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Predicting Phosphorus Sorption Characteristics in Highly Weathered Soils of South-Eastern Nigeria

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Abstract: This study investigated Phosphorus (P) sorption characteristics of 60 soil samples formed over 6 different parent materials in south-eastern Nigeria relating that to some soil properties. Soils were analyzed for pH, clay, Bulk Density (BD), Organic Carbon (OC), Mehlich-3 extractable calcium (Ca_{M3}) ammonium oxalate and Mehlich-3 extractable P, aluminium (Al) and iron (Fe). The oxalate and Mehlich-3 extractable elements were used in estimating Phosphorus Saturation Index (PSI). There were significant relationships between P saturation indices and soil attributes in the study site at $p \leq 0.01$ and $p \leq 0.05$. However, these correlations were least in shale-derived soils due to high content of Ca_{M3}. A P-sorption capacity model resulted from a multiple regression analysis using soil attributes as independent variables. The model showed high predictive ability ($r^2 = 0.77$; RMSE = 3.70) with little underestimation (bias = -0.09).

Key words: Desorbability, modelling, phosphorus saturation, south-eastern Nigeria, sustainable agriculture, ultisols

INTRODUCTION

Phosphorus (P) is a critical element in natural and agricultural ecosystems throughout the world. It is a key component of cellular compounds and vital to both plant and animal life. It is next to nitrogen considering its importance for profitable yields (Brady and Weil, 1999). Although P is considered to be relatively immobile in the soil system (Johnson *et al*., 1997), there are mechanisms through which it can leave the soil through plant uptake, loss in surface runoff, erosion of sediment and leaching through the soil (2005). Application of P-fertilizers in excess of crop requirement leads to its build-up in soils and increases the chances of P-loss from the soil system (Sharpley *et al*., 1999) and its entry into the runoff is a primary source of non-point soil pollution (Daniel *et al*., 1994) and eutrophication of water bodies (Sharpley *et al*., 1999).

The degree to which P becomes available in soils is governed by one or a combination of chemical and mineralogical properties, such as clay type content, iron and aluminium oxides, organic carbon, pH and calcium carbonate content (Burt *et al*., 2002). Significant correlations have been reported between soil P adsorption and soil pH (Brennan *et al*., 1994; Dodor and Oya, 2000; Khare *et al*., 2004), organic carbon (Dodor and Oya, 2000), aluminium and iron oxide content (Sanyal *et al*., 1993; Borling *et al*., 2001). The presence of organic matter reduces the phosphate sorption capacity of highly weathered tropical soils such as oxisols and ultisols possibly due to direct result of competition for sorption sites between phosphate and organic ligands (Gillman *et al*., 1989). But these tropical soils have suffered drastic reductions in soil organic matter due to soil erosion and inappropriate land uses (Mbagwu, 1992; Lal, 1995; Styczen, 1992) thereby making P-predictions inconsistent in most tropical soils (Oti, 2002).

Most soil properties used in predicting soil P are interrelated and this makes it difficult to identify the principal components contributing to P-availability in soils. Several studies used path analysis (Cramer and Wehner, 2000; Zheng *et al*., 2002; Garcia del Moral *et al*., 2003) and multiple regressions to evaluate the effect of different combinations of soil properties on P adsorption (Brennan *et al*., 1994; Dodor and Oya, 2000; Borling *et al*., 2001). The major objective of this study was to ascertain sorption characteristics in highly weathered, soils of south-eastern Nigeria and relating components of the prediction to P-sorption capacity.

MATERIALS AND METHODS

Site

The lowland states of south-eastern Nigeria, namely Abia and Imo States lying between latitudes 4°40^1 and 8°15^{1}N and longitudes 6°40^1 and 8°15^1 E (Federal Department of Agricultural Land resources, 1985) were chosen for the study. The parent materials underlying soils of the study area are Alluvium, Coastal Plain Sands, Shale, Lower Coal Measures, Upper Coal Measures and Falsebedded Sandstones (Ofomata, 1987). The site belongs to the humid tropics and its climate and vegetation pattern have been reported by Igwe and Stahr (2004). Pedogenic characterization of soils of the area has been done using 30 pedons and soil classes identified include Typic Udipsamments (Dystric Fluvisols), Arenic Paleudults/Typic Paleudults (Dystric Nitisols), Arenic Rhodic Paleudults (Dystric Acrisols), Dystrustepts/Typic Paleustults (Dystric Cambisols), Vertic Paleudults (Vertic Nitisols) and Typic Paleustults (Plinthic Nitisols) (Onweremadu, 2006). These classifications were done using Soil Taxonomy (Soil Survey Staff, 2003) and correlated with FAO/UNESCO legend, (FAO, 1998) implying that these are highly weathered soils. Farming is a major socio-economic activity in the area.

Field Sampling

Sixty soil samples were collected representing the diversity of soils of the study area under 4 years of fallow. Ten soil samples were collected over each of the 6 main parent materials of the study site. The soils were sampled from plow layer (0-20 cm) air-dried and sieved to pass a 2 mm mesh sieve.

Laboratory Determinations

Soil pH was measured in 1: 2.5 suspension of soil in 0.1 M KCl (Hendershot *et al*., 1993). Total C (g kg^{-1}) was measured by combustion with an Elementar CNS analyzer (Elementar America, Inc. Mt. Laurel, N.J) according to the methods described by Nelson and Sommers (1996). Percent clay content was determined by Bouyoucos hydrometer method (Gee and Or, 2002). Bulk density was estimated by core method of Grossman and Reinsch (2002).

Phosphorous adsorption isotherm was estimated according to the method of Graetz and Nair (2000). A gram of soil sample was equilibrated with 25 mL of varying concentrations of P in 0.01 $CaCl_2$ solution in 50 mL centrifuge tubes. The following concentrations of the solutions were used: 0.0, 0.5, 1.0, 10.00, 15.0 and 20.0 mg P l^{-1}.

The centrifuge tubes were shaken for 1 day on an end-to-end shaker at 150 oscillations per minute. The samples were centrifuged for 10 min at 5211 x g and the supernatant was decanted. Quantification of P in solution was done colourimetrically according to the procedures of the ascorbic acid method (Kuo, 1996). Phosphorous adsorbed was measured as the difference between initial and final amounts of P in solution. All these analyses were duplicated on all studied soils.

Extractable P, Aluminium (Al) and iron (Fe) were determined by shaking duplicate 1.5 g samples of soils with 30 mL of 0.5 M acidified ammonium oxalate $(COONH_4)_2$. H_2O at pH 3.0 in 50 mL centrifuge tubes (Schoumans, 2000). Later samples were shaken for 120 min in the dark on an end-to-end shaker at 150 oscillations per minute and centrifuged for 10 min at 5211 x g. Resulting supernatants were analyzed for P, Al and Fe using a TJA-9000 inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Again extractable P, Al and Fe were estimated by shaking duplicate 2 g samples of soil and 20 mL Mehlich-3 solution (M3) in 50 mL centrifuge tubes for 10 min on an end-to-end shaker at 150 oscillations per minute. Then, samples were centrifuged at 5211 x g and supernatants analyzed by ICP-AES.

Computations

Phosphorus Saturation Index (PSI) was calculated based on ammonium oxalate extraction (Schoumans, 2000). It is given by the formula:

$$\mathrm{PSI}_{\mathrm{M3}} = \frac{\mathrm{P}_{\mathrm{OX}}}{\mathrm{AI}_{\mathrm{OX}}+\mathrm{Fe}_{\mathrm{OX}}} \text{....1}$$

Where PSI_{ox} = P saturation index (oxalate)

P_{ox}, Al_{ox} and Fe_{ox} = oxalate extractable P, Al and Fe, respectively

Phosphorous saturation index was also computed using Mehlich-3 extractions of P, Al and Fe (Kleinman and Sharpley, 2002). This is given as follows:

$$\frac{\mathrm{P}_{\mathrm{M3}}}{\mathrm{AI}_{\mathrm{M3}}+\mathrm{Fe}_{\mathrm{M3}}} \text{....2}$$

Where $\mathrm{PSI}_{\mathrm{M3}}$ = P saturation index (Mehlich-3)

P_{M3}, $\mathrm{Al}_{\mathrm{M3}}$ and $\mathrm{Fe}_{\mathrm{M3}}$ = Mehlich-3 extractable P, Al and Fe, respectively

Data Analyses

Soil data were subjected to correlation and multiple regression analyses using SAS computer package (SAS, 2000). Root Mean Square Error (RMSE) was used to evaluate average prediction uncertainly of the model while bias of the model was used to assess overestimation or underestimation (Moldrup *et al*., 2004).

RESULTS AND DISCUSSION

Soil Properties

Clay content ranged from 60-400 g kg^{-1} indicating variability in the genesis of soils. Sandier parent materials such as Upper Coal Measures, Alluvium and Coastal Plain Sands gave rise to less clayey soils. Soils were moderately to strongly acidic (4.2-5.8) which could be attributed to the combined influence of parent materials and climate on pedogenesis. Shale-derived soils in the study area have intercalations of limestones which are inherently alkaline.

However, heavy rainfall and the attendant leaching may have washed away basic cations from the pedon thereby making soils acidic. Ranged after bulk density from 1.31 to 1.44 M gm^{-3} in response to differential distribution of organic carbon among soil groups (Table 1).

Phosphorous Sorption Characteristics

Phosphorous extracted by acidified ammonium oxalate (P_{ox}) ranged from 51.0 to 151.0 mg kg^{-1} soil with a median value of 120 mg kg^{-1} while Al_{ox} and Fe_{ox} varied from 191.0 to 951.0 and 221.0 to 2201.0 mg kg^{-1} soils, respectively. Phosphorus saturation index using ammonium oxalate extractant varied from 4.0 to 31.0%. Mehlch-3 extraction showed variation in distribution and as follows: P_{M3} (13-70 mg kg^{-1}), $\mathrm{Al}_{\mathrm{M3}}$ (191-661 mg kg^{-1}), $\mathrm{Fe}_{\mathrm{M3}}$ (28-341 mg kg^{-1}) and $\mathrm{PSl}_{\mathrm{M3}}$ (1.9-240%). These distributions were considered irrespective of soil group (Table 2).

Table 1: Selected properties of soils studied (mean values of soil groups)

Soil group	Clay (g kg^{-1})	BD (mg m^{-3})	pH	OC (g kg^{-1})	Ca (mg kg^{-1})
Alluvium	80	1.38	4.5	16	96.1
Coastal plain sands	90	1.41	4.3	14	91.8
Shale	400	1.34	5.8	20	525.3
Lower coal measures	280	1.31	5.3	26	387.2
Upper coal measures	60	1.44	4.2	10	88.6
Falsebedded sandstones	140	1.35	4.8	18	184.7

PM = Parent Material, BD = Bulk Density, OC = Organic Carbon, a = soil group represents all soils collected over the same parent material

Table 2: Phosphorus sorption characteristics of soils studied (mean values of soil groups)

	Acidified ammonium oxalate				Mehlich-3				
Soil group	P_{ox}	Al_{ox} (mg kg^{-1})	Fe_{ox}	Psl_{ox} (%)	P_{M3}	Al_{M3} (mg kg^{-1})	Fe_{M3}	Psl_{M3} (%)	Psat (%)
Alluvium	73	420	580	9.10	20	410	85	3.8	7.0
Coastal Plain sands	69	291	671	9.7	32	281	341	6.1	28.0
Shale	151	951	221	12.0	13	361	28	2.9	7.0
Lower coal Measures	121	191	281	31.0	70	191	131	24.0	75.0
Upper coal Measures	51	271	241	12.0	25	351	70	5.6	40.0
Falsebedded Sandstones	91	901	220	4.0	17	661	131	1.9	75.0
Mean	92.6	504.1	699.1	12.9	29.5	168.6	131	7.4	38.6
Median	82.0	355.5	430.5	10.8	22.5	506.0	108	4.7	34.0
Minimum	51.0	191.0	221.0	4.0	13.0	191.0	28	1.9	7.0
Maximum	151.0	951.0	2201.0	31.0	70.0	661.0	342	24.0	75.0

Phosphorus saturation (Psat) in the study site ranged from 7 to 75%. High Psat values indicate that soils derived from Lower Coal Measures and Falsebedded Sandstones are greatly filled with P when compared with other soil groups. Phosphorus saturation is a measure of potential desorbability of soil P (Beauchemim and Simard, 1999). Phosphorus desorption correlates highly with P saturation (Sibbesen and Sharpley, 1997) stating that P description increases with higher degrees of P saturation. The environmental implication of this in the study site is that more P is available for runoff and consequent non-point pollution and eutrophication in soils formed over Lower Coal Measures, Falsebedded Sandstones and Upper Coal Measures.

Table 3 shows the degree of relationship between Psat and some soil properties, indicating a varying influence of soil properties on Degree of P Saturation (DPS). In these tropical soils, organic carbon and clay exhibited profound relationships with Psat having $r = -0.90$ and $r = +0.82$, respectively. Similar findings were made by Dodor and Oya (2000). The presence of organic matter reduces the phosphate sorption capacity of oxisols and ultisols (Gillman *et al*., 1989). This could be the direct result of competition for sorption sites between phosphates and organic ligands. Organic matter (organic carbon) reduces positive charge on variable charge surfaces by lowering pHo (pH value at which the net charge due to variable charge components is zero) thus decreasing attraction of phosphates to the soil surface. The influence of organic matter on cation exchange capacity is not as pronounced in ultisols as in oxisols, as it has little effect on pHo.

There was significant negative correlation between Ca and Psat ($r = -0.46$), showing that competition exists between them and other polyvalent cations and anions. Giesler *et al.* (2005) reported that competition between phosphate and other anions may affect P sorption capacity thereby confirming the works of Shang *et al.* (1990) and Celi *et al.* (2003) that organophosphorus compounds, such as inositol phosphates. Again, ionic strength influences nature of competition. Previous studies

Table 3: Correlation coefficients between P saturation (Psat) with selected soil properties (n = 60)

Factors correlated	Correlation coefficient (r)	Level of significance
Psat vs pH	-0.66	**
Psat vs Ca	-0.46	*
Psat vs OC	-0.90	**
Psat vs BD	+0.51	*
Psat vs clay	+0.82	**

vs = Versus, ** Significant at $p<0.01$, * Significant at $p<0.05$

Table 4: Correlation coefficients between phosphorus saturation indices (n = 60)

Factors correlated	Correlation coefficient (r)	Level of significance
Psat vs PSI_{ox}	0.82	**
Psat vs PSI_{M3}	0.89	**
P_{M3} vs PSI_{ox}	0.84	*
P_{ox} vs PSI_{ox}	0.79	**
Al_{ox} vs PSI_{ox}	0.82	**
Fe_{ox} vs PSI_{ox}	0.87	**
Al_{M3} vs PSI_{ox}	0.85	**
Fe_{M3} vs PSI_{ox}	0.84	**

vs = Versus, ** Significant at $p\leq 0.01$, * Significant at $p\leq 0.05$

(Beck *et al*., 1999; Arbestain *et al*., 2002) have shown that phosphate can displace Dissolved Organic Carbon (DOC) from sorption sites. Decrease in ionic strength decreases DOC concentration (Kalbitz *et al*., 2000) which is explained by a reduction in divalent cations, such as Ca^{2+} thereby increasing phosphate sorption. Highly weathered soils of the humid tropics have modest amounts of Ca, Mg and K hence characterized by high P sorption capacity.

Relationships Among Psat Indices

Table 4 shows the degree of correlation between Psat indices in the study site. Phosphorus saturation using acidified ammonium oxalate was highly correlated ($r = 0.89$; $\geq$ 0.01) with PSl_{M3} for all 60 soil samples from the study site. These results are consistent with the reports of Maguire and Sims (2002). The same trend was observed between Psat and PSl_{ox} ($r = 0.82$; $p\leq 0.01$). Again, P sorption characteristics had significant positive correlations in the study area. However, correlation coefficients between P saturation indices varied among soil groups (Table 5). Least correlation values were recorded on soils derived from Shale and Low Coal Measures. These soil groups contained higher values of Ca extracted with M3, having 525.3 and 387.2 mg kg^{-1}, respectively, suggesting that soils contained greater concentrations of carbonates which may have interfered with Mehlich-3 and oxalate extractions of Al and Fe. Soils derived from Alluvium, Coastal Plain Sands and Upper Coal Measures are highly weathered based on low silt-clay ratios reported by Onweremadu (2006).

These highly weathered soils are generally subjected to harsh climate to produce clay fractions consisting of low activity minerals such as kaolinite, Al and Fe oxides (Gillman *et al*., 1989). These Al and Fe form surface sites where organophosphates sorb (Cali *et al*., 2003; Giesler *et al*., 2005).

Modelling

Step-wise multiple regression analysis using soil pH, OC, Al_{ox}, Fe_{ox}, clay and B.D. were used to attempt modelling of P sorption capacity in these tropical soils (Table 6). With fairly low coefficient of alienation ($1-R^2 = 0.23$), high prediction certainty was achieved (RMSE = 3.70) with little underestimation (bias = -0.09). Because the soils of the study site have an abundance of Fe and Al (Igwe *et al*., 2005) which affect solubility of phosphorus (Giesler *et al*., 2005) this model becomes relevant in estimating P availability to plants and micro-organisms (Giesler, 2002) and ground water discharge rate (Pellerin, 2002) and possible transfer of P from terrestrial to aquatic ecosystem (Lyons *et al*., 1998).

Table 5: Correlation coefficients between phosphorus saturation indices among soil groups (n = 10)

Factors correlated	Correlation coefficient (r)	Level of significance
Alluvium		
Psat vs PSl_{ox}	0.83	**
Psat vs PSI_{M3}	0.80	**
P_{ox} vs PSI_{M3}	0.79	*
Al_{M3} vs PSI_{ox}	0.81	**
Fe_{M3} vs PSI_{ox}	0.82	*
Coastal plain sands		
Psat vs PSI_{ox}	0.85	**
Psat vs PSI_{M3}	0.86	**
P_{ox} vs PSI_{M3}	0.77	**
Al_{M3} vs PSI_{ox}	0.84	**
Fe_{M3} vs PSI_{ox}	0.85	**
Shale		
Psat vs PSI_{ox}	0.62	*
Psat vs PSI_{M3}	0.48	*
P_{ox} vs PSI_{M3}	0.68	*
Al_{M3} vs PSI_{ox}	0.60	*
Fe_{M3} vs PSI_{ox}	0.62	*
Lower coal measures		
Psat vs Psl_{ox}	0.68	*
Psat vs PSI_{M3}	0.66	*
P_{ox} vs PSI_{M3}	0.70	*
Al_{M3} vs PSI_{ox}	0.65	*
Fe_{M3} vs PSI_{ox}	0.667	*
Upper coal measures		
Psat vs PSI_{ox}	0.87	**
Psat vs PSI_{M3}	0.92	**
P_{ox} vs PSI_{M3}	0.82	*
A_{lM3} vs PSI_{ox}	0.79	**
Fe_{M3} vs PSI_{ox}	0.76	*
Falsebedded sandstones		
Psat vs PSI_{ox}	0.73	**
Psat vs PSI_{M3}	0.58	*
P_{ox} vs PSI_{M3}	0.68	**
Al_{M3} vs PSI_{ox}	0.62	*
Fe_{M3} vs PSI_{ox}	0.71	**

Table 6: Phosphorus sorption capacity model attributes

Attribute	Value
R	0.88
R^2	0.77
$1\text{-}R^2$	0.23
Dependent mean	6.87
CV (%)	53.91
RMSE	3.70
Bias	-0.09

CONCLUSION

A good knowledge of P sorption capacity of highly weathered tropical soils is helpful in agronomyand environment. Soil properties such as pH OC, clay, Al and Fe oxides, Ca and BD showed significant relationships with P sorption characteristics. However, there relationships differed among soil groups in the study site with soils formed over Shale and Lower Coal Measures having least relationship. The measured soil attributes had a good relationship with P sorption characteristics hence of great importance in modelling and monitoring agricultural and environmental activities as they affect soils.

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