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USE OF RADIOACTIVE ^{32}P TECHNIQUE TO STUDY PHOSPHATE ROCK DISSOLUTION IN ACID SOILS

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Abstract. A laboratory experiment was conducted to evaluate the dissolution of six sources of phosphate rock in two acid soils (Ultisols): a sandy soil and a red clay soil. Labile P was determined using the radioactive ^{32}P technique for Pi extractable P and resin extractable P. Incubations were conducted for 0, 1, 2, 3, 4 and 5 weeks for ^{32}P exchangeable technique, 0 and 5 weeks for Pi technique and 5 weeks for resin technique. Rates of PR were 0 and 400 mgP/ha. The results showed that labile P in the sandy soil decreased from 0-1 weeks for all the PRs except Hahotoe PR and Hazara PR's. Between 1 and 5 weeks labile P remained relatively constant. The ranking of labile P from PRs was: North Carolina = Kouribga > Matam > Hahotoe = Hazara> Patos de Minas. In the red soil, labile P from all PRs appeared to be relatively unchanged during the 0-5 week incubation. Pi extractable P in sandy soil showed no significant differences due to incubation time. In the red clay soil, there was a significant decrease in Pi-P extracted from soil mixtures with PRs after 5 weeks as compared to 0 weeks. Results of the Resin-extractable P in both sandy and red soils were in agreement with labile P as measured by ^{32}P exchange technique.

1. INTRODUCTION

In sustainable agriculture, phosphate rock (PR) is a potential natural resource that can be utilized to supply phosphorus to plants and to increase crop yields. It has been shown that direct application of phosphate rock may be more cost-effective than the use of expensive water-soluble phosphate (P) fertilizers, especially in tropical developing countries, under certain soil, crop and agroclimatic conditions. Major factors affecting the agronomic effectiveness of PR for direct application are PR inherent factors, soil properties, climatic conditions and crop species.

Reactivity of PR varies widely with PR deposits. An understanding of PR reactivity is essential to the selection of proper sources of PR for direct application. Use of the radioactive ^{32}P technique is one means to measure the potential reactivity of PR. The total amount of phosphate ions in the soil (solid phase plus soil solution) that can undergo isotopic exchange is called the "Labile Phosphate" [1, 2]. Labile phosphate (E value of Russell et al. [3]) is often determined by the direct method of equilibrating soil with a solution of ^{32}P labelled orthophosphate. It is assumed the phosphate ions in solution exchange with solid phase phosphate and the added ^{32}P comes in equilibrium with the total exchangeable pool of P in the soil [4]. The P-fixing capacity of the acid soils can be determined at the same time by this technique. The objective of this study was to evaluate the dissolution of various phosphate rocksin acid soils utilizing the ^{32}P exchange technique.

2. MATERIALS AND METHODS

Laboratory studies were conducted at Auburn University, Auburn, Alabama and the International Fertilizer Development Center, Muscle Shoals, Alabama. Six sources of phosphate rock (PR) were incubated with two acid (Ultisols) sandy and red clay soils. The sandy soil was a Trovys loamy sand

and the red clay soil was a Hiwassee clay loam classified as a clayey, kaolinite, humic, rhodic, kanhapludults. A short description of main characteristics of PR and soils is given in Tables I and II.

Ten gram subsamples of soil were weighed in triplicate and mixed well with the Phosphate rock (PR) sources as listed in Table 1 Each source was applied to supply 400 mg P/kg soil. Distilled water was added to bring the soil moisture content to 80% of field capacity (5% for sandy soil and 10% for red clay soil). Soil mixtures were incubated for 0, 1, 2, 3, 4 and 5 weeks at a temperature of 68°F to 78°F

Incubated soil samples were set up for determination of labile P pool using ^{32}P exchange technique, available P determination by resin technique and Pi strip technique, and P fixation. Incubation times were 0-5 weeks for the ^{32}P exchange technique. Incubation time was 5 weeks for the resin method. Incubation times were 0 and 5 weeks for the Pi strip and P fixation methods.

TABLE I. CHEMICAL ANALYSIS OF SIX VARIOUS SOURCES OF PHOSPHATE ROCK

Symbol	PR source		% Total P	NAC - soluble P*
PR_1	North Carolina	(USA)	13.0	2.91
PR_2	Khouribga	(Morocco)	14.5	2.43
PR_3	Matam	(Senegal)	12.5	1.96
PR_4	Hahotoe	(Togo)	15.9	1.56
PR_5	Hazara	(Pakistan)	12.3	1.00
PR_6	Patos de Minas	(Brazil)	9.4	0.70

* NAC - soluble P = Neutral ammonium citrate – soluble P as % of rock.

TABLE II. SELECTED SOIL PROPERTIES (TYPIC ULTISOLS)

						CDR***		
		P*	K*	Mg*	Ca*	Fe_2O_3	Al_2O_3	CEC
Soil	pH	mg/kg				g/kg		meq/100 g soil
Sandy soil	4.7	12	13	17	85	62.0	9.3	3.45
Red clay Soil	5.8	26	140	211	640			8.44

* = Pi extractable P. ** = NaOAc pH 7. *** = Citrate - Dithionite - Bicarbonate extractable.

Labile P attributed to PR alone was determined using the ^{32}P exchange technique without any incubation. The purpose of this step of the experiment was to evaluate labile P from PR dissolution by measuring isotopically exchangeable.

For labile P via ^{32}P for each incubation time, soil mixtures (10 g soil) were equilibrated in 100 ml of ^{32}P solution with 10^{-4} M KH_2PO_4 as a carrier. The activity of ^{32}P in the 100 ml was 1.4 µci/subsample. The soil suspensions were shaken for 24 hr at low speed. A portion of the suspension was centrifuged at 2500 rpm for 1 hr. The supernatant was filtered using 0.2 µm pore filter paper, and 1 ml of supernatant was pippetted into 10 ml of liquid scintillant solution in glass vials. The activity of ^{32}P left in the equilibration solution was measured using a liquid scintillation counter (Beckman model L S 3800).

The total P determinations in the extracts were made colorimetrically using the ammonium molybdate ascorbic acid method. Absorbance was measured at 880 nm.

Labile P was determined from
Labile P = [(Si/Sf - 1) B]

where Si = the initial specific activity, SF = the final specific activity, and B = the amount of P in the solution added to the soil in the ^{32}P exchange technique.

2.1. Phosphorus determination by resin technique

One-half g of soil (soil mixture with phosphate rock at 400 mg P/kg at 5 weeks incubation time) was weighed in a 50 ml centrifuge tube. Resin strip was added to soil together with 30 ml of deionized water, and shaken for 16 h.

Resin was removed and washed are move any adhering soil .The washed resin strips were in 50 ml tubes and extracted with 20 ml 0.5M HCl. After setting 1 h to allow gas to escape, the tubes were capped and shaken in overnight. Phosphorus was determined by the Murphy - Riley method.

2.2. Pi strip technique for ^{31}P determination as labile P pool

Soil with PRs were mixed and incubated for 0 and 5 weeks. One g of soil was to a 100 ml shaking bottle with screw cap. Forty ml of 0.02 M KCl solution was added to the bottle. A Pi strip was placed in the bottle and shaked for 16 h at low speed. The Pi strip was removed and rinsed with distilled water to remove soil particles on the strip. The strip was dried, but it was not necessary to dry completely. The strip was transferred to another bottle and extracted with 40 ml of 0.2 N $H_2 SO_4$ and shaking for1 h. The supernatant was filtered through a 0.2 µm pore filter paper and the filtrate was analysed for total P by the Murphy - Riley method at a wavelength of 880 nm.

2.3. Soil phosphorus fixation capacity

Soil mixtures were incubated for 0 and 5 weeks. After incubation the treated samples (10 g of soil) were transferred into 500 ml plastic bottles. Two hundred ml of 100 ppm P (KH_2PO_4) was added to each sample, and shaken for 6 hr. at low speed. The suspension was centrifuged at 10,000 rpm for 5 min. The supernatent was filtered through millipore (0.02 µm). The total P was determined in the filtrate using the Murphy Riley (1962) procedure.

Phosphorus fixation was calculated as

$$\% \text{ P fixed} = (\text{OPC} - c)/\text{OPC} \times 100$$

where OPC = original P concentration of 100 ppm P and c = concentration of P found in supernatant.

3. RESULTS AND DISCUSSION

Labile P decreased from incubation at time zero to 1 week for all the PRs except PR (4) [Hahotoe (Togo)] and PR (5) [(Hazara (Pakistan)] in the sandy soil (Fig. 1). Between 1 week and 5 weeks, labile P remained relatively constant. During this period of time, labile P obtained from various PRs followed the order: PR (1) = PR (2) > PR (3) > PR (4) = PR (5) > PR (6), which approximately agreed withthe PR solubility (Table I). A decrease in labile P from 0 week to 5 weeks indicated that isotopically exchangeable P in the surface of PR was initially greater than labile P associated with the surface of reactive products formed after PR dissolution. A relatively unchanged labile P from 1 week to 5 weeks suggests that PR dissolution did not continue after 1 week incubation.

In the red soil, labile P obtained from all PRs appeared to be relatively unchanged during 5 weeks of incubation (Fig. 2). This suggests that only P on the surface of PR use all of the soil mixture exchanged with ^{32}P, but not the P on the surface of reaction products formed from PR dissolution. The fact that labile P at 0 week was about the same as that at 1 week suggests that PR dissolution also occurredat 0 week during the 24 h equilibration for labile P measurement. Again, the order of labile P obtained from various PRs during 5 week incubation followed : PR (1) = PR (2) > PR (3) > PR (4) = PR (6).

Figure 3 shows a significant linear corelation between labile P measured with PR alone and PR's solubility for all the PRs, except PR(1). This indicated that labile P as measured by the radioactive ^{32}P technique confirmed the PR sources varied widely in solubility. It is not known why PR(1), which had the highest solubility, did not have a high correlation between labile P and solubility.

Figure 4 shows that labile P obtained with the various PR sources correlated well with PR solubility at time zero in the sandy soil but not in the red soil. However, average labile P during the 1-5 week incubation correlated well with PR solubility in both the sandy and red soil (Fig.5).

At the end of the 5 week incubation, PR dissolution apparently reduced the P-fixing capacity of the sandy soil (Fig. 6). This suggests that P released from PR dissoluition occupied P-sorption sites and reduced further P adsorption. The effect of PR dissolution on reducing soil P-fixing capacity increased with increasing solubility of PR. However, PR dissolution did not affect the P-fixing capacity of the red soil (Fig. 7). It should be pointed out that the red soil had a higher P-fixing capacity (27.5%) from the sandy soil (12.5%). Thus, the effect of PR dissolution on soil P - fixing capacity was only observed in the sandy soil.

The Pi data in Table III show that no significant PR dissolution occurred after 5 weeks incubation in the sandy soil. The amounts of Pi-P obtained at 0 week and 5 weeks probably reflect P released from PR during the Pi extraction. This appears to contradict to the results as shown in Fig. 1, which suggests
.that PR dissolution occurred in the sandy soil.

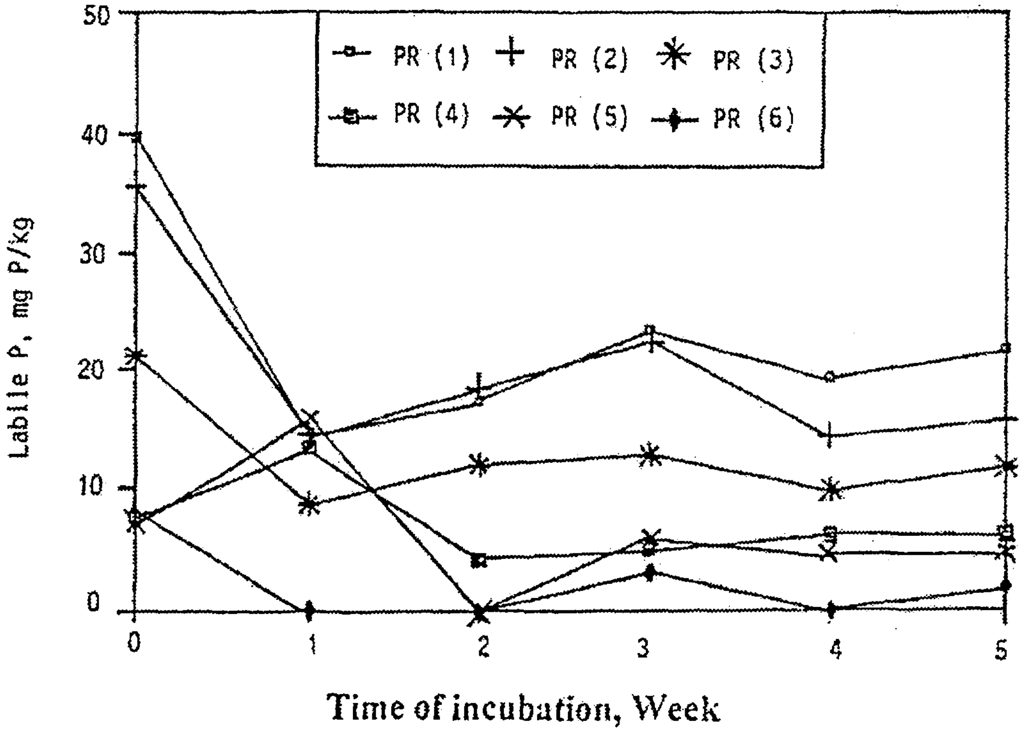

Fig. 1. Labile ^{32}P isotopic exchangeable P after incubating the mixtures of six sources of phosphate rock (PRs) and a sandy soil for 0-5 weeks.

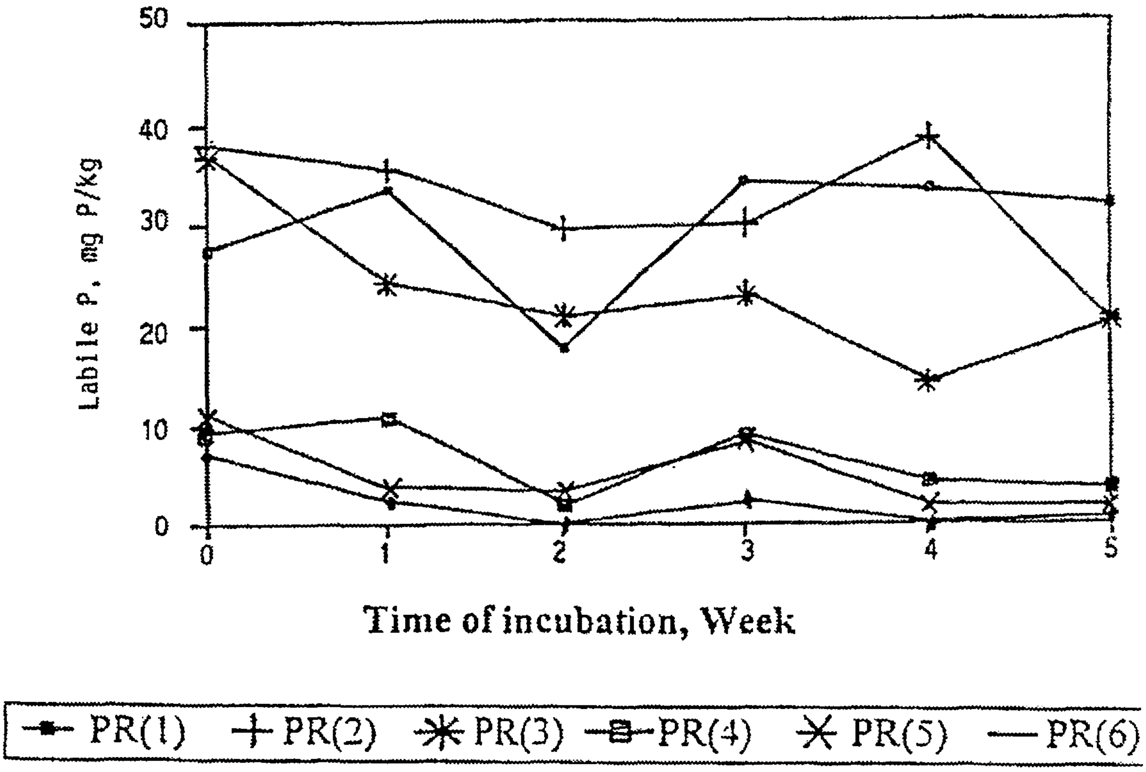

Fig. 2. Labile P (isotopically exchangeable) after incubation the mixtures of six sources of phosphate rock with a red soil.

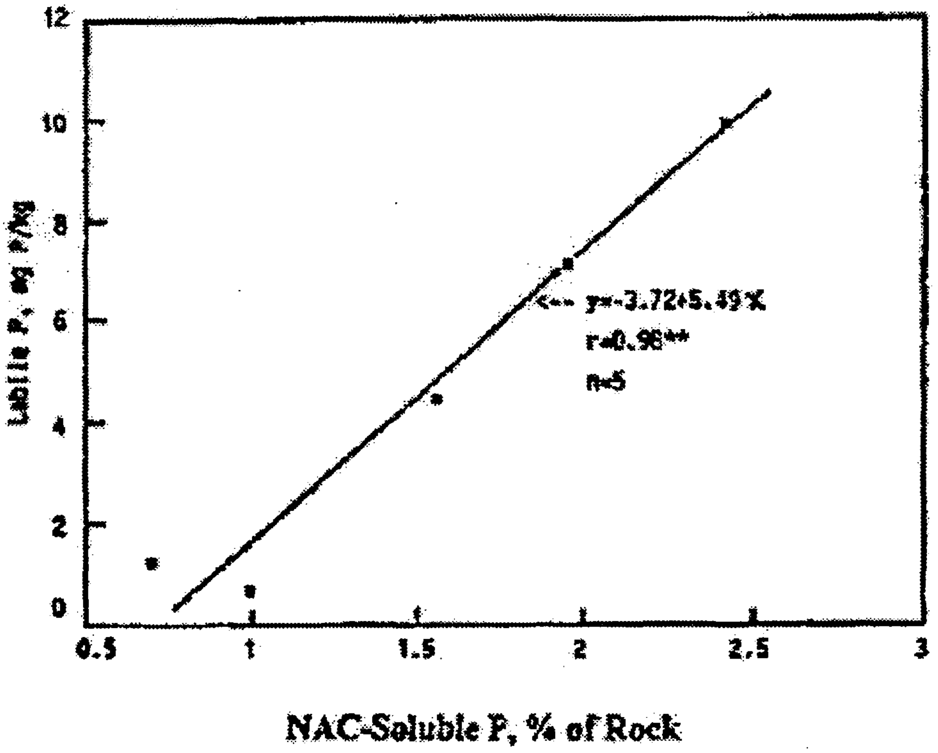

Fig. 3. Labile P (^{32}P technique) from six sources of phosphate rock compared with neutral ammonium citrate-souble P (NAC-soluble P).

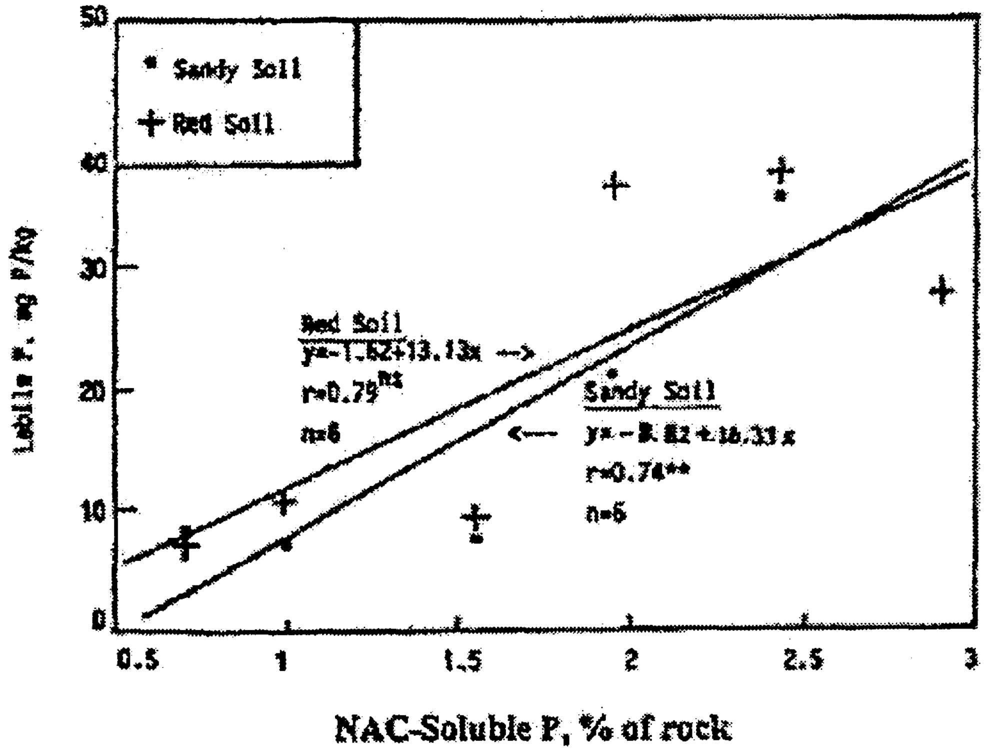

Fig. 4. Labile P (^{32}P technique) at 0 week incubation compared with neutral ammonium citrate soluble P (% of rock).

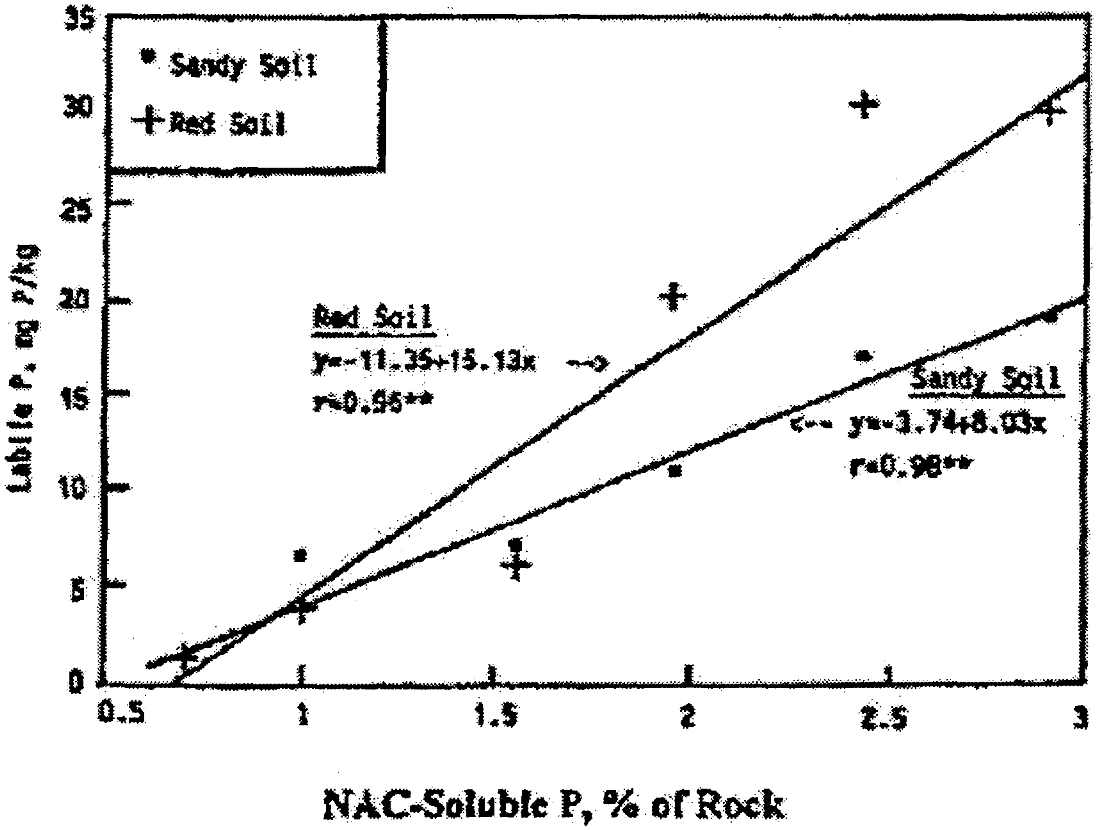

Fig. 5. Comparison of labile P (^{32}P technique) with NAC-soluble P determined on mixtures of various sources of phosphate rock with a sandy and a red soil.

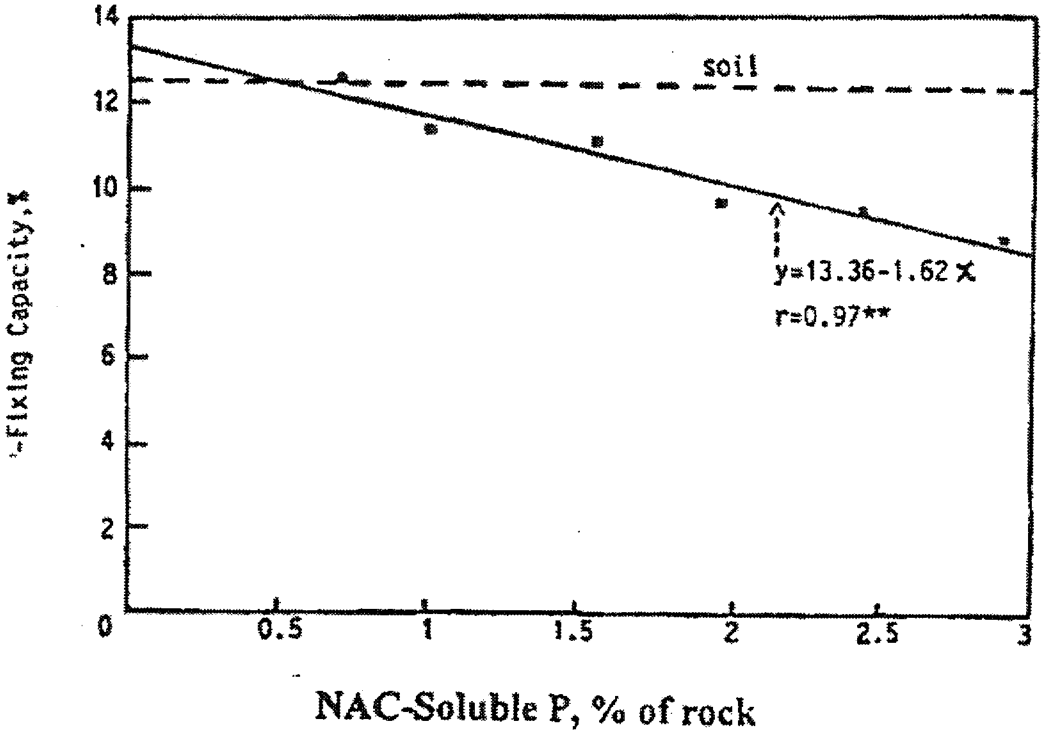

Fig. 6. Comparison of soil P-fixing capacity and phosphate rock solubility after 5 weeks incubation in a sandy soil.

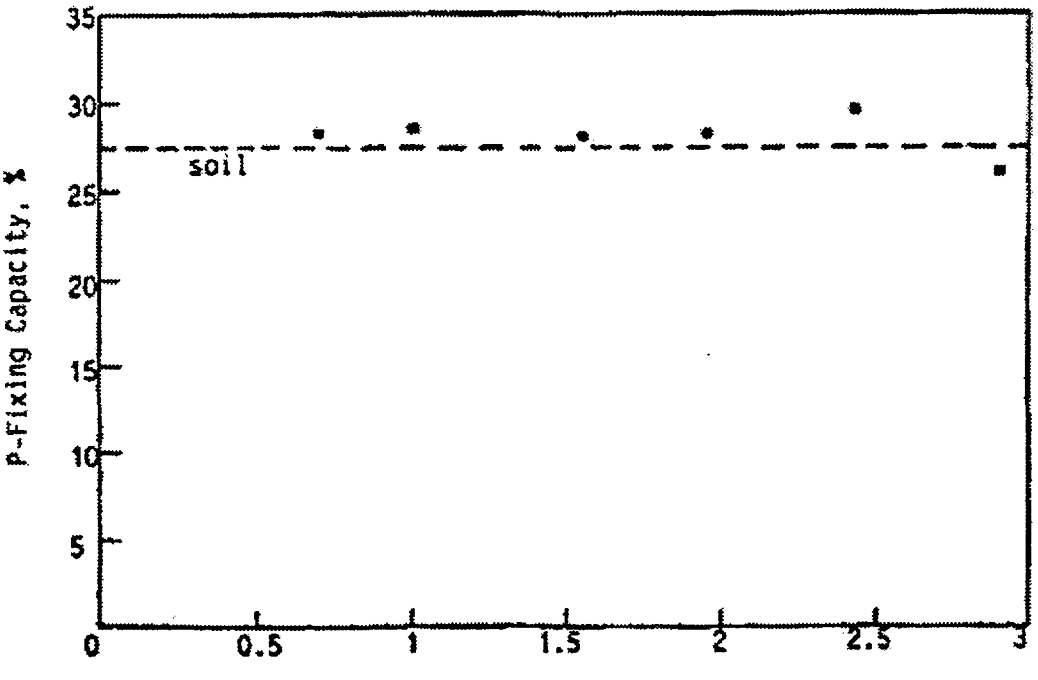

Fig. 7. Comparison of soil P-fixing capacity with phosphate rock solubility after 5 weeks incubation in a red soil.

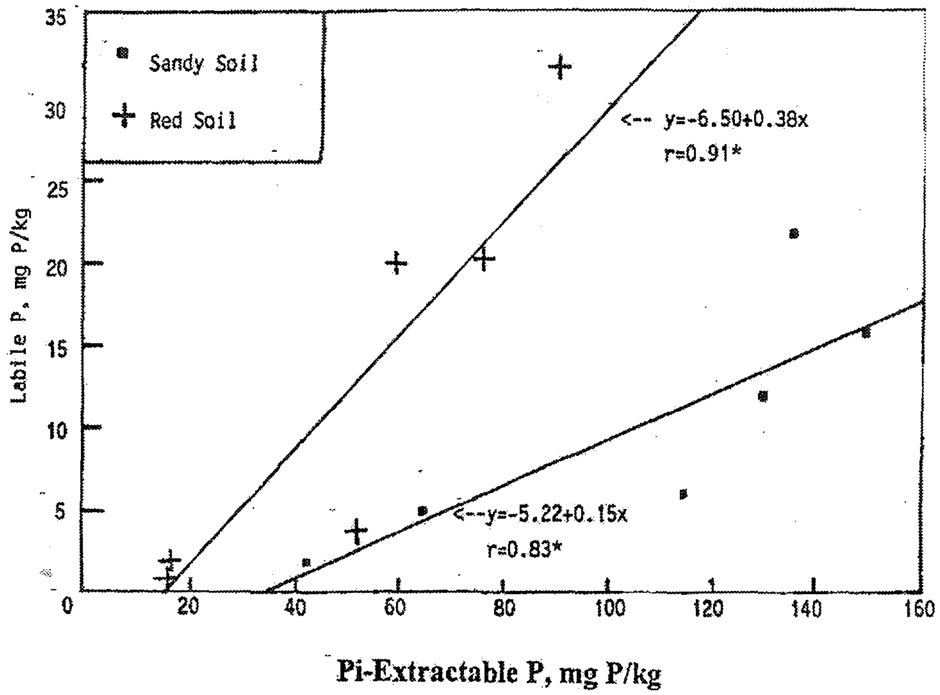

Fig. 8. Comparison of labile P from the ^{32}P *isotopic exchangeable P technique with Pi-extractable P after 5 weeks incubation in a sandy soil and a red soil.*

TABLE III. Pi SOIL PHOSPHORUS TEST IN SANDY SOIL AND RED CLAYEY SOIL MIXED WITH PRs AT RATE OF 400 mg P/kg AT 0 AND 5 WEEKS

Source of P	Sandy soil Pi (mg P/kg)		Red clayey soil Pi (mg P/kg)	
	0 weeks	5 weeks	0 weeks	5 weeks
Control (just soil)	1.9	1.9	4.1	4.1
North Carolina (USA)	142	136	102	80
Khouribga (Morocco)	154	149	104	76
Matam (Senegal)	130	130	100	59
Hahotoe (Togo)	110	115	61	52
Hazara (Pakistan)	50	65	35	16
Patos de Minas (Brazil)	42	49	23	15

TABLE IV. RESIN-EXTRACTABLE P IN SANDY SOIL AND RED CLAYEY SOIL MIXED WITH VARIOUS PRs AT 400 mg P/kg AFTER 5 WEEKS OF INCUBATION

PR	% P	
	Sandy soil	Red soil
North Carolina	28.6	30.2
Khouribga	27.0	41.0
Matam	16.7	19.0
Hahotoe	12.3	11.1
Hazara	4.8	8.4
Patos de Minas	7.8	7.3

Alternatively, PR dissolution could have occured in the sandy soil and Pi strip was able to extract all of the P from the reaction products formed after PR dissolution. In the red soil, a significant decrease was observed for Pi-P extracted from soil mixtures with PRs after 5 weeks compared to the amounts of Pi-P extracted at week 0 (Table III). Our results suggest that Pi strips extracted less P from the reaction products formed from PR dissolution in the red soil than the P extracted by Pi strips from PRs. This is probably due to the very strong P adsorption by the red soil.

Data of resin-extractable P obtained with various PR sources in the sandy and red soils after 5 weeks incubation are shown in Table IV. In general, resin-extractable P followed the same trend of PR solubility. Many researchers have used resin-P as labile P in P modeling work.

Labile P from the ^{32}P technique was compared with Pi - strips extractable P in sandy soil and red soil incubation for 5 weeks (Fig. 8). There was a significant corelation in the sandy soil and red soil ($r = 0.83$ and 0.91 respectively). It could be suggested that the ^{32}P isotopic technique can be used as another technique to study the dissolution of PRs in acid soils.

4. CONCLUSIONS

The results of labile P as measured by the ^{32}P isotopic exchange technique agree well with the results obtained with conventional techniques Pi – strip and P-resin utilized in this study to measure available P released from PR dissolution during a 5 week incubation in two acid Ultisols. The labile P from PR alone also correlated well with the PR's solubility as measured by neutral ammonium citrate (NAC). Thus the ^{32}P isotopic exchange technique provides another tool that can be used as reference to study the dissolution of PR in acid soils and evaluating their reactivity.

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