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STUDIES ON THE PERFORMANCE OF TWO PHOSPHATIC FERTILIZERS ON TEA SOILS WITH RESPECT TO THE P-ADSORPTION, MINERALOGY AND PLANT SPECIES USING ^{32}P LABELLED FERTILIZER

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Soils representing a wide range of phosphorus adsorption capacities were sampled from tea growing areas of Sri Lanka from three depths 0-15, 15-30 and 30-45 cm. Their mineralogy, P-availability and P-adsorption were studied. Predominant mineral in the clay fraction was Kaolinite. Whereas a hydroxy interlayered vermiculite was observed in equal abundance in St Coombs soil, gibbsite and quartz were found as minor components. From a clay mineralogical point of view Passara and Kandy soils were very similar. St Joachim and Kottawa soils were also similar with a varying gibbsite content. St Coombs soil was different from both the above types. Surface areas of the soils were above 20 m^2/g except in Kottawa soils. P-adsorption maximum obtained by using Langmuir adsorption isotherms ranged from 896 µg/g for Kottawa soil to 1400 µg/g for St Coombs soils. The native P-availability by A-value technique in St Coombs soil was much higher than in Kottawa soil. The two types of fertilizers showed comparable availability by the A-value technique for tea plants. When sorghum and bean plants were used fertilizers behaved differently. At normal levels of P application Eppawela apatite seems to be either comparable or better for tea than rock phosphate in concurrence with earlier observations (Sivasubramaniam, *et al.*, 1978.)

INTRODUCTION

The annual rock phosphate requirements for the tea industry in Sri Lanka is around 14,000 tonnes. In the past all this requirement was met by imports from the Middle East. In 1971, an apatite deposit was discovered in Sri Lanka with an estimated reserve of about 50 million tonnes. The primary crystalline apatite mineral of the deposit has been fluorapatite rich in chlorine (Deans, 1975). The phosphorus content of the finely ground material is rather variable and ranges from 25-35% total P_20_5 and 2.8 to 5.2% citric and soluble P_20_5.

Based on the results of incubation experiments and classical greenhouse experiments (Sivasubramaniam, *et al.*, 1978) the tea industry has substituted all its rock phosphate requirements by Eppawela apatite.

The maximum yield response for tea occurs at a phosphate rate of 34 kg P_2O_5/ha/annum, (Eden, 1949). Also it was shown that both rock phosphate and superphosphate were equally efficient for tea (Tolhurst, 1963). This rather low level of response for P and also the high P fixation capacities of these soils with the introduction of new phosphatic fertilizer warrants special attention in relation to tea nutrition. This study was therefore undertaken to investigate the main factors affecting the phosphorus availability in soil, namely the mineralogy of the clay fraction, surface area, surface charge, P-adsorption capacity and availability indices A and E_t values in relation to the soil types, P-fertilizers used, and also the plant species.

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MATERIALS AND METHODS

Soils

Six soils from the tea growing areas of Sri Lanka, consisting of two soils from Up-Country (St Coombs) one from Mid-Country (Kandy), one from Uva (Passara) and two from Low-Country were selected and sampled. Soil materials free of gravel were air dried and passed through a 2 mm sieve.

Particle size analysis and clay fractionation

Ten gram samples of soil was ultrasonically dispersed in water at pH 9, the pH being adjusted with NaOH, and fractionated by standard sieve and sedimentation techniques (Jackson, 1956). Clay sub-fractions were flocculated, dialyzed and washed using a series of solvents, 50% ethanol, 70% ethanol, 90% ethanol, 100% ethanol, acetone and Benzene and finally dried under a slow draught of air. This clay fraction was utilized for the mineralogical study.

Chemical analysis

Organic C was determined by Walkely & Black method.

Iron removal from the clay fraction of the soils was effected by three sequential extractions with sodium dithionite-citrate-bicarbonate (D CB) (Mehra and Jackson, 1960).

Phosphorus adsorption properties of the soils were studied by constructing the phosphorus adsorption isotherms. Duplicate 5g samples of soil were weighed directly into 100 ml polyethylene centrifuge tubes, appropriate quantities of 1N KCl and P-stock solution were added to make solutions that were 0, 10, 20, 30, 40, 60 and 80 ppm in respect to P final solution volume adjusted to 50 ml and solution pH to 4.5 in all cases. One drop of toluene was added and the tubes were sealed with polyethylene covered corks, placed in an insulated chest and shaken longitudinally for 24 hours. The suspensions were then centrifuged and analyzed for P by heteropoly blue method of Watanabe and Olson (1965).

Fractionation of P in the P added soils were effected by the method described by Chang and Jackson (1957) after two months of adding 100 ppm P as ^{32}P single super phosphate to the soil.

^{32}P Studies

(*a*) *Et Values.*—Et values of the soils were determined by using ^{32}P labelled KH_2PO_4 solution (IAEA 1976, Russel, *et al.*, 1954).

(*b*) *A Values.*—The evaluation of the fertilizers is based on the proposition that 'A' values (Fried and Dean, 1952) gave a quantitative measure that can be added or substracted. The method finally involves a determination of 'A' values of soils with and without addition of the source to be evaluated using the same standard of labelled phosphate, (Fried M. 1954).

The mathematical calculations are as follows :—

$$A_1 = B(1-Y_1)/Y_1$$

$$A_1 + A_2 = B(1-Y_2)/Y_2$$

When A_1 = amount of available P in the soil
A_2 = amount of available P in the fertilizer
B = amount of P applied as standard

Y_1 and Y_2 = proportion of the phosphorus in the plant derived from the standard.

Therefore $A_2 = B/Y_2 - B/Y_1$

gives the amount of 'available' phosphorus in the applied fertilizer in terms of the standard. Thus any number of fertilizers could be compared.

Greenhouse experiment

2.5 kg of dry soil was mixed thoroughly with the ^{32}P labelled single superphosphate at a rate of 100 ppm P and transferred into polythene lined pots. Eppawela apatite and rock phosphate were mixed wherever necessary in order to make P level 100 and 1000 ppm respectively. After three days of fertilizer application moisture content was brought to 90% field capacity and sorghum (*Sorghum vulgare*) and bean (*Fasciolus vulgaris*) seedlings were transplanted into the pots. In the case of tea plants (*Camellia sinensis* L.) plants were established in pots prior to the experiment and the fertilizers were incorporated only into the top 1 cm layer of the soil. Top dressings of ammonium sulphate and potassium sulphate were given at the rate of 100 ppm each N and K respectively. All treatments were given in triplicate, except in the case of tea, where establishment of plants posed a problem, limiting the number of replicates to one.

In addition to the A value, all the other possible data, including dry matter yield total P uptake, total P-concentration and P derived from fertilizer were measured.

CLAY MINERALOGICAL ANALYSIS

X-ray diffraction

Clay mineralogy was determined on parallel oriented 50 mg samples of clay on glass slides by X-ray diffractometry using Ni filtered Cu-K radiation. The diffraction assembly included a beam divergence slit, a medium resolution soller slit, and a diffraction beam monochromator. Standard chemical and thermal sample pretreatments were employed (Jackson, 1956).

Differential thermal analysis

Differential thermal analysis was done on 10 mg samples of clay in an atmosphere of N_2 at a heating rate of 10°C/mt. Gibbsite and Kaolinite percentages were estimated by measuring the area under the respective endotherms in relation to a standard.

Surface area determination

Surface areas were measured by N_2 gas adsorption using a quantachrome BET surface area analyzer.

RESULTS AND DISCUSSION

Mineralogy of clay fraction

Clay mineralogy of these tea soils has not been worked out in detail. Though it was known that these soils are mostly Kaolinitic, the X-ray diffraction data (Table 1) suggests that except in St Coombs, in all the other soils the predominant clay mineral is Kaolinite. Whereas in St Coombs a hydroxy interlayered vermiculite (V/C) was found in equal proportions with Kaolinite. Gibbsite was a minor component in all soil clays except the surface horizons of St. Joachim and Kottawa where the Gibbsite content was appreciable. Small peaks due to goethite was observed in all the soils except Kottawa. This is in conformity with the earlier observations of Kottawa soils which fixes P-mostly in the form of Ca and Al-bound P and not Fe-bound P (T. C. Z. Jayman, personal communication). Even in the cases of soils where goethite was found the peaks were not sharply defined probably due to the fine subdivision of these mineral crystallites, whereas Gibbsite exhibited a sharp diffraction peak showing its well crystallised nature. Because of this fine subdivision of goethite one would expect a relatively large specific surface area of this oxide mineral being available for the reaction with phosphate ions.

TABLE 1 — *Mineralogy of the Clay Samples*

Sample			*XRD (+Fe)**	*XRD (-Fe Clays)***	
1	0—15	St Coombs P_0	go. (?)	K = V/C, g, q	Essentially identical mineralogy
2	15—30	,,	go.	V/C = K, g, q	
3	30—45	,,	go. (?)	V/C = K, g, q	
4	0—15	St Coombs P_{60}	go. (?)	K = V/C, g, q	
5	15—30	,,	go. (?)	V/C = K, g, q	
6	30—45	,,	go. (?)	K = V/C, g, q	
7	0—15	Passara	go.	K, (v/c, v/mi, g) (trace)	Very similar mineralogy
8	15—30	,,	go. (?)	K, q (trace)	
9	30—45	,,	go. (?)	K, q (trace)	
10	0—15	Panwila	go. (?)	K, q, g, mi (trace)	
11	15—30	,,	go. (?)	K, (g, q, mi, v/c) (trace)	
12	30—45	,,	go. (?)	K, (g, q, mi) (trace)	
13	0—15	St Joachim	go.	K > G, v, q	Very similar but gibbsite varies ; the vermiculite is complex, since it disappears with heat
14	15—20	,,	go.	K, v, g, q (trace)	
15	30—45	,,	go.	K, v, g, q(trace)	
16	0—15	Kottawa	—	K > G, v, q	
17	15—30	,,	—	K, g, v, q (trace)	
18	30—45	,,	—	K, g, v, q, (trace)	

* Deferrated and non-deferrated samples gave similar results, except that there was some slight evidence for goethite in some samples (see column 1). Question mark means there is some uncertainty.

**K — kaolinite ; V/C = hydroxy-interlayered vermiculite ; G = gibbsite ; GO. = goethite Q = quartz ; Mi = mica. Upper case letters mean major component lower case = minor.

Note.—(trace) refers to the immediate preceding mineral, or where several minerals are enclosed in parenthesis, to all of the enclosed minerals.

It is interesting to note that the overall mineralogy of the soils could be broadly divided into three categories, where the two upcountry soils resemble each other very much, and the two mid-country soils from Passara and Panwila also have very similar mineralogy. Then the two low country soils St Joachim and Kottawa are very similar in silicate mineralogy though the Gibbsite content varies from sample to sample. Also the vermiculite is complex as the peak disappears on heating. From the differential thermal analysis data (DAT) St Coombs soils have the highest Gibbsite content in the clay fraction whereas Kaolinite content is highest in Passara, Panwila, St Joachim and Kottawa soils. Because of the variation in the mineral contents and also their differences in P-adsorbing power it is rather difficult to predict the P-adsorption on this mineralogical data alone.

Surface area of soils

Surface area of soils is determined mainly by the clay size fraction of the soils. Surface areas determined by the ethylene glycol retention method was closely correlated to the phosphate adsorption maxima of the soils (Olson and Watanabe, 1957). The BET surface areas of the soils reported here (Table 2) are not that well related to the phosphorus adsorption maxima of these soils, (SA vs. PAM, $r^2 = 0.60$). This lower correlation compared to that obtained by Olson and Watanabe ($r^2 = 0.94$) is due to the fact that ethylene glycol estimates most of the polar surface on clay and oxide minerals which constitutes hydroxyls, whereas N_2 gas adsorption determines the total area. However, a better correlation was obtained when the regression was done separately for 0—15 cm depth and 30—45 cm depth.

r^2 (0—15) = 0.79, PAM = 817.82 + 13.33 (SA)

r^2 (0—45) = 0.99, PAM = 632.14 + 33.42 (SA)

According to Parfitt *et al.*, (1975) the P-adsorption is via replacement of surface hydroxyls. Therefore naturally one would expect a better correlation of P-adsorption maxima versus ethylene glycol surface area.

Phosphorus adsorption

P-adsorption data obtained gave the Langmuir parameters P-adsorption maximum, and K, the constant related to the bond energy of P-in the soil (Table 2). The plots of adsorption versus solution P-concentration are given on Fig. 1 and 2. Here also the grouping according to the mineralogy is fairly closely followed. The two St Coombs soils (0—15 cm) fall as the highest P-adsorbing soil, Passara and Panwila falls next, last two are the St Joachim and Kottawa soils. Since fixation is the lowest in Kottawa soils, added fertilizer will remain in the same form for a longer period than in other high P fixing soils. The St Coombs soil fixes about 1400 μg/g of soil. The two soils from St Coombs belong to an experiment, where one soil was treated with P for the last 50 years with P-fertilizers STC P_{60} at the rate of 67 kg P_2O_5/ha/annum and the other was treated with no P-fertilizer STC P_{60}. Yet it is interesting to note that long years of addition of P has not changed the P-adsorption capacity of this high P fixing soil to any appreciable extent. Where P_0 soil had a P-adsorption capacity of 1432 μg/g and P_{60} soil 1402 μg/g. This clearly indicates that it is difficult to saturate the P-buffering capacity of these soils at the present rate of addition of fertilizer. And also it may be futile to add a highly available form of P, due to the fact that all the P will be fixed into unavailable forms in a rather short period. Therefore it may be economical to add a cheap less readily available form like rock phosphate as observed by Tolhurst (1963). Since the major difference between Eppawela apatite and rock phosphate is the presence of chlorine in the former, one of the objections for its use is the toxicity imparted by chloride. Yet the mature tea can tolerate fairly high levels of chloride, and hence Eppawela apatite should be as suitable as rock phosphate for tea.

TABLE 2 — *Measured physical and chemical parameters for the soils*

	depth (*cm*)	*Soil*	% *clay*	% *Gibbsite*	% *Kaolinite*	*SA* m^2/g	*PA max.* µg/g	µg/g*K*	*Et* µg/g
1.	0—15	St Coombs P_0	38.7	3.87	8.90	35.2	1432	1.13	208.4
2.	15—30	"				43.5			
3.	30—45	"	46.9	5.63	9.85	51.0	2380	1.26	
4.	0—15	St Coombs P_{60}	31.5	3.15	5.67	50.9	1402	1.04	252.5
5.	15—30	"				36.0			
6.	30—45	"	54.7	4.92	10.94	46.4	2365	1.55	
7.	0—15	Passara	49.4	<0.5	29.6	30.0	1311	1.34	249.2
8.	15—30	"				33.2			
9.	30—45	"	44.7	<0.45	19.67	29.7	1678	9.08	
10.	0—15	Panwila	44.7	0.45	27.4	25.9	1128	0.46	228.7
11.	15—30	"				28.4			
12.	30—45	"	50.4	0.50	29.23	33.8	1411	0.44	
13.	0—15	St Joachim	27.3	1.91	8.39	20.6	989	0.33	172.0
14.	15—30	"				24.0			
15.	30—45	"	31.8	2.23	18.13	24.8	14.05	0.67	
16.	0—15	Kottawa	17.8	1.25	9.43	6.2	896	0.37	137.1
17.	15—30	"				7.3			
18.	30—45	"	16.2	0.97	8.26	9.8	1099	0.64	

P-fractionation

Al-bound P Iron-bound P and Ca-bound P as determined by Chang and Jackson procedure (Table 3) on P-added St. Coombs and Kottawa soil show a marked difference. In St Coombs soil, Al and Fe-bound P derived from the added fertilizer was 9.8 and 11.4%, respectively. Whereas P-derived from fertilizer constituted 100% of Fe and Al-bound P in Kottawa soils. This indicates that in the original soil there is no Fe and Al-bound P to dilute the added P. If we consider the relative amounts of Fe and Al bound P, the latter is much greater in St. Coombs soil than in Kottawa. Therefore, the comparative amounts of Al and Ca phosphate in Kottawa soils are greater than that in St Coombs.

TABLE 3 — *Fractions of fixed labelled P in Soils*

Type of P (*Chang & Jackson 1957*	*St Coombs*			*Kottawa*		
	Amount of P µ*g*/*g soil*	*SP activity dpm*/µ*g P*	*P. derived from Fert.* %	*Amount of P* µ*g*/*g soil*	*SP activity dpm*/µ*g P*	*P. derived from fert.*%
Total P	616	5.3	4.0	232	51.59	39.33
KCl-extraction	ND	—	—	ND	—	—
AL-P	59	12.88	9.82	30	131.67	100.00%
Fe-P	164	14.93	11.38	36	140.97	100.00
Ca-P	48.5	1.96	1.49	18	19.4	1.48
Organic-P*	344.5	—	—	148	—	—

Each value is an average of three determinations.
* Estimated by difference method.
ND — Not detectable.

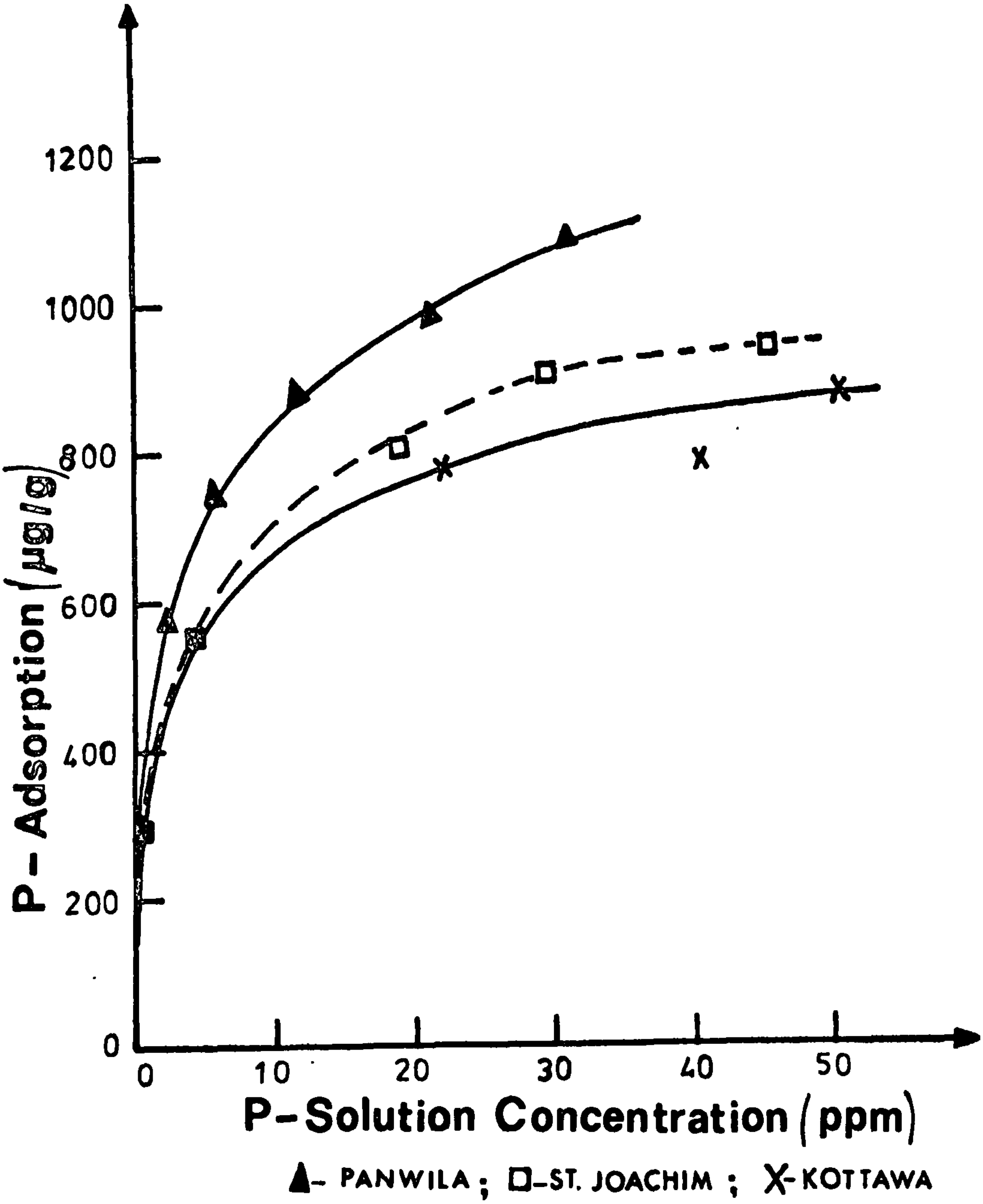

Fig. 2 — P adsorption isotherms of Panwila, St Joachim and Kottawa Soils.

E_t values

As seen from the Table 2, E_t values closely follow the phosphorus adsorption maxima (Table 2). The low E_t value soils respond to P-fertilization whereas in high value soil responses are quite low. E_t value can provide a valid explanation for the

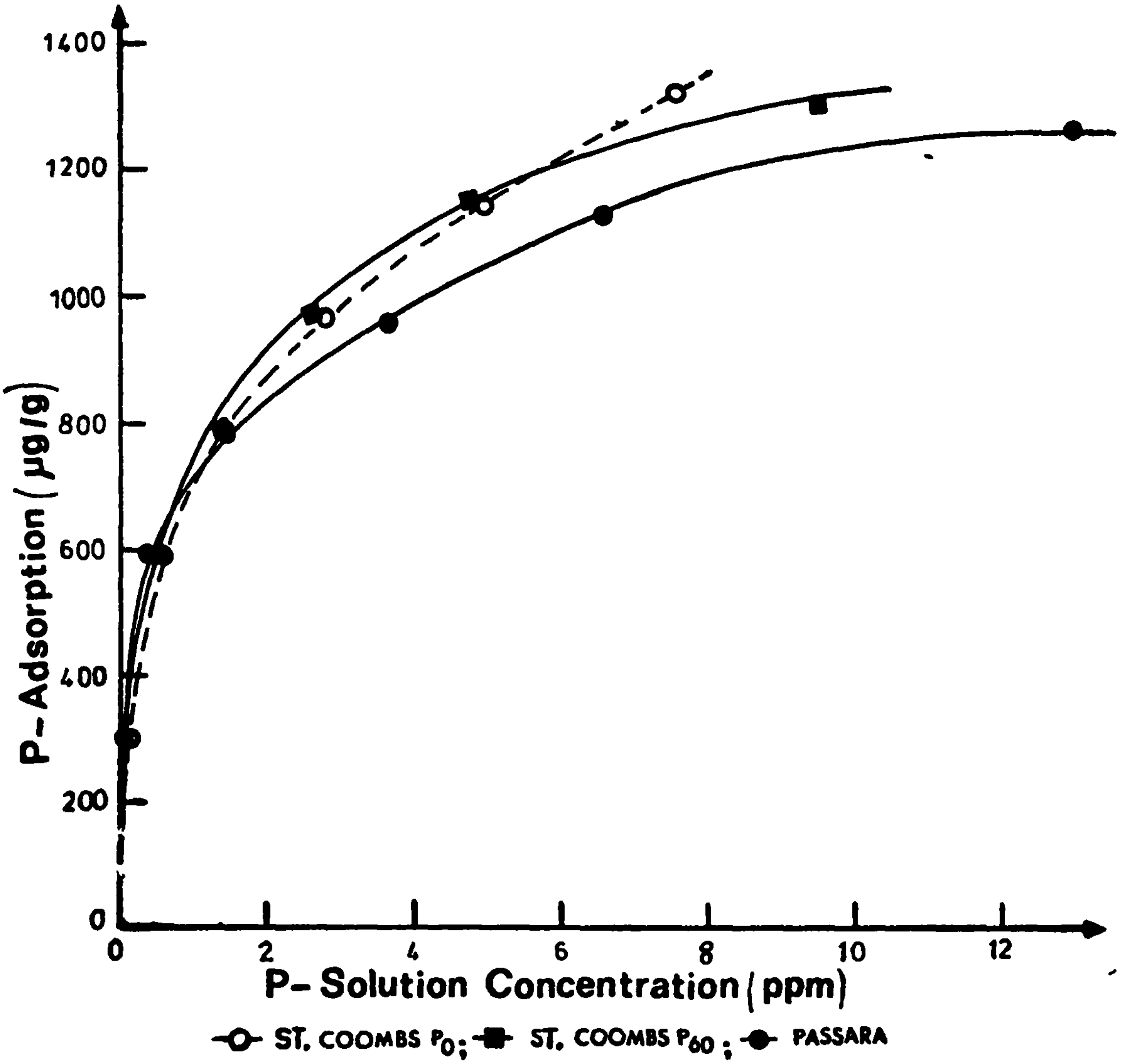

Fig. 1 — P adsorption isotherms of St Coombs and Passara Soils.

field P responses of tea yields. Heavily fertilized STC P_{60} soil shows a marked increase in E_t values over the STC P_0 though the P-adsorption capacities are very close in the two cases.

A values

A values were determined for soils using two plant species, replicated three times, and for tea, replicated once with only one level of P. A number of problems were encountered in the interpretation of the A-value data. In a number of instances the A value of the soil was higher than the 'A' value in the presence of the fertilizer (Table 4). This was true always in the case of St Coombs soil where the native P and the P-adsorption capacity was very high. Whereas in the low P-fixing Kottawa soil there was always a +ve A value. In Kottawa soils, rock phosphate was superior, to Eppawela apatite for beans and sorghum. But with tea plants, Eppawela apatite showed a better availability than that of rock phosphate in both soils. Since tea being a unique plant able to sustain life under very low pH conditions in soil, it must be having a different mechanism for uptake of largely unavailable P from soil from that of other annuals like bean and sorghum, Though this method of comparing fertilizers have been criticised widely (Nagarajah. *et. al.*, 1978) this clearly shows at least in the case of tea plants availability of P in Eppawela apatite is comparable to or even greater than that of rock phosphate at 100 ppm level of P-application. Also it shows that no other crop can be used as the test crop for availability of P in assessing P requirements of tea. This is in accordance with the A-value data calculated by previous workers for different crop species, (Anderson and Thomsen, 1978). A-value data in this case supports the previous evidence obtained by Sivasubramaniam, *et. al.*, (1974/78) by classical greenhouse experiments.

TABLE 4 — *A - Values (ppm)*

Plant Species	*Soil*	*Rock Phosphate*		*Eppawela Apatite*		*Control*	*LSD* (<*0.05*)
		100 ppm	*1000 ppm*	*100 ppm*	*1000 ppm*		
Bean (*Fasciolus vulgaris*)	Kottawa	$233^{(79)}$	$296^{(142)}$	$157^{(3)}$	$175^{(21)}$	154	540
	St Coombs	$1168^{(-ve)}$	$831^{(-ve)}$	$1165^{(-ve)}$	$1460^{(-ve)}$	2227	
Sorghum (*Sorghum vulgare*)	Kottawa	$27^{(23)}$	$65^{(21)}$	$7^{(3)}$	$20^{(16)}$	4	205
	St Coombs	$172^{(-ve)}$	$158^{(-ve)}$	$563^{(9)}$	$536^{-(ve)}$	554	
Tea (*Camellia sinensis L.*)	Kottawa	$782^{(663)}$	—	$983^{(864)}$	—	119	—
	St Coombs	$5518^{(2274)}$	—	$5550^{(2306)}$	—	3244	

* Values in parenthesis indicates A_2 (calculated).

Dry matter yield P, uptake and leaf P-concentration

All the above criteria did not show a significant difference between the two fertilizer types.

CONCLUSIONS

Mineralogy of the tea soils constitutes relatively few clay minerals namely Kaolinite and a hydroxy interlayered vermiculite in relatively large proportions, and also Gibbsite and Goethite in minor quantities. In Passara soil only Kaolinite was found at depths 15—30 and 30—45 cm and a trace of mica was found in Panwila soils. The Kaolinite, Gibbsite and Goethite are mainly responsible for the phosphorus fixation of these soils. Surface area of these soils are also related to the P-adsorption, probably suggesting a surface reaction on these clay minerals.

Phosphorus adsorption capacities of 0—15 cm layer of these soils range from 896 μg/g P for Kottawa soil into 1439 μg/g P for St Coombs soil whereas at 30—45 cm depth same soils ranges 1099 μg/g soil to 2380 μg/g soil. Probably this large P-fixation down the horizon suggests it is best to broadcast than to fork in the P-fertilizers. The Langmuir constant K-which is related to the bond strength of P to the soil, also follows the same trend as P-adsorption maximum.

K value clearly indicates that the P in Kottawa soil should be loosely bound than that in St Coombs. BET surface area showed a direct relationship towards P-adsorption though not as good as that with Ethylene Glycol area reported by Olson and Watanabe (1957). Fractionation of fixed P in these soils showed that, in both Kottawa and St Coombs soils organic P constituted the largest fraction. Most of the organic P fixed in Kottawa soil came from added fertilizer, except Ca-bound P. Whereas the P derived from fertilizer in St Coombs was about a tenth of the total of inorganic P.

E^t values for soils, and A values by using tea plants, both supported the use of Eppawela apatite on tea soils. Also to find the availability of P to tea, we cannot use the short term annual crops like bean and sorghum as the test crop. As the A values determined for these crops are quite different from that found using tea.

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