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SORPTION STUDIES OF TETRAOXOPHOSPHATE (V) IONS ON SOME AGRICULTURAL SOILS IN AKWA IBOM STATE, EASTERN NIGER DELTA, NIGERIA.

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ABSTRACT

The phosphate sorption capacity regulates principally the phosphorus concentration and available phosphorus in any soil solution. This work aims to study the phosphate sorption characteristics of five agricultural soils in Akwa Ibom State, Nigeria. The phosphate adsorption isotherm was obtained by shaking each soil sample with 20, 40, 60, 80, 100 and 120 mgL^{-1} for 24 h with 20 mL of KH_2PO_4 in 0.01 M $CaCl_2$ solution. The Langmuir, Freundlich, Van Huay and Temkin isotherms were applied to study the PO_4^{3-} sorption characteristics of the soil samples. The Freundlich model provided the best choice for phosphate sorption with mean R^2 value of 0.9872. Results obtained for the phosphate sorbed (µg g^{-1} soil) with 120 mgL^{-1} solution, heterogeneity factor of adsorption sites (n_F), and the Freundlich constant (K_F) (Lg^{-1}) were 101(84.3), 0.515 and 7.355 for Onna soil; 62.8(52.3), 0.641 and 2.464 for Ikot-Amama 2; 60.6(50.5), 0.708 and 3.985 for Ogu-Itumbonuso soil; 59.3(49.5), 0.652 and 2.505 for Ikot-Amama 1 soils; 58.0(48.3), 0.704 and 3.682 for Ikot-Nkon soils, respectively. The equilibrium concentration for phosphates (EC-P) were used as desorption index to determine whether the soils could serve as potential sources for their bioavailability to plants and results ranged from 5.0 to 9.90 mgL^{-1}, indicating high vulnerability to phosphate loss. The relationship between phosphate sorption parameters and soil physicochemical properties showed that the Freundlich adsorption intensity factor, n_F, strongly correlated negatively with organic carbon and organic matter (r = -0.953 and -0.947; P<0.01), Fe and Mn (r = -0.911 and -0.812, P<0.05). The EC-P correlated strongly with soil $pH_{(H_2O)}$ (r = 0.959, P<0.01), clay (r = 0.913, P<0.05), cation exchange capacity (CEC) (r = -0.824, P<0.05), Mn (r = -0.792, P<0.05) and Fe (r = -0.826, P<0.05). The study illustrated that soil management practices which involves the using organic fertilizers as the basis for PO_4^{3-} sorption in relation to soil properties can be a useful tool for sustainable crop production and environmental soil-water contamination.

Keywords: Sorption, adsorption, phosphates, agricultural soils

INTRODUCTION

Phosphorus as a non-metallic element is very essential for the nutrition of most biological organisms including animals, microbes and plants and it is associated with the eutrophication of both surface and groundwater systems (McMahon and Read, 2013; Wang *et al.*, 2013; Dapeng and Yong, 2014). Phosphorus reactivity, solubility and availability vary depending on the dominant chemical fractions present in soils and sediments (Camelo *et al.*, 2015). Sulphate and nitrates play complementary roles in plants because they are essential for protein synthesis. When sulphate is absence in soil (hence plant), protein synthesis cannot take place (Odoemelam *et al.*, 2020). Most agricultural soils in the study area do not meet crop demands for phosphorus hence its improvement through organic manure and chemical fertilizer application is therefore necessary. Generally, plants absorb most phosphorus as $H_2PO_4^-$ and smaller amount as HPO_4^{2-} depending on the soil pH. Lower soil pH values (acidic) increase the absorption of $H_2PO_4^-$ ion, while higher pH values will increase the absorption of HPO_4^{2-} ion (Radojevic and Bashkin, 1999).

Although total phosphorus content in different soil types can be high, only a small fraction of it is bioavailable for plant utilization because phosphorus is bound either as incompletely weathered mineral particles, or adsorbed on mineral surfaces, and or made unavailable by secondary mineral formation over the time of soil formation (Yang *et al.*, 2013). The potential of significant soil phosphorus loss into water depends on both the initial soil-phosphorus concentration and the soil phosphorus-sorption capacity. The soil sorption characteristics of phosphorus have been extensively studied for agronomic and for environmental purposes (Fox and Kamprath, 1970, Zhang *et al.*, 2005). According to Zhou and Li (2001), phosphorus sorption isotherms were found useful in describing phosphorus sorption characteristics in soils and to predict the risk of phosphorus loss to fresh water.

In most tropical agricultural soils, liming is frequently used to raise soil pH thereby increasing phosphorus bioavailability (Sanchez and Uehara, 1980). With increasing pH, phosphorus sorption was reported to both decrease (Mora *et al.*, 1999) and increase (Pereira and De-Faria, 1998; Curtin and Syers, 2001). For highly weathered and acid soils, research data available supports the hypothesis that exchangeable aluminium (Al^{3+}) is the main factor that determines the pattern of phosphorus sorption with changing pH (Chen and Barber, 1990). The application of lime to soils with low exchangeable Al^{3+} leads to the precipitation and neutralization of Al^{3+} ion and hydroxy-Al species to form aluminium hydroxide, thereby reducing the number of sorption sites for phosphorus. Therefore, Haynes (1984) reported that liming decreases phosphorus sorption in soils with low exchangeable Al^{3+} content, but increases phosphorus sorption in soils with initial high exchangeable Al^{3+}. Pierzynski *et al.* (2005) reported that about 35–70% of total soil phosphorus is inorganic and are bonded to metal oxides in acidic and highly weathered soils; and strong phosphorus adsorption and retention by metal oxides may render phosphorus less available for plant uptake (Luengo *et al.*, 2006; Mustafa *et al.*, 2008).

MATERIALS AND METHODS

Agricultural soil samples from five selected sites were collected from a soil profile pit of different types of agricultural soils from selected locations in Akwa Ibom State, the tropical region of Nigeria (Lat. 04° 09.845´N; Long. 009° 17.634´E) (Table 1 and Fig. 1). The sample sites were selected based on different agricultural practices such as Rice farming in the area. Each soil sample was air-dried in the laboratory and ground in an agate mortar to pass through a 2.0 mm sieve. Samples were analysed for some physicochemical properties including pH (soil $H_2O/CaCl_2$ ratio of 1:2.5) using electrometric method, organic carbon was determined by potassium dichromate ($K_2Cr_2O_7$) oxidation method of Walkley Black method. Organic matter was estimated by multiplying organic carbon by a factor of 1.724 (Udo *et al.*, 2009). Total concentration of phosphorus was determined by wet digestion method (Kuo, 1996). Exchangeable cations, Ca, and Mg were determined by using atomic absorption spectrophotometer while flame photometer was used for the determination of Na and K, Exchangeable acidity was analysed by KCl method and particle size distribution was determined using Bouyoucos Hydrometer Method (Anderson and Ingram, 1993; Day, 1965) Crystalline Fe and Al oxides were determined spectrophotometrically after extraction with dithionite ($Na_2S_2O_4$) and sodium citrate pentahydrate powder, while amorphous Fe and Al oxides were determined after reduction with ammonium oxalate in the dark using FAAS. Phosphate was determined by the ascorbic acid molybdate blue method (Kuo, 1996; Udo *et al.*, 2009). All chemicals and reagents used were analytical grade.

Table 1. Site location and their geographical co-ordinates

S/N	Code	Site	Location/Description	Latitude/ Longitude
1	SS-1	Ikot-Nkon	Proposed Rice Farm, Ikpe Ikot Nkon, Ini LGA.	5º23'2.65164" N 7º46'29.20656" E
2	SS-2	Ogu-Itumbonuso	Muddy clay soil, Obot Ananamong, Ogu-Itu Mbonuso, Ini LGA.	5º25'6.11616"N 7º46'59.77812" E
3	SS-3	Ikot-Amama 1	Rocky clay soil, Use Ikot Amama, Ibiono Ibom LGA.	5º23'52.59768" N 7º49'57.48312" E
4	SS-4	Ikot-Amama 2	Swampy soil, Use Ikot Amama, Ibiono Ibom LGA.	5º22'51.00636" N 7º54'0.81432" E
5	SS-5	Onna	Wetland soil, East-West Road, Onna LGA.	4º38'50.29692" N 7º55'15.27528" E

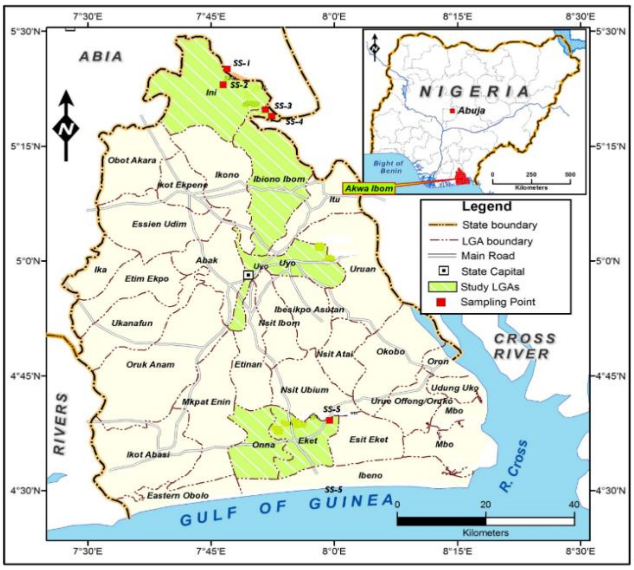


Figure 1. Map of study area

Batch Adsorption Study – Adsorption and desorption isotherms

The phosphate ion adsorption data was obtained after equilibration of 1.0 g each of the five soil samples with 20.0 mL solution of KH_2PO_4 in 0.01 M $CaCl_2$, as background electrolyte at room temperature. The KH_2PO_4 concentrations in equilibrating solutions ranged between 0 and 120.0 mg L^{-1} (20, 40, 60, 80, 100 and 120 mg L^{-1}) and the solution pH was adjusted to 6. The suspension was shaken for 24 h, centrifuged at 6,000 rpm. for 30 min at intervals of 8 h and filtered through acid-washed filter paper. Phosphorus concentration in the equilibrium solution was determined by visible spectrophotometry with ammonium molybdate-ascorbic acid reduced method (using Thermo Scientific GENESYS 50) as described by Kuo (1996) and Udo *et al.* (2009). Each soil sample was analysed in duplicate. The adsorbed phosphorus at equilibrium, Q_s, was calculated by the difference between the initial (added P) and the final concentration after equilibration. The mean concentration recorded is calculated using Equation (1):

$$Q_s = (C_i - C_e)\,{}^{V}\!/_{W}. \quad - \qquad - \qquad - (1)$$

where, Q_s = amount of solute adsorbed per unit mass of soil at equilibrium (mg g^{-1}), C_i is the initial liquid-phase solute concentrations (mg L^{-1}), C_e is the blank corrected solute concentrations at equilibrium (mg L^{-1}), W is the mass of the air-dried soil adsorbent (g) and V is the volume of the solution (L). Desorption experiments were carried out in soil samples previously equilibrated with various phosphate concentrations. After removing the supernatant solution, 20.0 mL solution of KH_2PO_4 in 0.01 M $CaCl_2$ solution adjusted to the soil pH were added, the suspensions shaken for 24 h, centrifuged at 6,000 rpm. for 30 min, and filtered through acid-washed filter paper. Phosphorus was determined in the equilibrium solution as in the sorption experiments. The phosphate concentration remaining in the adsorbed phase was calculated from the concentration adsorbed after the sorption equilibrium and the concentration released to the solution, making a correction to take into account the solution embedded in the solid after sorption equilibrium. Adsorption and desorption isotherms were obtained by plotting the phosphorus concentration in the adsorbed phase with the solution concentration at equilibrium. The isotherms were fitted to four different mathematical sorption models - the Langmuir, Freundlich van Huay and Temkin isotherms.

The Langmuir isotherm describes the adsorbate-adsorbent relationship where the extent of adsorbate coverage is limited to only one molecular layer before reaching the relative pressure of unity and is expressed by Equation (2),
$Q = Q_{max} * K_L * C_e/(1 + K_L * C_e)$ - - - (2)
where Q is the concentration of the adsorbed anion (mg g^{-1}), C_e is the concentration of solute in solution at equilibrium (mg L^{-1}), K_L is a constant related to the adsorption energy and Q_{max} is the maximum adsorption capacity (mg g^{-1}). The linear form of Equation (2) is written as

$\frac{Q_e}{Q} = \frac{1}{(Q_{max}*K_L)} + \frac{C_e}{Q_{max}}$ - - - - (3)
According to Goldberg (2005), the Langmuir model assumes the adsorption of a monolayer, that all the adsorption sites have the same adsorption energy and that there is no interaction among the adsorbed molecules (or ions).
The Freundlich isotherm is expressed by the equation as
$Q = K_F * C_e^{1/n_F}$, - - - - - (4)
where Q and C_e have the same meaning as in the Langmuir equation, K_F is the adsorption constant and n_F is a constant whose value varies between 0 and 1. The linearized form of equation (4) by taking the natural logarithm of both sides is written as
$\ln Q = \ln K_F + 1/n_F \ln C_e$ - -- - - (5)
The Freundlich model assumes that the adsorption surface is heterogeneous and that the adsorption energy decreases exponentially as the concentration in the adsorbed phase increases. It does not predict an adsorption maximum (Goldberg, 2005).
The Van Huay isotherm is expressed as
$Q/m = m + n\sqrt{C_e}$ - - - - (6)
where, Q = amount of solute adsorbed per unit mass of dry soil (mg g^{-1}), C_e = the solution concentration of solute at equilibrium (mg L^{-1}), n = Van Huay adsorption coefficient (L g^{-1}) and m = Van Huay constant parameter.
The Temkin isotherm is expressed as:

$Q = (RT/b)\ln(A_T C_e) = (RT/b)\ln A_T + (RT/b)\ln C_e$ - (7)
where Q and C_e have the same meaning as in the Langmuir equation, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (25 °C) and A_T is Temkin isotherm constant (Lg^{-1}) and b is the Temkin constant related to the heat of adsorption (J mol^{-1}). It considers that the adsorption surface is heterogeneous and that the adsorption energy decreases linearly with the concentration in the adsorbed phase. There is no maximum adsorption (Goldberg, 2005).

RESULTS AND DISCUSSIONS

Soil Physicochemical properties

The mean concentrations of soil physicochemical parameters for the selected agricultural soils are presented in Table 2. The total soil $pH_{(H_2O)}$ and $pH_{(CaCl_2)}$ for the five soil samples studied ranged from 3.03 to 4.91 (4.25±0.73) and 3.04 to 4.08 (3.68±0.40) respectively, showing high acidity. This showed that most agricultural soils in Akwa Ibom State were predominantly acidic, indicative of nutrients leaching from topsoil into the lower depths. In general, the mean soil pH compares favourably with reports that showed pH range from 3.27 to 4.35 for other soils from Akwa Ibom State (Udoh, 2015). Notably, soil pH is known to affect phosphate sorption parameters, as lower pH results in increasing positive charge on hydrous oxides thereby attracting phosphate anions (Sparks, 1995). The organic matter content ranged from 1.80 to 8.18 % with mean value of 4.17±2.54 %. The soil effective cation exchange capacity (ECEC) had a mean of 13.4±2.21 cmol Kg^{-1} with highest contribution in samples from Onna and Ikot-Nkon. The mean clay content of the soils was highest at Ikot-Amama 1 (36.0±2.52 %) and Ikot-Amama 2 (31.0±4.16 %); while highest mean silt content was recorded at Ikot-Nkon (74.7±13.0 %) and Ogu-Itumbonuso (18.0±14.7 %) respectively. All five soil samples recorded high levels of available NO_3^-, PO_4^{3-} and SO_4^{2-} with values ranging from 580 to 823 $mgKg^{-1}$, 720 to 1477 $mgKg^{-1}$ and 407 to 3390 $mgKg^{-1}$ respectively while highest mean concentrations of SO_4^{2-} was 2828±795 mg Kg^{-1} and was found in Onna soil (Table 2). Exchangeable aluminium recorded mean concentrations ($cmolKg^{-1}$) 2.02±1.30 while that of Mn, Fe, Ca and Mg were 64.3±43.3, 83.1±54.8, 7.28±0.87 and 2.43±0.29 respectively. However, Fe_2O_3 and Al_2O_3 recorded mean crystalline concentrations of 0.07±0.01 % and 0.04±0.03 % respectively, while the amorphous form had 0.21±0.06 and 0.088±0.024 % respectively. The particle size distribution recorded percentage mean values (range in parenthesis) of 68.4±11.0 (59.4-87.4), 4.78±4.82 (0.98-12.9) and 26.8±11.7 (9.64-35.6) for sand, silt and clay respectively. The texture of the five studied soils were sandy loam for Ikot-Amama 2 and Onna; loamy sand, sandy loam, sandy-clay loam for Ikot-Nkon, Ogu-Itumbonuso and Ikot-Amama 1 respectively.

Phosphate Adsorption and Desorption

The experimental results corresponding to the sorption-desorption behaviour of phosphate-phosphorus (PO_4-P) on to the studied agricultural soils for batch experiment with initial concentration of 80 mg PO_4 L^{-1} is presented in Tables 3, 4 & 5. As shown by Figure 2, the sorption of PO_4-P from solution on to the soils was relatively rapid in the first few minutes and remained constant until equilibrium sorption was reached. The sorption properties of soils were estimated through two parameters in the Langmuir equation, the maximum sorption capacity (Q_{max}) and the binding energy coefficient (K_L) (Brenner, 2019). The gradual reduction in PO_4-P sorption rate with time may be a result of occupation of the active sorption sites on the soils and sediments particles. For these soils, most of PO_4-P is adsorbed during the first 8 hours of sorption. Moreover, at any rate, sorption equilibrium is reached within 48 hours for all soils. Similar result was reported by Zhou *et al.* (2005) for sorption kinetics of PO_4-P onto sediments from Chinese Taihu Lake, considering that equilibrium conditions were attained within 48 hours.

Table 2: The mean ($\bar{x}$±SD) levels of physicochemical properties of studied agricultural soils

Soil properties	Soil sampling sites					($\bar{x}$±SD)	Range
	SS-1	SS-2	SS-3	SS-4	SS-5		
$pH_{(H_2O)}$	4.08±0.13	4.48±0.08	4.77±0.08	4.98±0.06	3.00±0.05	4.25±0.73	3.03-4.91
$pH_{(CaCl_2)}$	3.53±0.10	3.78±0.06	3.94±0.12	4.15±0.19	2.95±0.13	3.68±0.40	3.04-4.08
Ex. acidity (cmol Kg^{-1})	5.44±0.42	2.01±0.08	2.09±0.29	2.05±0.39	7.28±3.96	3.01±1.74	1.60-5.28
Organic matter (%)	2.78±1.18	1.51±0.62	3.86±1.78	2.54±1.97	8.54±0.51	4.17±2.54	1.80-8.18
Organic carbon (%)	1.62±0.70	0.85±0.38	2.24±1.04	1.56±1.03	4.94±0.30	2.42±1.47	1.04-4.73
ECEC (cmol Kg^{-1})	18.1±3.99	13.1±0.30	12.7±1.99	12.3±0.09	18.3±3.28	13.4±2.21	10.6-16.0
Total P ($mgKg^{-1}$)	53.6±3.44	16.9±8.09	194±150	19.1±0.82	43.3±16.3	30.5±15.3	18.2-56.1
Avail. P ($mgKg^{-1}$)	9.81±0.67	4.39±1.56	15.6±9.28	4.85±0.16	8.60±1.44	6.72±2.26	4.66-10.2
Base Saturation (%)	63.5±6.52	82.8±3.03	81.5±2.86	83.2±3.37	61.6±14.8	78.6±9.41	65.4-87.0
Ex. Mn ($mgKg^{-1}$)	71.4±22.1	34.0±1.23	27.3±0.74	60.6±12.2	133±1.39	64.3±43.3	26.5-134
Ex. Al (cmol Kg^{-1})	3.90±0.53	1.18±0.09	1.58±0.52	1.74±0.68	3.28±0.11	2.02±1.30	0.96-3.52
Ex. Fe ($mgKg^{-1}$)	59.0±10.3	58.2±4.93	55.2±6.03	53.9±3.35	204±34.3	83.1±54.8	50.1-180
Ex. Ca (cmol Kg^{-1})	7.87±0.61	7.17±0.06	7.13±0.99	7.27±0.31	8.00±0.57	7.28±0.87	6.00-8.40
Ex. Mg (cmol Kg^{-1})	2.62±0.20	2.39±0.01	2.38±0.33	2.43±0.09	2.67±0.19	2.43±0.29	2.00-2.80
Fe_2O_3 (%) ^{c}	0.07±0.02	0.10±0.02	0.12±0.04	0.10±0.04	0.09±0.01	0.07±0.01	0.05-0.09
Fe_2O_3 (%) ^{a}	0.13±0.01	0.15±0.07	0.25±0.01	0.21±0.06	0.16±0.03	0.21±0.06	0.14-0.27
Al_2O_3 (%) ^{c}	0.04±0.03	0.04±0.02	0.03±0.01	0.06±0.04	0.03±0.02	0.04±0.03	0.01-0.08
Al_2O_3 (%) (10^{-2}) ^{a}	0.70±0.20	1.00±0.10	1.00±0.20	1.10±0.10	1.10±0.10	0.88±0.24	0.50-1.10
Avail. NO_3^- ($mgKg^{-1}$)	618±34.0	657±24.0	619±23.4	653±148	619±5.30	661±99.2	580-823
Avail. SO_4^{2-} ($mgKg^{-1}$)	497±358	866±124	820±102	838±190	2828±795	1283±1200	407-3390
Av. PO_4^{3-} (mg Kg^{-1})	1194±424	994±218	1628±487	658±121	593±179	930± 472	720–1477
PSD: Sand (%)	74.7±13.0	60.4±2.65	62.7±2.08	63.7±4.04	69.4±2.83	68.4±11.0	59.4-87.4
Silt (%)	4.98±5.29	18.0±14.7	1.31±0.58	5.31±0.58	13.0±0.00	4.78±4.82	0.98-12.9
Clay (%)	20.3±9.45	21.6±12.2	36.0±2.52	31.0±4.16	17.6±2.83	26.8±11.7	9.64-35.6
Soil texture	Loamy sand	Sandy loam	S. clay loam	Sandy loam	Sandy loam		

Table 3: Equilibrium amount of sorbed (Q_s) and desorbed (Q_d) phosphate per unit mass of air-dried soil sample

Ci (mg L^{-1})	Reaction type	Amount of PO_4^{3-} sorbed, Q_s at equilibrium (μg g^{-1})				
		SS-1	SS-2	SS-3	SS-4	SS-5
20	Adsorbed	140 (34.8)	143 (35.6)	134 (33.6)	138 (34.4)	263 (65.6)
	Desorbed	54.0 (38.6)	56.0 (39.1)	52.0 (39.0)	54.0 (39.5)	120 (45.3)
40	Adsorbed	320 (40.1)	340 (42.3)	314 (39.2)	326 (40.8)	625 (78.1)
	Desorbed	190 (59.5)	164 (48.3)	175 (55.6)	180 (55.3)	450 (71.8)
60	Adsorbed	540 (44.9)	558 (46.5)	538 (44.8)	554 (46.2)	947 (78.9)
	Desorbed	378 (70.1)	380 (68.0)	378 (70.3)	398 (71.9)	760 (80.5)
80	Adsorbed	798 (49.9)	771 (48.2)	792 (49.5)	820 (51.2)	1313 (82.0)
	Desorbed	757 (78.4)	460 (59.8)	603 (76.2)	662 (80.5)	1140 (86.7)
100	Adsorbed	994 (49.7)	1040 (52.0)	1030 (51.5)	1057 (52.8)	1682 (84.1)
	Desorbed	757 (76.1)	663 (63.8)	706 (68.5)	873 (82.6)	1452 (86.3)
120	Adsorbed	1160 (48.3)	1187 (49.5)	1212 (50.5)	1256 (52.3)	2024 (84.3)
	Desorbed	880 (75.9)	740 (62.5)	782 (64.5)	1020 (81.1)	1745 (86.2)
Mean±SD	Adsorbed	658±395	673±404	670±417	692±431	1142±660
	Desorbed	502±341	411±270	449±296	531±385	944±616
Range	Adsorbed	139-1159	143-1187	134-1212	138-1256	263-2024
	Desorbed	54.0-880	56.0-741	52.0-782	55.0-1019	119-1745

Values in parentheses are percentages of adsorbed (% S) and desorbed (% D) species

The phosphate-phosphorus sorption process showed a particular trend and provided a clear foundation for understanding such sorption. However, phosphates bioavailability to plants, to a very large extent, is a function of PO_4^{3-} desorption.

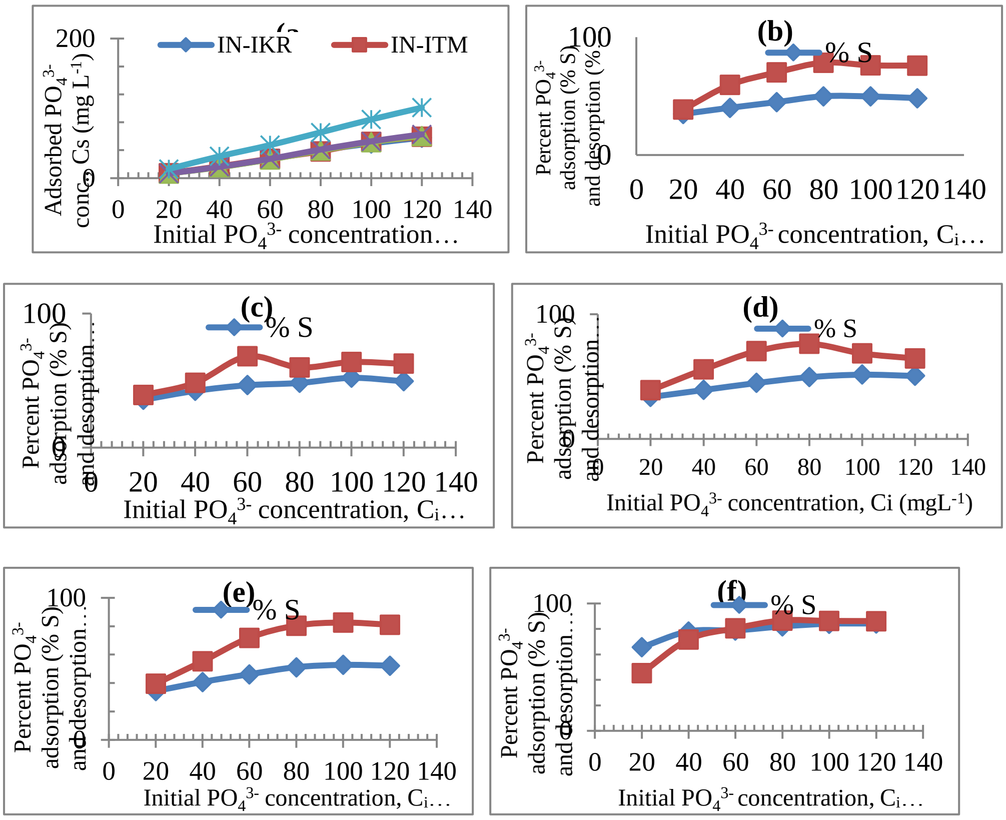
Effect of Initial Concentration on Phosphate Adsorption and Desorption

The variation of amount of phosphate ion adsorbed with initial concentration are shown in Figure 2. The plots indicated increase in the amount of sulphate ion adsorbed with concentration. The results of batch experimental procedures showing the effect of initial concentration of added KH_2PO_4 (ranged from 20 to 120 mg L^{-1} at selected pH of 5.5 with 2.0 g air-dried soil sample equilibrated for 12 hours) on adsorption and desorption of phosphate-phosphorus on selected agricultural soils under study are presented in Table 4. Results obtained showed increased concentration of PO_4^{3-} higher in Onna soil with values ranged from 13.1 to 101 mg L^{-1} (57.1±33.0 mg L^{-1}). Results of PO_4^{3-} concentration sorbed showed 84.1 mg L^{-1} for Onna soil sample while Ikot-Nkon soil showed least adsorbed PO_4^{3-} ions with mean value 32.9±19.8 (6.95-58.0) mg L^{-1} followed by Ikot-Amama 1, 33.5±20.9 (6.71-60.6) mg L^{-1}. Result showed that at very low concentration, less than 40% of the PO_4^{3-} concentration in equilibrium was sorbed onto soils except for Onna which recorded about 65.6% sorption at 20 mg L^{-1} aqueous solution.

Table 4: Effects of initial concentration (mg L^{-1}) on PO_4^{3-} ion adsorption and desorption

PO_4^{3-} initial conc. (mgL^{-1})	Reaction type	Adsorbed Phosphate ion concentration (mg L^{-1})				
		SS-1	SS-2	SS-3	SS-4	SS-5
20	Adsorbed	6.95(34.8)	7.13(35.6)	6.71(33.6)	6.88(34.4)	13.1(65.6)
	Desorbed	2.69(38.6)	2.79(39.1)	2.62(39.0)	2.72(39.5)	5.95(45.3)
40	Adsorbed	16.0(40.1)	16.9(42.3)	15.7(39.2)	16.3(40.8)	31.3(78.1)
	Desorbed	9.54(59.5)	8.18(48.3)	8.70(55.6)	9.0(55.3)	22.4(71.8)
60	Adsorbed	27.0(44.9)	27.9(46.5)	26.9(44.8)	27.7(46.2)	47.4(78.9)
	Desorbed	18.9(70.1)	19.0(68.0)	18.9(70.3)	19.9(71.9)	38.1(80.5)
80	Adsorbed	39.9(49.9)	38.5(48.2)	39.6(49.5)	41.0(51.2)	65.6(82.0)
	Desorbed	29.5(78.4)	23.1(59.8)	30.1(76.2)	32.9(80.5)	56.9(86.7)
100	Adsorbed	49.7(49.7)	52.0(52.0)	51.5(51.5)	52.8(52.8)	84.1(84.1)
	Desorbed	37.9(76.1)	33.1(63.8)	35.3(68.5)	43.7(82.6)	72.6(86.3)
120	Adsorbed	58.0(48.3)	59.3(49.5)	60.6(50.5)	62.8(52.3)	101(84.3)
	Desorbed	44.0(75.9)	37.1(62.5)	39.1(64.5)	51.0(81.1)	87.2(86.2)
Mean	Adsorbed	32.9±19.8 (44.6±6.1)	33.6±20.2 (45.7±5.9)	33.5±20.9 (44.8±7.2)	34.6±21.5 (46.3±7.4)	57.1±33.0 (78.9±7.0)
	Desorbed	23.8±16.2 (66.5±15.2)	20.5±13.5 (56.9±10.9)	22.5±14.8 (62.3±13.3)	26.5±19.2 (68.5±17.5)	47.2±30.8 (76.1±16.2)
Range	Adsorbed	6.95-58.0 (34.8-49.9)	7.13-59.3 (35.6-52.0)	6.71-60.6 (33.6-51.5)	6.88-62.8 (34.4-52.8)	13.1-101 (65.6-84.3)
	Desorbed	2.69-44.0 (38.6-78.4)	2.79-37.1 (39.1-68.0)	2.62-39.1 (39.0-76.2)	2.72-51.0 (39.5-82.6)	5.95-87.2 (45.3-86.7)

* Values in parentheses are percentage adsorbed and desorbed PO_4^{3-}.



F igure 2: (a) Sorption behaviour for all studied soils and percentage PO_4^{3-} adsorption and desorption for (b) Ikot-Nkon (c) Ogu-Itumbonuso (d) Ikot-Amama 1 (e) Ikot-Amama 2 and (f) Onna soils

At higher concentration of added adsorbate, the percentage fraction of phosphate sorbed onto the soils showed a corresponding rise to >50 mg L^{-1}. The trend showed higher sorption with increasing initial concentration of added PO_4^{3-} ion. The sorption pattern of phosphate ions (mg L^{-1}) in the studied soils followed the order: 57.1±33.0(SS-5) > 34.6±21.5(SS-4) > 33.6±20.2(SS-2) > 33.5±20.9(SS-3) > 32.9±19.8(SS-1).

Generally, the phosphate sorption pattern showed increased sorption with increasing concentration. Phosphate sorption was reported to be greatly influenced by the amount and type of clay fraction minerals, soil pH, soil organic matter, soil temperature, time of reaction, exchangeable Al^{3+} and soil redox condition (Sanchez and Uehara, 1980). Hence, the low phosphate sorption exhibited by most soil samples could be explained especially with high acidic (low pH) nature of the samples except for Onna soil (pH 3.00) which recorded highest phosphate sorption ranged between 65.6 – 84.3% within the initial concentration ranged from 20 to 120 mg L^{-1}. Also, the Onna soil sample (SS-5) recorded higher mean value of 3.28±0.11 cmol Kg^{-1} for exchangeable Al^{3+} which affects sorption capacity of phosphate. Similarly, the redox potential (Eh) value for Onna soil, 144±5.66 mV reported as the highest is a factor to consider in terms of high phosphate sorption ratio. Since liming increased soil pH, thereby increasing phosphate sorption in soils, we therefore can say that low pH values do not favour phosphate-phosphorus sorption, hence low pH values hinder phosphate sorption. According to Sato (2003), soil liming of a low exchangeable Al^{3+} soil, the neutralization and precipitation of Al^{3+} ion and of hydroxy–Al species to form $Al(OH)_3$ which reduces the number of phosphorus sorption sites. With high exchangeable Al^{3+} values, the formation of amorphous Al with highly active sorbing surfaces may exceed any decrease in the sorbing capacity of the original sorbing surfaces resulting in increased phosphate sorption with increasing pH.

Phosphorus Desorption

The amount of desorbed phosphate varied among the different soil samples in relation to the amounts adsorbed with lower concentration (in µgg^{-1}) at equilibrium than the adsorbed. The range of phosphate desorption in this study varied between 52.0 and 1745 µg g^{-1} (Table 3), with the wetland soil sample from Onna showing the highest recorded concentration (944±616 µgg^{-1}) followed by Ikot-Amama 2 (531±385 µgg^{-1}). The proposed Rice project farm, Ikot-Nkon (502±341 µgg^{-1}), Ikot-Amama 1 (441±296 µgg^{-1}) and Ogu-Itumbonuso (411±270) µgg^{-1}) recorded minimal concentration in soil. The percentage desorption for phosphate ions in soils varied from 45.3 to 86.7 (76.1±16.2) % in Onna soil and 31.1 to 68.0 (56.9±10.9) % in Ogu-Itumbonuso soil. Results showed that highest percentage phosphate desorption value, 86.7% (of the 56.9 %) adsorbed in Onna soil sample was recorded at initial PO_4^{3-} concentration of 80 mg L^{-1} while 63.8% (of the 33.1 % adsorbed) was desorbed in Ogu-Itumbonuso (SS-2) soil at initial PO_4^{3-} concentration of 100 mg L^{-1} (Table 4 and Figure 2). The desorption process describes phosphates bioavailability index to crop plants and soil microorganisms. This study, therefore, reveals that higher phosphate desorbability enhances higher phosphate bioavailability to crop plants and other soil microorganisms, thereby leading to surrounding surface and underground water contamination.

Effect of Soil-Solution pH on Phosphate Adsorption

Soil pH is very important for understanding phosphate mobility in agricultural soils. In tropical soils, liming is most frequently used, to raise soil pH hence increasing phosphate-phosphorus bioavailability to crop plants (Sanchez and Uehera, 1980). The phosphate sorption characteristics as affected by variable soil pH were investigated and results obtained are presented in Table 5. Results obtained for the amount of sorbed PO_4^{3-} by agricultural soils following the addition 25 mL of 125 mg L^{-1} KH_2PO_4 for all soil samples ranged from 157 to 482 (395±83.9) (µg g^{-1}) per unit mass of 2.0 mm air-dried soil sample. The sorbed concentration and percentage sorption (mean value in parentheses) ranged from 15.7 to 48.3 (39.5±8.39) mg L^{-1} and from 31.5 to 96.5 (78.9±16.8) % respectively (Figure 2). Across the five soil samples under study, the highest mean sorption value, 440±75.6 (260-483) µg g^{-1} was recorded at Ikot-Amama 2 soil followed by 421±81.1 (231-468) µg g^{-1} from Ogu-Itumbonuso soil representing 88.0±15.1% and 84.2±16.2% sorption respectively. The mean percentage sorption (% S) across the five studied soils followed the order: 88.0±78.9 (SS-4) > 84.2±16.2 (SS-2) > 402±82.5 (SS-5) > 370±78.9 (SS-1) > 340±78.8 (SS-2).

Table 5: Effect of pH on sorbed PO_4^{3-} with 25 mL of 125 mg L^{-1} KH_2PO_4 (pH = 5.5, W = 2.0 g, T = 25ºC)

Soil	Reaction type	Amount of PO_4^{3-} sorbed (Q_s) with 125 mg L^{-1} KH_2PO_4 added									Mean±SD	Range
		2.5	3.5	4.5	5.5	6.5	7.5	8.5	9.5	10.5		
SS-1	Q_s (µgg^{-1})	187	292	386	407	413	414	412	410	408	370±78.9	187-414
	% S	(37.5)	(58.5)	(77.2)	(81.4)	(82.6)	(82.9)	(82.4)	(82.0)	(81.6)	(74.0±15.7)	(37.5-82.9)
SS-2	Q_s (µgg^{-1})	231	346	431	456	464	468	465	464	463	421±81.1	231-468
	% S	(46.2)	(69.3)	(86.2)	(91.2)	(92.8)	(93.6)	(93.1)	(92.8)	(92.5)	(84.2±16.2)	(46.2-93.6)
SS-3	Q_s (µgg^{-1})	157	263	354	382	386	387	381	375	372	340±78.8	157-387
	% S	(31.5)	(52.5)	(70.8)	(76.5)	(77.2)	(77.5)	(76.3)	(75.0)	(74.5)	(68.0±15.8)	(31.5-77.5)
SS-4	Q_s (µgg^{-1})	260	377	451	473	479	483	482	480	477	440±75.6	260-483
	% S	(52.1)	(75.5)	(90.2)	(94.5)	(95.8)	(96.5)	(96.3)	(96.0)	(95.4)	(88.0±15.1)	(52.1-96.5)
SS-5	Q_s (µgg^{-1})	210	322	415	437	448	449	448	446	440	402±82.5	210-449
	% S	(42.0)	(64.5)	(83.1)	(87.4)	(89.5)	(89.7)	(89.5)	(89.2)	(88.1)	(80.3±16.5)	(42.0-89.7)

*Values in parentheses are percentages sorbed.

The optimum pH value for phosphate sorption was between 6.0 and 7.5, that is, PO_4-P sorption was not favoured by low pH ranges. At very low pH values, 2.5 to 3.0, only less than 50 % sorption of phosphate ions was obtained implying that highly acidic soil does not favour PO_4^{3-} sorption in tropical soils. At higher pH values (> 7.5), phosphate-phosphorus sorption experienced a decline due to increased hydroxyl concentration and increased competition between the hydroxyl groups and phosphate ions for specific sorption sites on the soil mineral surface (Sato, 2003).

On the other hand, the decline in PO_4^{3-} sorption could be attributed to neutralization and precipitation of Al^{3+} and hydroxyl-Al as $Al(OH)_3$ during liming process which leads to a decrease in the number of phosphorus sorption sites (Naidu *et al.*, 1990; Sato, 2003).

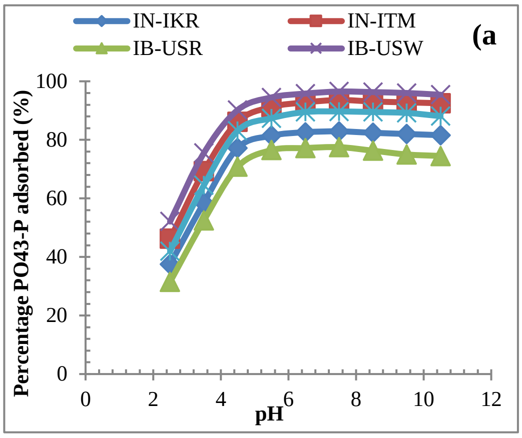


Figure 3: Effect of pH on percentage phosphate adsorbed onto soil samples

In acid weathered soils of pH 4.2 to 4.6, Chen and Barber (1990) reported that phosphate sorption increased when the pH was adjusted to between 6.0 and 6.2, but showed decreased sorption at higher pH values (pH 8.3). The authors ascribed this increase to the formation of amorphous hydroxyl-Al with highly active sorbing surfaces; while the subsequent decrease was attributed to increased competition of OH^- ions with PO_4^{3-} ions for sorption sites. At solution concentration of 125 mg PO_4 L^{-1} at pH 6.5, the amounts of PO_4^{3-} sorbed by the five soils were 479, 464, 448, 413 and 386 μg g^{-1} for SS-4, SS-2, SS-5, SS-1 and SS-3 soil samples respectively (Table 5). Since PO_4-P sorption decreases with increasing pH under normal soil conditions, results obtained from this study showed that increased sorption with soil pH between pH 5.5 and 7.5 for plant uptake of available phosphates.

Effect of Contact Time on PO_4^{3-} Sorption

The effect of contact time on PO_4-P sorption after 24 hours equilibration time was investigated using 25 mL of 125 mg L^{-1} KH_2PO_4 at controlled pH of 5.5 and varied contact-time interval from 0 to 1920 minutes. Mean results obtained are presented in Table 6. Results showed the adsorbed PO_4-P concentration, C_s (mean in parentheses) which ranged from 104 to 120 (111±3.75) mg L^{-1} and the percentage sorption ranged from 83.5 to 95.9 (89.0±3.00) %, indicating increased sorption level in the first-four hours of contact with the soil after 24 hours equilibration. Nearly all soil samples under study recorded up to 88.0% mean sorption except for Onna (SS-5) soil with 93.1±3.72% (116±4.65 mg L^{-1}) sorption. The mean amount of phosphate sorption onto the adsorbent, Q_t (in μg g^{-1} dry weight of soil) followed the order: 1454 (SS-5) > 1383 (SS-2) >1372 (SS-1) >1371 (SS-3) > 1370 (SS-4). This showed that all samples recorded above 80 % capacity to withdraw (sorbed) phosphate ions from solution. The sorption capacity of each soil sample was almost a constant after 480 minutes (8.0 h) staying between 82 and 100 % for all samples (Figure 4). Soil samples from Ikot-Nkon and Ogu-Itumbonuso showed similar behaviour due to proximity and related soil characteristics.

Table 6: Effect of contact-time on phosphate sorption with 125 mg L^{-1} KH_2PO_4 added to soil (pH = 5.5, W = 2.0g, V = 25 mL and T = 25°C)

Soil	Reaction type	Adsorbed (C_s) and equilibrium (C_e) conc. of PO_4^{3-} with time (minutes)								Mean±SD	Range
		0	30	60	120	240	480	960	1920		
SS-1	C_s (mg L^{-1})	104	106	109	110	111	112	113	113	110±3.15	104 – 113
	C_e (mg L^{-1})	20.7	18.5	16.4	15.4	13.7	12.8	12.2	12.0	15.2±3.15	12.0 – 20.7
SS-2	C_s (mg L^{-1})	107	108	109	110	112	113	113	113	111±2.48	107 – 113
	C_e (mg L^{-1})	18.4	16.8	16.0	14.6	13.4	12.2	12.0	11.7	14.4±2.48	11.7 – 18.4
SS-3	C_s (mg L^{-1})	108	108	109	109	110	111	111	111	101±1.31	108 – 111
	C_e (mg L^{-1})	17.1	16.8	16.1	15.8	15.0	14.1	13.9	13.8	15.3±1.31	13.8 – 17.1
SS-4	C_s (mg L^{-1})	108	109	109	110	110	110	110	111	110±0.89	108 – 111
	C_e (mg L^{-1})	16.9	16.4	15.8	15.2	14.8	14.8	14.6	14.5	15.4±0.89	14.5 – 16.9
SS-5	C_s (mg L^{-1})	107	113	116	117	119	120	120	120	116±4.65	107 – 120
	C_e (mg L^{-1})	18.4	12.2	9.37	7.76	6.12	5.2	5.16	5.13	8.67±4.65	5.13 – 18.4

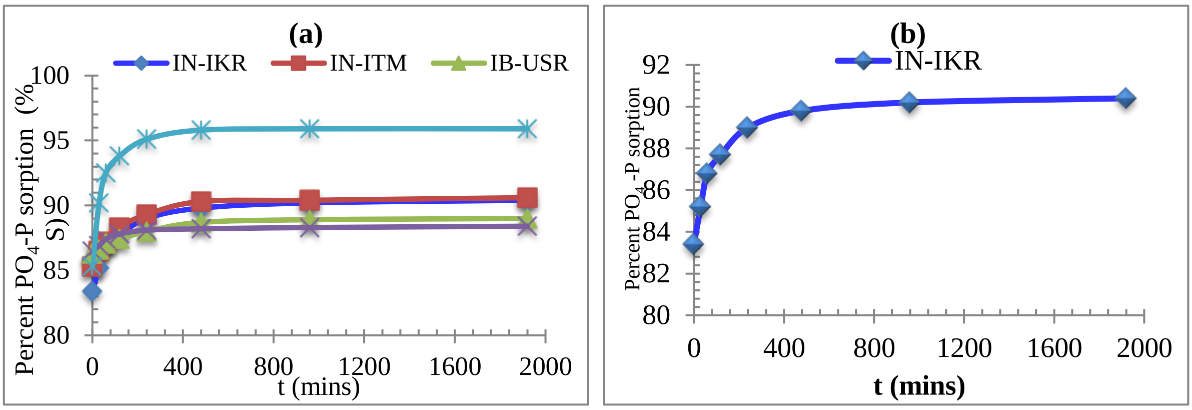


Figure 4: Effect of contact time on phosphate sorption (a) for all soil samples, and (b) for Ikot-Nkon soil (invisible in (a)).

The highest amount of phosphate sorbed onto soils, Q_t (µg PO_4 g^{-1} dry weight) was recorded for Onna soil, a wetland swampy soil from East-west Road, Onna. According to Otero *et al.* (2013), soils with lower bulk density which are likely to have high organic matter levels will show higher phosphate-phosphorus sorption velocity. This explains why soil sample from Onna showed higher adsorption capacity for phosphate-phosphorus being sample with highest organic matter content as explained by Otero *et al.* (2013). On the other hand, the authors also reported that total Fe and Fe-oxide contents in soils are the most determining properties influencing PO_4^{3-} sorption. From results of chemical properties (Table 2), Onna soil sample recorded the highest concentration of exchangeable Fe^{2+}, 204 mg Kg^{-1} with about 0.10 % and 0.16 % levels of both crystalline and amorphous Fe_2O_3 respectively.

The Equilibrium Concentration (EC) and Equilibrium Buffering Capacity (EBC) of PO_4^{3-} in Soils

The equilibrium concentration of phosphate (EC-P) is a useful parameter to predict the probability of soil samples acting as potential sinks or as a source of phosphate bioavailability to crop plants or simple the release of phosphate to the surrounding surface water bodies. It is used to predict the environmental risk of phosphate concentration in studied soils (Brand-Kilibanski *et al.*, 2007).

At low PO_4^{3-} concentration in soil solution, the relationship between PO_4^{3-} in aqueous phase, C_e (mg L^{-1}) and PO_4^{3-} sorbed onto solid phase, Q_s (µg g^{-1}) is described by Equation (8),

$Q_s = KC_e - Q_i$ - - - - - (8)

where: Q_i = the initial amount of phosphate sorbed on to soils (µg g^{-1}), Q_s = the sorbed nitrates on to solid phase (µg g^{-1}), C_e = phosphate concentration remaining in aqueous solution after 24 hours equilibrium (mg L^{-1}), K = phosphate equilibrium buffering capacity, EBC-P, (mL g^{-1}) (i.e., the slope of the plot).

The equilibrium concentration of phosphate (EC-P) and the linear regression model for estimating EC and EBC of phosphate for the five soils under study are presented in Table 7. The EC-P values obtained ranged between 5.00 and 9.90 mg L^{-1}. Soil samples from Ikot-Amama 1 and Ikot-Amama 2 recorded highest EC-P values of 9.80 mg L^{-1} and 9.90 mg L^{-1} respectively, while Onna soil (SS-5) recorded the least EC-P value, 5.00 mg L^{-1}. Higher EC-P values from renders the soil samples most vulnerable to phosphate loss. However, values obtained in this study were generally higher than those reported elsewhere which was quite below 1.0 mg L^{-1} (Hongthanat, 2010)

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Table 7**:** A linear regression model used to estimate equilibrium concentration (EC) and equilibrium buffer capacity (EBC) for NO_3^-, SO_4^{2-} and PO_4^{3-}.

Site	Linear equation	R^2	EBC-P (L g^{-1})	Q_i (µg g^{-1})	EC-P (mg L^{-1})
Ikot-Nkon	y = 22.104x - 161.24	0.9832	22.1	-161.24	7.40
Ogu-Itumbonuso	y = 23.124x - 168.15	0.9837	23.1	-168.15	7.54
Ikot-Amama 1	y = 24.905x - 239.38	0.9863	24.9	-239.38	9.80
Ikot-Amama 2	y = 26.879x - 260.21	0.9878	26.9	-260.21	9.90
Onna	y = 146.24x - 741.96	0.9793	146.2	-741.96	5.00

4.5.3 Equilibrium Modeling for Phosphate Adsorption

The Onna soil sample, which recorded the lowest EC-P value of 5.0 mg L^{-1}, was obtained from a wetland swampy soil along Eket-Onna-Ikot Abasi Road, characterized by high organic matter content and other decayed plants and animals leading to eutrophication. Soil samples with very high EC-P values showed high susceptibility or tendency for phosphate loss, therefore, samples from Ikot-Amama 2, Ikot-Amama 1, Ogu-Itumbonuso and Ikot-Nkon possessed the greatest capacity to act as phosphate sources by releasing phosphate ions to the crop plants, surrounding surface water and underground water sources. Therefore, the use of phosphate fertilizers poses threat to the surrounding surface water bodies and the ecosystem in general. Also, the index known as the equilibrium buffering capacity of phosphate (EBC-P) is the ability of soil samples to resist the change in solute concentration in solution. The linear regression model used to estimate the equilibrium concentration (EC) and the equilibrium buffering capacity (EBC) parameters of phosphate ions in different soil samples under study are presented in Table 7. The equilibrium buffering capacity of phosphate (EBC-P), which represents the ability of soil samples to buffer the additional phosphates in aqueous soil system for the five studied soil samples ranged between 22.1 and 146.2 L g^{-1} (Table 7). Higher EBC-P value was indicative of greater ability of the soil to sorb phosphate ions. The Onna soil sample (SS-5) with EBC-P value 146.24 L g^{-1} recorded the highest capacity to sorb additional phosphate ions; while Ikot-Nkon (22.1 L g^{-1}) and Ogu-Itumbonuso (23.1 L g^{-1}) recorded the lowest capacity to sorb additional phosphate. The phosphate sorption characteristics in the studied soil samples with variable initial concentration were calculated using the Langmuir, Freundlich, modified Freundlich, Van Huay and Temkin adsorption models. The sorption data with addition of 25 mL of variable initial concentration (from 20 to 120 mg L^{-1} KH_2PO_4 after 24 hours equilibration time at pH 5.5) for the different models are presented in Table 8 and Figures 5 – 9. The range of R^2 values (mean in parenthesis) recorded for the different models were 0.9659 to 0.9943 (0.9872), 0.9657 to 0.9758 (0.9696), 0.9175 to 0.9463 (0.9307) and 0.7088 to 0.8504 (0.7852) for Freundlich, Van Huay, Temkin and Langmuir model respectively. From the four isotherms used, the Freundlich model gave highest results compared to the other three isotherms with respect to the linearity of the plot in terms of R^2 values.

Table 8: Values of Langmuir, Freundlich, modified Freundlich, Van Huay and Temkin adsorption constants for phosphate sorption of selected soils

Soil samples	Freundlich			Langmuir			Van Huay			Temkin		
	R^2	K_F	$1/n_F$	R^2	K_L	Q_{max}	R^2	n	m	R^2	a	b
Ikot-Nkon	0.9893	3.682	1.421	0.7514	-0.008	-1250	0.9758	254	-850	0.9373	-1724	681
Ogu-Itumbonuso	0.9930	3.985	1.413	0.7674	-0.009	-1250	0.9730	262	-867	0.9337	-1743	695
Ikot-Amama 1	0.9936	2.505	1.534	0.8478	-0.010	-909	0.9657	281	-985	0.9175	-1915	740
Ikot-Amama 2	0.9943	2.464	1.561	0.8504	-0.012	-833	0.9664	298	-1041	0.9186	-1999	777
Onna	0.9659	7.355	1.941	0.7088	-0.041	-833	0.9671	1006	-2419	0.9463	-3069	1685
Mean	0.9872	3.998	1.574	0.7852	-0.016	-1015	0.9696	420	-1232	0.9307	-2090	916

K_F = Freundlich adsorption constant (L g^{-1}); K_L = Langmuir adsorption constant (L mg^{-1}); $1/n_F$ = measure of intensity of adsorption; **n** = Van Huay adsorption coefficient (L g^{-1}), **m** = Van Huay constant parameter; **a** = amount of P adsorbed (μgg^{-1}), **b** = buffer capacity of Temkin model (mLg^{-1}); Q_{max} = maximum adsorption capacity (μg g^{-1}).

Goodness of fit in the linear form of the equation is compared on the basis of the mean correlation values (r) for all the isotherm equations in use. Since the choice among model equations is often made based on the goodness of fitted data, the Freundlich model provided the best choice for phosphate sorption calculation in all samples except for Onna soil (mean R^2 = 0.9872). The highest correlation value, r, was found in Ikot-Amama 2 soil (R^2 = 0.9943) followed by Ikot-Amama 1 soil (R^2 = 0.9936). The least R^2 value (R^2= 0.9659) was from Onna soil which showed highest percentage sorption value, 84.3 % (2024 μg g^{-1}) with 120 mg L^{-1} KH_2PO_4 added and 65.6 % (μg g^{-1}) with 20 mg L^{-1} KH_2PO_4 added. From the linear Freundlich model, the value of $^1/n_F$, being a measure of the intensity of adsorption, in this study varied from 1.413 to 1.941 for all soil samples. This was responsible to the concave shape of non-linear adsorption isotherm, which is more favorable at lower equilibrium concentration (Bhatt *et al.*, 2012; Mohsenipour *et al.*, 2015).

The phosphate sorption constant derived from the Freundlich model showed that the K_F values varied from 2.464 to 7.355 L g^{-1} in all sample soils under study (Table 8). The Freundlich constant, K_F, which is related to the stability constant for complexes showed highest value in Onna soil (7.355 L g^{-1}) soil. The constant K_F is dependent on the phosphate solution concentration through which the value of K_F varied from sample to sample. However, K_F is the amount of PO_4^{3-} sorbed that would be available to sustain a unit PO_4^{3-} concentration in equilibrium solution. The measure of the intensity of adsorption, $1/n_F$, for all soil samples were greater than 1 (i.e., $1/n_F > 1.0$). This showed that the shape of the non-linear adsorption isotherm was concave implying that adsorption is favored at lower equilibrium concentration (Bhatt *et al.*, 2012). This study, therefore provided that the adsorption of PO_4^{3-}P was dominated in aqueous phase. Consequently, the Freundlich equation was used to calculate the phosphate sorption capacity for Ikot-Amama 2 soil sample, where K_F = 2.464 Lg^{-1} a, nF = 0.641 and $^1/n_F$ = 1.561

$$\mathbf{Q_e = K_F C_e^{1/n};} \quad = 2.464\ \mathrm{L\ g^{-1}} * C_e^{1.561} \quad - \quad - \quad - (9)$$

Since the intensity of adsorption, $^1/n_F$ is greater than 1 for all studied soil samples, the shape of non-linear adsorption isotherm in concave and adsorption of phosphates is favorable at lower equilibrium concentrations, hence, chemisorption resulted. The Van Huay parameters, that is, Van Huay adsorption coefficient (n), Van Huay constant parameter (m) and R^2 values computed from the data plotted on Fig. 5c-9c are shown in Table 2. There was a high correlation for all soil samples with values of R^2 >0.90, indicating apparent greater relationship between the adsorption data and the Van Huay model

The sorption coefficient (n) ranged from 254 L g^{-1} for Ikot-Nkon rice project soil to 1006 L g^{-1} for Onna, indicating that higher Van Huay sorption coefficient leads to higher amount of phosphorus adsorbed.

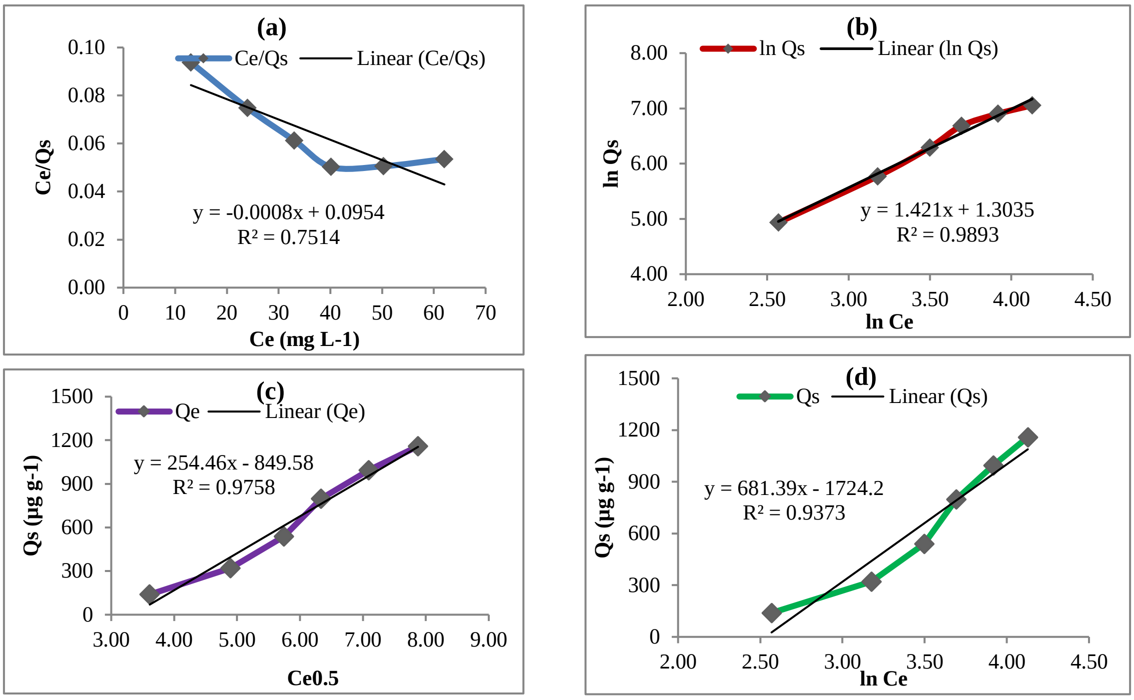

Figure 5. Linear fit for (a) Langmuir, (b) Freundlich, (c) Van Huay and (d) Temkin isotherms of PO_4^{3-} sorption for Ikot-Nkon (SS-1) soil

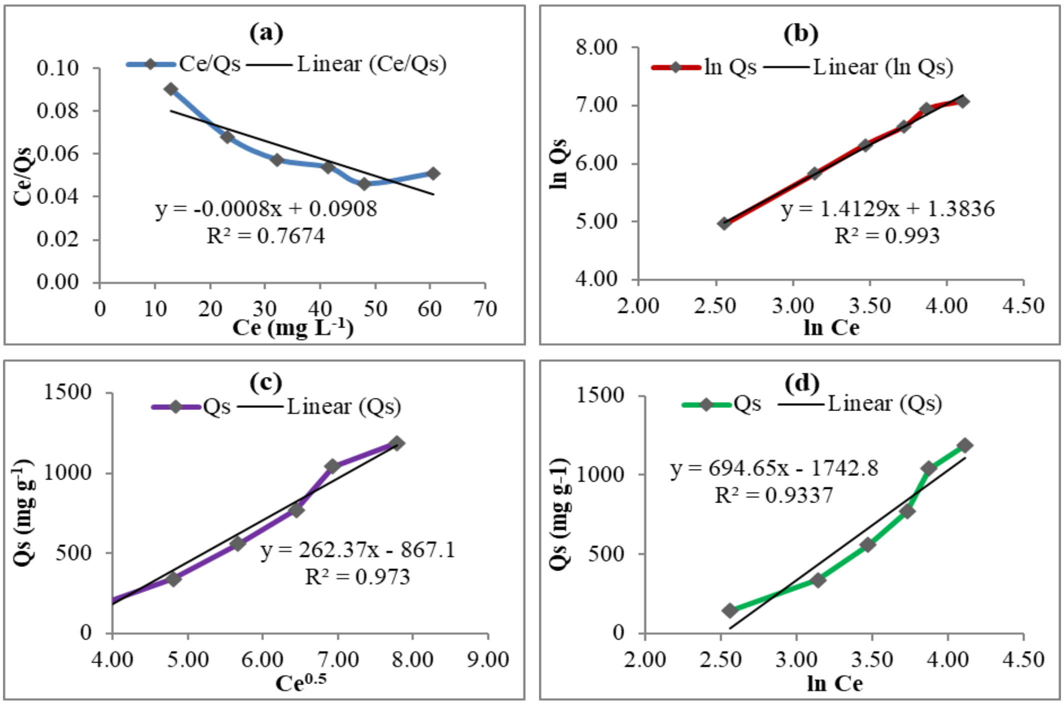

Figure 6. Linear fit for (a) Langmuir, (b) Freundlich, (c) Van Huay and (d) Temkin isotherms of PO_4^{3-} sorption for Ogu-Itumbonuso (SS-2) soil

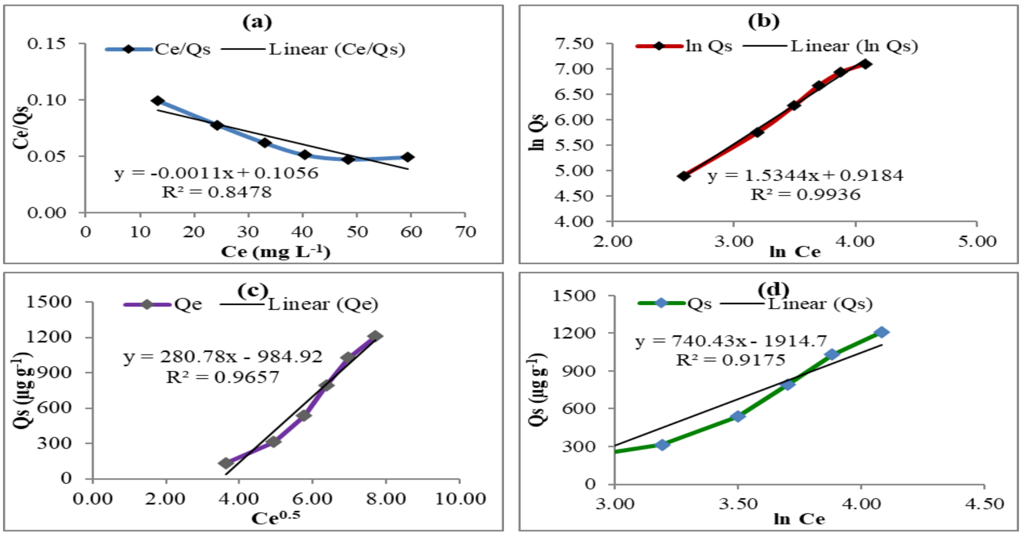

Figure 7. Linear fit for (a) Langmuir, (b) Freundlich, (c) Van Huay and (d) Temkin isotherms of PO_4^{3-} sorption for Ikot-Amama 1 (SS-3) soil.

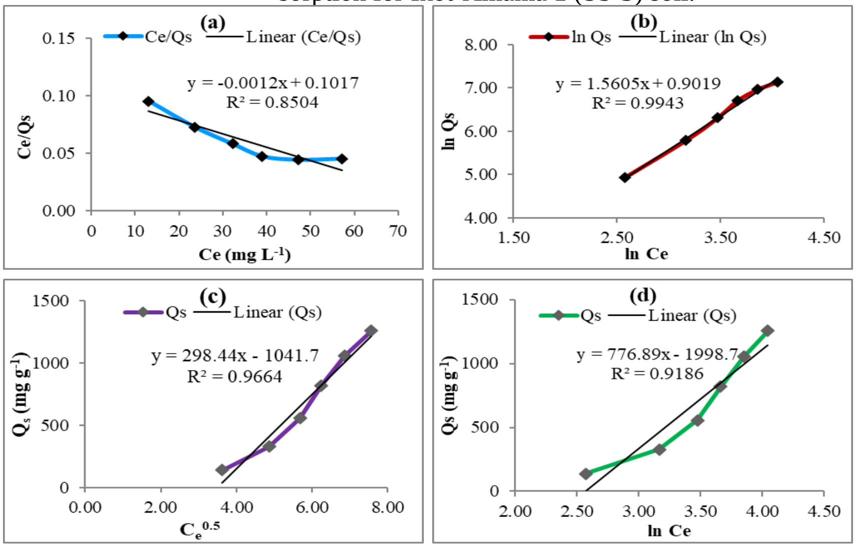

Figure 8. Linear fit for (a) Langmuir, (b) Freundlich, (c) Van Huay and (d) Temkin isotherms of PO_4^{3-} sorption for Ikot-Amama 2 soil

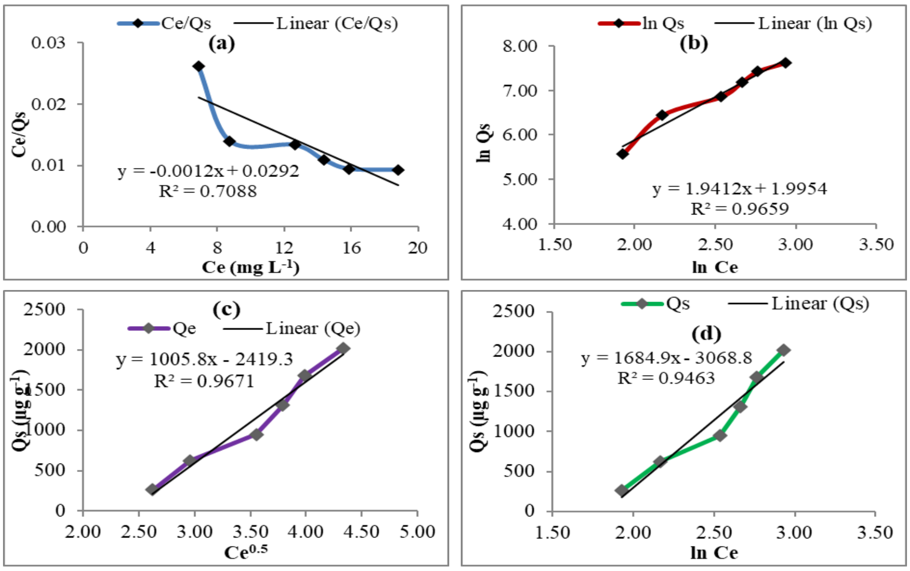

Figure 9. Linear fit for (a) Langmuir, (b) Freundlich, (c) Van Huay and (d) Temkin isotherms of PO_4^{3-} sorption for Onna (SS-5) soil.

Relationship Between Sorption Parameters and Soil Physiochemical Properties

In order to understand the sorption of phosphate ions on to agricultural soil samples, the Langmuir, Freundlich, Van Huay and Temkin sorption parameters - Q_{max} and K_L, n_F and K_F, n and m, a and b, EC-P and EBC-P were applied to study their relationships with soil physiochemical properties. The Langmuir sorption maxima (Q_{max}) showed very weak correlation with most soil properties except for EC (r = 0.709), OC (r = 0.611), OM (r = 0.594), TN (0.615), amorphous Fe_2O_3 (r = 0.660), amorphous Al_2O_3 (r = 0.606) and SO_4^{2-} (r = 0.533) ($P<0.05$). This, however, suggests that the sorption maximum increased with increasing concentration of amorphous oxides of Fe and Al in the samples together with electrical conductivity (Table 9). The Langmuir bonding energy index, K_L, showed strong negative correlation with available SO_4^- (r = -0.991), statistically significant at $P<0.01$, exchangeable Fe (r = -0.991, $P<0.01$), OC and OM (r = - 0.952, $P<0.01$), TN (r = - 0.956, $P<0.01$), EC (r = - 0.911, $P<0.05$), and exchangeable Mn (r = - 0.893, $P<0.05$) (Table 9). This implies that the bonding energy index increased with decreasing soil physiochemical variables. On the other hand, exchangeable Na (r = 0.609), K (r = 0.655), base saturation (r = 0.599) and available PO_4^{3-} (r = 0.593) showed strong positive non-significant relationship with K_L whereas soil pH showed very strong correlation (r = 0.854) significant at $P< 0.05$.

The Freundlich adsorption capacity (K_F) showed very strong positive significant correlation with Eh (r = 0.896, $P<0.05$), OC (r = 0.814, $P<0.05$), OM (r = 0.823, $P<0.05$), TN (r = 0.817, $P< 0.05$), Mn (r = 0.862, P<0.0.05), Fe (r = 0.949, $P<0.01$), available SO_4^{2-} (r = 0.908, $P<0.05$). Also, EC (r = 0.724), Ca (r = 0.747), Mg (r = 0.752) CEC (r = 0.732 and silt (r = 0.585) showed a strong positive relationship (though not significant) with the Freundlich's sorption capacity, K_F. The clay fraction, available PO_4^{3-}, amorphous Fe_2O_3, crystalline Al_2O_3, and base saturation showed non-significant strongly negative correlation with K_F, with r values of - 0.783, - 0.545, - 0.515, - 0.504, - 0.727 respectively; while soil pH showed very strong significant association (r = - 0.967, $P<0.01$). The data showed that an increase in the amount of exchangeable Fe, available PO_4^{3-}, SO_4^{2-}, exchangeable Mn and reduction potential of soil samples were responsible for increasing phosphate sorption capacity of the studied soils. The factor representing the intensity of adsorption in the Freundlich's isotherm, n_F, also showed very strong negative relationship, significant at $P<0.01$, with TN (r = - 0.957), OC (r = - 0.953), OM (r = - 0.947), and SO_4^{2-} (r = - 0.939), while EC (r = - 0.926), Fe (r = - 0.911) and Mn (r = - 0.812) showed significance at $P<0.05$ (Table 9). This relationship indicated that increasing the concentration of these parameters will lead to low adsorption intensity for phosphates ($n_F < 1$) leading to chemisorption.

The Van Huay adsorption coefficient (n) showed very strong positive relationship with Eh (r = 0.900, $P<0.05$), EC (r = 0.888, $P<0.05$), OC (r = 0.955, $P<0.01$), Mn (r = 0.897, $P<0.05$), OM (r = 0.956, $P<0.01$), TN (r = 0.958, $P<0.01$), Fe (r = 0.996, $P<0.01$) and sulphate (r = 0.991, $P<0.01$). The Van Huay sorption constant parameter (m) showed strong negative significant correlation, significant at $P<0.05$ with Eh (r = -0.885, $P<0.05$), EC (r = -0.907, $P<0.05$), Mn (r = -0.888, $P<0.05$), OC (r = -0.962, $P<0.01$), OM (r = -0.956, $P<0.01$), TN (r = -0.965, $P<0.01$), Fe (r = 0.989, $P<0.01$) and sulphate (r = -0.991, $P<0.01$).

Table 9: Pearson correlation (r) between phosphate sorption parameters and soil physicochemical properties

Soil parameters	Correlation (r) value									
	Q_{max}	K_L	n_F	K_F	n	m	a	b	EC-P	EBC-P
pH_W	-0.079	0.854*	0.686	-0.967‡	-0.879*	0.847*	0.799	-0.863*	0.959‡	-0.888*
Eh	0.297	-0.891*	-0.787	0.896*	0.900*	-0.885*	-0.861*	0.894*	-0.844*	0.903*
EC	0.709	-0.911*	-0.926*	0.724	0.888*	-0.907*	-0.928*	0.901*	-0.512	0.881*
OC	0.611	-0.952‡	-0.953‡	0.814*	0.955‡	-0.962‡	-0.962‡	0.957‡	-0.652	0.953‡
OM	0.594	-0.952‡	-0.947‡	0.823*	0.956‡	-0.962‡	-0.960‡	0.958‡	-0.665	0.955‡
TN	0.615	-0.956‡	-0.957‡	0.817*	0.958‡	-0.965‡	-0.966‡	0.961‡	-0.652	0.956‡
TP	0.241	0.170	0.009	-0.325	-0.161	0.137	0.114	-0.155	0.401	-0.165
Avail. P	0.194	0.028	-0.091	-0.139	-0.009	-0.005	-0.013	-0.008	0.183	-0.009
Ex. Al	-0.110	-0.392	-0.287	0.500	0.421	-0.394	-0.355	0.406	-0.598	0.430
CEC	-0.159	-0.562	-0.393	0.732	0.597	-0.558	-0.503	0.576	-0.824*	0.608
Ex. Mn	0.367	-0.893*	-0.812*	0.862*	0.897*	-0.888*	-0.872*	0.894*	-0.792	0.899*
Ex. Fe	0.441	-0.991‡	-0.911*	0.949‡	0.996‡	-0.989‡	-0.971‡	0.993‡	-0.826*	0.998‡
Cryst. Fe_2O_3	0.467	0.127	-0.062	-0.372	-0.153	0.110	0.057	-0.133	0.561	-0.165
Cryst. Al_2O_3	0.072	0.392	0.300	-0.504	-0.430	0.404	0.360	-0.412	0.504	-0.439
Amorp.Fe_2O_3	0.660	0.156	-0.122	-0.515	-0.188	0.128	0.053	-0.159	0.723	-0.203
Amorp. Al_2O_3	0.606	-0.318	-0.429	0.089	0.283	-0.320	-0.366	0.304	0.146	0.272
Avail. PO_4^{3-}	-0.311	0.593	0.529	-0.545	-0.569	0.571	0.578	-0.576	0.466	-0.566
Avail. SO_4^{2-}	0.533	-0.992‡	-0.939‡	0.908*	0.991‡	-0.991‡	-0.983‡	0.992‡	-0.748	0.990‡
Sand	-0.175	-0.256	-0.162	0.370	0.285	-0.259	-0.221	0.270	-0.491	0.294
Silt	-0.327	-0.340	-0.109	0.585	0.349	-0.309	-0.259	0.332	-0.631	0.357
Clay	0.415	0.486	0.215	-0.783	-0.514	0.460	0.389	-0.489	0.913*	-0.528

‡ and *. Correlation is significant at the 0.01 and 0.05 level (1-tailed), ^{a} = amorphous, ^{c} = crystalline, pH_w = pH_{water}, EA = exchangeable acidity.

The amount of solute adsorbed of Temkin model (a), showed significant negative relationship with Eh ($r = -0.861$, $P<0.05$), EC ($r = -0.928$, $P<0.05$), Mn ($r = -0.872$, $P<0.05$), OC ($r = -0.962$, $P<0.01$), OM ($r = -0.960$, $P<0.01$), TN ($r = -0.966$, $P<0.01$), Fe ($r = -0.971$, $P<0.01$) and sulphate ($r = -0.983$, $P<0.01$). The buffer capacity of Temkin model (b) showed strong positive relationship with Eh ($r = 0.894$, $P<0.05$), EC ($r = 0.901$, $P<0.05$), OC ($r = 0.957$, $P<0.01$), Mn ($r = 0.894$, $P<0.05$), OM ($r = 0.958$, $P<0.01$), TN ($r = 0.961$, $P<0.01$), Fe ($r = 0.993$, $P<0.01$) and sulphate ($r = 0.992$, $P<0.01$) (Table 9).

The equilibrium concentration of phosphates (EC-P) showed very strong positive significant association with soil pH ($r = 0.960$, $P<0.01$), clay ($r = 0.913$, $P<0.05$) but not significant with base saturation ($r = 0.795$), amorphous Fe_2O_3 ($r = 0.723$), crystalline Fe_2O_3 ($r = 0.561$) and crystalline Al_2O_3 ($r = 0.504$). The equilibrium buffering capacity of phosphate (EBC-P) showed perfectly strong positive correlation with Eh ($r = 0.903$), $P<0.05$), EC ($r = 0.881$, $P<005$), OC ($r = 0.953$, $P<0.01$), OM ($r = 0.955$, $P<0.01$), TN ($r = 0.956$, $P<0.01$), Fe ($r = 0.998$, $P< 0.01$), available SO_4^{2-} ($r = 0.990$, $P<0.01$), Mn ($r = 0.899$, $P<0.05$) (Table 9). This implied that buffering capacity was greatly influenced by the organic matter, organic carbon, exchangeable Fe, total nitrogen and electrical conductivity content of the studied soils.

CONCLUSION

Results of soil physicochemical characteristics showed that the studied soils were high acidic with high available phosphates (720 to 1477 $mgKg^{-1}$). The acidity was far higher than rice needs of 5.5-6.5 soil pH, hence, the need for soil improvement. The sorption studies revealed that phosphate adsorption increased with increasing concentration of added phosphates but decreased at a certain higher concentrations level due to soils lacking capacity to adsorb more phosphates. Samples showed high phosphate sorption related to active aluminium and iron species, while crystalline iron and aluminium oxides were mainly responsible for sorption in the Onna soil. The high desorption levels in Onna (SS-5) and Ikot-Amama 2 (SS-4) soils were indicative of a high risk of phosphorus leaching thereby posing serious threat to surrounding surface and underground water bodies. The degree of fitness (R^2) of the phosphate adsorption data for the different adsorption models was of the order Freundlich>Van Huay>Temkin>Langmuir. Therefore, the Freundlich isotherm model was the best fit to describe PO_4^{3-} sorption processes in the studied soils. Phosphorus requirements for rice yield was not favourable due to high desorption rate despite high P level in soils. In order to have a more reliable information on soil properties for prediction of likely environmental contamination, the need for more intensive survey and development of multiple regression relationships between PO_4^{3-} adsorption and physicochemical, and mineralogical soil properties was recommended. This will help to prevent both surface and groundwater contamination for sustainable surface and groundwater use.

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