COMPARISON OF AVAILABLE SOIL PHOSPHORUS BY ANION EXCHANGE RESIN AND BRAY 20:1 PROCEDURES

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CHAPTER I

INTRODUCTION

Phosphorus is found in the soil in different forms. Most of these forms present in soils are unavailable to plants. Also, if a soluble form of phosphorus is added to the soil in the form of fertilizer most of it is usually "fixed" or rendered unavailable to plants. To be absorbed by plants, the precipitated phosphoric acid must be dissolved. This can be achieved in the following way: A very small amount of phosphate is dissolved on coming in contact with the soil solution, it is absorbed by the plants, thus displacing the chemical equilibrium and causing a fresh minute quantity of phosphate to be dissolved.

Soils differ widely regarding the properties of their "available" phosphate probably due to the following:

1) The specific surface of the phosphate and its distribution in the soil (particle size; as the particle size gets smaller the specific surface and the solubility increase and vice versa).

2) The content of the other ions (e.g., Ca, Al, Fe, etc.).

3) The percentage of soil colloids (2:1 clay particles may fix phosphate, this can be achieved either by chemical precipitation, adsorption by simple addition or by anion exchange).

Various chemical methods have been devised for determining the available phosphorus present in the soil by using chemical extracting reagents with the assumption that these methods are analogous to the processes which are believed to proceed near the roots of plants.

In devising an analytical method for practical use, one should endeavor to imitate the manner in which the substance is made available, and at the same time interfere as little as possible with soil conditions, in other words, the method should be analogous to the processes which proceed near the roots of plants.

Based upon the principles and the assumptions which have been made for determining available phosphate, different methods and techniques can be grouped into four broad categories:

1) Chemical extraction techniques
2) Bioassay techniques
3) Radio-isotope-phosphorus techniques
4) Resins or anion exchange techniques

The principal objective of this study is to compare the performance of the exchange resin method of Amer et al (1)* with that of Bray (7) 20:1 (solution to soil ratio) method, to see whether the supposed advantages of the resin method will be sustained by applying it to dissimilar soils.

*Numbers in parentheses refer to literature cited.

CHAPTER II

REVIEW OF LITERATURE

Chemical Extraction Techniques

According to Russell (49) and Dean (16) chemical techniques are based on the following assumptions:

1) Dilute acids dissolve all calcium phosphates present except the apatites.

2) Concentrated solutions of acids dissolve the apatites.

3) Fluorides displace phosphate from the surface of hydrated aluminum oxides and subsequent treatment with alkali displaces it from the surface of hydrated ferric oxides.

4) Reducing solutions containing an iron chelating agent will remove phosphate present below the surface of iron oxide films and, in particular, phosphate present in nodules of hydrated oxide.

Keeping these points in mind researchers started to devise techniques to extract phosphorus from soils. The earliest attempt to determine the readily available phosphorus in the soil was made by Troug (57). He extracted the soil with a 0.002N solution of H_2SO_4 buffered with ammonium sulfate to pH 3.0.

Fisher and Thomas (24) also made an early attempt to extract available phosphorus. They used acetic acid-sodium acetate buffer at pH 5.6 and dilute H_2SO_4 at pH 2.0.

Harper (29) extracted non-calcareous soils with 0.1N acetic acid. Harper obtained good correlation between crop response to fertilizer applied and the phosphorus extracted by the acetic acid method.

Extraction of the soils with solutions with less solvent power, such as one percent citric acid employed by Dyer (22), and 0.20N nitric acid of Fraps (25), have been used and recommended by many workers as good indications of the available phosphorus in the soil.

Morgan (41) developed the so-called universal soil extracting solution for the evaluation of available phosphorus as well as several other nutrients within the soil. The universal soil extracting solution consists of 0.50N acetic acid solution, buffered at pH 4.8 with sodium acetate.

Das (15) proposed a method for determining available phosphorus by extracting the soil with a potassium carbonate solution and compared it with a citric acid method. Das concluded that the potassium carbonate method is equally applicable to all types of soils, whereas, the citric acid method breaks down as a discriminating agent for evaluating the available phosphates of alkali and calcareous soils.

Different quick tests have been introduced by many workers for phosphorus as well as other nutrients. These methods include: 0.7-0.8N HCl of Bray et al (8), 0.135N HCl of Spurway (54) and buffered perchloric acid extractant of Mile (38) and 0.3N HCl of Bauer (4).

Dickman and Turk (18) described a method for determining the organic phosphorus content of soils by decomposing the organic matter with hydrogen peroxide and subsequently extracting phosphorus with 0.2N H_2SO_4.

Bray and Kurtz (7) made the distinction between adsorbed and acid soluble phosphorus; on these bases they divided their test into two methods:

1) Extraction of the adsorbed phosphorus by using a mixture of 0.03N NH_4F and 0.025N HCl.

2) Extraction of acid-soluble plus adsorbed phosphorus by using a mixture of 0.03N NH_4F and 0.1N HCl.

Rubins and Dean (46) compared different chemical methods with the Neubauer biological method on different soils from Maine. Rubins and Dean reported that the acetic acid method and Truog method extracted a greater fraction of the total phosphorus than the Morgan method. They concluded that results with different chemical methods correlate with each other to a certain extent, but no significant correlation was obtained between results with the Neubauer biological method and the different chemical methods.

Distilled water saturated with CO_2 has been used on many calcareous soils (35,10). Good correlations between phosphorus applications and the amount of phosphorus extracted have also been obtained. McGeorge and Breazeale (35) concluded that the solvent action of carbonic acid on soil phosphorus in calcareous soils is mainly a function of soil reaction.

Olsen et al (45) proposed a new method for extracting soil phosphorus by using 0.5M solution of sodium bicarbonate adjusted to pH 8.5. They claimed that their method gave better correlations with plant response in both calcareous and acid soils than the Bray method.

Miller and Axley (39) attempted to determine the soluble phosphorus in soils by using a modification of the Bray, Kurtz, and Troug methods. Their extractant was a mixture of 0.3N H_2SO_4 and 0.03N NH_4F.

Breland and Sierra (10) compared the relative effects of eight extractants on the removal of phosphorus from seven major soil types of Florida. Breland and Sierra concluded that HCl-NH_4F and HCl-H_2SO_4 solutions extracted more phosphorus than the $NaHCO_3$, NaOAc, NH_4OAc, distilled water, or distilled water and CO_2 methods.

Bioassay Techniques

The relative availability of a nutrient in different soils can be investigated by using bioassay techniques of which there are two types using:

1) Higher plants

2) Microorganisms.

Higher Plants

The use of this method is based on the principle that a biological response may increase linearly with the dose of active ingredient.

The real development of this concept started when Liebig formulated his law of the minimum which stated that the nutrient present in least relative amount is the limiting nutrient. It implied that all the other nutrients were present in excess until the deficient or limiting nutrient was made adequate, whereupon, the one present in the next least relative amount became the deficient nutrient, and so on. This law stimulated the interest of other workers in the field to evaluate the availability of a given nutrient in the soil by determining plant response and total nutrient uptake.

According to Black (5) and Bray (9) Mitscherlich and later Spillman arrived independently at the following conclusion: A unit increase in supply of a plant nutrient results in an increase in the yield. The increase in the yield is to be proportional to the decrement from the maximum yield that can be produced as the supply of the nutrient is increased indefinitely. Mitscherlich expressed this mathematically as:

$$\log (A - y) = \log A - C(x + b)$$

where:

y = the yield associated with the soil available phosphorus, with or without added fertilizer

x = units of added fertilizer

b = available phosphorus present in the soil

A = maximum yield that can be produced as x increases indefinitely

C = a parameter

The A and b variables and the "C" parameter can be calculated and obtained in the simplest case by using the following formula:

$$A^* = \frac{y_1^2 - (y_o)(y_2)}{2y_1 - y_o - y_2}$$

$$C^* = \frac{\log(A - y_o) - \log(A - y_1)}{x_1 - x_o}$$

$$b^* = \frac{\log A - \log(A - y_o) - Cx_o}{C}$$

where y_o, y_1, y_2 are the yields corresponding to the added phosphorus x_o, x_1, x_2, respectively. Thus, it is apparent that the available soil phosphorus can be calculated by knowing the other components of the

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*These formula can be used only when $x_1 - x_o = x_2 - x_1$.

equation.

Bray (6) and Arnold and Schmidt (2) have used the Mitscherlich equation with considerable success in the correlation of chemical soil tests with results of field experiments with fertilizers.

Based upon the assumption that plants presented with two sources of a nutrient, namely the soil and fertilizer, will absorb this nutrient in proportion to the amounts available, Dean (17) developed a curve to estimate the available soil phosphorus in terms of phosphorus applied as a fertilizer. If the yield of phosphorus curves are extrapolated to their intersection with x-axis, this likewise should give a measure of the amount of phosphorus in the soil as available as the source applied as a fertilizer.

According to Stewart et al (55) and Bould (11) Neubauer proposed his seedling techniques for evaluating phosphorus availability in the soil. The Neubauer method is based on the principle of intensive uptake of plant nutrients by a large number of seedlings grown on a small quantity of soil. Neubauer asserted that 95 to 100 rye seedlings will extract in 14 days all of the available nutrient elements in 100 grams of soil. Neubauer found that the phosphorus and potassium taken up by the seedlings is dependent on the soil and appears to be a constant value for each sample of the same soil under a standard technique.

Microorganism Techniques (Soil Plaque Method)

The microorganism techniques are based on the fact that microorganisms have some similarities in their requirements for certain elements, such as K, P, N, etc., as plants do. Any deficiency in one of the required nutrients, therefore, will retard and reduce their growth.

According to Nicholas (43) Butkeric and Korceleckii were pioneers in using microbiological methods for the determination of mineral nutrients in soils. Butkeric and Korceleckii used *Aspergillus* for the study of available phosphorus in Russian soils.

According to Sackett and Stewart (50) Winogradsky and Ziennieka demonstrated that spontaneous colonies of *Azotobacter* grow luxuriantly on soil plaques if suitable energy and nutrient elements are provided. Winogradsky and Ziennieka found that there was a close correlation between the limiting factors for *Azotobacter* and those for growing plants.

Sackett and Stewart (50) modified Winodradsky's method for the study of elemental deficiencies in Colorado soils. They used *Azotobacter* colonies as a nutrient element indicator. Sackett and Stewart concluded that the *Azotobacter* soil-plaque method was a satisfactory means of determining deficiencies in phosphate, calcium, and probably potassium.

Stewart (55) compared the soil plaque technique for phosphorus and potassium deficiency determinations with the Neubauer and Hoffer corn stalk method. The results showed that both tests are equally reliable, however, the soil-plaque technique is faster and cheaper to run that the Neubauer test.

According to Smith et al. (53) Niklas et al used the growth of *Aspergillus niger* in culture solution to which soil had been added as an indication of the phosphorus needs of the soil. Niklas et al. obtained quite satisfactory results which were in close agreement with the results secured by the Neubauer method.

Dalberg and Brown (14) compared the soil-plaque technique with the Neubauer method, on different western soils. Dalberg and Brown concluded that the soil plaque method gave a satisfactory comparison with the Neubauer method for phosphorus deficient soils, but not for soils with higher phosphorus contents.

Mehlich (37) modified Niklas' method by using Cunning-hamella instead of Aspergillus niger, for quantitative determinations of available phosphorus in soils. He compared this method (Cunning- hamella) with the Aspergillus niger method, a chemical method, and field test. The results obtained with a large number of soils from widely separated areas showed good agreement with field test results but not with the chemical method.

Halversen and Hoge (28) modified Sackett and Stewart's method (50) by replacing the water by hot agar solution to give a smooth surface for colony growth and uniformity of appearance of the plaque.

Tchan (56) described a new biological soil test in which a mixed culture of algae is used. Algae and higher plants show similar growth responses in the presence of different quantities of nutrients. The test involves adding 5-10 grams of air dry soil to 50 ml of complete nutrient solution (minus the nutrient element under test, e.g., phosphorus). The pH of the medium is adjusted to that of the soil. A mixed culture of algae is then added and the flasks are incubated under conditions of constant light and temperature for two to three weeks. The results of the test are compared with a standard series, thus, a prediction of the plant's response when fertilizer is supplied to a particular soil can be obtained.

Radio-Isotopes-Phosphorus Technique

Soil solution phosphorus is in dynamic equilibria with the solid phase phosphorus of soil. The equilibration takes place as a result of dissociation of phosphate groups from the site of binding in the soil, and their replacement for the solution phase by other phosphate groups (1). Thus isotopic tracers are of value in following the exchange reactions which take place between surfaces and components of the continguous solutions.

McAuliffe (34) applied this principle to soil reactions involving phosphate and hydrogen by using P^{32} and deuterium. McAuliffe found that the inorganic phosphate ions in the soil solution exchange continuously with the inorganic phosphate ions held by the solid phase of the soil. After McAuliffe's findings a fundamentally new approach to the problem of estimating soil phosphorus availability was made possible using P^{32}.

Larsen (31) stated that isotopic exchange between mono- and dicalcium phosphates and soil phosphate was so extensive that the exchangeable phosphate content of the soil could be determined by comparing the specific activity of labelled phosphate, subsequently absorbed by plants. Larsen developed the following equation to calculate exchangeable phosphate:

$$y = \frac{(Co - 1)}{C} X$$

where:

y = the amount of exchangeable phosphorus originally present in the soil

X = amount of phosphate added as fertilizer

Co = the content of radio phosphorus in the fertilizer

C = radio-phosphorus isolated from the plant

Larsen concluded that "this calculated value of exchangeable soil phosphorus" is independent of the amount of phosphate added, provided that a definite fraction of the soil phosphorus takes part in the isotope dilution.

Based on the same principle that Larsen used to calculate the exchangeable phosphorus in the soil, Fried and Dean (26) proposed a similar method for measuring the amount of available phosphorus in soils. This involved the introduction of a known quantity of standard source of nutrient under consideration into a soil, growing the desired crop, determining the proportion of the total nutrient absorbed that was derived from the standard source, and then calculating the amount of available nutrient (phosphorus) in the soil by applying the following formula:

$$A = \frac{B(1 - y)}{y}$$

where:

A = the amount of available phosphorus in the soil

B = the amount of phosphorus supplied as fertilizer

y = the fraction of the phosphorus in plant derived from fertilizer only

Thus, by knowing that part of phosphorus which is taken by plants from the fertilizer added (by applying radioactive tracer techniques) the A value can be determined.

Russell et al (47) argued that the simple isotopic exchange relation:

$$\frac{\text{(A) soil}}{\text{(B) soil}} = \frac{\text{(A) plant}}{\text{(B) plant}}$$

developed by Larsen, Dean, and others, is only applicable under very specific conditions; where soil phosphorus and added phosphorus fertilizer have the same availability coefficient. Russell et al suggested the modification of this simple relation by introducing the availability coefficient into the equation, thus, it will be applicable under all conditions. The equation will take the following form:

$$\frac{\text{(A) soil}}{\text{(B) soil}} = X\,\frac{\text{(A) plant}}{\text{(B) plant}}$$

where X is the availability coefficient.

Amer et al (1) compared P^{32} and the anion exchange resin method for characterization of soil phosphorus. Amer et al found both methods gave satisfactory results, but, they concluded that the resin method may be preferable because of the time required for equilibration.

Russell et al (48) investigated the relationship between the absorption of phosphate by plants and labile soil phosphate in four different soils. Russell et al concluded that tracer methods appear to be subjected to limitations similar to those of the older extraction procedures. Russell et al attributed these limitations to the slow migration of the labile phosphate between sites with different characteristics. This slow migration will cause the presence of different labile fractions with different activation energies. Also under slow migration true equilibrium will never be attained.

Caldwell and Jones (12) compared the labile phosphate result with the responses obtained in field experiments for peaty and chalky boulder clay soils. Their results showed that the responsiveness of the soils in the field to applied phosphate was not reflected in the labile values obtained on the peaty soils, but the labile method was more successful in chalky boulder clays than the soil analysis method.

Anion Exchange Method (Resin)

Ion exchange can be defined as a reversible exchange of ions between solid and liquid phases in which there is no substantial change in the structure of the solid (19).

Synthetic ion exchange resins are a special type of polyelectrolytes, i.e., cross-linked polyelectrolytes that can be visualized as an elastic three dimensional hydrocarbon network to which are attached a large number of ion active groups (19). The ion active group is always fixed to the high molecular weight polymer and is immobile.

The electrical charge of the ion active groups is always balanced by an equivalent number of oppositely charged ions which are mobile and can be exchanged with other ions of a similar charge. The ion active groups determine the chemical behavior of the ion exchange resins (e.g. cation exchange or anion exchange).

Types and Chemical Composition of Resins

Resins are made by copolymerization of styrene and divinyl benzene. In general there are four major types of resins (19):

a) Strong acid resins: made up by the nuclear sulfonation of styrene-divinyl benzene heads (e.g., Dowex 50 and Dowex 50W)

b) Strong base resins: a quaternary ammonium functionality (e.g. Dowex 1, Dowex 2, Dowex 21K)

c) Weak base resins: tertiary amine resin built on a condensed epi-amine backbone (e.g., Dowex 4)

d) Weak acid resins: containing carboxylic groups as the functional sites

The method of using anion exchange resins as a means for determining available soil phosphorus is based on the following principles. If the soil in aqueous suspension is treated with a substance capable of an ionic exchange such as organic resins and inorganic Na-zeolites, and with a reaction (neutral or slightly basic) almost the same as that of soil, this substance can remove the phosphorus from the soil solution. Its action will be more nearly analogous to that of the plant root than any other method in which an equilibrium is being set up between phosphorus in the extracting solutions and phosphorus in the solid phase. The resin would remove phosphate from the solution in exchange for the anions initially present on the resin, e.g. Cl^-, $SO_4^=$, or $CO_3^=$.

In 1952 Moller and Mogensen (40) suggested the use of Na-zeolite as ionic exchange substance for determining available phosphorus in soil. The Na-zeolite used is insoluble and neutral or slightly alkaline in aqueous suspension and the process results in minimum interference with the colloid-chemical condition in the soil. They proceeded with their analysis by shaking 10 grams of air dried soil in 250 ml distilled water with 5, 10, or 20 grams of Na-zeolite (Na-Z) for various times. Finally, they determined the phosphate concentration colorimetrically. Taking $Ca_3(PO_4)_2$ as an example of one of the soil phosphorus fractions present in the soil, the overall reaction may be represented as follows:

$$6NaZ + Ca_3(PO_4)_2 \rightarrow 3CaZ_2 + 2Na_3PO_4$$

Moller and Mogensen concluded that 1:1 ratio (soil:Na-Z) and shaking for six hours gave the best results.

Amer, Bouldin, Black and Duke (1) used Dowex-2, the Cl^- form of the strong base anion exchange resin. They shook one gram soil (100 mesh) with one gram resin (32 mesh) with 100 ml of water. The suspension was shaken continuously on a wrist action shaker and, after the adsorption period, the resin was separated from the soil by washing the suspension through 82 mesh bolting cloth mounted on a Buchner funnel. Phosphorus adsorbed by the resin was exchanged by digesting the resin on a steamplate with 25 ml of 10% solution of NaCl for 45 minutes, followed by leaching with additional portions of NaCl solution until 100 ml of filtrate was collected. From this experiment Amer et al concluded the following:

1) 1:1 ratio between resin and soil is the best ratio for maximum rate of phosphorus removal.

2) The rate of phosphorus adsorption by resin agitated in solution is proportional to the P concentration in solution, and is independent of the rate of diffusion of adsorbed P in the resin.

3) The rate of phosphorus adsorption by the resin is controlled by the rate of phosphorus released from the soil.

4) The quantities of phosphorus adsorbed from the soil by the resin after varying intervals of time were less than those equilibrated with P^{32} during the same time interval.

Nevertheless, Amer et al, found very close agreement ($r = 0.95$) between P adsorbed by the resin and phosphorus availability as measured by the isotopic dilution method of Fried and Dean (26).

Moser et al (42) compared the performance of the exchange resin method of Amer with that of Bray and Kurtz (0.1N, HCl, 0.03N NH_4F), Olsen's method (0.5M, $NaHCO_3$), and the phosphate potential method of Schofield, Aslyng using sorghum's growth on cultures of 22 soils in the greenhouse. Moser et al based their comparisons on the precision of predicting the yield of phosphorus in which they arranged the results in order of decreasing precision as follows:

1) Anion-exchange resin method of Amer and coworkers
2) 0.5M $NaHCO_3$ method of Olsen
3) Phosphate potential method of Schofield and Aslyng
4) 0.1N HCl, 0.3N NH_4F method of Bray and Kurtz

Van Diest, White, and Black (58) used the Bray and Kurtz method (0.03N NH_4F, 0.025 NHCl) and the anion-exchange resin method of Amer and coworkers as the basis for predictingthe yields of phosphorus in plants grown on the soils in the greenhouse. The resin method gave more precise predictions of P yield than the 0.03N NH_4F, 0.025N HCl method of Bray and Kurtz, but the regression coefficient was smaller for alkaline soils than for acid soils. This difference may have been due to the effect of pH on the relative amounts of $H_2PO_4^-$ and $HPO_4^=$ present.

Lathwell, Sanchez, Risk, and Peech (32) used the strongly basic anion-exchange resin Amberlite to investigate the amounts of available phosphorus in 21 New York surface soils, and subsequently compared this method with the sodium bicarbonate method. Lathwell et al found that the amounts of phosphorus extracted by the resin gave the highest degree of correlation with response measured in terms of yield and phosphorus uptake for all methods they used. These workers also found a very high correlation between the Fried and Dean 'A' value and the results of their resin method.

Sidorina (52) used the weak base anion exchange resin EDE-10P to determine the available phosphate in some Russian soils. Sidorina found that the exchange was very slow when the ratio between soil to resin was 10:2, however, by changing the ratio to 1:1 a rapid exchange was noted. Sidorina concluded that plants make use of the resin-phosphate just as readily as water soluble phosphate.

Williams (60) used Dowex-2 (X4) resin to give an indication of the residual availability of previous applications of phosphorus in the following forms: water soluble phosphate (superphosphate), relatively insoluble form of phosphate (ground mineral phosphate, G.M.P.), di-calcium phosphate, and basic slag. He compared the availability with mean yields of potatoes over a period of six years. Williams found that there was a fairly good linear relationship between the yield of potatoes and resin phosphorus values.

Duplessis and Burger (20) compared the performance of eight chemical extraction procedures with phosphorus experimental data from 34 top soils of the Orange Free State Region (South Africa). The soils varied in clay content from four to five percent and in pH values from 5.2 to 8.5. The eight chemical methods which they used are:

1) one percent citric acid
2) 0.5N sodium bicarbonate at pH 8.5
3) 0.1N HCl + 0.03N NH_4F (Bray and Kurtz)
4) 2.5 percent acetic acid
5) 0.1M calcium lactate
6) 0.1N sodium hydroxide
7) 0.002N sulfuric acid
8) anion-exchange resin (the chloride form of the strong base

anionic exchange resin, IRA-400)

Data of Duplessis and Burger revealed that all the methods, except NaOH, were almost equally effective for estimation of total phosphorus uptake when all soil classes were considered. However, if only heavier soils were considered, the $NaHCO_3$ and resin methods were significantly better-correlated with total phosphorus uptake than results of the other methods. Duplessis and Burger also found that the $NaHCO_3$ and anion exchange resin methods gave the highest correlation with both percentage yield and total phosphorus uptake.

Duplessis and Burger (21) conducted another experiment to determine which phosphorus fraction in the soil was mainly utilized by the plants and to obtain an extractant for available phosphate which will dissolve all these fractions. Many different extractants were used for these investigations. Included were one percent citric acid 0.5M $NaHCO_3$ (Olsen method), 0.1M calcium lactate, 0.5N NH_4F plus 0.1N HCl (Bray and Kurtz), 2.5 percent acetic acid (Williams and Stewart), 0.002N H_2SO_4 (Troug), 0.1N NaOH (Saunders), and the anion-exchange resin method (Amer et al). All these methods correlated with total phosphorus uptake by plants. The findings of these investigations revealed that the Al-P and Fe-P compounds may be more available to plants than Ca-P compounds in alkaline soils while in acid soils Ca-P may be highly available. Therefore, it can be assumed that an extractant which dissolves Al-P and Fe-P compounds in alkaline soils and Ca-P compounds in acid soils would be the most suitable for the determination of available phosphorus for both soils. Duplessis and Burger concluded that the anion exchange resin extraction method for the determination of available phosphorus gave the best correlation with plant uptake. The method may be applicable in acid as well as alkaline soils.

Each of the techniques mentioned has its own advantages and limitations, which may be briefly summarized as follows:

1) Chemical extraction techniques: Chamical extractiontechniques are fast and rather simple to perform but have the following limitations:

a) The soil is extracted with organic or an inorganic acid which affect and alter the normal soil-chemical conditions.

b) Solubility is really induced by using these chemicals which do not normally exist under natural conditions.

c) Different results can be obtained from the same soil by using different reagents.

d) Most of the extraction techniques do not correlate well with plant response.

2) Bioassay technique: Although this method may give better correlation with plant response, it has the following limitations:

a) It is time consuming, allowing for growth of the organism.

b) It requires many replications.

c) In case of the microorganism adjustments need to be made such as pH and organic matter to permit rapid growth.

d) When two different sources of nutrient are used (soil and fertilizer) organism use is frequently influenced more by relative availability than total availability.

3) Radio-active method: This method has many advantages, such as making the measurements without the addition of the acids, bases, complexing or precipitating reagents which are commonly employed in chemical extraction procedures that alter the measurement of availability.

Its main limitations are:

a) Calculations of the quantity of soil phosphorus with which the added phosphorus has equilibrated is strictly valid only at equilibrium. Since the process continues indefinitely the required condition of equilibrium does not prevail.

b) The extent of kinetic exchange of phosphate for phosphate may not be entirely satisfactory as an estimate of soil phosphorus availability because of the tendency of limitation to "surface" exchange.

c) Phosphorus released may well be replaced by $SiO_3^{=}$ or OH^-.

4) Anion exchange resin: Although this method is more laborious and time consuming than the chemical method, on the average it gives better correlation with phosphorus uptake than most chemical extractant tests. However, the resin method is still new, and additional work is needed to test its use under different conditions.

CHAPTER III

MATERIALS AND METHODS

Thirty-six soil samples representing central and western Oklahoma wheatland soils were used for this investigation. All samples were taken from the top six inches of the profile. All samples tested were air dried and passed through a 2 mm. sieve.

Phosphorus Analysis

Anion Exchange Resin Method

Dowex 1 (X-8), strongly basic anion exchange resin containing eight percent of divinyl benzene in Cl-form was used in this study. Three grams of 50-100 mesh dry resin, three grams of soil and 100 ml of deionized water were shaken continuously on a wrist-action shaker for two hours. After the adsorption period, the resin was separated from the soil by washing the soil suspension through a 100 mesh sieve. After the resin was separated from the soil it was transferred from the sieve into a 250 ml beaker. Phosphorus adsorbed by the resin was removed by digesting the resin with 50 ml of 12% Na_2SO_4 solution on a steam plate for 45 minutes, followed by leaching with an additional 12% Na_2SO_4 solution until 100 ml of filtrate was obtained. Phosphorus extracted was determined by the Watanabe and Olsen ascorbic acid method (59).

Bray #1 Method

One gram of oven dry soil was shaken with 20 ml of Bray solution (7) consisting of 0.025N HCl in 0.03N NH_4F for five minutes. The soil suspension was filtered with a Whatman #2 filter paper and the resultant solution collected in a test tube. Color was developed using the ascorbic acid method of Watanabe and Olsen (59).

pH Determination

Soil pH values were determined using 1:1 soil:1N KCl and soil-distilled water pastes with Corning pH Meter, Model 10, at 25°C.

Greenhouse Study

Number 10 polyethylene lined cans were used in the greenhouse as experimental pots. Two and one-half kilograms of soil (oven dry) were placed in each can. On September 28, 1969 twenty seeds of Piper sudangrass (sorghum sudanese) were planted in each can. One hundred seventy mg nitrogen as NH_4NO_3 was applied to each can as starter fertilizer, and all cans (108 cans) were arranged in a completely randomized design in the greenhouse. Each soil was kept moist throughout the experiment. Moisture additions were based on the predetermined approximate field capacity.

Ten days after planting, the plants were thinned to ten plants per pot. A further thinning was made 20 days after planting, leaving seven plants per can. On October 20, three hundred forty mg of nitrogen were applied to each can as NH_4NO_3 to make a total of 510 mg of nitrogen added per pot.

The plants were harvested on November 8, 1968, after a 42 day growing period. The plant samples were oven dried at 75-80°C in a forced air oven for four days and the oven-dry weight recorded.

Total Phosphorus Uptake Determination

Total phosphorus uptake by the plants was determined colorimetrically using the vanadomolybdophosphoric method described by Jackson (30) after wet ashing by the method of Chapman (13).

CHAPTER IV

RESULTS AND DISCUSSIONS

Anion Exchange Resin Method

Soil-Resin Ratio

A preliminary experiment was designed to determine the ratio of soil to resin required to produce optimum phosphorus removal from the soil. Three grams of soil in 100 ml of deionized water were shaken with two, three, four, five, and six grams of resin for two hour periods. Resin was separated from the soil and analyzed for phosphorus.

Results of this investigation (Table I) show that by decreasing the soil:resin ratio from 3:2 to 3:3 a significant increase in phosphorus adsorption was obtained. However, a further decrease in soil:resin ratio resulted in very slight but not significant improvement in phosphorus removal. Thus, it became apparent that a 1:1 ratio of soil to resin supplied enough resin for efficient and reproducible removal of available phosphorus. Hence, the quantity of phosphorus adsorbed by the resin and the rate of adsorption was apparently dependent upon the release of phosphorus from the soil in question.

Adsorption Period

Another preliminary study was conducted to determine the minimum time required to remove most of the available phosphorus from the soil.

Results in Table II show that by increasing the time of adsorption beyond two hours, only a slight increase in the phosphorus adsorption occurred. The increase does not justify the additional time involved. Also, since the resin rapidly adsorbs phosphorus present in solution (42) most of the phosphorus adsorbed during any time interval is released from the solid phase during that same time interval. Thus, it can be assumed that phosphorus adsorbed by the resin during a two hour interval can be used to represent the phosphorus available to plants.

TABLE I

PHOSPHORUS ADSORBED BY RESIN FROM SOILS UNDER DIFFERENT SOIL:RESIN RATIOS (2 HRS SHAKING)

Soil:Resin Ratio (in grams)	Microgram of Phosphorus Adsorbed
3:2	35
3:3	41
3:4	41
3:5	41.5
3:6	42.0

TABLE II

ADSORPTION OF PHOSPHORUS BY RESIN FROM SOIL AT DIFFERENT ADSORPTION PERIODS

Adsorption Period (hr)	Micrograms of Phosphorus
2	41
3	44
4	45
6	46.5

Grouping of Soils

In any soil there may be one or more forms of inorganic phosphorus which may be regarded as available phosphorus. It has been found that Al-P and Fe-P are the available forms in alkaline soils; Al-P and Ca-P for acid soils, and all of these forms are supposed to be available in neutral soils (21,33,51). For this reason the samples were separated into acid soils (pH 4-6), slightly acid soils (pH 6-7) and slightly alkaline soils (pH 7-8). Correlation studies were carried out separately on each group in an attempt to investigate the behavior of the two methods under different situations.

Correlation of Anion Exchange Resin-P with P-Uptake

The data in Tables III, IV and V indicate the types of the thirty-six soils, their available phosphorus content according to anion

TABLE III

AVAILABLE SOIL PHOSPHORUS ADSORBED BY RESIN, PHOSPHORUS UPTAKE AND AVERAGE DRY WEIGHT PER POT FOR SLIGHTLY ACID SOILS (pH 6-7)

Soil No.	Soil Type	pH Water Paste	pH KCl	p-ppm Adsorbed by Resin	P Uptake Per Pot (mg)	Average Dry Wt. Per Pot (g)
1	Kirkland silt loam	6.70	6.15	21	7.03	7.0166
3	Oswego silt loam	6.6	6.05	18.7	7.21	6.27
7	Carwile loam	6.8	6.15	18.67	8.11	6.76
12	Oswego silt loam	6.15	5.43	7.20	3.57	3.720
13	Kay silt loam	6.10	5.65	47.0	12.23	6.120
18	Reinach silt loam	6.4	5.75	11.30	4.69	5.21
27	St. Paul Clay loam	6.7	6.1	27.7	10.79	7.71

TABLE IV

AVAILABLE SOIL PHOSPHORUS ADSORBED BY RESIN, PHOSPHORUS UPTAKE, AND AVERAGE DRY WEIGHT PER POT FOR ACID SOILS (pH 4-6)

Soil No.	Soil Type	pH Water Paste	pH KCl	p-ppm Adsorbed by Resin	P Uptake Per Pot (mg)	Average Dry Wt. Per Pot (g)
2	Renfrow silt loam	5.28	6.15	7.0	2.59	2.73
4	Kirkland silt loam	4.75	4.38	16.0	2.02	1.39
5	Tabler silt loam	4.78	4.18	9.83	3.26	3.84
6	Port silty clay loam	5.60	5.0	23.00	4.69	4.58
10	Oswego silt loam	5.10	4.53	18.3	4.36	6.01
11	Oswego silt loam	5.30	4.80	13.7	3.76	5.57
17	Reinach very fine sandy loam	5.28	4.50	13.0	3.44	4.72
19	Nash very fine sandy loam	5.55	4.85	11.0	4.11	5.31
20	Pond Creek silt loam	5.0	4.35	22.7	3.99	4.77
21	Pond Creek silt loam	5.45	4.65	15.0	3.95	5.85
22	Pond Creek silt loam	4.90	4.15	19.7	3.05	5.09
23	Pond Creek silt loam	5.15	4.62	11.7	2.33	2.91
30	Dalhart sandy loam	5.95	5.68	26.7	8.22	5.22

TABLE V

AVAILABLE SOIL PHOSPHORUS ADSORBED BY RESIN, PHOSPHORUS UPTAKE AND AVERAGE DRY WEIGHT PER POT FOR SLIGHTLY ALKALINE SOILS (pH 7-8)

Soil No.	Soil Type	pH Water Paste	pH KCl	p-ppm Adsorbed by Resin	P Up-take Per Pot (mg)	Average Dry Wt. Per Pot (g)
8	Kingfisher silt loam	7.8	7.10	9.83	2.67	1.35
9	Grant very fine sandy loam	7.20	6.65	20.0	7.18	6.68
14	Vernon clay loam	7.70	7.10	11.30	6.63	4.21
15	Renfrow clay loam	7.55	6.85	11.0	9.48	6.65
16	Derby fine sandy loam	7.45	6.95	25.0	6.34	4.01
24	Spur heavy loam	7.65	7.30	18.5	1.92	.99
25	Richfield silt loam	7.30	7.20	26.30	10.25	6.53
26	Carwile heavy silt loam	7.05	6.50	17.30	9.48	8.07
28	Woodward loam	7.80	7.30	17.7	5.45	4.45
29	Richfield silt loam	7.55	6.85	10.3	7.8	6.0
31	Cary silt loam	7.28	6.85	25.3	8.44	6.37
32	Richfield heavy silt loam	7.40	7.03	21.7	8.94	7.36
33	Richfield loam	7.55	7.05	38.0	7.91	5.95
34	Ulysses sandy clay loam	7.85	7.18	19.8	4.33	3.36
35	Boise sandy loam	7.95	7.5	12.3	.69	.69
36	Woodward silty clay loam	7.4	6.90	25.0	10.65	7.35

exchange resin method, average dry weight of plants and total phosphorus uptake from soils which received no phosphate fertilizer.

The correlation data in Table VI and Figures 1 through 4 reveal a significant correlation at 1% level ($r = 0.9375$) between phosphorus taken up by plants and phosphorus adsorbed by anion exchange resin from slightly acid soils. Good correlation (significant at 5% level) was also obtained between anion exchange -P and P-uptake for acid soils ($r = 0.6817$), however, it was considerably lower than that of slightly acid soils. A deterioration in the correlation was observed for slightly alkaline soils ($r = 0.3801$). Despite the drop of the correlation coefficient from 0.9375 to 0.3801 on acid to slightly alkaline soils when the correlation coefficient is calculated over all soils a significant correlation at the 1% level was obtained.

The variation in "r" values at different pH ranges can probably be attributed to the effect of pH on the relative amounts of $H_2PO_4^-$ and $HPO_4^=$ present. While resin adsorbs all phosphorus species unselectively and with no discrimination, in case of plants we are facing a much more complex absorption system. There may be different binding sites or carriers involved in the absorption of $H_2PO_4^-$ and $HPO_4^=$ (27). The monovalent species ($H_2PO_4^-$) is absorbed through one site and the divalent species ($HPO_4^=$) through another. The presence of two or more sites for phosphorus adsorption suggests that the divalent and the monovalent species will not be absorbed equally by plants. This has been confirmed by McGeorge (36). McGeorge studied the pH value of both the cell sap of plants and the feeding zone of the root tip. The following conclusions were made:

TABLE VI

CORRELATION COEFFICIENT (r), REGRESSION COEFFICIENT (b) AND REGRESSION EQUATIONS BETWEEN PHOSPHORUS EXTRACTED BY ANION EXCHANGE RESIN METHOD AND P-UPTAKE BY PLANTS

Soil Group	pH	d.f. n-2	r	b	Regression Equations
Slightly acid soils	6-7	5	.9375**	.2221	$\hat{y} = 2.8522 + .2221x$
Acid soils	4-6	11	.6817*	.1809	$\hat{y} = .9393 + .1809x$
Slightly alkaline soils	7-8	14	.3801	.1512	$\hat{y} = 3.8368 + .1512x$
All soils		34	.6268**	.2238	$\hat{y} = 1.7207 + .2238x$

*Significant at 5% level.

**Significant at 1% level.

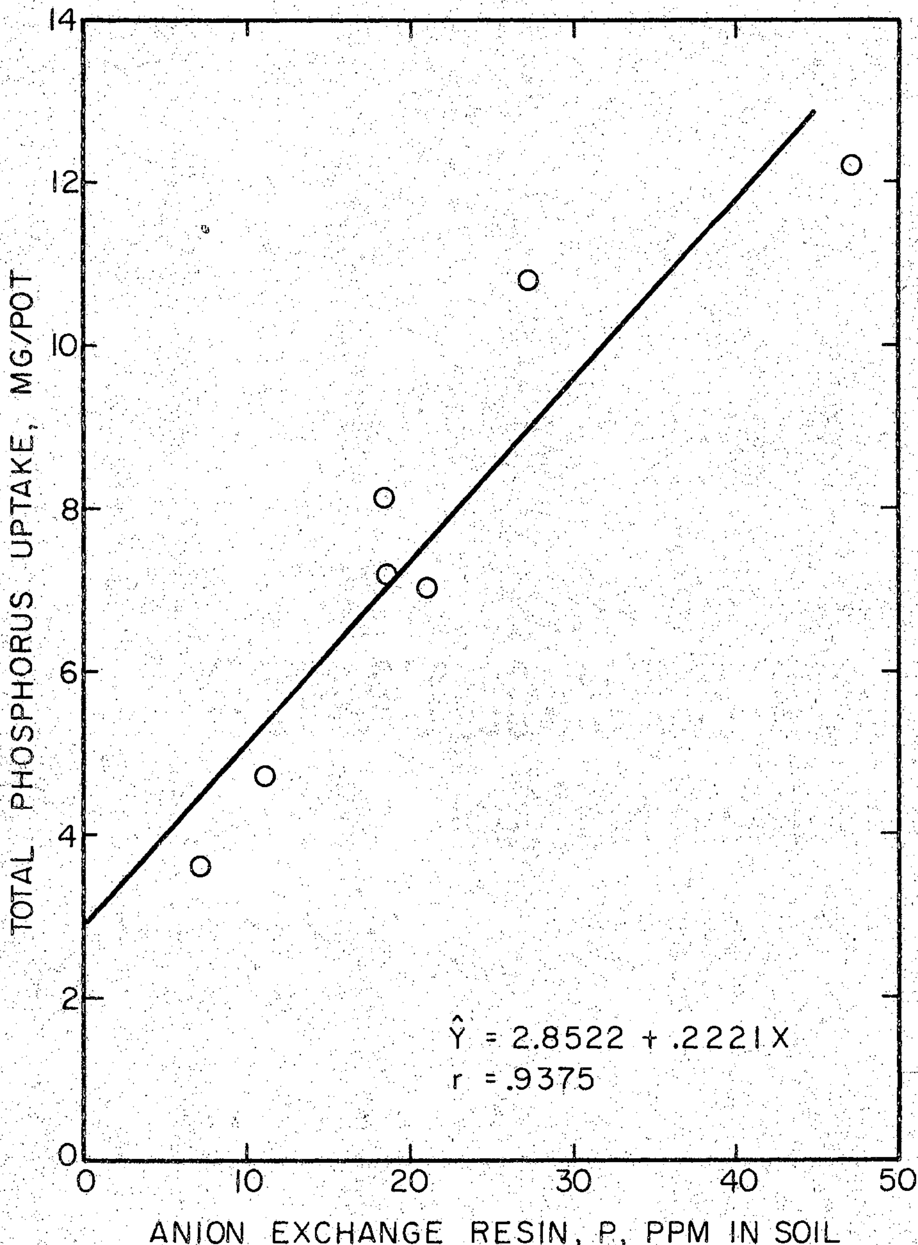

Figure 1. Relation Between Anion Exchange Resin-P and Total Phosphorus Uptake in Slightly Acid Soils

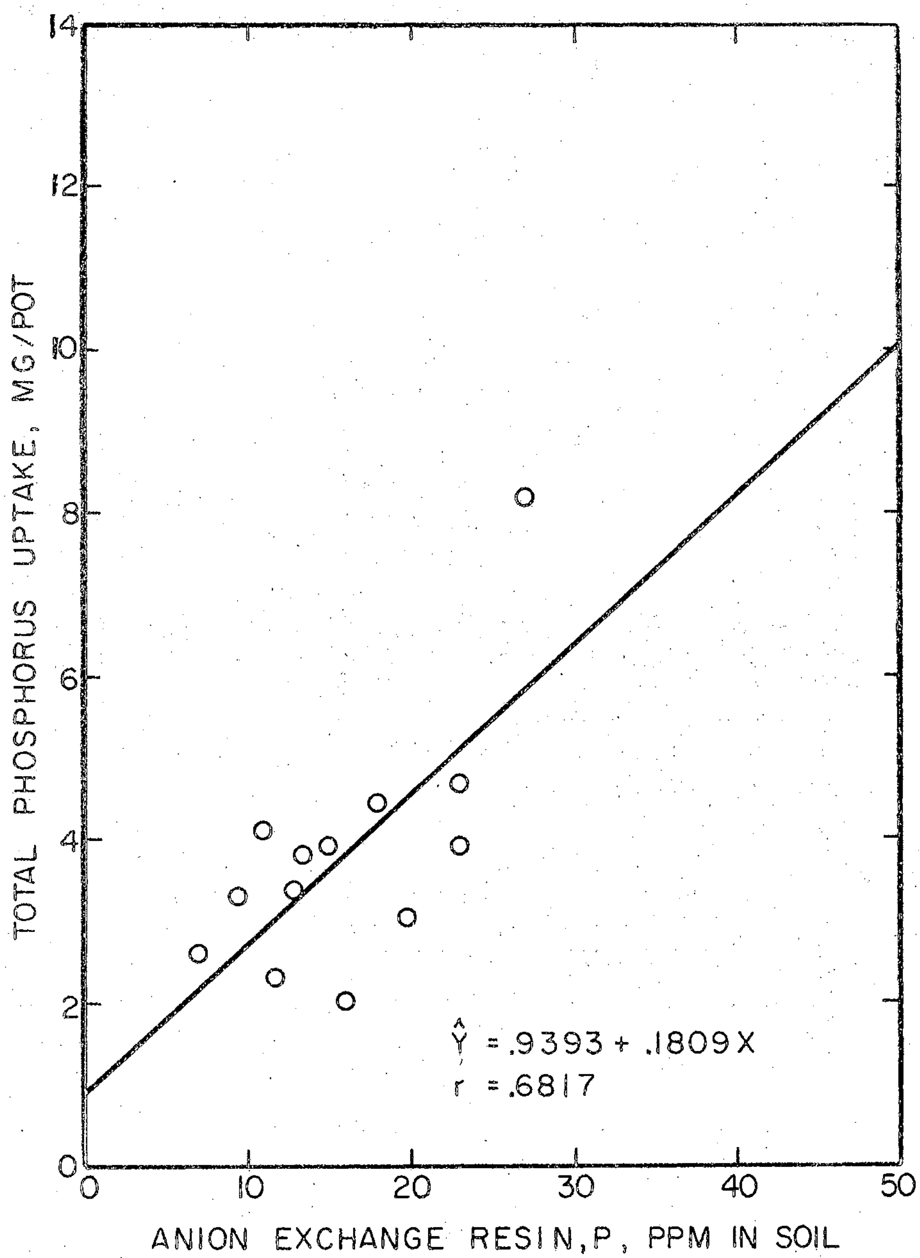

Figure 2. Relation Between Anion Exchange Resin-P and Total Phosphorus Uptake in Acid Soils

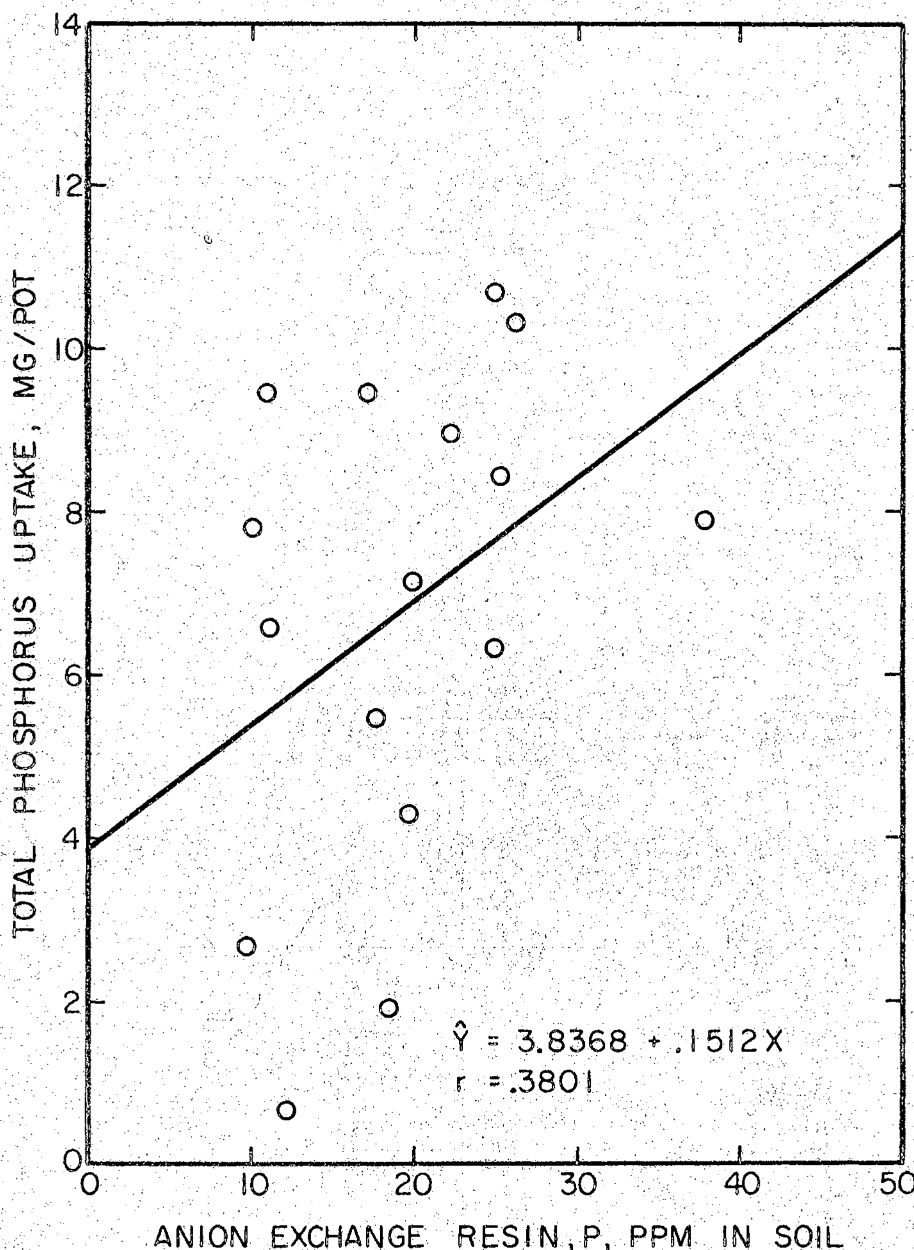

Figure 3. Relation Between Anion Exchange Resin-P and Total Phosphorus Uptake in Slightly Alkaline Soils

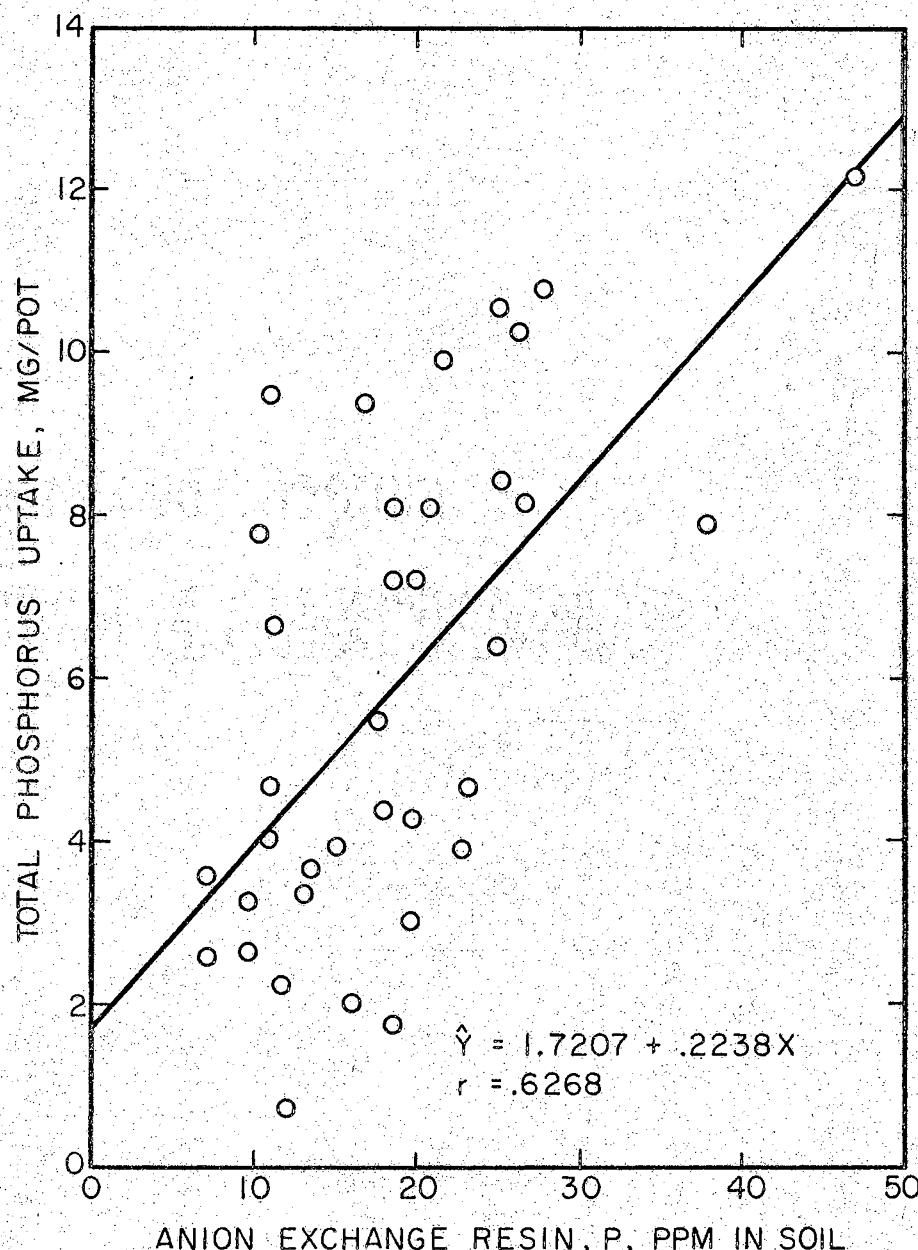

Figure 4. Relation Between Anion Exchange Resin-P and Total Phosphorus Uptake in All Soils

1) In acid soils available phosphate is present mainly as the $H_2PO_4^-$ ion while in alkaline soils $HPO_4^=$ is the important ion.

2) The monovalent species ($H_2PO_4^-$) is the dominant ion in plant sap, thus plants may prefer the $H_2PO_4^-$ ion for nutrition purposes.

3) Plants assimilate phosphate most readily at reactions close to neutrality (preferably slightly acid), less readily under acid conditions and least readily under alkaline conditions.

The findings of this study and the concludions of McGeorge may suggest that the use of anion exchange resin for practical application may require separate calibration for soils differing in pH values. As an alternative procedure correlations may be made on the basis of relative amounts of $H_2PO_4^-$ and $HPO_4^=$ present rather than total phosphorus (3). This has been suggested by many workers. Moser et al (42) found that the precision of prediction of the available soil phosphorus was improved by using the $H_2PO_4^-$ concentration instead of the total inorganic phosphorus. Van Diest et al (58) reported that an improvement in regression fit was obtained by subdividing the phosphorus into two components, $H_2PO_4^-$ and $HPO_4^=$, but not by including pH as an independent variable. Thus, the anion exchange resin method might be modified and be applicable over a much wider soil pH range.

Correlation of Anion Exchange Resin-P with Average Dry Weight

Table VII and Figures 5 through 8 reveal that the average dry weight has a low degree of correlation with the amount of available phosphorus determined by anion exchange resin method over all pH ranges. The r values are not significant (for acid soils, r = 3.553, slightly acid soils, r = .4957, and slightly alkaline soils, r = .3872).

TABLE VII

CORRELATION COEFFICIENT (r), REGRESSION COEFFICIENT (b) AND REGRESSION EQUATIONS BETWEEN PHOSPHORUS EXTRACTED BY ANION EXCHANGE RESIN METHOD AND AVERAGE DRY WEIGHT

Soil Group	pH	d.f. n-2	r	b	Regression Equations
Slightly acid soils	6-7	5	.4957	.0501	$\hat{y} = 5.031 + .0501x$
Acid soils	4-6	11	.3553	.0839	$\hat{y} = 3.1208 + .0839x$
Slightly alkaline soils	7-8	14	.3572	.1118	$\hat{y} = 2.8398 + .1118x$
All soils		34	.3965*	.0915	$\hat{y} = 3.3236 + .0915x$

*Significant at 5% level.

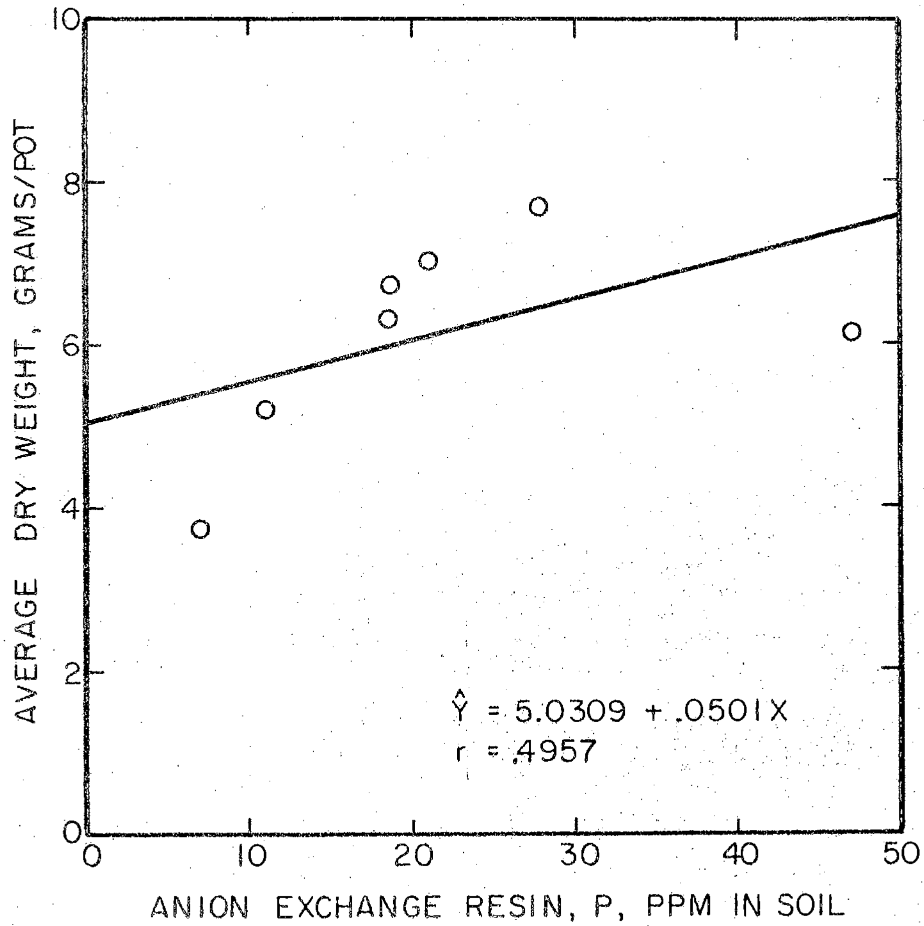

Figure 5. Relation Between Anion Exchange Resin-P and Average Dry Weight in Slightly Acid Soils

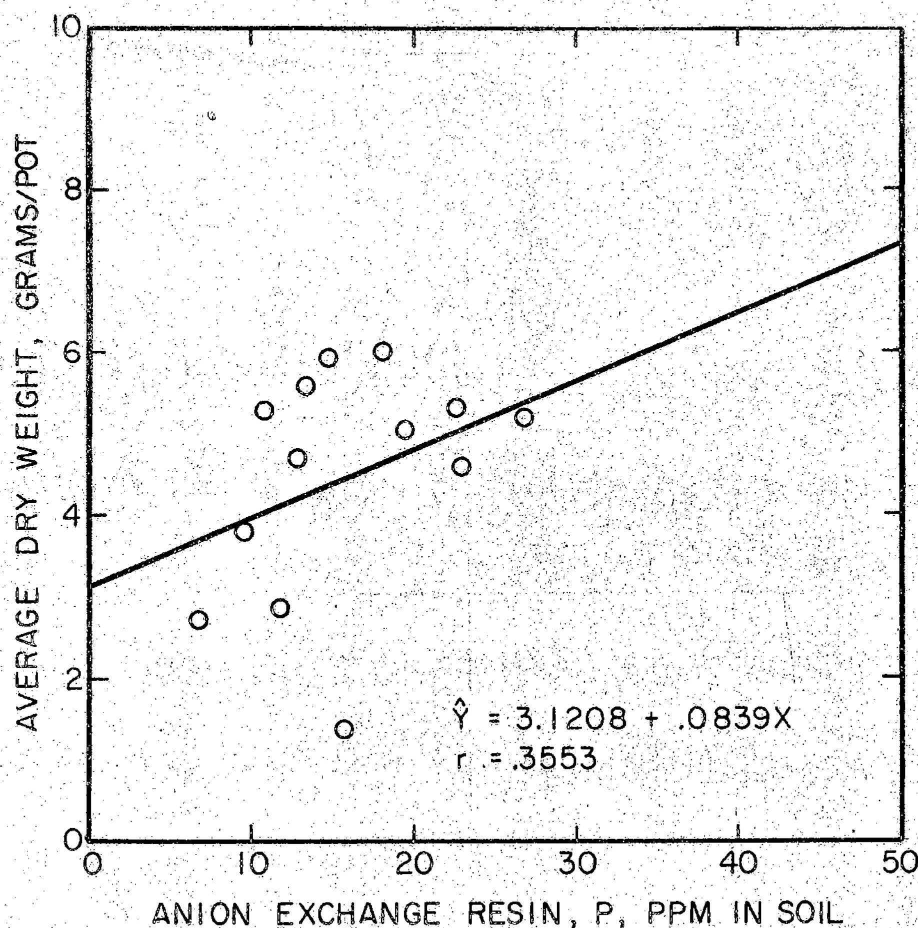

Figure 6. Relation Between Anion Exchange Resin-P and Average Dry Weight in Acid Soils

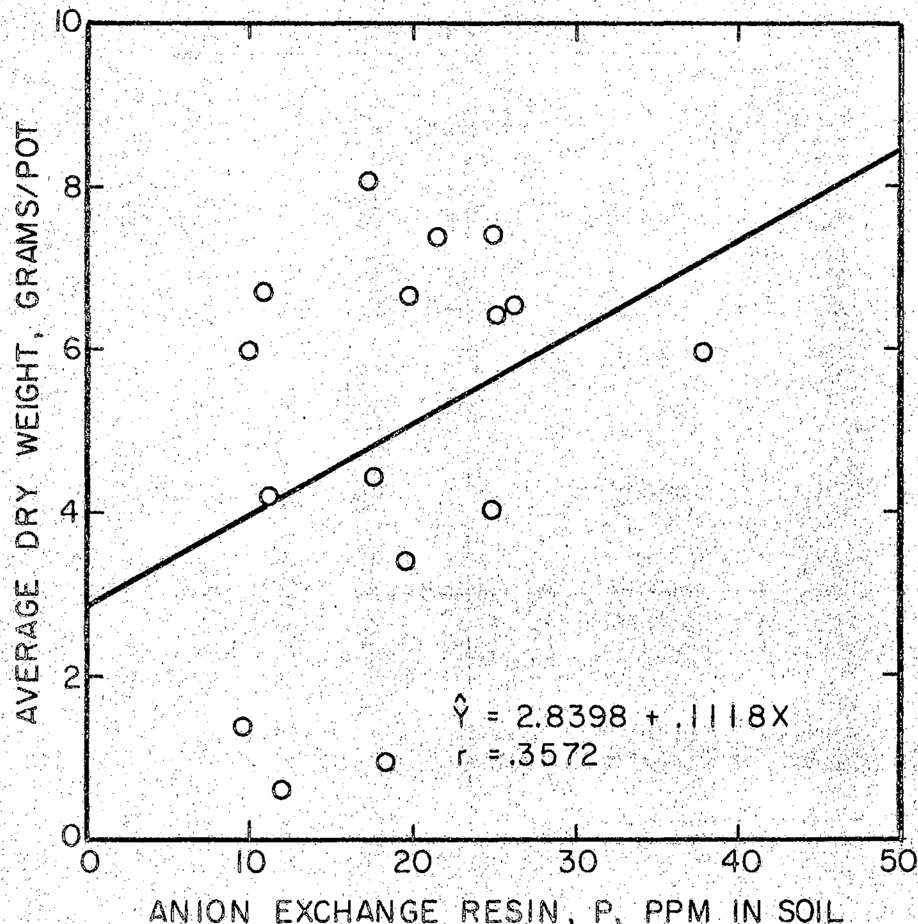

Figure 7. Relation Between Anion Exchange Resin-P and Average Dry Weight in Slightly Alkaline Soils

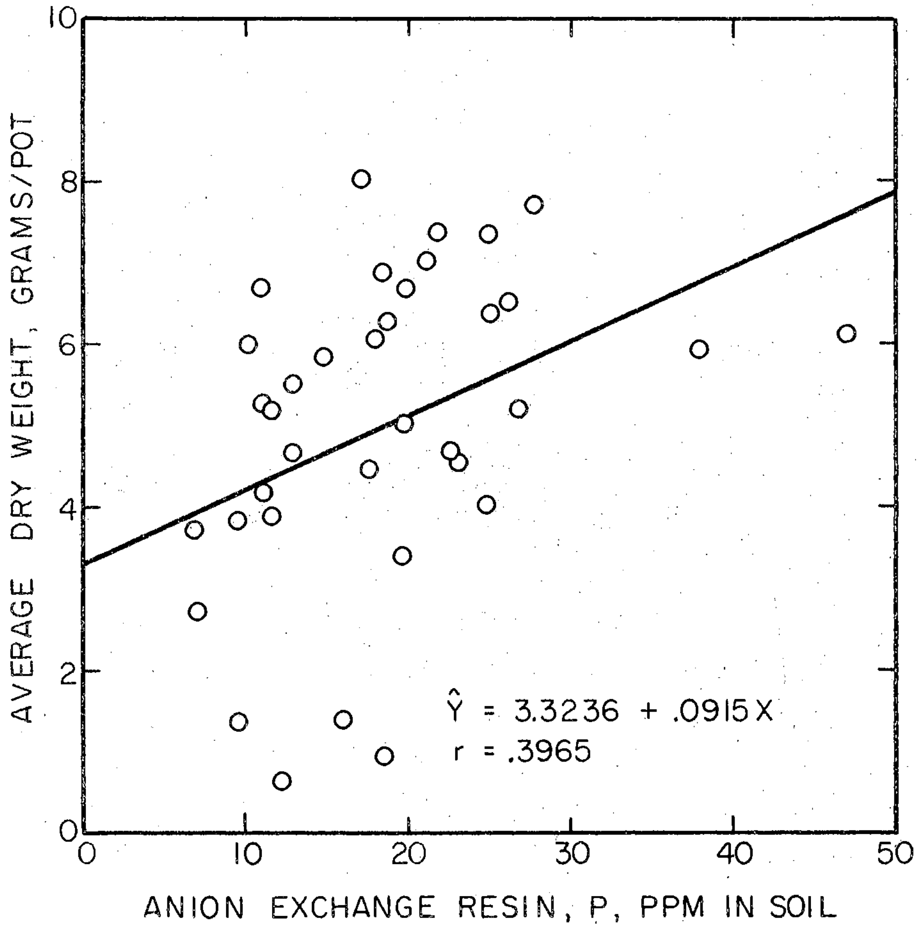

Figure 8. Relation Between Anion Exchange Resin-P and Average Dry Weight in All Soils

However, when all soils were pooled together "r" was significant at the 5% level (see Table VI and Figure 8). These poor correlations may be attributed to the fact that the yield of the plants is likely to be affected by many variables in addition to phosphorus. Thus, as in any system of several related variables, measurements of one variable are inadequate to describe the behavior of the system without control or correction for other variables. The significance at the 1% level in the correlation when all soils were pooled is due to the increase in the degrees of freedom. It is questioned that the "significance" under these circumstances has any real meaning in regard to phosphate measurement or management. Based on these findings it was felt that phosphorus uptake by plants should provide the most reliable indication of the phosphorus supplying power of the soils.

Correlation of Phosphorus Uptake by Plants with Average Dry Weight

It can be seen from Table VIII and Figures 9 through 12 that total phosphorus uptake under slightly alkaline conditions gave the best correlation with average dry weight (r = .9586). Good correlations were also obtained for acid soils and for all soils when pH was disregarded. The failure of the correlation for slightly acid soils to be significant was unexpected. Although the value of "r" was .7056, which is much higher than that of acid soils (r = .5673), it is still not significant, undoubtedly a result of insufficient degrees of freedom.

TABLE VIII

CORRELATION COEFFICIENT (r), REGRESSION COEFFICIENT (b) AND REGRESSION EQUATIONS BETWEEN P-UPTAKE AND AVERAGE DRY WEIGHT

Soil Group	pH	d.f. n-2	r	b	Regression Equations
Slightly acid soils	6-7	5	.7056	.3007	$\hat{y}$ = 3.8119 + .3007x
Acid soils	4-6	11	.5673*	.5050	$\hat{y}$ = 2.5274 + .5050x
Slightly alkaline soils	7-8	14	.9586**	.7538	$\hat{y}$ = -.0944 + .7538x
All soils		34	.8097**	.5231	$\hat{y}$ = 1.9487 + .5231x

*Significant at 5% level.
**Significant at 1% level.

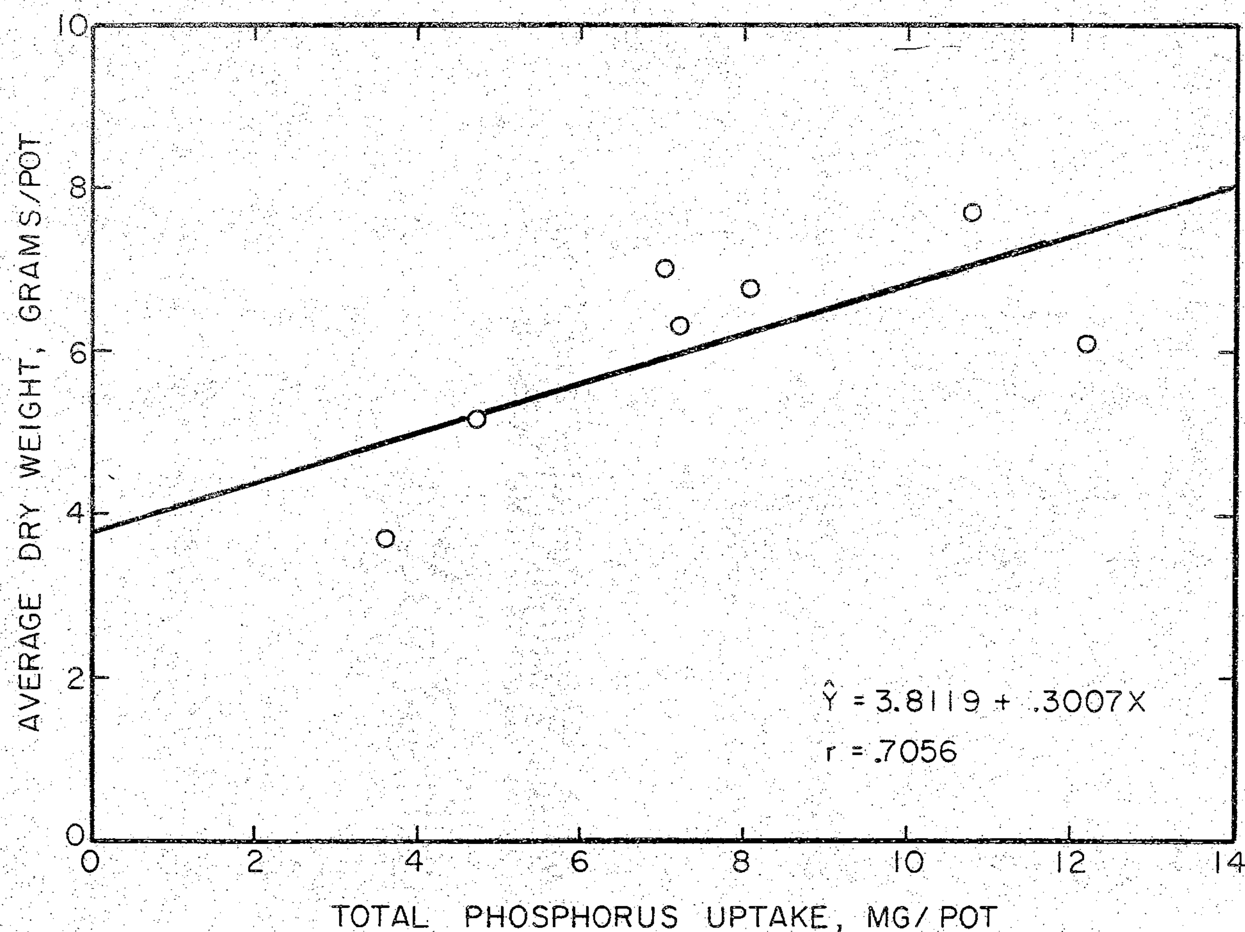

Figure 9. Relation Between Total Phosphorus Uptake and Average Dry Weight in Slightly Acid Soils

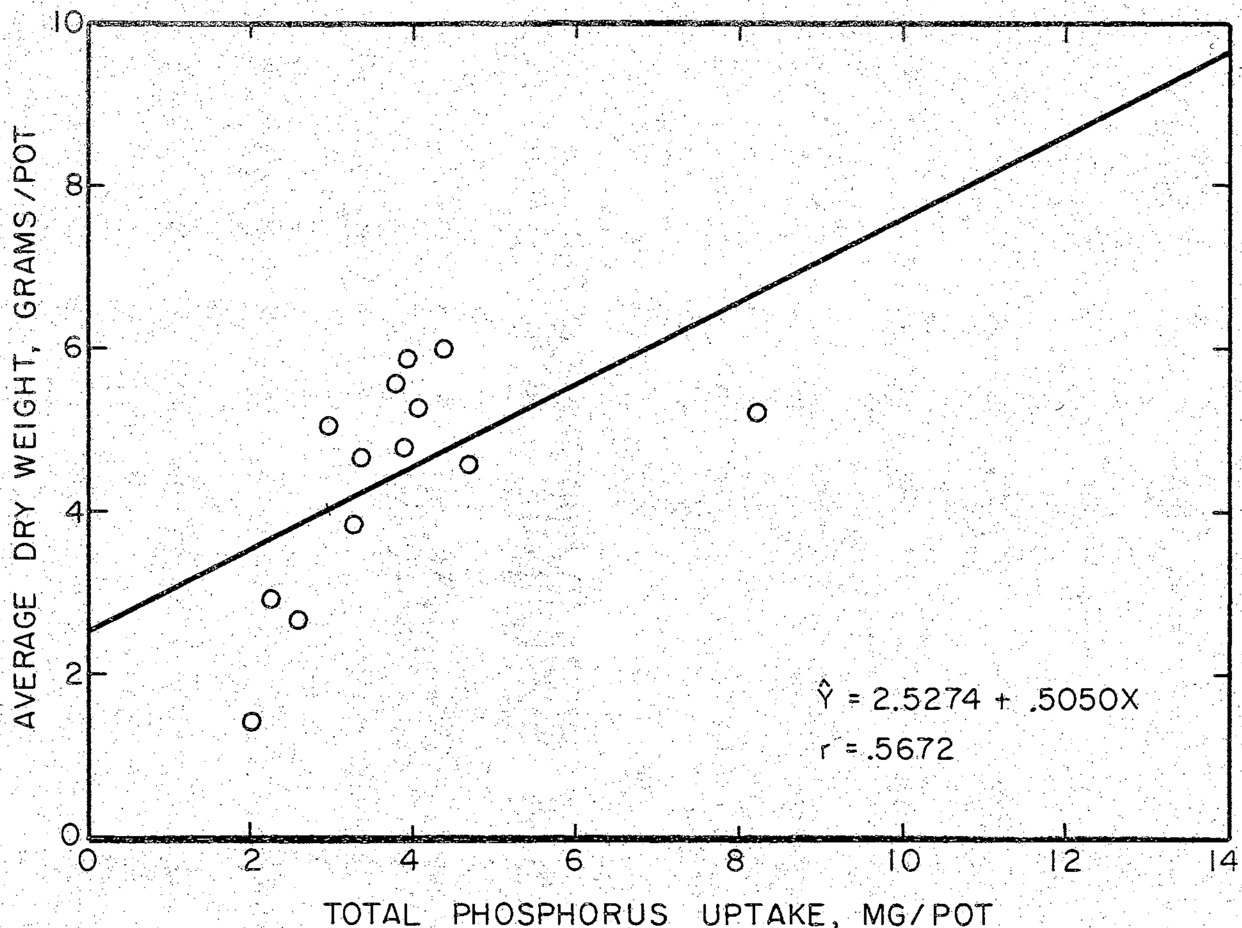

Figure 10. Relation Between Total Phosphorus Uptake and Average Dry Weight in Acid Soils

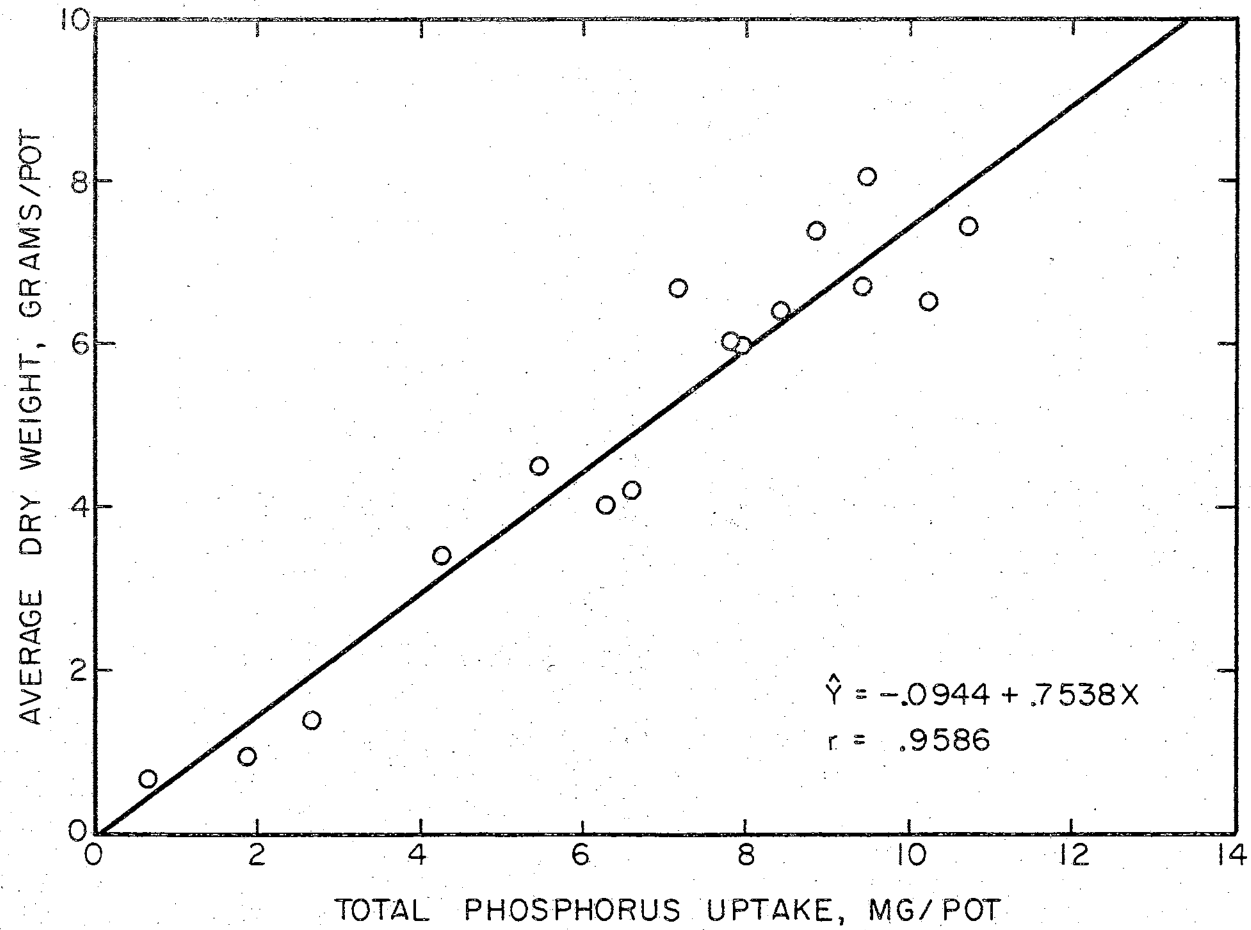

Figure 11. Relation Between Total Phosphorus Uptake and Average Dry Weight in Slightly Alkaline Soils

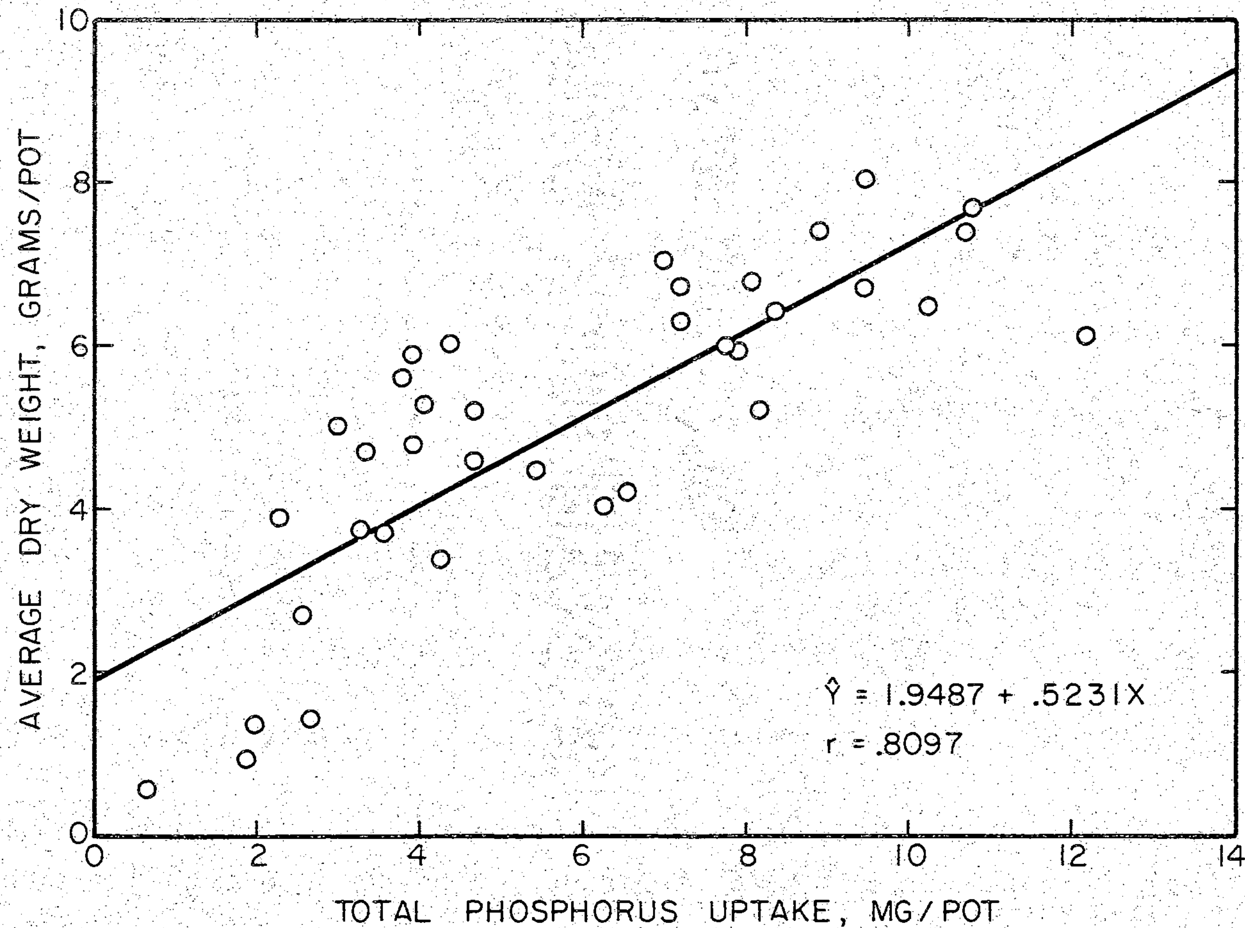

Figure 12. Relation Between Total Phosphorus Uptake and Average Dry Weight in All Soils

Bray Method

Available phosphorus was determined by the commonly used chemical extraction technique of Bray (7). This procedure employs the reagents 0.025N HCl and 0.03N NH_4F. The Bray procedure was used to establish a basis for evaluating the exchange resin method for determining phosphorus availability. Soil:extractant ratio of 1:20 was used. This ratio has been shown to be suitable for Oklahoma soils (44). Use of the 1:20 ratio will supply sufficient H^+ to neutralize the $CaCO_3$ expected in most Oklahoma soils. Also, five minutes of shaking was employed to ensure a short extraction period and to prevent the possible secondary precipitation reactions (45).

Correlation of Bray-P with Total Phosphorus Uptake by Plants

The data in Tables IX, X and XI show soil types, available phosphorus content of the soils according to Bray method, pH, average dry weight, and phosphorus uptake by plants.

Statistical analysis (Table XII and Figures 13 through 16) for this investigation demonstrates excellent correlation between Bray-P and total phosphorus uptake in slightly acid soils (r = .9094). Good correlation was also obtained with slightly alkaline soils, and when all soils were considered. Poor correlation was shown for acid soils. The low value of "r" for acid soils may be attributed to the forms of available phosphorus which can be found for this pH range and the chemical nature of the extracting solution. As was stated earlier, Al-P and Fe-P are the main available forms of phosphorus under alkaline conditions, Al-P and Ca-P are the main available forms for acid soils.

TABLE IX

AVAILABLE SOIL PHOSPHORUS EXTRACTED BY BRAY METHOD, PHOSPHORUS UPTAKE AND AVERAGE DRY WEIGHT PER POT FOR SLIGHTLY ACID SOILS

Soil No.	Soil Type	pH Water Paste	pH KCl	p-ppm Extracted	P Uptake Per Pot (mg)	Average Dry Wt. Per Pot (g)
1	Kirkland silt loam	6.7	6.15	35.4	7.03	7.02
3	Oswego silt loam	6.6	6.05	29.0	7.21	6.27
7	Carwile loam	6.8	6.15	27.6	8.11	6.76
12	Oswego silt loam	6.15	5.43	16.8	3.57	3.72
13	Kay silt loam	6.10	5.65	78.8	12.23	6.12
18	Reinach silt loam	6.4	5.75	26.4	4.69	5.21
27	St. Paul clay loam	6.7	6.1	52.4	10.79	7.71

TABLE X

AVAILABLE SOIL PHOSPHORUS EXTRACTED BY BRAY METHOD, PHOSPHORUS UPTAKE, AND AVERAGE DRY WEIGHT PER POT FOR ACID SOILS

Soil No.	Soil Type	pH Water Paste	pH KCl	p-ppm Extracted	P Uptake Per Pot (mg)	Average Dry Wt. Per Pot (g)
2	Renfrow silt loam	5.28	4.70	15.6	2.59	2.73
4	Kirkland silt loam	4.75	4.38	52.8	2.02	1.39
5	Tabler silt loam	4.78	4.18	25.6	3.26	3.84
6	Port silt clay loam	5.60	5.0	49.6	4.69	4.58
10	Oswego silt loam	5.10	4.52	35.2	4.36	6.01
11	Oswego silt loam	5.3	4.80	34.0	3.76	5.57
17	Reinach very fine sandy loam	5.28	4.50	33.8	3.44	4.72
19	Wash very fine sandy loam	5.55	4.85	28.4	4.11	5.31
20	Pond Creek silt loam	5.0	4.35	52.4	3.99	4.77
21	Pond Creek silt loam	5.45	4.65	41.4	3.95	5.85
22	Pond Creek silt loam	4.90	4.15	49.4	3.05	5.09
23	Pond Creek silt loam	5.15	4.62	33.8	2.33	2.91
30	Dalhart sandy loam	5.95	5.68	53.2	8.22	5.22

TABLE XI

AVAILABLE SOIL PHOSPHORUS EXTRACTED BY BRAY METHOD, PHOSPHORUS UPTAKE AND AVERAGE DRY WEIGHT PER POT FOR SLIGHTLY ALKALINE SOILS

Soil No.	Soil Type	pH Water Paste	pH KCl	p-ppm Extracted	P Up-take Per Pot (mg)	Average Dry Wt. Per Pot (g)
8	Kingfisher silt loam	7.80	7.10	12.8	2.69	1.35
9	Grant very fine sandy loam	7.20	6.65	34.0	7.18	6.68
14	Vernon clay loam	7.70	7.10	22.4	6.63	4.21
15	Renfrow clay loam	7.55	6.85	18.0	9.48	6.65
16	Derby fine sandy loam	7.45	6.95	38.4	6.34	4.01
24	Spur heavy loam	7.65	7.30	4.0	1.92	.99
25	Richfield silt loam	7.30	7.20	55.6	10.25	6.53
26	Carwile heavy silt loam	7.05	6.50	34.0	9.48	8.07
28	Woodward loam	7.80	7.30	29.4	5.45	4.45
29	Richfield silt loam	7.55	6.85	30.0	7.8	6.0
31	Cary silt loam	7.28	6.85	45.6	8.44	6.37
32	Richfield heavy silt loam	7.40	7.03	44.0	8.94	7.36
33	Richfield loam	7.55	7.05	60.0	7.91	5.95
34	Ulysses sandy clay loam	7.85	7.18	30.40	4.33	3.36
35	Boise sandy loam	7.95	7.5	20.0	0.69	0.69
36	Woodward silty clay loam	7.40	6.90	43.6	10.65	7.35

TABLE XII

CORRELATION COEFFICIENT (r), REGRESSION COEFFICIENT (b) AND REGRESSION EQUATIONS BETWEEN P-EXTRACTED BY BRAY METHOD AND PHOSPHORUS UPTAKE BY PLANTS

Soil Group	pH	d.f. n-2	r	b	Regression Equations
Slightly acid soils	6-7	5	.9094**	.1334	$\hat{y} = 2.5845 + .1334x$
Acid soils	4-6	11	.3716	.0478	$\hat{y} = 1.9709 + .0478x$
Slightly alkaline soils	7-8	14	.6804**	.1357	$\hat{y} = 2.3311 + .1357x$
All soils		34	.5056**	.0984	$\hat{y} = 2.3223 + .0989x$

**Significant at 1% level.

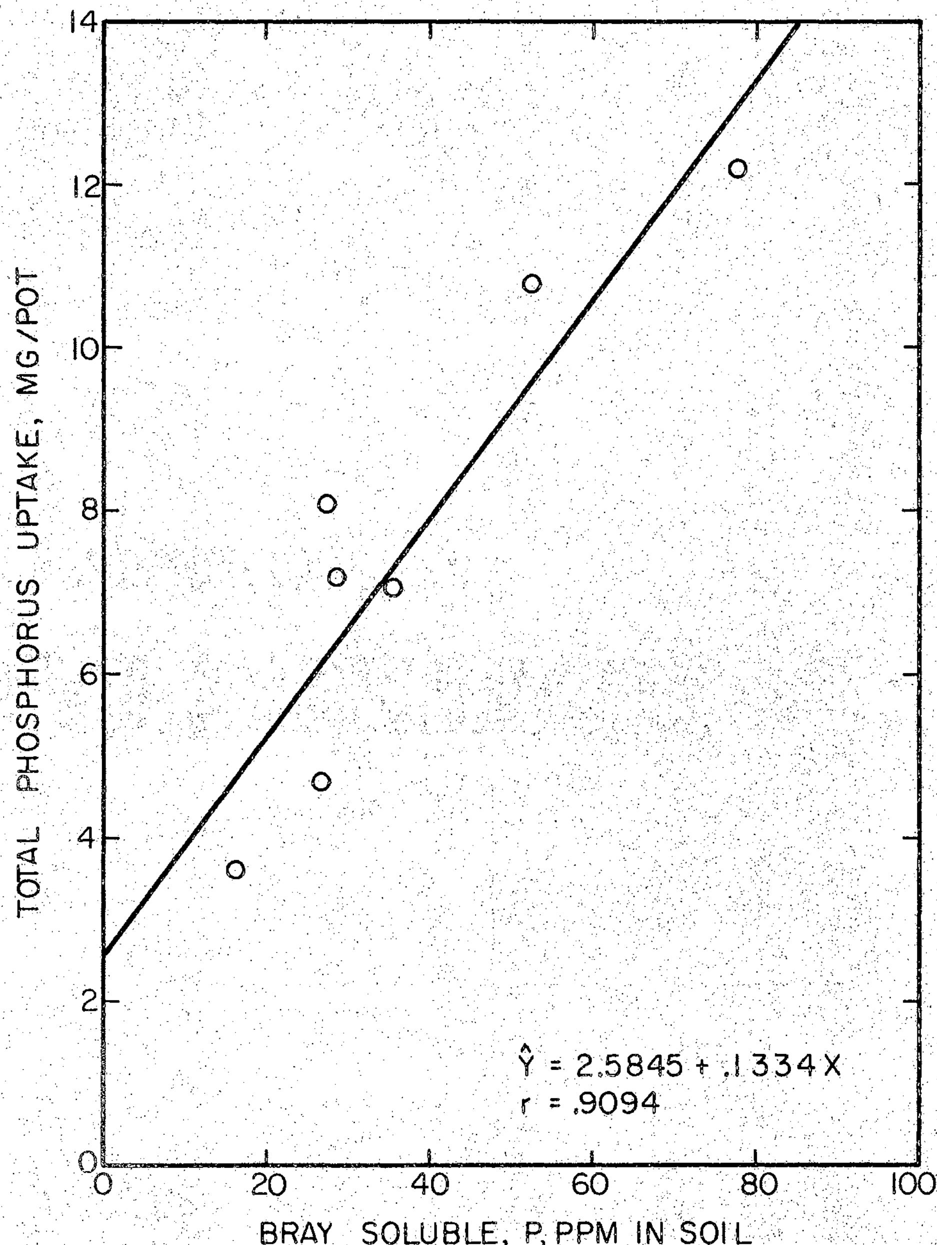

Figure 13. Relation Between Bray Soluble P and Total Phosphorus Uptake by Plants in Slightly Acid Soils

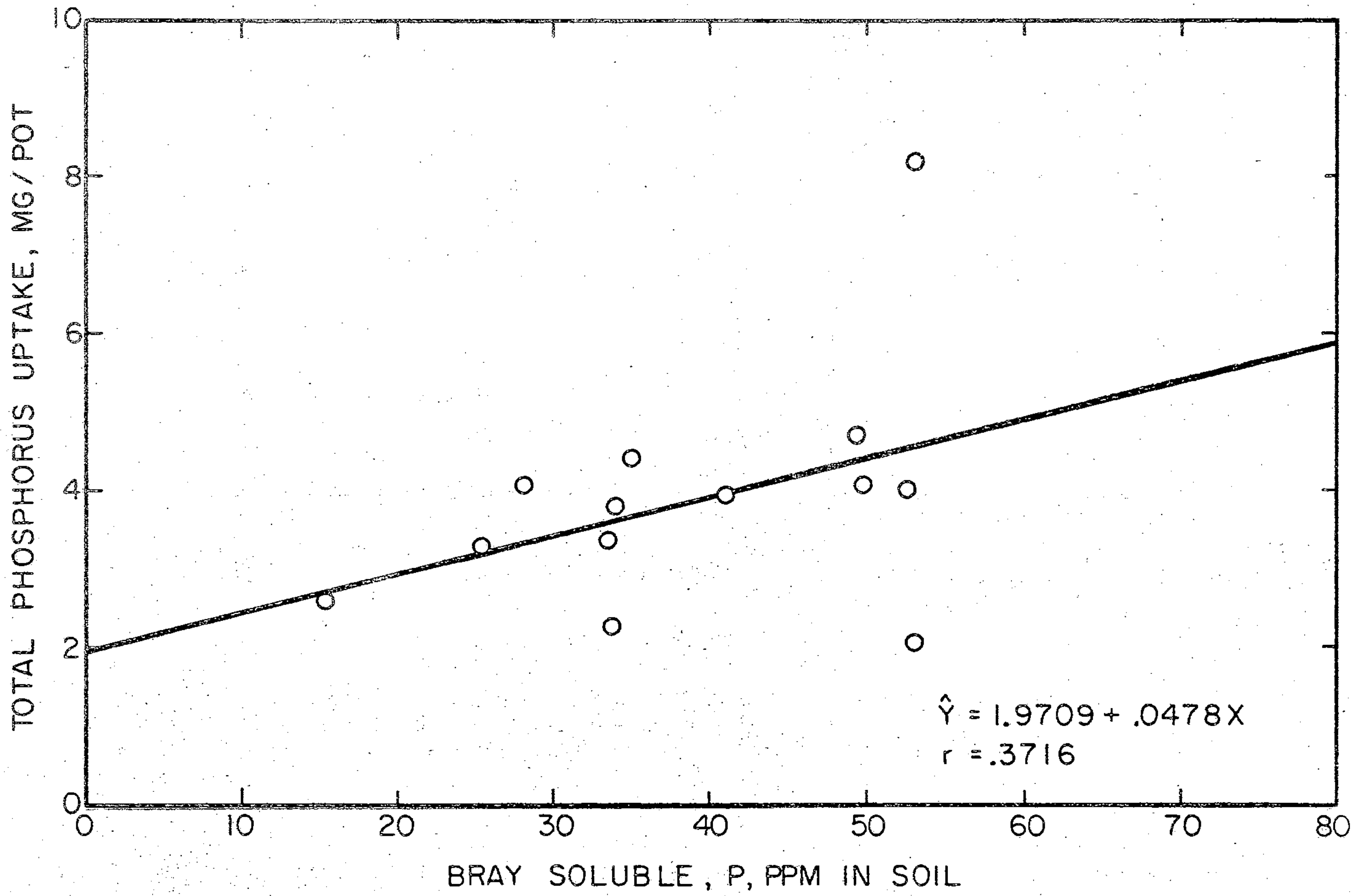

Figure 14. Relation Between Bray Soluble P and Total Phosphorus Uptake in Acid Soils

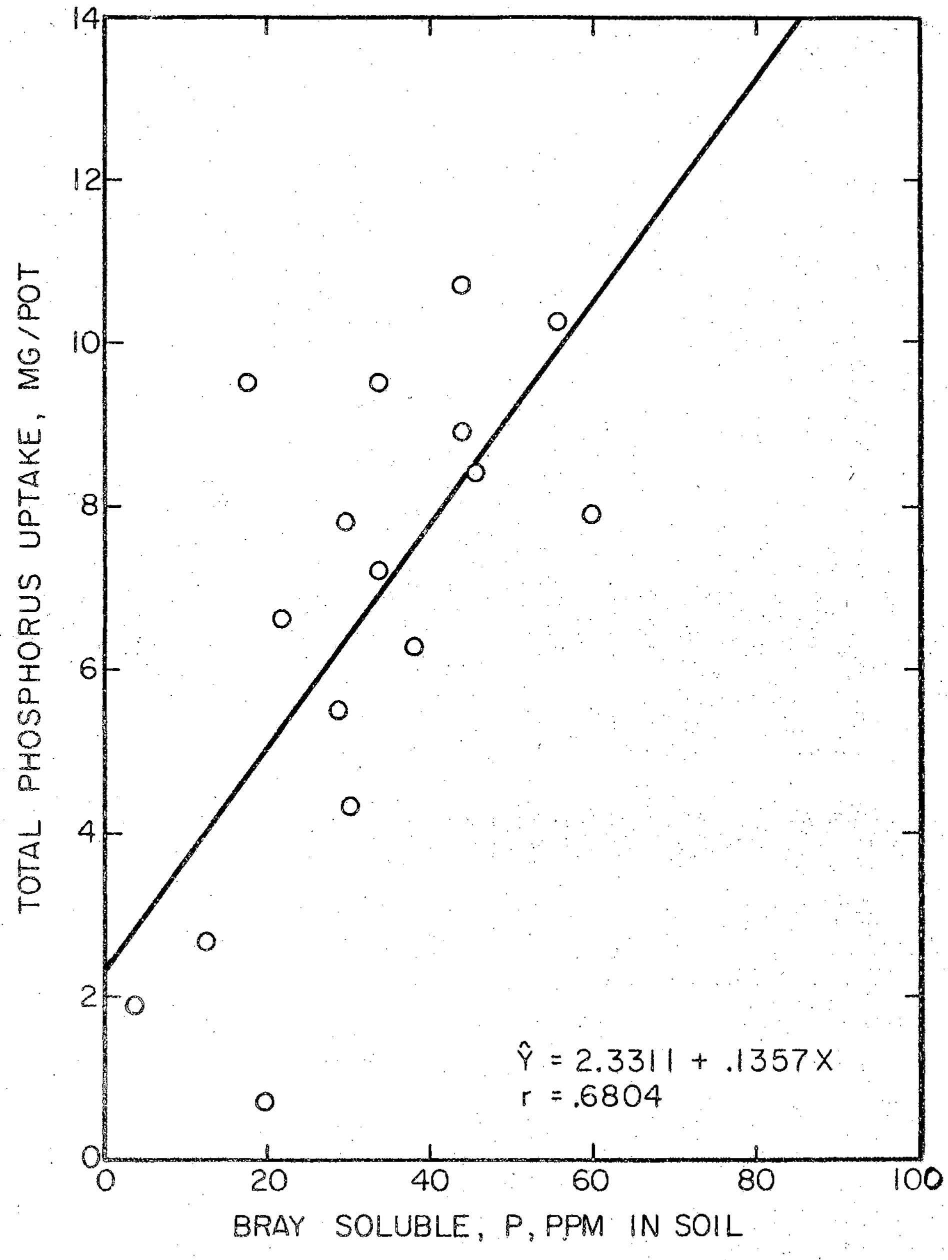

Figure 15. Relation Between Bray Soluble P and Total P Uptake in Slightly Alkaline Soils

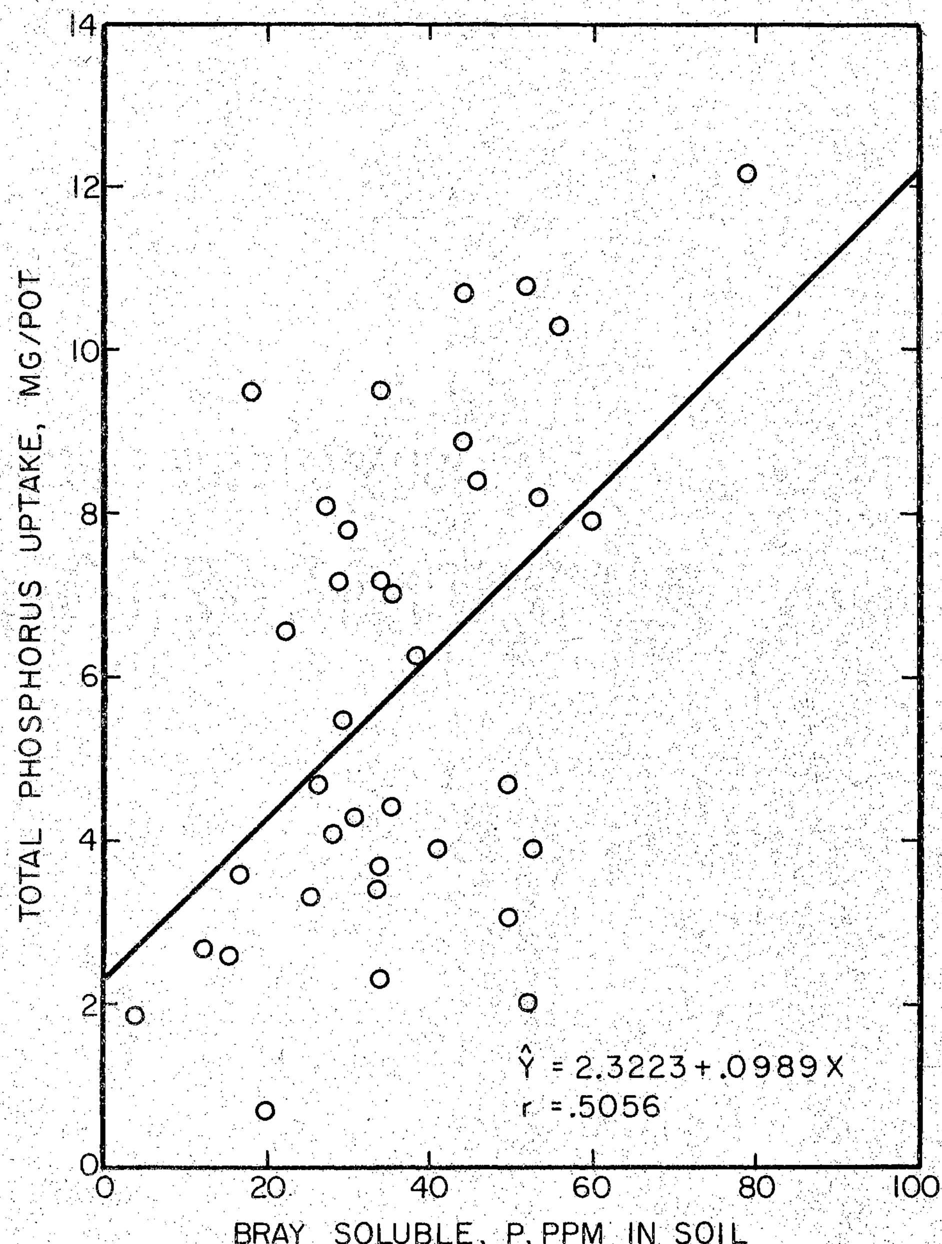

Figure 16. Relation Between Bray Soluble P and Total P Uptake in All Soils

All of these forms are supposed to be available under near neutral conditions. The good correlation obtained for slightly acid soils can be explained on the assumption that dilute acid-fluoride mixture effectively extracted the available forms. With calcareous soils the Bray method probably derived its good correlation because the fluoride anion had a definite repressive effect on the solubility of fluorapatite of rock phosphate and tribasic phosphate which are considered to be unavailable forms for alkaline soils. Thus, it can be seen that while the acid part of the extracting solution will dissolve the Fe-P and Al-P and possibly the monobasic Ca-P the fluoride ion represses teh solubility of the unavailable compounds. In the case of acid soils the presence of fluoride anions resulted in greater increase in solubility of phosphorus contained in both Fe-P and Al-P. These two forms are not as available in acid soils as in alkaline soils, especially Fe-P which is considered a completely unavailable form for plants in acid soils (21).

Correlation of Bray-P with Average Dry Weight

As stated earlier, it is almost impossible to correlate a given soil test for phosphorus with the average dry weight of the plants where the latter is a function of many variables. The results with the Bray method (Table XIII and Figures 17 through 20) confirm the findings of the anion exchange method in this study. The data of Table XIII also reveal interesting results. A good correlation was obtained under slightly alkaline conditions and with pooled soils. Improvement in correlation for slightly alkaline soils may result because these soils are more uniform and similar in their chemical compositions than the other soils. This, also, has been confirmed when phosphorus uptake was

TABLE XIII

CORRELATION COEFFICIENT (r), REGRESSION COEFFICIENT (b) AND REGRESSION EQUATIONS BETWEEN P-EXTRACTED BY BRAY METHOD AND AVERAGE DRY WEIGHT

Soil Group	pH	d.f. n-2	r	b	Regression Equations
Slightly acid soils	6-7	5	.4464	.0279	$\hat{y} = 5.0539 + .0279x$
Acid soils	4-6	11	.0949	.0109	$\hat{y} = 4.0372 + .0109x$
Slightly alkaline soils	7-8	14	.6675**	.1047	$\hat{y} = 1.5842 + .1047x$
All soils		34	.4362**	.0552	$\hat{y} = 3.0393 + .0552x$

**Significant at 1% level.

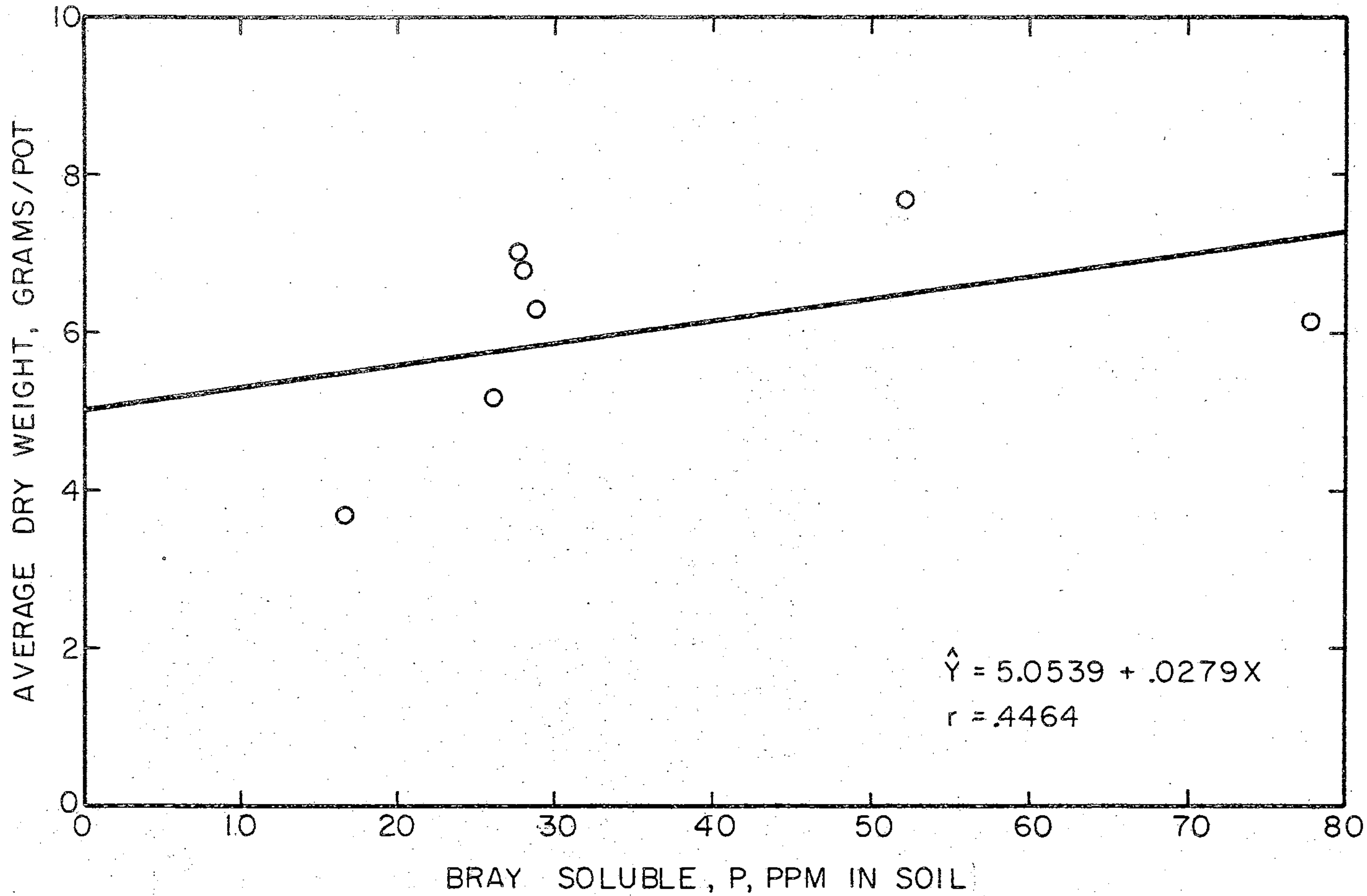

Figure 17. Relation Between Bray Soluble P and Average Dry Weight in Slightly Acid Soils

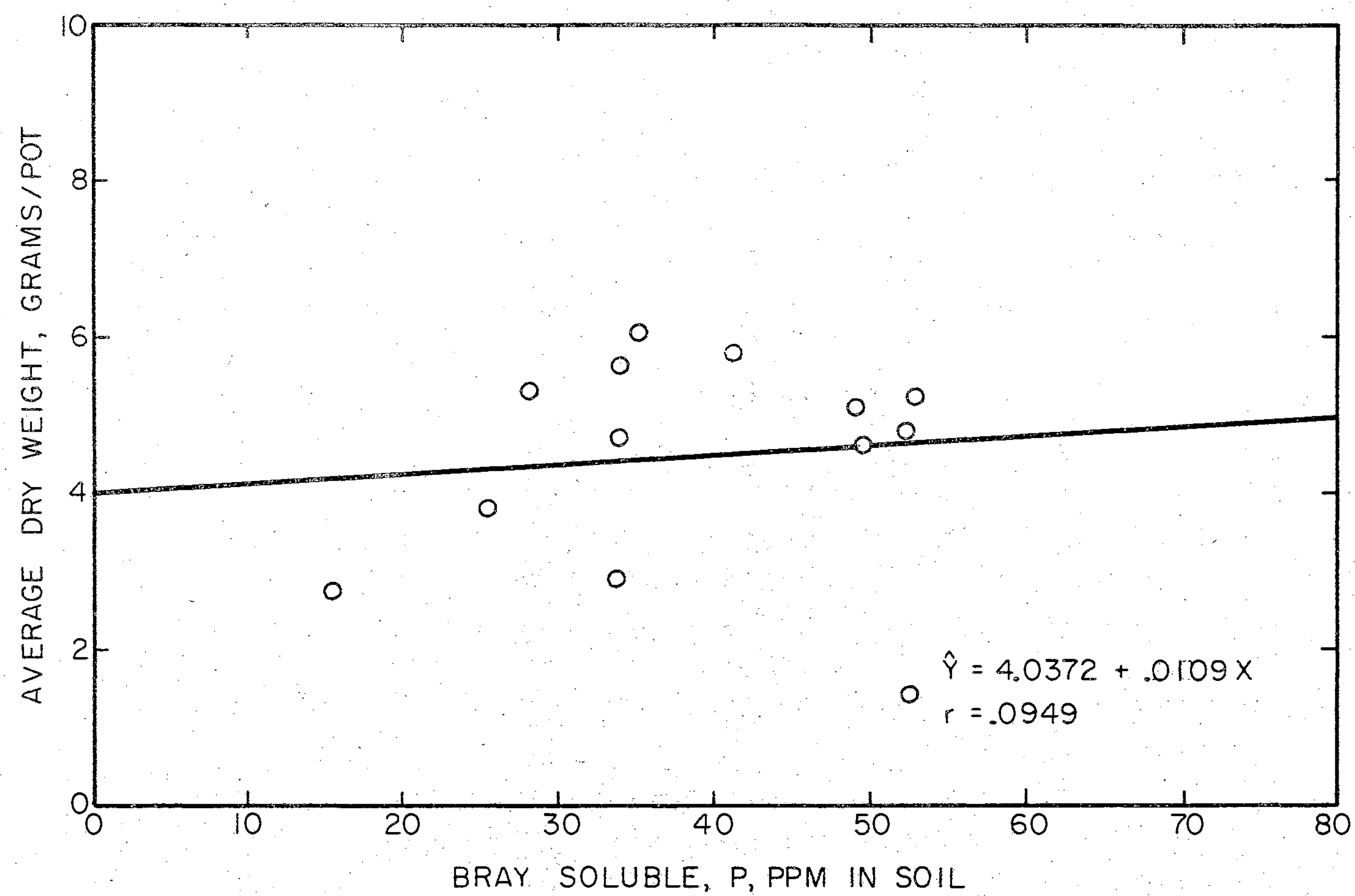

Figure 18. Relation Between Bray Soluble P and Average Dry Weight in Acid Soils

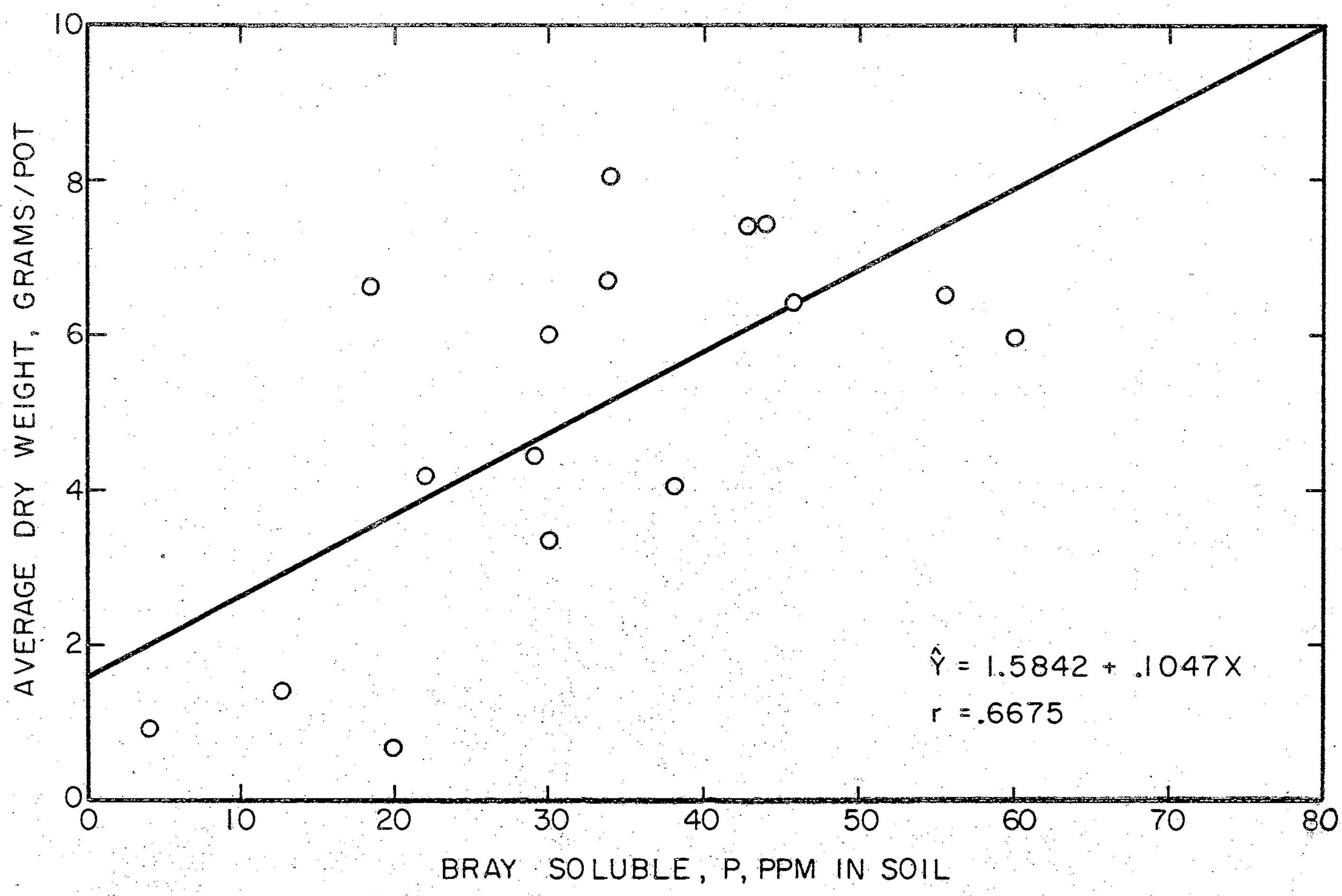

Figure 19. Relation Between Bray Soluble P and Average Dry Weight in Slightly Alkaline Soils

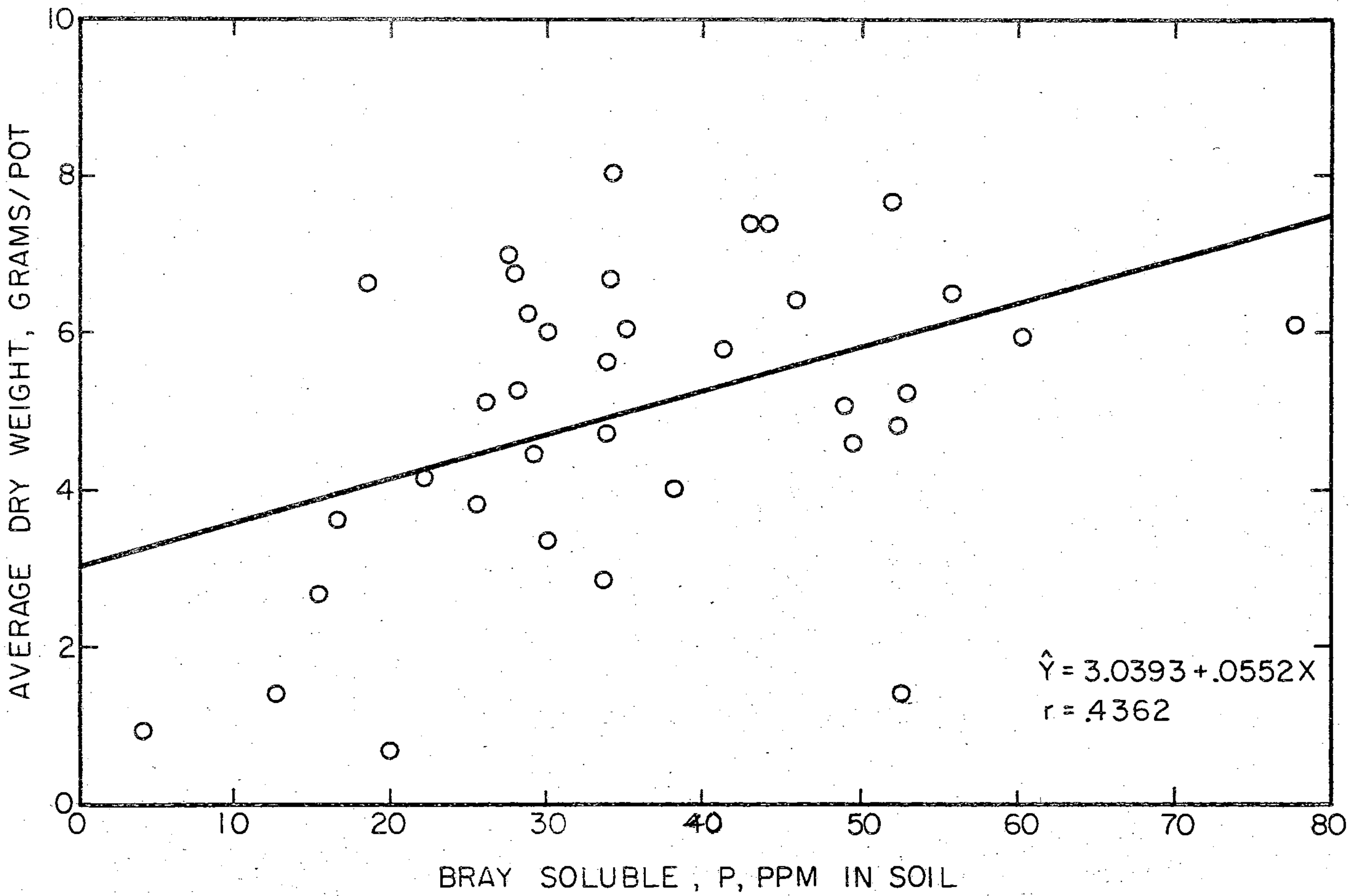

Figure 20. Relation Between Bray Soluble P and Average Dry Weight in All Soils

correlated with average dry weight (see correlation of average dry weight versus total uptake). The highest correlation (r = .9586, Table VIII) was obtained for slightly alkaline soils. The improvement in the significance of the correlation between dry weight and Bray-P (Table XIII) when all soils were considered is merely due to an increase in the degrees of freedom. The "r" value for all soils is still small (r = .4362).

Comparison Between Anion Exchange Method and Bray Method

The correlation data for phosphorus uptake (Table XIV) reveals that both the Bray and resin methods are almost equally effective for estimation of available phosphate under slightly acid conditions. However, when acid and slightly alkaline soils were considered a lowering of the correlation coefficient occurred. In the case of acid soils only the anion exchange resin method correlated significantly with phosphorus uptake. The Bray method yielded a rather poor correlation for acid soils. This may be due to the forms of phosphorus present under this condition, and the chemical nature of the Bray extractants, as was explained earlier. In the case of alkaline soils, an opposite result was revealed. Good correlation was obtained with Bray (r = .6804), where poor correlation was noticed with anion exchange (r = .3801). The low "r" value for anion exchange under slightly alkaline conditions, as was discussed earlier, may be due to the predominant phosphate species ($HPO_4^{=}$) present in the slightly alkaline soils which are not preferred by plants. When the classification of soils into neutral, acid, and alkaline is ignored, anion exchange resin method shows a better correlation (r = .6268) than Bray method (r = .5056). The findings of this study suggest that the two tests together may complement each other. Anion exchange resin can be used for slightly acid and acid soils, while Bray method may be best used for slightly alkaline soils.

TABLE XIV

COMPARISON OF THE CORRELATION OF THE AVAILABLE PHOSPHORUS DETERMINED BY THE BRAY AND THE RESIN METHODS WITH PHOSPHORUS UPTAKE

Soil Groups	pH	Anion Exchange Resin	Bray
Slightly acid soils	6-7	.9375**	.9094**
Acid soils	4-6	.6817*	.3716
Slightly alkaline soils	7-8	.3801	.6804**
All Soils		.6268**	.5056**

*Significant at 5% level.
**Significant at 1% level.

In spite of its present poor correlation under alkaline soils, on the average the anion exchange resin method gave the best results overall. If the anion exchange resin method is modified where it can be suitably applied for alkaline soils, and if this modification is verified by further trial, the anion-exchange resin method may yield enough better results to justify its use for routine analysis.

The correlation data between the two methods and the average dry weight (Table XV) show similar results for both test methods. Both methods show rather poor correlations with the average dry weight except under alkaline conditions where Bray gave good correlation. Significant correlations were obtained for both tests when all soils were considered. These results were discussed earlier where the good correlation under alkaline soils was attributed to the possibility of more uniformity and similarity in the chemical composition among the soils of this group. The significance in the correlations obtained for both tests when all soils were considered may be due to the increase in the degrees of freedom. Good correlations with the average dry weight should not be expected, since many other variables are involved.

TABLE XV

COMPARISON OF THE CORRELATION OF THE AVAILABLE PHOSPHORUS DETERMINED BY THE BRAY AND THE RESIN METHODS WITH AVERAGE DRY WEIGHT

Soil Groups	pH	Anion Exchange Resin	Bray
Slightly acid soils	6-7	.4957	.4464
Acid soils	4-6	.3553	.0949
Slightly alkaline soils	7-8	.3572	.6675**
All soils		.3965**	.4362**

**Significant at 1% level.

CHAPTER V

SUMMARY AND CONCLUSIONS

This study was conducted to compare the performance of the anion exchange resin method of Amer et al with that of Bray 20:1 solution:soil ratio method to see whether the supposed advantages of the resin method will be sustained by applying it to dissimilar soils.

Thirty-six soil samples representing central and western Oklahoma wheatland soils were used for this investigation. The amount of available phosphorus in these soils was determined by the anion exchange resin method and the Bray method. The results of the soil tests were correlated with the phosphorus uptake by plants and average dry weight obtained from plants grown in the greenhouse. Also, correlation studies were made between phosphorus uptake by plants and average dry weight.

Tests were also conducted to determine the best ratio between resin and soil and the minimum time required to produce the optimum phosphorus removal from soil.

The findings of this study lead to the following conclusions:

1) Two hours of shaking and 1:1 ratio of resin to soil seem to be efficient and reproducible for removal of available phosphorus.

2) Both methods are suited for determining the status of the available phosphorus for slightly acid to neutral soils.

3) Anion exchange resin method is best suited for acid soils.

Although this method is not suited for alkaline soils under its present condition, hopefully some modification might be introduced for improvement under alkaline conditions.

4) The Bray 20:1 method is best suited for alkaline soils.

5) Over all soils the anion exchange resin method gave better results than the Bray method. This may justify its use for routine work.

6) Good correlations were obtained between phosphorus uptake and average dry weight over wide pH ranges.

7) A high correlation between soil chemical test data and average dry weight was not obtained and should not be expected since many other variables come into play.

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