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Parker F. Pratt
SOLUBILITY AND PHYSIOLOGICAL AVAILABILITY OF PHOSPHATES IN SODIUM AND CALCIUM SYSTEMS

by

Parker F. Pratt

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Parker F. Pratt
TABLE OF CONTENTS

I. INTRODUCTION .................................................. 1

II. REVIEW OF LITERATURE .......................................... 2

   A. Solubility of Phosphates .................................... 2
      1. Solubility in calcium systems ............................ 2
      2. Solubility in sodium systems ............................ 4
      3. The importance of anion exchange ....................... 5

   B. Physiological Availability ................................ 5
      1. In solution cultures .................................. 5
      2. Physiological availability of $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ ions .......................... 7

III. THE SOLUBILITY OF PHOSPHATES IN SUSPENSIONS OF CLAY WITH DIFFERENT DEGREES OF SODIUM AND CAJCIUM SATURATION .......................... 10

   A. Method ................................................... 10
   B. Results .................................................. 11

IV. THE PERMEABILITY OF PHOSPHORUS TO ROOTS OF BEAN AND TOMATO PLANTS OVER A pH RANGE FROM FOUR TO NINE ...................................... 14

   A. Method ................................................... 14
   B. Results .................................................. 16
      1. pH relationships .................................... 16
      2. Concentration relationships .......................... 20

V. DISCUSSION .................................................... 24

VI. SUMMARY ...................................................... 27

VII. Literature Cited ............................................. 28
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PHOSPHATES IN SODIUM AND CALCIUM SYSTEMS

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INTRODUCTION

One of the principal fertility problems of calcareous soils is the lack of available phosphates. The factors which control this availability are not completely understood. One hindrance to the solution of the problems involved results from confusion of the concepts of solubility and availability. Availability is the net effect of the chemical state of a plant nutrient element and the ability of the plant to utilize the forms of the element present under the existing chemical and physical environmental conditions. In this paper, the term solubility will be used to designate the chemical solubility of an element in water or in specified extracting reagents. The term physiological availability will be used to designate the ability of the plant to assimilate the soluble forms of the element, and the term net availability will be used to designate the net effect of chemical solubility and physiological availability.

These limited definitions seem justified in this study because the sodium and calcium systems investigated are alkaline and plants growing in these systems would probably be largely limited to soluble phosphates. Solubility is known to be one of the main factors which control availability of phosphates, but there is no conclusive evidence as to the importance of physiological availability.

Some investigators (26,13)\(^1\) have produced evidence which they claim supports the hypothesis that the \(\text{H}_2\text{PO}_4^-\) ion is the only phosphate ion

\(^1\)Numbers in parenthesis refer to "Literature Cited".
absorbed by plants. Since the relative concentration of this ion decreases as the pH increases above neutrality, they then conclude that physiological availability is largely a function of pH. Other investigators (41, 7) have produced evidence which suggests that solubility is probably the only factor which limits the availability of phosphates in alkaline and calcareous soils. The purpose of this study is to add evidence which will help clarify the relative importance of solubility and physiological availability of phosphates in sodium and calcium soils.

REVIEW OF LITERATURE

Solubility of Phosphates

Solubility in calcium systems

The solubility of phosphates in calcium dominated systems is very low, especially in alkaline conditions. Bucher (13), from purely theoretical treatment, has calculated that, in the system CaHPO₄-CaCO₃-H₂CO₃, the phosphate concentration at equilibrium is directly proportional to the hydrogen ion concentration and inversely proportional to the calcium ion concentration. The results of this theoretical treatment are in agreement with the work of Teakle (40), who found that, in a calcium dominated soil system, the main factors in the depression of the solubility of phosphates are calcium ion concentration and hydroxyl ion concentration. He also found that if the hydroxyl ion concentration was increased, without additions of calcium ion, the solubility of phosphates is increased. With various cations in the soil, Teakle found that those soils which contained calcium were the only ones which showed a decrease in soluble phosphates as the pH was raised above 7. Bennet, Perkins, and King (8) found that calcium oxide was more effective than calcium carbonate in reducing phosphate solubility. They explained this on the basis of the low solubility of calcium carbonate compared to the solubility of
calcium oxide. They also found that when calcium oxide was added, the minimum solubility of phosphates was reached at a pH of 7.36 and remained at the same level as the pH was increased.

Cameron and Bell (14), in 1907, made an extensive study of soil phosphates. They stated that soil phosphates, whether solid solutions or definite chemical compounds, are of such a nature as to give very small quantities of soluble phosphates. They suggested that soil phosphates are of the nature of hydroxyapatite or carbonate apatite. Bassett (5) concluded that since the soil reaction range is well within the range in which hydroxyapatite is the stable calcium phosphate, this form of phosphate is the only one that can exist permanently in the soil. McGeorge and Breaseale (29) say that the low solubility of phosphates in calcareous soils results from the formation of carbonate apatite, which has the formula $3Ca_3(PO_4)_2\cdot CaCO_3$. They state that carbonate apatite is the least soluble form of phosphate in calcareous soils, and that its solubility is governed by the common ion calcium and the solid phase calcium carbonate. McGeorge and Breaseale assign a definite structural formula to carbonate apatite. Kramer and Shear (23) point out that it is incorrect to assign a definite formula to carbonate apatite. Logan and Taylor (25) say that the composition of carbonate apatite or hydroxyapatite is not constant and depends on the concentration of such ions as $Ca^{++}$, $HPO_4^{2-}$, $OH^-$, $CO_3^{2-}$ in the solution at the time of precipitation. Eisenberger, Lehrman and Turner (18) suggest that the apatites are not stoichiometric compounds, but types of crystal lattices which form continuous series of solid solutions. They cite the apatite family as an example of an ionic crystal capable of dissolving a large variety of components, in large or small proportions, without fundamental change in lattice.

Ensminger and Larson (19) in studying crop response to phosphate
fertilization found that soils containing 0.5 to 1.0 percent lime showed least response, soils containing 1.0 to 2.0 percent lime showed medium response, soils containing 2 percent or more lime showed good response, and that there was no increase in response as the percent lime increased above 2 percent. This suggests that 2 percent lime may be just as effective as higher percentages in reducing the soluble phosphates in soils.

**Solubility in sodium systems**

The solubility of phosphates in soil systems dominated by exchangeable sodium or sodium carbonate is much higher than in calcium dominated soil systems. In a sodium system there is a decrease in calcium ion concentration and a release of phosphates into the soil solution. This decrease of calcium ion concentration and increase in soluble phosphorus is well illustrated by the work of Thorne (41,42) who found that, when the exchangeable sodium increased, the calcium content of plants decreased and the phosphorus content increased. Bower and Turk (9) report that naturally occurring soils, high in exchangeable sodium, may not furnish an adequate supply of calcium to plants even though calcium carbonate is present. Teakle (40) found that removal of the calcium ions from the soil solution with oxalate caused a 20 to 50 fold increase in soluble phosphates. Williams (44) conducted an examination of the solubility of various phosphatic materials and found that the only types which can be placed in the sodium hydroxide insoluble category are those having an apatite structure. Gardner and Kelly (20) say that because of the low concentration of calcium ion in sodium soils, the rate of formation of carbonate apatite is greatly reduced if not stopped completely, and therefore soluble phosphates accumulate. Kobe and Doumani (22) found that the solubility of calcium phosphates in sodium carbonate solutions increased...
as the concentration of sodium carbonate increased, and that grinding the phosphates increased their solubility. Other investigators (36, 26, 28, 8) agree that phosphates are more soluble in sodium than in calcium dominated soils.

The importance of anion exchange

In sodium and calcium dominated soils, anion exchange is not an important factor in reducing the solubility of phosphates. Stout (39), working with kaolinite clay, found that the ability of this clay to fix phosphate as an exchangeable anion was greatly reduced in alkaline solutions. Stout reports that the phosphate fixed at pH values of 7, 8, 9, 10, and 11 was 14.7, 5.9, 4.3, 3.2, and 0 percent respectively of the amount fixed at pH 5. This is in agreement with the results obtained by Murphy (30) who conducted a similar investigation with the same type clay. Dean and Rubins (17) state that the phosphates retained by soils as exchangeable anions are almost completely removed by hydroxide solutions. Ravikovitch (36) found that, when calcium hydroxide or sodium hydroxide is added to an acid soil, the exchange reaction takes place in two steps. The first step is a cationic reaction which proceeds until the hydrogen ions are completely removed from the clay. When there are no hydrogen ions being released to unite with the hydroxyl ions being added, the second step begins. This step consists of an anionic exchange in which hydroxyl ions replace phosphate ions held as exchangeable ions. If calcium hydroxide is the base added, the released phosphates are precipitated as calcium phosphates. If sodium hydroxide is the base added, the released phosphates will remain in solution.

Physiological Availability

In solution cultures

The difficulty of measuring the physiological availability of nutrients
in such a complex system as the soil, has led to the use of solution cultures for such studies. Results obtained by the study of solution cultures cannot, in all cases, be applied directly to the soil. But with phosphates in calcareous and alkaline soils, where plants are probably limited to soluble phosphates, there should be some application.

The effect of pH on the physiological availability of phosphates in solution cultures has been studied by several investigators. Arnon, Fratzke, and Johnson (4) report the uptake of phosphates by lettuce, tomato and bermuda grass plants from solution over a pH range from 3 to 9. Plants were grown in a balanced nutrient solution until they were 5 weeks old. They were then placed in nutrient solutions in which the pH was controlled by additions of sodium hydroxide or sulfuric acid. The phosphate concentration was held at the same level in all solutions. The uptake of phosphates was measured for a period of 92 hours. Tomato and bermuda grass plants showed maximum absorption of phosphates at pH 7. Lettuce showed maximum absorption at pH 6. For all plants there was a significant decrease in phosphate uptake at pH levels above 7. At pH 8 the uptake was approximately 55 percent of the maximum uptake. At pH 9 the uptake was 7 percent of the maximum for tomato plants, 26 percent of the maximum for lettuce, and 12 percent of the maximum for bermuda grass. Arnon, Fratzke and Johnson conclude that, providing a supply of soluble phosphates is maintained, plants will be able to absorb adequate amounts of phosphates over a pH range from 4 to 8. This suggests that within this pH range the physiological availability is not as important as solubility in the control of phosphate availability.

McGeorge (26) reports that, with wheat plants in solution cultures, phosphates are absorbed most readily at pH values close to neutrality, less readily at acid reactions, and least readily at pH values of 3 to 9.
Tidmore (43) reports the absorption of phosphates from solution cultures by wheat and corn plants at pH values of 4, 5, 6, and 7.5. There was no appreciable difference in the absorption at pH values of 4, 5, and 6. But at pH 7.5 the absorption was significantly lower than at pH 6.

Breazeale (10) reports a decrease in phosphorus content of rye plants with increase in sodium carbonate content of solution cultures. An increase in sodium carbonate concentration is comparable to an increase in pH.

Samokhvalov (37) reports the absorption of phosphates from solution cultures by wheat and vetch. The highest absorption was at pH 7. At pH 5 and 8.4 the absorption was less than at pH 7.

Breazeale and McGeorge (11) conducted solution culture investigations in which the pH and phosphate concentration were determined every hour. From the results of this investigation, they concluded that phosphates in alkaline solutions are not absorbed by plants until the pH of the solutions has been reduced to at least 7.6. This report is contrary to the results obtained by Arnon, Fratzke, and Johnson (4), and Samokhvalov (37), who report phosphate absorption at pH values above 6.

Physiological availability of \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) ions

Duehrer (18), using the dissociation constants of phosphoric acid, has calculated the relative concentration of various orthophosphate ions over a pH range from 4 to 9. Figure 1 shows the relative concentrations of \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) ions at various pH values. Concentrations of \( \text{H}_3\text{PO}_4 \) and \( \text{PO}_4^{3-} \) are too small to be represented graphically. The positions of \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) curves depend mainly on the second dissociation constant of phosphoric acid. There is considerable variation among the values reported in the literature for this constant. Table I gives a list of values found. The solid line curves in Fig. 1 are based on calculations using a value of \( 1.95 \times 10^{-7} \), taken from Abbott and Bray (1), for the
Figure 1. The relative concentrations of $H_2PO_4^-$ and $HPO_4^{2-}$ ions at different pH values. Solid curves based on the highest value (1), broken curves based on the lowest value (34) found for the second dissociation constant of $H_3PO_4$. 
second dissociation constant of phosphoric acid, which is the highest value found; and the broken line curves are based on calculations using a value of $5.85 \times 10^{-8}$ taken from Prideaux and Ward (34), which is the lowest value found. Buehrer used the value reported by Abbott and Bray, which is much higher than any of the other values reported. The relative concentrations of the $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ ions are thus a function of pH, and the correct values probably lie within the range shaded in Fig. 1. The pH value at which the relative concentration of $\text{H}_2\text{PO}_4^-$ ion becomes small depends on the second dissociation constant of phosphoric acid.

McGeorge (26) concludes that the $\text{H}_2\text{PO}_4^-$ ion is the phosphate ion utilized by plants. He states that, since $\text{H}_2\text{PO}_4^-$ is the dominant phosphate ion in the pH range of plant sap, and since plants exist on lower concentrations of phosphates in slightly acid soils, plants prefer this ion for nutritional purposes. He states that physiological availability of phosphates is thus largely a matter of pH. Buehrer (13) states that alkaline solutions may affect the membranes of roots in such a way that they cannot readily absorb phosphates, but that it is equally convincing to argue that the roots don’t readily absorb phosphates from alkaline solutions because of the low concentration of $\text{H}_2\text{PO}_4^-$ ions.

Thorne (41) found a positive correlation between the pH of synthetic

### Table I. Values given for the second dissociation constant of phosphoric acid

<table>
<thead>
<tr>
<th>Source of Information</th>
<th>Value Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbott and Bray (1)</td>
<td>$1.95 \times 10^{-7}$</td>
</tr>
<tr>
<td>Britton (12)</td>
<td>$1.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>Sima (33)</td>
<td>$9.55 \times 10^{-8}$ at 25°C</td>
</tr>
<tr>
<td>Chemistry and Physics Handbook (15)</td>
<td>$7.35 \times 10^{-8}$ at 15°C</td>
</tr>
<tr>
<td>Cohn (16)</td>
<td>$6.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>Bates and Acree (6)</td>
<td>$6.53 \times 10^{-8}$ at 25°C</td>
</tr>
<tr>
<td>Nims (31)</td>
<td>$6.07 \times 10^{-8}$ at 20°C</td>
</tr>
<tr>
<td>Prideaux and Ward (34)</td>
<td>$5.85 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
soils and the concentration of phosphorus in plants grown in these soils. The pH values were closely related to the degree of sodium saturation of the soils. Since with calcium carbonate in the soil there was no close relationship between pH and phosphorus content of plants, Thorne concludes that the primary cause of the increased phosphorus uptake was the degree of sodium saturation with the resulting increase in soluble phosphates. He states that the pH was probably only an accompanying relationship. This suggests that plants are able to absorb adequate amounts of phosphates regardless of the pH and the relative concentration of \( \text{H}_2\text{PO}_4^- \) ion, providing soluble phosphates are present. Behrens (7) grew oats in pure sand to which pure chemicals were added. Several phosphatic compounds were used with and without calcium carbonate. He concludes that the great decrease in phosphate utilization with calcium carbonate was a result of the solubility rather than pH.

McGeorge (27), using the Neubauer test, determined phosphate absorption from soils saturated with calcium, magnesium and sodium. Phosphate absorption from the calcium and magnesium saturated soils was about the same as from the original soil, but the absorption from the sodium saturated soil was appreciably lower. There is some question as to the validity of the Neubauer test under such conditions. The seedlings used in the tests probably made very poor growth, if any, on the sodium saturated soils. If there is poor growth, the total uptake of phosphates would be low regardless of their solubility or physiological availability.

THE SOLUBILITY OF PHOSPHATES IN SUSPENSIONS OF CLAY WITH DIFFERENT DEGREES OF SODIUM AND CALCIUM SATURATION

Method

The clay used in this investigation was a montmorillonite type of clay separated from a natural bentonite material obtained about three miles
north of Garland in Box Elder County, Utah. The clay was freed of bases by leaching with dilute hydrochloric acid and was suspended in water to facilitate handling. Sixteen M.E. of monopotassium phosphate per 100 gms. of clay was added to the suspension and the suspension thoroughly shaken in a mechanical shaker. Titration curves were made by plotting pH against M.E. of sodium hydroxide or M.E. of calcium oxide added per unit weight of clay in the suspension. Fifty mls. of clay suspension was put into each of 52 Erlenmeyer flasks. Half were treated with varying quantities of sodium hydroxide and half with varying quantities of calcium oxide. The amount of base added to each sample was calculated from the titration curves so as to give pH values ranging from 4 to 10 inclusive, at intervals of 0.5 pH unit. Duplicate samples were prepared for each pH value. Water was added to each sample to bring the clay-water ratio to 1:10. The samples were then stoppered and let stand for 5 days with vigorous shaking twice daily. A water extract was obtained by centrifuging a suitable portion of the samples in 100 ml. centrifuge tubes. Phosphorus was determined on the water extract, according to the method of Allen (3), using a Fisher A.C. model electrophotometer.

Results

The water soluble phosphorus in clay suspensions at different pH values and different degrees of sodium and calcium saturation is shown graphically in fig. 2. At all pH values the clay suspensions titrated with sodium hydroxide gave higher amounts of water soluble phosphorus than those titrated with calcium oxide. This difference was greatest over the alkaline pH range. The large increase in water soluble phosphorus in the clay suspensions titrated with sodium hydroxide, over the pH range from 7 to 10, probably results from the release of phosphate ions from the anion exchange complex. For every unit increase in pH there is a
Figure 2. The water soluble phosphorus in clay suspensions in relation to the pH induced by additions of different quantities of calcium oxide or sodium hydroxide.
ten fold increase in hydroxyl ion concentration. When the pH exceeds 7, the hydroxyl ion concentration reaches the point where, by mass action, they replace the phosphate ions held by the anion exchange complex (30, 17, 35).

The water soluble phosphorus in the clay suspensions treated with calcium oxide was less than 1 M.E. per 100 gms. of clay for all pH values over 4. From pH 7 to 8 there was a slight increase in soluble phosphorus. The probable cause of this increase is that the increment increase of phosphate ions released from the anion exchange complex for increment increase in pH is greater than the increment increase of calcium ion for the same increase in pH. Above pH 8 this relationship is reversed and the soluble phosphorus decreases with rise in pH. This relationship can be expressed as follows. For pH 7 to 8

\[
\frac{\text{Phosphates}}{\text{pH}} > \frac{\text{Ca}^{++}}{\text{pH}}
\]

and for pH values above 8

\[
\frac{\text{Phosphates}}{\text{pH}} < \frac{\text{Ca}^{++}}{\text{pH}}
\]

where parentheses are used to indicate ionic activity. At pH slightly above 8 the clay was 100 percent calcium saturated. Below this saturation point the cation exchange complex of the clay absorbs added calcium ions and greatly reduces their activity in the solution of the clay suspension. Above the saturation point the cation exchange complex has greatly reduced capacity to absorb added calcium ions and they remain free in increasing quantities to react with phosphate ions, thus reducing the water soluble phosphorus.

The results obtained are in general agreement with reports by Ravikovitch (35), who conducted similar studies with an acid soil.
The clay suspensions titrated with sodium hydroxide contained no calcium ions and those treated with calcium oxide contained no sodium ions. Therefore, the results represent extreme situations. In naturally occurring basic and alkaline soils, the chances of obtaining a soil with either sodium or calcium as the only exchangeable cation is rather improbable. However, the results are indicative of the solubility of phosphates in soils dominated by exchangeable sodium or exchangeable calcium. In soils which are dominated by calcium and contain considerable quantities of calcium carbonate, the water soluble phosphorus is undoubtedly lower than the values found in the clay suspensions treated with calcium oxide. In soils dominated by exchangeable sodium the activity of the calcium ions is greatly reduced, and therefore the results obtained represent trends of the solubility of phosphorus in sodium soils.

THE PERMEABILITY OF PHOSPHORUS TO ROOTS OF BEAN AND TOMATO PLANTS OVER A pH RANGE FROM FOUR TO NINE

Method

The method used in this study is a modification of a method developed and described by Lauritzen (24). Tomato and bean plants were grown in the greenhouse in gallon pots filled with pure quartz sand. Nutrients were supplied to the plants from a nutrient solution which was dripped onto the sand. The pots contained holes in the bottoms which allowed free drainage. The beans were allowed to grow for 6 weeks and the tomatoes for 8 weeks. Then, for a three-day period, they were given a nutrient solution to which no phosphates were added. At the end of this period, the tops of the plants were cut off, leaving about 2 inches of the stems standing above the sand. The pots were brought into the laboratory and the sand and roots washed with a solution of known pH and known phosphate
content. The washing was continued until the solution coming out of the sand was of the desired pH. The hole in the bottom of each pot was then sealed with a rubber stopper and sufficient solution was added to completely saturate the sand. The pots were then transferred to a pressure chamber. Rubber connections were used to connect the short stems to glass tubing which led to the outside. Twenty-five lbs. per sq. in. air pressure was then applied to the chamber and the solution forced through the roots. The solution which came from the roots was caught in small Erlenmeyer flasks. Figures 3 and 4 show the apparatus used. The pressure was maintained for a period of 4 hours. The solution was then drained from the sand and the pH determined. Samples were taken of the solution in the sand both before and after the pressure period. The pH of the solution in the sand during the four-hour period was assumed to be the mean of the pH before and the pH after. The samples of the sand solution and the samples of the solution which came through the roots were analyzed for phosphorus. The solution which came from the roots will be called the expressed solution and the solution in the sand will be called the solution around the roots.

Results

pH relationships

Figures 5 and 6 show the relationship between pH of the solution around the roots and the concentration of phosphorus in the expressed solution. The phosphorus concentration of the solution around the roots was held at approximately 46 p.p.m. Each small circle represents the results for one plant for one pressure period. Regression lines are shown where there is a significant correlation and no lines are shown where the correlation is not significant. The results obtained with tomato roots are not significantly different from the results obtained with bean roots.
Figure 3. Photograph of the apparatus used in forcing solution through plant roots. Apparatus is shown in operation.

Figure 4. Photograph of the apparatus used in forcing solution through plant roots. Apparatus is shown with the top of the pressure chamber removed showing the method of connecting roots to the delivery tubes.
Figure 5. The relationship between the pH of the solution around the roots and the phosphorus content of the solution after forcing through roots of bean plants. (Phosphorus content of solution around roots held at 45 p.p.m.)
Figure 6. The relationship between pH of the solution around roots and the phosphorus content of the solution after forcing through the roots of tomato plants. (Phosphorus content of the solution around roots held at 45 p.p.m.)
There was no measurable change in phosphorus content of the expressed solution with change in pH over the acid range. Over the alkaline range there was a decrease in phosphorus content of the expressed solution with increase in pH. There was no observed correlation between pH and the amount of expressed solution collected during a four-hour pressure period. The pH of the expressed solution, for all pH values of the solution around the roots, varied between 6.5 and 7.2.

The solution around the roots was prepared from a .0009 molar solution of acetic acid by adding phosphorus as orthophosphoric acid and titrating with sodium hydroxide to the desired pH. Substitution of potassium hydroxide for sodium hydroxide gave similar results. Furthermore, the addition of sodium bicarbonate and sodium carbonate to the sodium hydroxide solution to increase the buffering power in the alkaline pH range did not change the results. This indicates that the results obtained are not unique to sodium hydroxide induced alkalinity.

The decrease in phosphorus content of the expressed solution, with increase in pH of the solution around the roots over the alkaline pH range is interpreted as a decrease in permeability of the roots to phosphate ions. This decrease in permeability may be explained in at least two ways. The \( \text{H}_2\text{PO}_4^- \) ion may be the phosphate ion most easily assimilated by plants, and the decrease in permeability may result from the decrease in concentration of this ion; or, the increase in hydroxyl ion concentration, associated with increase in pH, may produce physiological changes in the root membranes resulting in a decreased permeability to phosphate ions. The data presented in figs. 5 and 6 do not favor the decrease in \( \text{H}_2\text{PO}_4^- \) ion as an explanation because in the pH range from 4 to 7 the relative concentration of this ion is decreased approximately 50 percent (see fig. 1), but there was no decrease in permeability over this pH range. A physiological change in the
root membranes, associated with increase in pH, seems a more logical explanation for the results obtained in this study. Buehrer (13) after a consideration of solution culture data presented by McGeorge (26) and Breaseale and McGeorge (11), discussed both of these possibilities and placed more emphasis on the explanation involving the $\text{H}_2\text{PO}_4^-$ phosphate ion. Data from a more recent solution culture study by Arnon, Fratzke, and Johnson (4) favor the explanation involving a physiological change in the root membranes, associated with increase in hydroxyl ion concentration, because only at pH values above 7 was there a significant decrease in phosphorus assimilation with increase in pH.

The results obtained agree with the work of Pierre and Pohlman (32), who analyzed the exuded sap from stems of corn, sorghum, and sudan grass and found no variation in phosphate content of the sap over a pH range from 4.6 to 6.6.

**Concentration relationships**

There was some difficulty experienced in keeping the solution around the roots at a constant phosphorus concentration. The solution always contained a higher concentration of phosphorus at the end of the pressure period than at the beginning. For a great majority of the tests the average of the phosphorus concentration at the beginning and the end of the pressure period was close to 45 p.p.m. Because the increase in phosphorus concentration was greatest at acid reactions most of it was attributed to the dissolving action of the buffer solution on the phosphates precipitated in the sand. Some of the increased phosphorus concentration in the solution around the roots probably resulted also from the relatively low phosphorus content of the expressed solution.

Because of the variations in phosphorus concentration in the solution around the roots a study was conducted to find the relationship between
such variations and the concentration of phosphorus in the expressed solution. The phosphorus concentration in the solution around the roots was varied from 1 to 85 p.p.m. with the pH held at 7 for one series of tests and at 9 for another series. The results obtained with roots of tomato plants are presented graphically in fig. 7 and those for bean roots in fig. 8. With tomato roots there was no significant correlation between the phosphorus concentrations of the expressed solution and the solution around the roots at either pH value. The phosphorus concentration in the expressed solution at pH 9 was consistently lower than that at pH 7, indicating that over the entire range of phosphorus concentration, the permeability of the roots to phosphate ions was less at pH 9 than at pH 7. Similar results were obtained with bean roots and with tomato roots, except that with beans in the pH 7 series a positive correlation was obtained between phosphorus in the expressed solution and that in the solution around the roots over the range of 45 to 85 p.p.m. No such trend was observed with tomato roots.

The absence of a positive correlation between the phosphorus concentration of the solution around the roots and the phosphorus concentration of the expressed solution suggests that the roots were able to concentrate or screen out phosphorus depending on the phosphorus concentration around the roots. It also suggests the possibility that the phosphorus content of the expressed solution depends to some extent on the amount of phosphorus already in the roots. There is evidence for and against this possibility. Tomato roots from six plants were washed clean of sand, wiped dry, and then placed without water in the pressure chamber. The expressed solution obtained would then be that which was already in the roots. Pressure was applied until no more solution could be obtained from the roots. From 6 to 14 mls. of expressed solution was obtained from each plant and
Figure 7. The phosphorus content of solution pressed through tomato roots in relation to the phosphorus content of the solution around the roots.
Figure 3. The phosphorus content of solution pressed through bean roots in relation to the phosphorus content of the solution around the roots.
these solutions varied in phosphorus concentration from 8 to 18 p.p.m. This shows that there was some phosphorus already in the roots which may have influenced the results and which undoubtedly caused some of the variations found. Another group of tomato roots from six plants were put under pressure with distilled water around the roots. The average phosphorus concentration of the expressed solution for the first two-hour period was 11 p.p.m. For the second two-hour period it was 7.5 p.p.m. and then it dropped to 4.4 p.p.m. This indicates that without a supply of phosphorus the phosphorus in the roots is soon washed out. However, all of the roots used in obtaining the results were used for three pressure periods, and most of them used for four pressure periods with no unusual results noted for the first period. Therefore, the phosphorus already in the roots probably can be dismissed as a major factor in producing the observed results.

The results presented do not agree with the results obtained by Pohlman and Pierre (35) who found a positive correlation between the exuded sap of corn plants and the water soluble phosphorus in the soil. The different type of plants used and the different technique and method used in collecting the sap may account for this discrepancy.

**DISCUSSION**

The physiological availability of phosphates, as measured by the permeability of roots to phosphates, is a function of pH. There was no change in permeability of roots to phosphates with change in pH from 4 to 7, but from pH 7 to 9 there was a decrease in permeability with increase in pH. This decrease does not seriously reduce the amount of phosphorus coming through the roots until the pH 8 is exceeded. Therefore, if the discussion is limited to pH values from 4 to 9, which is the range in which most plants grow, physiological availability is only of importance in the
alkaline range and of major importance only where pH 8 is exceeded.

The net availability of phosphates is a function of their solubility and physiological availability. From pH 4 to 7 the net availability is largely determined by solubility. From pH 7 to 8 solubility is probably the dominant factor with physiological availability taking a place of minor importance. When pH 8 is exceeded, solubility and physiological availability may be of equal importance. However, there is a possibility that, if a high level of soluble phosphates is maintained over the entire pH range, plants will be able to assimilate adequate amounts of phosphates. At high pH values, where the physiological availability of phosphates is low, plants are usually restricted in growth because of factors other than the lack of phosphates, producing a low phosphate requirement.

In a soil system dominated by sodium the net availability of phosphates probably is, in most cases of poor growth of plants, not the limiting factor. Solubility of phosphates in sodium soil systems is usually high and usually increases with increase in pH. When the pH of a sodium soil system is high enough that the physiological availability of phosphates is low, the plants are probably so restricted in growth by other factors that the physiological availability of phosphates is no hindrance to their nutrition. In fact, under these conditions plants may show an increase in phosphorus, on a percentage basis, with increase in pH (41).

In calcium dominated soils the net availability of phosphates is usually low because of their low solubility. If the pH is increased to the point where physiological availability is important, the net availability is reduced to an extremely low value because in a calcium system both solubility and physiological availability decrease with increase in pH. However, the pH of most naturally occurring calcareous soils in their natural state in the field probably seldom exceeds 8.5. Therefore, in
calcium dominated soils, physiological availability is undoubtedly not as important as solubility in determining net availability.

Phosphate solubility studies show that phosphate solubility in soils cannot be directly related to pH unless the type of soil system is specified. With a sodium system the solubility characteristics for certain pH ranges are directly opposite from the characteristics found in calcium systems. However, when the soil system is specified, pH may possibly have some value as an approximate index to the phosphate solubility.

Emphasis should be placed on reaction and changes which occur with change in pH rather than on pH itself. The physiological availability of phosphates is a function of pH, yet, over most of the pH range of importance to the culture of plants, solubility of phosphates is the most important factor and at any pH value the solubility may vary from one extreme to the other, depending on the type of soil system. Albrecht (2), in discussing the significance of pH, stated that pH cannot be closely related to crop production if the pH remains constant and other factors fluctuate widely. Hoagland and Arnon (21) state that pH can only have meaning when used as a measurement reflecting the interaction of several factors peculiar to a specific soil.

With many soils the water soluble phosphorus is seldom greater than 1 p.p.m. and most physiological availability studies have involved phosphorus concentrations higher than this. A more thorough understanding of how physiological availability affects the net availability of phosphates under conditions of low solubility, should be useful information.

The rate of movement of phosphate ions through plant roots has been suggested as a factor which may have affected the phosphorus concentration in the expressed solution obtained by forcing solution through roots. The use of radio-active phosphorus should give information on the rate of
movement of phosphate ions, under these specific conditions, which would undoubtedly help improve the method and help interpret the results obtained.

**SUMMARY**

1. Investigations of the solubility of phosphates in sodium and calcium clay suspensions and of the permeability of plant roots to phosphates over a pH range from 4 to 9 have been conducted. A measure of the permeability of roots to phosphates was obtained by forcing solution through roots of tomato and bean plants by means of air pressure.

2. The solubility of phosphates, for all pH values between 4 and 10, was higher in sodium than in calcium clay suspensions. This difference was greatest at alkaline reactions.

3. There was no measureable change in the permeability of roots to phosphate in the acid pH range. In the alkaline pH range there was a decrease in permeability with increase in pH.

4. The physiological availability of phosphates, as measured by the permeability of roots to phosphates, is a function of pH, and is important at alkaline reactions.

5. The net availability of phosphates is a function of their solubility and their physiological availability. Over the acid pH range from 4 to 7 the net availability is largely a function of solubility. Over the alkaline range from pH 7 to 9 physiological availability is important, but solubility is probably the more important of the two factors.

6. The physiological availability of phosphates in sodium and calcium soil systems may seldom be the limiting factor in plant growth, providing phosphate solubility is held at a high level.
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