

AN ABSTRACT OF THE THESIS OF

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Twelve Sri Lankan Alfisols were characterized for P. Soils were incubated for three weeks with sufficient P applied (P2) to elevate soil solution P to 0.2 ug P/g solution as determined by sorption curves, with 75 percent of P2 (P1), and without P (P0). For P0 treatments, (a) organic P, (b) 0.5 M NaHCO₃ extractable "labile" inorganic P, (c) 0.1 M NaOH extractable "moderately labile" inorganic P, and (d) concentrated HCl extractable residual P fractions contained 44, 10, 13, and 22 % of total P respectively. Fifty five percent of applied P (P1 and P2) was recovered in the inorganic 0.5 M NaHCO₃ fraction and 25 percent in the inorganic 0.1 M NaOH fraction. Significant amounts of applied P were recovered in the organic fractions of some soils. Factor analysis of P0 treatment fractionation data

suggested that inorganic and organic fractions were separate equilibrium systems. Both inorganic and organic systems, however, contributed significantly to P uptake in a Neubauer experiment. Moreover, applied fertilizer P appeared to increase contributions of organic P to P uptake.

Correlation of Neubauer plant uptake data to Olsen, Bray 1, Bray 2, CAL, and Double acid extractable soil P showed that P uptake was most highly correlated to Double acid extractable P. Regression analysis suggested that the higher correlation was due to the Double acid extractant's ability to measure the organic P contribution to P uptake. Phosphorus sorption by the soils ranged from low to medium and was described satisfactorily by either the Langmuir two surface or the Freundlich equation but not by the Langmuir one surface equation. Correlation analysis indicated that oxalate extractable Fe was the soil component most active in P sorption. Although organic matter and pH were correlated to sorption capacity and may have been directly involved in the P sorption mechanisms they could also have covaried with other components responsible for sorption. Although citrate-dithionite extractable Fe did not appear to be involved in P sorption its high correlation with residual P fractions suggests an involvement with "slow" sorption. Phosphorous sorption had no apparent influence on P uptake by foxtail millet from the 12 soils in a Neubauer experiment.

Phosphorus Characterization in Sri Lankan Alfisols:
Sorptions, Fractions, Plant Availability and
Soil Test Suitability

by

Robert R. Sattell

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PHOSPHORUS CHARACTERIZATION IN SRI LANKAN ALFISOLS:

SORPTION, FRACTIONS, PLANT AVAILABILITY AND SOIL TEST SUITABILITY

CHAPTER I

INTRODUCTION

Soil P is naturally low in Sri Lankan Alfisols (Panabokke and Nagarajah, 1964) and has limited yields in rice (Panabokke, 1963; Takijma and Gunawardena, 1971) and maize (Nagarajah et al., 1973). Government P fertilizer subsidies have resulted in high P fertilization rates in some areas (Bandaranaike, 1963). Phosphorus added to the soil often exceeds crop removal (Amarasiri and Perera, 1975), resulting in P accumulation over years. Consequently, present recommended P rates may be too high and in some cases residual P may be able to satisfy plant P requirements. Conversely newly developed areas that have not been fertilized heavily with P may benefit from higher P applications. Research that helps to identify critical soil P levels will save scarce resources. Characterization of soil P fractions and P sorption, and identification of a soil extractant that correlates well to plant available P will help guide further field calibration and crop management studies.

Sri Lankan Alfisols (Reddish Brown Earths and Non-calciic Browns in the national classification) are found exclusively in the Dry Zone (mean annual rainfall less than 1500 mm) and occur in sequences on an undulating plain (Somasiri, 1985). Rhodustalfs, Halplustalfs and Tropaqualfs are typically found in well drained, moderately and imperfectly drained, and poorly drained portions of the catena respectively.

To date P correlation and calibration studies in Sri Lanka (Rodrigo, 1967; unpublished Kumaragamage and Keerthisinghe, 1987, Department of Soil Science, University of Peradeniya, Sri Lanka) have grouped Wet, Intermediate and Dry Zone soils together and focused on poorly or imperfectly drained paddy soils. Wet and Intermediate Zone soils are highly weathered and are dominated by Ultisols whereas Dry Zone soils are predominantly Alfisols. This difference likely affects soil P chemistry and justifies P characterization and correlation research on Alfisols as a discrete group. Moderately to well drained soils that produce cereals, pulses and oil crops as well as poorly drained rice soils were utilized in this study.

Based on work by Chang (1964) and unpublished reports by Nagarajah (1963, 1964, Division of Chemistry, Department of Agriculture, Ceylon), Rodrigo (1967) used Olsen P in a

calibration experiment involving 25 rice soils of the Wet, Intermediate and Dry Zones in which he successfully predicted the response of rice to P fertilization. Today the Olsen extractant is used predominantly in Sri Lanka to test for available P. Kumaragamage and Keerthisinghe (1987, unpublished, Department of Soil Science, University of Peradeniya, Sri Lanka) correlated Olsen P (0.5 M NaHCO₃ at pH 8.5; Olsen et al., 1954), Bray 2 P (0.03 M NH₄F + 0.100 M HCl; Bray and Kurtz, 1945), and CAL P (0.1 M Ca lactate + 0.1 M Ca acetate + 0.3 M acetic acid; Schuller, 1969) to cumulative P uptake over 72 days by rye grass in pots using four soils, one of which was from the Dry Zone. They found that the CAL method was superior although the other methods also gave significant correlations.

Plant available P can be determined by the P uptake in Neubauer experiments. Phosphorus fractionation of soils that have been incubated with and without added P reveal the fate of applied P fertilizers (Hedley et al., 1982). The fractions important to the P uptake process can be identified by regressing P uptake on soil P fractions. Bowman et al. (1978) and Sibbesen (1978) found that the anion exchangeable fraction was the most biologically available. Tiessen et al. (1984) reported that the quantity of labile P was controlled by inorganic surface adsorbed and secondary P in Mollisols and by organic P pools in more highly weathered Ultisols. Other researchers (Agboola and

Oko, 1976; Adepetu and Corey, 1976; Dalal, 1979; Sharpley, 1985) have concluded that organic P may play an important role in P uptake, especially in tropical soils.

Phosphorus sorption isotherm curves quantify the partitioning between solution P and sorbed P as P is added to a soil. The amount of P applied to a soil to meet plant needs most efficiently, as well as the method of application, will depend on the P sorption properties of the soil.

The Langmuir one surface, Langmuir two surface, and the Freundlich models are often fit to experimental P sorption data. Their suitability to describe sorption behavior of Sri Lankan Alfisols was tested. They have not been shown to be theoretically applicable to P sorption in the soil but rather, they are simply methods to describe and summarize data (Sposito, 1982). Descriptions of the models follow.

1. Langmuir 1 surface

$$P \text{ sorbed} = kbC(1 + kC)^{-1}$$

where k and b are curve fitting parameters and C is the concentration of P in the soil solution.

2. Langmuir 2 surface

$$P \text{ sorbed} = k_1 b_1 C (1 + k_1 C)^{-1} + k_2 b_2 C (1 + k_2 C)^{-1}$$

where k_1 , k_2 , b_1 , and b_2 are curve fitting parameters and C is the concentration of P in the soil solution.

3. Freundlich

$$P \text{ sorbed} = AC^n$$

where A and n are curve fitting parameters and C is the concentration of P in the soil solution.

Functions derived from the models were used to calculate descriptive sorption values. Descriptive sorption values were used in correlation and regression analysis with soil properties to identify those properties that affected sorption.

The objectives of research presented in chapter II were to 1) describe the distribution of soil P fractions and determine the fate of applied P , 2) determine which of several P availability indices best correlates to plant

available P, and 3) determine which P fractions most influence plant available P and extractable P.

The objectives of the research presented in chapter III were to 1) describe P sorption, 2) test three curve fitting models for goodness-of-fit to experimental sorption data, and 3) identify soil components and properties that affect P sorption.

CHAPTER II

PHOSPHORUS FRACTIONS, AVAILABILITY INDICES, AND PLANT UPTAKE

Methods

Sampling and P Treatments

Composite samples consisting of 15 cores to a depth of 15 cm were taken in 100 m² areas from 30 Dry Zone fields. Fields from two to four positions within a catena were sampled. Soils were from the Rhodustalf and Haplustalf great groups. Samples were air-dried and ground to pass a 2 mm sieve. On the basis of initial laboratory determinations 12 soils exhibiting a wide range of characteristics were selected for further study. Descriptive soil properties appear in Table 1.

Three P treatments were applied to the 12 soils. In treatment P₀, no P was applied. Treatment P₂ received sufficient P to raise the soil solution to 0.2 ug P/g solution. P₁ treatments received 75% of the P₂ level and on average resulted in a soil solution containing 0.1 ug P/g soil. Phosphorus quantities added to each soil (Table 2) to obtain desired soil solution concentrations were adjusted according to sorption isotherms determined by the method that Fox and Kamprath (1970) outlined. For each soil, the

Table 1. Descriptive data for soils.

Soil no.	Location ^a	Catena position	Texture ^b	%clay	pH	OM ^c	CEC ^d	Na+	K+	Ca ²⁺	Mg ²⁺
						mg/g		-----cmol (+) kg ⁻¹ -----			
1	MIA	middle	SCL	24.0	5.3	15	8.3	0.1	0.8	4.6	1.8
2	MIA	middle	SCL	25.0	4.8	13	7.3	0.1	0.7	3.3	1.3
3	AK	middle	SCL	26.0	5.9	17	11.7	0.1	0.5	7.9	2.3
4	AK	middle	SL	15.1	5.8	14	7.2	0.1	0.6	4.9	1.5
5	A18	lower	SCL	25.6	7.0	21	9.9	0.8	0.2	9.4	2.8
6	A18	middle	SCL	23.3	6.4	18	8.3	0.3	0.2	5.5	2.5
7	A18	upper	SCL	20.7	5.7	16	7.0	0.1	0.2	4.4	1.6
8	MICC	upper	SCL	31.3	6.7	14	10.7	0.3	0.3	5.7	3.5
9	MICC	middle	SCL	20.8	6.2	8	8.0	0.4	0.1	5.2	3.3
10	ARAL	upper	LS	8.2	5.3	14	3.9	0.1	0.1	2.0	0.6
11	G	lower	SCL	29.3	6.9	28	13.4	0.5	0.3	12.6	3.6
12	G	upper	SCL	28.3	6.1	19	12.4	0.3	0.5	7.7	3.2

- a. MIA is Maha Illuppallama Research Station, alley crop experiment; AK is Angunakolapelessa, Kurudana Dryland site; A18 is Angunakolapelessa, Tract 18; MICC is Maha Illuppallama Research Station, Catchment C; ARAL is Aralaganwila, new undeveloped station area; and G is Galnewa, Block 304.
- b. SCL, SL and LS refer to sandy clay loam, sandy loam and loamy sand respectively.
- c. OM refers to organic matter.
- d. CEC refers to cation exchange capacity.

Table 2. Phosphorus added to treatment P2 before incubation. Sufficient P was added to P2 to achieve a soil solution concentration of 0.2 ug P/g soil solution as determined by sorption isotherm curves.

Soil	P added to Treatment P2
	ug P/g soil
1	98
2	98
3	59
4	29
5	158
6	158
7	128
8	99
9	91
10	51
11	141
12	79

appropriate P quantity as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was dissolved in 50 ml H_2O and mixed well with 330 g soil. Soils were incubated near field capacity [incubated soils contained 28% moisture by volume assuming bulk densities of 1.5 g cm^{-3} and 5% moisture by volume when air dried; Joshua (1988) reported that bulk densities of typical Sri Lankan Alfisols were 1.53 g cm^{-3} and field capacities were 26% moisture by volume] in plastic bags for 3 weeks at 28 to 30 °C with occasional mixing and aeration. Then they were air dried, ground to pass a 2 mm sieve, and used immediately in the Neubauer P uptake experiment, and for Bray 1 and Olsen extractions, all of which were carried out at the Maha Illuppallama Research Station in Sri Lanka. Subsequently the soil incubation procedure was replicated in a constant temperature room (29 °C) at Oregon State University where the remaining laboratory analyses were completed. Samples for laboratory work were kept refrigerated until needed.

Laboratory Analysis

Soil texture (hydrometer method; Gee and Bauder, 1986), organic matter (wet digestion; Walkley Black, 1934), exchangeable cations (2 g soil extracted with 1 M ammonium acetate for 30 minutes), cation exchange capacity (ammonium acetate saturation and displacement by 0.1 M HCl), and pH (soil:0.01 M CaCl_2 , 1:1 by weight), are in Table 1. Extracts were analyzed with atomic absorption spectroscopy.

Phosphorus availability indices were determined by extracting all treatments with Olsen, Bray 1, Bray 2, CAL and Double acid extractants as outlined in Table 3. They are referred to as Olsen P, Bray 1 P, Bray 2 P, CAL P, and Double P.

Anion exchangeable P (Resin P) was determined using Dowex 2-X8 20 to 50 mesh resin saturated with bicarbonate ions. Thirty ml distilled water, 0.5 g 100-mesh soil, and 0.5 g resin were added to centrifuge tubes. After shaking for 16 hours the resin was separated from the soil by washing the soil through a 60 mesh sieve that retained the resin. Phosphorus sorbed to the resin was displaced by equilibration with 10% NaCl.

Separate soil samples were fractionated sequentially using the method from Hedley et al. (1982) with slight modifications. Samples were extracted sequentially (Fig. 1) with 0.5 M NaHCO₃ buffered to pH 8.5, 0.1 M NaOH, 0.1 M NaOH with sonication, 1 M HCl, concentrated HCl, and concentrated HCl + 30% H₂O₂. In an attempt to differentiate between inorganic and organic residual P, residual P was removed with two extractions (concentrated HCl; concentrated HCl and 30% H₂O₂) rather than the single extraction (H₂SO₄ and 30% H₂O₂) proposed by Hedley et al.. Concentrated HCl was intended to extract inorganic residual P from Ca-P minerals

Table 3. Methods used for P availability extractions.

P availability index	Extracting solution	Shaking time	Soil extract ratio	Reference
		s	g/mL	
Olsen	0.5 M NaHCO ₃ at pH 8.5	1800	1.5/30	Olsen et al (1954)
Bray 1	0.03 M NH ₄ F + 0.025 M HCL	60	1/7	Bray and Kurtz (1945)
Bray 2	0.03 M NH ₄ F + 0.100 M HCL	60	1/7	Bray and Kurtz (1945)
CAL	0.1 M Ca lactate + 0.1 M Ca acetate + 0.3 M acetic acid	7200	1/15	Schuller (1969)
Double acid	0.5 M HCl + 0.0125 M H ₂ SO ₄	300	2.5/10	Nelson et al. (1953)

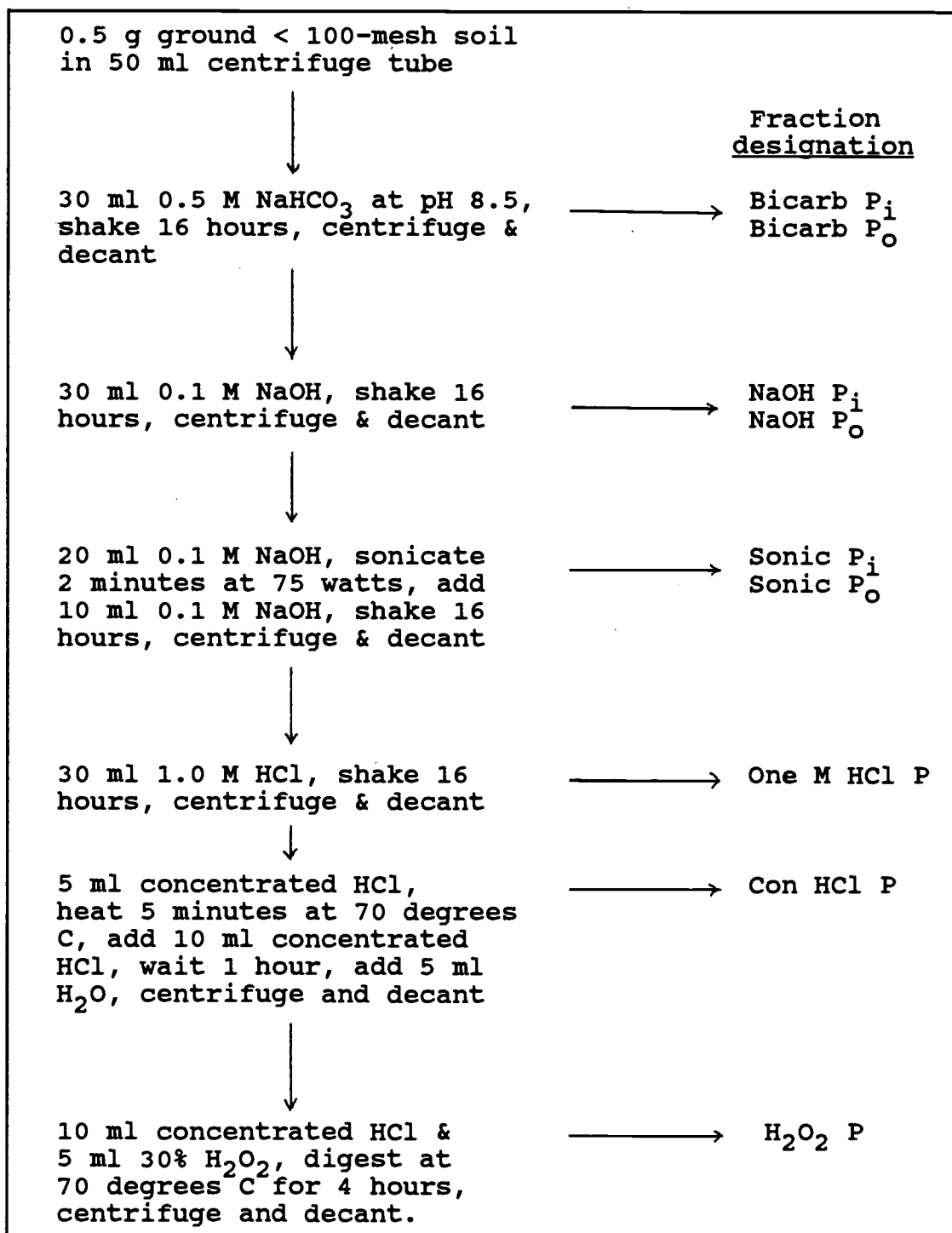


Fig. 1 - Modified Hedley sequential extraction.

or occluded P whereas digestion with concentrated HCl and 30% H₂O₂ was intended to remove residual organic P. Phosphorus extracts from the fractionation are referred to as Bicarb P, NaOH P, Sonic P, One M HCl P, Con HCl P, and H₂O₂ P.

The 0.5 M NaHCO₃, 0.1 M NaOH, and the 0.1 M NaOH sonicate extracts were analyzed for total P (EPA, 1986) as well as inorganic P. Organic P was calculated as the difference between total and inorganic P. When both inorganic and organic fractions were determined on an extract, subscripts i and o were used to differentiate between them.

Phosphorus in all extractions and fractions except the CAL extract was determined using the methods of Murphy-Riley (1962) and a Baush & Lomb flow through spectrophotometer. Extracts were neutralized when necessary using p-nitrophenol indicator. For extracts high in dissolved organic matter, P was determined immediately after neutralizing to minimize the possibility that inorganic P might precipitate with organic matter as described by Holtzclaw et al. (1978). When precipitation did occur during color development, test tubes were centrifuged and the color intensity of the supernatant read. The CAL extract was analyzed using the stannous chloride method. All analyses were carried out in duplicate.

Neubauer P Uptake Experiment

A greenhouse experiment using the methods of Neubauer (1923) as modified by Al-Abbas and Barber (1964) was conducted to determine P uptake by foxtail millet (*Setaria italica* (L.)) in the P0, P1, and P2 treatments of the soils. One hundred and fifty g of acid washed sand was placed in the bottom of 0.5-l plastic containers. A layer of 100 g air dried soil was placed over the sand, and another 50 g sand covered the soil and filled a 1 cm diameter drainage core through the soil to the sand below. One hundred foxtail millet seeds dusted with Captan (N-trichloromethylmercapto-4-cycloheximide-1,2-dicarboximide) to prevent fungal growth were planted in each pot with the aid of a planting mould. Seeds were then covered with an additional 50 g of sand. Twelve blank Neubauer pots (four per block) were filled the same as pots for other treatments except that 100 g acid washed sand was substituted for soil. All pots received forty ml water containing 12,500 ug N as urea and 12,500 ug K as KNO₃. All nutrients were reagent grade. Three replicates were arranged in a randomized complete block design. Pots were covered with plastic to inhibit evaporation.

After germination the plastic was removed and the pots were moved to a greenhouse bench. Moisture was maintained at 55 ml/pot by watering twice daily with distilled water.

Twice during the growing period 5 ml of a NH_4NO_3 solution containing 7,500 ug N were added to the pots. Blocks and treatments within blocks were rotated every 5 days. After 25 days the plants were harvested by washing sand and soil from the roots. Plant material was dried (80°C) to constant weight, ground, ashed, dissolved in HCl and analyzed for P.

Statistical Methods

Data were analyzed with version 6.03 of the SAS statistical package (SAS Institute Inc., 1987). Procedures CORR and FACTOR were used for correlation and factor analysis and procedures RSQUARE and REG were used for regression analysis.

Results and Discussion

Table 1 indicates that the soils were neutral to slightly acid and had low cation exchange capacities. Textures were sandy clay loams or coarser and organic matter ranged from 1 to 2 %.

Soil P Fractions

Ranges and means from the Hedley fractionation procedure for the P₀ treatments are presented in Table 4. Mean organic P (Bicarb P₀, NaOH P₀ and Sonic P₀) accounted for 44% of mean total P, of which the majority was found in the moderately available NaOH P₀ fraction. The "labile" Bicarb P_i and "moderately labile" NaOH P_i fractions were of approximately equal size comprising 10 and 13% of total P respectively. Calcium bound P and physically inaccessible P represented by the One M HCl and Sonic P_i fractions respectively contributed little to total P. The majority of the residual P (23% of total P) was extracted in the Con HCl P fraction.

Hedley et al. (1982) and Tiessen et al. (1984) reviewed the literature regarding the source of extracted P for each fraction. They reported that Resin P is biologically available P. Bicarb P_i and Bicarb P₀ are thought to be labile P sorbed on sesquioxide and Ca surfaces. Bicarb P₀ is easily mineralizable. NaOH P_i and P₀ are chemisorbed to Fe and Al surfaces and are more stable than Bicarb fractions. Sonic P_i and P₀ are hypothesized to be physically inaccessible P and One M HCl P is predominantly Ca bound P though it may contain occluded P in weathered soils.

Table 4. Phosphorus means and ranges from modified Hedley fractionations and from P availability indices determined on 12 soils.

	Treatment P0 ^a		Treatment P1		Treatment P2	
	Mean	Range	Mean	Range	Mean	Range
----- ug/g -----						
<u>Modified Hedley fractions</u>						
Resin P	14	9-28	49	24-74	64	32-97
Bicarb P _i	18	12-29	57	30-78	73	41-109
Bicarb P _o	8	4-13	10	5-17	11	6-21
NaOH P _i	24	14-42	45	15-73	50	17-77
NaOH P _o	61	32-100	66	30-104	68	30-106
Sonicate P _i	5	1-11	7	1-11	7	1-11
Sonicate P _o	15	6-25	14	5-25	13	6-23
One M HCl P	10	4-14	13	6-21	15	6-25
Conc HCl P	42	8-60	45	10-61	47	11-68
H ₂ O ₂ P	8	3-12	8	1-13	7	1-11
Total P ^b	190	127-228	263	193-210	289	218-344
<u>P availability indices</u>						
Olsen	5	2-11	27	15-39	36	20-56
Bray 1	5	1-16	27	14-44	36	20-54
Bray 2	8	3-24	35	24-53	47	32-70
CAL	3	0-8	16	12-25	28	16-43
Double	4	1-15	19	11-27	27	16-38

- a. P0, P1, and P2 refer to P applications. For P2 sufficient P was added to elevate soil solution P to 0.2 ug P/g solution. Seventy five percent of P2 was applied to P1 treatments. No P was applied to P0 treatments.
- b. Calculated as the sum of all fractions except Resin P.

The high degree of covariance among fractions is evident from Table 5. Given these high correlations, factor analysis was used to identify three hypothetical variables, or factors, that grouped the nine sequentially extracted fractions of the P0 treatments by their covariances. Factor loadings (Table 6) indicate the degree of correlation between the factors and each fraction. The inorganic fractions Bicarb P_i, NaOH P_i and Sonic P_i were associated with the first factor, the organic fractions with the second factor and residual fractions (Con HCl P and H₂O₂ P) with the third factor. One M HCl P was not associated with any factor. These results are similar to those obtained by Tiessen et al. (1984) from an analysis of 168 USDA-SCS benchmark soils from the USA representing eight soil orders of the Soil Taxonomy. Tiessen et al. (1984) stated that the high degree of covariance of fractions within a system suggests that the fractions are in equilibrium with each other.

To select four soils representing the range of labile inorganic and organic P fractions among the twelve soils, factor analysis was repeated with the One M HCL P, Conc HCl P and H₂O₂ P fractions excluded. The factor scores for each soil were plotted in a scatter diagram (Fig. 2) which was used to identify four soils contrasting in the inorganic and organic fractions. Soil 10 was chosen over other soils with

Table 5. Pearson's correlation coefficients for P fractions of P0 treatments (no P applied). Values with P <0.05 are presented in bold type.

	Res P ^a	B P _i	B P _o	NH P _i	NH P _o	S P _i	S P _o	1MHCl	Con	H2O2
Res P		0.89^b	-0.41	0.79	-0.05	0.73	-0.04	0.25	0.15	0.08
B P _i			-0.46	0.74	-0.15	0.66	-0.28	0.33	0.02	0.11
B P _o				-0.41	0.83	-0.59	0.63	-0.37	-0.37	-0.43
NH P _i					-0.21	0.80	0.08	-0.08	0.23	0.19
NH P _o						-0.52	0.70	-0.19	-0.52	-0.64
S P _i							-0.25	0.04	0.55	0.40
S P _o								-0.27	0.05	-0.18
1MHCl									0.20	0.17
Con										0.84

a. Res, B, NH, S, 1MHCl, Con, and H2O2 refer to Resin P, Bicarb, NaOH, Sonic, One M HCl P, Con HCl P and H₂O₂ P respectively.

b. For $r < 0.58$, $P > 0.05$; for $0.58 < r < 0.70$, $0.01 < P < 0.05$; for $0.69 < r < 0.81$, $0.001 < P < 0.01$; for $r > 0.80$, $P < 0.001$.

Table 6. Factor loadings for P fractions of P0 treatments (no P applied) generated by the procedure SAS FACTOR.

Fraction	Factor1	Factor 2	Factor 3
Bicarb Pi	0.88^a	-0.29	-0.14
Bicarb Po	-0.41	0.74	-0.36
NaOH Pi	0.96	0.11	0.15
NaOH Po	-0.14	0.70	-0.61
Sonic Pi	0.82	-0.17	0.43
Sonic Po	-0.04	0.92	0.00
One M HCl P	0.02	-0.56	0.03
Con HCl P	0.13	0.00	0.95
H2O2	0.08	-0.18	0.90

a. Values greater than or equal to 0.70 are highlighted.

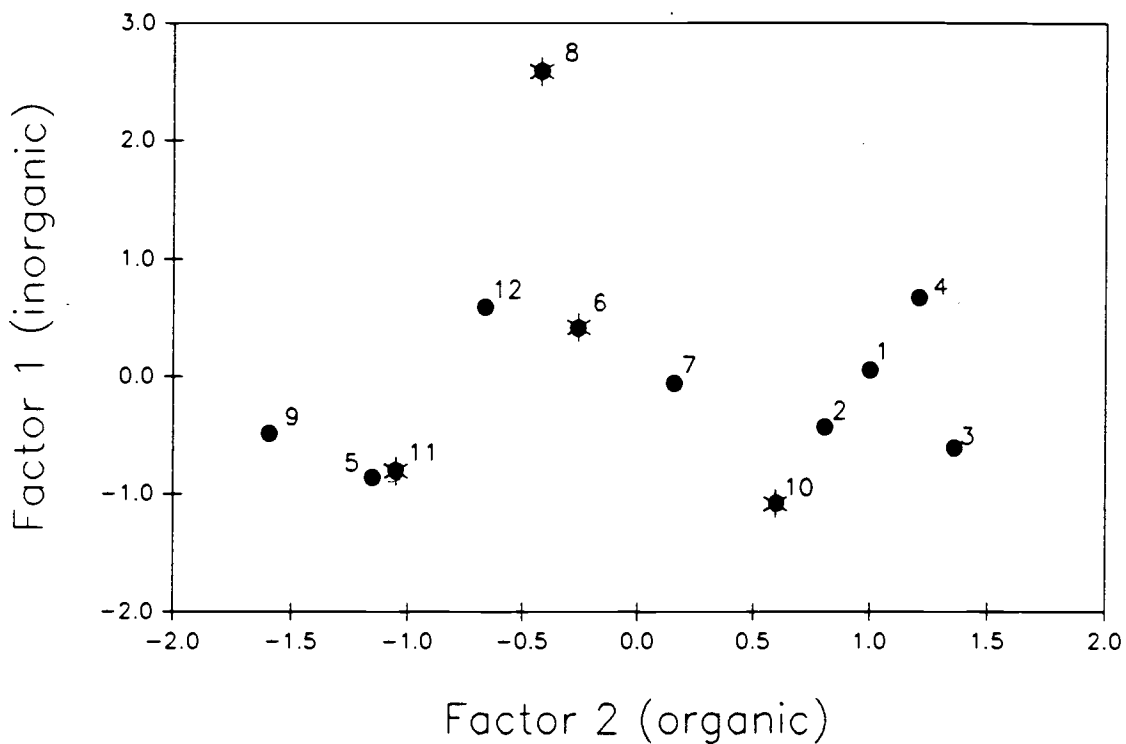


Fig. 2. Scatter diagram of factors produced by factor analysis representing inorganic and organic P forms. Numbers refer to soils. Starred data points represent soils used in distribution and fate of applied P bar graphs (Fig.'s 3 and 4).

higher Factor 2 scores because it was different than all other soils with respect to texture, CEC, extractable cations, and oxalate and citrate dithionite Fe and Al. Fig. 3 illustrates the distribution of soil P in the P₀ treatment of these four soils. Major differences were observed in the NaOH P_i fraction between soils 6 and 8 and soils 10 and 11, and in the NaOH P_o fraction between soil 10 and soils 6, 8 and 11. Soil 10 had very little Con HCl P in comparison to the other soils but this fraction was not expected to contribute significantly to P uptake in the short term because of its residual nature. Differences among soils in other fractions were relatively minor.

The fate of P applied to the P₁ treatments of the four representative soils after three weeks incubation is summarized in Fig. 4. The percentage of P added in the P₁ treatment that was recovered in a particular fraction, F, was defined as Recovered P and calculated as

$$\text{Recovered P} = \frac{F_{P_1} - F_{P_0}}{\text{sum over all F of } (F_{P_1} - F_{P_0})} \times 100\%$$

where F represents a fraction from the sequential fractionation, F_{P₁} is the P in fraction F of treatment P₁, and F_{P₀} is the P in fraction F of treatment P₀.

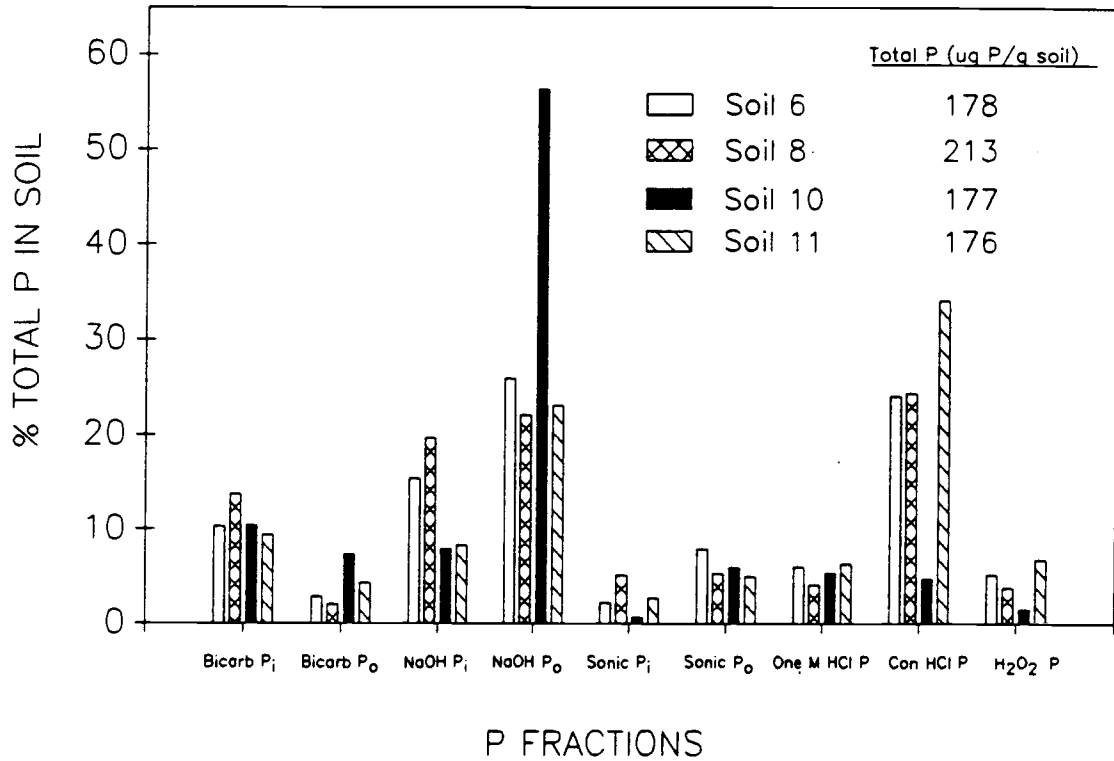


Fig. 3. Phosphorus fraction distribution in P₀ treatments (no P applied) of four representative soils.

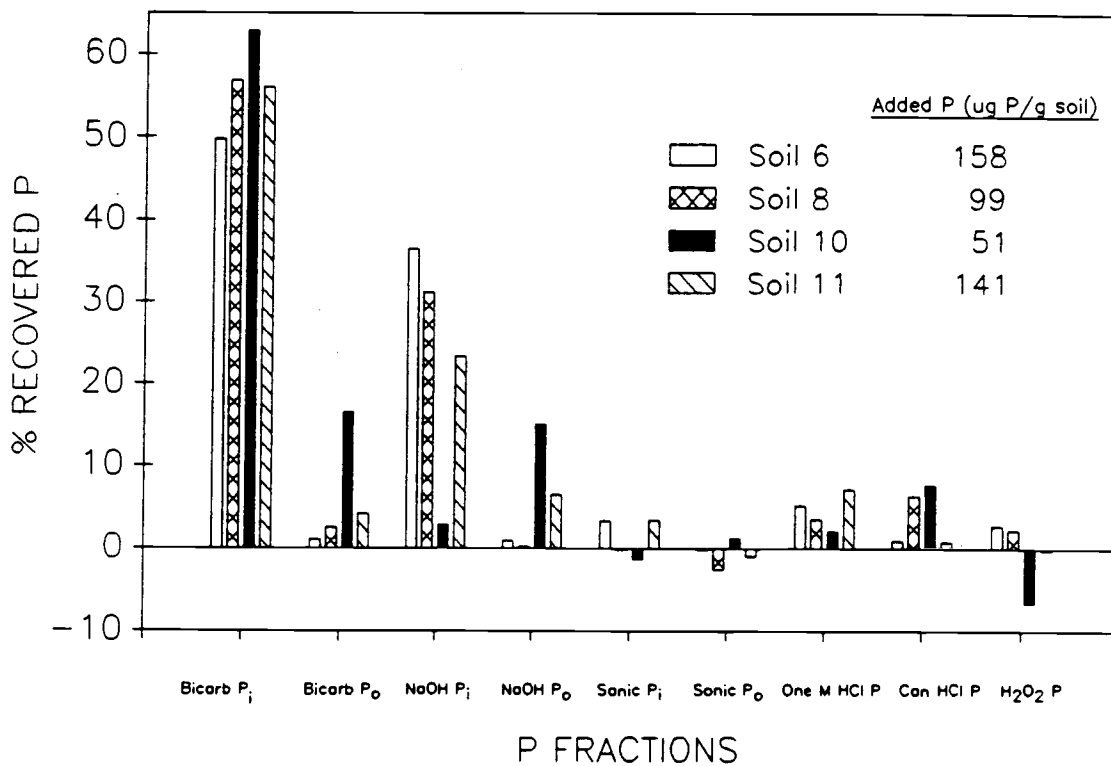


Fig. 4. Fate of P applied to P_i treatments of four representative soils after a three week incubation.

Over half of the applied P was recovered in the Bicarb P_i fraction and 20-30 % of applied P was recovered in the NaOH P_i fraction in all soils but soil 10. The P recovered in the Bicarb P_i and NaOH P_i fractions was probably sorbed on Fe and Al oxides (Chang and Juo, 1963; McLaughlin et al., 1977). For five soils (soils 3,4,7,10,12), 18-32% of P added in the P1 treatment was recovered in the Bicarb P_0 and NaOH P_0 fractions. Added P recovered in organic fractions was either incorporated into the microbial biomass (Hedley et al., 1982; Bowman and Cole, 1978) or reacted directly with organic matter (Harter, 1969). As expected, only small amounts of P were recovered in the sonicate or residual fractions. It is likely that with time however, more of the applied P would move into the less labile fractions. The fate of P applied to P2 treatments was similar to that of P applied to P1 treatments.

Total Plant Uptake versus Extracted Soil P

Total plant P was determined as the total P in the roots and shoots of all plants in a Neubauer pot and will be referred to as Plant P. Plant P means for treatments P0, P1, and P2 were 1586, 2427, and 2745 ug P/pot respectively. The 12 blanks derived P from the seed and acid washed sand and had a mean Plant P of 1534 ug P/pot (SE=117). P uptake means (Plant P minus blank P) for treatments P0, P1, and P2 were 52, 893, 1212 ug P/pot respectively.

Phosphorus treatments significantly increased Plant P variance (Bartlett's test, $P < 0.05$). Therefore a log transformation was applied to Plant P data (Bartlett's test after transformation, $P > 0.97$). This transformation was applied to total uptake without adjusting for P in blanks because the adjusted values were negative in 20 of the P0 pots. These were cases in which extractable soil P was low (Double acid P < 3.8 , mean = 2.3, Olsen P < 6.5 , mean = 4.5) and may be the result of P efflux from the plant to the soil solution. Moores (1938) commented that after the adjustment for P in blanks the Neubauer method often gave zero P uptake values for soils low in P.

The means and ranges of measured P from P availability indices are presented in Table 4. Correlation coefficients between P availability indices and log Plant P are presented in Table 7. In all groupings of treatments, Double P consistently exhibited the highest correlation with Plant P, and Olsen P the lowest. The correlation difference was especially marked when only treatments receiving additions of P were considered. In that case Olsen P was not significantly correlated to Plant P while Double P had a correlation of 0.71 ($P < 0.001$). Scatter plots and regression lines of Double P and Olsen P vs log Plant P appear in Fig. 5.

Table 7. Pearson's correlation coefficients between P availability indices and log Plant P from Neubauer experiment.

P availability index	No P added treat 0	P added treat 1 & 2	All treatments treat 0, 1 & 2
Olsen	0.52	0.28	0.77***
Bray 1	0.68*	0.48*	0.85***
Bray 2	0.72**	0.43*	0.85***
CAL	0.68*	0.45*	0.80***
Double acid	0.74**	0.71***	0.90***

*, **, *** Significant at the 0.05, 0.01 and 0.001 levels, respectively.

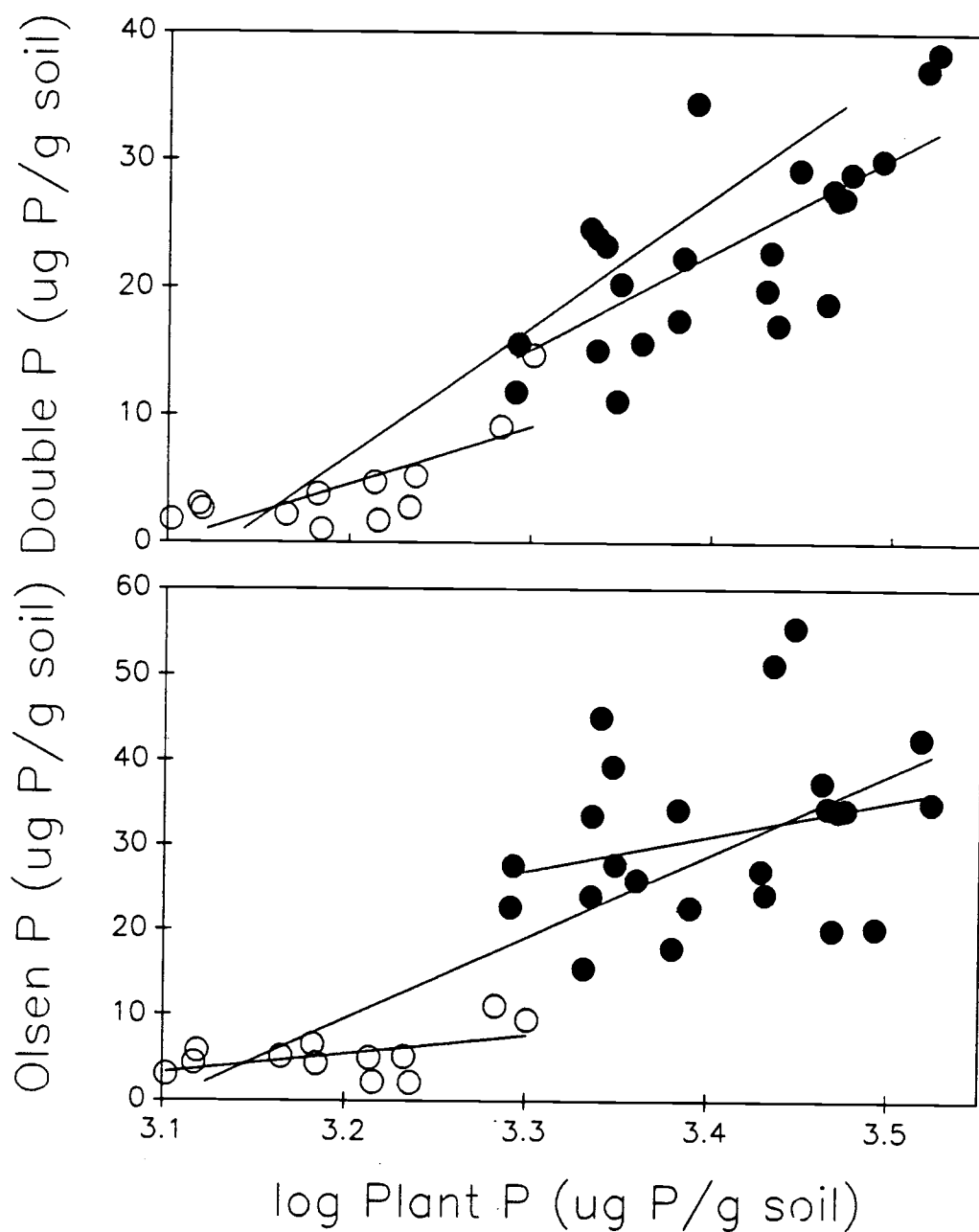


Fig. 5. Scatter diagram of Double P and Olsen P with log Plant P. Open circles represent P0 treatments (no P applied) and filled circles represent P1 and P2 treatments (P applied). Lines represent regressions for P0 treatments only, P1 and P2 treatments combined, and all treatments combined.

Applied P, which differed for soils (Table 2), did not correlate significantly to log Plant P ($r=0.11$, $P=0.60$) indicating that applied P reacted differently among soils and/or that native sources of P contributed significantly to P uptake. Applied P did correlate significantly with Olsen P ($r=0.92$, $P<0.001$) and Resin P ($r=0.88$, $P<0.001$) which were both highly correlated to Bicarb P_i (Fig. 6). Bicarb P_i is considered to be the "labile" P fraction. The bicarbonate extractant is especially efficient at removing P sorbed on Fe and Al oxides (Chang and Juo, 1963), the likely site of much of the sorbed added P. However the poor correlation of Olsen P and Resin P with log Plant P (Fig. 6) indicates that they extracted P not available to plants, or failed to extract P that was available to plants, or both. Double P was not significantly correlated to applied P or Bicarb P_i but was highly correlated to log Plant P ($r=0.71$, $P<0.001$) (Fig 6). The double acid extractant removed different proportions of the applied P and Bicarb P_i fraction in different soils and/or extracted varying amounts of P fractions other than the Bicarb P_i fraction that contributed significantly to P uptake.

To identify soil fractions that contributed to Plant P and extracted soil P in P0 treatments, treatments P1 and P2 combined, and all treatments combined, all possible regressions were generated for the models

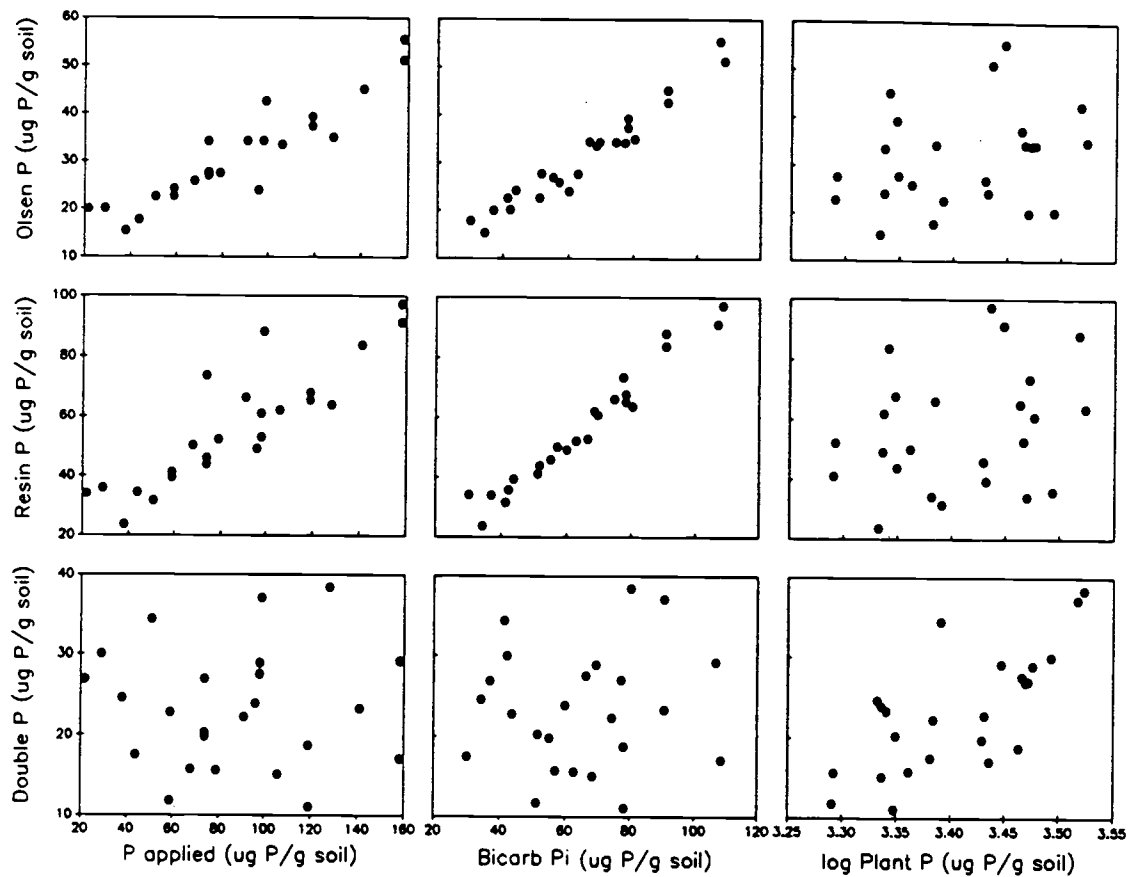


Fig. 6. Scatter plots of Olsen P, Resin P, and Double P with P applied, Bicarb P_i , and log Plant P.

log Plant P = fn(Bicarb P_i, Bicarb P_o, NaOH P_i,
NaOH P_o, Sonic P_i, Sonic P_o, One M HCL)

extracted soil P = fn(Bicarb P_i, Bicarb P_o,
NaOH P_i, NaOH P_o, Sonic P_i, Sonic
P_o, One M HCL)

Because Double P was more highly correlated to log Plant P than other P availability indices, results from the models log Plant P = fn(fractions) and Double P = fn(fractions) were of the most interest. Significant regressions from those models are presented in Table 8 while other results are discussed only. The best single independent variable regressions for either of these two dependent variables always selected an inorganic fraction, and in four of the five cases this was Bicarb P_i. The best two variable regressions selected both an inorganic fraction, usually Bicarb P_i, and an organic fraction, usually NaOH P_o, to predict log Plant P and Double P. The only exception was the two variable regression on log Plant P from the P₀ treatments. Two organic fractions, Bicarb P_o and NaOH P_o were selected for this model. The additional explained sum of squares gained by the inclusion of the NaOH P_o fraction in the log Plant P and Double P models is evidence that this fraction contributed to P taken up by the plants and P extracted by the double acid method. Standardized regression coefficients (Table 8) suggest the organic

Table 8. Standardized coefficients of significant one and two variable regression models for log Plant P and Double P, using P fractions (excluding Con HCl P and H₂O₂ P) as potential independent variables. Variables not selected in the regression model are indicated with a dashed line.

Dependent variable	Independent variables				R ²
	Bicarb P _i	Bicarb P _o	NaOH P _i	NaOH P _o	
<u>Treatment P0 only (no P applied)</u>					
log Plant P	0.58	----	----	----	0.34*
log Plant P	----	-1.25	----	1.22	0.52*
Double P	0.66	----	----	----	0.44*
Double P	0.75	----	----	0.57	0.76**
<u>Treatments P1 and P2 only (P applied)</u>					
log Plant P	----	----	0.44	----	0.19*
log Plant P	----	----	0.79	0.64	0.47**
Double P	0.74	----	----	0.91	0.42**
<u>Treatments P0, P1 & P2 (all treatments combined)</u>					
log Plant P	0.74	----	----	----	0.55***
log Plant P	----	----	0.69	----	0.48***
log Plant P	0.87	----	----	0.45	0.74***
log Plant P	----	----	0.83	0.45	0.66***
Double P	0.68	----	----	----	0.47***
Double P	----	----	0.56	----	0.32***
Double P	----	----	----	0.35	0.12*
Double P	0.84	----	----	0.55	0.75***
Double P	0.77	0.49	----	----	0.70***
Double P	----	0.62	0.78	----	0.66***

*,**,*** significant at the 0.05, 0.01, and 0.001 levels, respectively.

fractions contributed 30 to 50 % of the P taken up by the foxtail millet in all treatments.

The best 2 variable models regressing Bray 1 P, Bray 2 P and CAL P on P fractions also included Bicarb P_i and NaOH P_o . However NaOH P_o did not explain as much of the variability within those extracts (as determined by the standardized coefficients) as it did within the Double P extract. The best significant single variable regression model for Olsen P in the P0 treatment group selected the Bicarb P_i fraction ($R^2=0.63$, $P<0.01$) as did the only significant regression models for Olsen P in the other two treatment groupings (P1 and P2 treatments combined, $R^2=0.95$, $P<0.001$; all treatments combined, $R^2=0.97$, $P<0.001$). Given that only extraction time and soil:solution ratios differ between the Olsen extraction and the Bicarb P_i fraction, this was not unexpected. Apparently Olsen P failed to predict plant available P in this experiment because of its inability to measure the contribution from organic fractions.

Many workers have reported that organic P plays a significant role in P uptake, especially in the tropics. Agboola and Oko (1976) reported that P uptake by rice in a pot experiment on Nigerian soils was more correlated to organic P than to Bray 1 P though both were significant.

They concluded that both inorganic and organic P contributed to P uptake.

Adepetu and Corey (1976) reported that 80% of the variation of P uptake in 4 successive maize crops from pots of Southern Nigerian soils could be explained by mineralized P. Mineralized P was highly correlated to organic P. When Bray 1 P was included in a multiple regression with organic P, prediction of P uptake for the first crop was improved but prediction of the cumulative uptake for four crops was not. Organic P in the test soils may have built up as they had not been cultivated for several years.

Dalal (1979) found that solution organic and inorganic P (0.01 M CaCl₂ extracted) levels both decreased considerably in the presence of growing plants and concluded that solution organic P made a significant contribution to P uptake.

Sharpley (1985) observed the seasonal variation of inorganic and organic P in the field using 20 soils from Texas and Oklahoma. Organic P was found to be greater during the winter than during the summer because of additions of plant residues in the fall and lower mineralization rates in the winter. Organic P variation was explained by changes in the moderately labile organic P pool, while labile and resistant pools remained constant.

Sharpley (1985) hypothesized that the moderately labile organic P pool can rapidly replenish the labile organic P pool as it mineralizes in response to plant P uptake. He also found that organic P can contribute significantly to Bray 1 P, especially in unfertilized soils.

The regression analyses for Plant P indicated that organic P contributed significantly to P uptake in both the no P added (P₀) and P added (P₁ and P₂) treatments. If organic P contributed one third of P uptake in the P added treatments as suggested by standardized regression coefficients, then 300 ug P/pot came from organic fractions. This value is six times greater than the mean net P uptake of P₀ treatments [(mean Plant P of P₀ treatments) - (mean Plant P of blank pots)], or 50 vs 300 ug P/pot.

Applied P may have increased the P mineralization rate, and in effect made more organic P available. Although Wier and Black (1968) found no increase in P mineralization with applications of inorganic P in organic and mineral soils of the USA, others have reported this phenomenon. McCall et al. (1956) found that organic P mineralization in a Histosol during a 2 to 4 month incubation increased as applied monocalcium phosphate increased. Acquaye (1963) incubated several Ghana soils (top 5 cm) without P and with 2 levels of added P at 27 °C for 28 days. Mineralization increased as applied P increased. Mineralization of organic P was

significantly different between no P added and P added treatments and between different levels of P. Enwezor (1966) measured P mineralization over 12 weeks on a coarse textured Nigerian soil to which 0, 50 and 150 ug P/g soil had been added. Some samples were amended with additions of organic material. Mineralization was elevated in treatments receiving P. For the first 3 weeks P was immobilized in soils amended with organic materials but thereafter it mineralized at a greater rate than that of unamended soil. The effects of applied P on organic P mineralization reported by Enwezor and Acquaye were sufficiently large to explain the results found in this experiment.

The fractionations indicated that part of the added P may have been immobilized during incubation. The microbial biomass produced by added P may have had a lower C:P ratio than original organic matter, increasing its subsequent mineralization rate (Thompson et al., 1954). Air drying the incubated soils before the Neubauer experiment may have lysed microbes and increased the mineralization rate. Abbott (1978) reported that P uptake from soils incubated for 20 days at 24 to 35 °C was lower than P uptake from nonincubated soils because microbes immobilized soil P. However drying soils before the subsequent crop increased organic P mineralization especially in the incubated soil. Because more P was presumably immobilized by microbes in the

P added treatments, more P would be available to plants upon lysing.

Resin P has been shown to be correlated to plant available P (Bowman, et al., 1978; Sibbensen, 1978). In this experiment Resin P was highly correlated to Bicarb P_i ($r=0.99$, $P<0.001$) but was not significantly correlated to Plant P. Apparently Resin P does not measure organic contributions to P uptake. Organic P fractions appear to have contributed significantly to P uptake in this experiment even when Resin P levels were high.

Resin P may have overestimated the inorganic P available to the plant root. According to Sibbensen (1978), phosphate desorption is the rate limiting step in anion exchange extraction. For inorganic P uptake from the soil, however, it is likely that the rate limiting step is the diffusion of phosphate to the plant root (Mengel and Kirkby, 1987).

If organic P is more available than inorganic P it may continue to be an important contributor to Plant P even when fertilizer P is added to the soil. Because inorganic P concentrations in soil solution are very low, contributions of mass flow to inorganic P uptake are small. Organic P forms are often present in the soil solution at higher concentrations, and are more mobile than inorganic forms

(Hannapel et al., 1964). If soil solution organic P concentrations are high, mass flow may become an important factor in moving P to the plant root. Data reported by Furlani et al. (1987) agree with the notion of greater mobility, but also suggest that organic P may be taken up more readily for other reasons. They observed that P from organic compounds (ethylammonium, glyceryl, and phenyl phosphates) was more available to sorghum than P from inorganic compounds (potassium dihydrogen, tribasic and pyro calcium, ferric, and aluminum phosphate). Sorghum supplied with organic P took up more P than did plants supplied with inorganic P, whether in hydroponic or soil culture.

Conclusions

Analysis of P fractionation data suggested that inorganic and organic fractions are in equilibrium among themselves. Both inorganic and organic systems contributed significantly to P uptake, corroborating evidence of other researchers that organic P is an important source of plant P in tropical soils. Application of fertilizer P appeared to increase contributions of organic P to P uptake. Resin P and Olsen P measured only inorganic contributions to P uptake and were poorly correlated to log Plant P. Bray 1, Bray 2, CAL, and Double P measured inorganic and organic contributions to P uptake and all were better correlated to log Plant P than Olsen or Resin P. Double P correlated best to log Plant P

and should be evaluated along with Olsen P (the extractant presently used in Sri Lanka) in future calibration experiments on Sri Lankan Alfisols.

CHAPTER III

PHOSPHORUS SORPTION AND SOIL PROPERTIES

Methods

Twelve Sri Lankan Alfisols were sampled and analyzed for selected soil properties. Descriptive soil data and a summary of sampling methods are in chapter II of this text. Citrate-dithionite extractable Fe and Al (Olsen and Ellis, 1982) and oxalate extractable Fe and Al [method of Tamm (1932) as modified by McKeague and Day (1966), and 1:100 soil:extractant ratio by weight] were determined with atomic absorption spectroscopy. They are identified with the subscripts d and o respectively (Fe_d , Al_d , Fe_o , Al_o).

For each soil, a P sorption isotherm curve was determined using the methods of Fox and Kamprath (1970). Anion exchangeable P (Resin P) in chapter II was added to P sorbed to account for native sorbed P. The procedure NLIN from the SAS statistical package (SAS Institute, 1987), a nonlinear regression method, was used to fit P sorption data to the Langmuir one surface, Langmuir two surface, and Freundlich sorption isotherm models.

The residual root mean square error (RMSE) was proposed by Kinniburgh (1986) as a measure of goodness-of-fit for P

sorption curves estimated by nonlinear regression. It is defined as

$$\text{RMSE} = [\text{RSS}(\text{o-p})^{-1}]^{1/2}$$

where RSS is the residual sum of squares from the nonlinear regression, o is the number of observations and p is the number of parameters in the model. Lower RMSE values are indicative of better fit to experimental data. The RMSE was calculated for the three curve fitting models on each of the 12 experimental sorption isotherms.

Results and Discussion

Citrate-dithionite and oxalate extractions are used to characterize the amorphous-crystalline nature of Fe and Al in sesquioxides. Oxalate extracts only amorphous sesquioxides (Mckeague and Day, 1966; Schwertman 1964) while citrate-dithionite extracts amorphous, crystalline, and slightly crystalline sesquioxides. Amorphous oxides are most active in P sorption (Ballard and Fiskell, 1974) although the slightly crystalline phase of the citrate dithionite Fe and Al oxides also participate in P retention.

Citrate-dithionite and oxalate extractable Fe and Al values appear in Table 9. Extractable Fe values were higher than corresponding extractable Al values except that Al₀ was

Table 9. Extractable Fe and Al values.

Soil	Fe _d ^a	Al _d	Fe _o	Al _o
	----- mg/g soil -----			
1	18.8	1.9	2.2	0.8
2	17.7	1.9	1.9	0.9
3	18.1	2.1	0.9	0.8
4	7.8	1.1	0.9	0.6
5	15.7	1.6	3.9	0.8
6	13.1	1.5	2.7	0.6
7	12.6	1.7	1.2	0.6
8	17.4	2.1	1.9	0.9
9	9.8	1.1	2.4	0.6
10	2.2	1.2	0.3	1.5
11	14.9	1.8	2.0	0.9
12	16.3	1.3	3.0	1.0

a. Fe_d, Al_d, Fe_o, and Al_o refer to citrate dithionite extractable Fe and Al, and oxalate extractable Fe and Al respectively.

higher than Fe_o in soil 10. Soil 10, a Non-calcic Brown soil in the national classification, had much less Fe_d and Fe_o than the other soils. Citrate-dithionite Fe levels in the twelve Alfisols were much higher than Fe_o levels, indicating that there were more crystalline than amorphous Fe oxides. Mean values for the 12 Sri Lankan Alfisols were $Fe_d = 13.7$, $Fe_o = 1.9$, $Al_d = 1.6$, and $Al_o = 0.8$ mg/g soil. Loganathan and Fernando (1980) reported values for two Sri Lankan Alfisols [Reddish Brown Earth, $Fe_d = 8.7$, $Fe_o = 3.8$, $Al_o = 3.2$ mg/g soil; Non-calcic Brown, $Fe_d = 2.8$, $Fe_o = 1.2$, $Al_o = 1.0$ mg/g soil]. Keramidas and Polyzopoulous (1983) reported a mean value of $Fe_d = 11.4$ for 14 Greek Alfisols, while Torrent (1987) reported mean values of $Fe_d = 50$, $Fe_o = 2.1$, and $Al_o = 2.6$ for 13 Spanish Alfisols.

Nonlinear regression parameters for the three curve fitting models and RMSE values appear in Tables 10 and 11 respectively. Using RMSE as the criterion for fit, the Langmuir two surface model fit best for eight soils and the Freundlich model fit best for the remaining four. For all soils the Langmuir two surface and the Freundlich models fit the data much better than the Langmuir one surface model. The difference in curve fitting ability was apparent when estimated curves of a representative soil (soil 6) were graphed with experimental data (Fig. 7). The Langmuir one surface model underestimated sorbed P at low and high soil solution P concentrations and overestimated sorbed P at mid

Table 10. Parameters generated by nonlinear regression for the Langmuir one surface, Langmuir two surface, and Freundlich models.

soil	<u>Langmuir one</u>		<u>Langmuir two</u>				<u>Freundlich</u>	
	b	k	b1	b2	k1	k2	A	n
1	283	1.15	130	275	7.60	0.120	143	0.289
2	294	1.59	111	267	20.71	0.255	160	0.287
3	210	1.65	84	228	20.19	0.177	116	0.304
4	134	1.42	51	129	15.91	0.192	70	0.292
5	553	2.31	294	567	10.75	0.117	316	0.283
6	456	3.12	176	402	69.37	0.419	292	0.249
7	283	1.49	108	247	46.95	0.234	157	0.255
8	356	1.03	108	306	29.40	0.296	178	0.282
9	294	1.79	100	256	44.05	0.368	168	0.268
10	265	2.08	95	250	24.80	0.299	147	0.293
11	626	1.39	215	616	30.41	0.244	334	0.291
12	473	1.24	139	443	66.46	0.294	246	0.286

Table 11. Root mean square error goodness-of-fit values for the fitted Langmuir 1 surface, Langmuir 2 surface, and Freundlich P sorption curves.

Soil no.	RMSE		
	Langmuir 1	Langmuir 2	Freundlich
1	21.8	2.5	3.4
2	25.9	3.1	4.3
3	19.9	4.2	2.3
4	12.3	2.0	2.4
5	55.6	12.6	22.3
6	52.5	14.9	10.3
7	31.3	9.0	5.9
8	25.5	5.1	8.1
9	27.8	5.0	5.5
10	25.6	5.4	9.0
11	68.6	9.9	18.6
12	42.8	9.2	7.8

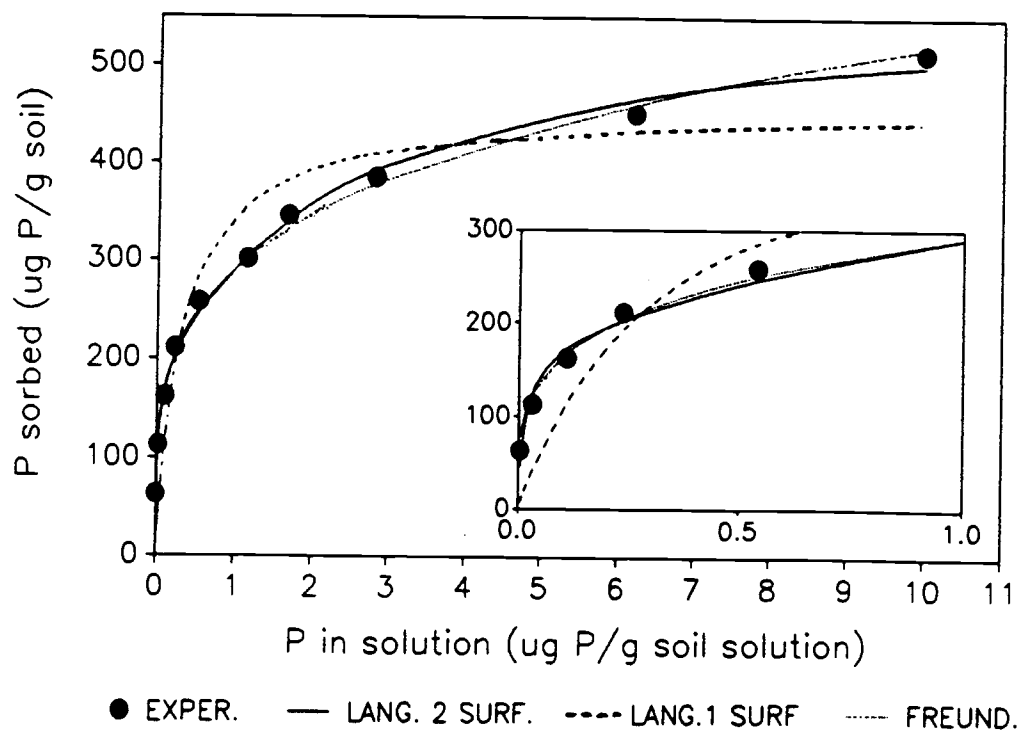


Fig. 7. Curve-fitting of soil 6 experimental sorption data by the Langmuir one surface, Langmuir two surface, and the Freundlich models. The Langmuir one surface model is biased, and the other two models are not.

range solution P levels. Langmuir two surface and Freundlich models both fit the data with negligible bias.

These results corroborate evidence of Mead (1981), Polyzopoulos et al. (1985), and Ryan et al. (1985) that the Langmuir one surface model often deviates systematically from experimental data. Harter (1984) concluded that in the presence of systematic deviation, adsorption maxima estimates may have 50% or greater error. Mead (1981), Polyzopoulos et al. (1985), and Kinniburgh (1986) also found that the Langmuir two surface and Freundlich models fit true sorption behavior well.

Assuming Freundlich sorption behavior, an advantage of the Freundlich model is that its parameters may be estimated from a log [P sorbed] vs log [P in solution] plot. Since the resultant plot is linear only two experimental points are necessary to estimate the curve (Mead, 1981). Where soils have been shown to fit Freundlich sorption behavior this two point estimation offers a relatively simple index of P sorption. There is, however, no a priori way of knowing whether or not a soil will exhibit Freundlich sorption behavior.

An advantage of the Langmuir two surface model is its capability of representing any sorption curve "if the distribution coefficient for an ion sorbed by a soil is a

finite, decreasing function of the amount sorbed, q , and extrapolates to zero at some finite value of q " (Sposito, 1982). Since this is invariably the case for P sorption the greater flexibility of the Langmuir two surface model makes it more suitable for standard reporting of research results. The proliferation of personal computers and nonlinear regression packages makes solving for the four parameters in the model less problematic than it once was.

Phosphorus sorption isotherms for four soils, representative of the range among the 12 soils, are presented in Fig. 8. Estimated curves were given by the Langmuir two surface model. For all soils, sorption was low or medium (Juo and Fox, 1977).

Workers have derived the following functions from curve fitting models to characterize sorption.

1. Maximum buffer capacity (MBC) is defined as the slope of the sorption curve when solution P concentration equals zero and for the Langmuir two surface model is estimated as

$$\text{MBC(L2)} = k_1 b_1 + k_2 b_2$$

where k_1 , k_2 , b_1 , and b_2 are the parameters defined for the Langmuir two surface model.

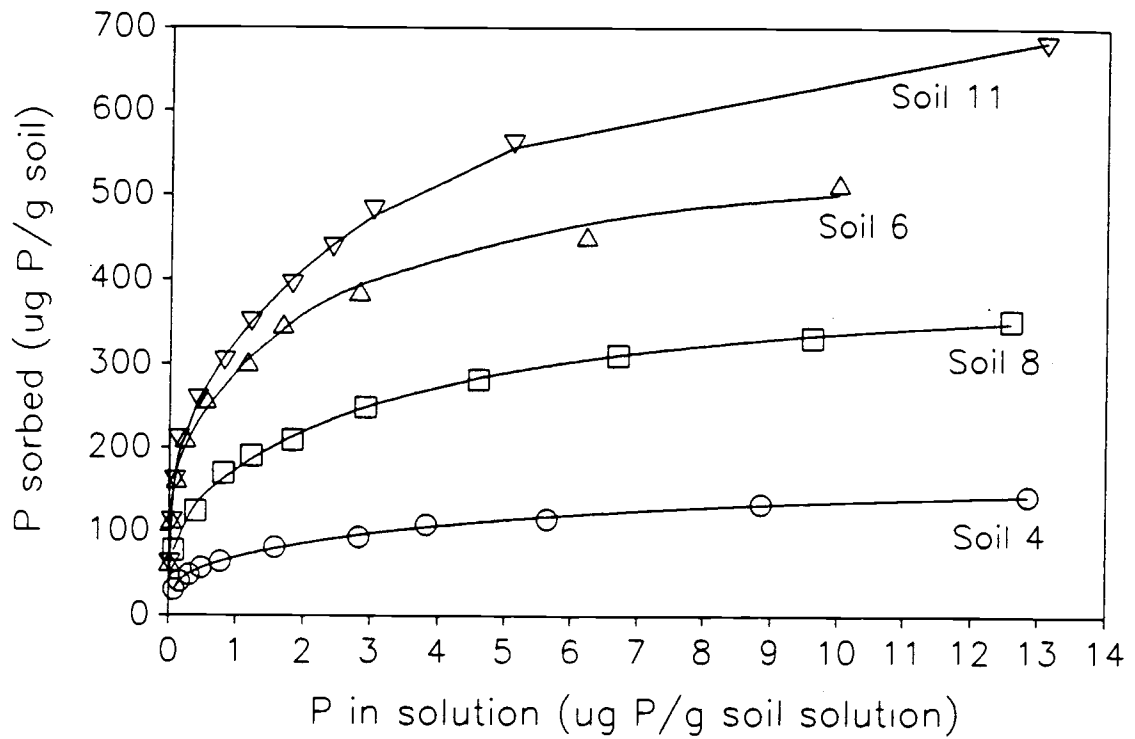


Fig. 8. Phosphorus sorption isotherms for four representative soils - experimental data and estimated Langmuir two surface curves.

2. Sorption maxima (SM) is defined as the maximum quantity of P a soil can sorb and is estimated for the Langmuir one surface model as

$$SM(L1) = b$$

where b is the curve fitting parameter (Loganathan and Fernando, 1980), and for the Langmuir two surface model as

$$SM(L2) = b_1 + b_2$$

where b_1 and b_2 are the parameters defined for the Langmuir two surface model (Sposito, 1982).

3. Tangential buffering capacity (TBC) is defined as the slope of the Langmuir two surface curve at some P concentration other than zero (Keramidas and Polyzopoulos, 1983). It may be calculated by substituting the desired solution P concentration (C) into the first derivative of the sorption model equation. For the Langmuir two surface model and C equal to 0.2 ug P/g solution

$$TBC(L2) = k_1 b_1 [(1 + (k_1)(0.2))^2]^{-1} + k_2 b_2 [(1 + (k_2)(0.2))^2]^{-1}$$

where k_1 , k_2 , b_1 , and b_2 are the estimated parameters from the Langmuir two surface model.

For the Freundlich model and C equal to 0.2 ug P/g solution

$$TBC(F) = (n)(A)(0.2)^{(n-1)}$$

where A and n are estimated parameters from the Freundlich model.

4. P retention value (PRV) is defined as the quantity of P sorbed at a given P solution concentration (C) and may be calculated by substituting the desired value of C into the sorption model equation (Juo and Fox, 1977; Ryan et al., 1985). For the Langmuir two surface model and C equal to 0.2 ug P/g solution

$$PRV = k_1 b_1 (0.2) [1 + k_1 (0.2)]^{-1} + k_2 b_2 (0.2) [1 + k_2 (0.2)]^{-1}$$

and for the Freundlich model and C equal to 0.2 ug P/g solution

$$PRV = A(0.2)^n$$

where k_1 , k_2 , b_1 , and b_2 , and A and n are parameters estimated from the Langmuir two surface and Freundlich models respectively.

The relationships between these functions are depicted in Fig. 9. The functions were used to compute descriptive sorption values for each of the 12 soils (Table 12).

With the exception of MBC(L2) descriptive sorption values were highly correlated regardless of the model used to generate them (Table 13). Although the Langmuir one surface model did not describe sorption behavior accurately its sorption maxima were highly correlated with all other sorption values except those of the MBC(L2) function.

Correlations between these descriptive sorption values and Fe_d , Al_d , F_o , Al_o (Table 9), pH, CEC, % clay, OM (Table 1) and Hedley fractions (Table 4) were computed. Significant correlations with F_o , pH, OM and NaOH P_o were obtained (Table 14). The MBC(L2) again differed from the other parameters by not correlating significantly to any soil property except NaOH P_o . This correlation was negative.

Researchers working with different sets of soils have found variously that P sorption was best correlated to Al_o (Saunders, 1965), Fe_o (Ryan et al., 1985; Sree Ramulu et

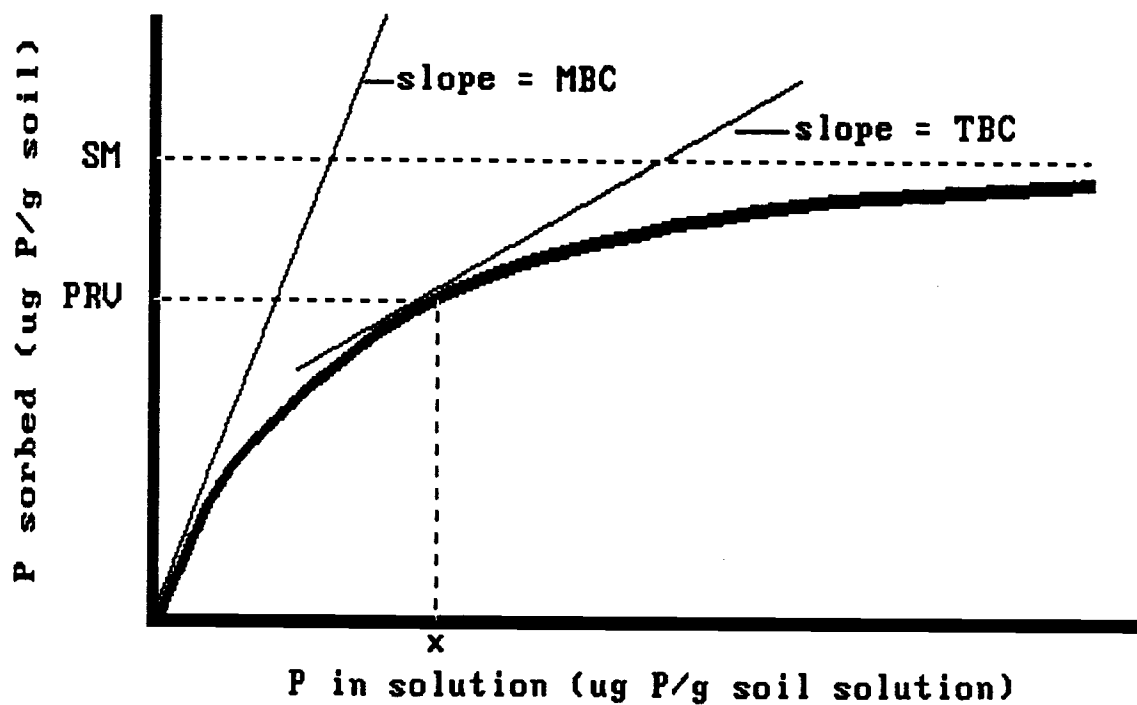


Fig. 9. Descriptive sorption functions used to calculate descriptive sorption values. MBC, SM, TBC, and, PRV are maximum buffer capacity, sorption maxima, tangential buffer capacity at x, and P retention value at x respectively.

Table 12. Descriptive sorption values for the fitted Langmuir one surface, Langmuir two surface, and Freundlich sorption curves.

Soil	MBC(L2) ^a	TBC(L2)	TBC(F)	SM(L2)	SM(L1)	PRV(L2)	PRV(F)
	ug P sorbed/ug P soln			-----ug P/g soil-----			
1	1023	187	130	405	283	85	90
2	2359	149	145	379	293	102	101
3	1738	104	108	312	210	75	71
4	838	70	63	180	134	44	44
5	3231	382	284	861	553	214	200
6	12384	198	244	577	456	195	195
7	5128	100	133	355	282	109	104
8	3262	148	159	414	356	109	113
9	4517	128	146	356	294	108	109
10	2431	133	134	345	265	93	92
11	6692	267	304	831	626	213	209
12	9361	161	222	581	473	154	155

a. MBC(L2), TBC(L2), TBC(F), SM(L2), SM(L1), PRV(L2), and PRV(F) refer to maximum buffer capacity estimated by the Langmuir two surface model, tangential buffer capacity estimated by the Langmuir two surface model at 0.2 ug P/g solution, tangential buffer capacity estimated by the Freundlich model at 0.2 ug P/g solution, sorption maxima estimated by the Langmuir two surface model, sorption maxima estimated by the Langmuir one surface model, and P retention value at 0.2 ug P/g solution as estimated by the Langmuir two surface and Freundlich models respectively.

Table 13. Pearson's correlation coefficients for descriptive sorption values.

	MBC(L2)	TBC(L2)	TBC(F)	SM(L2)	SM(L1)	PRV(L2)	PRV(F)
MBC(L2)		NS	0.63 ^a	NS	0.61	0.68	0.71
TBC(L2)			0.85	0.93	0.83	0.84	0.82
TBC(F)				0.98	0.99	0.99	0.99
SM(L2)					0.97	0.96	0.95
SM(L1)						0.97	0.97
PRV(L2)							1.00

a. For $0.58 < r < 0.70$, $0.01 < P < 0.05$; for $0.69 < r < 0.81$, $0.001 < P < 0.01$; for $r > 0.80$, $P < 0.001$.

Table 14. Pearson's correlation coefficients between descriptive sorption values and, soil properties and P fractions.

	Fe _o	Fe _o +Al _o	pH	OM	NaOH P _o
MBC(L2)	NS	NS	NS	NS	-0.59 ^a
TBC(L2)	0.75	0.78	0.59	NS	NS
TBC(F)	0.71	0.74	0.68	0.65	-0.71
SM(L2)	0.72	0.76	0.68	0.67	-0.66
SM(L1)	0.71	0.72	0.69	0.67	-0.74
PRV(L2)	0.72	0.74	0.69	0.61	-0.72
PRV(F)	0.73	0.73	0.69	0.67	-0.73

a. For $r < 0.70$, $0.01 < P < 0.05$; for $r > 0.69$, $0.001 < P < 0.01$.

al., 1967), or Fe_d (Solis and Torrent, 1989; Torrent, 1987). Often sorption parameters are correlated to more than one of the sesquioxide groups (Ballard and Fiskell, 1974; Evans and Smillie, 1976; Maraikar et al., 1983; Saunders, 1965; Sree Ramulu et al., 1967; Torrent, 1987; Udo and Uzo, 1972). In any particular soil several or all of the sesquioxide groups are probably involved in the sorption process.

The contribution of oxalate or citrate-dithionite extractable Fe or Al to P sorption in a particular group of soils depends upon their absolute and relative quantities and the degree of crystallinity of the citrate-dithionite extractable oxides. The correlations between descriptive sorption parameters [except for MBC(L2)] and soil properties suggest that of the sesquioxides, amorphous Fe oxides dominated the sorption process in the sampled Alfisols. Oxalate Fe was highly correlated to sorption parameters but Al_o , Fe_d and Al_d were not. The correlation of [$Fe_o + Al_o$] to sorption parameters was only slightly greater than Fe_o alone.

Citrate-dithionite iron did not improve the regressions of sorption parameters on Fe_o when included as a second independent variable in the regression models. Either 1) Fe_d was not actively involved in P sorption, 2) the degree of crystallinity of Fe_d , and thus its reactivity with P, varied inconsistently among sampled soils, or 3) the range

of measured Fe_d values was too narrow to detect a relationship to P sorption. Fe_d was highly correlated to the residual P fractions Con HCl P ($r=0.89$ $P<0.001$) and H_2O_2 P ($r=0.59$ $P<0.05$) suggesting that slightly crystalline and crystalline Fe oxides may act as a sink for a "slow" sorption reaction in which labile P is transformed to less available forms. Barrow (1989) hypothesized that initial P sorption takes place on variably charged surfaces and is followed by a slow diffusion of P into the soil particle. P added to Sri Lankan Alfisols may be sorbing on amorphous oxide coatings of more crystalline oxides. With time and inward diffusion or crystal accretion, the sorbed P may move into the crystalline structure.

P sorption in the slightly acid to neutral Alfisols in this experiment was found to be positively correlated to pH. Barrow (1984) found that increasing the pH above 5.5 increased P sorption in 3 out of 4 tested soils. Barrow (1989) assumed that HPO_4^{2-} has a greater adsorption affinity than does $H_2PO_4^-$. Since HPO_4^{2-} levels increase rapidly with pH above 5.5, sorption should also increase. However this is offset by increases in the negative surface charge of adsorption surfaces which repel the phosphate anions. Barrow (1989) concluded that the net effect of these two processes may be determined by the background electrolyte solution. Divalent cations are more able to mask negative surface charge and increase sorption than are monovalent

cations. Sorption isotherms presented in this paper were made using a divalent cation solution, 0.01 M CaCl_2 .

Udo and Uzu (1972) and Ballard and Fiskell (1974) reported negative correlations between P sorption and pH in acid soils. The increase in P sorption with decreasing pH may be due to rapidly increasing levels of exchangeable and acetate extractable Al below pH 5.5 (Lopez-Hernandez and Burnham, 1974). Loganathan and Fernando (1980) reported that sorption in acid Sri Lankan soils was significantly correlated to "active" Al [1 M NH_4OAc (pH 4.8) extractable Al - 1 M KCl extractable Al]. Above pH 5.5 activity of Al^{3+} and $\text{Al}(\text{OH})^{2+}$ is very low.

Researchers (Ahenkorah, 1968; Ballard and Fiskell, 1974; Lopez-Hernandez and Burnham, 1974; Maraikar et al, 1983; Saini and MacLean, 1965; Saunders, 1965) have reported significant positive correlations between organic matter and P sorption. Harter (1969) suggested that phosphate ions could replace hydroxyl ions on organic matter in an anion exchange type of reaction. He hypothesized that P sorbed on organic matter reacted with sesquioxides over time and became less available.

Regression models using P sorption parameters as dependent variables and soil properties as independent variables showed that coefficients for OM and pH were not

significant if Fe_0 was in the model. Covariance between Fe_0 , OM and pH may be due to factors independent of sorption. Illuviated cations are deposited in low terrain positions and tend to increase pH. Low terrain positions are also saturated for greater periods of the year than higher positions, resulting in increased Fe_0 and OM levels.

None of the descriptive sorption values were significantly correlated to log Plant P. Log Plant P was regressed on Double P in separate combinations with each sorption parameter but none of the sorption parameter coefficients were significant. Keramidas and Polyzopoulos (1983) studied Greek Alfisols and found that including descriptive sorption parameters in a regression of P uptake on P concentration or E value did not improve the fit significantly. These results do not preclude the possibility that sorption properties affect P uptake. The soil groups used in this investigation and by Keramidas and Polyzopoulos (1983) were relatively homogeneous, restricting the range over which the relationships between P sorption and uptake could be tested. Nair and Mengel (1984) choose a very heterogeneous set of soils and measured buffer power as the slope of CAL extractable P (Schuller, 1969) vs electro-ultrafiltration P. They found that when buffer power was included in a regression of P uptake on soil test P that the R^2 improved significantly.

Conclusions

Phosphorus sorption in Sri Lankan Alfisols was low to medium and was described satisfactorily with either the Langmuir two surface or the Freundlich equation. The Langmuir one surface equation was not suitable for describing sorption behavior because of model bias. Correlation analysis of descriptive sorption values and selected soil properties indicated that Fe_0 was the soil component most active in P sorption. Organic matter and pH were also highly correlated to descriptive sorption values. They may be directly involved in the P sorption process, or they may covary with P sorbing components in the soil due to factors independent of sorption. Although Fe_d did not appear to be involved in measured P sorption its high correlation with residual P fractions suggests it may be involved in the "slow" sorption reaction. Phosphorus sorption had no apparent influence on P uptake by foxtail millet in a Neubauer experiment.

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