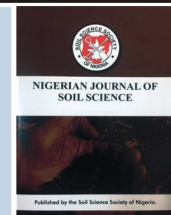




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Kinetics of Phosphorus Sorption in Selected Soils of Southeastern Nigeria

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ABSTRACT

This study investigated the phosphorus sorption kinetics of soils of varying parent material and soil depth in south east Nigeria. The parent materials studied were: Coastal Plain Sand, Basalt, Shale and Sandstone and the depths were: 0 – 20cm, 20-40cm and 40-60cm. Soil samples were collected from the different parent material in three replicates and a total of thirty-six composite samples were collected. The experimental design was a 4 x 3 factorial in Randomized Complete Block Design. Both parent material and soil depth as lone factors significantly influenced the rate constant (K_i), but their interactive effect was not significant. The means K_i values occurred in the following order: Shale (5.05m^{-1}) > Basalt (4.67m^{-1}) > Sandstone (3.55m^{-1}) > Coastal Plain Sand (1.08m^{-1}). The rate constant (K_i) generally increased with soil depth. Relating the rate constant (K_i) to clay mineralogy showed that the values of K_i were highest in soils derived from Shale and Basalt which also had the highest concentration of Fe and Al oxides.

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1.0 Introduction

The process of soil P sorption has been widely studied over the last few years, particularly because physicochemical adsorption to soil surface is the main process underlying phosphate retention, resulting in low P availability (Agbenin and Tiessen, 1994; Farias *et al.*, 2009). Despite the numerous studies on P sorption characteristics of tropical soils (Osodeke and Ubah, 2005; Frank *et al.*, 2015; Zinabu and Wassie, 2015; Aghimien *et al.*, 2015), little attention has been paid to the rate of this process, which is very relevant in planning of phosphate fertilization strategies (Santos *et al.*, 2011). Chemical kinetics is the study of chemical processes and the factors that affect the speed of reaction as well as the mechanism of chemical reaction. It

refers to the time, how fast or slow reactants are consumed and the products formed (Anacleto, 2010). It encompasses the reaction pathways, how the rates respond to changes in the condition or presence of a catalyst and the steps by which reactions take place (Anacleto and Godwin, 2002).

Adsorption and precipitation which are the principal reactions in soil P retention begin immediately after P addition to the soil (Santos *et al.*, 2011). The rate of both adsorption and precipitation of added P in the soil environment is known as kinetics of sorption of P (Henry and Smith, 2004). The kinetics of P sorption is characterized by an initial fast reaction, followed by a slow reaction which continues for a long time (Henry and Smith, 2004). In the

first stage, P applied to the soil is rapidly adsorbed, most of it in the first hour of contact with soil. In the second and slower phase, the recently adsorbed P is more strongly retained in the soil, forming non-labile P (Goncalves *et al.*, 1985). This latter reaction is responsible for the continuous removal of P from the soil solution, even when the concentration of P has fallen below the solubility thresholds at which P precipitation reaction cease (Henry and Smith, 2004).

The pace at which P is sorbed, not only to the soil, but also to other materials, has been the subject of several studies around the world, primarily to understand this phenomenon, which is a matter of great concern, and secondly to estimate the capacity and rate of various materials in removing excessive P amount that cause pollution in the environment (Karaca *et al.*, 2004; Cheung and Venkitachalam, 2006; Wang *et al.*, 2009).

The continuing slow reaction of P in soils is a major contributory factor to the loss of the effectiveness of P fertilizer application over time (Barrow, 1980a). This is because it reduces the availability of the residues of past P fertilizer applications to plants, and hence, progressively extinguishes their residual value over time (Henry and Smith, 2004). The rate of both the fast and slow P reactions in soil has been found to vary widely between different soils (Barrow, 1980), including tropical soils. These variations may be attributed to the differences in physical, biological, chemical and mineralogical properties of soils. According to Ruan and Gilkes (1995), the variations on P kinetics among soils may be related to the type, amount, crystal, morphology and specific surface area of clay minerals, including Fe, Al oxides and kaolinite.

To obtain an index of the rate of P kinetics is of obvious interest. Firstly, the identification of P kinetics differences among soils could serve as a basis to select the most ap-

propriate fertilization philosophy for each soil which is of immense economic importance (Henry and Smith, 2004). Secondly, independently of its role in choosing a fertilization philosophy, the possibility of estimating an index of the kinetics of P from soil properties could lead to its inclusion in the soil parameters routinely determined by soil testing laboratories. This would be a useful aid in formulating P fertilizer recommendations, which are meant to last for more than one season, such as in situations where the fertilizer cannot annually be incorporated into the plough layer (Henry and Smith, 2004). Allowing for the differences in P kinetics between soils when making P fertilizer recommendations would be an improvement compared to the current situation where it is assumed that no differences in residual value of the additional P fertilizer exist between different soils (Henry and Smith, 2004; Wang *et al.*, 2009).

The primary bases for P sorption kinetics study lies on the fact that the faster the process of P sorption to soil surfaces, the lower the amount of plant-available P in short periods (Santos *et al.*, 2011). Since clay mineralogy and parent materials are strong factor in P kinetics, evaluation of P sorption kinetics for soils of contrasting clay minerals is necessary to determine the retention times among soils which will guide in formulating viable P fertilization programmes. This informs the choice of this study.

2.0 Methodology

2.1 Study area

The study area, southeastern Nigeria lies between latitudes 4°20' and 7°25'N and longitudes 5°25' and 9°51'E (Nwagbara, 1997). It is made up of Abia, Akwa Ibom, Anambra, Cross River, Ebonyi, Enugu, Imo, and River States and occupies a land mass of about 12% of the total land area of Nigeria (Fig.1) (Odurukwe *et al.*, 1995). It

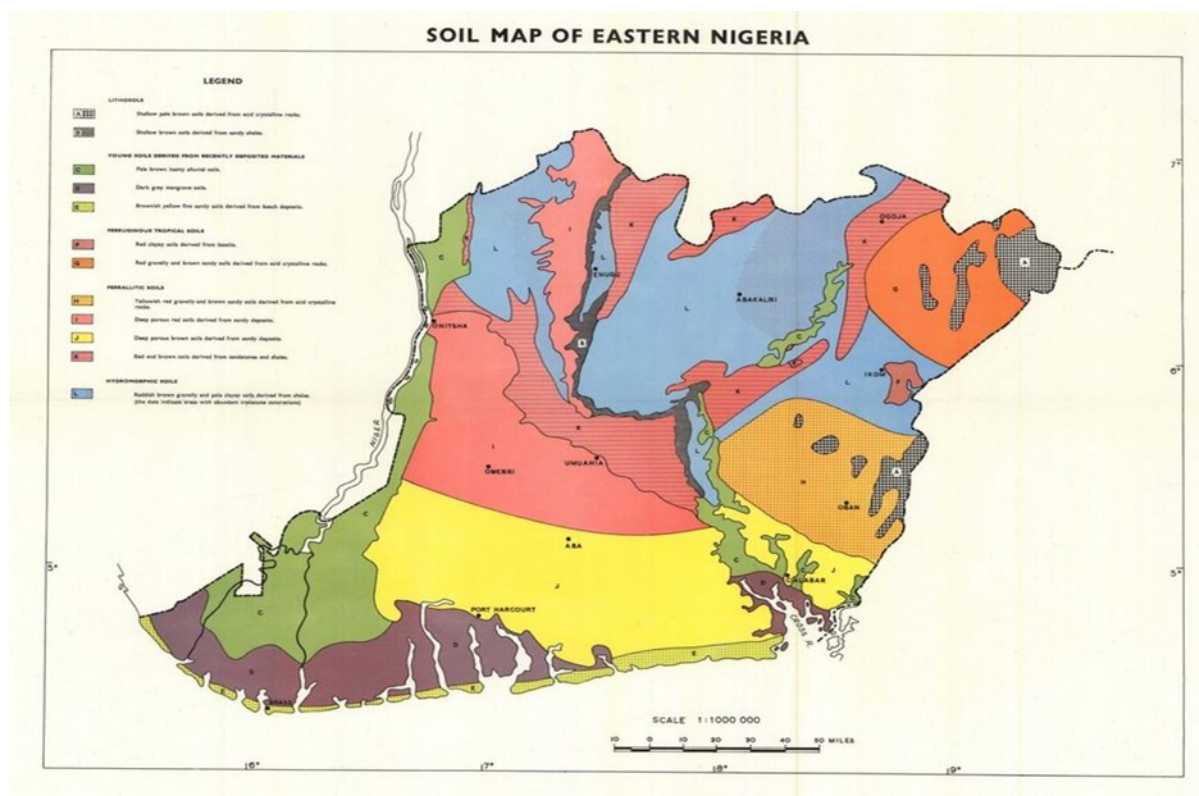


Fig. 1. Map of Southeastern Nigeria showing sample locations.

covers an area of about 37,845km² land mass with 60 per cent of this area covered by the tropical rainforest (Njoku *et al.*, 2006).

The climate is essentially humid Tropical with annual rainfall total not exceeding 3500mm (Njoku, *et al.*, 2006). Air temperature over this area is generally high all year round and changes slightly during the year (Njoku *et al.*, 2006). Current mean maximum temperature of the area is 32°C while the mean minimum is 21°C, and a relatively high mean annual relative humidity, exceeding 75% (Njoku *et al.*, 2006). The underlying geology consist of heterogeneous materials, namely Basement Complex, Beach Sands, Coastal Plain Sand, Mangrove Swamp Deposits, Sandstones, Somberirio Warri Deltaic Deposits, Recent and Sub-recent Alluvium (FDALR, 1990). Vegetation stretches from mangrove swamp in the coast through rainforest to derived savanna in the interior. According to Okorie and Okpala, (2000), the vegetation is essentially secondary forests tending towards derived savannah because of population pressure and repeated annual bush burning.

The chemical characteristics of the soils tend to reflect the nature of the parent materials. Most soils of this area belong to the order “Ultisol” and are classified as typic Hap-ludult (Federal Department of Agriculture and Land Resources, 1985; Nwaogu and Ebeniro, 2009).

Soils types consist of Lithosols found around Oban, Ogoja and some parts of Enugu State, young soils derived from recently deposited materials (Alluvial soil, mangrove and beach deposits) found around Ikwo and Oguta, Brass and Bonny respectively, Ferruginous tropical soils (Basalt) found around Ikom, Ferrallitic soils found around Afikpo and Hydromorphic soils (shale) found around Abakiliki (FDLR, 1990). Soils formed on coastal plain sand and sandstone occupy most of Imo, Abia and Akwa Ibom States, a reasonable part of Rivers, Bayelsa States and a little of Cross River State. These soils are usually acidic, have low CEC, low base saturation and low fertility status (Okunami, 1981). Soils formed on shale are reddish-brown and gravelly. They have high clay content, poorly drained, acidic with high exchangeable cations but are generally fertile

Table 1. Some physical and chemical properties of the soils used for the study

Parent Material	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Texture	pH H ₂ O	pH CaCl ₂	OC (%)	OM (%)	TN (%)	TEB Cmol/kg	TEA Cmol/kg	ECEC cmol/kg	BS %
Basalt	0-20	40.7	26.5	32.8	CL	4.03	5.03	1.90	3.27	0.22	4.70	2.72	7.42	63
	20-40	26.3	20.3	53.4	CL	3.43	4.33	1.27	2.13	0.16	4.18	3.32	7.50	55
	40-60	24.6	16.3	59.3	CL	3.10	4.07	0.90	1.53	0.10	2.41	3.47	5.88	41
CPS	0-20	77.1	10.3	12.6	ScI	3.93	4.90	1.83	3.30	0.13	3.55	2.45	5.67	59
	20-40	72.7	10.1	17.4	ScI	4.20	5.13	1.40	2.30	0.18	4.41	2.42	7.00	64
	40-60	69.6	11.1	19.3	ScI	4.00	5.00	1.10	1.43	0.16	3.19	3.11	6.29	51
Shale	0-20	44.4	19.4	36.2	CL	4.67	5.83	2.50	4.33	0.27	6.83	2.81	9.64	68
	20-40	30.1	16.6	53.3	CL	4.40	5.30	1.53	2.73	0.23	5.30	3.43	8.73	59
	40-60	23.8	14.6	62.2	CL	3.43	4.90	1.13	2.00	0.12	3.74	3.95	8.03	48
Sandstone	0 - 20	56.9	19.2	23.9	ScI	4.10	5.03	1.97	3.40	0.18	5.08	3.03	8.44	60
	20-40	51.0	16.6	32.7	CL	3.63	4.70	1.70	2.97	0.14	4.92	3.31	8.56	57
	40-60	45.4	12.4	42.2	CL	3.50	4.57	1.13	1.97	0.08	4.20	3.43	7.63	54
Mean		46.9	16.1	37.1		3.87	4.90	1.53	2.61	0.17	4.38	3.12	7.57	56
LSD (0.05)														
PM		8.41	4.67	6.56		0.257	0.203	NS	NS	0.04	NS	NS	1.413	NS
DE		7.28	NS	5.68		0.222	0.176	0.34	0.58	0.03	NS	NS	NS	6.1
PM X DE		NS	NS	NS		0.445	0.351	NS	NS	NS	NS	NS	NS	NS

Source: Azu *et al.*, (2018)

Table 2. Mineralogical properties of the soils used for the study

Parent Materi	Depth (cm)	Halloysite	Chlorite	Goethite	Gibbsite	hermatite	Illite	Kaolinite	Mica	Montmorillonite	others	Quartz	Vermiculite,
Basalt	0-20	0.263	0.000	13.94	7.57	11.00	0.00	27.44	0.00	0.00	0.827	42.50	0.513
	20-40	0.00	0.00	24.54	3.82	14.88	0.00	28.08	0.00	0.00	0.290	32.80	0.560
	40-60	0.00	0.383	26.48	10.31	23.14	0.08	14.64	0.00	0.67	0.620	23.70	0.00
CPS	0-20	0.103	0.000	1.41	0.36	0.75	0.00	9.94	0.02	0.00	0.220	87.30	0.000
	20-40	0.000	0.000	2.84	1.33	2.56	0.00	19.83	0.00	0.00	0.513	72.60	0.000
	40-60	0.00	0.00	8.81	1.23	3.46	0.00	28.83	0.40	0.00	0.907	56.40	0.000
Shale	0-20	0.017	0.050	23.58	9.62	20.39	0.68	6.89	0.377	14.37	1.137	22.50	0.523
	20-40	0.027	0.047	24.43	12.10	21.65	0.92	5.09	0.290	20.09	0.537	13.40	1.283
	40-60	0.337	0.483	25.09	8.48	24.19	1.26	3.56	0.000	21.88	0.053	8.20	0.627
Sandstone	0-20	0.210	0.000	7.77	1.70	4.58	0.31	31.26	0.557	0.00	1.267	51.80	0.600
	20-40	0.000	0.307	12.12	3.66	10.57	0.16	30.63	0.683	0.00	0.357	38.70	1.793
			0.867	14.87	5.23	14.62	0.13	26.42	0.643	0.16	0.227	35.40	1.017
Grand Mean		0.071	0.178	15.49	5.42	12.65	0.29	18.97	0.248	4.76	0.579	40.50	0.576
LSD (0.05)													
PM		NS	NS	3.614	2.303	2.993	0.734	3.828	0.431	1.775	NS	6.00	0.529
DE		NS	0.328	3.129	NS	2.592	NS	NS	NS	1.537	NS	5.20	NS
PM X DE		NS	NS	NS	3.900	NS	NS	6.630	NS	3.074	NS	NS	NS

Source: Azu *et al.*, (2018)

2.2 Soil sampling

Thirty six soil samples representative of twelve (12) locations of contrasting parent materials comprising of Abakiliki, Afikpo and Bende (Shale), Ikom, Etung and Nssuka (Basalt), Umudike, Ikot-Ekpene and Aba (Coastal plain sand) and Amaeke, Ohafia and Okigwe (Sandstone), at three depths (0-20cm, 20-40cm and 40-60cm) were collected using soil auger.

2.3 Phosphorus sorption kinetic study

2.1g of soil was weighed into a 125ml Erlenmeyer flask and horizontally shaken with 25ml of 0.01M CaCl_2 solution containing 60mgL^{-1} of P in the form of KH_2PO_4 . Two drops of Toluene were added to suppress biological activity.

The flasks were shaken for different time intervals (5, 30, 60, 90, 120, 1320, 1350, 1380, 1410 and 1440 minutes). At the end of each equilibrating period, aliquot of 2ml from the supernatant solution was taken, filtered and the final P concentration in the equilibrium solution determined according to Murphy and Riley (1962) as described by Udo *et al.*, (2009). The amount of P adsorbed in each soil at each time interval was calculated by the difference between the P concentration in the equilibrium solution at the beginning and ending of the shaking period as shown in Equation 1:

$$q_e = \frac{(c_0 - c) \cdot v}{m} \quad (1)$$

where q_e is the amount of phosphorus sorbed in mg/g, c_0 is the initial P concentration and c is the measured P concentration at the specified time, with both concentration being in mg/L. V is the volume of P solution in liters and m is the mass of soil used in kg.

Phosphorus Sorption Kinetic Modelling.

A first-order model was used to model the kinetics of P sorption using the following equation (Eljamal *et al.*, 2013).

$$\frac{dq}{dt} = k_i (q_e - q) \quad (2)$$

where k_i is the rate constant of pseudo first-order sorption (min^{-1}), q is the amount of P sorbed at time t in mg/g, q_e is the amount of sorption at equilibrium in mg/g, and t is the contact time in minutes. After integration of Equation 2 for the boundary conditions $q = 0$ at $t = 0$ and $q = q_e$ at $t = t$,

Equation 2 becomes;

$$q = q_e (1 - e^{-k_i t}) \quad (3)$$

Equation 3 was fitted to the average sorption data using a minimization of least square fitting procedure. The minimization was performed using the solver function of Microsoft Excel and varying the q_e and k_i parameters. Statistical analysis of variance was performed using SPSS to determine if either the extent of P sorption or the amount of sorption at any measured times were statistically different among the various soils of contrasting parent materials and at different depths.

3.0 Result and discussion

3.1 Effects of time on equilibrium concentration

The equilibrium phosphorus concentration is the point at which the rate of P sorption is equal to the rate of desorption, and it will appear that the soil is unable to sorb more P. This value provides the maximum extent to which soil can accumulate P at a certain solution concentration (Regan and Anderson, 2013). Figures 1-13 show the amount of P sorbed by the different soil of contrasting parent materials and depths over a period of 1444 minutes. The results indicated that even though the soils varied in their sorption characteristics, the extent of phosphorus sorption did not differ significantly ($P < 0.05$) between the various soils with respect to parent material and depth, but the rate at which sorption occurred differed significantly ($P < 0.05$) among the various soils with respect to parent material and depth. The sorption isotherms of the investigated soils showed that the rate of P sorption increased with an increase in incubation time, but at a certain point, the sorption of P became almost constant as the maximum sorption capacity was reached and the typical shapes of these reactions are illustrated in Figures 1-13. The graphs showed that samples rapidly sorbed P during the first few minutes (5-120 minutes) of contact time for all soils irrespective of parent material and depth and slowed down in subsequent minutes when equilibrium was reached, as widely reported in the literature (Santos *et al.*, 2011; Karaca *et al.*, 2004; Cheung and Venkitachalan, 2006; Wang *et al.*, 2009; and Regan and Anderson, 2013). According to Cheung and Venkitachalan (2006), the decrease in P sorption rate over time suggest that factors such as the penetration of P into the pores of soil micro aggregates and the P saturation of the adsorbent surface hamper P sorption for each increment of soil P application.

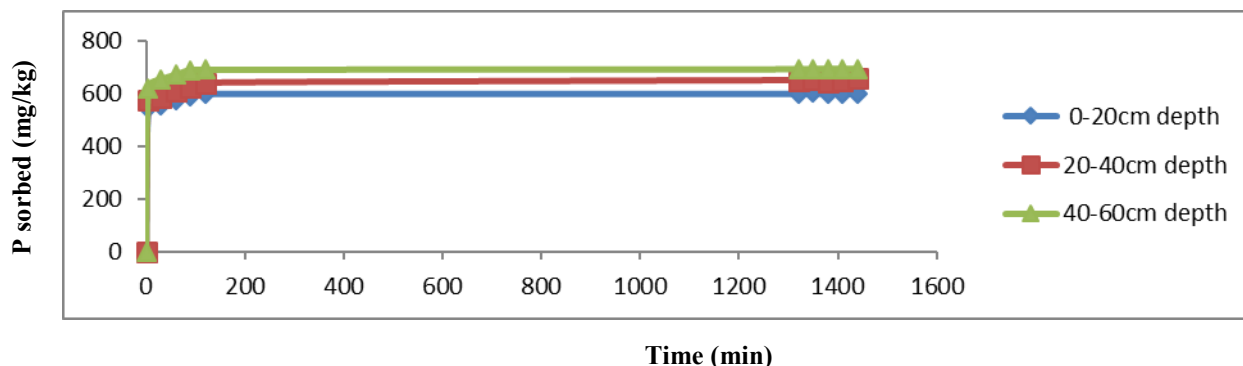


Fig 2. P sorbed against equilibrium time at different depths for soil of Aba

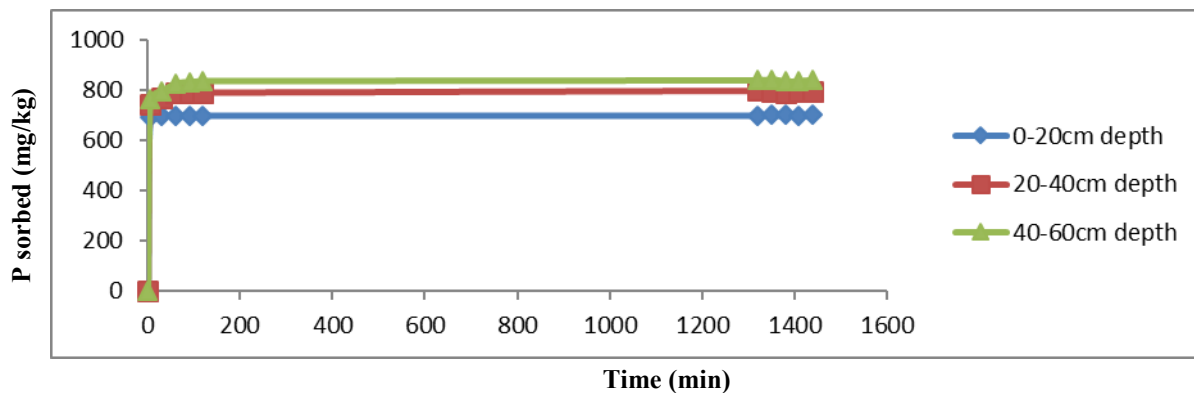


Fig 3. P sorbed against equilibrium time at different depths for soil of Abakaliki

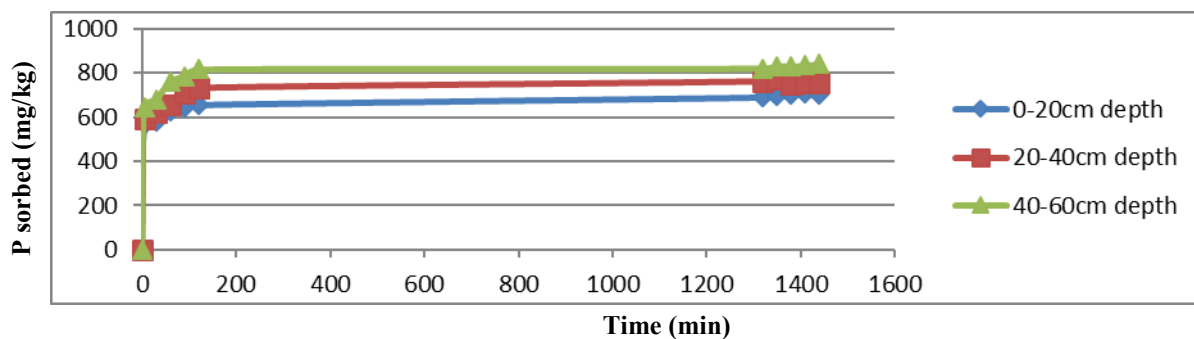


Fig 4. P sorbed against equilibrium time at different depths for soil of Amaeke

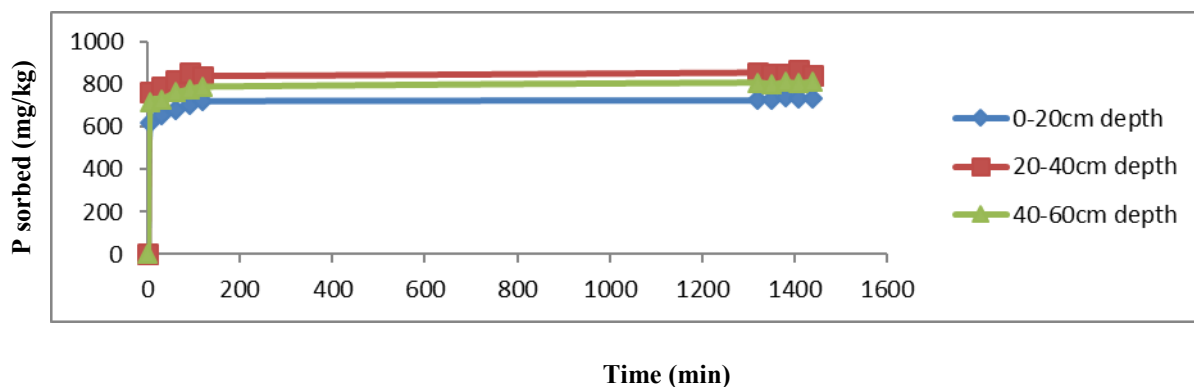


Fig 5. P sorbed against equilibrium time at different depths for soil of Bende

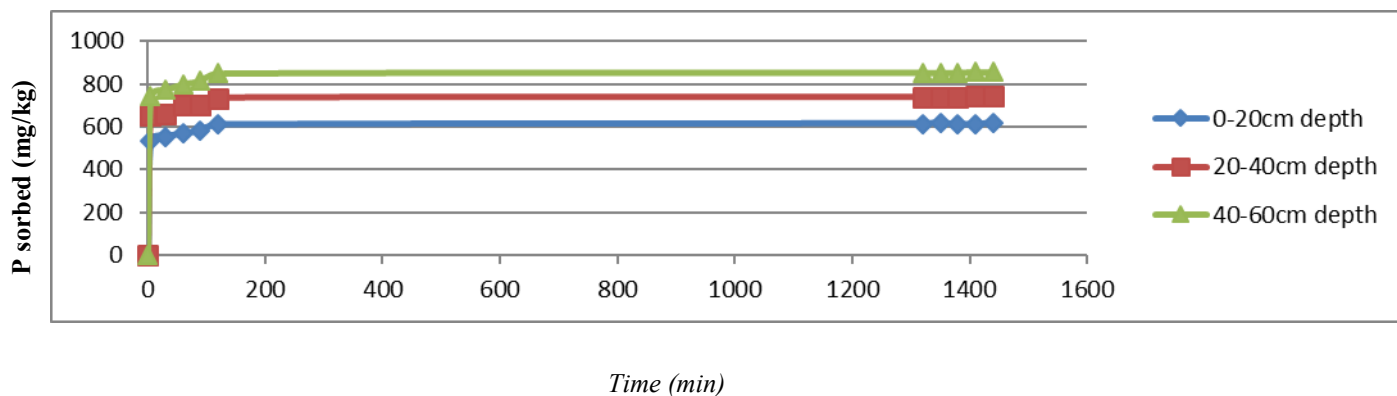


Fig 6. P sorbed against equilibrium time at different depths for soil of Etung.

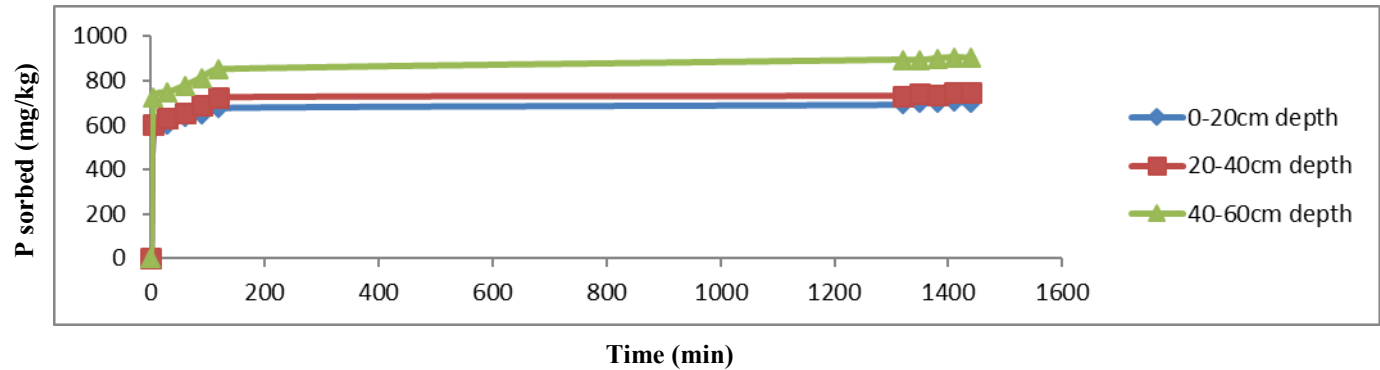


Fig 7. P sorbed against equilibrium time at different depths for soil of Ikom.

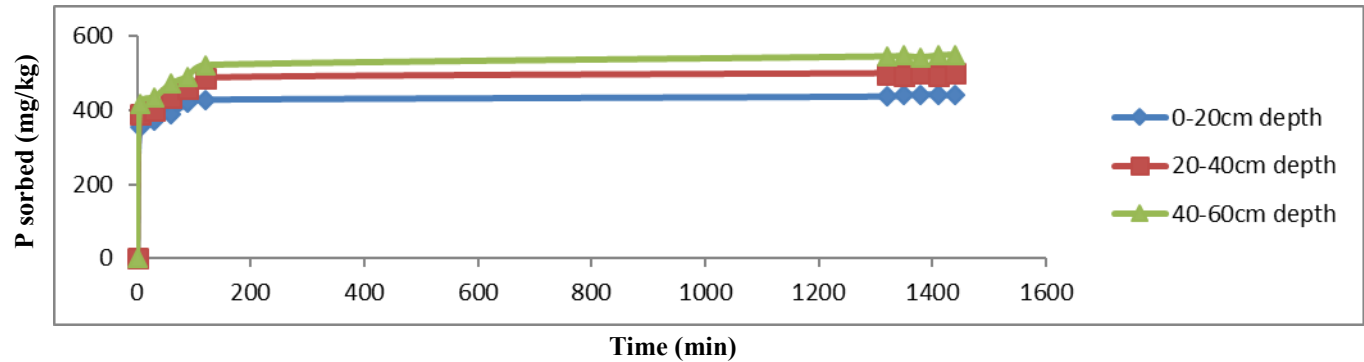


Fig 8. P sorbed against equilibrium time at different depths for soil of Ikot-Ekpene.

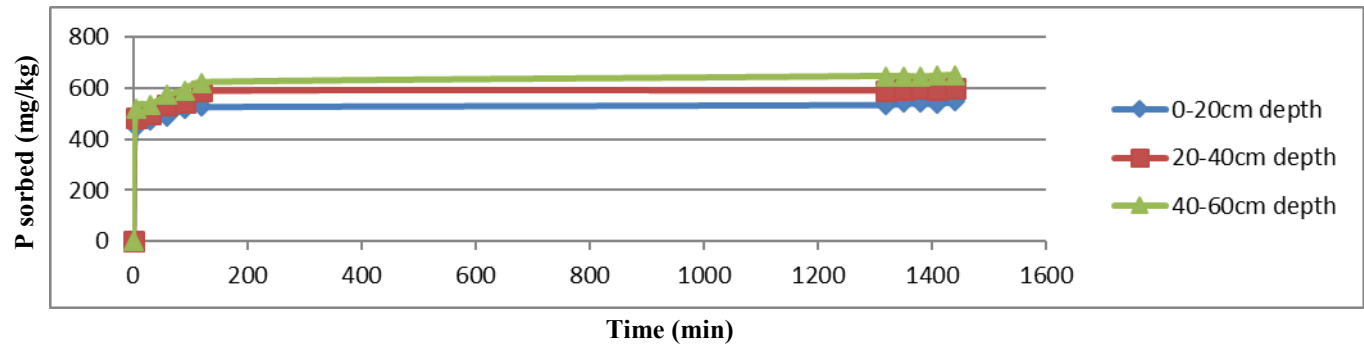


Fig 9: P sorbed against equilibrium time at different depths for soil of Ohafia.

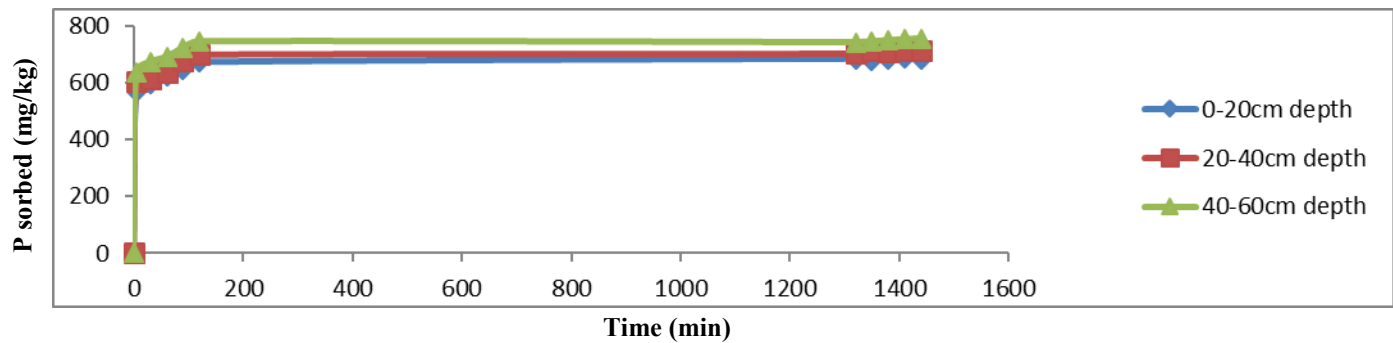


Fig 10 P sorbed against equilibrium time at different depths for soil of Okigwe.

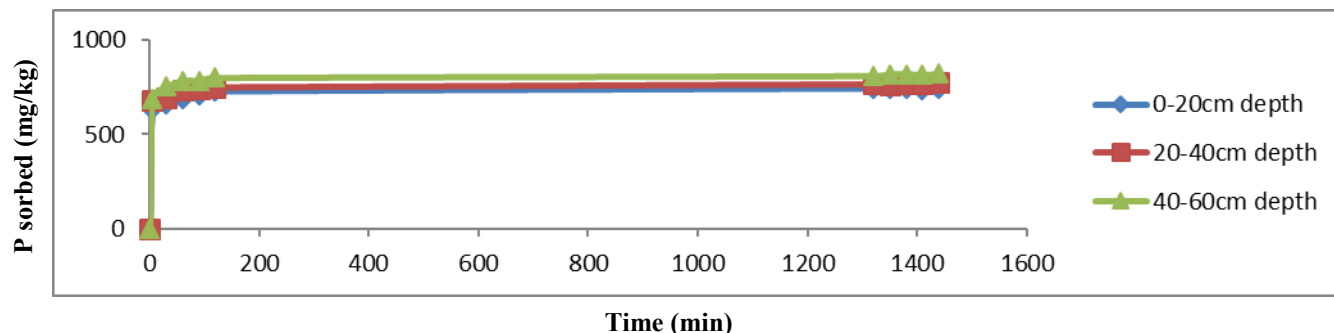


Fig 11. P sorbed against equilibrium time at different depths for soil of Nsukka.

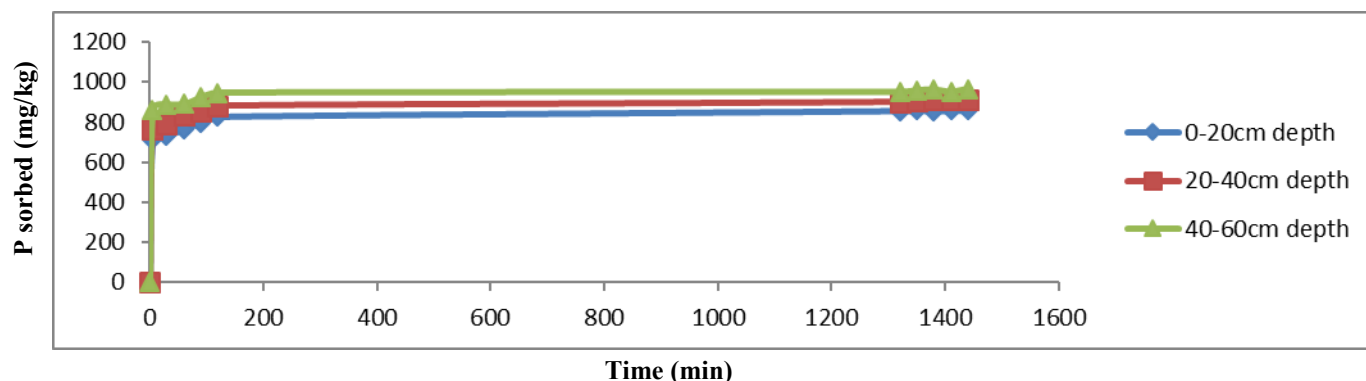


Fig 12 P sorbed against equilibrium time at different depths for soil of Afikpo

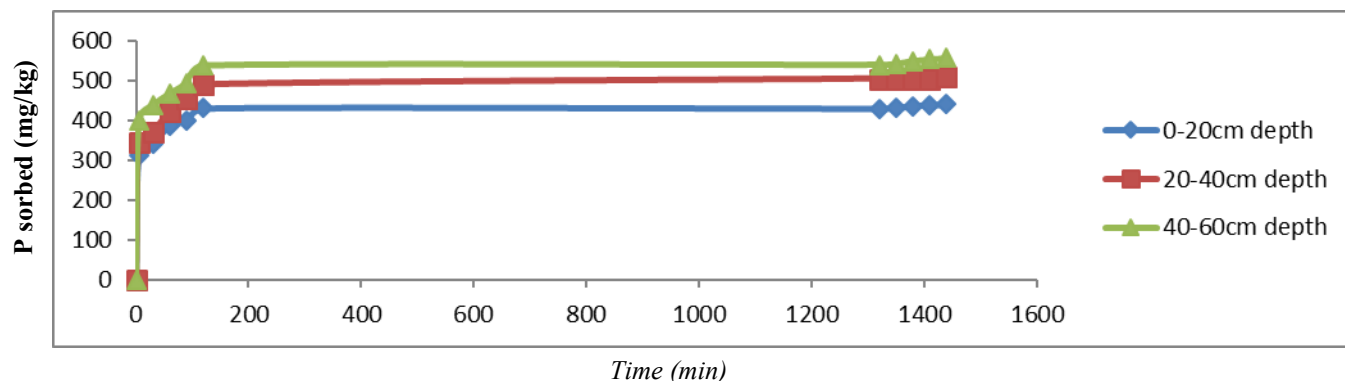


Fig 13. P sorbed against equilibrium time at different depths for soil of Umudike

3.2 Effect of parent materials and depth on P kinetics

Table 4 shows the rate constants and amount of sorption at equilibrium for soils of contrasting parent materials at three soil depths. Results showed that the rate of P sorption varied widely in soils of different parent materials and depth. The parent material and soil depth as lone factors showed significant ($P < 0.05$) effect on the rate constant (k_i), but their interaction had no significant effect. The rate constant (k_i) varied from $1.08 \text{ (m}^{-1}\text{)}$ in soil of coastal plain sand to $5.05 \text{ (m}^{-1}\text{)}$ in soil of shale formation.

The mean values of the rate constant (k_i) with regards to specific parent material showed that soils formed from shale had the highest values as against soils formed from coastal plain sand which had the least values.

The means of the rate constant (k_i) occurred in the following order shale (5.05 m^{-1}) > basalt (4.47 m^{-1}) > sandstone (3.55 m^{-1}) > coastal plain sand (1.07 m^{-1}). It can be seen that soils from shale and basalt exhibited a more expedient sorption of P than soil samples from sandstone and coastal plain sand. This tendency was confirmed in an assessment

of the rate constant (k_i) values, which is the reaction rate at constant concentration. The lowest and highest rate constant (k_i) values as observed in this study were found in soils from coastal plain sand and shale respectively.

When the rate of P sorption was compared based on soil depth, it was observed that top soil horizons had lower values of rate constant (k_i), indicating that the rate of P sorption is inversely related to soil depth. The values of rate constant (k_i) for top soils (0-20 cm) ranged from 0.74 m^{-1} to 4.62 m^{-1} , middle layer (20-40cm), 1.02 m^{-1} to 5.59 m^{-1} and the lowest depth (40-20cm) had values ranging from 1.47 m^{-1} to 5.38 m^{-1} indicating that sorption rates increased with increasing depth of soil development as reported by Slazak and Freese (2014). The soil depth significantly ($P < 0.05$) influenced the rate constant (k_i). The implications of the variability of the rate constant (k_i) values with respect to soil types and depth, is that, while the concentration of P in solution at a given time is similar among different soils, differences in concentrations can appear as time goes by because the rate of reaction not only depends on the concentration of P in solution, but also on the clay sesquioxide content and soil pH (Regan

and Andersen, 2013).

While the isotherm approach to recommending P fertilizer has proved to be correlated well with plant performance in

the season during which the application of the fertilizer is made, differences in P kinetics between soils could mean that the availability of the fertilizer residues to plants in the following season of the application differs

Table 4. Variables used in modeling P sorption kinetics with a pseudo first-Order model. Parameters include the rate constant and sorption capacity

Parent Material	Depth (cm)	Rate Constant (ki) (m ¹)	Amount of sorption at equilibrium (mg P/kg Soil)
Basalt	0 - 20		
	20 - 40		
	40 - 60		
Mean		4.67	706.10
CPS	0 - 20	0.74	683.50
	20 - 40	1.02	777.60
	40 - 60	1.47	690.50
Mean		1.08	717.20
Shale	0 - 20	4.62	702.10
	20 - 40	5.59	707.00
	40 - 60	4.94	711.20
Mean		4.67	706.10
Sandstone	0 - 20	2.51	691.20
	20 - 40	3.73	697.90
	40 - 60	4.42	704.80
Mean		3.55	706.10
Ground mean		3.58	698.00
LSD (0.05) PM		0.687	NS
LSD (0.05) DEPTH		0.595	NS
LSD (0.05) PM X DEPTH		NS	NS

This in turn means that, over time, differences in crop responses could occur between soils of different kinetics characteristics although they have in principle been fertilized to achieve the same level of P concentration in solution (Henry and Smith, 2004).

Based on the above principle, it can be deduced that soils with high values of Ki absorb P rapidly from soil solution than those with low Ki values and therefore have better capacity to accumulate labile P in soils, even though, they may require more frequent P fertilizer application than those with very low Ki values. On the other hand, soils

with low Ki values though may have more P concentration in solution depending on the texture, may be confronted with the problem of P loss through leaching and run-off.

The rate constant (Ki) and the amount of P sorbed at equilibrium concentration were correlated with some soil properties and the results showed that Ki correlated significantly but negatively with organic carbon and percent sand ($r = -0.510^{**}$ and -0.798^{**}), but positively with clay ($r = 0.798^{**}$) indicating the influence of these properties on rate of P sorption (Table 4.9).

Table 5. Coefficients of Simple Linear Correlation between Soil Properties and Variables used in Modeling P Sorption Kinetics with a 1st order Model

	pH	Org. C	ECEC	TEA	SAND	SILT
CLAY						
ASE	-0.194	-0.489**	0.183	0.548	-0.904*	0.305
Ki	-0.114	-0.510 ⁸⁸	0.129	0.328	-0.798**	0.282

Ki is rate constant, ASE is amount of P sorption at equilibrium (mg/kg), and TEA is total exchangeable acidity.

This corresponds to the report of Santos *et al.*, (2011) who found similar relationships in some tropical soils. The rate constant (Ki) also correlated positively with ECEC, TEA and silt, but these correlations were not significant. Similarly, the amount of P sorbed at equilibrium (ASE) correlated significantly and negatively with organic carbon and sand ($r = -0.486^{**}$, -0.904^{*} respectively), but positively with clay. These soil properties may reflect P sorption rate in the soil and therefore can be used as P sorption indices.

When values from this study was compared, it was observed that soils with higher clay content had higher values of Ki than other soils as observed in their correlations and the order of the amount of Ki in relation to soil types is basalt > shale > sandstone > coastal plain sand.

4.0 Conclusion

Phosphate adsorption kinetics is an important soil chemical process that determines the rate of phosphorus removal from soil solution. This study revealed that most soils of southeastern Nigeria have high rate of P adsorption and thus low P availability to crops. Values of rate constant shows that soils of shale and basalt removes P rapidly than soils of coastal plain sand and sandstone formations. Reducing that rate of P adsorption through liming, organic manure application and saturation of P sorption sites through continuous external P fertilizer application is recommended.

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