

Evaluation of bioavailable phosphorus in some acid soils of Ghana using ^{32}P isotopic exchange method

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ABSTRACT

An adequate knowledge about bioavailable soil P of highly weathered tropical acid soils is a pre-requisite to their sustainable management for food production. The objective of this study was to characterize the bioavailable soil P status of six highly weathered low activity clay (LAC) soils from SW Ghana by using an isotopic exchange method. The bioavailable P was characterized by three factors, i.e. intensity, quantity, and capacity inferred from experimental parameters that describe the dynamics of soil phosphorus through isotope exchange of phosphate ions and represented by a functional model with five compartments in which the pools have been defined according to their mean exchange time with the phosphate in soil solution. The results indicated that all the LAC acid soils had very low P fertility status as reflected by the low P concentration in solution, C_p ($<0.02 \text{ mg P l}^{-1}$), low exchangeable P, E_{min} ($<5.0 \text{ mg P kg}^{-1}$), and high P fixation capacity, r_1/R (0.24) with the exception of one soil. The compartmental analysis also showed that an average of 45 % of the total P pool could not be exchanged within 1 year while 0.53 % of it was exchangeable within 1 min. These results are consistent with the numerous exchange sites located on the oxides of the LAC acid soils. In addition, the study showed that the r_1/R parameter correlated significantly with P_{max} derived from P sorption isotherms and the SPR, i.e., the amount of P sorbed at a concentration of 0.2 mg P l^{-1} . It was concluded that the ^{32}P isotopic exchange method was useful for the determination of bioavailable P and also for estimating soil-fixing capacity of these low-activity clay acid soils of Ghana.

RÉSUMÉ

OWUSU-BENNOAH, E., FARDEAU, J. C. & ZAPATA, F.: *Evaluation de phosphore biodisponible en quelques sols acides du Ghana employant la méthode d'échange isotopique de ^{32}P* . Une connaissance adéquate du P de sol biodisponible des sols acides de tropique fortement érodés est une condition préalable à leur exploitation soutenue pour la production alimentaire. L'objectif de cette étude était de caractériser l'état du P de sol biodisponible de six sols d'argile de moins d'activité (AMA) fortement érodés du Sud-Ouest du Ghana employant une méthode d'échange isotopique. Le P biodisponible était caractérisé par trois facteurs, c.-à-d. intensité, qualité et capacité inférées des paramètres d'expérience qui décrivent le dynamisme de phosphore de sol à travers l'échange d'isotope d'ions de phosphate et représenté par un modèle fonctionnel avec cinq subdivisions dans lesquels les pools ont été défini selon leurs temps d'échanges moyens avec le phosphate en solution de sol. Les résultats indiquaient que tous les sols acides d'AMA avaient de très bas niveaux de fertilité de P comme traduit par la basse concentration de P en solution, C_p ($< 0.02 \text{ mg P l}^{-1}$), P échangeable bas, E_{min} ($<5.0 \text{ mg P kg}^{-1}$) et une capacité élevée de la fixation de P, r_1/R (0.24) à l'exception d'un sol. Les analyses de subdivisions montraient également qu'un moyen de 45 % de la totalité du pool de P ne pourrait pas être échangé en une année alors que 0.53 % en ai échangé dans 1min. Ces résultats sont en accord avec la présence de plusieurs sites d'échange situés sur les oxides de l'AMA des sols acides. En plus, l'étude montrait que le paramètre de r_1/R corrélait considérablement avec P_{max} dérivé d'isothermes de l'absorption de P et le SPR c.-à-d. la quantité de P absorbée à une concentration de 0.2 mg P l^{-1} . La conclusion était tirée que ^{32}P méthode d'échange isotopique était utile pour la détermination de P biodisponible et aussi pour l'estimation de la capacité de fixation de sol de ces sols d'argile de moins d'activité du Ghana.

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Introduction

An estimated 10-15 per cent of the 23.9 million hectares of potentially arable land in Ghana comprises highly weathered soils of low-base status (Oxisols and Ultisols). These soils are in the humid rainforest agro-ecological zone of the country. The major constraint to increased food-crop production in this area is the inherently low soil fertility status (Owusu-Bennoah *et al.*, 1997). Phosphorus (P) is one of the most limiting nutrients for sustained crop production in these acid soils. Low solution P concentration and a high P sorption capacity are the two common problems in these acid soils. For sustainable management and the formulation of P fertilizer recommendations, it is necessary to evaluate and characterize P-availability in the soil for crops, and to know the relationship between the bioavailability, fertilization, and crop yields. Bioavailable soil P has been defined by Fardeau (1981) as the P that can contribute to the phosphate nutrition of plants, and can be considered as the mainstay of the P cycle for sustainable agriculture.

Although the characterization of soil phosphate availability has been the subject of numerous studies elsewhere, a gap in knowledge still exists for the highly weathered LAC acid soils of Ghana. At present, there is no generally standard, reliable P soil test for the acid soils of Ghana.

Currently, P availability is measured by chemical extraction which uses AB-DTPA (Ammonium bicarbonate-diethylene-triamine pentaacetic acid), NaHCO_3 , mild acids (e.g. Bray P-1), and saturation paste with water. According to Corey (1978), the P measured by using any of these chemical methods gives a fraction of the total soil P and is operationally defined by the extractant used. The isotopic dilution P method, however, has advantage over the chemical extractants because it does not interfere with the soil physico-chemical components, and there is an identity between isotopically exchangeable P and the phosphate ions absorbed by plants

(Russell, Rickson & Adams, 1954; Fardeau, 1981). In addition, the chemical methods measure static P pools without providing any estimate of the dynamic components of bioavailability. Nye & Tinker (1977) and Barber (1984) have cited diffusion rate as a limiting factor for P availability in soils.

A complete characterization of bioavailable soil P requires an estimation of the intensity, quantity, and capacity factors. Recently, an isotopic dilution technique has been developed which makes it possible to estimate these factors simultaneously as the P content in solution, the isotopically exchangeable E value, and the labile pool of available P in a single procedure (Fardeau & Jappe, 1976; Fardeau, 1993). ^{32}P isotope exchange kinetics method provides an estimation of the P sorption capacity as determined by the ratio of the radioactivity remaining in the solution after 1 min exchange to the total radioactivity added (r_1/R). Another kinetic factor n indicating the decrease of radioactivity remaining in the solution versus time can also be measured with this procedure. According to Tran, Fardeau & Giroux (1988), the Fardeau procedure offers potential to describe both the soil P status and P kinetic parameters.

This study was undertaken by using the ^{32}P isotopic exchange model in six major acid soils of SW Ghana.

Materials and methods

Samples of the top layer (0-15 cm) of six soil series from the South-western part of the Western Region of Ghana were used in the study. Table 1 shows the classification and selected characteristics of the soil series. The samples were air-dried in a greenhouse and ground to pass through a 2-mm mesh screen before analysis. The modified Bouyoucos method as described by Day (1965) was used to analyze particle size distribution. The exchangeable bases were determined by $1\text{ M NH}_4\text{OAc}$ (pH 7.0) method (Chapman, 1965). Soil pH was measured in a soil/water (1:1) mixture and organic carbon content by the Walkley and Black

TABLE I
Selected Physical and Chemical Characteristics of the Studied Soils

Soil series	Classification	Particle size (%)			Org.C								Exchangeable cations (c mol _e kg ⁻¹)	Oxalate extractable (m mol _e kg ⁻¹)	Dithionite-citrate extractable (m mol _e kg ⁻¹)	P adsorption maxima (mmol kg ⁻¹)
		Sand	Silt	Clay	pH	Ca	Mg	K	H+Al	ECEC	Fe	Al				
Abenia	Typic Hapludox	66	7	27	3.7	26	0.57	0.43	0.13	2.5	3.8	29	28	145	70	17.0
Ankasa	Typic Hapludox	75	5	20	3.7	22	0.63	0.31	0.13	1.55	2.9	13	27	88	61	13.8
Aiyinasi	Typic Hapludox	77	5	18	4.0	22	0.63	0.47	0.12	2.0	3.4	16	29	40	40	13.1
Boi	Typic Hapludox	48	12	40	3.5	17	0.54	0.31	0.10	2.60	3.7	28	30	660	177	17.2
Kwaben	Typic Hapludox	81	2	17	4.6	14	1.22	0.6	0.22	0.15	2.5	14	15	55	34	9.3
Tikobo	Typic Hapludox	79	3	18	4.9	10	1.23	0.6	0.10	0.10	2.6	10	14	168	78	10.3

oxidation procedure (Allison, Bollen & Moodie, 1965). Amorphous Fe and Al were extracted in a solution of ammonium oxalate/oxalic acid as described by McKeague (1978). The soil P was extracted by Bray-1 method (0.03 M NH₄F + 0.025 M HCl, Bray & Kurtz, 1945). Dithionite-extractable Fe and Al were determined by using a citrate-bicarbonate-dithionite (CDB) extract (Mehra & Jackson, 1960).

Phosphorus absorption isotherms were constructed by equilibrating for 24 h, 1.0 g of soil in 50-ml centrifuge tubes with 25 ml of a 0.01-M CaCl₂ solution of increasing P concentrations covering the range 0 - 0.1 mM P l⁻¹ at equilibrium. The tubes with contents were centrifuged and the supernatant filtered through Whatman No. 42 filter paper. Aliquots from the filtrate were analyzed for P by the method of Murphy & Riley (1962). Theoretical sorption maxima were calculated by fitting data to the linear form of the Langmuir equation:

$$C/X = (BX_M)^{-1} + (C/X_M)$$

where C is the P concentration in the equilibrium solution, X is the P sorbed per mass of soil, X_M is the sorption maximum, and B is a constant. A plot of C/X versus C, with a slope of (X_M)⁻¹ was used to calculate the sorption maximum of each soil.

The isotopic exchange kinetic model

It has been shown that after the addition of

initial radioactivity R into a steady soil-solution system, the remaining radioactivity of the isotope in soil solution at time t, i.e. r_t, can be described by the following equation:

$$r_t/R = (r_1/R) [t + (r_1/R)^{1/n}]^{-n} + r/R \quad (1)$$

where r₁ is the radioactivity in solution 1 min after the addition of the isotope into the system, and r/R is the maximum dilution limit of phosphorus in the system which is equal to the ratio of solution phosphorus to soil total P (Fardeau, 1993):

$$r/R = 10C_p/P_T \quad (2)$$

where C_p is the P concentration in the soil solution, P_T is the total P of the soil sample, and 10 is the ratio of liquid to soil. In the Eq. (1), if r₁/R is below 0.7 and n > 0.1, the value of (r₁/R)^{1/n} will be very low, and hence for most soils, Eq. (1) can be expressed as follows:

$$r_t/R = (r_1/R)t^n \quad (3)$$

After taking the logarithm of Eq. (3), the following expression will be obtained:

$$\log(r_t/R) + \log(r_1/R) - n \log t \quad (4)$$

By determining the residual ³²P in the solution at different time (r_t), Eq. (4) can be solved.

The exchange behaviour of the phosphate ion within the solid-liquid interface can be further

characterized by the mean exchange rate, K_m (min^{-1}); the mean flux of exchange of phosphate between the soil solution and the solid phase, F_m ($\text{mg}(\text{kg} \cdot \text{min})^{-1}$); and the mean sojourn time in solution, T_m (min);

$$K_m = n/(r_1/R)^{\frac{1}{n}} \quad (5)$$

$$T_m = 1/K_m \quad (6)$$

$$F_m = 10C_p K_m \quad (7)$$

According to the isotope exchange theory, the amount of phosphate exchangeable with ^{32}P within time t , E_t , can be calculated by the following equation:

$$E_t = 10C_p (R/r_1)t^n \quad (8)$$

Based on Eq. (8), the whole phosphate ion content of the soil can be further sub-divided into five pools (Fardeau, 1993): i.e., the pool of free phosphate, which is approximated by the quantity of phosphate isotopically exchangeable within 1 min (E1min) (Salcedo, Bertino & Sampaio, 1991; Tran *et al.*, 1988); phosphate exchangeable between 1 min and 1 d (E1min-1d); phosphate exchangeable between 1 d and 12 wk (E1d-12 wk); phosphate exchangeable between 12 wk and 1 yr (E12wk-1yr); and phosphate that is not isotopically exchangeable within 1 yr ($E > 1$ yr). The size of each pool is calculated as described by Fardeau (1993).

Isotope exchange kinetic experiment

The experimental procedure used in this study as described in detail by Fardeau & Jappe (1980) is as follows:

Ten grams of each sample was weighed into 150 ml polyethylene bottles in triplicate. To each of these bottles was added 99 ml of deionized water and the suspension shaken for 18 h. The ^{32}P tracer (1 ml of carrier-free solution of $^{32}\text{PO}_4$ having a radioactivity level (R) of about 0.1-1 MBq) was then added at time $t = 0$ and mixed well with a magnetic stirrer with continuous shaking. At times t corresponding to 1, 10, 40, and 100 min

respectively of isotopic exchange, 8 ml of the mixture were removed subsequently with a polyethylene syringe and the solution immediately separated from soil by a Millipore filter (0.2- μm pore size and 47-mm diameter). A constant period of 10 sec was allowed to complete the sampling and filtration steps. Radioactivity (r) remaining in the solution at each time (t) was measured by Cerenkov counting on 1 ml of solution in a liquid scintillation counter. The quantity of phosphate in solution (C_p) was determined after the last sampling of the isotopic exchange by the ammonium molybdate and ascorbic acid method (Murphy & Riley, 1962).

Results and discussion

The soils used in this study are all highly weathered tropical Oxisols, with low cation exchange capacity due to the dominance of 1:1 clays, crystalline and amorphous iron and aluminium oxides. They also contain low organic carbon and low base saturation (Table 1). Levels of crystalline Fe and Al oxides are high for Boi series, which also has the highest clay and silt, aluminium oxides and P-sorption maximum. Phosphorus sorption was better correlated with oxalate-extractable Al and Fe ($r=0.89^*$ and 0.79^* , significant at $P=0.1$, respectively) than with dithionite extractable Al and Fe ($r=0.75$ and $r=0.73$ ns, respectively), confirming the more significant role of the amorphous oxides in P sorption in these soils. The adsorption isotherms of these soils and their standard P requirement (SPR) have been reported elsewhere (Owusu-Bennoah *et al.*, 1997). Phosphorus adsorption maximum ranged from 9.3 to 17.2 mmol kg^{-1} with a mean value of 13.45 mmol kg^{-1} .

The isotope kinetic characteristics of P in the soils

Table 2 shows the results obtained by the ^{32}P isotope exchange kinetics method. The C_p values, i.e. the intensity factor ranged from 0.013 mg P l^{-1} in Ankasa series to 0.090 mg P l^{-1} in Kwaben series. Based upon the considerable range of C_p values

TABLE 2

Isotopic Exchange Kinetic Parameters and Distribution of Isotopically Exchangeable P+ in the Studied Soils

Soil series	Soil P status parameters			P kinetic parameters					P compartment			
	Cp mg P l ⁻¹	r ₁ /R	n	Elmin mg P kg ⁻¹	El/Cp l/kg. min ⁻¹	K _m min ⁻¹	T _m min	F _m mg P min ⁻¹	Elmin.1 d	E1d-12wk	E12wk-1yr	E>1 yr
Abenia	0.017	0.19	0.44	0.92	54.12	19.0	0.05	3.2	18.3	59	42	48
Ankasa	0.013	0.16	0.42	0.81	62.31	33.0	0.03	4.3	14.3	47	20	56
Aiyinasi	0.038	0.34	0.50	1.10	28.95	4.3	0.23	1.6	31.0	66	14	18
Boi	0.024	0.16	0.41	0.66	27.50	35.8	0.03	8.0	5.0	77	32	92
Kwaben	0.090	0.68	0.20	1.30	14.44	1.4	0.72	1.2	4.2	8	6	265
Tikobo	0.028	0.37	0.39	0.75	26.69	5.0	0.20	1.4	11.2	40	20	90

+Elmin = phosphate isotopically exchangeable within 1 min; Elmin1d = phosphate exchangeable between 1 min and 1 d; E1d-12 wk = phosphate exchangeable between 1 d and 12 wk; E12 wk-1 yr = phosphate exchangeable between 12 wk and 1 yr; E > 1 yr = phosphate not exchangeable, within 1 yr.

among the six soils, they were divided into three arbitrary groups: low intensity soils of <0.02 mg P l⁻¹, Group 1, comprising Ankasa and Abenia series; intermediate intensity soils, 0.02 - 0.04 mg P l⁻¹, Group 2 which includes Boi, Tikobo and Aiyinasi series; and high intensity soils of >0.04 mg P l⁻¹, Group 3, example Kwaben series. It has been shown that P becomes a limiting factor to P nutrition of many agricultural crops whenever the Cp is lower than 0.02 mg P l⁻¹ (Barber, 1984). The aforementioned results, therefore, suggest that with the exception of Kwaben series, all the other soils could be considered to be low or very low P in soil solution.

Table 2 shows the quality index, E (1 min), which is a good approximation of the quantity of P readily exchanged into the soil solution without chemical transformation to plants (Tran *et al.*, 1988; Salcedo *et al.*, 1991; Fardeau & Frossard, 1992). The soils show values ranging between 0.66 and 1.3 mg P kg⁻¹ (mean 0.92 mg P kg⁻¹). There was a high significant correlation between Elmin and Cp ($r = 0.76^*$), but the relationship between Elmin and Bray-1 was not close. The r value was only 0.569 ($P > 0.05$). The results indicate that the isotopically exchangeable P values were generally low in the six acid soils (Table 2). Tran *et al.* (1988) and Fardeau, Guiraud & Marol (1995) have reported E

(1 min) value lower than 5 mg P kg⁻¹ to be very poor in available soil P.

The capacity factor, El/Cp, which is 10 R/r₁, was also derived from the data in Table 2. The capacity values varied between 14.4 and 63.3 (mean 35.7). The values show that they were negatively related to the intensity factor, Cp. The correlation coefficient between El/Cp and Cp was ($r = -0.792^*$) (Table 3). The higher the buffer capacity of the soils (e.g. Abenia and Ankasa soil series), the lower was the P soil solution concentration and *vice versa*. The capacity factor also was related to Bray-1 P ($r = -0.761^*$), suggesting that the extractant tended to desorb more phosphate from soils with low buffer capacity (e.g. Kwaben) and less from those with high capacity values (Table 2). These results confirm the suggestion that bioavailable P is a direct function of the quantity factor and an inverse function of buffering capacity (Holford, 1997).

Table 2 presents the kinetic parameters, r₁/R and n values of the soils. The r₁/R values measure the radioactivity that remains in the solution after 1 min of isotopic exchange over the total radioactivity added. The value ranged between 0.16 and 0.68 (mean 0.32). With the exception of the Kwaben soils, the mean value for the soils is 0.24 which is close to the figure suggested by

TABLE 3
Simple Correlation Coefficient between Isotopic Kinetic Parameters, P_{max} and SPR

	C_p	$E1min$	$E1/C_p$	r_i/R	n	$1/r_i/R$	P_{max}	SPR	Bray 1
C_p	1								
$E1min$	0.760*	1							
$E1C_p$	-0.792	-0.389	1						
r_i/R	0.917***	0.799*	0.734*	1					
n	-0.827**	-0.501	0.512	-0.790*	1				
$1/r_i/R$	0.907**	0.660	-0.557	0.864**	0.979***	1			
P_{max}	-0.579	-0.488	0.0452	-0.805*	0.638	-0.646	1		
SPR	-0.593	0.673	0.438	-0.833**	0.510	-0.578	0.949***	1	
Bray 1	0.788*	0.596	-0.761*	0.934***	-0.719	0.747*	-0.914**	0.878**	1

Fardeau & Jappe (1980) and Fardeau *et al.* (1983) for high P-fixing African soils. The correlation between C_p and r_i/R was very significant ($r=0.917***$). This implied that the sorption capacity of these soils were far undersaturated and strongly controlled the P activity in soil solution.

The n value, a kinetic parameter, which indicates the decrease of the radioactivity remaining in the solution over time, varied from 0.2 to 0.5. The n values decrease with an increase in C_p values ($r=-0.827**$) (Table 3). The set of n versus C_p values was described by

$$n = 0.504 - 3.028 C_p; r = -0.827**$$

A higher n value suggested a stronger P sorption capacity of the soils with time. The correlation between n and r_i/R was, therefore, also significant ($r=-0.790*$). Fardeau & Jappe (1976, 1978) observed that soils having an n value close to 0 are already rich in available P or may easily be enriched by phosphate fertilizers, while those having an n value close to 0.50 will fix much of the added phosphate fertilizers. The foregoing results indicate that with the exception of Kwaben soil series, the rest of the soils may be considered to have high ability to fix water-soluble phosphatic fertilizers.

The kinetic data derived from Eqs. 5 - 7 (Table 2) show that the mean exchange rate of phosphate

ions in solid-solution interface K_m was higher for soils with higher P-fixing capacity such as in Boi and Ankasa soil series, and the mean sojourn time of phosphate ions in solution T_m was shorter; the reverse was true for soils with low-fixing capacity as in Kwaben soil series. There was high, significant correlation coefficient between T_m and C_p ($r = 0.954***$). This may indicate that phosphate ions would stay longer if the soil had a higher content of phosphate in the solution. Both aspects would favour plant absorption. Similar results have been reported by Sat (1995) and Xiong, Fardeau & Zhigao (1997). The mean flux of exchange of phosphate ions between the soil solution and the solid phase of the soil (K_m and F_m) had significant correlation with the clay content (0.731* and 0.919***, respectively).

The compartments of soil phosphate pools

Table 2 shows the results of compartmental analysis for the six soils. These results show very large differences between the soils. Average values calculated from the six soils showed that 0.53 per cent of P in the total pool was exchangeable within 1 min, 10.76 per cent was in the E1min-1 d pool, 30.17 per cent in the E 1d-12 wk pool, 13.1 per cent in the E12wk-1yr pool, and 45.3 per cent in the E > 1yr pool. Similar results have been reported by Sinaj, Frossard & Fardeau (1997). From plant nutrition point of view, E > 1yr,

therefore, may be considered as the compartment which could hardly be made available for plant use, as the phosphate may be occluded or strongly bound to the inner surface of the soil absorbents. The diffusion of these phosphate ions to the outer surface or to the soil solution is very difficult. Distribution of exchangeable phosphate in all the five pools of isotopically exchangeable phosphate may reflect numerous exchange sites located on the oxides of the LAC acid soils, clay, and organic matter (Xiong *et al.*, 1997; Owusu-Bennoah *et al.*, 1997; Sinaj *et al.*, 1997).

Relationships between r_i/R , P_{max} and SPR

In this study, the relationships between r_i/R , P_{max} and $P_{0.2}$ (standard P requirement) were examined, since previous studies have observed good agreement between the kinetic parameter r_i/R and phosphate sorption capacity (P_{max}) estimated by classical Langmuir isotherm (Tran *et al.*, 1988; Morel *et al.*, 1989; Salcedo *et al.*, 1991; Frossard *et al.*, 1993). The three parameters showed wide variations among the six soils (Tables 1 and 2). r_i/R varied from 0.68 to 0.16 with a mean of 0.32; P_{max} varied from 17.2 to 9.3 mmol kg^{-1} , with a mean of 13.5 mmol kg^{-1} ; and standard P requirement at 0.2 mg l^{-1} P (SPR) from 6.0 to 1.5 mmol kg^{-1} , with a mean of 3.0 mmol kg^{-1} (Owusu-Bennoah *et al.*, 1997). High degree of correlation ($r = -0.805^*$) was observed between r_i/R and P_{max} , and between r_i/R and SPR ($r = -0.833^{**}$). The correlation coefficient between P_{max} and SPR was also highly significant (0.949***). Each of the three parameters, i.e. r_i/R , P_{max} and SPR, correlated significantly with soil pH and oxalate-extractable Al (Table 4), but not with either DCB-extractable Fe, clay or organic matter contents of the soils contrary to the findings of Frossard *et al.* (1993). The conclusion from the results, however, tend to confirm the observation by Frossard *et al.* (1993) that the phosphate sorption capacity generally can be expressed by any of these parameters.

In summary, it could be concluded that the isotopic kinetic models may be used to characterize the bioavailable P pools of tropical

TABLE 4
Correlation Coefficient between r_i/R , P_{max} , SPR, and Selected Soil Properties

Soil properties	r_i/R	P_{max}	SPR
Soil pH	0.746*	-0.963***	-0.853**
0.2 μ m clay	-0.588	0.802*	0.909**
Org. carbon	-0.556	0.682	0.489
Al ₀	-0.766*	0.885**	0.762*
Fe _d	-0.450	0.575	0.743

acid soils from Ghana. The model was also found to be appropriate in measuring the phosphate sorption capacity of the acid soils.

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