AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON, D. C. 20523

BIBLIOGRAPHIC INPUT SHEET

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1. SUBJECT CLASSIFICATION

A. PRIMARY: Agriculture

B. SECONDARY: Soils and Fertilizers

2. TITLE AND SUBTITLE

Inorganic and organic phosphorus occurrence in some highly weathered soils of Puerto Rico

3. AUTHOR(S)

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4. DOCUMENT DATE	5. NUMBER OF PAGES	6. ARC NUMBER
1974	12p.	ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS

Cornell University
Dept. of Agronomy
Ithaca, New York 14850

8. SUPPLEMENTARY NOTES *(Sponsoring Organization, Publishers, Availability)*

Published in tropical agriculture vol.52, no.2, Apr.1975

9. ABSTRACT

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10. CONTROL NUMBER

PN-AAB- 236

11. PRICE OF DOCUMENT

12. DESCRIPTORS

Oxisols, Ultisols, Soil Phosphorus, Reductant-Soluble Iron, Aluminum Oxides, Phosphorus Adsorption

13. PROJECT NUMBER

931-17-120-505

14. CONTRACT NUMBER

AID/CSD-2490

15. TYPE OF DOCUMENT

Research paper

AID 590-1 (4-74)

Trop. Agric. (Trinidad) Vol. 52, No. 2, April 1975

REPRINTED FROM

TROPICAL AGRICULTURE

THE JOURNAL OF THE FACULTY OF AGRICULTURE (IMPERIAL COLLEGE OF TROPICAL AGRICULTURE) UNIVERSITY OF THE WEST INDIES

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Published on behalf of the Faculty by
IPC SCIENCE AND TECHNOLOGY PRESS LTD
GUILDFORD
1974

*Inorganic and organic phosphorus occurrence in some highly weathered soils of Puerto Rico**

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Seven oxisols and ultisols of Puerto Rico were analysed for inorganic P fractions, organic P, and P adsorption characteristics. Reductant-soluble or iron occluded P was the predominant inorganic form followed by Fe-P, adsorbed P, Ca-P, and Al-P. The adsorbed P ($NaHCO_3$ extractable) was apparently associated with iron and aluminium oxides and its removal prior to fractionation caused a decrease in the Al-P and Fe-P fractions. The decrease in Al-P and Fe-P fractions as a result of the removal of adsorbed P was most pronounced on the soils that had received fertilizer P additions within two years prior to sampling. Organic P, as determined by three different methods, constituted 25 to 50 per cent of the total soil P. Adsorption isotherms indicated that these soils had a high retention capacity for phosphorus. Amorphous or non-crystalline forms of aluminium oxides were more correlated with P adsorption characteristics than those of iron.

INTRODUCTION

PHOSPHORUS is generally recognized as being one of the major limiting nutrients for plant growth on the highly weathered ultisols and oxisols of the humid tropics (OLSEN and LNGELSTAD, 1972). This results from the phosphorus of these soils being present in forms that are relatively unavailable to plants and also from the immobilization or fixation by iron and aluminium oxides of added fertilizer P. Recent field experiments on some highly weathered soils of Puerto Rico, however, have failed to show a consistent response to phosphate fertilizer applications. This was in spite of the fact that glasshouse trials and chemical extractions for available phosphorus indicated that a definite response should have occurred. Various explanations could be advanced for the lack of P response in the field, such as the presence of forms of inorganic phosphorus that may become available to the plant over the growing season but are not extracted by routine tests for available P (FIGARELLA *et al.*, 1964); fixation of added P fertilizers (FOX *et al.*, 1971); or mineralization of organic P (ACQUAYE, 1963; FRIEND and BIRCH, 1960). Before investigation of any of these in detail it would be desirable and

* Agronomy Paper No. 1062. Contribution from the Dept. of Agronomy, New York State College of Agriculture and Life Sciences, Cornell University.

Table 1. Some chemical properties of soils studied

Soil series and subgroup	pH		Organic matter	Dithionite–citrate		Tamm		0·5 M $CaCl_2$ at pH 1·5		Phosphorus		
	H_2O	KCl	(%)	Fe (%)	Al (%)	Fe (%)	Al (%)	Fe (%)	Al (%)	Bray No. 2 (p.p.m.)	Olsen (p.p.m.)	Total (p.p.m.)
Catalina Tropeptic Haplorthox	4·7	4·1	5·1	8·3	0·9	0·38	0·26	0·05	0·24	0·8	5·3	500
Coto Tropeptic Haplorthox	4·8	4·1	4·2	9·3	1·5	0 14	0·16	0 01	0·14	4·9	5·0	1420
Daguey Orthoxic Tropohumult	5·4	4·6	5·8	7·6	1·0	0 90	0·21	0·08	0·15	0·8	7·5	708
Humatas Typic Tropohumult	4·9	4·6	5·1	3·6	1·3	0·33	0·15	0·08	0·17	3·6	7·1	602
Nipe Typic Acrorthox	5·0	4·5	5·2	23·0	3·9	0·20	0·28	0 02	0·20	1·4	4·5	583
Pina Typic Haplorthox	4·5	4·3	1·4	1·0	0·4	0·09	0·04	0·02	0·10	104	76·0	530
Torres (1) Orthoxic Palehumult	4·3	4·0	4·4	6·9	1·0	0·57	0·36	0·05	0·19	5·8	8·5	525
Torres (2) Orthoxic Palehumult	4·9	4·5	—	—	—	—	—	—	—	33·0	62·0	744

beneficial to have some background knowledge of the phosphorus parameters of the highly weathered soils of Puerto Rico. Currently this information is not available in the literature. Hence it was the purpose of the present investigation to determine: (1) the amount and forms of inorganic P; (2) the organic P content; and (3) the P adsorption characteristics of some representative oxisols and ultisols of Puerto Rico.

MATERIALS AND METHODS

Soil samples

The seven ultisols and oxisols selected for study (*Table 1*) were from the northern portion of the island of Puerto Rico where the average annual temperature is approximately 24 C and the average annual rainfall is 1600 to 2000mm. All of the soils except the Piña and Nipe have been formed from volcanic andesitic parent materials. Sandy deposits derived from weathered limestones and quartzitic sandstones were the parent materials of the Piña while the Nipe was formed by the weathering of serpentinite rocks. Surface soil samples were collected from 0 to 15cm with the exception of the Nipe from which the 0 to 30cm depth was collected.

The Catalina, Coto, and Humatas samples were taken from open pits adjacent to fertility plots, while the Daguey and Nipe samples were taken from exposed road banks. The Piña sample was taken from a fertility plot that had received P at 165kg/ha as triple superphosphate over a two year period prior to sampling. The Torres (1) sample was taken from the control treatment of a fertility trial while the Torres (2) was sampled from a treated plot that had received P at 360kg/ha applied as triple superphosphate four months prior to sampling. The Piña, Torres (1) and Torres (2) samples were included in the study in order to have some idea of the fate of applied phosphate fertilizers in these soils.

For purposes of characterization of the soils, total organic matter content was determined by the modified Walkley Black method (GRIEWELING and PEECH, 1965); pH was determined in H_2O and 1N KCl at a 1 : 2 soil : solution ratio; available P by the Olsen and Bray No. 2 methods (JACKSON, 1958); and total P by HF H_2SO_4 digestion (PRUDEN and KING, 1969). Crystalline iron oxides and associated aluminium oxides were determined by the citrate bicarbonate dithionite (*CBD*) procedure of JACKSON (1956). Tamm's acid oxalate procedure (GORBUNOV *et al.*, 1961) and the procedure of TWENHOFEL *et al.* (1967) were used to determine amorphous or less-ordered iron and aluminium oxides.

Inorganic phosphorus fractionation

Inorganic phosphorus fractions were determined according to the method of CHANG and JACKSON (1957) as modified by PETERSEN and CORLY (1966). Two changes, however, were made in the fractionation procedure. First, the initial NH_4Cl extraction for soluble P was replaced by five sequential 30min extractions with 0·5N $NaHCO_3$ of pH8·5 to remove adsorbed P as suggested by ROBARGE (1971). Secondly, the re-adsorption of P by active

iron oxides during the extraction of Al–P was corrected by the procedure of WILLIAMS *et al.* (1967).

The ascorbic acid method of WATANABE and OLSEN (1965) was used to determine the P in the extracts. In order to determine P in the *CBD* extracts by the ascorbic acid method, additional ammonium molybdate solution was added as suggested by WEAVER (1974) to eliminate interference from citrate.

Organic phosphorus

Total organic phosphorus content of highly weathered soils can vary widely depending upon the method used for determination (ROBERTS and WEAVER, 1973). Because of this and the limited data available on comparative studies of organic phosphorus methods on highly weathered soils, three different methods for total organic phosphorus were used in this study. The first two methods were the ignition procedures of SAUNDERS and WILLIAMS (1955) in which the soil sample is ignited at 550 C for one hour followed by an overnight extraction with 2N H_2SO_4 or 0.2N H_2SO_4 at a 1 : 50 soil : solution ratio. The difference in the phosphorus extracted from an unignited sample as compared to the ignited sample is taken as the organic phosphorus content. The extraction procedure of MEHLICH *et al.* (1954) as modified by ANDERSON (1960) was the third method used to determine total organic phosphorus.

Phosphorus adsorption isotherms

Phosphorus adsorption isotherms were determined in a manner similar to that given by FOX *et al.* (1971). This method involved equilibration of 3g samples of soil at 25 C in 30ml of 0.01M $CaCl_2$ containing 500 to 4000 μg P and two drops of toluene. Samples were shaken 30min daily. After six days equilibration the samples were centrifuged and P in solution was analysed by the ascorbic acid method. Phosphorus sorbed (x/m, p.p.m.) was plotted against the logarithm of the solution P concentration (c, p.p.m.).

For calculation of adsorption maxima the following form of the Langmuir equation was used:

$$c/(x/m) = 1/kb + c/b$$

where c = final supernatant solution P concentration, x/m = P adsorbed by soil, b = adsorption maximum, k = a constant related to the bonding energy of the soil for phosphorus. A plot of $c/(x/m)$ against c should give a straight line with slope of $1/b$ and an intercept of $1/kb$.

RESULTS AND DISCUSSION

Inorganic phosphate fractions

The results of the inorganic phosphate fractionation (*Table 2*), excluding the Piña and Torres (2) soils which had received recent additions of P fertilizers, showed that reductant-soluble P or that occluded within iron oxides was the predominant form with a mean value of 232 p.p.m. Although it is the largest proportion of inorganic P in these soils, the reductant-soluble P is of little importance as a source of plant available P except under reducing conditions as might occur under paddy rice production. Of the so-called

Table 2. Inorganic phosphate fractions (p.p.m.) of some highly weathered soils of Puerto Rico

Soil	Adsorbed-P	Al-P Uncorrected	Al-P Corrected	Fe-P	Ca-P	Reductant soluble-P	Total
Catalina	21	8	24	80	13	137	275
Coto	18	11	16	234	28	475	771
Daguey	20	2	10	76	18	192	316
Humatas	23	4	9	59	25	133	249
Nipe	15	2	8	39	8	304	374
Piña	125	68	68	119	21	85	418
Torres (1)	24	7	23	89	24	155	315
Torres (2)	105	16	40	172	32	155	504

'mobile' inorganic P fractions, the Fe-P was the largest with an average value of 96 p.p.m. P, followed by adsorbed P (20 p.p.m.), Ca-P (19 p.p.m.), and Al-P (14 p.p.m.). With the exception of the adsorbed P fraction, this distribution of inorganic P fractions is consistent with other results on highly weathered soils (CHANG and JACKSON, 1958). Presumably in acid soils, Ca-P weathers to form Al-P, Fe-P, and reductant soluble P with the amounts increasing in that order with increasing degree of chemical weathering.

The proportion of adsorbed P in the soils was much greater than values usually associated with soluble P extracted by 1 N NH_4Cl from highly weathered soils. This was especially true for the recently P fertilized Piña and Torres (2) soils. To determine the nature of the adsorbed P, the extractions for Al-P, Fe-P and Ca-P were repeated but with 1 N NH_4Cl extraction in place of $NaHCO_3$. When this was done, it was found that the sums of the inorganic P fractions (*Table 3*) were approximately equal to those obtained

Table 3. Comparison of the effect of initial extraction by 1 N NH_4Cl and 0·5 N $NaHCO_3$ on the determination of inorganic P fractions (p.p.m.)

Soil	1 N NH_4Cl Soluble-P	Al-P	Fe-P	Ca-P	Total	0·5 N $NaHCO_3$ Adsorbed-P	Al-P	Fe-P	Ca-P	Total
Catalina	—	28	93	13	134	21	24	80	13	138
Coto	1	21	247	29	298	18	16	234	28	296
Daguey	—	11	83	18	112	20	10	76	18	124
Humatas	—	11	81	26	118	23	9	59	25	116
Nipe	—	8	41	7	56	15	8	31	8	62
Piña	13	95	192	21	321	125	68	119	21	333
Torres (1)	1	29	105	25	160	24	23	89	24	160
Torres (2)	2	70	249	31	352	105	40	172	32	349

when initial $NaHCO_3$ extractions had been used. The NH_4Cl extractions, however, caused increases in the Al-P and Fe-P fractions in comparison to those obtained when $NaHCO_3$ extractions were used, while the Ca-P fractions remained essentially unchanged. Apparently for these soils, as also noted by ROBARGE (1971) for some acid soils of New York, the P extracted by $NaHCO_3$ is that which would normally be extracted as Al-P or Fe-P in the original CHANG and JACKSON (1957) procedure or the PETERSEN and COREY (1966) modification. In as much as the bicarbonate extraction has been shown (ROBARGE, 1971) not to remove any appreciable amount of P from crystalline Al-P (variscite) or Fe-P (strengite), it seems likely that the

$NaHCO_3$ extractable P is that which is associated with surface active iron and aluminium oxides. Whether or not this P fraction should be considered as adsorbed P or 'colloidal' forms of Al–P and Fe–P that are soluble in 0·5N $NaHCO_3$ may be an academic question only. The important point is that the inclusion of the bicarbonate extraction enabled an additional distinction to be made on the reactivity of P that is associated with Fe and Al. This could be quite significant since labile phosphate forms, which would include those mobilized by bicarbonate extraction, are much more active in maintaining the pool of solution P for plant growth than are crystalline or more ordered forms (MURRMAN and PELCH, 1969). Therefore, the prior removal of adsorbed P should make a decided improvement in the use of inorganic P fractionation for characterization of P forms present in soils and also for monitoring P transformations in soils following applications of P fertilizers. The latter is pointed out quite strongly in the present case for the Piña and Torres (2) samples which had received recent additions of P fertilizer. Failure to take into account the adsorbed P fraction would have led to an overestimate of the amount of applied P that had reacted to form Al–P and Fe–P. This has probably been the case in other studies (LUCAS and BLUE, 1972; UDO and UZU, 1972) in which applied P on acid soils was reported to be retained almost entirely as Al–P and Fe–P. It is also very likely that in situations in which Al–P and Fe–P have been identified as sources of plant available P (SHELDON and COLEMAN, 1968) it was the adsorbed P associated with Al and Fe oxides rather than Al–P or Fe–P (extractable by 0·5N NH_4F and 0·1N NaOH, respectively, but not by 0·5N $NaHCO_3$) that was utilized by plants.

Organic phosphorus

The values for organic P (*Table 1*) showed that this fraction constituted a significant proportion of the total soil P. The amount for any one soil, however, varied depending upon the method used for its determination. If past results on highly weathered soils are used as a criterion (ENWEZOR and MOORE, 1966), then the ANDERSON–MEHTA values should probably be taken as the most accurate. That is, this procedure has been found to give the

Table 4. Organic, inorganic and total extracted phosphorus content (p.p.m.) of some highly weathered Puerto Rican soils

Soil	Total extracted P			Inorganic P			Organic P		
	I*	II†	III‡	I	II	III	I	II	III
Catalina	303	163	476	63	25	261	240	138	215
Coto	658	577	1291	99	44	931	559	533	360
Daguey	241	166	657	66	26	297	175	140	360
Humatas	373	266	631	79	43	343	294	223	298
Nipe	205	79	472	27	11	231	178	68	241
Piña	467	419	585	362	266	467	105	153	118
Torres (1)	387	203	526	135	61	300	252	142	226
						Mean	258	200	260

* I: Ignition at 550°C and extraction with 2N H_2SO_4 (SAUNDERS and WILLIAMS, 1955)
† II: Ignition at 550°C and extraction with 0·2N H_2SO_4 (SAUNDERS and WILLIAMS, 1955)
‡ III: Alkaline plus acid extraction (ANDERSON, 1960)

maximum extraction of organic P with a minimum of hydrolysis or mineralization during extraction in comparison to ignition procedures.

Incomplete extraction of organic P appears to have occurred with 0·2N H_2SO_4 extraction following ignition as these values were generally low compared to the other two methods. A probable reason for the incomplete extraction is that during ignition, a portion of the organic P which is mineralized may combine with the abundant amounts of iron and aluminium oxides present in these soils to form a secondary reaction product which is not solubilized by 0·2N H_2SO_4 (BORNEMISZA and IGUE, 1967). Accordingly, the generally greater values for organic P when 2N H_2SO_4 extraction followed ignition probably resulted from the increased acid concentration being more effective in recovery of the organic P released upon ignition. For two of the soils, Daguey and Nipe, even the 2N H_2SO_4 extraction following ignition gave organic P values that were much lower than the ANDERSON-MEHTA values. This is not unusual, however, as it has been observed that even repeated extraction with 2N H_2SO_4 may not extract all of the organic P from some highly sesquioxidic soils (SAUNDERS and WILLIAMS, 1955). The Piña soil was exceptional in that it had a higher organic P content with 0·2N H_2SO_4 extraction following ignition than with 2N H_2SO_4 extraction. Possibly for this soil the stronger acid extraction may have caused the hydrolysis of acid-labile organic P compounds during extraction of the unignited sample (ANDERSON, 1960).

The Coto soil was also unusual as its ANDERSON-MEHTA organic P value was much lower than that of either ignition procedure. An explanation for this difference could be the presence of the plumbogummite group of phosphate minerals (NORRISH, 1968). When these minerals are heated to temperatures above 400°C, they lose their structural water and become amorphous. In this form they are likely to be extracted by either 0·2N H_2SO_4 or 2N H_2SO_4 and would cause ignition organic P values to be greater than ANDERSON-MEHTA extraction values. An attempt was made to determine the presence of the plumbogummite minerals in the Coto soil by concentration with HF and X-ray diffraction powder analysis as recommended by NORRISH (1968). No characteristic diffraction lines of the plumbogummite minerals were observed and apparently the greater ignition values, as compared to those of the ANDERSON-MEHTA method, may be related to the nature of the organic P present in the Coto soil.

Excluding the fertilized Piña soil, the organic P content as given by the ANDERSON-MEHTA procedure ranged from 25 to 51 per cent of the total soil P with an average value of 42 per cent. These values are similar to those for other soils of tropical regions where similar extraction techniques have been used. For example, BORNEMISZA and IGUE (1967) reported 12 surface soils of Costa Rica as having an organic P content that was 14 to 77 per cent of the total soil P with an average value of 51 per cent. In 23 southern Nigerian surface soils OMOROSO (1971) found organic P to represent 21 to 74 per cent of the total soil P with an average value of 40 per cent.

Even though organic P makes up a significant proportion of the total soil P, it is difficult to make any definite predictions as to whether or not mineralization of organic P would occur in these soils, based only on the amount or proportion of organic P. This is because numerous other factors are also

involved, notably temperature, moisture, soil reaction, and the supply of energy material. Nevertheless, the studies in which organic P mineralization has been shown to be significant (ACQUAYE, 1963; FRIEND and BIRCH, 1960) have involved soils in which organic P formed a major proportion of the soil P. Furthermore, ENWEZOR (1967) found for some Nigerian soils, that mineralization of organic P was positively correlated with organic P expressed as a percentage of total P. Therefore, it would seem likely that mineralization could have a significant role in supplying plant available P

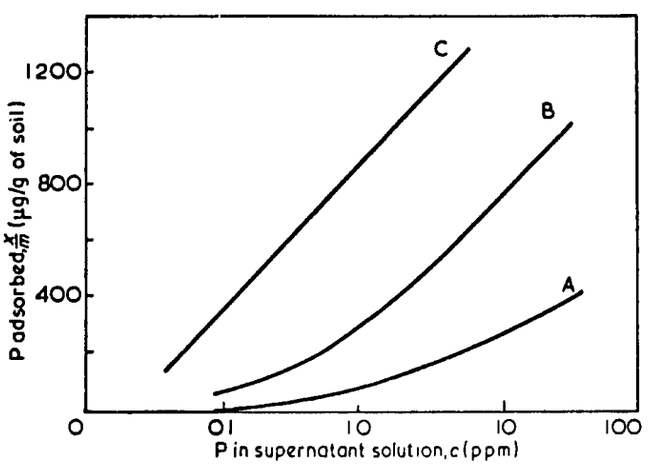

Figure 1. Phosphorus adsorption isotherms for some highly weathered soils of Puerto Rico. A, Piña, B, Humatas; C, Catalina

in these highly weathered Puerto Rican soils under the appropriate conditions and that further field and laboratory studies to elucidate the exact role of organic P mineralization in these soils would be desirable.

Phosphorus adsorption isotherms

The phosphorus adsorption isotherms of the soils plotted as the amount of P adsorbed (x/m) against the logarithm of the equilibrium solution concentration (c) were linear or slightly concave curves. Some examples are shown in *Figure 1*. When values of $c/(x/m)$ were plotted against c in order to determine adsorption maxima, it was evident that the soils had two distinct isotherms as evidenced by those of the Catalina and Humatas (*Figure 2*). As reported by SYERS *et al.* (1973) the existence of at least two adsorption isotherms is not uncommon for soils and is an indication of two distinct populations of adsorption sites with widely different affinities for phosphorus. The sites responsible for the adsorption of P at low equilibrium concentration values (approximately less than 3 p.p.m. P) have a much higher affinity for P than those sites at higher equilibrium concentrations. The presence of two different populations of adsorption sites would mean that each soil will have two different adsorption maxima and that the P adsorption capacity of a given soil should be the overall sum of the individual maxima. The adsorp-

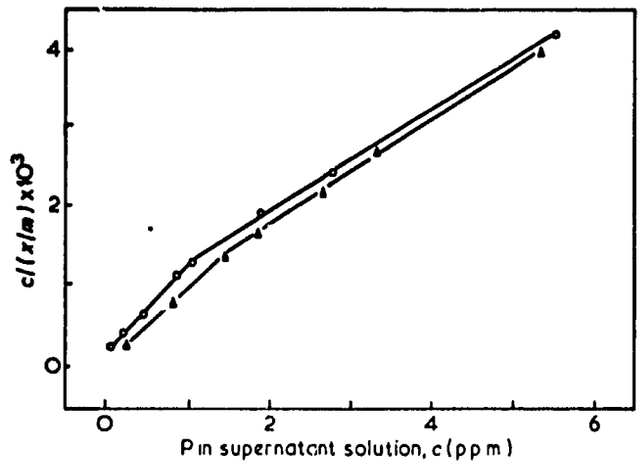

Figure 2. Langmuir plot of the phosphate adsorption data for the Catalina (○) and Torres (1) (▲) soils

tion maxima reported in *Table 5* are largely based upon the population of adsorption sites at the higher concentration values and therefore should represent values for the overall P adsorption capacities of the soils. The values (*Table 5*) indicated that these soils have a relatively high adsorption capacity for phosphorus and are quite similar in magnitude to those reported for some highly weathered soils of Hawaii (Fox *et al.*, 1971) and Jamaica

Table 5. Phosphorus adsorption isotherm data (p p.m.) for some highly weathered soils of Puerto Rico

Soil	*Adsorbed P at 0·1 p.p.m. solution P*	*Adsorption maximum*
Catalina	360	1100
Coto	220	637
Daguey	310	700
Humatas	50	730
Nipe	360	1070
Piña	0	375
Torres (1)	410	1020
Torres (2)	240	900

(WEIR, 1972). The Piña, inevitably, was an exception as a result of its coarse texture (sandy clay) and recent P fertilizer applications.

From an immediate fertility standpoint the amount of adsorbed P at a given single solution P value may be of more significance than the adsorption maxima. According to North Carolina and Hawaiian investigators (Fox and KAMPRATH, 1970) the requirements for maximum yields on highly weathered soils can be estimated as the amount of P that must be added to give a solution value of 0·2 p.p.m. P. Recent results by Hawaiian investigators (SILVA, personal communication, 1972) have suggested that 0·1 p.p.m. solution P may be adequate for maximum crop production, and accordingly

the amount of adsorbed P at 0·1 p.p.m. solution P is given for the Puerto Rican soils in *Table 5*. It is not known whether this method for determination of P requirements will apply to Puerto Rican soils. Some recent field results on the Torres soil suggest that it does not, as there was no consistent or large response to P even though the unfertilized soil had less than 0·005 p.p.m. solution P and sufficient P was added to raise the solution level to 0·1 p.p.m. P as indicated by the adsorption isotherm.

Regression analysis was used to relate the P adsorption parameters to the amount and type of sesquioxides present in the soils. Only the amounts of amorphous or non-crystalline aluminium oxides extracted by the TAMM or TWENEBOAH procedures were significantly correlated with any of the P adsorption parameters. The TAMM extractable Al was significantly correlated with the adsorption maxima ($r=0{\cdot}95$; $P=0{\cdot}01$) as was the TWENEBOAH extractable Al ($r=0{\cdot}91$; $P=0{\cdot}01$). Neither the TAMM or TWENEBOAH extractable Al was significantly correlated with adsorbed P at 0·1 p.p.m. solution P at the $P=0{\cdot}05$ level. The failure to find any significant correlation of amorphous iron oxides with any of the P adsorption parameters even at the $P=0{\cdot}10$ level may be in part a consequence of the small number of samples used in the study. The present results, however, are in general agreement with other studies (SYERS *et al.*, 1971) in that amorphous Al oxides appear to be more active in the immediate adsorption of P than iron oxides.

CONCLUSIONS

Overall, the analyses for available P, the inorganic P fractions, and adsorption isotherms show that these highly weathered soils of Puerto Rico are low in available P; have a large proportion of their inorganic P in a highly unavailable form (reductant-soluble) and have a fairly high capacity to immobilize applied fertilizer.

The results suggest two aspects that may eventually help explain the lack of field response to phosphorus on these or similar soils of Puerto Rico. The first is the origin and significance of the adsorbed or bicarbonate extractable P associated with aluminium and iron oxides and ordinarily determined as Al–P or Fe–P. The second is the possible mineralization of the organic P which made up a significant proportion of the total soil P. The mineralization of at least some portion of the soil organic P would seem likely in consideration of results in other tropical areas (ACQUAYE, 1963; FRIEND and BIRCH, 1960). It may well be that mineralization of organic P gives rise to a substantial part of the adsorbed P fraction in these soils. It was shown that a large amount of the applied fertilizer P in the Piña and Torres (2) soils existed as adsorbed P. In an analogous manner, it would seem that one of the results of organic P mineralization would be an increase in the adsorbed P fraction. The latter would be a dynamic process, no doubt, with portions of the adsorbed P being converted to forms non-extractable with bicarbonate while at the same time mineralization processes could replenish or increase the adsorbed P fraction. Although the exact relationship between the adsorbed P fraction and organic P mineralization cannot be definitely

elucidated from the present results, the possible significance of such a relationship in extension of knowledge of P behaviour in highly weathered soils should merit further research in this area.

ACKNOWLEDGEMENT

This study is part of the work supported by the U.S. Agency for International Development under research contract csd-2490 entitled: Soil Fertility Requirements to Attain Efficient Production of Food Crops on the Extensive, Deep, Well Drained, but Relatively Infertile Soils of the Humid Tropics.

(*Received September 1973*)

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