

Factors Controlling Phosphate Fixation and Release in Selected Soils under Rubber Cultivation

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Four soils under rubber cultivation, used in this study, contain high amounts of Fe and Al. More than 50% of the free dithionite-citrate-bicarbonate extractable Fe was found to be dissolved by Tiron, which relates to the amount of the amorphous iron oxide in the soils. The P adsorption maxima of the soils ranged from 324 μgP to 507 μgP per gramme soil.

The total P contents of the soils were low; and, more than 60% of this P was found in the Fe-P fraction. The amounts of P extracted by four soil available P testing methods were also found to be low.

Freshly adsorbed P in the soils was readily extracted by Bray and Kurtz 2 and ammonium lactate reagents. Drying had little influence on the amount of adsorbed P extractable by the two reagents. Overcoating the phosphated samples with a prepared Fe (III) sol reduced greatly the amount of extractable P. The irreversible fixation of P in soils may involve such an overcoating process by iron oxides.

Malaysian soils especially those under rubber cultivation are mostly highly weathered soils. In general, these soils are classified as Ultisols or Oxisols; some Inceptisols are also cultivated with rubber^{1,2}. Since these soils contain high amounts of sesquioxides, the phosphate adsorption capacity of these soils can be expected to be high.

Owen^{3,4} showed that phosphate availability was one of the major problems in the management of soil fertility for rubber cultivation. Most of the soils were found to be responsive to phosphate fertiliser application^{5,6}. Pushparajah *et al.*⁷ reported that phosphate fertiliser applications not only increased yields but also improved the latex quality.

Total phosphate contents of most of these soils were reported to be variable, with the majority being less than 500 μgP per gramme soil⁸. The amount of available P, as estimated by Bray and Kurtz 2 extraction, was also found to be low. Response to phosphate fertiliser application by rubber trees was expected when the amount of Bray and Kurtz-extractable P was less than 11 μgP per gramme soil⁹. However, in some soils no response was detected although this amount was only 5 μgP per gramme soil. This led to investigations into the possibility of using other P availability indices^{10, 5}.

In the present study some basic investigations on phosphate sorption processes in four soils were carried out. Factors related to the P availability or fixation were also considered.

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MATERIALS AND METHODS

Four soils used in this study were collected from areas under rubber. Organic matter content of the soils was determined by Walkley and Black wet digestion method. Cation-exchange capacity was determined using the Ba-133 isotopic exchange method¹¹. Soil pH was determined in a 1:5 soil to water ratio. Total P and Fe contents were determined after digesting the soils with 18% HClO₄. Phosphate fractionation was done by the method of Chang and Jackson¹². Phosphate availability indices were determined by Bray and Kurtz 1 and 2 methods, Olsen's method (0.5 M NaHCO₃) and ammonium lactate reagent. Phosphate was analysed by the method of Scheel¹³, and iron by the hydroxylamine-phenantroline method¹⁴. Amorphous iron and aluminium (hydr)oxides were removed by extracting the soils with Tiron¹⁵ and acid ammonium oxalate single extraction in the dark¹⁶. Total free iron and associated aluminium were extracted twice with the dithionite-citrate-bicarbonate method (DCB) of Mehra and Jackson¹⁷. Analyses of Fe and Al in all the extracts were done after digesting the samples with 2 ml concentrated HClO₄. Aluminium in the extracts was determined by the eirochromcyanine method¹⁸.

Phosphate adsorption on the soils was determined on the untreated soils and on the soil samples after the removal of Fe and Al as outlined above. The processed soil samples were prepared for P adsorption by washing the samples several times with 0.02 M NaCl at pH 4.20 and finally equilibrating the soils overnight with the same electrolyte concentration and adjusting to the same pH. The amount of soil sample used for each adsorption treatment was about 1 gramme. The final volume of the reacting suspension was

40 ml, containing upto about 15 μ mole P. After P was applied the samples were allowed to equilibrate for about 24 hours. The same procedure was followed for the untreated soils (controls). Phosphate sorption maxima of the soils were estimated using a linearised form of the Langmuir equation.

After the phosphate sorption maxima of the various samples had been calculated, enough P was added to the four untreated soil samples to get 50% P saturation. The soil samples were then washed a few times with 0.02 M NaCl at pH 4.20.

Fresh samples, samples after vacuum-drying and samples after overcoating with Fe (III) sol prepared as described elsewhere¹⁹ were extracted by Bray and Kurtz 2 and ammonium lactate reagents. Two Fe (III) sol rates were applied to give 50% and 100% Fe (III) sol coating.

RESULTS AND DISCUSSION

Some of the basic characteristics of the soils are given in *Table 1*. All the soils are acid in nature having pH ranging from 4.4 to 4.7. The low total P content of the soils (13.5 mg to 28.2 mg P per 100 g soil) reflects a short fertiliser history and low P content of the parent materials. The C.E.C. values as estimated from the Ba-133 isotopic exchange method are much lower than other reported values on the soils²⁰ involving the use of 1 N ammonium acetate. The discrepancies between the two methods are attributed to the different pH conditions of the solutions involved. In the determination of C.E.C. using 1 N ammonium acetate, the pH of the solution is 7; while using the Ba-133 method the pH of the final equilibrating solution is normally around pH 4.5. The near approximation of the solution pH used in the Ba-133 method to the soil pH, in our opinion, gives a

TABLE 1. SOME BASIC PROPERTIES OF THE SOILS

Soil	Order	Clay (%)	C.E.C. (M-equiv./100g)	pH (H ₂ O)	Organic C (%)	Total analyses		
						P (mg/100g)	Fe (mg/100g)	Al (mg/100g)
Rengam	Ultisol	24	3.5	4.70	1.38	20.9	1 209	7 775
Jerangau	Oxisol	43	3.0	4.53	1.54	28.2	3 451	7 905
Kulai	Ultisol	38	3.2	4.44	1.39	13.5	1 488	5 817
Yong Peng	Ultisol	50	2.2	4.68	1.42	21.8	4 686	8 828

better estimate of the C.E.C. of the soils.

More than 80% of the total Fe was extractable by DCB, indicating that most of the Fe was in the free oxide form (Table 2). Ammonium oxalate and Tiron extractable Fe and Al, which are supposed to extract the amorphous (non-crystalline) Fe and Al oxides, differed greatly in amount. It should be noted that Schwertmann¹⁶ stressed that the acid ammonium oxalate method only measures the relative amount of the amorphous Fe and Al oxides. On the other hand, Biermans and Baert¹⁵ realised that Tiron extraction also dissolves a small fraction of the crystalline forms. A second extraction was proposed by the authors to correct for the amount of crystalline Fe or Al oxides dissolved during the first extraction. However, in

this work the second extraction was not done because the samples after extraction were used for phosphate sorption experiments. Hence, the values of amorphous Fe and Al reported here are overestimates of the actual amounts. In any case, this amount probably exceeds 50% of the total free Fe and Al which tends to relate better to the Tiron extraction method.

The amount of extractable Al using Tiron exceeds that obtained by the DCB method. This may be taken to indicate misuse of the amount of DCB-extractable Al, by some authors, as being the total free Al. If the DCB-extractable Al is the total free Al, then the amount extracted by this reagent must exceed that of the Tiron extraction, but not otherwise.

TABLE 2. IRON AND ALUMINIUM EXTRACTED BY VARIOUS REAGENTS

Soil	DCB		Tiron		Tamm	
	Al (mg/100g soil)	Fe (mg/100g soil)	Al (mg/100g soil)	Fe (mg/100g soil)	Al (mg/100g soil)	Fe (mg/100g soil)
Rengam	230	1 000	570	640	100	60
Jerangau	690	3 080	910	1 700	180	190
Kulai	340	1 370	620	980	150	210
Yong Peng	870	3 896	1 370	2 630	190	130

Table 3 summarises the amount of P extracted by the various routine methods and by the P fractionation method. Bray and Kurtz 1 and 2 reagents are the most efficient due to the low pH and presence of fluoride ions. Ammonium lactate extracted higher amounts compared to the Olsen method due to the complexing power of lactate for Fe and Al. Probably most of the P extracted by these reagents came from the free-P and the Al-P fractions, since none of the soils showed an amount of P extracted greater than the Al-P fraction. Most of the phosphate, virtually more than 60% of the total P, was in the rather 'unavailable' Fe-P fraction.

It is evident that the amount of P extracted by all the tests was low. But based on the Bray and Kurtz 2 extraction, Rengam and Jerangau series soils may have sufficient amounts of 'readily available' P to sustain normal growth of rubber plants, if the limit of $11\mu\text{g}$ P per gramme soil extracted by this reagent as suggested by Guha and Yeow⁹ is applicable.

The phosphate sorption maxima of the untreated soils (control) varied from $324\mu\text{g}$ P in the Rengam series soil to $507\mu\text{g}$ P per gramme soil, in the Yong Peng series soil (*Table 4*). In general,

adsorption was better related to the Fe content than to the Al content. Removal of Fe and Al by different methods reduced the amount of the P sorption capacity of the various soils, more than 70% reduction in P adsorbed, based on the average, on the soils extracted by the DCB method. This indicates the importance of Fe and Al oxides in the soils in controlling the P sorption capacity of these soils.

It is, however, difficult to make definite conclusions on the nature of decrease in the P sorption maxima after extraction by Tamm and Tiron methods. The two methods, although extracting different amounts of amorphous Fe and Al oxides, adsorbed a comparable amount of phosphate. Probably other parameters, for example, the surface area and the clay content may influence the P sorption characteristics after the extraction procedures. However, it is difficult to single out the individual factors based on the limited number of samples used here. In any case, the relationship between the amount of Al and Fe oxide extracted and the P sorption capacity was very evident.

The result in *Table 5* indicates that soils possess the ability to adsorb high amounts of prepared Fe (III) sol. The capacity of the soils to adsorb the iron particles was

TABLE 3. PHOSPHATE EXTRACTED BY VARIOUS METHODS AND PHOSPHATE IN DIFFERENT FRACTIONS

Soil	Phosphate (mg/100g soil)							
	Bray 1	Bray 2	Olsen	Ammonium lactate	Free-P	Al-P	Fe-P	Ca-P
Rengam	1.55	1.84	0.81	1.38	0.25	1.91	12.9	1.9
Jerangau	0.83	1.22	0.61	0.66	0.24	1.81	14.1	2.4
Kulai	0.81	1.09	0.57	0.76	0.16	1.09	7.9	1.9
Yong Peng	0.45	0.70	0.31	0.26	0.16	0.84	15.6	3.7

TABLE 4. PHOSPHATE ADSORPTION
MAXIMA AFTER DIFFERENT
TREATMENTS

Soil	P adsorption maximum ($\mu\text{g P/g soil}$)			
	DCB	Tiron	Tamm	Control
Rengam	73.6	212.2	161.1	324.1
Jerangau	146.8	267.9	261.0	479.3
Kulai	84.7	159.4	177.3	437.7
Yong Peng	235.2	339.1	355.7	506.6

hardly influenced by the presence of the adsorbed phosphate. Freshly adsorbed phosphate, amounting to more than 90%, was readily extracted by Bray and Kurtz 2 reagent, except in Yong Peng series soil where only 70% of the adsorbed P was extracted (Table 6). Ammonium lactate, a weaker extractant, extracted about 68% to 86% of the adsorbed P. Drying the samples had little influence on P recovery by Bray and Kurtz 2 reagent, but there was a noticeable difference on the amount of ammonium lactate-extractable P. Only Yong Peng series soil exhibited a lower fraction of extractable P with both reagents.

The influence of Fe (III) sol overcoating on the extractability of the adsorbed P was very evident. As the

amount of Fe (III) sol overcoating increased, the amount of extractable P decreased with both the reagents. At 50% Fe (III) sol saturation, about 50% of the adsorbed P was extractable by Bray reagent, while 35% was extractable by ammonium lactate. In Yong Peng series soil, a lower percentage was extractable. At 100% Fe (III) sol saturation, the percentage of adsorbed P that was extractable decreased further; some 30% remained extractable by Bray reagent and only about 20% was recovered by ammonium lactate.

Several authors^{21, 22} proposed that readjustments of the adsorbed phosphate ions on the oxide surfaces, for example by bridging or multidentate formation, was the reason for the irreversible fixation of P in soils. This explanation may only be a partial contribution to the overall process of fixation, depending on the type of soils e.g. Yong Peng series soil which easily turns part of the added P into an unextractable form. This soil contains a much higher amount of total Fe and Al compared to other soils. For the other soils, this study showed that the Fe (III) sol overcoating contributed a major factor in the non-extractability of the adsorbed P. Hence, it is an important reaction leading to the irreversible fixation of phosphate in soils.

The ability of the soils to adsorb the Fe (III) sol may also be used to explain the observations made by several authors that on ageing, the Al-P fraction is converted to the Fe-P fraction. Considering that iron phosphate compounds are less soluble than aluminium phosphate compounds, the precipitation of iron oxides from the soil solution onto the phosphated soil surfaces will occur faster than the precipitation of aluminium. As a result of this preferential precipitation of

TABLE 5. AMOUNT OF FE (III) SOL
ADSORBED BY THE SOILS

Soil	Fe adsorbed (mg/g soil)	
	Non-phosphated	Phosphated
Rengam	7.4	7.8
Jerangau	9.7	10.2
Kulai	10.8	10.0
Yong Peng	8.3	10.3

TABLE 6. PERCENTAGE OF ADSORBED PHOSPHATE EXTRACTED AFTER DRYING AND
FE (III) SOL OVERCOATING

Soil	Non Fe (III) sol-coated				Fe (III) sol-coated (dried)			
	Fresh		Dried		50%		100%	
	A	B	A	B	A	B	A	B
Rengam	100	86	100	70	57	40	39	19
Jerangau	91	68	87	57	53	35	31	19
Kulai	100	86	100	71	57	44	35	22
Yong Peng	69	55	63	40	34	22	18	14
Average	90	74	88	60	50	35	31	19

A = Bray and Kurtz 2 extraction

B = ammonium lactate extraction

iron oxides on the phosphated surfaces, more P will be found in the Fe-P fraction with time.

As soils are chemically dynamic in that iron can be constantly released through pedogenic and biological processes, an overcoating process by Fe (III) oxides is a possible reaction. A recent report by McLaughlin and Syers²³ serves as a reference to support this observation. By dialysing several phosphated iron oxides against Fe gel these authors observed a formation of a short-range order material of iron (hydr)oxide surrounding the phosphated materials after about twenty days. Using this scale of time in their observation, the formation of an overcoating on phosphated surfaces can be a rather rapid process. Therefore, it is very probable that this overcoating process contributes a major factor in determining the extent of phosphate fixation in soils.

Another important consequence of this over-coating process by iron oxides, or perhaps aluminium oxides too, is that it is not advisable to apply P fertilisers, especially the more soluble forms, in high amounts intended for prolonged P supply

to plants grown on high sesquioxide-rich soils. This is because much of the applied P will be immediately adsorbed and when coatings of iron oxides are formed the applied P will be rendered unavailable. The current phosphate fertiliser recommendation by the Rubber Research Institute of Malaysia (RRIM) involving the split method of application and using the less soluble rock phosphate instead of the more soluble superphosphate, is therefore justified^{24, 25, 26}. This method of fertiliser application may help to minimise the effect of the applied P being overcoated by iron (or aluminium) oxides. Therefore, more response per unit of P input can be obtained. This is observed in many of the RRIM experiments comparing rock phosphates with superphosphate as P sources for *Hevea*. The better response from the rock phosphate in the long run, may be due to minimised overcoating of the applied P.

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