = -0.44) there was no serious relationship between S_o and other soil properties and with only P accounting for more than 50% of it. Sulphate sorption processes were elucidated using thermodynamic parameters (Table 5). Separation coefficient (K_R), a thermodynamic factor that determines whether sorption is favourable decreased with added S (Table1). Reduction in K_R with increased S indicates a more favourable sorption at high initial concentration as have been reported for Zn sorption (Cassagrande et al., 2008). Mean K_R ranged from 0.216-0.267 and 0.212-0.373 in the top and sub soils under the land uses (Table 5), with values for both soil depths less than unity. It has been reported that sorption reaction is favourable and spontaneous when $K_R < 1$while values of $K_R > 1$indicate absence of spontaneity of sorption reaction (Singh and Pant 2004; Cassagrade et al., 2008). Also sorption process could be described as unfavourable ($K_R > 1$), linear ($K_R =1$), favourable ($0 < K_R <1$ or irreversible ($K_R = 0$) (Ho et al., 2002; Cassagrande et al., 2008). Mean K_R values (0.216-0.373) of the soils studied indicated that sorption reaction was spontaneous and favourable in both top and sub soils but with the former better than the later. Hence the soils were efficient systems for S sorption, with the degree varying as Oil palm < rice < fallow < cassava and rice < fallow < oil palm < cassava for top and sub soils respectively.

Gibbs free energy (ΔG^o), a measure of the extension or force that guides sorption reaction ranged from-324.63- -4752.92 and -49.06- -3124.96kJ mol^{-1}in the top and sub soils respectively, with mean values of -216.14- -2148.30 kJ mol^{-1}. In the soils of the various land uses, values of ΔG^o were negative, indicating the feasibility and spontaneity of S sorption and with energy released for the conversion of the less stable S forms in solution to the sorbed form with greater stability. Similar observation has been reported for Cd and Zn (Cassagrande et al., 2008). Spontaneity of S sorption was higher in the top than the sub soil probably due to high pH and OM content of the surface soil. It has been reported that as temperature increases, sorption process becomes more thermodynamically spontaneous leading to increase in the driving force for ion sorption (Cassagrande et al., 2008). Enthalpy (ΔH^o) for sulphate sorption was negative and ranged from -0.71- -68.76 J mol^{-1} $k^{-1}$for the various land use types. This included values of -4.7- -68.76(mean = 21.56) and -0.71—45.21(14.10) J mol^{-1} $k^{-1}$for the top and sub soils respectively. The negative values indicated that sulphate sorption was exothermic, contrary to endothermic reaction reported for metal cations by other workers (Adhikari and Singh, 2003: Unlu and Ersoz, 2006; Dandanmozd and Hosseinpur, 2010).

The exothermic reaction could be ascribed to the fact that the energy needed to dehydrate sulphate ion is less than the exothermicity of the ions attaching to the soil surface. For according to Kumar et al. (2013), the Simple Correlation (r)and Coefficient of Determination (r2) between Sorption Parameters and selected Soil Properties

Table 4.

	Clay		ECEC		pH		N		OM		P		Sand		Silt	
	r	r^2	r	r^2	r	r^2	r	r^2	r	r^2	r	r^2	r	r^2	r	r^2
b	0.56	0.31	-0.53	0.28	-0.04	0.00	0.3	0.09	0.26	0.07	0.07	0.00	0.78	0.61	-0.53	0.28
EPC_o	0.51	0.26	-0.19	0.04	-0.53	0.28	0.003	0.00	0.39	0.15	-0.43	0.18	-0.23	0.05	-0.49	0.24
MBC	0.62	0.38	-0.20	0.04	-0.20	0.04	0.60	0.36	0.74	0.55	-0.59	0.35	0.21	0.04	-0.65	0.42
K_d	0.28	0.08	0.001	0.00	0.63	0.40	0.45	0.20	0.39	0.15	0.54	0.29	0.64	0.41	0.03	0.00
K_f	0.82	0.67	-0.37	0.14	0.34	0.12	0.52	0.27	0.41	0.17	0.36	0.13	0.79	0.62	-0.54	0.29
n	0.72	0.52	-0.35	0.12	0.43	0.18	0.53	0.28	0.41	0.17	0.41	0.17	0.86	0.74	-0.46	0.21
K	0.60	0.36	-0.17	0.03	-0.26	0.07	0.49	0.24	0.31	0.10	-0.56	0.31	0.07	0.00	-0.61	0.37
So	0.22	0.05	0.11	-0.01	-0.52	0.27	0.11	0.01	-0.11	0.01	-0.72	0.52	-0.44	0.19	-0.25	0.06

Table 5.

Land use	Soil Depth cm	K_R	ΔG^o kJ mol^{-1}	ΔH^o $Jmol^{-1}k^{-1}$	ΔS^o $Jmol^{-1}k^{-1}$
Cassava	0-15	0.216	-492.67	-7.13	1.63
	15-30	0.212	-3124.96	-45.21	10.33
	Mean	0.214	-2148.3	-31.08	7.1
Fallow	0-15	0.247	-4752.92	-68.76	15.72
	15-30	0.346	-512.89	-7.4	1.72
	Mean	0.297	-3447	-49.87	11.4
Rice	0-15	0.256	-324.63	-4.7	1.07
	15-30	0.373	-213.51	-3.09	0.71
	Mean	0.315	-280.79	-4.07	0.93
Oil Palm	0-15	0.267	-388.99	-5.63	1.29
	15-30	0.278	-49.06	-0.71	0.16
	Mean	0.273	-216.14	-3.42	0.78

Thermodynamic Parameters of the Soils Studied at 25o C endothermicity of U (VI) sorption was arrogated to the complete solvation of the ion in water and the assumption that the energy needed for dehydration exceeded the exothermicity of the ions attaching to the soil surfaces. Values for ΔS^o were positive and ranged from 1.07-15.72 (4.93) in the top soil and 0.16-10.33(3.23) kJ mol^{-1} in the sub soil. Positive ΔS^o values indicate increased randomness at solid-solution interface during the sorption. According to Abou-Mesalam, (2003), a decrease in the degree of randomness causes an increase in ion sorption capacity on the sorbent. Also ΔS^o values determines whether associative or dissociative mechanisms control sorption reaction, with dissociative mechanism occurring at values greater than -10KJ mol^{-1} (Hue et al., 2010; Yang et .al., 2012). Thus the high

ΔS^o values obtained indicated that dissociative mechanism control sulphate sorption on the soils studied.

CONCLUSION

Soils were generally acidic with high P content probably due to inorganic P application. Sulphate sorption and equilibrium S concentrations increased with added sulphur probably due to the saturation of sorption sites. Sulphate sorption capacity using the sorption maximum (b) decreased in the order fallow > cassava > rice > oil palm and rice > fallow > cassava > oil palm in the top and sub soils respectively. Also, the tenacity with which sorbed S was held decreased as cassava > fallow > rice > oil palm and cassava > oil palm > fallow > rice in the top and sub soils respectively, with cassava better in both soil depths. Soil b, MBC, Kf, K, and n were higher in the top than the sub soil whereas the reverse was the case for the EPCo, indicating that S availability and mobility will be higher in the sub than the top soil. Soil properties; sand, silt, clay, pH, OM, ECEC, N and P affected S sorption parameters (b,K, kf, n, MBC and EPCo) in different ways. Sulphate sorption process was favourable, exothermic and spontaneous and controlled by dissociative mechanism. The spontaneity of the process was greater in the top than the sub soil

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