Correlation of soil and plant measurements of phosphorus availability

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CORRELATION OF SOIL AND PLANT MEASUREMENTS
OF PHOSPHORUS AVAILABILITY

by

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A dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Soil Fertility

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1956
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INTRODUCTION

For a considerable length of time, agronomists have been faced with the problem of attempting to estimate the availability of soil P to plants. Numerous methods have been developed with this end in view. P probably exists in a great variety of compounds in the soil; and because each method employs a different means of extracting the P, it is not surprising that the various methods yield different results on a given soil, and that with a group of soils the correlation between results obtained by different methods may be rather low.

All methods are intended to simulate the action of plant roots as far as evaluating P availability is concerned. Since the mechanism of root action is still largely unknown, however, it becomes difficult to devise laboratory methods that will have the desired action in extracting the soil P. Because an anion-exchange resin method had been developed at Iowa State College in an attempt to simulate root action more closely than the usual methods, and since preliminary results involving this method seemed promising, it was desired to test this method in comparison with others in current use to determine whether or not it was better for indicating the availability of soil P to plants. This thesis is concerned with a comparison of chemical methods for predicting the response of plants in the greenhouse.

Correlations between soil P and plant P for a number of soils will usually be high for most methods of soil P extraction provided the range of properties of the soils is restricted sufficiently, but in general
the correlation becomes poorer as the soil properties diverge. To assure a wide divergence of soil properties, and hence a rigorous test of the methods employed in this work, a wide variety of soils from different areas of the United States were used.
REVIEW OF LITERATURE

A general objective for those who are involved in soil P research is to learn how to predict the response of plants to P fertilization in the field. The availability of soil P is an important factor in determining this response. Evaluation of the availability of soil P in the field can be accomplished only by tests in the field using, for example, Mitscherlich (1930) b values, or some other means. For advisory purposes the availability of soil P in the field is usually estimated from chemical tests made in the laboratory, after these have been correlated with results of field experiments. For obtaining a preliminary evaluation of different laboratory methods, however, responses of plants grown in the greenhouse are often employed as a substitute for field experiments. Using greenhouse experiments in this way involves the assumption that methods which are superior for predicting plant response in the greenhouse are superior also in the field.

Methods that have been proposed to estimate the availability of soil P in relation to plants may be divided into two main types, chemical and biological. Since biological methods are not under investigation in this thesis, no further discussion will be given of these methods. A review of the biological methods may be found in a paper by Vandeavee (1948).

Chemical methods may be categorized on the basis of the type of extractant employed, e.g., (a) $\text{H}_{2}\text{O}$, (b) acids, bases, and buffered solutions, and (c) cation- and anion-exchange resins. These extractants will be discussed in the order named.
A number of investigators, including Bingham (1949), Jenny et al. (1950), and Burd and Murphy (1939), have developed methods based on extraction of soil P with water. Schofield (1951) proposed a method in which the extractant is a dilute CaCl₂ solution. This method was described in detail by Aslyng (1954). Since this method is essentially an H₂O extraction procedure it will be classified in that way. The method involves the concept that the P in solution in soil is in equilibrium with a much larger amount of P in the solid phase, and that the condition of the P in the soil solid phase can be characterized by the activity of P in solution, after account has been taken of the activities of other ions. The latter may be done by means of the solubility product concept. The solubility product for CaH₂PO₄, for example, may be represented in the following manner:

\[ p\text{Ca} + p\text{H₂PO₄} = a \]

where \( a \) is constant at a given temperature. The second dissociation constant of H₃PO₄ at a given temperature may be represented as follows:

\[ pH + p\text{HPO₄} = p\text{H₂PO₄} + b \]

where \( b \) is constant. By solving the above equation for pHPO₄, substituting the result in the solubility-product equation, and rearranging, the equation

\[ (pH - \frac{a}{2}p\text{Ca}) - (\frac{b}{2}p\text{Ca} + p\text{H₂PO₄}) = b - a \]

is obtained. Since \( b - a \) on the right-hand side of the equality is constant, the difference between the two terms on the left-hand side of the equality is constant likewise. The terms \( pH - \frac{a}{2}p\text{Ca} \) and
are known as the lime potential and the monocalcium phosphate potential (or simply the phosphate potential), respectively. Aslyng (1954) found also that the lime and phosphate potentials of acid soils are independent of CaCl$_2$ concentrations if the latter are extremely low.

There are several advantages for the use of a dilute solution of CaCl$_2$. One advantage for using such a solution instead of H$_2$O is that the analysis for Ca is not required. The use of $\text{anH}_2\text{O}$ extraction would necessitate an analysis for Ca. A second advantage is that the concentration can be high enough to maintain soils in a flocculated state without exceeding the limit to which the activity coefficients can be applied.

A possible limitation in the value of water-soluble P methods lies in the fact that since the total amount of P taken up by plants is much greater than the P in solution at any one time (Burd and Martin, 1923; Pierre and Parker, 1927), the water-soluble portion may not give a good estimate of the total.

Most chemical methods devised to estimate P availability in soils use as extractants acids, bases, or buffered solutions.

A large number of methods employing acid extractants have been proposed. Some that involve the use of organic acids are the CH$_3$CHOHCO$_2$H method of Egner (1941), and the CH$_3$COOH method of Hibbard (1931). Some that employ the use of mineral acids are the 0.01 N HNO$_3$ method of Von Sigmond (1929), the 0.01 N H$_2$SO$_4$ method of Keur and Steiglitz (1939), and the 0.7 N HCl method proposed by Olson (1946). Many workers have
employed buffered acids. The Truong (1930) method uses 0.002 N \( \text{H}_2\text{SO}_4 \) buffered at pH 3 with \((\text{NH}_4)_2\text{SO}_4\), the Pechoh and English (1944) method uses \( \text{CH}_3\text{COOH} \) buffered at pH 4.8 with NaC\(_2\text{H}_3\text{O}_2\), and the Bray and Kurtz (1945) method uses HCl buffered with NH\(_4\)F.

Originally acid extractants for soil P were used because their action was thought to be similar to that of organic acids excreted from roots. More recently this idea has been abandoned, and no particular similarity to the action of plants is claimed.

In general, acid extractants give relatively poor results with calcareous soils. The acids decompose some or all of the CaCO\(_3\), and are neutralized in the process, with accompanying reprecipitation of phosphate (Wild, 1950). Reprecipitation of dissolved phosphate may occur in acid soils also. The presence of NH\(_4\)F in the HCl extractants used by Bray and Kurtz (1945) and of 8-hydroxyquinoline in the CH\(_3\)COOH extractant used by Ghani (1943) reduce the reprecipitation, and facilitate the phosphate extraction by competing with phosphate for the cationic substances by which the phosphate is held in the soil.

Several methods (Das, 1930; Rhoades, 1939; Olsen, 1954) have been developed for estimating P availability in alkaline soils. Das (1930) recommended a 1 per cent \( \text{K}_2\text{CO}_3 \) solution for extracting P. Rhoades (1939) proposed a 0.01 M Na\(_2\text{CO}_3 \) solution buffered with enough H\(_3\text{BO}_3 \) to give the solution the same pH as the soil. Olsen et al. (1954) suggested a 0.5 M solution of NaHCO\(_3 \) for use on both alkaline and acid soils.

Probably the main effect of the alkaline carbonate and bicarbonate extractants on alkaline soils is to decrease the Ca activity, which in
turn increases the solubility of P. In the case of acid soils, these extractants probably bring about the hydrolysis of Fe and Al phosphates. There may exist competition between the OH and the phosphate ions for attachment to the hydrous oxides of Fe and Al in the soil. The use of an alkaline extractant will increase the OH concentration, which in turn causes the balance to move toward OH retention, and thereby increases the equilibrium concentration of phosphate in solutions. Except for Rhoades' (1939) method, the effect of the extractant on soil pH depends on the initial pH of the soil. The extractant thus affects different soils to different degrees.

A fourth type of chemical method for the determination of soil P availability uses synthetic ion-exchange materials for extracting the P. Both cation-exchange resins and anion-exchange resins have been used.

Møller and Mogensen (1953) described the use of a synthetic zeolite for estimating P availability in soils. If a sample of soil is treated with NaZ, sodium zeolite, the interaction with Ca₃(PO₄)₂ may be represented as follows:

\[ 6\text{NaZ} + \text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{CaZ}_2 + 2\text{Na}_3\text{PO}_4. \]

The Na₃PO₄ is soluble. The increase in solubility of P in the presence of the resin thus results indirectly from the reaction between the resin and cationic constituents with which the P is combined.

Amer (1953) described an anion-exchange resin method, in which the resin is the strongly-basic type, and is used in the Cl-form. In the soil, the Cl on the resin is replaced in part by phosphate. Some other ion such as silicate or OH probably takes the place of the phosphate in
the soil solid phase. Anions (Lindsay and D'Amico, 1951) are removed by this
type of resin over a wide pH range. The resin is slightly buffered over the
usual pH range of soils.
MATERIALS AND METHODS

The study was made on 22 soils that were obtained from various regions of the United States. The soils had been used previously in the cooperative uniform P experiments of 1951 (Dean, 1952) and 1952 (Dean, 1953), and were chosen on the basis of results obtained from these experiments. The soils were selected to produce a low correlation between the A value of Fried and Dean (1952) and the soil P extracted by the Bray and Kurtz (1945) method No. 1A. Table 1 shows the soils used, their location, their Iowa numbers, their U. S. Dept. of Agriculture numbers, and their pH values. The U. S. Dept. of Agriculture numbers are included for reference purposes only, since the samples were taken from locations adjacent to the 1951 experiments, and are not identical with the samples taken originally in connection with these experiments.

Soil samples were taken from the plowed layer. Samples used in the greenhouse experiment were air dried, crushed to pass an 8-mesh screen, and then stored in covered metal cans until ready for use. Soils that were used for laboratory work involving a dry treatment were air dried, crushed to pass a 60-mesh screen and stored in quart jars. Soils that were used in the experiments involving a moisture equivalent treatment were crushed to pass a 2-mm. screen.

Two treatments were employed in the laboratory experiments. In one treatment an air-dry sample was used. The second treatment involved the adjustment of soils to the moisture equivalent by the method described by Bouyoucos (1935). A Büchner funnel, 15 cm. in diameter, was filled with
Table 1. Soils used in thesis.

<table>
<thead>
<tr>
<th>U.S.D.A. No.</th>
<th>Iowa No.</th>
<th>pH</th>
<th>Soil Type</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>51526</td>
<td>F-2811</td>
<td>6.75</td>
<td>Barnes loam</td>
<td>South Dakota</td>
</tr>
<tr>
<td>51562</td>
<td>F-2815</td>
<td>5.69</td>
<td>Cinebar silt loam</td>
<td>Washington</td>
</tr>
<tr>
<td>51563</td>
<td>F-2816</td>
<td>5.30</td>
<td>Puyallup silt loam</td>
<td>Washington</td>
</tr>
<tr>
<td>51567</td>
<td>F-2817</td>
<td>8.10</td>
<td>Nibley clay loam</td>
<td>Utah</td>
</tr>
<tr>
<td>51569</td>
<td>F-2818</td>
<td>8.20</td>
<td>Draper loam</td>
<td>Utah</td>
</tr>
<tr>
<td>51572</td>
<td>F-2819</td>
<td>6.10</td>
<td>Lloyd clay loam</td>
<td>Alabama</td>
</tr>
<tr>
<td>51574</td>
<td>F-2820</td>
<td>8.20</td>
<td>Nunns silty clay</td>
<td>Montana</td>
</tr>
<tr>
<td>51576</td>
<td>F-2821</td>
<td>5.65</td>
<td>Mardin silt loam</td>
<td>New York</td>
</tr>
<tr>
<td>51582</td>
<td>F-2822</td>
<td>6.40</td>
<td>Davidson clay loam</td>
<td>Virginia</td>
</tr>
<tr>
<td>51583</td>
<td>F-2823</td>
<td>6.10</td>
<td>Appling fine sandy loam</td>
<td>Virginia</td>
</tr>
<tr>
<td>51585</td>
<td>F-2824</td>
<td>6.40</td>
<td>Yooemento silt loam#</td>
<td>Kansas</td>
</tr>
<tr>
<td>51586</td>
<td>F-2825</td>
<td>7.50</td>
<td>Huffine silt loam</td>
<td>Montana</td>
</tr>
<tr>
<td>51588</td>
<td>F-2826</td>
<td>6.45</td>
<td>Carrington clay loam</td>
<td>Nebraska</td>
</tr>
<tr>
<td>51589</td>
<td>F-2827</td>
<td>6.50</td>
<td>Moody silty clay</td>
<td>Nebraska</td>
</tr>
<tr>
<td>52592</td>
<td>F-2828</td>
<td>8.35</td>
<td>Declo loam**</td>
<td>Idaho</td>
</tr>
<tr>
<td>51615</td>
<td>F-2829</td>
<td>6.00</td>
<td>Palouse silty clay loam</td>
<td>Idaho</td>
</tr>
<tr>
<td>51616</td>
<td>F-2830</td>
<td>5.76</td>
<td>Waukegan silt loam</td>
<td>Minnesota</td>
</tr>
<tr>
<td>51627</td>
<td>F-2831</td>
<td>6.25</td>
<td>Fox sandy loam</td>
<td>Michigan</td>
</tr>
<tr>
<td>51633</td>
<td>F-2832</td>
<td>5.90</td>
<td>Lloyd clay loam</td>
<td>Georgia</td>
</tr>
<tr>
<td>51634</td>
<td>F-2833</td>
<td>5.50</td>
<td>Orangeburg sandy loam</td>
<td>Georgia</td>
</tr>
<tr>
<td>51652</td>
<td>F-2834</td>
<td>5.70</td>
<td>Norfolk loamy sand</td>
<td>North Carolina</td>
</tr>
<tr>
<td>51745</td>
<td>F-2835</td>
<td>6.21</td>
<td>Walla Walla silt loam</td>
<td>Washington</td>
</tr>
</tbody>
</table>

* Formerly called Manjor silt loam.

**From the 1952 experiments (Dean, 1953); all others from the 1951 experiments (Dean, 1952).*
air-dry soil. The base of the funnel was gently tapped against a table top to pack the soil. The soil was leveled with the top of the funnel. The funnel then was placed in a liter beaker, into which distilled H₂O was poured until it almost reached the level of the soil. The water that was placed in the beakers was adjusted in such a way that the temperature was the same in all beakers at the beginning of the incubation. A 17-cm. watch glass was placed on top of the funnel to decrease evaporation. The soil sample was allowed to soak for a period of 24 hours. After this period, the soil was placed under vacuum suction for a period of 15 minutes, and the watch glass was maintained in place. The funnel then was removed from the suction rack. The soil was scraped into a pint jar, a moisture sample was taken, and the jar was tightly closed. The rewetted soils were allowed to incubate at room temperature for a period of 7 days. On the 6th day, moisture samples were taken again to ascertain whether or not there had been an appreciable loss of moisture. It was found that the moisture content did not change during the incubation to any great extent. The weights of rewetted soils used in the analyses were adjusted so that the quantity of dry soil was equal to that used in the dry treatment.

Extraction procedures of Aslyng (1954), Bray and Kurtz (1945), Olsen et al. (1954), and Amer (1953) were used in this study. These methods will be discussed in the order mentioned.

The first procedure that was used was the "phosphate potential" method of Schofield (1951), as described in detail by Aslyng (1954). The extracting agent was a 10⁻² M CaCl₂ solution. Twenty- and 40-gram
samples of soil were weighed into large test tubes (22 mm. x 175 mm.). Fifty ml. of a 10^{-2} M CaCl\textsubscript{2} solution were then added. The test tubes were shaken for a period of 30 minutes on a wrist-action shaker, and then were centrifuged at 4000 r.p.m. for a period of 10 minutes. The supernatant solution was filtered through No. 42 Whatman filter paper, 15 cm. in diameter. Extra samples were treated in the same fashion at the same time, and the pH of the suspension was determined. The P concentration of the filtrate was determined by a modification of the Truog and Meyer (1929) method. The reagents used were those described by Truog and Meyer (1929).

A 15-ml. aliquot of the sample was pipetted into a test tube, and to this was added 0.7 ml. of (NH\textsubscript{4})\textsubscript{2}MoO\textsubscript{4}·H\textsubscript{2}SO\textsubscript{4} solution. The resulting mixture was shaken three times. One drop of SnCl\textsubscript{2} solution was added, the mixture was shaken, and the amount of P was determined by use of a colorimeter exactly 10 minutes after the color-producing reagent was added. Because many of the extracts were somewhat colored by organic matter, the double tube-reading procedure of Dyer and Wrenshall (1938) was employed.

To avoid dilution effects, the procedure was carried out using two different amounts of soil. The molar phosphate concentration then was plotted on the Y axis against the reciprocal of the amount of soil on the X axis. The straight line passing through the experimental points was extended to the X axis as a means of obtaining the phosphate concentration present at "zero dilution". The resulting value was used to calculate the phosphate potential, which is described by the equation:

\[
\text{phosphate potential} = \frac{1}{2} p\text{Ca} + p\text{H}_2\text{PO}_4
\]
where

\[ \frac{1}{2} \gamma_{\text{Ca}} = \frac{1}{3} \gamma_{(\text{Ca})} + \frac{1}{3} \gamma_{\gamma} \]

The activity coefficient, \( \gamma \), is obtained by using the equation:

\[ \gamma = z^2 A \sqrt{\frac{\varepsilon}{2}} \]

where \( z \) signifies the valency and \( \varepsilon \) the concentration. \( A \) is usually 0.5 at room temperature.

The term \( \text{pH}_2\text{PO}_4 \) is obtained from the equation:

\[ \text{pH}_2\text{PO}_4 = \text{p}(\text{H}_2\text{PO}_4) + 0.5 \sqrt{\mu} \]

where

\[ \mu = 0.5z^2c^2 \text{ and} \]

\[ \text{p}(\text{H}_2\text{PO}_4) = \text{pF} + \text{p}(\frac{\text{H}}{\text{KW} + \text{H}}) \]

where the numerical value of \( \text{p}(\text{H}/(\text{KW} + \text{H})) \) at different pH values is obtained from a table given by Aslyng (1954).

The phosphate potential is then obtained by combining the terms \( \frac{1}{2} \gamma_{\text{Ca}} \) and \( \text{pH}_2\text{PO}_4 \).

The second procedure employed was method 2A of Bray and Kurtz (1955) for the determination of "adsorbed- and acid-soluble-P". The reagents used were those described by Bray and Kurtz (1955), but the procedure was modified slightly for convenience.

To 5 grams of soil in a 250-ml. Erlenmeyer flask, 35 ml. of extracting solution (0.03 N \( \text{NH}_4 \text{F} \) in 0.01 N HCl) were added. The resulting mixture was shaken by hand (approximately 20 times) for a period of 40 seconds, and then was filtered immediately through No. 42 Whatman filter paper, 15 cm. in diameter.

To a 5-ml. aliquot, 1 ml. of saturated \( \text{H}_3\text{BO}_3 \) solution (Kurtz, 1952)
was added. The mixture was diluted to 35 ml. in a test tube, and was mixed thoroughly by shaking. To the resulting solution 10 ml. of the Dickman and Bray (1940) (NH₄)₂MoO₄ - HCl solution were added, and the solutions were mixed. Two drops of SnCl₂ solution (made up in concentrated form so that two drops contained the quantity added by Dickman and Bray in 5 ml. of diluted solution) were added to the solution, the mixture was shaken, and the amount of P was determined using the colorimeter exactly 20 minutes after the SnCl₂ had been added.

The third method employed was the NaHCO₃ method described by Olsen et al. (1954), in which the P is extracted with a solution of 0.5 M NaHCO₃ buffered at a pH of 8.5. The reagents used were those described by Olsen et al. (1954).

A 5-gram sample of soil, to which 100 ml. of 0.5 M NaHCO₃ adjusted to a pH of 8.5 had been added, was placed in a 250-ml. Erlenmeyer flask. One teaspoonful of carbon black (Darco G-60) was then added, and the flask was shaken for 30 minutes. The resulting mixture was filtered immediately through Whatman No. 42 filter paper, 15 cm. in diameter. It was found that 1 ml. of 20 per cent HCl should be added to the aliquot in the test tube for each 5 ml. of aliquot used. After addition of the HCl the sides of the test tubes were washed down, and the test tubes were placed in a hot water bath for 1 hour. The tubes were then allowed to cool to room temperature. The resulting mixture was diluted to 35 ml. with distilled H₂O, and was shaken. Reagents were added as described in the preceding method, and the amount of P was determined by use of a colorimeter exactly 12 minutes after the color-producing reagent was added. In the event that a 5-ml.
aliquot proved to have too high a concentration a smaller aliquot was
used, and the amount of NaHCO₃ solution was adjusted so that the total
remained the same as before.

The fourth procedure used was the anion-exchange resin method as
described by Amer (1953). The anion-exchange resin used was the Cl-form
of Dowex 2, which is made by the Dow Chemical Company, Midland, Michigan.
It is strongly basic resin which is a quaternary ammonium salt (Wheaton
and Bauman, 1951) of the type \( \text{HR}^+ \text{R}^2 \text{R}^3 \text{R}^4 \text{N}^+ \text{A}^- \) in which one of the \( \text{R}^i \)s
is cross linked with divinylbenzene to render the resin insoluble in aqueous
and nonaqueous solutions. The resin is a highly-dissociated organic base
(Lindsay and D'Amico, 1951), in which the large cationic body is limited in
movement and the relatively small, and mobile anions exchange freely over a
wide pH range.

The resin was obtained in a 20 to 50-mesh spherical form, light yellow
in color, with a density of 1.15, and a moisture content ranging from 35
to 50 per cent. The resin was air dried and sifted through a 32-mesh screen.
Only the fraction that remained on the screen was used in analysis.

Resin and soil were mixed in a 1:1 ratio, in which 1 gram of soil was
added to 1 gram of resin. To the mixture 100 ml. of distilled H₂O were
added, and the suspension was shaken for periods of 5, 10, 15, and 30
minutes, 1, 2, 6, 12, 24, 36, 48, and 72 hours. At the end of the given
time interval the 250-ml. Erlenmeyer flask was removed from the shaker
and the mixture was washed through a 50-mesh stainless steel screen. The
soil was washed away from the resin by additions of distilled H₂O. The
resin was then allowed to dry on the screen. Once dry, it was transferred
quantitatively to a 250-ml. Erlenmeyer flask to which were added 25 ml. of a 10 per cent NaCl solution. The flask was then placed on a steam plate for a period of 45 minutes. The solutions were allowed to cool, and then were filtered through a No. 42 Whatman filter paper, 15 cm. in diameter. The resin on the filter paper was leached with portions of 10 per cent NaCl solution until the volume of the filtrate totaled 100 ml. Aliquots of the filtrate were diluted in such a way that the final concentration in the colorimeter tube did not exceed a concentration of 4 per cent NaCl. P was determined colorimetrically by the method of Dickman and Bray (1940), making all percentage transmission measurements 20 minutes after the addition of the color-producing reagent.

A greenhouse experiment was utilized in this study as a basis for evaluating the chemical methods employed. The soils used in this experiment are listed in Table 1. The pots that were used were No. 10 tin cans that had been lined with polyethylene bags. To each pot, 2300 grams of white quartz sand was added. The sand was obtained from a local lumber company. Four hundred grams of soil and 1000 grams of sand were mixed in a twin shell dry mixer for a period of 2 minutes, and then were placed in the tin cans. Three hundred ml. of a nutrient solution lacking P (Hoagland and Arnon, 1938) were added to each can. This solution contained N, K, Ca, Mg, and S at concentrations of 196, 234, 160, 48, and 64 p.p.m. respectively. One ml. of a minor-elements solution describer by Hoagland and Arnon (1938) was added to each liter of nutrient solution. Jacobson (1951) reported that 5 to 10 p.p.m. of Fe provided in the form of an ethylenediamine tetra-acetic acid complex provided enough iron for adequate plant growth and did not
produce detrimental symptoms. The solution was prepared by dissolving in 
\( \text{H}_2\text{O} \) 36.4 grams of Na-Fe salt of ferric ethylenediamine tetra-acetic acid 
containing a minimum of 12 per cent Fe. The total volume of the solution 
was diluted to 1 liter. One ml. of this solution was added to each liter 
of nutrient solution used.

On the wet surface of the soils 300 ml. of distilled \( \text{H}_2\text{O} \) were added. 
Then 35 sorghum seeds of Red Bine 60 variety were seeded in a circular 
pattern. The seeds were then covered with 300 grams of white quartz sand, 
and then 100 ml. of distilled \( \text{H}_2\text{O} \) were added. The weight of the pots was 
found to vary from 1900 to 5000 grams.

Ten replicates of each soil were prepared in the above fashion, and 
were placed in the greenhouse in a randomized block design. Pots within 
replications were rerandomized daily, and replications were rerandomized 
weekly. Pots were weighed daily, and losses in weight were adjusted by 
additions of distilled \( \text{H}_2\text{O} \). Distilled \( \text{H}_2\text{O} \) was added to the pots by use 
of a modified shower sprayer that had been shortened. A funnel was con­
ected through tubing to the spray type mechanism.

The experiment was started on September 28, 1955. It was found 
necessary to add N and K at frequent intervals. These elements were added 
in the form of a solution that contained half the N as \text{NH}_4\text{NO}_3 \) and the 
other half as \text{KNO}_3 \). The first addition of 42 milligrams of K and 50 
milligrams of N was made on October 18. Similar additions were made on 
November 7 and 25. One hundred milligrams of N and 84 milligrams of K 
were added to all pots on both November 29 and December 20.

The temperature range that occurred in the greenhouse during the 
early period of growth was 90° to 112° F. In the later stages of growth
the temperature ranged from 60° to 70° F. during the day and 50° to 70° at night. In the early days of the fall, it was found necessary to wash down side walks and tables in the greenhouse to keep the temperature down.

Aphids and red spider disease made it necessary to fumigate with Nicofume on October 19. Various leaf blight diseases, probably of Helminthosporium origin, also occurred. Temperature was kept down during this time, and plants were not watered so frequently.

It was decided that the plants should be allowed to grow until they were P deficient, and were growing slowly. Height measurements were begun on November 16, and were made weekly to ascertain whether or not the plants had ceased growth. It was found that the height on December 19 was essentially the same as it had been on December 12, from which it was inferred that growth had essentially stopped. Pots at this period were losing about 50 grams of H₂O per day.

Plants were harvested on December 21. The surface sand was discarded, and the plants were cut with a pair of scissors at the point where the stalk was connected to the seed. By so doing, it was felt that much error would be avoided, since all plants would be cut at the same point. The cut portions were placed in No. 10 paper bags, and were allowed to dry for a period of 72 hours in ovens adjusted to 65° C.

A few samples at a time were removed from the oven and placed in a desiccator. After they had almost cooled, the contents of each bag were weighed on a torsion balance in a tin foil cup which weighed 50 grams. Each sample was then ground in a Wiley mill to pass a 20-mesh screen and was stored in a sample bottle for subsequent analysis.
To determine P the ground plant material first was placed in a forced-air-draft oven for a period of 48 hours. A few samples at a time were removed and allowed to cool in a desiccator. Then, following the procedure described by McCants (1955), 0.5 gram from each sample was weighed on an analytical balance. All samples were duplicated. The weighed sample was placed in a 30-ml, beaker. To each beaker were added 5 ml, of a 5 per cent Mg(C$_2$H$_3$O$_2$)$_2$ solution. The beakers were placed on a steam plate, and the solution was allowed to evaporate to dryness. The beakers then were placed in a cool muffle furnace, the temperature of which was gradually raised to 200$^\circ$ C. After charring was completed the temperature was raised to 500$^\circ$ C and held there for a period of 2 hours. After cooling, the samples were moistened with 1 ml, of 1 N HNO$_3$, placed on a steam plate, and allowed to evaporate to dryness. Samples were then placed in a muffle and heated to 500$^\circ$ C, for approximately 1 hour. To the cooled ash 10 ml, of 1 N HCl were added. Watch glasses were placed on the beakers, and the covered beakers were placed on a steam plate for 3 hours. Samples were then cooled, and the contents were transferred to 100-ml, volumetric flasks. Beakers were washed and policed. The solution was made up to volume and shaken. To allow the sediment to settle the flasks were allowed to stand for a period of about 12 hours.

The Dickman and Bray (1940) method was used for the analysis of P in the plant material. Five-ml, aliquots were used. Enough HCl was placed in the test tubes which contained solutions of standard P so that all test tubes would have the same concentration of the acid.
RESULTS AND DISCUSSION

Four methods for extracting soil P were investigated to determine their relative values in predicting plant response. Each method was used on dry samples and on premoistened samples. Table 2 shows the moisture content at which the premoistened samples were incubated. Samples of soil were equilibrated with distilled H₂O for 7 days, and then the P content was determined for each sample by the extracting procedures suggested by Aslyng (1954), Bray and Kurtz (1945), and Olsen et al. (1954). At a later date samples were again equilibrated with distilled H₂O to determine the amount of P in premoistened soils obtained by using the extraction procedure suggested by Amer (1953). The two separate equilibrations were made because of the length of time required for carrying out the experimental work.

The P extracted by each method was correlated with the yield of plant P in milligrams, shown in Table 3. The methods were rated in accordance with the magnitude of the correlation coefficients. The results obtained by the methods suggested by Aslyng (1954), Bray and Kurtz (1945), Olsen et al. (1954), and Amer (1953) will be discussed in the order indicated.

Schofield (1955) has stated that perhaps it is not the amount of available P in the soil that is of primary importance in the ability of plants to extract P, but rather the amount of energy that plants must exert to extract it from the soil. Therefore, he suggested the chemical potential or free-energy concept of P utilization by plants from soils. He suggested that the availability of soil phosphates to plants may be
Table 2. Moisture content of premoistened samples. Extractions were made by the Bray and Kurtz (1945) method, the Olsen et al. (1954) method, and the Aslyng (1954) method on samples prepared in the first equilibration. Extractions were made by the Amer (1953) method on samples prepared in the second equilibration.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Moisture content of soil in per cent</th>
</tr>
</thead>
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</tr>
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<td>52</td>
</tr>
<tr>
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<td>F-2818</td>
<td>19</td>
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<td>29</td>
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<td>F-2820</td>
<td>38</td>
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<td>F-2821</td>
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<td>F-2822</td>
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<tr>
<td>F-2835</td>
<td>28</td>
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Table 3. The yield of dry matter and the yield of P in sorghum plants grown on the soils listed.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Yield of dry matter per culture, grams</th>
<th>Yield of P per culture, milligrams</th>
</tr>
</thead>
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<tr>
<td>F-2814</td>
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<td>8.0</td>
<td>5.5</td>
</tr>
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<td>F-2816</td>
<td>18.5</td>
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<td>9.4</td>
</tr>
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<td>F-2819</td>
<td>7.6</td>
<td>5.6</td>
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<td>F-2820</td>
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<td>5.0</td>
</tr>
<tr>
<td>F-2821</td>
<td>11.0</td>
<td>10.5</td>
</tr>
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<td>F-2822</td>
<td>6.8</td>
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</tr>
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<td>F-2823</td>
<td>5.3</td>
<td>2.3</td>
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<tr>
<td>Blank</td>
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<td>1.8</td>
</tr>
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</table>
determined by the appropriate chemical potential, and by its rate of decrease as phosphate is withdrawn.

Aslyng's (1954) method, which was originally proposed by Schofield (1951), was used as an extraction procedure for the 22 soils used in this study. The results obtained using this procedure may be found in Tables 4, 5, and 6. Tables 4 and 5 show the results obtained when 20- and 100-gram samples of soil were used, as well as the extrapolated value for zero dilution. The extrapolation was performed by plotting the molar phosphate concentration against the reciprocal of the quantity of soil used. The straight line obtained was extended to the x axis, which represented the molar concentration of phosphate with an infinite quantity of soil, i.e., with zero dilution. The purpose of this procedure was to eliminate differential effects of dilution on the phosphate concentration of different soils.

In almost all cases the P extracted from 20 grams of soil was considerably higher than that extracted from 100 grams. More P was extracted from the initially dry samples than from the premoistened samples of 100 of the 22 soils where 20-gram samples were employed. No consistent statement can be made concerning all soils that differ from the majority in this respect. A possible explanation for the fact that a higher P concentration was obtained with the initially dry samples in the majority of cases is that the premoistening may have permitted slow hydration of some of the Fe and Al oxides, which in turn increased the adsorption capacity of the soil for P, and therefore decreased the P concentration in solution. This explanation evidently does not account for the reverse behavior observed with a number
Table 4. P extracted by $10^{-2} \text{ M CaCl}_2$ solution from samples of different soils that were dry initially.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>P extracted, p.p.m. of air-dry soil</th>
<th>Concentration of P in solution at zero dilution, M x 10^6</th>
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<tbody>
<tr>
<td></td>
<td>20 grams soil</td>
<td>40 grams soil</td>
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<tr>
<td></td>
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<tr>
<td>F-2814</td>
<td>0.108</td>
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<td>0.171</td>
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<td>0.574</td>
<td>0.374</td>
</tr>
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</tr>
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</tr>
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<td>F-2819</td>
<td>0.097</td>
<td>0.054</td>
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<td>0.083</td>
<td>0.054</td>
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<td>F-2821</td>
<td>0.086</td>
<td>0.045</td>
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<td>0.446</td>
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<td>W</td>
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<td>6%</td>
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<tr>
<td>10.00</td>
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*T. P. extracted by 10% NaCl solution from samples of different soils that had been premoistened.*

Table 5. P. P. extracted by 10% NaCl solution from samples of different soils.
Table 6. The pH, lime potential (pH - \( \frac{1}{2}pCa \)), and phosphate potential (\( \frac{1}{2}pCa + pH_2PO_4 \)) obtained with the Aslyng (1954) method using initially dry and premoistened samples of different soils.

<table>
<thead>
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<th>Soil No.</th>
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<th>Premoistened samples</th>
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<td></td>
<td>pH</td>
<td>pH - ( \frac{1}{2}pCa )</td>
<td>( \frac{1}{2}pCa + pH_2PO_4 )</td>
<td>pH</td>
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</tr>
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<td>5.61</td>
<td>4.45</td>
<td>6.86</td>
<td>5.50</td>
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</table>
of soils. Some of the soils that did not follow the trend of the majority contained high amounts of P extractable by the other procedures. Yet others that were high in P followed the trend of the majority. On the other hand some soils with which the P concentration was greater with premoistened than with initially dry samples had the lowest extractable P content of all soils studies and with all the other methods employed. Some of the soils in which the P concentration was greater with premoistened than with dry samples are alkaline.

In the case of 10 soils, the P at zero dilution was higher with the initially dry samples than with the premoistened samples. Half of these soils had pH values of 7.5 or more, and the other half were slightly acid. Those soils that showed a large increase of P at zero dilution with the premoistened samples as compared to the initially dry samples were alkaline, with the exception of one soil. Some of these soils were the same as those that showed an increase in P concentration in the premoistened samples as compared to the dry samples in the direct measurements made at the different dilutions. Some of the soils that showed this increase had a large amount of P according to all methods, but not all soils that showed the increase were high in P.

Table 6 shows the pH, lime potential, and phosphate potential obtained for the 22 soils. The relation between the lime potential and the pH is such that as the pH increases, or the H⁺ activity decreases, the lime potential increases. From the data shown in Table 6 it would be difficult to make any general observation concerning the differences exhibited in results between the dry and premoistened treatments. With
Soils a higher lime potential was obtained with initially dry samples than with premoistened samples. Only ten showed a similar increase in phosphate potential. With some soils, as the lime potential increased the phosphate potential decreased; with other soils, as the lime potential increased, the phosphate potential increased as well; and for still other soils, as the lime potential increased, the phosphate potential remained essentially the same.

Table 10 shows the correlations obtained between the various P measurements of the Aslyng (1954) method and the yield of P in milligrams in the plants grown on the various soils. The results are contrary to the ideas that Aslyng (1954) set forth in his paper. The correlations between plant P and P obtained using 20- and 40-gram samples of soil respectively for both treatments are about the same, and are much higher than the correlation between plant P and P obtained at zero dilution. A possible reason for this situation may be that the effects of experimental error become more important in the extrapolation than in the individual values. It may also be noticed that for these soils the phosphate potential gave essentially no correlation with the yield of P in the plants. It would appear from the data presented in this paper that this method is unable to withstand the rigorous test presented by employing soils with widely differing properties.

The results obtained from the use of the Bray and Kurtz (1945) method may be found in Table 7. It may be noted that some figures appear to be abnormally high. In a number of cases the high P values are associated with high soil pH values. With such soils the high concentration of the acid used probably would bring about a dissolution of much of the Ca
Table 7. P extracted by the Olsen et al. (1954) method and the Bray and Kurtz (1945) method from initially dry and premoistened samples of different soils.

<table>
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<th>Soil No.</th>
<th>Olsen method</th>
<th>Bray and Kurtz method</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Initially dry samples</td>
<td>Premoistened samples</td>
</tr>
<tr>
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<td>39.2</td>
<td>35.6</td>
</tr>
<tr>
<td>F-2815</td>
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<td>16.5</td>
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</tr>
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<td>F-2818</td>
<td>31.7</td>
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<td>F-2820</td>
<td>7.5</td>
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<td>F-2821</td>
<td>20.0</td>
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phosphates. The samples in which the extractable P were low by the Bray and Kurtz (1945) method were low also by the Olsen et al. (1954) and Amer (1953) methods.

Table 10 shows the correlation between the yield of P in the plants and the soil P extracted using the Bray and Kurtz (1945) method. The correlation obtained with the initially dry samples was higher than that with the premoistened samples, but both correlation coefficients were low, indicating that the laboratory measurements were of little value in predicting the yield of phosphorus in the plants.

Table 7 shows the result obtained by use of the extracting procedure discussed by Olsen et al. (1954). With this procedure the P obtained from the dry and premoistened samples do not differ greatly from each other. The greatest difference is 5 p.p.m.

Table 10 shows the correlation obtained between soil P extracted by the method of Olsen et al. (1954) and the yield of P in the plants. The correlation is somewhat higher with the premoistened samples than with the dry samples. The correlations obtained by use of this method are higher than the ones discussed previously.

The results obtained by the extraction method of Amer (1953) are shown in Tables 8 and 9. Figures 1 to 6 show some typical curves obtained by plotting P adsorbed by the resin on the Y axis and time along the X axis. The curves may be grouped into four main types on the basis of the shapes of the curves.

Group 1 consists of soils for which the P extraction curves reach a maximum with both the dry and premoistened samples before 72 hours. The soils in this group are Appling fine sandy loam (F-2823) and Carrington
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Table 9. P adsorbed from premoistened samples by Dowex 2 over different lengths of time.

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clay loam (F-2826).

Figure 1 shows the P extraction--time curve for Appling fine sandy loam. The curves for the dry and premoistened samples reach the same maximum although the maximum is attained earlier with the premoistened samples than with the dry samples. In the case of the premoistened samples, the maximum is essentially obtained at 2 hours. With the initially dry sample 48 hours are required to reach the maximum. In the dry treatment no P is extracted by the resin during the first 8 hours. This is not the case with the premoistened treatment, where some P is extracted within the first 5 minutes. The two curves cross at 0.17 hour.

Group 2 consists of soils in which no maxima are reached within 72 hours. The soils in this group are Barnes loam (F-2814), Cinebar silt loam (F-2815), Puyallup silt loam (F-2816), Wibley clay loam (F-2817), Lloyd clay loam (F-2819), Mardin silt loam (F-2821), Moody silty clay (F-2827), Palouse silty clay loam (F-2829), Waukegan silt loam (F-2830), and Norfolk loamy sand (F-2834).

Several different subtypes of curves occur in this group. These subtypes are not mutually exclusive. The first subtype is illustrated by the curves obtained with Palouse silty clay loam. As shown in Figure 2 both curves in the longer times of adsorption exhibited almost a straight line relationship between P adsorbed and time. This behavior was exhibited only by Palouse silty clay loam. The curve representing the dry samples crossed the curve representing the premoistened samples at 1 hour and again at 36 hours. Between 1 and 36 hours more P was extracted from the dry sample than from the premoistened sample treatment.
Figure 2. P adsorbed from Palouse silty clay loam by Dowex 2.
SOIL PHOSPHORUS ADSORBED BY RESIN,
P.P.M. OF SOIL

PALOUSE
SILTY
CLAY
LOAM

PREMOISTENED
DRY

TIME IN HOURS
Another subtype within this group consists of soils in which the rate of P adsorption from initially dry samples definitely decreases with increasing time throughout the 72 hours, and in which the rate of P adsorption from the premoistened samples increases almost linearly with time over the longer time intervals. Soils of this category are Puyallup silt loam (see Figure 3), Cimbar silt loam, Orangeburg sandy loam, Moody silty clay, Lloyd clay loam, and Waukegan silt loam.

The third subtype within group 2 consists of soils in which P adsorbed increased at a decreasing rate with respect to time with both the initially dry and premoistened samples. Soils in this category are Barnes loam, Mibley clay loam, Mardin silt loam, Norfolk loamy sand, and Fox sandy loam (see Figure 4).

Group 3 consists of soils in which the P adsorbed—time curve reaches a maximum within 72 hours with the dry samples but not with the premoistened samples. Soils of this category are Nunn's silty clay (F-2820), Yocemento silt loam (F-2821h), Hufnins silt loam (F-2825), Lloyd clay loam (F-2832), and Walla Walla silt loam (F-2835).

One of the subtypes of soils within this group is Nunn's silty clay (Figure 1). More P was adsorbed from the dry sample than from the premoistened treatment throughout the entire 72-hour extraction period. No P was extracted from the premoistened sample before 0.50 hour; with the longer times of adsorption, P was extracted at a diminishing rate.

In the remainder of the soils in group 3 the P adsorption over the longer time intervals increases almost linearly with the premoistened samples. Figure 5 shows the P adsorbed—time curves for Walla Walla silt
Figure 3. P adsorbed from Puyallup silt loam by Dowex 2.
Figure 4. P adsorbed from Fox sandy loam by Dowex 2.
SOIL PHOSPHORUS ADSORBED BY RESIN,
P.P.M. OF SOIL

TIME IN HOURS

0 10 20 30 40 50

0 10 20 30 40 50

FOX SANDY LOAM

DRY

PREMOISTENED
Figure 5. P adsorbed from Walla Walla silt loam by Dowex 2.
WALLA WALLA SILT LOAM

SOIL PHOSPHOROUS ADSORBED BY RESIN, P.P.M. OF SOIL

TIME IN HOURS

PREMOISTENED

DRY
loan. P extracted from the initially dry soil was greater than that extracted from the premoistened soil during the first 24-hour adsorption interval. After that time the curves crossed, and more P was extracted from the premoistened soil than from the initially dry soil.

Group I consists of soils in which the P adsorbed--time curve reaches a maximum within 72 hours with the premoistened samples but not with the initially dry samples. Soils in this group are Draper loam (F-2818), Davidson clay loam (F-2822), and Declo loam (F-2828). Figure 6 shows the results obtained with Declo loam. More P was extracted from the premoistened soil than from the dry soil throughout the 72 hour period, except for the 2-hour adsorption interval.

Table 10 shows the correlation coefficients between soil P obtained by using Amer's (1953) method and yield of P in the plants grown in the greenhouse. The correlation coefficients were about the same for all time intervals and for initially dry and premoistened samples. A possible explanation for this result is that the amount of P extracted over any given time interval is approximately proportional to the P extracted over any other time interval.

The primary reason for determining the P extracted by the resin over the various time intervals was not to find which extraction time gave the highest correlation, but rather to investigate the applicability of more complex methods of analysis. The simple correlation is based on a mathematical relationship of the form

\[ Y = a + bZ \]

where \( Y \) is the yield of P in the plants grown in the greenhouse, \( Z \) is the P
Figure 6. P adsorbed from Declo loam by Dowex 2.

SOIL PHOSPHORUS ADSORBED BY RESIN,
P.P.M. OF SOIL

TIME IN HOURS

DECLO LOAM

DRY
PREMOISTENED
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<td>23:00</td>
<td>23:00</td>
<td></td>
</tr>
</tbody>
</table>

*Zero distribution (extrapolated)
*10 grams solid in 50 ml
*20 grams solid in 50 ml
*Phosphate potential
*Free and Aqueous

**Table 10.** Correlation coefficient (r) between P extracted from solutes in the soil in the greenhouse by different methods and the yield of P in plant grown on soil.
extracted from the soil, and \( a \) and \( b \) are constants. The more complex relationship has the form

\[
Y = a + b_1Z_1 + b_2Z_2 + \ldots + b_nZ_n
\]

where \( Y \) is the yield of \( P \) in the plants as before, \( Z_1, Z_2, \ldots Z_n \) are different quantities of soil \( P \), and \( a \) and \( b_1, b_2, \ldots b_n \) are constants.

Two different approaches of the more complex type were tried. In the first the curves were segmented into different time intervals, on the basis that \( P \) extracted during the early part of the extraction period might have greater availability to plants than \( P \) extracted during the latter part. Accordingly \( Z_1, Z_2, Z_3, \) and \( Z_4 \) were allowed to represent, respectively, the amounts of \( P \) extracted during the time intervals 0.0 to 0.25 hour, 0.25 to 2 hours, 2 to 24 hours, and 24 to 72 hours. These intervals were chosen on the basis of rate changes within the total curves obtained for the 22 soils.

A multiple correlation of these variables with plant \( P \) in milligrams was then obtained. The results are described in Tables 11 and 12. When the data were treated in this fashion, the \( b \) values for some of the variables were found not to differ significantly from zero. In the case of the dry samples, only \( b_2 \) and \( b_4 \) differed significantly from zero. With the premoistened samples only \( b_4 \) proved to be significantly different from zero. These findings are indicated in the upper part of the tables. Because some of the variables proved not to be significant in estimating plant \( P \), the data were again rearranged, this time with two variables. For the dry samples, the first variable was obtained by adding \( Z_1 \) and \( Z_2 \), and the second variable was obtained by adding \( Z_3 \) and \( Z_4 \). For the
Table 11. Multiple correlation coefficients (R) and partial correlation coefficients (r_{ij}) between yield of P in plants (Y) and P removed from initially dry samples of soil during different intervals of time (Z).

<table>
<thead>
<tr>
<th></th>
<th>$Z_1$</th>
<th>$Z_2$</th>
<th>$Z_3$</th>
<th>$Z_4$</th>
<th>Y</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{1j}$</td>
<td>1.00</td>
<td>0.90***</td>
<td>0.79***</td>
<td>0.69***</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>$r_{2j}$</td>
<td>1.00</td>
<td>0.60***</td>
<td>0.56***</td>
<td>0.81**</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{3j}$</td>
<td>1.00</td>
<td>0.62</td>
<td>0.84***</td>
<td>0.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{4j}$</td>
<td>1.00</td>
<td></td>
<td>0.86***</td>
<td>0.68*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$Z_1 + Z_2$</th>
<th>$Z_3 + Z_4$</th>
<th>Y</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{1j}$</td>
<td>1.00</td>
<td>0.73***</td>
<td>0.80***</td>
<td></td>
</tr>
<tr>
<td>$r_{2j}$</td>
<td>1.00</td>
<td>0.67</td>
<td></td>
<td>0.81***</td>
</tr>
</tbody>
</table>

*Significant at 10 per cent level
**Significant at 5 per cent level
***Significant at 1 per cent level
Table 12. Multiple correlation coefficients ($R$) and partial correlation coefficients ($r_{ij}$) between yield of P in plants ($Y$) and P removed from premoistened samples of soil during different intervals of time ($Z_i$).

<table>
<thead>
<tr>
<th>$Z_1$</th>
<th>$Z_2$</th>
<th>$Z_3$</th>
<th>$Z_4$</th>
<th>$Y$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{1j}$</td>
<td>1.00</td>
<td>0.63***</td>
<td>0.91***</td>
<td>0.84***</td>
<td>0.77</td>
</tr>
<tr>
<td>$r_{2j}$</td>
<td>1.00</td>
<td>0.66***</td>
<td>0.53**</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>$r_{3j}$</td>
<td>1.00</td>
<td>0.92***</td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{4j}$</td>
<td>1.00</td>
<td>0.86***</td>
<td>0.87***</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$Z_1$ * $Z_2$ * $Z_3$</th>
<th>$Z_4$</th>
<th>$Y$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{1j}$</td>
<td>1.00</td>
<td>0.88***</td>
<td>0.77</td>
</tr>
<tr>
<td>$r_{2j}$</td>
<td>1.00</td>
<td>0.86***</td>
<td>0.86***</td>
</tr>
</tbody>
</table>

**Significant at 5 per cent level
***Significant at 1 per cent level
premoistened samples the first variable consisted of the sums of \( z_1, z_2, \) and \( z_3 \). The second variable was \( z_4 \). Multiple correlation tests indicated that in each instance only one of the new variables was of significant value in predicting \( y \), independently of the other. The multiple correlation coefficients \((R)\) were slightly lower than the ones obtained with all four variables, but nevertheless exceeded the simple correlations.

The second approach of the more complex type was based on the procedure described by Amer et al. (1955) for representing a single extraction curve as the sum of a group of simultaneous first-order reactions. Amer et al. (1955) found only three simultaneous reactions in the soils they examined. The shortest time interval over which they made measurements was 0.25 hour in length. In the present investigation shorter time intervals were employed, and as a result some soils were found to produce extraction curves that could be broken down into four simultaneous reactions. Thus in the present work the general equation of the extraction curve may be represented by the form

\[
P_r = P_\infty - (C_3 \times 10^{-k_3 t} + C_2 \times 10^{-k_2 t} + C_1 \times 10^{-k_1 t} + C_0 \times 10^{-k_0 t}),
\]

where \( P_r \) signifies the amount of P adsorbed by the Dowex 2 in time \( t \), and \( P_\infty \) is the limiting amount of \( P \) adsorbed by the Dowex 2 as \( t \) approaches infinity. \( C_3, C_2, C_1, \) and \( C_0 \) refer to the maximum amount of \( P \) that can be adsorbed by Dowex 2 in the slow, first intermediate, second intermediate, and fast reactions, respectively. The symbols \( k_3, k_2, k_1, \) and \( k_0 \) refer to the slopes obtained for the slow, first intermediate, second intermediate, and fast reactions, respectively.

The parameters of the foregoing equation for the individual soils
and treatments may be found in Tables 13 and 14. The values of $P_2$ calculated using these parameters agree closely with the observed data, thus indicating that a satisfactory fit has been obtained.

Of the $h_4$ curves analyzed, some consisted of four reactions, some of three, some of two, and some of one. The fast reaction in all cases was essentially completed within the first 5 minutes. The second intermediate reaction was essentially completed in a time interval greater than 5 minutes but less than 12 hours. The first intermediate reaction was essentially completed within a time interval greater than 12 hours but less than 72 hours, and the slow reaction was essentially completed at some time beyond 72 hours.

In the correlation analysis the $G$ values obtained for the various reactions were employed as the independent variables and the yield of $P$ in the plants grown on the soils in the greenhouse was employed as the dependent variable. The results are summarized in Tables 15 and 16. The upper part of the tables gives the results with the independent variables taken individually. The lower parts show the results obtained when the independent variables were grouped (by addition) in different ways.

The $R$ values in Table 15 are no greater than the $r$ values obtained in Table 10, which shows that no improvement in prediction value resulted from applying the complex method of analysis to data obtained on the initially dry samples. The $R$ values in Table 16 obtained with the four independent variables taken individually or grouped into three independent variables were the highest of all the correlations obtained in this investigation. Their superiority over the simple correlations in Table 10 and the multiple correlations in Table 12 suggest that the curve analysis procedure
<table>
<thead>
<tr>
<th>Parameter</th>
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<th>0.0</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>7.0</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 12: Parameter of P adsorbed - time curves for water samples of different soils.
Table 14. Parameters of P adsorbed--time curves for premoistened samples of different soils.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>$P_\infty$</th>
<th>$C_3$</th>
<th>$k_3$</th>
<th>$C_2$</th>
<th>$k_2$</th>
<th>$C_1$</th>
<th>$k_1$</th>
<th>$C_0$</th>
<th>$k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-2811h</td>
<td>61.0</td>
<td>35.1</td>
<td>0.016</td>
<td>8.7</td>
<td>0.23</td>
<td>0.0</td>
<td>0.0</td>
<td>17.2</td>
<td>5.0</td>
</tr>
<tr>
<td>F-2815</td>
<td>6.1</td>
<td>4.4</td>
<td>0.008</td>
<td>1.6</td>
<td>0.75</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>2.9</td>
</tr>
<tr>
<td>F-2816</td>
<td>60.2</td>
<td>12.2</td>
<td>0.010</td>
<td>9.4</td>
<td>0.30</td>
<td>0.0</td>
<td>0.0</td>
<td>8.6</td>
<td>15.9</td>
</tr>
<tr>
<td>F-2817</td>
<td>62.3</td>
<td>30.7</td>
<td>0.007</td>
<td>21.3</td>
<td>0.16</td>
<td>1.0</td>
<td>0.38</td>
<td>9.3</td>
<td>24.6</td>
</tr>
<tr>
<td>F-2818</td>
<td>41.9</td>
<td>18.1</td>
<td>0.052</td>
<td>11.0</td>
<td>0.15</td>
<td>2.8</td>
<td>5.18</td>
<td>10.0</td>
<td>7.4</td>
</tr>
<tr>
<td>F-2819</td>
<td>17.4</td>
<td>11.2</td>
<td>0.011</td>
<td>3.2</td>
<td>0.07</td>
<td>2.0</td>
<td>2.51</td>
<td>1.1</td>
<td>18.5</td>
</tr>
<tr>
<td>F-2820</td>
<td>17.5</td>
<td>12.1</td>
<td>0.021</td>
<td>4.0</td>
<td>0.22</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4</td>
<td>2.5</td>
</tr>
<tr>
<td>F-2821</td>
<td>24.2</td>
<td>18.1</td>
<td>0.020</td>
<td>1.9</td>
<td>1.11</td>
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<td>0.0</td>
<td>4.3</td>
<td>16.7</td>
</tr>
<tr>
<td>F-2822</td>
<td>9.2</td>
<td>7.8</td>
<td>0.017</td>
<td>0.0</td>
<td>0.00</td>
<td>0.0</td>
<td>0.0</td>
<td>1.5</td>
<td>3.4</td>
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<tr>
<td>F-2823</td>
<td>2.6</td>
<td>2.6</td>
<td>0.000</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>F-2824</td>
<td>43.6</td>
<td>28.5</td>
<td>0.016</td>
<td>6.3</td>
<td>0.20</td>
<td>0.0</td>
<td>0.0</td>
<td>8.8</td>
<td>20.4</td>
</tr>
<tr>
<td>F-2825</td>
<td>108.2</td>
<td>63.0</td>
<td>0.000</td>
<td>25.1</td>
<td>0.32</td>
<td>7.9</td>
<td>2.37</td>
<td>12.2</td>
<td>9.5</td>
</tr>
<tr>
<td>F-2826</td>
<td>5.0</td>
<td>2.5</td>
<td>0.050</td>
<td>1.9</td>
<td>2.10</td>
<td>0.0</td>
<td>0.0</td>
<td>0.6</td>
<td>10.0</td>
</tr>
<tr>
<td>F-2827</td>
<td>20.4</td>
<td>12.1</td>
<td>0.009</td>
<td>4.7</td>
<td>0.09</td>
<td>0.0</td>
<td>0.0</td>
<td>3.6</td>
<td>0.5</td>
</tr>
<tr>
<td>F-2828</td>
<td>27.5</td>
<td>15.0</td>
<td>0.051</td>
<td>8.5</td>
<td>2.50</td>
<td>0.0</td>
<td>0.0</td>
<td>4.0</td>
<td>10.0</td>
</tr>
<tr>
<td>F-2829</td>
<td>92.9</td>
<td>59.6</td>
<td>0.011</td>
<td>7.5</td>
<td>0.35</td>
<td>0.0</td>
<td>0.0</td>
<td>25.8</td>
<td>19.5</td>
</tr>
<tr>
<td>F-2830</td>
<td>138.7</td>
<td>75.0</td>
<td>0.003</td>
<td>22.0</td>
<td>0.10</td>
<td>2.6</td>
<td>1.26</td>
<td>38.9</td>
<td>21.8</td>
</tr>
<tr>
<td>F-2831</td>
<td>48.6</td>
<td>33.1</td>
<td>0.008</td>
<td>8.2</td>
<td>0.11</td>
<td>1.6</td>
<td>0.57</td>
<td>8.4</td>
<td>11.3</td>
</tr>
<tr>
<td>F-2832</td>
<td>43.9</td>
<td>18.1</td>
<td>0.003</td>
<td>3.5</td>
<td>0.22</td>
<td>1.7</td>
<td>1.60</td>
<td>0.7</td>
<td>25.4</td>
</tr>
<tr>
<td>F-2833</td>
<td>27.4</td>
<td>15.9</td>
<td>0.008</td>
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<td>0.0</td>
<td>0.0</td>
<td>6.6</td>
<td>14.1</td>
</tr>
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<td>18.1</td>
<td>0.037</td>
<td>7.2</td>
<td>1.57</td>
<td>0.0</td>
<td>0.0</td>
<td>10.6</td>
<td>9.7</td>
</tr>
<tr>
<td>F-2835</td>
<td>77.7</td>
<td>50.1</td>
<td>0.005</td>
<td>17.9</td>
<td>0.23</td>
<td>0.0</td>
<td>0.0</td>
<td>9.7</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Table 15. Multiple correlation coefficients (R) and partial correlation coefficients (r_{1j}) between yield of P in plants (Y) and C values calculated from P extracted by Dowex 2 for initially dry samples from different soils.

<table>
<thead>
<tr>
<th></th>
<th>C_3</th>
<th>C_2</th>
<th>C_1</th>
<th>C_0</th>
<th>Y</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>r_{1j}</td>
<td>1.00</td>
<td>0.55**</td>
<td>0.58***</td>
<td>0.42</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>r_{2j}</td>
<td>1.00</td>
<td>0.24</td>
<td>0.73***</td>
<td>0.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{3j}</td>
<td>1.00</td>
<td>0.33</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{4j}</td>
<td>1.00</td>
<td>0.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>C_3</th>
<th>C_2 + C_1</th>
<th>C_0</th>
<th>Y</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>r_{1j}</td>
<td>1.00</td>
<td>0.71***</td>
<td>0.42</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>r_{2j}</td>
<td>1.00</td>
<td>0.78***</td>
<td>0.77*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_{3j}</td>
<td>1.00</td>
<td>0.62</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>C_3 + C_2</th>
<th>C_1 + C_0</th>
<th>Y</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>r_{1j}</td>
<td>1.00</td>
<td>0.64***</td>
<td>0.73**</td>
<td></td>
</tr>
<tr>
<td>r_{2j}</td>
<td>1.00</td>
<td>0.70**</td>
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<td></td>
</tr>
</tbody>
</table>

#Significant at 10 per cent level
**Significant at 5 per cent level
***Significant at 1 per cent level
Table 16. Multiple correlation coefficients ($R$) and partial correlation coefficients ($r_{ij}$) between yield of P in plants ($Y$) and C values calculated from P extracted by Dowex 2 for premoistened samples from different soils.

<table>
<thead>
<tr>
<th></th>
<th>$C_3$</th>
<th>$C_2$</th>
<th>$C_1$</th>
<th>$C_0$</th>
<th>$Y$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{1j}$</td>
<td>1.00</td>
<td>0.74***</td>
<td>0.20</td>
<td>0.81***</td>
<td>0.83****</td>
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</tr>
<tr>
<td>$r_{2j}$</td>
<td>1.00</td>
<td>-0.01</td>
<td>0.60***</td>
<td>0.47**</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{3j}$</td>
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<td>0.06</td>
<td>0.02</td>
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<td></td>
</tr>
<tr>
<td>$r_{4j}$</td>
<td>1.00</td>
<td>0.80*</td>
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<td></td>
<td>0.90***</td>
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</table>

<table>
<thead>
<tr>
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<th>$C_3$</th>
<th>$C_2 + C_1$</th>
<th>$C_0$</th>
<th>$Y$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{1j}$</td>
<td>1.00</td>
<td>0.76***</td>
<td>0.81***</td>
<td>0.83****</td>
<td></td>
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<td>$r_{2j}$</td>
<td>1.00</td>
<td>0.59***</td>
<td>0.45**</td>
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<td></td>
</tr>
<tr>
<td>$r_{3j}$</td>
<td>1.00</td>
<td>0.80**</td>
<td></td>
<td></td>
<td>0.90***</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$C_3 + C_2$</th>
<th>$C_1 + C_0$</th>
<th>$Y$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
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<td>$r_{1j}$</td>
<td>1.00</td>
<td>0.79***</td>
<td>0.77**</td>
<td></td>
</tr>
<tr>
<td>$r_{2j}$</td>
<td>1.00</td>
<td>0.75*</td>
<td></td>
<td>0.81***</td>
</tr>
</tbody>
</table>

*Significant at 10 per cent level  
**Significant at 5 per cent level  
***Significant at 1 per cent level  
****Significant at 0.1 per cent level
for obtaining the independent variables enhances the precision with which
the yield of $P$ in plants can be predicted. Their superiority over the
multiple correlations in Table 15 suggests that premoistened soils are
more suitable than initially dry soils for predicting the yield of $P$
in plants grown on the soils.
SUMMARY AND CONCLUSIONS

The research described in this thesis was concerned with a comparison of the value of different methods of soil phosphorus extraction and different methods of calculation for predicting the yield of phosphorus in plants grown in the greenhouse. The main objective of the work was to evaluate an anion-exchange method developed by Amer, by comparing it with other methods in current use. The basis of comparison was the correlation coefficients between the yield of P in plants grown on a group of soils and the results of laboratory measurements made by the various methods on the same soils.

Since most methods will give results that correlate well with plant response if the range in the properties of the soils is restricted sufficiently, a group of 22 soils with widely divergent properties was selected from different regions of the United States as a means of providing a rigorous test of the methods. The soils were selected from those used in the 1951 and 1952 cooperative uniform P experiments carried out nationally. The soils were selected to produce a poor correlation between Fried and Dean A values and soil P extracted by method 1A of Bray and Kurtz.

The experimental technique utilized in the greenhouse was designed to make P the limiting factor by adding ample quantities of nutrients other than P, and restricting the quantity of soil to 400 grams in a mixture with 3600 grams of quartz sand. Sorghum (variety Red Bine 60) was used as a test plant. The plants were allowed to grow until all were strongly deficient in P. The plants were then harvested and analyzed.
for P.

Four extraction procedures were used: (1) the buffered 0.5 M NaHCO₃ extraction method of Olsen et al., (2) the 0.1 N HCl + 0.03 N NH₄F extracting procedure of Bray and Kurtz, (3) the 10⁻² M CaCl₂ extracting method of Schofield, as described by Aslyng, and (4) the anion-exchange resin method of Amer. Each method was employed with soil samples that were dry initially, and with soil samples that had been adjusted to moisture equivalent, and allowed to incubate at room temperature for a period of 7 days.

The method suggested by Aslyng involves the use of two different weights of soil in a fixed volume of 10⁻² M CaCl₂. The molar phosphate concentration in solution with the different quantities of soil was plotted against the reciprocal of the weight of soil to obtain a straight line that was extended to the Y axis. The intersection of this line with the Y axis gave the molar phosphate concentration at "zero dilution." From this value, together with knowledge of the pH and the Ca activity in the CaCl₂ solution, the phosphate potential (2pCa⁺ pH₂PO₄⁻) was calculated.

Schofield stated that perhaps it is not the amount of available phosphate in a soil that primarily controls the uptake of P by plants, but the work needed to withdraw it from the soil. Hence he conceived of the phosphate potential or free-energy concept of plant utilization of soil P. Aslyng stated that this potential should give a good estimate of soil P available to plants. The correlations between the phosphate potential and the yield of P indicated, however, that essentially no relationship existed between the two sets of data; the correlations were
\( r = 0.07 \) and \( r = -0.08 \) for the dry and premoistened samples, respectively. Therefore, it may be concluded that this method was not able to withstand the rigorous test presented by using soils that have widely divergent properties. The linear correlations (\( r \)) obtained between P extracted for 20- and 40-gram weights of soil and the yield of P in milligrams were 0.61 and 0.63 respectively for the dry treatment and 0.64 and 0.59 respectively for the premoistened treatment. The correlations obtained between P extracted at "zero dilution" and the yield of P were 0.30 and 0.44 for the dry and premoistened treatments respectively.

The correlations between yield of P and soil P extracted by the Bray and Kurtz method were low; the correlation coefficients were \( r = 0.38 \) and \( r = 0.14 \) for initially dry and premoistened samples, respectively. The unduly large amount of P extracted from some of the alkaline soils appeared to be primarily responsible for the low correlations.

Correlations between yield of P in the plants and soil P extracted by the 0.5 M NaHCO\(_3\) method of Olsen et al. were higher than those described above, and were essentially the same with both the dry samples and the premoistened samples (\( r = 0.74, r = 0.77 \), respectively).

The method of Amer involved extracting P from soils by a strong-base type anion-exchange resin (Dowex 2) employed in chloride-form. The simple correlations between yield of P in the plants and P extracted from the soils over different lengths of time ranging from 5 minutes to 72 hours were about \( r = 0.78 \) and \( r = 0.79 \) with the dry and premoistened samples, respectively.

Two more complex types of correlations were investigated with the
Amer method. In the first of these the P adsorbed from the soil by the resin was classified into different categories according to the time interval during which adsorption occurred. The intervals employed were 0.0 to 0.25 hour, 0.25 to 2 hours, 2 to 24 hours, and 24 to 72 hours. The P extracted during various time intervals was correlated with the yield of P in the plants by the method of multiple linear correlation. The multiple correlation coefficients \( R \) obtained by arranging the data in this fashion were 0.86 and 0.87, for the dry and premoistened samples, respectively. These values are higher than the simple correlations described above.

The second multiple correlation analysis was made on the basis of quantities of soil P found in a different way. The overall P extraction-time curve was broken down into component curves on the assumption that the process of P adsorption by the resin under the conditions found in the soil is first order with respect to P. From one to four separate first-order reactions for each soil were found in this way, each reaction being characterized by a rate and by a maximum or limiting value that is approached as the time increases indefinitely. The limiting values were classified into four categories according to rate, and a multiple linear correlation was made between the limiting values as independent variables and the yield of P in the plants as the dependent variable. The multiple correlation coefficient was found to be \( R = 0.79 \) where the independent variables were derived from analyses on samples of dry soil, and \( R = 0.90 \) where the independent variables were derived from the samples of premoistened soil. Although the former is no higher than the simple correlation coefficients
obtained with the P extracted during the fixed length of time; the latter is the highest of all the correlation coefficients encountered in this investigation.

The results show that the yield of P in plants grown on a group of widely different soils was predicted more precisely by the Amer anion-exchange resin method for estimating soil P availability than by any of the other methods investigated. Predictions from measurements made by the Amer method appear to be somewhat improved by the use of premoistened soil samples instead of dry samples, and by breaking down the overall P extraction vs. time curve into a series of separate first-order reactions.
LITERATURE CITED


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ACNOWLEDGEMENTS

The author wishes to express her sincere appreciation to Dr. C. A. Black for his suggestions during the investigation, and for his helpful advice during the preparation of the manuscript.

The author is indebted to the following agronomists for having provided soils for this investigation: Dr. L. E. Ensminger of Alabama; Dr. H. D. Morris of Georgia; Dr. J. V. Jordon and Dr. L. I. Painter of Idaho; Dr. P. L. Brown of Kansas; Dr. Kirk Lawton of Michigan; Dr. A. C. Caldwell of Minnesota; Dr. J. C. Hide, Mr. T. S. Aasheim, and Mr. P. Pederson of Montana; Prof. R. A. Olson of Nebraska; Dr. A. Mehlich of North Carolina; Dr. D. J. Lathwell of New York; Dr. L. O. Fine of South Dakota; Dr. H. B. Peterson of Utah; Dr. C. L. Rich of Virginia; and Dr. R. L. Hausenbuiller, Dr. H. M. Reisenauer, and Dr. W. P. Mortensen of Washington.

The author also wishes to thank Miss L. D. Swain and Mr. G. L. Cowgill for their assistance in the laboratory.