INFLUENCE OF ROCK PHOSPHATE ON AVAILABLE PHOSPHORUS AS MEASURED BY PLANT UPTAKE AND SOIL EXTRACTANTS

By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTERS OF SCIENCE

Department of Crop and Soil Science

1979

ABSTRACT

INFLUENCE OF ROCK PHOSPHATE ON AVAILABLE PHOSPHORUS AS MEASURED BY PLANT UPTAKE AND SOIL EXTRACTANTS

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A greenhouse and laboratory study was conducted to determine the response of corn grown in three sandy loam soils to application of five rock phosphates (RP). The ACS solubility index for the five RP ranged from 22.6 to 1.2

Addition of RP to the Marlette and Tracy soils increased plant growth slightly and markedly increased total P uptake. RP addition to the Granby soil produced very little response.

Solubility of the RP had a marked influence on the response observed. The most soluble RP, North Carolina and Central Florida, gave the best response. Idaho and Tennessee RP produced only slight responses while Missouri, the least soluble RP, gave a slightly negative response.

Yield and total P uptake correlated very well with the amount of P extracted by Bray - 1 solution, water and 0.5 M ammonium citrate when North Carolina and Central Florida RP were applied. The correlations were quite low when the less soluble RP were used. Each of the three extractants reflected reasonably well the rate of RP added to the

three soils. The highest correlation coefficients were obtained when the most soluble RP were applied. Water soluble P correlated with total P uptake as well or better than Bray - 1 and ammonium citrate extractable P.

DEDICATION

to my wife Teresa and my lovely children

Jose and Paul.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to INIAP (Instituto Nacional de Investigaciones Agropecuarias) for its financial support and stimulation that made this graduate study possible.

A grateful acknowledgment is extended to Dr. D. Warncke, my major professor, for his valuable guidance, patience, and understanding that made my educational experience at Michigan State University rewarding.

The author also thanks Dr. B. G. Ellis and Dr. S. Portch members of my thesis committee.

Finally, appreciation is expressed to all MSU soil testing laboratory personnel for their help and friendship.

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INTRODUCTION

Many soils in the tropical areas of the world are strongly acid, and as a consequence phosphorus (P) deficient. Liming and heavy applications of superphosphates have been used in correcting this problem, but the results have been contradictory.

Direct application of rock phosphate on acid soils as a source of P could be another approach which can solve the problem. Many deposits of rock phosphates are located in developing countries, and this fact can make the use of rock phosphate economically attractive. Until now most of the P applied to the soils in the tropical areas has been in the form of superphosphate processed from rock phosphate. The investment and the energy expended in the processing of rock phosphate could be considerabley less if direct application of rock phosphate is made to the soil.

For many years research has been done to evaluate the agronomic effectiveness of rock phosphate. The response obtained with applications of rock phosphate has proved to be less than that obtained with the soluble superphosphate. However, the results have not always been satisfactory and some erractic patterns in the results has caused some researchers to doubt the effectiveness of the rock phosphates.

A better understanding of the rock phosphate structure and their solubility has led to promising results in the use of rock phosphate. Not only the properties of the rocks tested, but the properties of the soils have also proved to be important. Of special importance are pH and the influence of Ca in solution.

As the use of rock phosphates for direct application on soils becomes popular, a good soil P extractant for these soils is necessary. The initial availability of P applied as rock phosphate is initially low, but as the rock phosphate reacts with the soil, P is slowly released to a more available form. This fact makes it difficult to determine the amount of available P in soils after application of rock phosphate.

The objectives of this study were to:

1. Evaluate the effectiveness of five rock phosphate materials for improving corn growth and phosphorus uptake.
2. Evaluate three different soil extractants for their ability to measure the availability of P in soil which has had rock phosphate applied.
3. Relate growth responses, P uptake and extractable P to the rock phosphate properties.

LITERATURE REVIEW

Large areas in Ecuador, located in the coastal and the oriental parts of the country are tropical with strongly acid soils that are deficient in phosphorus. A number of experiments conducted in this area using superphosphate have found that a lot of the P applied forms insoluble compounds in the soil and it is necessary to apply a lot of fertilizer in order to obtain the quantity of P necessary for plant growth.

Rock phosphate is an inexpensive source of P and it has a promisory future improving phosphprus availability. Hammond (15) indicates that broadcast applications of finely ground rock phosphate can result in increased yields of many crops grown in P deficient soils, and the use of more reactive rock phosphate can produce yields that are economically attractive when compared to those obtained with the costly superphoshpate.

Howeler and Woodruff (16) mention that rock phosphates are derived from apatite but they can be found as igneous sedimentary and metamorphic rocks. The igneous apatites are derived directly from molten magmas and consit of $Ca_5(PO_4)Cl$ or $Ca_5(PO_4)_3F$. When the fluorapatite is partly calcined, the product is hydroxyapatite,

$Ca_5(PO_4)_3OH$. The sedimentary apatite which is the most commercially mined rock phosphate is found as amorphous marine deposits containing mainly fluor- and hydroxy-apatite, and impurities like calcite clay, quartz and mono and dicalcium phosphate. The metamorphic rock is only mined in small quantities.

For many years investigators have done research in order to measure the effectiveness of different rock phosphates as sources of P.

Cook (9) indicates that the native and soluble P applied as fertilizer are available at pH above 6.5 and rock phosphate is usually more available in slightly acid soils. Paauw (22) suggested that soil pH needed for a good efficiency of rock phosphate is too acid for plant growth. Ellis et al. (13) found that rock phosphate should be applied to the soil at an acid pH in order to let acidulation take place and after that soil can be limed to a most desirable pH.

Barnes and Kamprath (2) limed an acid soil to pH 6.0 before application of rock phosphate and no response to the addition of the rock was found. They indicated that at pH 6.0 the soil was uncapable of acidulating the rock making it more available. These authors also indicate that not only P availability is influenced when rock phosphate reacts with the soil, but also with acidulation Ca and pH are increased and Al is decreased. All of these changes depend on the rate of application and in the efficiency of acidulation of the rock.

Chien (6) concluded that the dissolution of apatites is stimulated by a driving force, which is H^+, and in acid soils this driving force is provided. Hence, in the pH range between 3.5 to 6.5 rock phosphate is most responsive.

Caro and Hill (5) tested particle size, surface area, exchangeable P and chemical solubility of rock phosphate against yield and found a good correlation with citric acid solubility and bound CO_3 content of the apatite. No correlation was found for surface area and readily exchangeable P.

Bennett et al. (3) in a greenhouse experiment tested the availability of seven rock phosphates on two soils with and without lime. They found some effect of lime and soil type on the availability of the rocks, but they concluded that the source of rock phosphate was even more important. They also found no correlation between fluorine content or specific surface area of the sources of rock phosphate and their availability to plants. They concluded that chemical solubility evaluates better than physical properties the availability of rock phosphate.

Research by Ensminger et al. (12) lead to the conclusion that the effectiveness of rock phosphates varied widely among soils but was no more than one fourth of that of superphosphate at the same rate.

Howeler and Woodruff (16) tested the P availability of Missouri apatite of igneous origin relative to that of Florida and Arkansas rock phosphate of sedimentary origin. The absence of carbonate in the Missouri apatite crystal resulted in a very strong crystaline structure. A greenhouse study with corn and soybeans as well as incremental dissolution with diluted HCl indicated that this source of rock phosphate releases its P very slowly. The small degree of crystallinity of the sedimentary rocks allowed the dissolution more easily.

Barnes and Kamprath (2) comparing North Carolina and Florida rock phosphates against superphosphate in an acid soil found that dry weight production and P uptake by corn were highly correlated with rates of application of rock. They concluded that North Carolina rock phosphate was 90 percent as effective as superphosphate, and Florida was only 25 percent. Chien and Hammond (8) indicate that corn responded strongly to increased rates of application of P both from North Carolina and Sechura rocks. They also found an increase in response with decreasing granule size.

Paauw (22) testing Gafza and Florida rock phosphates in an acid humic soil showed that application of rock phosphate increased the amount of water soluble phosphorus in the soil. He also concluded that equilibrium is obtained after a short period of time of contact between the soil and the rock. After that the degree of solubility change only slightly. Solubility of rock phosphates in different chemical solutions has been correlated with their reactivity in soils. Caro and Hill (5), Arminger and Fried (1), Engelstad et al. (11), and Lehr and McCellan (19) concluded that ammonium citrate and citric acid solubility tests are an effective measure of P availability.

Lehr and McCellan (19) indicate that in the past years the basis to select rock phosphate for direct application and the analytical methodology used to evaluate availability of rock phosphates "have contributed to erratic patterns of agronomic response." Characterization studies have demonstrated that apatitic phosphate minerals change markedly. These authors concluded that the solubility of rock phosphate is due to structural substitution of PO_4 by CO_3 and F. Accordingly a statistical derived new model that relates citrate solubility to apatite composition was obtained; the Absolute Citrate Solubility index (ACS) and is defined as the ratio of citrate soluble P_2O_5 to the theoretical P_2O_5 content of any given rock.

$$\text{ACS} = \frac{\text{AOAC citrate solubility } P_2O_5\%}{\text{Theoretical } P_2O_5\% \text{ of apatite}}$$

In this way the authors used the solubility index based on apatite composition and did not relate "the citrate soluble P_2O_5 as a fraction of the total P_2O_5 content (grade) of the particular rock sample.

It was also found that the length of the "a" axis of the apatite unit cell, a_o, determined by X-ray diffraction is statistically related to the ACS by

$$ACS = 421.4(9.369 - a_o)$$

Greenhouse evaluations were done by Terman et al. (25) with the principal objective of testing the validity of the Absolute Citrate Solubility reacting scale. A range of apatite compositions was used. Response of rice demonstrated a close agreement between predicted reactivities of rock phosphates and dry matter production and phosphorus uptake.

Hammond (15) after his research in Colombiam soils concluded that rock phosphate can be described as having high, medium or low reactivity. Citrate soluble P_2O_5 in the range of 5.4 to 6.5 percent of the total rock was considered high, 3.2 to 3.4 medium and 1.9 to 2.7 low. The same author also indicated that rock phosphates chosen for direct application on the basis of citrate solubility will show erratic and unpredictable crop response unless applied at high rates. He also concluded that crop response could be influenced by reduced Al saturation and increased exchangeable Ca.

Wilson (28) conducted a laboratory study with six rock phosphates of a wide range of solubility according to the ACS index, and concluded that North Carolina and Central Florida rocks are very soluble; Tennessee, India, and Idaho have a lower solubility; and Missouri rock is almost insoluble. He also found that with increasing Ca activity in solution there is decreasing phosphate solubility. An example was given to illustrate the practical implications of the Ca activity on the solubility of rock phosphates. Assuming 50 ppm phosphorus are needed for plant growth, then this level of available P could be obtained with Ca activities of 3.6×10^{-3} $\underline{M}$, 6.8×10^{-3} $\underline{M}$, and 9.1×10^{-3} $\underline{M}$ for the India, Idaho, and Tennessee rocks, respectively. Missouri rock phosphate will not solubilize 50 ppm of P at any practical activity of Ca. On the other hand North Carolina and Central Florida rocks will release that amount of P with any practical Ca activity.

Wilson also concluded that another factor to be considered before rock phosphate application is the Ca:P molar ratio. If a wide ratio is present (Missouri rock) the Ca activity will increase to a larger extent than if a narrow Ca:P is present in the rock. It is necessary to take into account not only the solubility of the rock but also the amount of Ca which will be released.

Smith et al. (24) indicated that no specific attention has been given to evaluate the P availability of soils which have had rock phosphate applied. Barnes and Kamprath (2) mentioned that after rock phosphate applications the amount of available phosphorus is difficult to determine.

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Ellis et al. (13) reported that 0.002 N H_2SO_4 extracted solubilized unreacted rock phosphate in soils.

Bray and Kurtz (4) developed an extracting solution, "Bray 1" (0.03 N NH_4F + 0.025 N HCl), which has been widely used in the determination of available P. Fitts (14) indicates that "Bray 1" gives results that are highly correlated with crop response to phosphate fertilization.

Smith et al. (24) concluded that "Bray 1" appeared to be a good evaluating method of P availability in soils to which rock phosphate has been added, and it seems to measure the release of unavailable phosphorus in rock phosphate to an available soil form.

Peaslee (23) on the other hand, found a poor correlation between the plant availability coefficient ratio and "Bray 1" extracting coefficient ratio for Iowa soils to which a Florida rock phosphate had been applied. They found a better correlation with an anion exchange resin.

Ensminger et al. (12) referring to the soil extractants used in evaluating the effectiveness of rock phosphate concluded that, since the forms of accumulated P resulted from superphosphate and rock phosphate may be quite different, the extractants used were selected because they tend to be selective in dissolving certain forms of P. Dilute acids dissolve calcium phosphate, but are not very effective in dissolving iron and aluminum phosphate. The opposite is true for neutral ammonium flouride. These authors report that for most of the soils used in their investigation, neutral ammonium fluoride extracted considerably less P from the rock phosphate treated soils than it did from soils that had received the same amount of P_2O_5 from superphosphate. They concluded that much of the rock phosphate had not reacted with the soil. They also reported that the amount of P released to an anion exchange resin was related to the total water soluble P present in the soil.

As cited previously, when Barnes and Kamprath (2) limed an acid soil to pH 6.0 no response to the addition of rock phosphate was observed. Soil pH had the same effect in soil analysis with "Bray 1". The acid soil had more available P than the limed soil. On the other hand the double acid extractant (0.05 $\underline{N}$ HCl + 0.025 H_2SO_4) extracted the same amount of P from the limed and unlimed soils.

Chien (7) mentioned that the combination of HCl and NH_4F in "Bray 1" is designed to remove easily acid soluble forms of P largely calcium phosphates, other than apatite and a portion of the iron and aluminum phosphates. He also indicated that in the past many attempts to measure the available phosphorus with "Bray 1" on soils treated with rock phosphate were made in limed soils or neutral to slightly acid soils, and the rock phosphates were unreactive. Poor results were obtained because "Bray 1" cannot dissolve the unreacted rock phosphate. The conditions change when acid soils and relatively reactive rock phosphate are used.

An experiment of incubation, rate of application, and time of reaction of different rock phosphates was made by Chien (7) to prove the above statements. The results of the incubation indicated that incubation increases the amount of "Bray 1" extractable P from a soil treated with eight different rocks. The amount of "Bray 1" extractable P varied with the source of rock phosphate from 9.6 ppm with Tapira rock phosphate to 93.7 ppm with the North Carolina rock. This represents 1.1 to 11.6 percent of added P.

The results of rate of application were obtained testing North Carolina and Tennessee rock phosphates which represent high and low solubility. The amounts of "Bray 1" extractable P from the North Carolina rock were greater than those with Tennessee rock, both before and after incubation. The amount of "Bray 1" extractable P also increased as the application rates increased.

The time of reaction experiment showed that the reaction of the rock phosphate with the soil seems to approach a maximum at about 90 days of incubation at room temperature.

Since unreacted rock phosphate in the soil may still be in the original form and only a small portion of added phosphate was extracted by "Bray 1", Chien suggested that a comparison of "Bray 1" extractable P from the soil treated with rock phosphate before and after incubation may be used to estimate the P contributed by the unreacted phosphate rock to the total "Bray 1" extractable phosphorus. He concluded that although "Bray 1" does not significantly dissolve the unreacted rock phosphate in the soil in terms of total phosphorus added, it may dissolve some and contribute to the total "Bray 1" extractable P. Both sources, unreacted rock phosphate and reaction products, can provide available P to the plant, especially in strongly acid soils with low buffering capacity and if the rock phosphates are relatively reactive in a short period of time.

Chien also mentioned that it can be seen in the literature that many workers report a good correlation between the reactivities of rock phosphate as measured by neutral ammonium citrate and plant growth. He tested a correlation between "Bray 1" extractable P for a soil treated with eight different rock phosphates, before and after incubation, and their ammonium citrate solubility. He found a very good correlation so he suggested that "Bray 1" extractable P should correlate in the same fashion with crop response.

Mehlich (21) working with pure North Carolina and Florida rock phosphates found that, after five minutes of shaking, the double acid (0.05 $\underline{N}$ HCl + 0.025 $\underline{N}$ H_2SO_4) and "Bray 2" (0.1 HCl + 0.03 $\underline{N}$ NH_4F) achieve a complete dissolution of both rocks. Using 0.025 $\underline{N}$ HCl 92 percent of the

North Carolina rock and 93 percent of the Florida rock were dissolved. "Bray 1" (0.025 N HCl + 0.03 NH_4) dissolved 43 percent of North Carolina and 27 percent of Florida rock. 0.05 N NH_4 dissolved 0.3 percent of North Carolina and 0.1 percent of Florida. One hour and overnight shaking did not give significant change in the analytical results.

MATERIALS AND METHODS

An experiment with corn grown in three different soils was conducted in the greenhouse to compare five different rock phosphates as sources of P. Yield and total P uptake were obtained to evaluate the response of the soils to the direct addition of rock phosphates. Three soil extractants: Bray-1, water soluble, and ammonium citrate were tested on the three soils and correlated with yield and total P uptake.

The three Michigan soils used in the experiment are: Marlette sandy loam, Granby sandy loam, and Tracy sandy loam. The characteristics of the soils are described in Table 1.

The five rock phosphates used in this experiment: Idaho, Central Florida, North Carolina, Tennessee, and Missouri, were selected to represent a range of P solubility. They were characterized by Lehr and McCellan (1972). Missouri rock phosphate is of an igneous origin and the others are sedimentary. Their P_2O_5 content varies from 29.9 to 34.7%. The apatite composition and theoretical citrate solubility are given in Tables 2 and 3.

Table 1. Soil Properties

	Marlette Sandy Loam	Granby Sandy Loam	Tracy Sandy Loam
U.S. Classification	Glossoboric Hapludalf, Fine Loamy Mixed Mesic	Typic Haplaquoll Sandy, Mixed Mesic	Ultic Hapludalf Coarse-Loamy Mixed Mesic
Clay (%)	18.4	14.4	16.4
Silt (%)	22.0	13.0	21.0
Sand (%)	59.6	72.6	62.6
pH	6.6	6.9	5.6
Total P (ppm)	260.0	310.0	400.0
Bray P-1 (ppm)	11.0	25.0	26.0
Exch K (meg/100gm)	0.087	0.092	0.307
Exch Ca (meg/100gm)	38.5	82.5	33.4
Exch Mg (meg/100gm)	3.81	16.66	5.7
Zn (ppm)	2.0	2.0	7.0
Mn (ppm)	10.0	34.0	59.0
Cu (ppm)	1.0	3.0	2.0
Fe (ppm)	20.0	48.0	36.0
C.E.C. (meg/100gm)	8.85	17.75	7.18
Organic Matter (%)	1.3	14.82	1.67

Table 2. ACS Solubility Index*

TVA No.	Rock Phosphate Source	a_o^s	Solubility Index (ACS) x-ray	Solubility Index (ACS) Chemical
MR-464	Central Florida (Polk County Peeble)	9.345	10.1	14.0
MR-465	Idaho Shale Phosphate	9.356	5.48	9.37
MR-467	North Carolina clastic phosphorite	9.322	19.8	22.6
MR-468	Tennessee Brown (Columbia, Tenn)	9.358	5.06	13.7
MR-505	Missouri (by product concentrate)	9.373	1.20	1.20

a_o^s = length of a axis of apatite unit cell.

*From Lehr and McCellan (19)

Table 3. Rock Phosphate Composition*

Component	ROCK PHOSPHATE Central Florida	North Carolina	Tennessee	Missouri	Idaho
CaO	47.5	48.6	42.3	50.1	46.8
P_2O_5	32.7	29.9	30.7	34.7	32.3
F	3.6	3.5	3.2	3.4	3.2
CO_2	3.3	5.4	1.4	2.8	2.4
Na_2O	0.66	0.99	0.40	0.27	0.96
K_2O	0.15	0.13	0.65	0.16	0.36
MgO	0.32	0.55	0.28	0.63	0.37
Al_2O_3	1.20	0.46	1.40	0.34	1.10
Fe_2O_3	1.45	0.68	1.20	2.60	0.44
SiO_2	5.2	1.6	10.00	2.8	5.4
S	0.4	1.1	0.2	0.08	0.9

* From Lehr and McCellan (19)

Greenhouse Experiment

The soils upon arrival at the greenhouse were air-dried, screened, and mixed. Three kilograms of soil were weighed into plastic bags. Each of the sources of P was added to the soils at rates to supply 50, 100, 200, and 400 ppm P_2O_5, mixed, and left to incubate for two months.

Solutions of KNO_3, NH_4NO_3, $MnSO_4$, and $ZnSO_4$ were applied to the soils to supply 57 mg K/kg, 32 mg N/kg, 3 mg Mn/kg, and 2 mg Zn/kg for the Marlette soil;
57 mg K/kg, 32 mg N/kg, and 2 mg Zn/kg for the Granby soil;
15 mg K/kg, 32 mg N/kg, and 2 mg Zn/kg for the Tracy soil.
All solutions were thoroughly mixed with the soil prior to planting.

After incubation the soils were transferred to plastic pots and planted with corn, Variety-Pioneer 3780. Ten seeds were planted per pot and thinned to four plants per pot 10 days after emergence. The pots were arranged in a complete randomized design with four replications.

The corn was harvested, oven dried, and weighed seven weeks after planting. Soil samples were collected from the pots after harvesting.

Laboratory Procedures

Plant analysis:

The oven dried plant samples were ground and analyzed following a digestion of 1.0 gm of plant tissue with a mixture of nitric and percloric acids. The digested material was diluted to 50 ml with distilled water. P was analyzed by the use of a Technicon-Autoanalyzer II (880 nm), employing the ascorbic acid-molybdate colorimetric method. From the results total P uptake was calculated.

Soil analysis:

All soil samples were air-dried, ground and sieved to pass a 20 mesh sieve.

Extractions with Bray 1, water, and ammonium citrate solutions were made for each soil sample. Bray 1 extractable P was extracted for 10 minutes with the Bray 1 solution (0.03 $\underline{N}$ NH_4F + 0.025 $\underline{N}$ HCl) at a 1:10 soil-solution ratio.

Water soluble P was determined in a 1:10 soil-water ratio after 10 minutes of shaking. The soil water mixture was first filtered through a Whatman #40 filter paper and then spun down for 15 minutes in an International centrifuge.

Ammonium citrate extractable P was extracted for one hour with 0.5 $\underline{M}$ ammonium citrate at pH 5.5 A 5 ml aliquot of the extract was dried in a sand bath and ashed in a muffle furnace at 400^{o}C. The ash was then brought into solution and analyzed for P (Wilson, 1979).

Statistical Analysis

A statistical analysis of variance was conducted for the data collected from the greenhouse experiment. A Duncan's Multiple Range Test was used to identify statistical differences between treatments.

Simple correlations were calculated to test association between rate of rock phosphate application and yield, total P uptake, Bray P-1 extractable P, water soluble P, and ammonium citrate extractable P. In the same way correlations of yield and total P uptake with Bray 1 extractable P, water soluble P, and ammonium citrate extractable P were also calculated.

RESULTS AND DISCUSSION

Five rock phosphates were evaluated in the greenhouse in three different soils using corn as the test plant.

In Michigan it was difficult to find soils with low P contents, especially in combination with acid pH. The soils selected for this study were chosen for their relative low P content for the region, but only one soil, a Tracy sandy loam had an acid pH. The other two soils, a Marlette sandy loam and a Granby sandy loam had 6.6 and 6.9 pH's, respectively (Table 1).

Increasing rates of rock phosphate resulted in differing growth and total P uptake responses. Average dry weights and total P uptake values are presented in Tables 4 and 5 for the Marlette soil and in Tables 6 and 7 for the Tracy soil. An analysis of variance confirmed that statistically significant differences in yield and total P uptake occurred in response to rock phosphate addition to these two sandy loam soils. The degree of response in total P uptake is illustrated by the linear regression lines in Figures 1 and 2.

According to a Duncan's Multiple Range test for yield the order of response in the Marlette soil (Table 4) was: North Carolina rock phosphate (RP) Central Florida RP =

Tennessee RP Missouri RP Idaho RP. When treated by total P uptake (Table 5) the order was: North Carolina RP Central Florida RP = Tennessee RP Idaho RP = Missouri RP.

The Tracy soil showed (Table 6 and 7) North Carolina RP Central Florida RP = Tennessee RP = Idaho RP = Missouri RP for both yield and total P uptake. In this soil only North Carolina Rock phosphate is statistically different from the others. Looking at the results it can be seen that there is a marked increasing trend in yield and total P uptake with increasing rates of application for Central Florida rock phosphate. It is also interesting to observe that for both Marlette and Tracy soils the trend with the Missouri rock phosphate is negative. As the rate increases both yield and total P uptake decreases. This aspect will be discussed later.

The rock phosphates produced responses according to what was expected on the basis of the absolute citrate solubility defined by Lehr and McCellan (19). North Carolina always gave the best response because it was the most soluble rock. On the other hand Missouri gave no response because of its low solubility. These results are also in agreement with those obtained by Wilson (28) in his laboratory study. He indicated that the pattern in rock phosphate solubility was North Carolina RP Central Florida RP Tennessee RP Idaho RP Missouri RP. He concluded that North Carolina and Central Florida rock phosphates are highly soluble while Missouri is almost

Table 4. Total Yield (Dry Weight) of Corn in the Greenhouse as Affected by Rate and Source of Phosphorus in Marlette Sandy Loam Soil.

	Rate of Application (ppm P_2O_5)				
	50	100	200	400	Average*
	g/pot				
Idaho Shale Phosphorite	11.5	12.0	11.6	12.9	12.0 d
Central Florida (Polk County Peeble)	13.1	15.8	16.2	19.1	16.2 b
North Carolina Clastic Phosphorite	16.2	19.0	19.6	20.4	18.8 a
Tennessee Brown (Columbia, Tenn)	12.9	15.4	14.4	16.1	14.7 bc
Missouri (by-product concentrate)	13.8	13.7	13.6	12.7	13.4 c

* Means with the same letter are not significantly different with Duncan's Multiple Range Test ($p = .05$)

Table 5. Total Phosphorus Uptake of Corn in the Greenhouse as Affected by Rate and Source of Phosphorus in Marlette Sandy Loam Soil.

	Rate of Application (ppm P_2O_5)				
	50	100	200	400	Average*
	mg/pot				
Idaho Shale Phosphorite	13.2	13.2	15.3	17.4	15.1 c
Central Florida (Polk County Peeble)	14.9	18.0	25.3	37.1	22.6 b
North Carolina Clastic Phosphorite	19.6	26.4	39.4	45.6	32.8 a
Tennessee Brown (Columbia, Tenn)	15.8	18.3	17.0	18.2	17.3 bc
Missouri (by-product concentrate)	14.3	13.8	13.1	12.0	13.3 c

* Means with the same letter are not significantly different with Duncan's Multiple Range Test (p = .05)

Table 6. Total Yield (Dry Weight) of Corn in the Greenhouse as Affected by Rate and Source of Phosphorus in Tracy Sandy Loam Soil.

	Rate of Application (ppm P_2O_5)				
	50	100	200	400	Average*
	g/pot				
Idaho Shale Phosphorite	8.1	7.5	8.7	9.1	8.3 b
Central Florida (Polk County Peeble)	8.4	8.0	9.4	10.5	9.1 b
North Carolina Clastic Phosphorite	12.0	11.2	12.8	11.1	11.8 a
Tennessee Brown (Columbia, Tenn)	7.6	7.2	7.8	7.9	7.6 b
Missouri (by-product concentrate)	7.7	7.6	8.5	8.2	8.0 b

* Means with the same letter are not significantly different with Duncan's Multiple Range Test ($p = .05$)

Table 7. Total Phosphorus Uptake of Corn in the Greenhouse as Affected by Rate and Source of Phosphorus in Tracy Sandy Loam Soil.

	Rate of Application (ppm P_2O_5)				
	50	100	200	400	Average*
	mg/pot				
Idaho Shale Phosphorite	7.0	7.2	7.9	8.8	7.7 b
Central Florida (Polk County Peeble)	7.6	7.9	10.4	13.6	9.9 b
North Carolina Clastic Phosphorite	14.3	18.1	23.9	21.4	19.4 a
Tennessee Brown (Columbia, Tenn)	6.4	6.0	6.3	7.5	6.6 b
Missouri (by-product concentrate)	6.2	6.5	6.3	6.0	6.3 b

* Means with the same letter are not significantly different with Duncan's Multiple Range Test (p = .05)

insoluble. The results obtained with the Marlette and Tracy soils study indicate that the more soluble the rock phosphate the greater the crop response to the direct application of rock phosphate.

In contrast to the Marlette and Tracy soils none of the rock phosphate materials produced a significant response in yield or total P uptake when applied to the Granby soil (Tables 8 and 9). The neutral pH and the high amount of exchangeable Ca may have had an adverse effect on the availability of P from the rock sources.

When rock phosphate is used as a P source in direct application on soils, it is necessary to look for a good soil extractant which can evaluate the real P availability reflected in a concommitant crop response. Thomas and Peaslee (26) mention that "when selecting a soil extractant one should always consider the degree of correlation of the extractant with plant response to soil and fertilizer P".

In this study, the degree of correlation between rate and yield, total P uptake, Bray - 1 extractable P, water soluble P and ammonium citrate extractable P was calculated (Tables 10, 11, 12). The Marlette (Table 10) and Tracy (Table 11) soils showed a high degree of association between rate and all the variables tested for North Carolina and Central Florida rock phosphates. In the Tennessee and Idaho rock phosphates the correlations were poor, while the Missouri rock phosphate gave a negative

Table 8. Total Yield (Dry Weight) of Corn in the Greenhouse as Affected by Rate and Source of Phosphorus in Granby Sandy Loam Soil.

	Rate of Application (ppm P_2O_5)				
	50	100	200	400	Average*
	g/pot				
Idaho Shale Phosphorite	8.9	8.1	8.9	9.9	8.9 a
Central Flofida (Polk County Peeble)	9.3	9.6	9.2	10.3	9.6 a
North Carolina Clastic Phosphorite	10.1	8.8	10.2	10.1	9.8 a
Tennessee Brown (Columbia, Tenn)	10.7	9.3	10.3	10.2	10.1 a
Missouri (by-product concentrate)	10.3	10.1	11.0	9.4	10.2 a

* Means with the same letter are not significantly different with Duncan's Multiple Range Test (p = .05)

Table 9. Total Phosphorus Uptake of Corn in the Greenhouse as Affected by Rate and Source of Phosphorus in Granby Sandy Loam Soil.

	Rate of Application (ppm P_2O_5)				
	50	100	200	400	Average*
	mg/pot				
Idaho Shale Phosphorite	8.2	7.4	7.5	9.3	8.1 a
Central Florida (Polk County Peeble)	8.8	10.1	9.1	9.8	9.4 a
North Carolina Clastic Phosphorite	10.3	8.5	9.1	10.0	9.5 a
Tennessee Brown (Columbia, Tenn)	10.7	8.4	11.1	8.9	9.8 a
Missouri (by-product concentrate)	9.5	9.1	9.1	8.7	9.1 a

* Means with the same letter are not significantly different with Duncan's Multiple Range Test (p = .05)

Table 10. Correlation Coefficients for P Rate, P Uptake, Dry Weight, Bray-1, Extractable P, Water Soluble P and Ammonium Citrate Extractable P in Various Combinations for the Marlette Soil.

	Uptake	Dry Weight	Bray P-1	Water Soluble	Ammonium Citrate
	mg P/pot	gm/pot	mg P/kg soil		
		Idaho			
Rate (mg P_2O_5/kg)	0.49	0.09	0.30	0.03	0.53
Uptake (mg P/pot)			0.05	0.22	0.32
Dry Weight (gm/pot)			0.13	0.20	0.31
		Central Florida			
Rate (mg P_2O_5/kg)	0.95	0.86	0.77	0.92	0.93
Uptake (mg P/pot)			0.75	0.94	0.94
Dry Weight (gm/pot)			0.58	0.85	0.83
		North Carolina			
Rate (mg P_2O_5/kg)	0.95	0.80	0.97	0.96	0.97
Uptake (mg P/pot)			0.96	0.92	0.90
Dry Weight (gm/pot)			0.81	0.78	0.70
		Tennessee			
Rate (mg P_2O_5/kg)	0.52	0.58	0.73	0.52	0.48
Uptake (mg P/pot)			0.10	0.45	0.55
Dry Weight (gm/pot)			0.10	0.49	0.60
		Missouri			
Rate (mg P_2O_5/kg)	-0.44	0.07	-0.65	0.01	0.25
Uptake (mg P/pot)			0.05	0.19	0.07
Dry Weight (gm/pot)			0.23	0.24	0.31

Table 11. Correlation Coefficients for P Rate, P Uptake, Dry Weight, Bray-1, Extractable P, Water Soluble P and Ammonium Citrate Extractable P in Various Combinations for the Tracy Soil.

	Uptake	Dry Weight	Bray P-1	Water Soluble	Ammonium Citrate
	mg P/pot	gm/pot	mg P/kg soil		
		Idaho			
Rate (mg P_2O_5/kg)	0.74	0.48	0.11	0.04	0.59
Uptake (mg P/pot)			0.03	0.28	0.21
Dry Weight (gm/pot)			0.04	0.25	0.08
		Central Florida			
Rate (mg P_2O_5/kg)	0.97	0.84	0.96	0.64	0.98
Uptake (mg P/pot)			0.91	0.63	0.93
Dry Weight (gm/pot)			0.79	0.50	0.84
		North Carolina			
Rate (mg P_2O_5/kg)	0.75	0.46	0.99	0.89	0.99
Uptake (mg P/pot)			0.80	0.85	0.67
Dry Weight (gm/pot)			0.46	0.56	0.37
		Tennessee			
Rate (mg P_2O_5/kg)	0.49	0.29	0.69	0.53	0.79
Uptake (mg P/pot)			0.25	0.26	0.22
Dry Weight (gm/pot)			0.05	0.12	0.17
		Missouri			
Rate (mg P_2O_5/kg)	-0.31	0.35	-0.05	0.01	0.05
Uptake (mg P/pot)			0.15	0.01	0.01
Dry Weight (gm/pot)			0.03	0.03	0.01

Table 12. Correlation Coefficients for P Rate, P Uptake, Dry Weight, Bray-1, Extractable P, Water Soluble P and Ammonium Citrate Extractable P in Various Combinations for the Granby Soil.

	Uptake	Dry Weight	Bray P-1	Water Soluble	Ammonium Citrate
	mg P/pot	gm/pot	mg P/kg soil		
		Idaho			
Rate (mg P_2O_5/kg)	0.14	0.03	0.08	0.28	0.79
Uptake (mg P/pot)			0.32	0.21	0.14
Dry Weight (gm/pot)			0.33	0.13	0.13
		Central Florida			
Rate (mg P_2O_5/kg)	0.02	0.18	0.18	0.63	0.73
Uptake (mg P/pot)			0.04	0.03	0.07
Dry Weight (gm/pot)			0.09	0.04	0.18
		North Carolina			
Rate (mg P_2O_5/kg)	0.03	0.13	0.98	0.43	0.97
Uptake (mg P/pot)			0.04	0.11	0.01
Dry Weight (gm/pot)			0.09	0.04	0.18
		Tennessee			
Rate (mg P_2O_5/kg)	0.10	0.06	0.43	0.23	0.33
Uptake (mg P/pot)			0.08	0.07	0.18
Dry Weight (gm/pot)			0.04	0.03	0.13
		Missouri			
Rate (mg P_2O_5/kg)	-0.22	-0.08	-0.27	0.23	0.28
Uptake (mg P/pot)			0.14	0.12	0.35
Dry Weight (gm/pot)			0.08	0.13	0.05

correlation when comparing rate vs. total P uptake (r = -0.44), and rate vs. Bray - 1 extractable P (r = -0.65).

Increasing rates of North Carolina rock phosphate applied on the Marlette soil correlated well with all the variables (Table 10): yield, r = 0.08; total P uptake, r = 0.95; Bray - 1 extractable P, r = 0.97; water soluble P, r = 0.96; and ammonium citrate extractable P, r = 0.97. Similar correlations in the Tracy soil (Table 11) were: yield, r = 0.46; total P uptake, r = 0.75; Bray -1 extractable P, r = 0.99; water soluble P, r = 0.89; and ammonium citrate extractable P, r = 0.99.

With the Central Florida rock phosphate the results are quite similar to those of North Carolina in both Marlette and Tracy soils. Increasing rates of Tennessee rock phosphate showed an appreciable correlation with Bray - 1 extractable P, r = 0.73 for the Marlette soil and r = 0.69 for Tracy soil, Chien (7) obtained similar results when he tested Bray - 1 as an extractant in soils applied with increasing rates of North Carolina and Tennessee rock phosphates. He concluded that Bray - 1 estimates P availability although the extractant does not dissolve all the unreacted rock phosphate in the soil in terms of P added, but it can dissolve some unreacted rock as well as reaction products of the dissolved rock.

As mentioned before the correlations of rate against all the variables with North Carolina and Central Florida rocks are quite similar. A significant statistical difference was found in the greenhouse. This difference in response due to the difference in solubility is not reflected in the correlation coefficients but in the absolute values of the variables. (Appendix Tables I, II, III). For the 400 ppm P_2O_5 rate in the Marlette soil (Appendix I) the North Carolina rock produced an average yield of 20.4 gm/pot while Central Florida produced 19.5 gm/pot. Total P uptake with North Carolina RP was 42.6 mg P/pot and was 32.1 mg P/pot with Central Florida RP. Bray - 1 extractable P was 55.7 ppm P with North Carolina RP and 29.5 ppm P with Central Florida RP. Water soluble P was 4.9 ppm P with North Carolina RP and 1.9 ppm P with Central Florida RP. Ammonium citrate extractable P was 202.2 ppm P with North Carolina RP and 97.5 ppm P with Central Florida RP.

The same effect was observed in the Tracy soil (Appendix II). Respective values for North Carolina and Central Florida rock phosphates were: yield 11.1 and 10.6 gm/pot; total P uptake 21.4 and 13.6 mg P/pot; Bray - 1 extractable P 42.2 and 19.0 ppm P; water soluble P 2.4 and 0.8 ppm P; ammonium citrate extractable P 186.0 and 82.5 ppm P. For both Marlette and Tracy soils total P uptake evaluated the availability of P from rock phosphates better than yield.

In the Granby soil (Table 12, as expected because of the lack of response to rock phosphate additions, almost all correlations were very poor. A significant correlation between rate of application and ammonium citrate extractable P was found for North Carolina, Central Florida, and Idaho rock phosphates with correlation coefficients of 0.97, 0.73 and 0.79, respectively. This indicates that ammonium citrate is dissolving unreacted rock phosphate. The correlation for rate of application vs. Bray - 1 extractable P proved to be significant in this soil only for North Carolina rock phosphate, r = 0.98. This indicates that Bray - 1 solution is dissolving some of the unreacted rock phosphate, and this fraction is related to the rate of application.

The Missouri rock phosphate applied on the Marlette soil (Table 10 and Figure 1) showed a negative correlation for rate vs. uptake, r = -0.44, and for rate vs. Bray - 1 extractable P, r = -0.65. In the Tracy soil (Table 11 and Appendix II) the negative trend can be seen but the correlations are very poor. Theses results, especially on the Marlette soil, agree with the results obtained by Wilson (28) in his laboratory study. He concluded that increasing amounts of Ca activity in the soil solution decreases the solubility of rock phosphate, and the use of a rock phosphate with a wide Ca:P molar ratio like Missouri (20:1) would add a larger amount of Ca to the solution upon dissolution than release of P. In this way, increasing rates of Missouri rock phosphate increased the Ca activity in the soil solution resulting in decreased phosphate solubility, and as a consequence a decreased total P uptake.

Yield and total P uptake were correlated against Bray - 1 extractable P, water soluble P, and ammonium citrate extractable P. (Tables 10, 11, 12). Significant associations were found with North Carolina and Central Florida rock phosphate for all the variables in the Marlette and Tracy soils. In all cases total P uptake rather than yield gave the better correlation. The relationships between total P uptake and Bray - 1 water soluble, and ammonium citrate extractable P for Marlette and Tracy soils are shown in Figures 3 and 14 where either North Carolina or Central Florida rock phosphate was applied. Comparing the regression equations for water soluble P versus total P uptake (Figures 7, 8, 9, 10) reveals that all data points fall along a common regression line. The slopes and intercepts of all four regression equations are quite similar. Comparing the regression equations for Bray - 1 and ammonium citrate extractable P reveals a less clear picture. The slopes and intercepts are quite variable between soils.

In the Granby soil no significant relationships existed between any of the extractants and total P uptake regardless of rock phosphate source. Hence, writing regression equations would be meaningless. Even with the poor correlations it was apparent that values obtained with the Granby soil were related to a regression line different from that for the Marlette and Tracy soils.

North Carolina and Central Florida rock phosphates, when applied on Marlette and Tracy soils, gave a response which correlated with all of the extractants tested. The difference between extractants is the amount of P they extracted from the soils. (Appendix I, II, III). Water soluble P ranged from 0.23 to 0.58 ppm P in the check samples which is relatively high because the soils before rock phosphate application had an appreciable amount of P (Table 1). However, response to the addition of North Carolina and Central Florida rock phosphates in the Marlette and Tracy soils was evident. These two rock phosphates are soluble enough to increase the amount of water soluble P which is readily available to the plant.

Bray - 1 extractable P is extracting the native P in the soil and the reaction products of the solubilized rock phosphate. Barnes and Kamprath (2) after their study with North Carolina and Central Florida rocks concluded that corn yield correlates well with Bray - 1 extractable P. They also mentioned that as the dissolution of rock phosphate is a slow process, the amount of P extracted with Bray - 1 is only a very small fraction of the total P applied.

On the other hand, the amount of P extracted by ammonium citrate is the largest for all extractants used, with both North Carolina and Central Florida rock phosphate treatments. At the rate of 400 ppm P_2O_5 of North Carolina rock approximately 80% of the P applied is extracted, and with Central Florida rock the average amount extracted for all three soils was 20%. These results indicate ammonium citrate is dissolving an appreciable amount of unreacted North Carolina rock phosphate.

The rate of solubilization of Idaho, Tennessee, and Missouri rock phosphates was not high enough to give a response in yield or total P uptake. Also, their small solubilities could not be detected in the three soils when extracted with ammonium citrate.

Using ammonium citrate directly as a soil extractant on soils fertilized with rock phosphate the amount of soluble rock phosphate can be detected. The effectiveness of this extractant in evaluating the available P is related to the solubility of the rock phosphate applied.

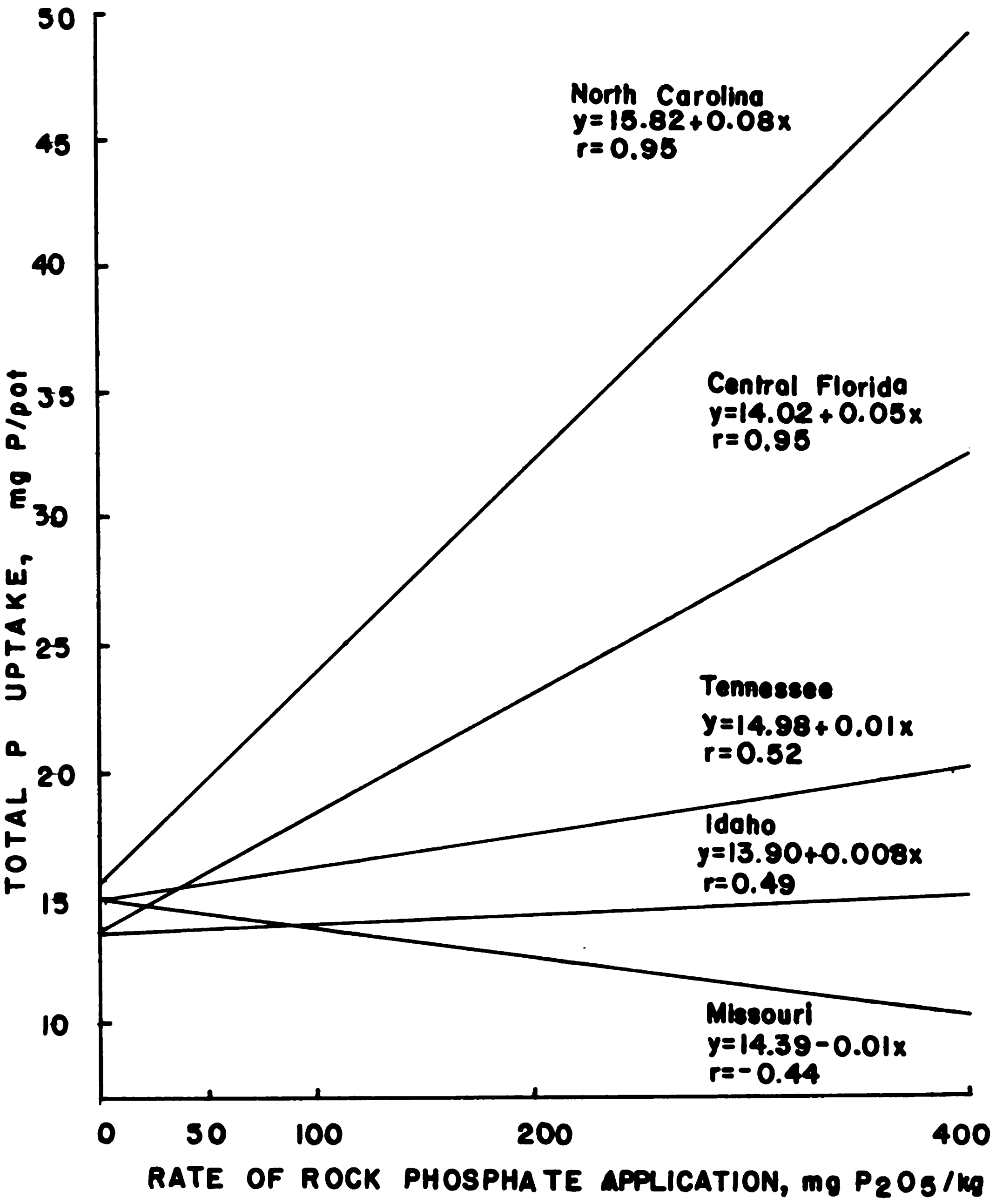

Figure 1. Relationship between the rate of rock phosphate application and total P uptake in Marlette soil.

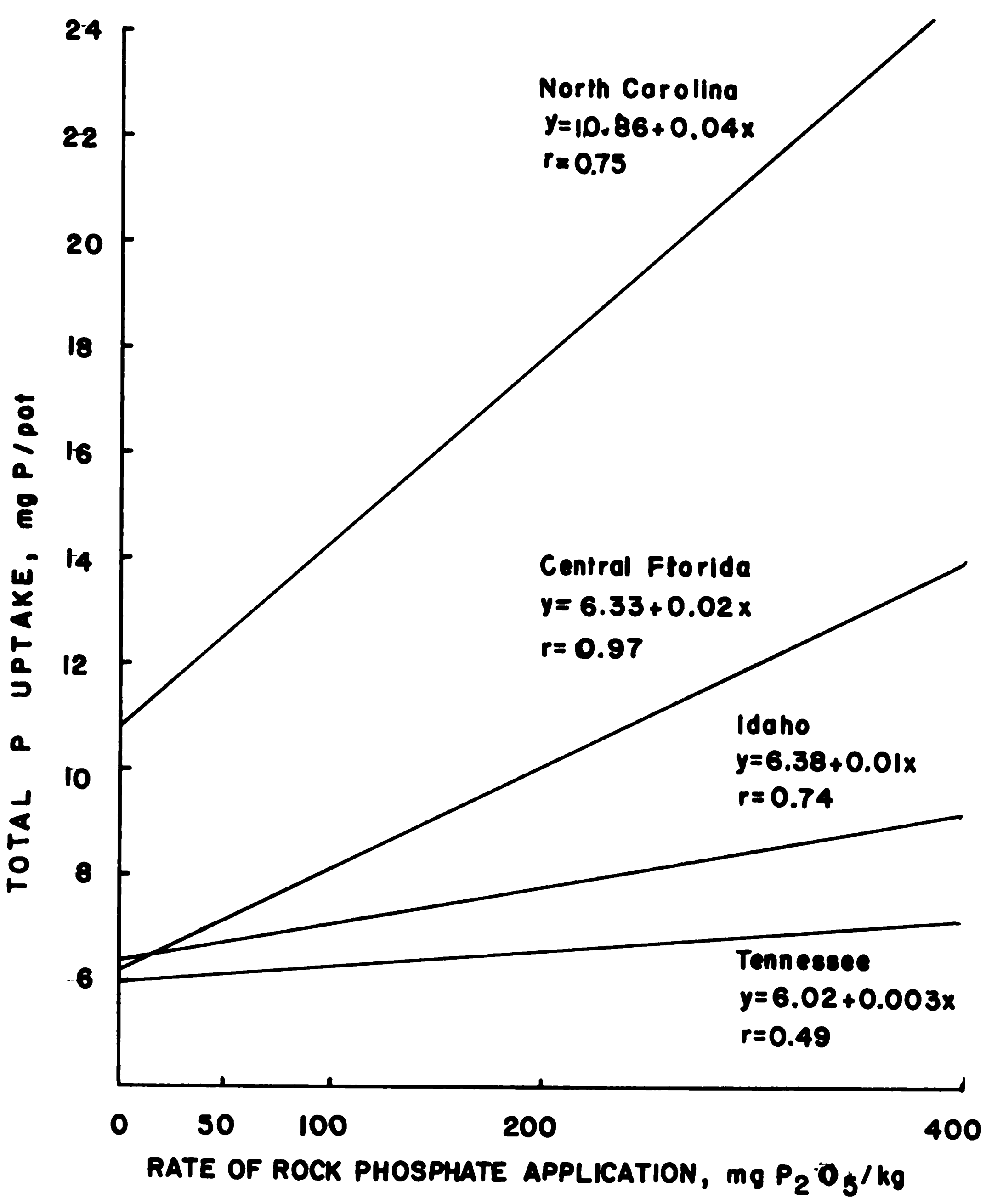

Figure 2. Relationship between the rate of rock phosphate application and total P uptake in Tracy soil.

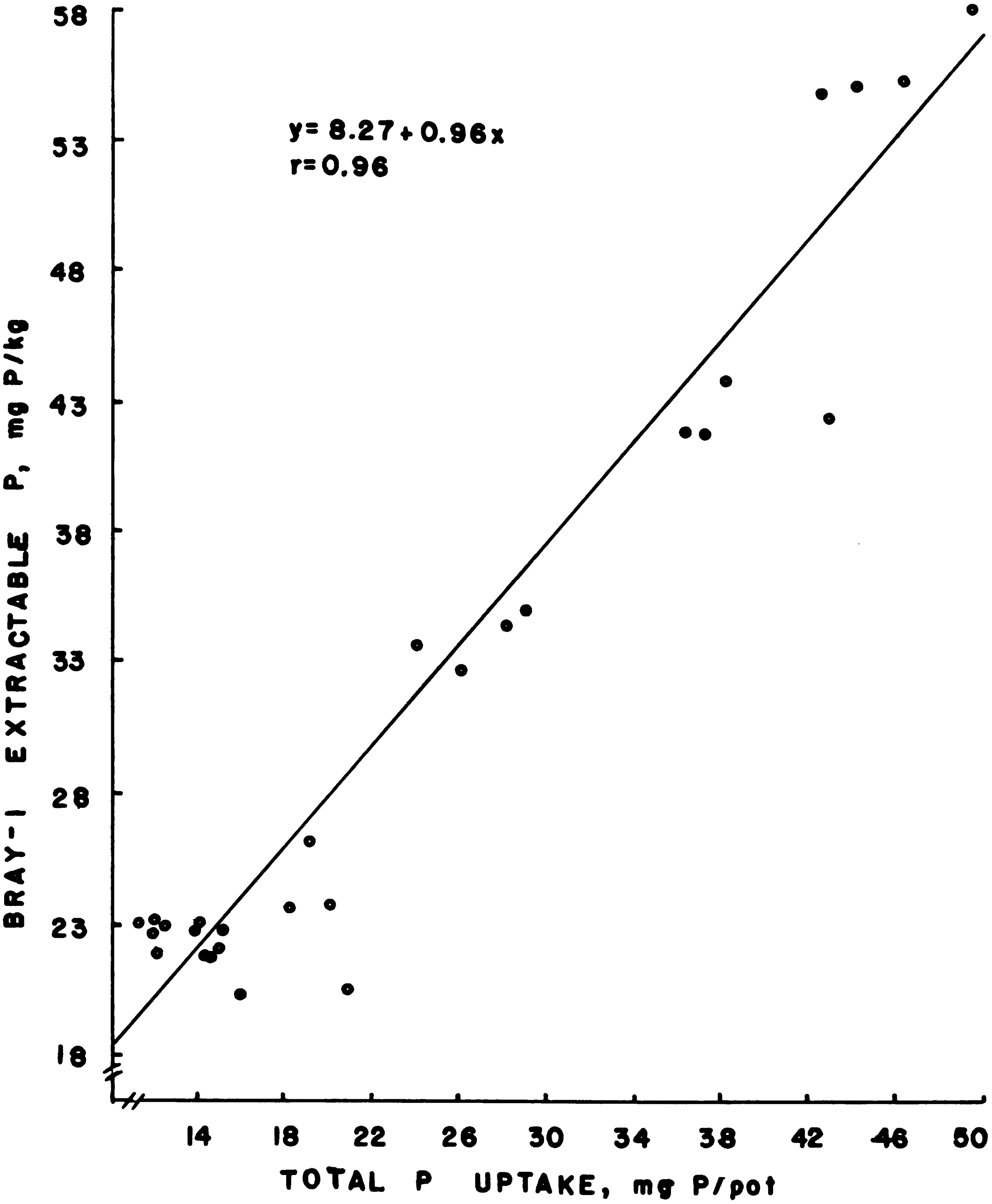

Figure 3. Relationship between total P uptake and Bray-1 extractable P for North Carolina rock phosphate in Marlette soil.

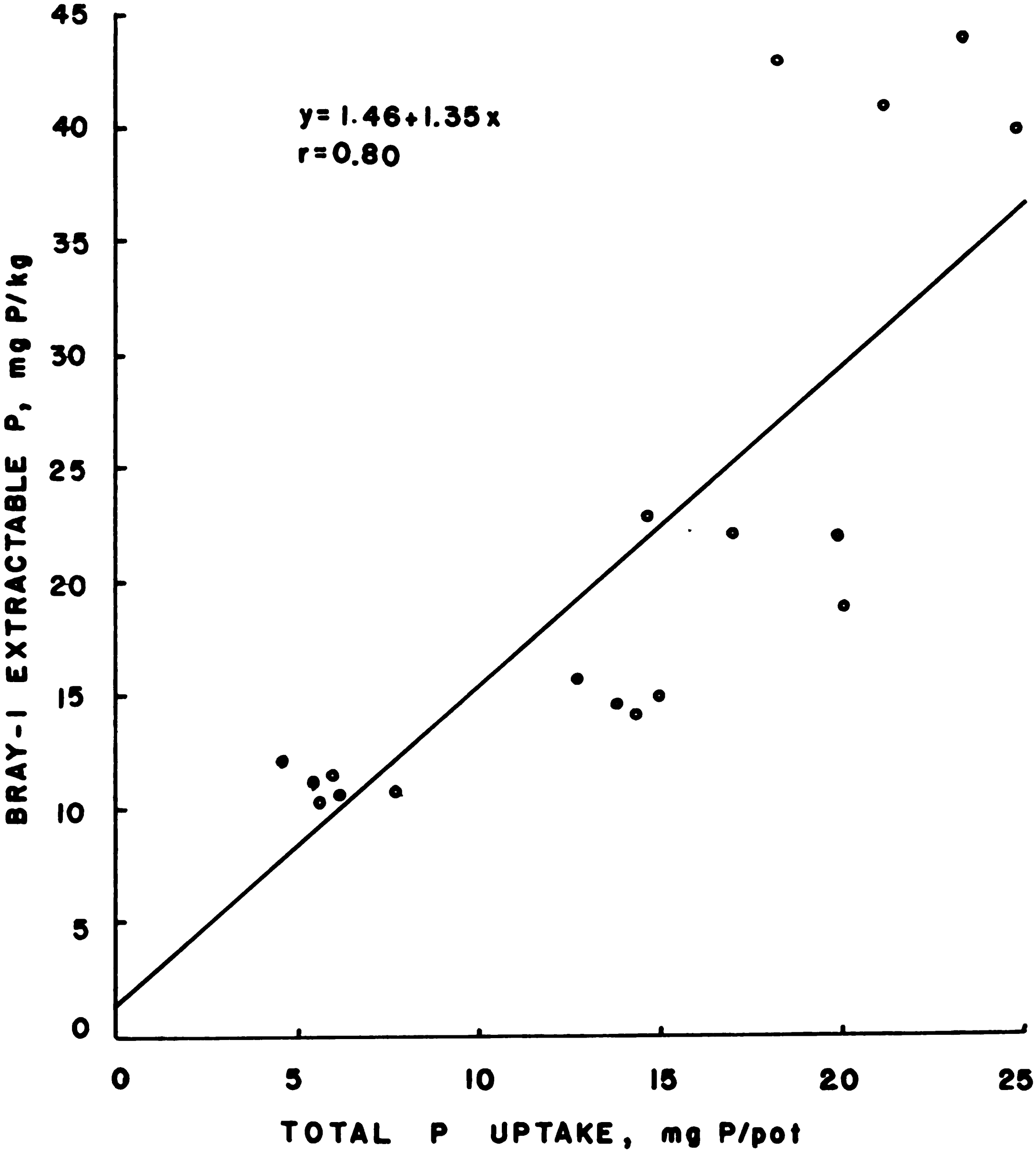

Figure 4. Relationship between total P uptake and Bray-1 extractable P for North Carolina rock phosphate in Tracy soil.

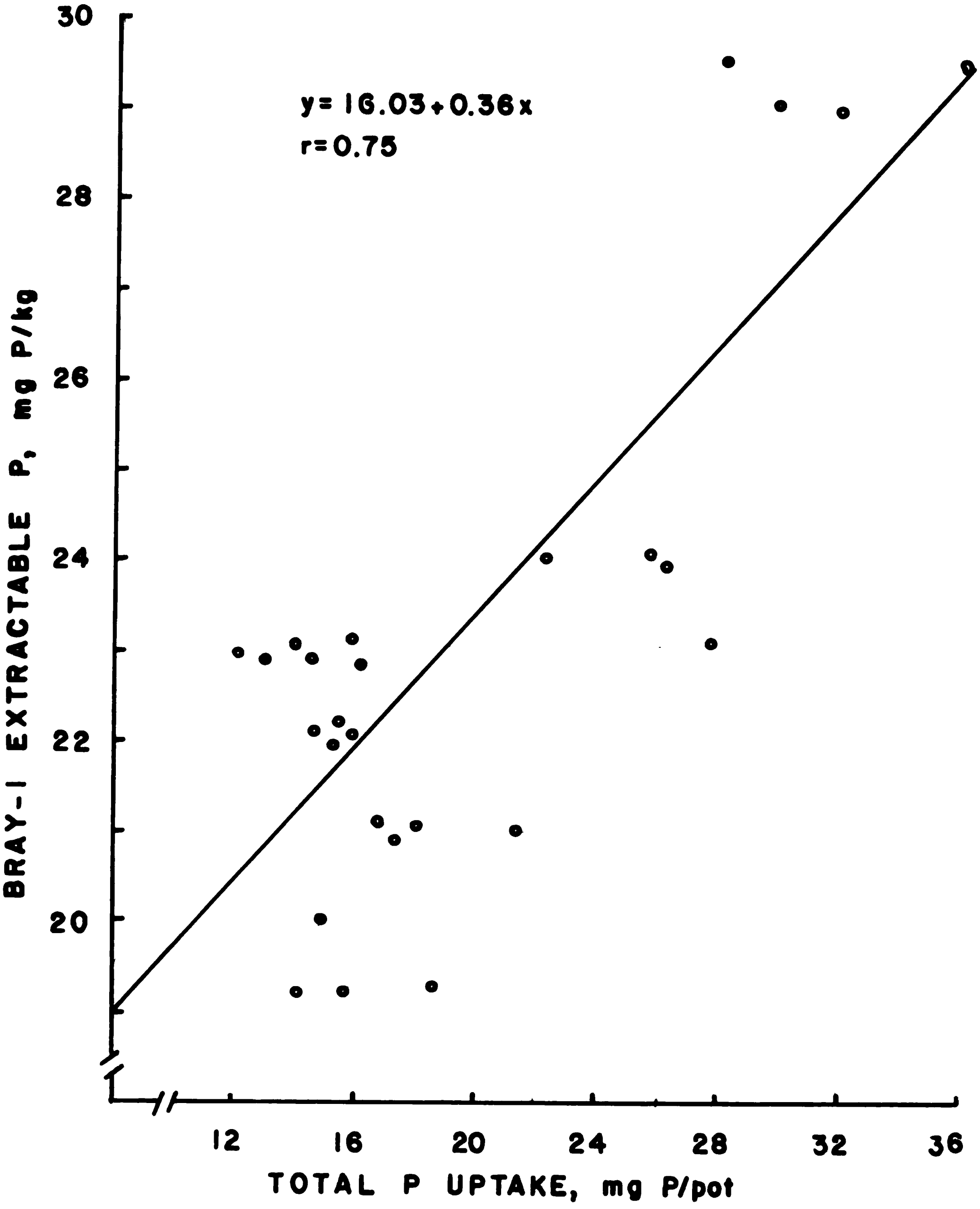

Figure 5. Relationship between total P uptake and Bray-1 extractable P for Central Florida rock phosphate in Marlette soil.

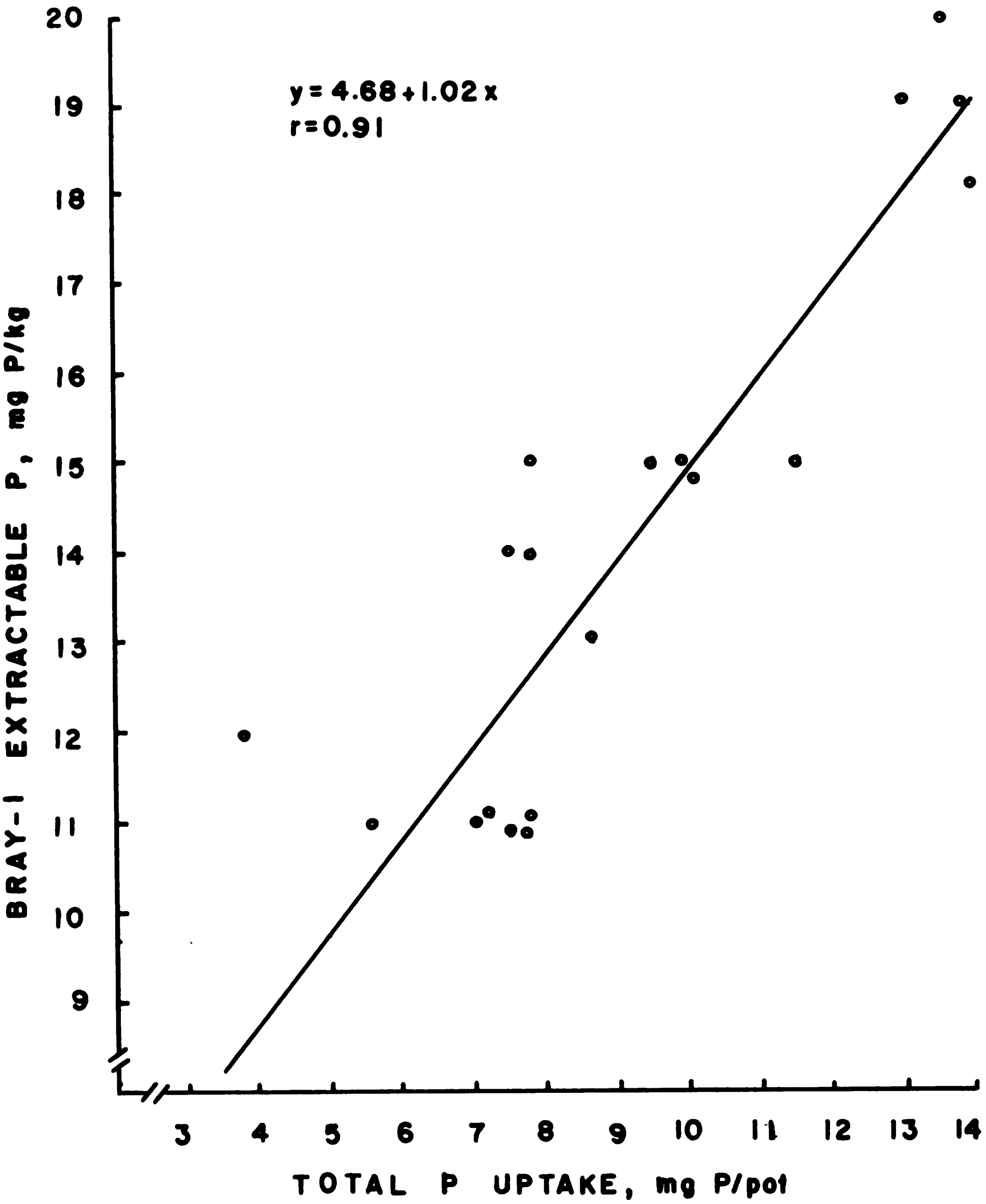

Figure 6. Relationship between total P uptake and Bray-1 extractable P for Central Florida rock phosphate in Tracy soil.

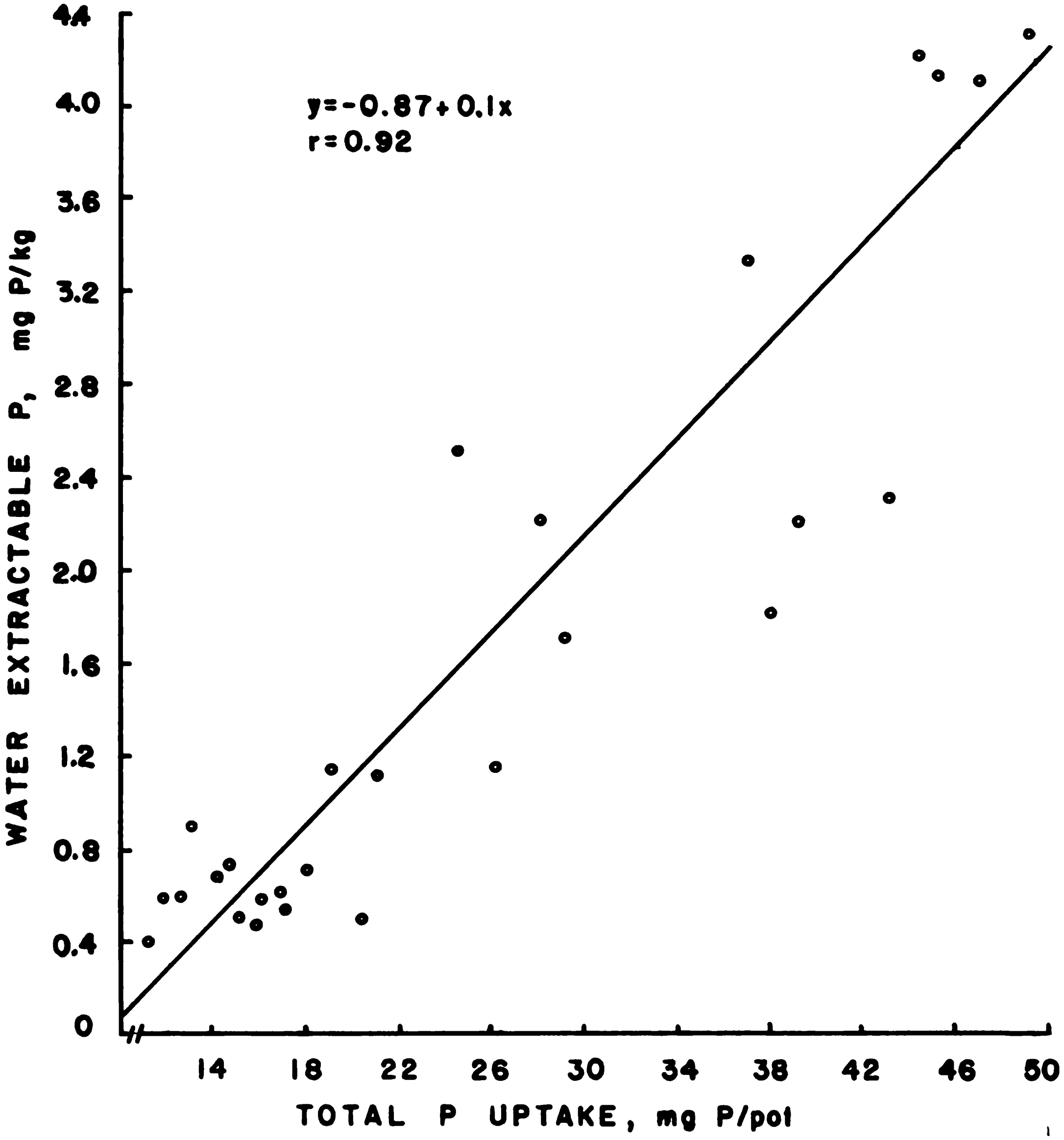

Figure 7. Relationship between total P uptake and water soluble P for North Carolina rock phosphate in Marlette soil.

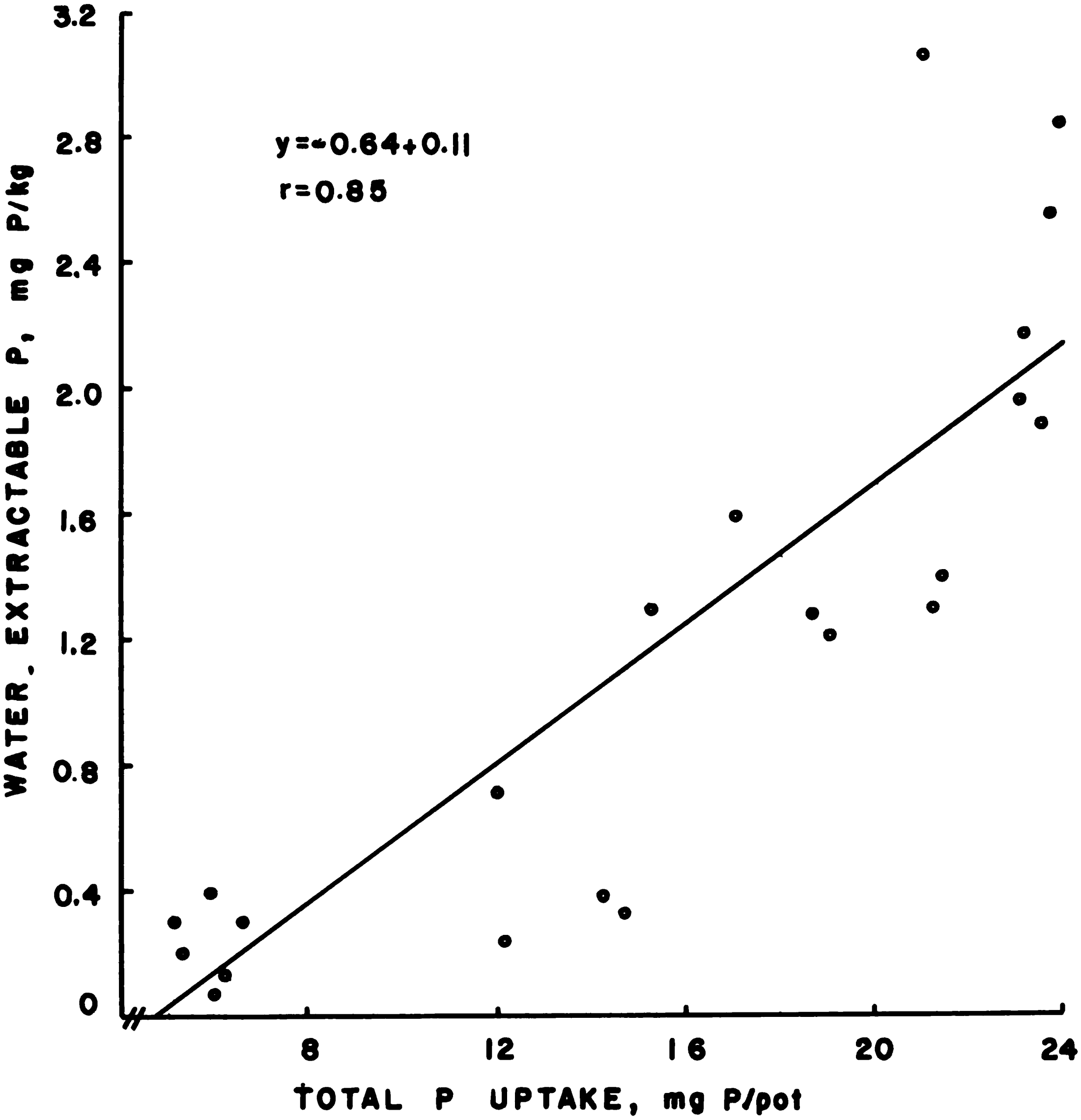

Figure 8. Relationship between total P uptake and water soluble P for North Carolina rock phosphate in Tracy soil.

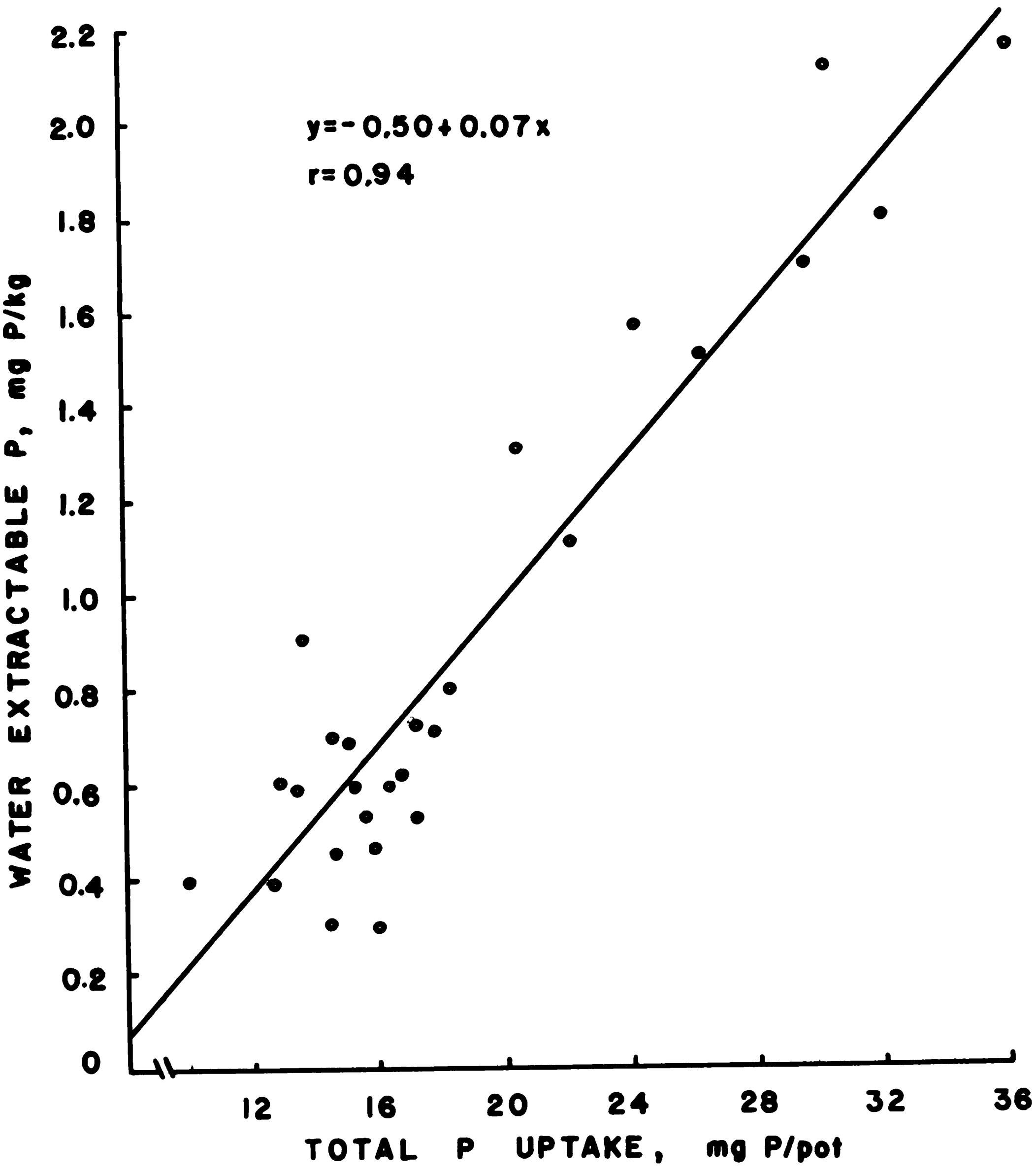

Figure 9. Relationship between total P uptake and water soluble P for Central Florida rock phosphate in Marlette soil.

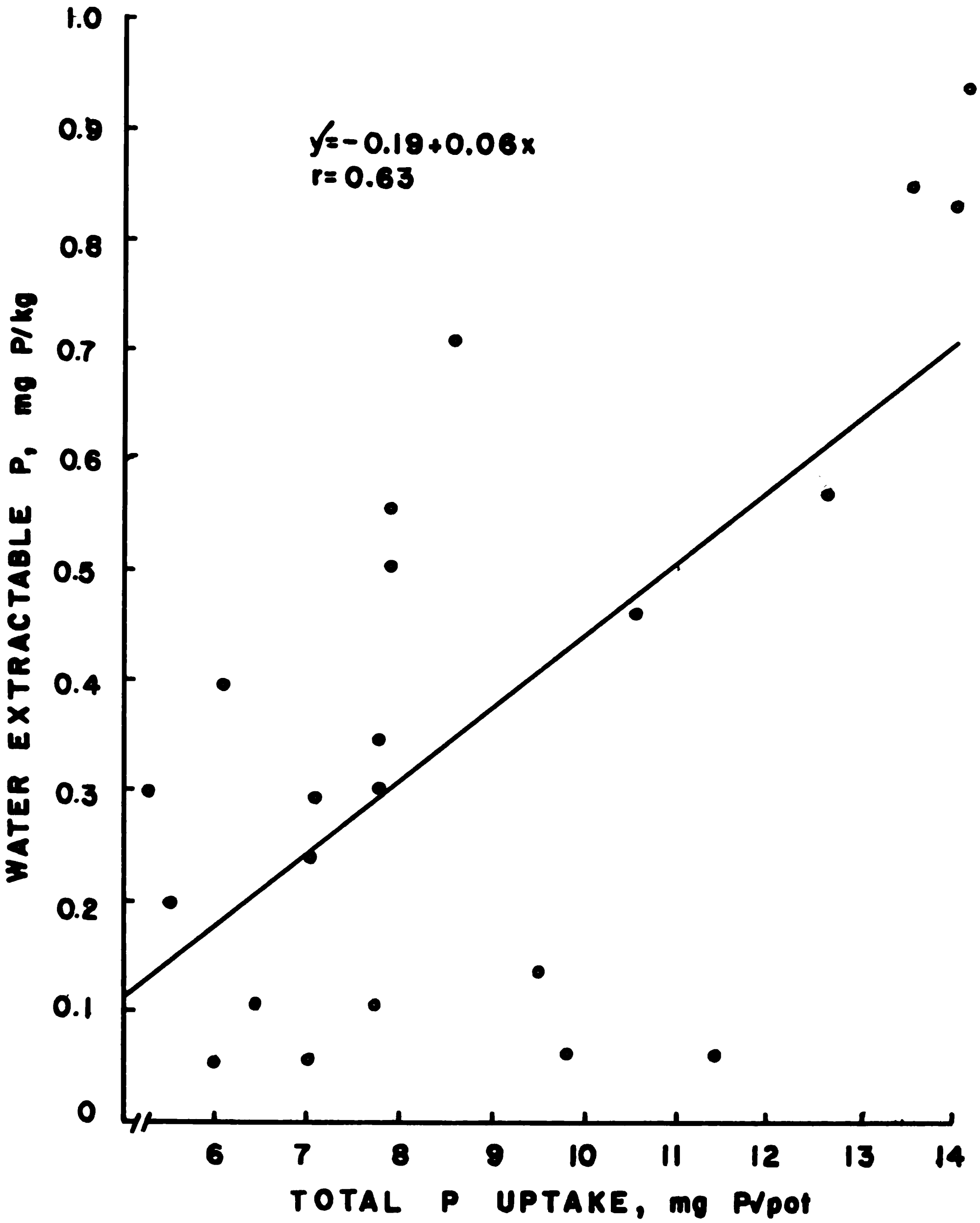

Figure 10. Relationship between total P uptake and water soluble P for Central Florida rock phosphate in Tracy soil.

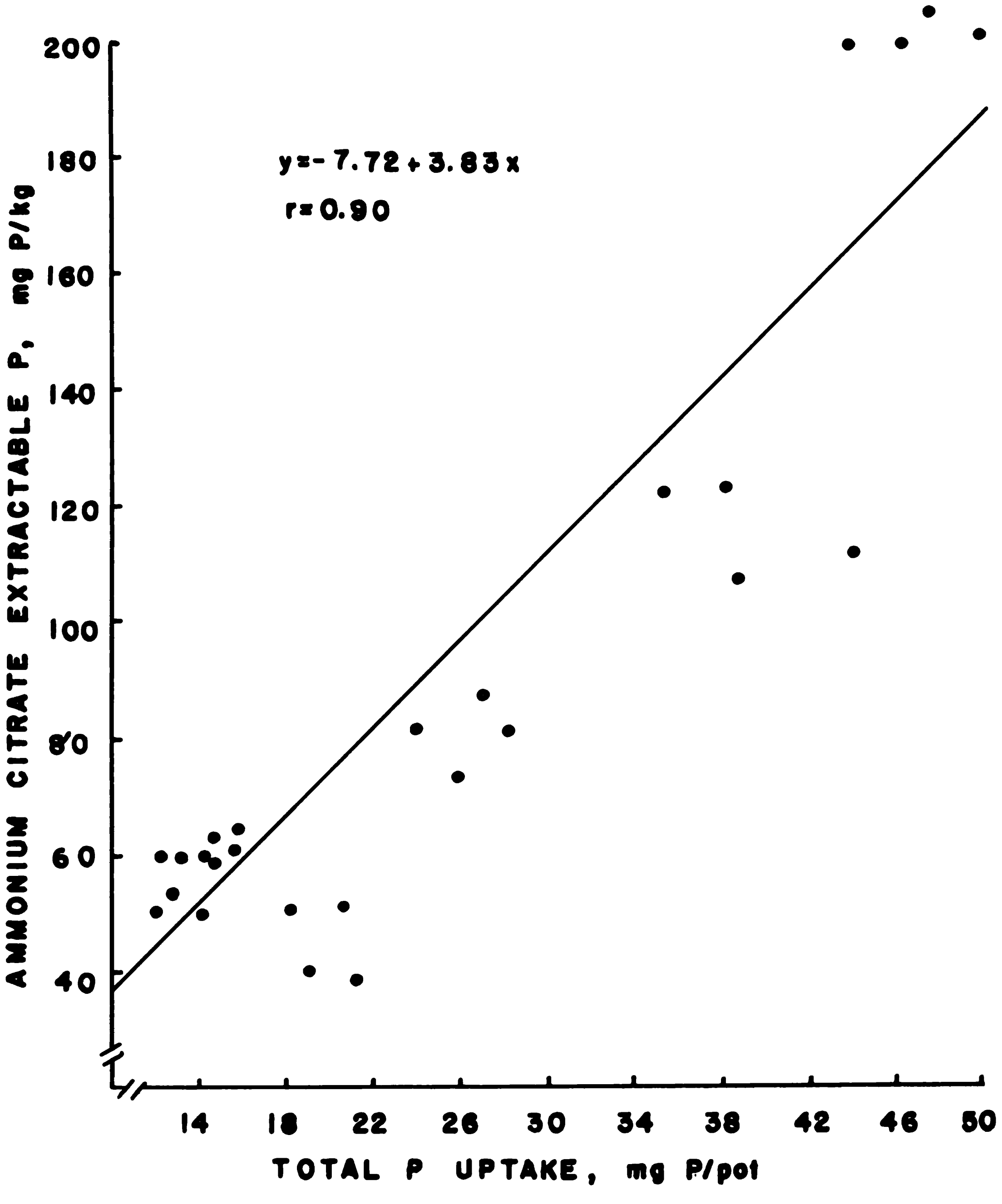

Figure 11. Relationship between total P uptake and ammonium citrate extractable P for North Carolina rock phosphate in Marlette soil.

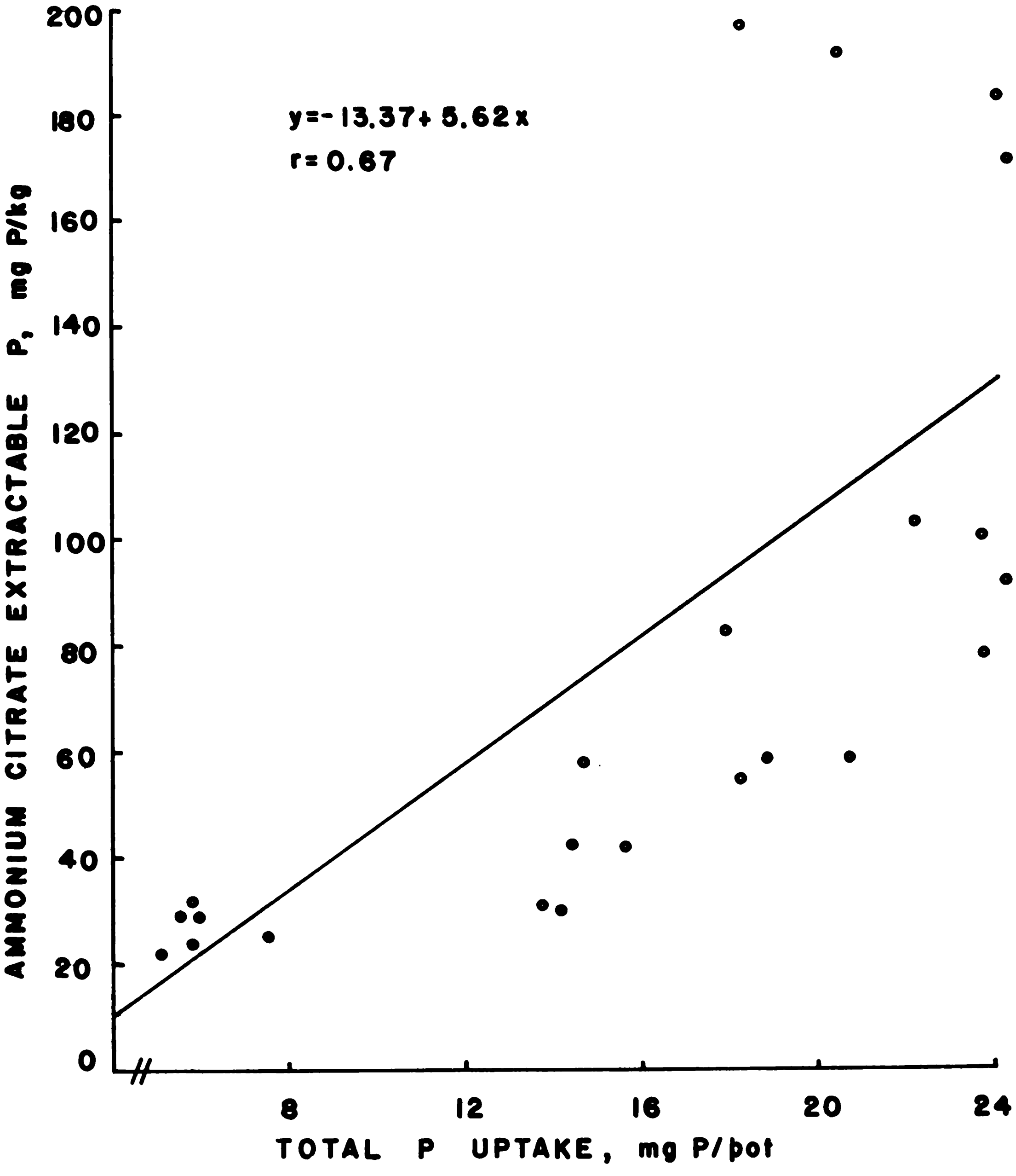

Figure 12. Relationship between total P uptake and ammonium citrate extractable P for North Carolina rock phosphate in Tracy soil.

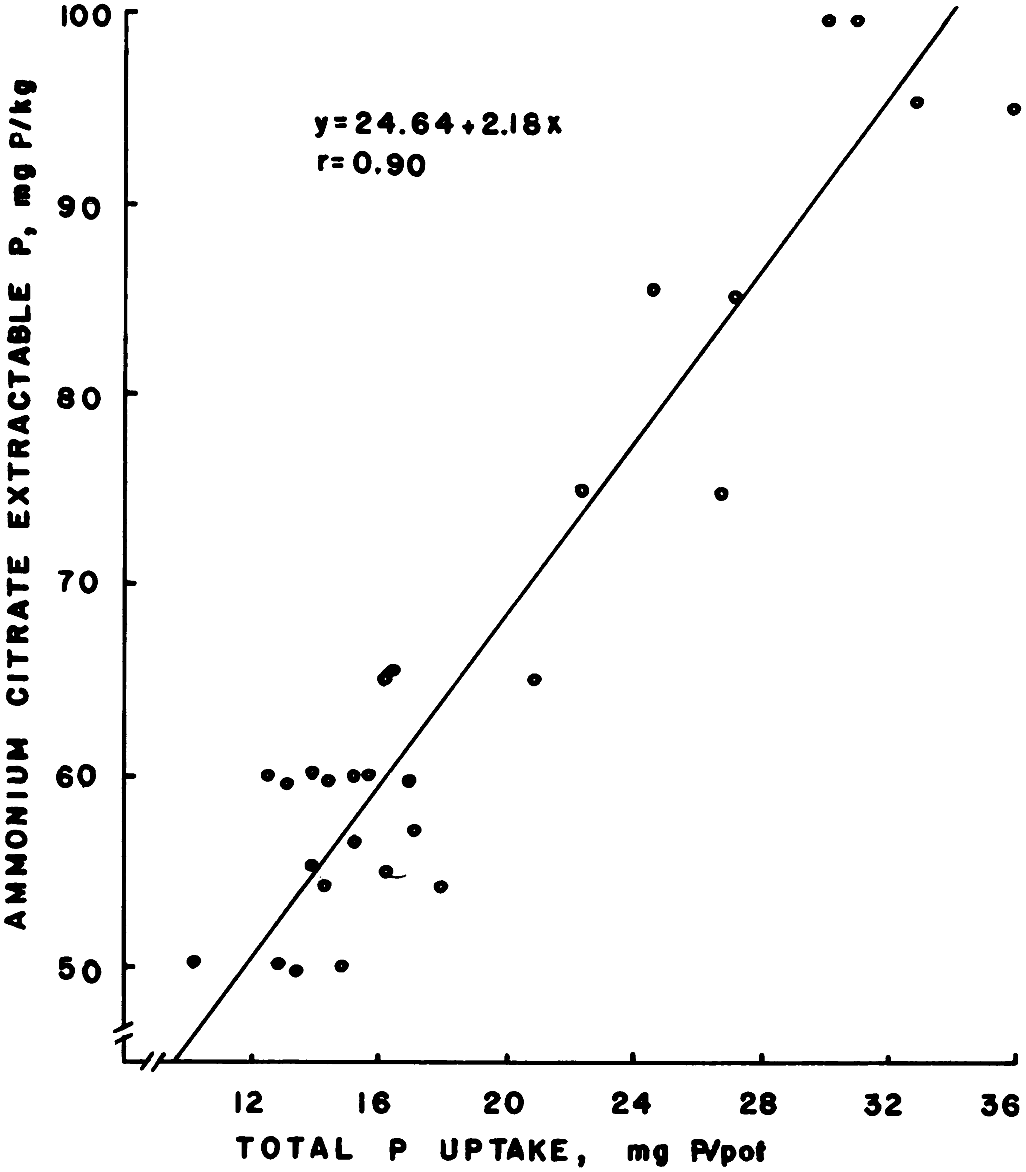

Figure 13. Relationship between total P uptake and ammonium citrate extractable P for Central Florida rock phosphate in Marlette soil.

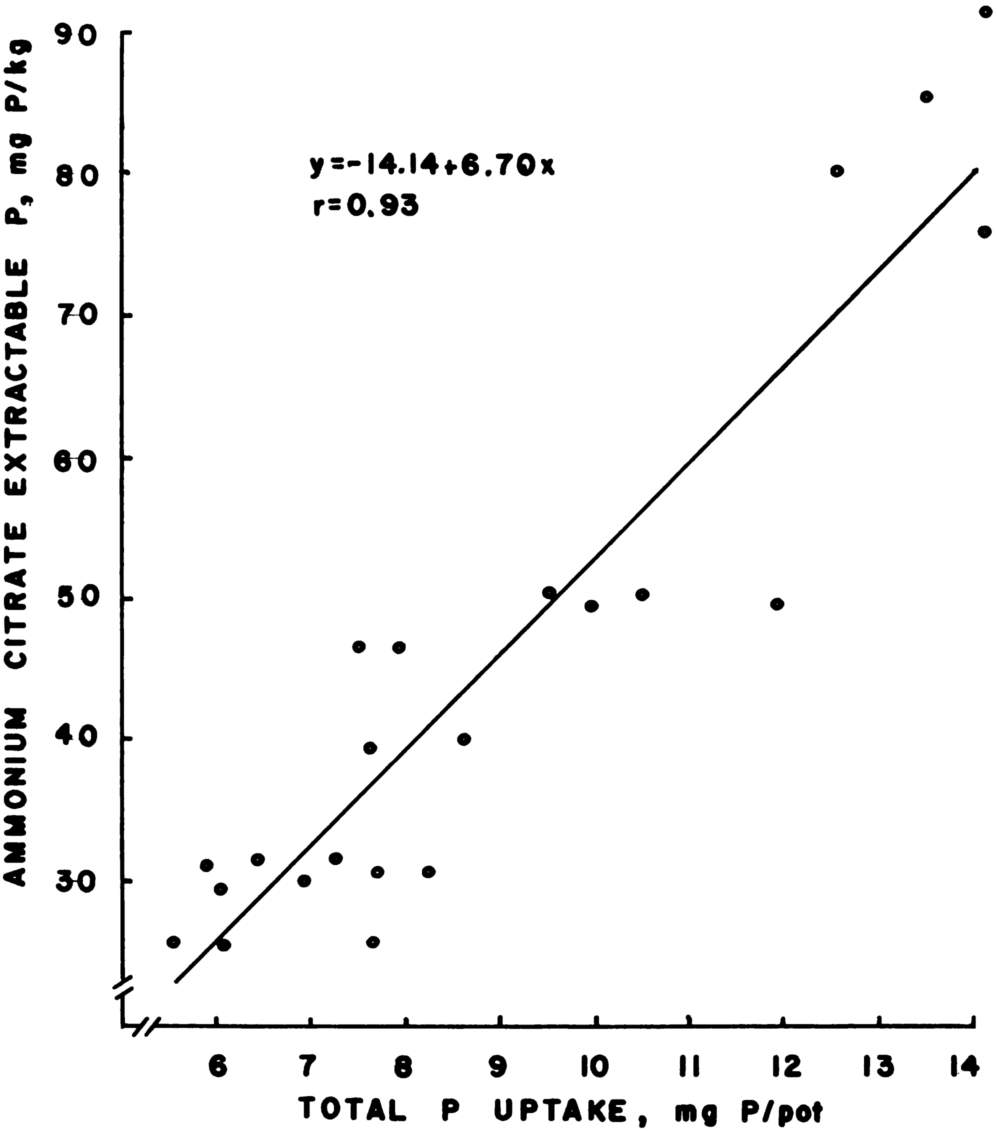

Figure 14. Relationship between total P uptake and ammonium citrate extractable P for Central Florida rock phosphate in Tracy soil.

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APPENDIX

APPENDIX I. Results and Experimental Data of Marlette Sandy Loam Soil*

Rate	Uptake	Dry Weight	Bray P-1	Water Soluble	Ammonium Citrate
mg P_2O_5/kg	mg P/pot	gm/pot	mg P/kg		
		Idaho			
0	14.2	12.4	22.5	0.5	57.0
50	13.9	11.5	16.2	0.4	57.5
100	13.6	12.0	16.2	0.4	62.5
200	15.3	11.5	18.5	0.3	60.5
400	17.4	12.9	19.7	0.6	65.0
		Central Florida			
0	14.2	12.4	22.5	0.5	57.0
50	14.9	13.1	18.7	0.4	54.2
100	18.0	15.8	20.5	0.8	60.5
200	25.3	16.2	27.7	1.3	80.0
400	32.0	19.5	29.5	1.9	97.5
		North Carolina			
0	14.2	12.4	22.5	0.5	57.0
50	19.5	16.2	23.5	0.8	45.0
100	26.3	19.0	33.5	1.8	78.7
200	39.4	19.6	42.7	2.4	115.2
400	45.6	20.3	55.7	4.3	202.2
		Tennessee			
0	14.2	12.4	22.5	0.5	57.0
50	15.8	12.8	23.2	0.9	59.2
100	18.3	15.4	22.7	0.9	61.0
200	16.9	14.3	23.7	0.8	57.0
400	18.2	16.0	25.0	1.2	66.2
		Missouri			
0	14.2	12.4	22.5	0.5	57.0
50	14.3	13.8	24.2	0.5	60.5
100	13.8	13.6	22.5	0.8	66.2
200	13.0	13.5	21.0	0.5	59.2
400	12.0	12.6	19.2	0.6	61.7

* Average of Four Replications

APPENDIX II. Results and Experimental Data of Tracy Sandy Loam Soil*

Rate	Uptake	Dry Weight	Bray P-1	Water Soluble	Ammonium Citrate
mg P_2O_5/kg	mg P/pot	gm/pot	mg P/pot		
		Idaho			
0	6.1	7.4	10.8	0.2	28.1
50	6.9	8.0	10.2	0.1	23.5
100	7.1	7.5	11.5	0.1	34.7
200	7.8	8.6	11.0	0.1	34.0
400	8.8	9.0	11.0	0.2	36.5
		Central Florida			
0	6.1	7.4	10.8	0.2	28.1
50	7.5	8.3	11.0	0.2	31.5
100	7.8	8.0	14.0	0.4	42.5
200	10.3	9.4	15.0	0.1	50.0
400	13.6	10.5	19.0	0.7	82.5
		North Carolina			
0	6.1	7.4	10.8	0.2	28.1
50	14.3	12.0	15.2	0.4	36.0
100	18.0	11.1	21.0	1.2	55.5
200	23.9	12.8	29.7	1.9	95.5
400	21.4	11.0	42.2	2.4	186.0
		Tennessee			
0	6.1	7.4	10.8	0.2	28.1
50	6.4	7.5	12.0	0.4	26.7
100	5.9	7.1	12.7	0.6	32.2
200	6.3	7.8	13.7	0.5	37.2
400	7.5	7.9	13.2	0.7	39.7
		Missouri			
0	6.1	7.4	10.8	0.2	28.1
50	6.2	7.7	11.0	0.3	36.7
100	6.5	7.6	11.2	0.4	28.7
200	6.2	8.5	10.7	0.3	29.2
400	6.0	8.1	11.0	0.4	30.0

* Average of Four Replications

APPENDIX III. Results and Experimental Data of Granby Sandy Loam Soil*

Rate	Uptake	Dry Weight	Bray P-1	Water Soluble	Ammonium Citrate
mg P_2O_5/kg	mg P/pot	gm/pot	mg P/kg		
		Idaho			
0	9.8	9.7	18.7	0.3	34.5
50	8.2	8.9	20.5	0.5	32.0
100	7.3	8.1	19.5	0.8	33.2
200	7.5	8.9	20.0	1.2	36.5
400	9.2	9.9	18.7	1.3	45.0
		Central Florida			
0	9.8	9.7	18.7	0.3	34.5
50	8.8	9.3	19.0	1.0	38.5
100	10.1	9.6	19.2	1.5	55.5
200	9.0	9.1	20.7	1.1	51.7
400	9.7	10.3	19.7	1.3	62.5
		North Carolina			
0	9.8	9.7	18.7	0.3	34.5
50	10.3	10.1	24.5	0.9	48.0
100	8.5	8.8	29.0	1.5	63.7
200	9.0	10.1	35.7	1.0	103.5
400	10.0	10.0	49.5	0.9	172.4
		Tennessee			
0	9.8	9.7	18.7	0.3	34.5
50	10.6	10.6	24.0	0.6	33.2
100	8.3	9.3	23.0	0.7	40.5
200	11.0	10.2	22.2	0.6	41.7
400	8.9	10.2	22.5	0.5	36.5
		Missouri			
0	9.8	9.7	18.7	0.3	34.5
50	9.5	10.3	20.7	0.6	40.5
100	9.0	10.1	20.7	0.3	39.7
200	9.1	10.9	21.5	0.4	38.7
400	8.6	9.4	20.0	0.6	37.0

* Average of Four Replications