

EFFECTS OF ORGANIC MATTER REMOVAL AND ADSORBATE SOLUTION COMPOSITION ON PHOSPHATE SORPTION BY SELECTED SOILS OF KWARA STATE, NIGERIA.

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ABSTRACT

The effects of organic matter removal and adsorbate solution composition on phosphate sorption by selected soils of Kwara State were studied. Organic matter was removed by treating the soils with hydrogen peroxide. These were the 'treated' samples. The 'untreated' samples were those to which hydrogen peroxide was not applied. The adsorbate solutions used were: $\text{KH}_2\text{PO}_4 + \text{KCl}$, KH_2PO_4 , $(\text{NH}_4)_2\text{HPO}_4 + \text{KCl}$ and $(\text{NH}_4)_2\text{HPO}_4$. The phosphate sorption data were fitted into the Langmuir II sorption model. The r^2 values from the Langmuir II sorption models were 0.95 for Ilorin, Omuaran and Erin-ile soils while Odoowa, Malete and Lanwa had 0.94, 0.93 and 0.89 respectively for the untreated soil samples. The r^2 values for the treated samples were 0.96 each for Omuaran, Erin-ile and Malete while Ilorin, Odoowa and Lanwa had r^2 values of 0.95, 0.94 and 0.91 respectively. There was no significant difference in the r^2 values of the treated and untreated samples except for Ilorin soil. The r^2 values obtained for the treated samples were generally higher than their untreated counterparts. The r^2 values for $\text{KH}_2\text{PO}_4 + \text{KCl}$ adsorbate solution were higher than those for other adsorbate solution compositions for both Omuaran and Lanwa soils. The highest adsorption maximum for the untreated soils was recorded for Omuaran, followed by Erin-ile, Malete, Odoowa and Lanwa in that order. In the treated soils, the values of the adsorption maxima were slightly greater than for untreated samples. Adsorption maxima and buffer capacity values were higher in $\text{KH}_2\text{PO}_4 + \text{KCl}$ and $(\text{NH}_4)_2\text{HPO}_4 + \text{KCl}$ adsorbate solutions than in KH_2PO_4 and $(\text{NH}_4)_2\text{HPO}_4$ adsorbate solutions. The k values were also higher in both $\text{KH}_2\text{PO}_4 + \text{KCl}$ and $(\text{NH}_4)_2\text{HPO}_4 + \text{KCl}$ adsorbate solutions than in KH_2PO_4 and $(\text{NH}_4)_2\text{HPO}_4$ adsorbate solutions for Omuaran and Lanwa soils. The k constant values were higher in Omuaran, Erin-ile and Ilorin than in Lanwa, Odoowa and Malete for both treated and untreated samples. Additions of KCl to the adsorbate solutions enhanced phosphate adsorption by the soils studied. Soils with higher phosphate adsorption will require increased phosphate fertilizer application to satisfy the phosphate needs of the crops.

KEY WORDS: Phosphate sorption, Langmuir II sorption model, adsorption maxima, k constant.

INTRODUCTION

Phosphorus (P) deficiency has been found to be widespread in the soils of the humid tropics (Olsen and Englestad, 1972) and in Nigeria, positive response to applied P has been experienced in all ecological zones (Udo, 1981). The low availability of P in the tropical soils is attributed to the nature of the chemical forms of P. The high contents of oxides of iron (Fe) and aluminium (Al) are associated with high P fixation (Brady and Weil, 1999). In acid soils, inorganic P in the soil solution becomes adsorbed to surfaces of Fe and Al oxides and clay minerals (Garcia, 1999), thereby becoming unavailable to the crop plants.

Adsorption is generally defined as the enrichment (positive adsorption) or the depletion (negative adsorption) of one or more chemical species in the region of an interface (Sposito, 1989).

Soils of the hot, humid tropics generally have small amounts of phosphate available to plants and correspondingly high capacities for phosphate sorption (Weir, 1977).

It is well established that cations like Fe and Al can hydrolyze to produce hydrous oxide polymers which function as ion exchanger and irreversibly sorb added phosphate (Wilson, 1968). Also, soils containing large quantities of clay (with large surface area) will fix or adsorb more P than soils with lower clay content (Ogunwale and Shamshuddin, 1999).

Phosphate sorption capacity has been found to change with the amount of extractable Al and Fe, irrespective of the organic matter content, and even the removal of organic matter did not alter the phosphate adsorption of some soils (Bolan *et al*, 1985). The release of adsorbed P by soil particles over time is affected by both the magnitude and the direction of the changes of solution P concentration (Murrman and Peech, 1969). These changes differed between soils, and for a given soil, between levels of added phosphate (Ahmad, 1982). He reported that the different soils of Malaysia reacted differently to different phosphate adsorbate solution compositions. Also in North Carolina (U.S.A.), Sample (1973) reported a similar observation to that of Ahmad (1982). Adsorbate solution composition influences the quantity of phosphate adsorbable by a soil. The use of adequate adsorbate solution gives reliable adsorption maximum of a soil and this enhances the predictability of the optimum quantity of phosphate fertilizer to apply to such a soil for maximum crop yield. Ogunwale *et al* (1998) gave information on the effects of organic matter removal on phosphate sorption by Tamkpafo soils which represent the red soils developed over sandstones and are found in two local government areas of Kwara State (Edu and Pategi). There is no information on phosphate sorption by soils derived from the basement complex rocks in Kwara State, Nigeria, which the soils used in this study represent. The selected soils are representative of areas of intensive agricultural activities in Kwara State. This study was carried out to determine the effects of organic matter removal on phosphate sorption by selected soils developed over basement complex rocks in Kwara State, and the effects of adsorbate solution composition on P sorption by Omuaran and Lanwa soils of Kwara State, Nigeria.

MATERIALS AND METHODS

Soil Sampling:

Surface soil samples (0 - 15cm) were collected from six locations in Kwara State. This consisted of 20 samples per hectare of cropped farmland bulked to make one composite sample. Such samples from 10 farmlands in each location were bulked and sampled to represent that location. The locations are: Ilorin Central Local Government Area (LGA), Omuaran in Ifelodun LGA, Erin-ile in Ilemo LGA, Lanwa in Ilorin East LGA, Odo-owa in Ekiti LGA, and Malete in Moro LGA (Fig 1). The samples were air-dried and sieved through a 2mm sieve then stored for subsequent laboratory analysis. Sub-samples of each soil were finely ground to pass through a 60-mesh sieve and stored for organic carbon determination and phosphate sorption studies.

Characterization of the soils:

Soil pH was determined in water and 0.1M KCl solution in 1:1 soil:water suspension using an electronic pH meter. Particle size analysis was done by the hydrometer method (Bouyoucos, 1962) and the texture was determined from the particle sizes with the aid of a textural triangle. Organic carbon was determined by the wet oxidation method (Jackson, 1958). Organic matter was calculated from the values obtained for organic carbon by multiplying the latter by a factor of 1.72 (Jackson, 1958)

Free aluminium (Al) and iron (Fe) oxides in the soils were extracted by dithionite-citrate-bicarbonate (DCB) method (McKeague and Day, 1966). A 10ml aliquot of the DCB extract was digested by 5ml M HCl and diluted to 100ml with distilled water. Iron in the digest was analyzed colorimetrically by the O-phenathroline method at a wavelength of 508nm and Al by the xylenol

orange method at a wavelength of 550nm (Hesse, 1971). The short range order (non-crystalline) Al and Fe in soils were extracted with acid ammonium oxalate in the dark (McKeague and Day, 1966). The extract was digested with 10% hydrogen peroxide and nitric acid. Aluminium and Fe in the digest were also analyzed colorimetrically as above.

Soil treatments before equilibration with P

The soil samples were treated for the removal of organic matter with hydrogen peroxide (H_2O_2). To 30g of soil, 50ml of distilled water and 10ml of 30% H_2O_2 were added. The mixture was stirred thoroughly and left to settle overnight. The supernatant liquid was carefully decanted, and the soil sediment was air dried and ground in a mortar. The ground soil was used for P equilibration studies.

Equilibration of treated and untreated soils with adsorbate solutions:

A 1g soil sample was weighed into each of nine 50ml capacity vials and 10ml of 0.04 M KCl was added to each sample. Eight samples received 10ml of 5, 10, 15, 20, 22, 25, 28, and 30 ppm P as KH_2PO_4 respectively. The ninth vial, which served as the control, received 10ml of distilled water. Each mixture received two drops of toluene to control the growth of fungi. Each container was covered tightly and agitated on an orbital shaker for 1 hour at 150rpm during the first day. For the next four days, the containers were shaken for 30 minutes daily. The mixtures were filtered through Whatman No. 42 filter paper on the sixth day. The filtrate was analyzed for phosphorus. For $(NH_4)_2HPO_4$ and KCl adsorbate solutions, each of the containers received 10ml of 0.04M KCl before receiving 10ml of 5, 10, 15, 20, 22, 25, 28 and 30 ppm P as $(NH_4)_2HPO_4$. The control vial received 10ml of distilled water without the addition of P.

Phosphorus analysis:

Sample filtrates were analyzed for P by the Murphy and Riley (1962) method at a wavelength of 882nm. The difference between the P added and that in the equilibrium solution was taken as the P sorbed.

Phosphate sorption isotherms:

The Langmuir II isotherm, expressed by the equation below, was used to describe phosphate sorption by the six soils studied:

$$\text{Langmuir II} = C/q = C/Q + 1/k Q_m \text{ (Bache and Williams, 1971)}$$

Where

q = the quantity of materials sorbed by a unit weight of adsorbent ($\mu\text{g P/g soil}$).

C = Equilibrium concentration of phosphate ion ($\mu\text{g P/g}$)

Q_m = Adsorption maximum ($\mu\text{g P/g}$) and

k = Constant which relates to sorption affinity in the equation.

Adsorption maximum was obtained directly by linear regression of P sorbed against P sorbed/equilibrium P. The intercept of the line with the ordinate gave a direct measure (Q_m) for each of the soils with the background electrolyte. The buffering capacities of the soils for P were obtained from the slope of the plot of P sorbed against the logarithm of equilibrium P (Arines and Sainz, 1987).

RESULTS AND DISCUSSION

General characteristics of the soils:

The gravel content of the soils ranged from 8.50 to 35.0% (Table 1). The highest gravel content (35.0%) was recorded in Omuaran and the least of 8.50% was recorded in Malete. Ilorin and Omuaran have sandy loam texture; Erin-ile, Odo-owa and Malete have loamy sand texture, while Lanwa has sandy texture. The sand particles ranged from 69.52 to 87.52% (Table 1). The silt contents

are comparatively lower than the sand components but higher than those of clay in all but Lanwa soil whose clay content is marginally higher than silt.

The pH of the soils ranged from slightly acidic to neutral. Omuaran had the lowest value in water of 4.8. This is acidic and the soil will sorb more P because the higher the soil acidity, the more the P sorbed by soils. This implies that more P fertilizer will be required in this soil than in Lanwa, which had the highest pH value of 7.3. Phosphate sorption will be lowest in Lanwa soil, hence more P will be available for crop uptake in that soil and less fertilizer P will be required.

Percentage organic matter ranged from 5.29mg/Kg (Omuaran) to 2.39mg/Kg (Ilorin). Organic matter will release locked-up plant nutrients as it decomposes, therefore it is expected that nutrient availability to crops on these soils will not be a problem. This level of organic matter should be maintained or even increased by the addition of organic materials as crop residues and organic manures.

The free iron (Fe) and aluminium (Al) oxides (DCB extractable) were higher than the amorphous (ammonium oxalate-extractable) Fe and Al oxides in the soils studied (Table 1). This indicates the presence of a greater percentage of crystalline materials in the soils than amorphous materials. The highest value of free Fe (66.14 mg/Kg soil) was recorded for Odo-owa soils, while the lowest (30.39 mg/Kg) was recorded for Lanwa. The highest value of free Al (44.89mg/Kg) was recorded for Erin-ile, while the lowest value (16.54mg/Kg) was recorded for Malete. Meanwhile, the greatest value of ammonium oxalate extractable Fe (short-range order Fe) was recorded for Odo-owa (33.08) and the least (16.09) was recorded for Lanwa. The highest value of amorphous Al was recorded for Ilorin soil (23.63) and the least was recorded for Lanwa and Omuaran soils (3.54mg/Kg) respectively.

Sorption isotherms and parameters for untreated soils

Phosphate sorbed by all the soils studied conformed to the Langmuir II sorption isotherm (Fig. 2). The adequacy or otherwise of the Langmuir II model may be assessed by the r^2 values of linear regression (Ogunwale and Shamshuddin, 1999). Three of the soils studied (Omuaran, Ilorin and Erin-ile) have r^2 values of 0.95 while the remaining three (Lanwa, Malete, and Odo-owa) have r^2 values of 0.89, 0.93 and 0.94 respectively (Table 2). These are all high r^2 values. Isotherms of all the soils are curved (Fig. 2a). This could be due to the possibility of the migration of sorbed P to the sub-surface layers of the adsorbent, as explained by Bache and Williams, (1971). The greatest value of adsorption maximum (14.3 mg P/Kg) and buffer capacity (7.86mg P/Kg) were recorded for Omuaran soil (Table 2). This may be due to the acidic nature of the soil. It has been recorded that the acidic soils of the humid tropics generally have small quantities of phosphate available to plants and correspondingly high capacities for phosphate sorption (Weir, 1977).

The adsorption maximum of Omuaran soil was the highest. This may be due to the high value of short-range order Al (23.63) recorded for that soil. It has been reported that cations like Al and Fe can hydrolyze to produce hydrous oxide polymers which function as an anion exchanger and irreversibly sorb added phosphate (Wilson, 1968). Short-range order hydrous metal oxides of Fe and Al sorb considerably greater values of P than their crystalline counterparts (McLaughline *et al*, 1981).

The sorption energy (k) values calculated from the Langmuir II isotherms varied among the soils from -1.19 to -0.66 (Table 2).

Sorption Isotherms and parameters for treated soils

The phosphate sorbed by the soils studied (from which organic matter had been removed) conformed to the Langmuir II adsorption isotherm (Fig 2b). The r^2 values recorded were greater than those obtained for the untreated samples (having organic matter intact) except for the Ilorin soil

in which the values remained the same (Table 2).

The adsorption maximum was also slightly greater than that of the untreated soils, except for Ilorin soil whose value did not change. The behaviour of Ilorin soil agrees with the report of Bolan *et al* (1985) where the removal of organic matter did not alter the phosphate adsorption of some soils. The higher adsorption maximum for the treated soils may be due to the removal of organic matter which exposes the surfaces of oxides of Fe and Al for P sorption (Ogunwale, 2003).

Buffering capacity was higher in the untreated samples than in the treated samples in the six soils studied. This may be due to the organic matter content which had been removed in the treated samples (Ogunwale *et al* 1998). The values ranged from 5.36 in Lanwa to 7.50 in Omuaran (Table 2).

Effect of solution composition on phosphate sorption by Omuaran and Lanwa soils

Omuaran soil

The ability of Omuaran soil (pH 4.8, water) to sorb added inorganic phosphate varied with the different solution compositions used (Table 3). The P sorbed also fitted the Langmuir II adsorption isotherm (Fig. 3a). The isotherms of these soils using the different solutions were curved. The $\text{KH}_2\text{PO}_4 + \text{KCl}$ solution composition had r^2 value of 0.95. The highest value of adsorption maximum (14.3) was also recorded when this solution was used. This is due to the effect of the adsorbate solution (KCl) which increases the ionic strength of the solution. Neue and Zhu (1990) reported that phosphate retention increases with increasing ionic strength. This same solution ($\text{KH}_2\text{PO}_4 + \text{KCl}$) gave the highest value of buffer capacity (7.86) while the least value of adsorption constant (k) was recorded from the $(\text{NH}_4)_2\text{HPO}_4$ solution.

Lanwa soil

The P sorbed by Lanwa soil (pH 7.3, water) with the different solution compositions used also fitted the Langmuir II adsorption isotherm (Fig. 3b). Like the Omuaran soil, the r^2 value was highest (0.89) for the $\text{KH}_2\text{PO}_4 + \text{KCl}$ solution. All the isotherms were curved when all the solutions were used (Fig. 3b). The highest value of adsorption maximum (12.7) was recorded when $\text{KH}_2\text{PO}_4 + \text{KCl}$ solution was used (Table 3). This was followed by $(\text{NH}_4)_2\text{HPO}_4 + \text{KCl}$ solution (11.9), KH_2PO_4 (10.4) and $(\text{NH}_4)_2\text{HPO}_4$ (9.76). The higher values of 12.7 and 11.9 obtained with P-sources containing KCl, may be due to the reason advanced above for Omuaran soil.

The $\text{KH}_2\text{PO}_4 + \text{KCl}$ solution composition gave the greatest value of buffer capacity (5.77), followed by $(\text{NH}_4)_2\text{HPO}_4 + \text{KCl}$, KH_2PO_4 and $(\text{NH}_4)_2\text{HPO}_4$ solutions respectively (Table 3). The adsorption constant, k was negative when all the solutions were used for P adsorption studies in the Lanwa soil. The highest value of k was obtained when $\text{KH}_2\text{PO}_4 + \text{KCl}$ adsorbate solution was used.

CONCLUSION

The Phosphate sorption data of Omuaran, Ilorin, Erin-Ile, Odo-Owa, Malete and Lanwa soils, all in Kwara state of Nigeria, fitted the Langmuir II adsorption model, regardless of whether the organic matter was left intact or removed. The effect of adsorbate solution composition on P sorption by two of the soils - Omuaran and Lanwa soils produced P sorption data that also fitted the Langmuir II adsorption model with significant r^2 values.

The highest phosphate adsorption maximum and buffer capacity values were recorded for Omuaran, and the least for Lanwa soils in both the treated and untreated samples. Adsorption maxima were slightly higher in the treated samples than in the untreated samples, except in Ilorin soil where the removal of organic matter did not affect the adsorption maximum. Removal of organic matter resulted in lower equilibrium P in the soils studied.

Phosphate adsorption maxima and buffer capacity values were higher when $\text{KH}_2\text{PO}_4 + \text{KCl}$ and $(\text{NH}_4)_2\text{HPO}_4 + \text{KCl}$ solution compositions were used than when KH_2PO_4 and $(\text{NH}_4)_2\text{HPO}_4$

solutions were used for Omuaran and Lanwa soils.

It therefore follows that in order to reduce phosphate adsorption in these soils, the organic matter should be left intact, and KCl should be used in all equilibration studies so as to obtain the highest possible adsorption maximum.

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Table 1: Textural and Some Chemical Characteristics of Selected Soils of Kwara State, Nigeria.

Sample Location	pH in H ₂ O	pH in KCl	Gravel	Sand	Silt	Clay	Organic matter	Texture	DCB* extractable		Ammonium oxalate extractable	
									Fe	Al	Fe	Al
									mg/Kg			
Ilorin	6.10	5.60	30.00	69.52	18.00	12.48	2.39	Sandyloam	35.75	28.53	21.45	23.63
Omuaran	4.80	4.20	35.00	69.52	18.00	12.48	5.29	Sandyloam	48.26	35.44	17.98	3.54
Erin-ile	6.10	5.40	33.00	83.52	10.00	6.48	4.81	Loamysand	33.96	44.89	16.99	4.73
Lanwa	7.30	6.60	17.00	87.52	6.00	6.48	4.19	Sand	30.39	42.53	6.09	3.54
Odoowa	6.70	6.30	21.00	83.52	10.00	6.48	4.47	Loamysand	66.14	33.08	33.08	12.99
Malete	6.80	5.90	8.50	81.52	12.00	6.48	3.43	Loamysand	51.84	16.54	14.30	9.45

*DCB = Dithionite-Citrate-Bicarbonate

Table 2: Phosphate Adsorption Parameters for Selected Soils of Kwara State

Sampling Location	Adsorption maximum	Buffer capacity	Adsorption constant	r ² values
Organic matter removed (treated)				
Ilorin	13.9	6.82	-0.84	0.95
Omu-Aran	14.3	7.86	-0.66	0.95
Erin-Ile	13.6	7.50	-0.73	0.95
Lanwa	12.7	5.77	-1.19	0.89
Odo-Owa	13.3	5.83	-0.92	0.94
Malete	13.6	6.25	-0.87	0.93
Organic matter intact (untreated)				
Ilorin	13.9	6.25	-0.67	0.95
Omu-Aran	14.4	7.50	-0.61	0.96
Erin-Ile	14.2	6.94	-0.65	0.96
Lanwa	13.7	5.36	-1.11	0.91
Odo-Owa	14.3	5.68	-0.88	0.94
Malete	14.1	5.68	-0.76	0.96

Table 3: Phosphate Adsorption Parameters for the effect of Solution Composition on Omuaran and Lanwa Soils

Solution Composition	Adsorption maximum	Buffer capacity	Adsorption constant (k)	r ² values
Omuaran soil				
KH ₂ PO ₄ + KCl	14.3	7.86	-0.66	0.95
KH ₂ PO ₄	12.1	5.00	-1.38	0.87
(NH ₄) ₂ HPO ₄ + KCl	13.9	5.70	-1.03	0.86
(NH ₄) ₂ HPO ₄	10.7	2.50	-1.63	0.81
Lanwa soil				
KH ₂ PO ₄ + KCl	12.7	5.77	-1.19	0.89
KH ₂ PO ₄	10.4	5.38	-1.58	0.81
(NH ₄) ₂ HPO ₄ + KCl	11.9	5.45	-1.47	0.88
(NH ₄) ₂ HPO ₄	9.76	5.00	-1.69	0.79

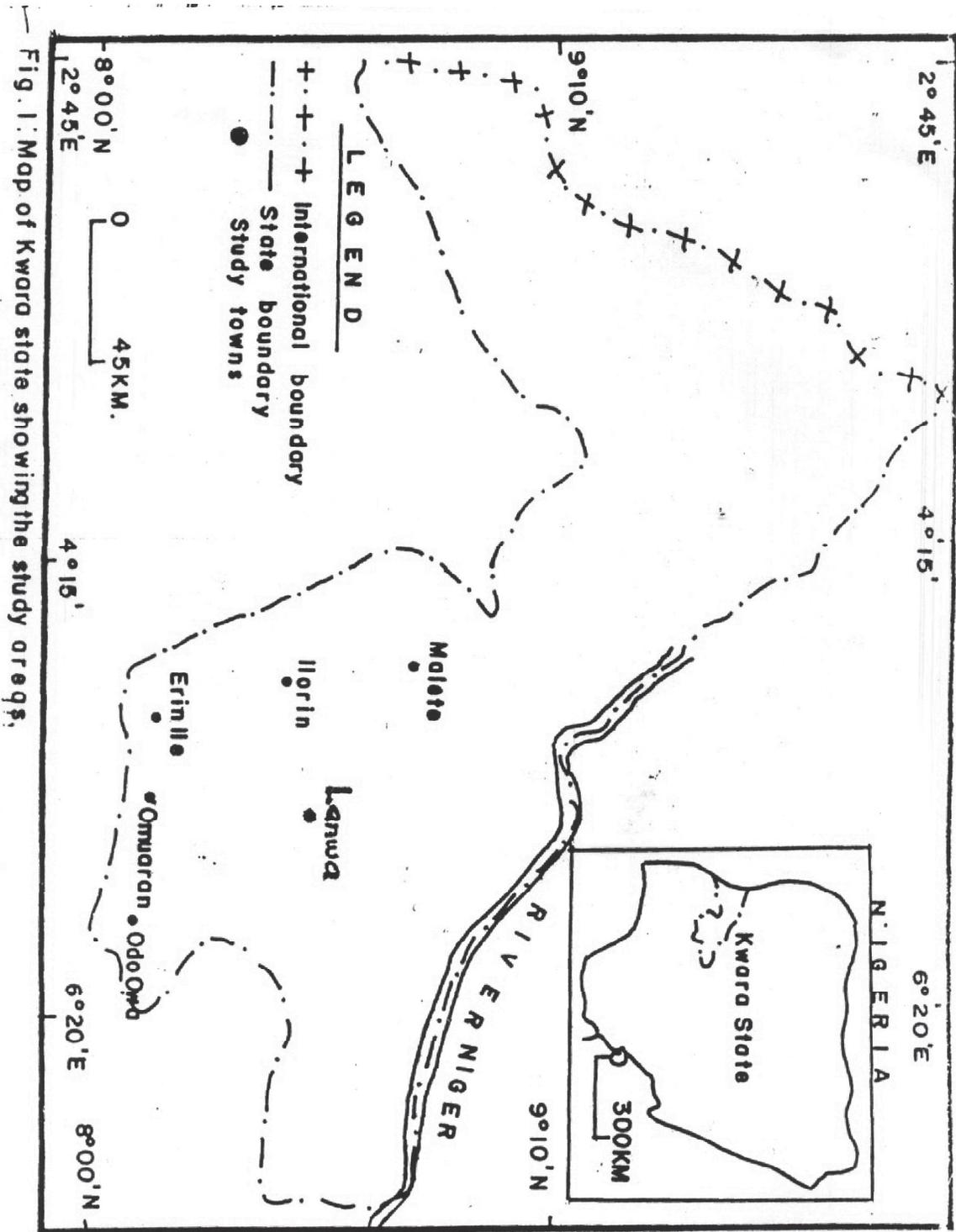


Fig. 1: Map of Kwara state showing the study areas.

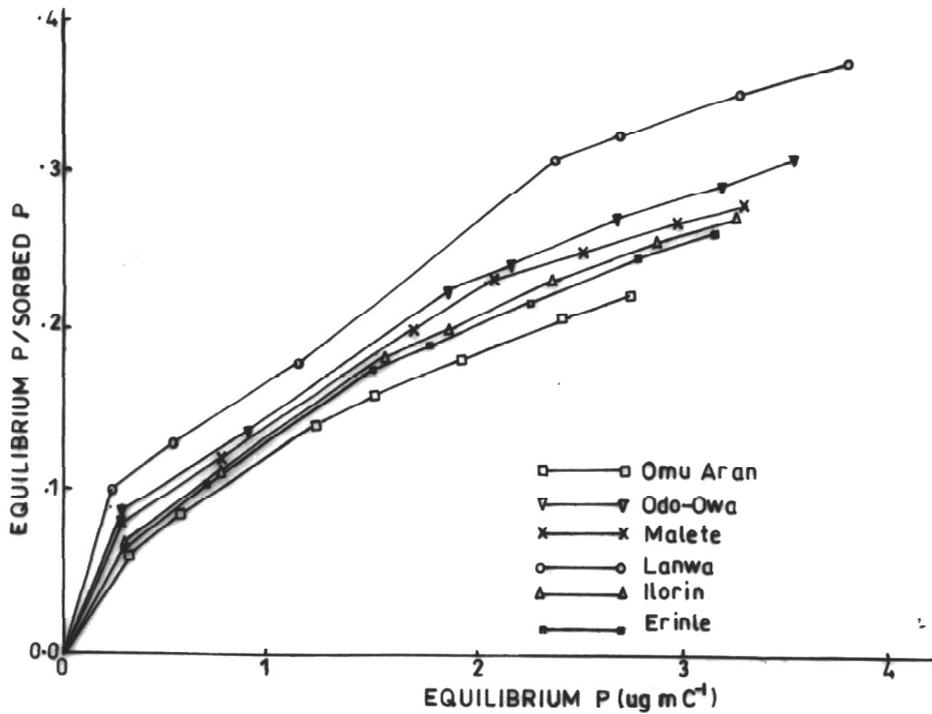


Fig 2a Langmuir II sorption isotherms for selected soils of Kwara state (organic matter not removed)

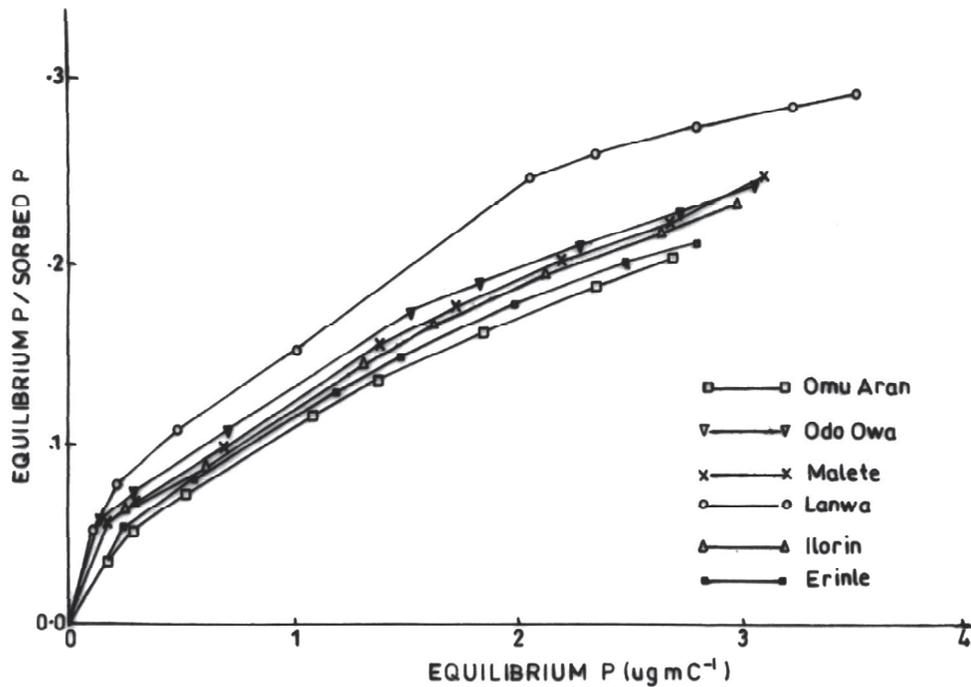


Fig. 2b Langmuir II sorption isotherms for selected soils of Kwara state (organic matter removed)

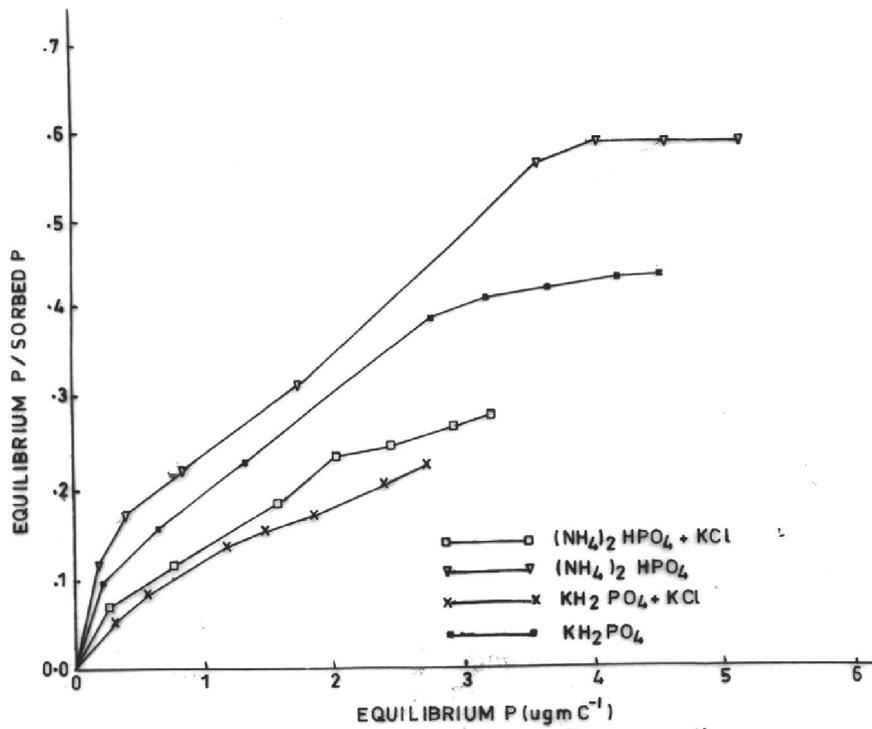


Fig3a Langmuir II sorption isotherms for the effect of solution composition on P sorption by Omuaran soil.

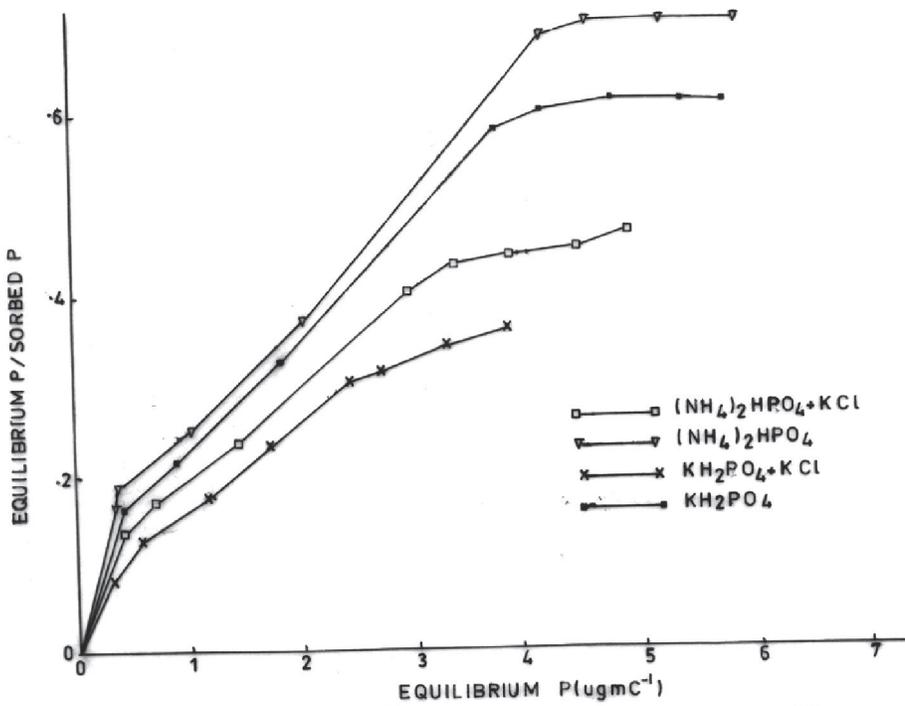


Fig3b Langmuir II sorption isotherms for the effect of solution composition on P sorption by Lanwa soil.