

# Fixation and Penetration of Phosphates in Vermont Soil

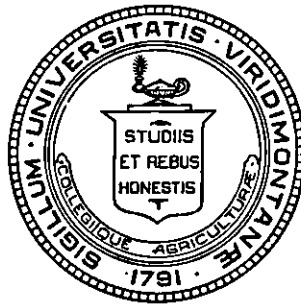
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FIXATION AND PENETRATION OF PHOSPHATES IN VERMONT SOILS

By V. L. WEISER



Studies were made of the penetration and fixation of phosphates in Vermont soils. Field plots were established and greenhouse and laboratory studies made of sundry phosphatic fertilizers. Plant and chemical studies of phosphate fixation were included and methods of overcoming such fixation were considered.

Field studies with super-, ammonium and sodium phosphates indicate that phosphate penetration is a problem of minor importance under field conditions in Vermont. However, laboratory results seem to show that superphosphate penetrates slowly into many Vermont soils.

Penetration of superphosphate may be enhanced by certain materials, such as certain sulphate and nitrate salts. Sodium, ammonium, and certain organic phosphates penetrate more quickly in soils than does superphosphate. Exposure of a phosphate to relatively large amounts of soil results in enhanced fixation.

Vermont soils are comparatively high fixers of phosphorus, being sometimes as potent in this respect as are lateritic soils. This may be explained by the presence of much of the B horizon in the surface soil, due to the loss of a considerable portion of the A horizon through cultivation and erosion. It is well understood that the B horizon of podzolized soils can fix large amounts of phosphorus, usually, it is thought, because of their iron and aluminum contents.

Certain hydrated oxides and precipitated salts of iron and aluminum fix large amounts of phosphorus. Certain silicates and minerals, as well as some sorts of organic matter, when applied to soils reduce their fixing power.

Liming increases the ability of a crop to recover phosphorus. However, chemical studies indicate that liming may sometimes increase fixation.

The influence of frequency of application on phosphate recovery was found to vary with the form of phosphatic fertilizer used. Recovery from sodium phosphate was greater when small and frequent applications were made, but recovery from superphosphate and Ammophos was greater when large and less frequent applications were made.

## BULLETIN 356: FIXATION AND PENETRATION OF PHOSPHATES IN VERMONT SOILS

By V. L. WEISER<sup>1</sup>

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The problems of phosphate fixation and penetration are often encountered in fertilizing practice. Various field studies (93) (60) have shown that many—perhaps most—Vermont soils respond to the application of available phosphoric acid. However, the amount recovered in crops may be much less than that applied in the fertilizer. Pasture fertilization studies on 13 Addison county farms (61) show an average increase of 1,100 pounds of dry grass the first year and of 674 pounds the second year following an average acre application of 554 pounds of superphosphate. Ellenberger *et al.* (16) state that the average pasture grass contained 0.32 percent phosphoric acid. Assuming that this figure may be applied to these 13 pasture soils, only one-sixth of the average phosphorus applied was recovered in two years' crops, but the carryover from the fertilizer during the following season might be expected to raise this figure. Gile and Smith (28) cite evidence of recoveries as low as 10 to 20 percent. Indeed on the Broadbalk wheat plots at Rothamstead, England (40) after 50 years of fertilization, the recovery amounted to but little more than two-thirds of the phosphorus which had been added, although very small amounts had been lost in the drainage waters.

Since the plants redeem only small fractions and since losses by leaching are almost invariably negligible, it is obvious that the fate of much of the applied phosphorus must be otherwise accounted for. The generally accepted explanation of this loss is that the phosphate is "fixed" by the soil in such form that it is made unavailable to plant growth. It may be fixed in a form upon which plants can not feed or in a position where the roots can not reach it. That soluble phosphates quickly revert in soils to difficultly soluble forms is a generally accepted fact, their availability being thus much impaired. This fixation may take place so rapidly that their surface applications are often held within the upper half inch of soil. In such cases the form in which the phosphorus is held may be such that plants can use it, but the location

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in which it is held may be such, being above the areas of the feeding roots, that it is positionally inaccessible.

This phenomena of positional unavailability of phosphates is thought in part to account for the poor response made during the initial year to topdressings of superphosphate on some of Vermont's heavier soils (61). Another factor which may account for greater yields during the second year is the improvement of the turf and herbage, especially white Dutch clover, which has a stoloniferous rooting habit, sending out new roots at the very surface of the soil. However, it seems likely that the slow penetration of phosphate to root depths has considerable, yet only temporary, influence. When one realizes that more than four-fifths of Vermont pasture soils are unplowable, thus necessitating surface applications if they are to be fertilized at all, one becomes impressed by the vital necessity to the solution of the pasture problem in Vermont of a thorough study of penetration phenomena.

Since fixation of phosphorus into unavailable forms is a more permanent condition and applies to both plowable and unplowable soils, it seems to have greater importance than slow penetration to root depths. However a consideration of methods whereby either positional or chemical availability of phosphates may be furthered should be worthy of attention.

The objective of the present study is the demonstration of the manner in which phosphates may become fixed in Vermont soils, as well as the best way in which to overcome this fixation and to facilitate penetration and recovery. In approaching these two problems the following plans of attacks were formulated:

1. Use more penetrating phosphates; on the ground that forms other than those commonly used may be less subject to immediate fixation and may leach to root depths before they are held by the soil.
2. Determine which compounds or soil constituents function most prominently in phosphate fixation in Vermont soils. A study of the process of soil formation in this area and a knowledge of the compounds active in phosphate fixation should indicate how phosphates are fixed.
3. Seek a means of decreasing fixation in soils. It may be possible to replace phosphate with some other anion in the fixation reaction, or else the fixing agencies of the soil may be destroyed or, rather, deactivated by definite soil treatments. Methods of applying phosphate and the use of insoluble forms may also decrease fixation.

## REVIEW OF LITERATURE

## PENETRATION

Penetration of phosphorus into the soil has been studied for many years. Perhaps the lack of downward movement may be better understood if one realizes how quickly soluble phosphates may revert to insoluble forms when applied to the soil.

Scarseth (74) in a laboratory trial used superphosphate at the rate of two tons per acre and after five months recovered less than one percent of its water-soluble phosphorus. Schmitt (75) found 98 percent converted to water-insoluble forms within two days and Crawley (9) states that immediately after irrigation complete reversion of a seven-ton application of double superphosphate occurred in certain Hawaiian soils. Gile and Smith (28) in pot experiments noted a 40 percent decrease in efficiency when phosphate was applied 30 days before planting as compared with application at planting time. Egorov (15) cites Stoklasa who puts the time limit for phosphate reversion at from 50 to 60 days and, also, Shapiro who claims that it is completed within 10 days. Egorov attributes these differences to the diverse nature of the soil used and sets the time limit with chernozem at 24 days. Some work done on a podzolized soil indicated a much more speedy reversion. Since Vermont soils are podzolic such findings seem especially applicable here. Wojtysiak (98) states that phosphate adsorption increases with time. He believes that there are two types of reversion; one which acts slowly in soils of a high calcium carbonate content and one acting more rapidly in calcium-free soils possessing a high iron content. Chernozem soils are high in, while podzol soils quite free of, calcium; hence his findings agree with that of Egorov.

Harper (35) applied superphosphate to Iowa soils and found that during a season of high rainfall its phosphorus did not leach beyond 4.5 inches and that under normal conditions very little left the surface inch. Crawley (9), in the case cited in the last paragraph when irrigation immediately followed application, found that half of the phosphate was held in the first inch, nine-tenths in the first three inches and all within the upper six inches. When, however, 15 hours elapsed between application and irrigation, nine-tenths were held in the surface inch. This observation indicates the influence which an immediate and heavy rainfall may have on penetration. Van Alstine (92) feels that phosphorus remains where it is placed until it is removed by crops or erosion. Heck and Truog (37) state that in soils of high fixing capacities, the downward movement is often restricted to the upper inch or

half inch of soil. Midgley (59) has shown the importance of positional availability. He worked superphosphate into an old blue-grass sod by slicing the sod with a knife and applying the phosphate in the grooves. The grass yield in the latter case was greater by 57 percent than that secured following surface application. The study of the phosphorus content in the different soil layers where surface applications had been made showed that very little had moved out of the upper inch at the end of six months and that most of it was held in the surface half inch. Sodium, ammonium and potassium phosphates penetrated two soils used in laboratory trials more rapidly than did superphosphate and an application of sodium nitrate greatly increased the downward movement of superphosphate in Miami silt loam.

Sen (79) and Harrison and Das (36) report only slight penetration in the calcareous soils of India. They suggest the use of such forms as di- and tri-sodium phosphate which they found—as did Midgley—penetrated much more than did superphosphate and which can not induce the formation of tri-calcium phosphate. Spencer and Stewart (82) at Nevada recognize the importance of positional availability of phosphate. They found that an organic phosphate of the general formula  $R(OH)_x \cdot (OPO_3M_y)_z$  was as available to plant growth as are ordinary fertilizers and that it penetrated soils more quickly and completely. And, finally, in connection with these attempts at enhancing penetration, Reifenberg (70) suggests that silicic acid may play an important rôle in phosphate movement, especially in semi-arid soils. He maintains that the silica exerts a protective action on the phosphoric acid in soil, preventing secondary aggregation or reversion. This peptization allows for more free movement of the phosphate.

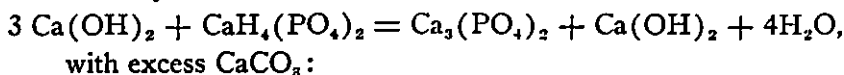
The foregoing review indicates clearly that much of a phosphorus application is apt to be held in the surface half inch of soil. That this is true is due chiefly to the rapidity of reversion. However, the time limit for reversion varies with the soil and the manner of fixation and, furthermore, the amount and distribution of rainfall may affect the outcome. The only factor which seems to be within human control is the form of phosphate used. However, by proper choice desirable positional availability may in some measure be secured.

#### FIXATION

Fixation is the term applied to the phenomenon whereby soluble phosphorus is removed from solution by soils. It is often designated by other terms, such as "absorption," "adsorption" and "reversion."

This removal has been attributed by some to chemical reaction with soil bases and by others to physical adsorption by the soil colloids. The availabilities of these fixed phosphates may vary considerably, depending upon the soil constituent responsible for the reaction. Phosphorus held by one compound may yield readily to the feeding roots while that held by a different substance may be almost entirely unavailable. This statement, of course, applies also to the surface fixation encountered in poor penetration. In other words, phosphorus may be both chemically and positionally fixed so that it is unavailable to plants.

*Calcium compounds.*—There is considerable evidence that soluble phosphates revert to insoluble forms in the presence of calcium carbonate, that is to say in soils which naturally have either a neutral or an alkaline nature. Thus Simmermacher (80) reports reduced assimilation by oats from dicalcium and tricalcium phosphates in the presence of lime. Nagaoka (62) found that calcium oxide reduced phosphorus assimilation by rice plants more than did calcium carbonate but that both considerably decreased phosphate availability. Gericke (26), working with germinating rye cultures, found that heavy lime applications increased assimilation in soils of very low phosphate concentration but that it decreased assimilation on soils of high concentrations. Schulze (78) as well as Westhauser and Zielstorff (96) also report decreases in phosphate availability coincident with lime applications. Arie (2) found that the lime content of the Brazilian soils with which he worked varied from 0.01 to 0.65 percent and that the more calcareous soils fixed about five percent more phosphate than did those of a lower calcium content. Egorov (15) states that mono-calcium phosphate in chernozem becomes progressively less soluble as the molecule takes up more calcium and suggests the possibility of the existence of a phosphate with a higher calcium content than  $\text{Ca}_3(\text{PO}_4)_2$ . Harrison and Das (36) found that mono-calcium phosphate reacts very rapidly with calcium carbonate to form dicalcic phosphate and that this in turn reacts more slowly to form the less soluble tricalcic combination. Austin (4) gives the reaction for the titration of mono-calcium phosphate with excess calcium hydroxide as follows:



$$3 \text{CaCO}_3 + \text{CaH}_4(\text{PO}_4)_2 = 2 \text{CaHPO}_4 + \text{Ca}(\text{HCO}_3)_2 + \text{CaCO}_3$$

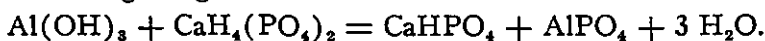
This, he feels, indicates that large amounts of carbon dioxide in calcareous soils should enhance phosphatic availability.



Teakle (86) removed calcium from the soil solution by the addition of ammonium oxalate and increased by fifty-fold the amount of phosphate in solution. McGeorge and Breazeale (55) found that upon acid extraction the calcareous soils of Arizona yield large amounts of phosphorus but that plant assimilation and water solubility may be very low. In a later publication (54) they state that unquestionably the phosphates exist in these soils in combination with larger amounts of calcium than exist in tricalcic phosphate and suggest the following formulae as possibilities:  $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$  and  $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$ . They state that these high calcium phosphates are quite insoluble and unavailable to plants at the reactions prevalent in these soils and that it seems quite probable that calcium plays an important part in fixation of phosphorus into unavailable forms in calcareous soils.

*Iron and Aluminum compounds.*—In acid soils, where calcium is relatively lacking, fixation is generally brought about by iron and aluminum compounds. Vanstone (94) states that soils of an acid reaction fix phosphorus in a form different from those in which soils high in calcium fix it. Nemec (65) maintains that soils high in calcium should contain more available phosphoric acid than those deficient in calcium and states that soils containing more than 50 milligrams of iron per kilogram of soil (one percent citric acid extraction) fail to respond to phosphoric acid treatments. Burgess (6) claims that phosphates fixed by calcium are more available to plant uses than those fixed by iron and aluminum compounds. Hall and Vogel (34) state that acid soils high in total iron give high phosphorus fixation. Martin and Doyne (49), studying fixation in lateritic soils, found that a high free aluminum content implied greater fixation.

McGeorge (53) mentions the work of Walker at the Hawaii station, who found the highest percentages of phosphorus in cane juices where the least active aluminum was present in the soil. Gosh and Bhat-tacharyya (29), working with di-hydrogen phosphate, found considerable phosphate fixation with aluminum hydroxide gels, a reaction similar to the following being indicated:



McGeorge and Breazeale (56), in a similar study with iron and aluminum hydrogels, found that they fixed large amounts of phosphorus, which was insoluble in water and was with difficulty ionized by electro-dialysis but was completely soluble in dilute hydrochloric acid. The gels were amphoteric, giving up the phosphate at alkaline reactions. Calcium carbonate added to either gel increased while sodium carbon-

ate reduced fixation. This observation helps explain the greater availability of phosphorus in black alkali spots. They conclude that iron and aluminum as well as calcium may be involved in phosphate fixation in these calcareous soils. Doughty (12) found iron phosphate to be least soluble at pH 4.0 and aluminum phosphate at pH 6.5, and inferred that when both are present a soil should have high fixing powers over quite a wide range of reaction.

Recently much attention has been directed toward fixation by the basic iron and aluminum oxides. Thus Ganssen (23) states that alumina fixes phosphate in soils. Meyer (57) at Louisiana reports the discovery of an iron compound which is responsible for the fixation of phosphates in southern soils. It exists in concretions and fixes phosphorus as a basic ferrous phosphate. In later work (58) he found that soils low in organic matter but high in sesquioxides may fix large quantities of soluble phosphates and maintain such low solubility as materially to hinder plant growth. Heck and Truog (37) found that phosphorus was fixed quite completely in acid soils as basic iron and aluminum phosphates and that liming made it more available. Gaarder (21) shows that phosphate is insoluble between the pH value of 4.0 and 7.5 in soils that are rich in active sesquioxides but, contrary to the observations of Heck and Truog and of Burgess, that liming does not always augment phosphate availability on such soils.

Ford (19) cites references to show that hematite ( $\text{Fe}_2\text{O}_3$ ), goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and bauxite ( $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ ) are the oxides usually present in soil. Hematite did not appear to fix phosphates, whereas goethite fixed large amounts. When bauxite became dehydrated to the monohydrate form (diaspore) it fixed more phosphorus than any other form of aluminum oxide. X-ray analysis of the minerals before and after phosphate application indicated that a crystalline phosphate of very low solubility was formed by the combination. He concludes that phosphates fixed by calcium and magnesium are relatively the most available, that those fixed by soluble iron and aluminum are of intermediary availability and that those fixed by goethite and bauxite are of very low solubility. These three forms of fixation summarized by Ford are, perhaps, the most important occurring in soils. However, other forms have been suggested.

*Organic matter.*—Roszman (72) found a decrease of phosphate adsorption by electrolyzed clay treated with sodium. Since this treatment brought more organic matter into solution, he concluded that the fixation was due to the organic matter. Dreyspring *et al.* (13)

found that less phosphorus was recovered by the plants growing upon 22 moorland soils than was present in the 100 rye seeds which were used and attribute the loss to fixation by the humus. However, Doughty (12) and Weidmann (95), working with peat and muck respectively, could account for fixation only by the bases in these soils. Das (11), of India, cites work to show that phosphorus in organic combination in soils remains more available to plants than inorganic phosphates and Meyer (58) found that organic matter was necessary in maintaining phosphate availability. Apparently fixation by organic matter is a moot point; indeed it may even enhance availability.

*Colloidal adsorption.*—Although it is generally recognized that soil colloids adsorb soil bases, there is considerable controversy over the importance, and even the existence, of adsorption of the ion. Arrhenius (3) found that soil colloids are amphoteric and concluded that they could adsorb either acid or base radicals. Mattson (51) (52), too, has shown that some soil colloids are amphoteric, among them the sesquioxides of iron and aluminum. These were able to adsorb phosphorus in acid solutions. But Ford has shown by X-ray analysis that phosphate added to these compounds forms a new mineral with a different crystal lattice, indicating that a chemical reaction takes place. Mattson's work with alumina-silicates and kaolin was done with pure colloids. The complexity of factors influencing phosphate fixation in a soil may mask the physical adsorption by colloids, hence in applying the laws of colloidal behavior to soils this fact must be kept in mind.

Wojtysiak (98) found that clay and chernozem soils adsorbed phosphate according to the Freundlich equation,  $\frac{x}{M} = KC^{1/n}$  where  $x$ —represents the grams of phosphate adsorbed,  $C$  the concentration in grams per c.c. of phosphate in solution, and  $K$  and  $n$  are constants. Russell and Prescott (73) conclude that the equation expresses the phenomena of phosphate fixation by soils, but Fisher (17) criticizes their work, feeling that the equation is not always a true index of adsorption. Comber (8) also sets forth what he deems to be fallacies in their paper, contending that only those acid radicals which form insoluble salts with soil bases are removed from solution. He asserts that this fact precludes the possibility of physical adsorption.

Starkey and Gordon (85) hold that many phenomena in soil chemistry have been attributed to adsorption, whereas the workers did not really know whether they were dealing with physical adsorption,

chemical reaction, or adsorption phenomena between charged aggregates. The first of these is a pure surface energy phenomenon not involving electrical charges, whereas the latter involves a neutralization of electrical charges and would seem to be closely related to chemical reaction. The only apparent difference between it and chemical reaction lies in the size of the aggregates involved.

Perhaps these differences in opinion as to the importance of colloidal adsorption are due to misunderstandings as to what the various investigators mean by the term "adsorption." Teakle (86) says that the evidence at hand does not permit the denial of the existence of colloidal adsorption, but that at best it can play only a minor rôle in most soils.

A summary of the cited literature would seem to indicate that chemical reaction with soil bases accounts for fixation in most soils. In calcareous soils the phosphorus exists in the form of a difficultly soluble high calcium phosphate. In acid soils fixation is due to iron and aluminum compounds.

#### REMEDIAL MEASURES

Sen (79) has suggested the use of sodium phosphates on calcareous soils, while McGeorge and Breazeale (56) state that ammonium and organic phosphates gave good results. Egorov (15) secured quite effective resistance to fixation in chernozems by the use of sodium, potassium, and magnesium phosphates. Gehring (24), Loew (46), and Kellogg (44) found that magnesium enhanced phosphate availability in such soils. Truog (90) attributes this effect to a better calcium-magnesium soil balance, in which event the plants are not forced to excess feeding on calcium in order to obtain phosphorus. Marais (48) holds that aluminum phosphate is more available than calcium phosphate in calcareous soils and Spencer and Stewart (82) found organic phosphates especially resistant to fixation.

Decreased fixation follows the use on acid soils of phosphates which have a low solubility in the soil solution yet yield readily to direct feeding by the plant roots. Nehring (63), Gericke (25), Meyer (58), and Ford (20) conclude that this is true. Ford reports yields from rock phosphate which, with some crops, exceed those secured with superphosphate. In this connection Truog (88) has shown that plants vary in their ability to feed on mineral phosphates and Whiting and Heck (97) suggest the use of a plant with a high feeding power as a green manure crop, before growing a more important crop with a lower feeding power for rock phosphate, for the reason that when the green

manure decomposes it leaves an available source of phosphorus for succeeding plants.

Gaither (22), Parker and Tidmore (68), Greenhill (32), Simon (81), and Ford (20) increased phosphate availability by liming acid soils; Truog and Parker (91), Heck and Truog (37), and Burgess (6) attribute this to the formation of calcium phosphate, thus preventing the formation of less soluble iron and aluminum phosphates. Gaarder (21), however, states that liming does not always enhance availability on soils which are very rich in sesquioxides. Wolkoff (99), using small amounts of lime, slightly increased phosphate recovery but when large amounts of lime were applied such recovery was inhibited. These workers have indicated that lime in ordinary amounts may not be sufficient to prevent fixation by sesquioxides and that, if used in large amounts, the conditions prevalent in calcareous soils may be approached wherein an excess of calcium itself may be detrimental.

Jensen (41) found that humus, freed of bases and phosphorus, increased phosphate availability. Thus when only three percent of green or stable manure was plowed into a soil and allowed partially to decompose, solubility was increased by from 30 to 100 percent. Other investigators, as Gaarder (21), Ganssen (23), Meyer (58), and Arie (2), have observed similar effects exerted by humus. Ganssen attributes its action to a deactivation of the sesquioxides. McGeorge and Breazeale (56), Spencer and Stewart (82), Schriener (77), and Whiting and Heck (97) found organic forms quite available to plants and less subject to fixation than the common forms of mineral phosphates.

Nemec (64) and McGeorge (53) found that in the presence of much soluble silica the availability of phosphorus in soils was distinctly enhanced. Schollenberger (76) added silicates to limed soils in pots and increased both the yields and the phosphorus content of the plants. Niklas *et al.* (66) increased the efficiency of superphosphate by adding from three to five percent of kiesselguhr in the manufacturing process. Hall and Morison (33) augmented plot yields by the application of sodium silicate to the soil. They looked upon its action as influencing the physiological functions of the plant, but Fisher (18), in a discussion of their paper, shows that as a matter of fact it influenced phosphorus availability in the soil.

Other compounds, also, have been found to enhance phosphate availability. Thus Spurway (84), Greaves and Carter (31), Van Alstine (92), Midgley (59), and Gracanic (30) found that sodium, potassium and magnesium salts were effective.

Phosphate placement as a means of retarding fixation has been demonstrated by Meyer (58), Overseth (67), and Buie (5). By placing the phosphate in localized areas in reach of the feeding roots, its availability to plant growth is maintained and at the same time less fixation occurs.

It would seem that phosphate fixation may be partially overcome in calcareous soils by the use of specific soluble phosphates, in acid soils by use of insoluble phosphates or additions of lime, and in either by phosphate placement, or applications of humus, silicates or other specific fertilizer salts.

#### DOWNWARD MOVEMENT OF PHOSPHATES

Several investigators, whose conclusions have been cited in previous pages, have indicated that crop yields may be much reduced by the failure of surface applications of phosphates to reach root depths. The lack of a satisfactory response during the first year from applications of superphosphate on several permanent pastures in Vermont is thought to be due to slow penetration. The trials now about to be discussed were instituted with a view of determining the effect of penetration on crop response and of devising methods whereby penetrability may be increased.

#### FIELD PLOTS

In the spring of 1930 three series of field plots were laid out on well established bluegrass-timothy pastures in as many localities for the purpose of studying penetration and plant response from surface applications of three different phosphates, namely: superphosphate, Ammophos, and sodium phosphate. At the same time a study was made of the rate and frequency of application, the results being set forth on page 23.

The Waterbury plots were located on a Merrimac sandy loam soil. It had a pH of 4.9, a lime requirement of 1.5 tons by the Jones method (42), and an available phosphorus content of 10 pounds per acre by the Truog method (89). The Middlebury plot was located on an Addison clay with a pH of 5.5, a lime requirement of 2.5 tons, and an available phosphorus content of 38 pounds per acre. The soil on the Brandon field is classed as a Pittsfield clay loam. Its pH was 5.9, its lime requirement two tons, and its available phosphorus 10 pounds per acre.

The sources and available phosphoric acid content of the phosphates used were as follows: Superphosphate-commercial, 16 percent;

Ammophos-commercial "A" and "B," 52.2 and 20.8 percents respectively; Disodium phosphate, U. S. P. grade, 19.8 percent. They were used at two rates; one equivalent to 600 pounds per acre of 16 percent superphosphate, applied at the outset to last for three years, the other equivalent to 200 pounds applied each spring during three successive years. At Middlebury and Waterbury applications were made both with and without lime, at Brandon only the unlimited series was used. All plots were  $\frac{1}{160}$  of an acre in size, i.e.,  $16\frac{1}{2} \times 16\frac{1}{2}$  feet. Muriate of potash was supplied on all the plots at the outset at rates sufficient to meet the plant needs and nitrogen added as ammonium sulphate twice each year, allowance being made, of course, for the nitrogen added as Ammophos.

The grass was cut four or five times a year, a lawn mower set to approximate grazing by animals being used. Samples of the cuttings from each plot were brought to constant weight in a forced hot-air drier, and yields computed as pounds per acre on dry basis.

The comparative yearly responses from the 600-pound applications should be the best indication of differences in penetration of the three phosphates. Table 1 summarizes these data.

TABLE 1.—YEARLY RESPONSE OF PASTURE HERBAGE TO SURFACE APPLICATIONS OF THREE PHOSPHATES. (RESULTS EXPRESSED AS PERCENTAGE INCREASE OVER CHECKS)

Plots	Year	Unlimed areas			Limed areas		
		Super-phosphate	Ammo-phos	Disodium phosphate	Super-phosphate	Ammo-phos	Disodium phosphate
Waterbury	1930	50.5	61.4	55.7	56.2	62.2	74.8
	1931	40.6	78.2	103.4	125.3	137.8	146.9
	1932	5.2	6.2	25.2	90.4	61.6	94.8
Three-year average		33.7	50.3	61.9	88.7	86.3	104.
Middlebury	1930	63.1	20.6	27.8	54.7	29.4	34.4
	1931	140.6	127.7	137.8	154.6	168.2	138.
	1932	92.8	106.7	122.	139.1	143.	141.9
Three-year average		105.8	94.4	103.8	124.8	125.9	115.2
Brandon	1930	117.1	80.1	49.2			
	1931	76.8	107.	107.2			
	1932	69.6	98.5	36.7			
Three-year average		76.1	106.8	78.3			

If first year yields alone are used as criteria, superphosphate would outrank its competitors on the Middlebury and Brandon plots, since greater penetration would be indicated, whereas on the Waterbury area

the other two phosphates proved to be slightly better than superphosphate. The increments of the second year may be attributed to the development of a better turf and on the lime plots to augmented clover growth. The lowered response in several instances during the third year may be ascribed to phosphorus insufficiency. Fixation into unavailable forms seems to have occurred since considerably more phosphate was applied than was removed by plant growth. No consistency exists in the results secured with the three phosphates, which would seem to indicate that penetration is not a very important factor under field conditions on these three soils. The amount and distribution of rainfall in Vermont may be such that penetration is a less vital issue than it is in some localities and especially in more arid regions. Most Vermont soils are sufficiently moist on the surface so that crops can feed near the surface where the phosphorus is held.

GREENHOUSE STUDIES

Greenhouse studies similar to those conducted on the field plots were instituted, using Addison clay placed in pots. They were designed to determine the differences in penetration and plant availabilities existing between calcium, ammonium and sodium phosphates on a limed and an unlimed soil. Calcium oxide was applied to the former at a rate equivalent to one ton per acre. Surface applications were made, each pot receiving the same dosages of phosphorus and of nitrogen. They were seeded to Hungarian millet. Water was applied at the surface in amounts sufficient to maintain 25 percent of the water-holding capacity of the soil which was used. The results are set forth below and in plate 1.

TABLE 2.—EFFECT OF DIFFERENT PHOSPHATES ON MILLET YIELDS

Pot treatments	Dry weight of plants, grams	Pot treatments	Dry weight of plants, grams
Superphosphate and ammonium sulphate .....	12.	Disodium phosphate and nitrate of soda .....	15.7
Superphosphate, ammonium sulphate and calcium oxide .....	9.1	Disodium phosphate, nitrate of soda and calcium oxide	10.2
Ammophos "B" .....	13.1	Check—No treatment .....	8.2
Ammophos "B" and calcium oxide .....	10.6		

Sodium and ammonium phosphates produced greater yields than the calcium phosphate, which may have been due either to their greater positional availabilities (penetration) or to increased chemical avail-



ability. Liming consistently depressed the yields. The relatively low yields secured with calcium phosphate and in the limed pots indicate rapid reversion in presence of calcium oxide and consequent poor penetration.

A second attempt to determine the importance of positional availability was made with a Mohawk clay loam, which had a pH of 5.8, a three-ton lime requirement and contained 34 pounds of available phosphorus per acre. Superphosphate equivalent to 600 pounds per acre was applied on the surface and, also, was mixed with the surface three inches. The pots were seeded with a pasture mixture of timothy, redtop, blue grass and white clover. The first cutting was not recorded because the young grasses were not uniformly sodded, as evidenced by the duplicate pots. The average yields of the duplicate pots for the succeeding cuttings are presented in table 3. Plate 2 shows the results secured at the time of the second cutting.

TABLE 3.—INFLUENCE OF TWO METHODS OF APPLYING SUPERPHOSPHATE ON POT YIELDS OF A PASTURE MIXTURE

Pot treatment	Dry weights, grams		Total percentage increases
	Second cutting	Third cutting	
Check (no phosphate) .....	3.2	2.9	...
Phosphate applied on surface.....	3.28	3.89	17.5
Phosphate mixed with top three inches.....	5.07	3.31	37.3

The admixture with the top three inches of soil gave the larger returns at the second cutting and the first cutting also showed the same trend. The lower yields secured as a result of surface applications in these two cuttings may be attributed to lack of penetration. However, by the time when the third cutting was made, the surface applied phosphorus had apparently penetrated sufficiently into the soil so that it had become more available to plant growth. Perhaps had this trial been continued the total yields might have been more nearly equal.

#### CHEMICAL STUDIES

The penetration of phosphates through different soil depths was the object of study in the laboratory as well as in the field and in the greenhouse. Available phosphorus determinations were made on soil samples taken at different depths from the large pasture plots (p. 13) and, also, from smaller pasture plots receiving surface applications. The results secured with these field samples were inconsistent, but



PLATE 1.—Response of Hungarian millet to surface applications of three phosphates on Addison clay. The phosphate treatments to each pot were as follows: 1, superphosphate; 3, ammophos; 7, disodium phosphate; 9, check (no phosphate). Sodium phosphate shows greater response than other treatments. This is attributed to its greater penetration to root depths.

PLATE 2.—Growth of grass-clover mixture in response to two methods of applying superphosphate on Mohawk clay loam. Poor response from the surface application is attributed to a lack of sufficient penetration of the phosphate to root depths.

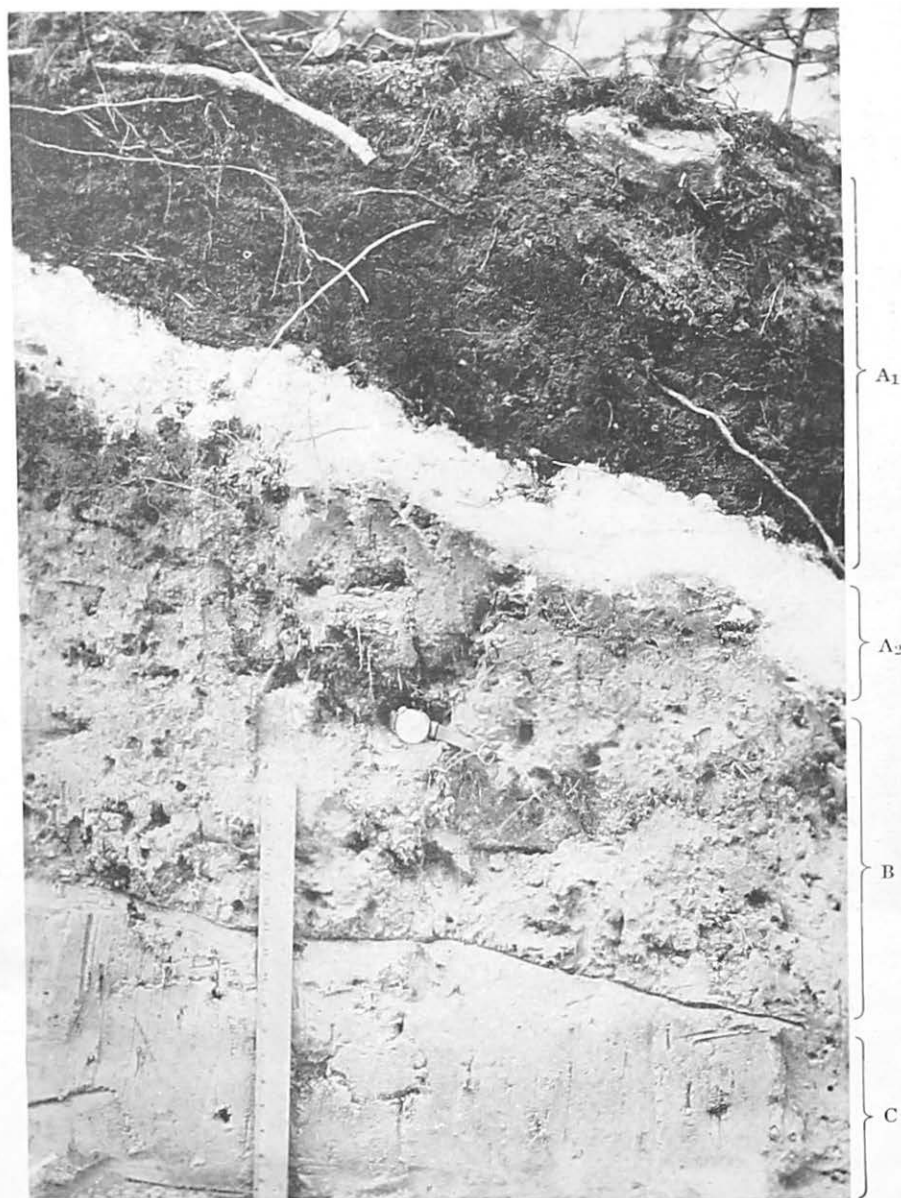


PLATE 3.—A typical well-defined podzol profile from Breadloaf, Addison Co., Vt. The organic horizon (A<sub>1</sub>) supplies large quantities of organic acids which dissolve and remove the bases (including iron and aluminum) from the A<sub>2</sub> horizon leaving a white ashy residue high in silica. The bases from the A<sub>2</sub> are deposited in the B horizon which is often highly cemented and colored red because of its high iron content. The C horizon consists of unweathered parent material.



PLATE 4.—Erosion on a podzolized soil near Lyndonville. Removal of the surface (A) horizons has exposed the lower (B) and (C) horizons. The B horizon has been found to have a very high fixing power for phosphorus. Such erosion, where the B horizon becomes the surface soil, helps explain the high fixing power of many Vermont soils.



PLATE 5.—Growth of turnips, showing effect of  $\text{CaSiO}_3$  and  $\text{CaCO}_3$  on response to rock phosphate in a Hermon fine sandy loam. Pot treatments: 1, rock phosphate; 2, rock phosphate and  $\text{CaSiO}_3$ ; 3, rock phosphate and  $\text{CaCO}_3$ .

PLATE 6.—Growth of rape plants, showing effect of  $\text{CaSiO}_3$  and  $\text{CaCO}_3$  on response to rock phosphate in an Addison clay soil to which iron oxide was added. The iron oxide has a high phosphate fixing power. Pot treatments: 6, rock phosphate; 7, rock phosphate and  $\text{CaCO}_3$ ; 8, rock phosphate and  $\text{CaSiO}_3$ .

laboratory trials carried on under controlled conditions gave more definite results.

The penetration of four phosphates, namely, superphosphate, Ammophos, disodium phosphate and silico-phosphate through a one-inch depth of Hermon fine sandy loam, was studied in the laboratory. The soil was placed in Buechner funnels and the four phosphates applied on the surface at rates so that each funnel received 33.65 milligrams of elemental phosphorus. The silico-phosphate was prepared in the laboratory by heating to red heat a 1:1 mixture of potassium silicate and rock phosphate. Five hundred cubic centimeters of distilled water were leached through each funnel in two days, the amount of phosphorus present in the leachates and the available phosphorus in the leached soils were then determined, the figures appearing in table 4. Clearly disodium phosphate was much more effective in penetration than its competitors and at the same time maintained quite a high availability in the soil. The silico-phosphate evidenced high availability but penetrated very slowly. Considering both penetration and availability the disodium phosphate proved superior.

TABLE 4.—PENETRATION AND AVAILABILITY OF FOUR PHOSPHATIC FERTILIZERS IN HERMON FINE SANDY LOAM

Phosphatic fertilizer	Phosphorus in leachate	Available phosphorus in soil after leaching	Total recovery of phosphorus	Percentage recovery
	mgs.	mgs.	mgs.	
Superphosphate .....	1.35	5.6	6.93	20.6
Ammophos .....	4.75	3.5	8.25	24.6
Disodium phosphate....	11.37	4.9	16.27	48.3
Silico-phosphate .....	trace	11.2	11.20	33.2

In a similar trial on Addison clay soil, iron-lacto, ferric-glycerol, and calcium-glycerol phosphates all exhibited greater penetrative powers and proved to be more available than did calcium, ammonium or sodium phosphates, which results are in full agreement with the observations of Spencer and Stewart (82), who found that organic phosphates gave better penetration than did mineral phosphates.

It is thought by many students of soil problems that increased penetration of phosphate in a soil may be accompanied by a greater amount of fixation, due to its exposure to more of the soil fixing agencies. This point was studied in the laboratory, using a clay loam of the Woodbridge series and the B<sub>2</sub> horizon of a well defined podzol profile of the Hermon series. Superphosphate was applied at an acre rate of 1,000 pounds to the Woodbridge soil and of 8,000 pounds

to the B<sub>2</sub> horizon, the larger amount being used in the latter case because the Hermon soil was found to fix considerably more phosphorus than did the Woodbridge. Similar amounts of phosphate were added to varying amounts of each soil to simulate exposure to one-, three- and six-inch depths. Fixation was induced by wetting and drying the samples in glass containers. Samples were taken after successive dryings and the available phosphorus determined on an equivalent amount of soil containing an equivalent amount of phosphorus. Correction was made for the available phosphorus present in the soil before treatment. The results are given in table 5.

TABLE 5.—INFLUENCE OF PENETRATION ON THE TOTAL AVAILABILITY OF SUPERPHOSPHATE IN TWO SOILS. (RESULTS EXPRESSED AS MGS. ELEMENTAL PHOSPHORUS RECOVERED)

Depth of soil to which phosphate was exposed	B <sub>2</sub> horizon of podzol		Woodbridge soil	
	Dried once	Dried three times	Dried once	Dried three times
6 inches	0.14	0.13	0.022	0.022
3 inches	0.17	0.15	0.047	0.031
1 inch	0.35	0.22	0.049	0.039

There was nearly twice as much chemically available phosphorus in both soils when the phosphate was placed at the one-inch depth as when it was mixed with the six-inch depth. Theoretically it might be expected that a highly penetrating phosphate would become chemically fixed to a greater extent than one of a less penetrating nature.

Since other fertilizer salts are usually applied to a soil at the same time as are phosphates, a study was made to determine their influence upon the penetration of superphosphate in an Addison clay soil. Superphosphate was applied on the surface of a half-inch layer of soil contained in Buechner funnels, then the several salts were added at the surface on an equivalent cation basis and slowly leached with 300 c.c. of distilled water. The amounts of phosphorus in the leachates are shown in table 6.

TABLE 6.—INFLUENCE OF EIGHT FERTILIZER SALTS ON PENETRATION OF SUPERPHOSPHATE IN ADDISON CLAY

Fertilizer salts applied with superphosphate	Milligrams phosphorus in 300 c.c. of leachate	Fertilizer salts applied with superphosphate	Milligrams phosphorus in 300 c.c. of leachate
Check (phosphate only)...	trace	Sodium sulphate .....	6.87
Sodium nitrate .....	7.97	Potassium sulphate .....	5.50
Potassium nitrate .....	7.45	Ammonium sulphate .....	3.72
Magnesium nitrate .....	3.49	Magnesium sulphate .....	3.46
Ammonium nitrate .....	1.40		

The nitrate and sulphate salts of sodium, potassium, ammonium, and magnesium tend to enhance the penetration of superphosphate, the salts of the first two proving more active in this respect than those of the other two cations. Any of these salts in field practice should increase the availability of surface applications of superphosphate, nitrogen as nitrate being more effective than as ammonia salts. If this observation is confirmed by further trials, this consideration may well be taken into account in making choice of a fertilizer.

#### FIXATION IN UNAVAILABLE FORMS

*Nature of Fixation.*—The object of this study was to determine, in so far as it was possible to do so, the nature of phosphate fixation in Vermont soils. Several workers (34) (49) (53) (65) have indicated that in acid soils iron and aluminum compounds are responsible for phosphate fixation. Since most of Vermont soils are acid, special attention was given to these compounds. Ford (19) found that hematite ( $\text{Fe}_2\text{O}_3$ ) does not fix phosphate while goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and diaspore ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) fix quite large amounts and suggested that some soils in the temperate zone may contain considerable hydrated oxides of iron. Marbut (50) has classified the soils of northern New England as podzols and Lunt (47) has also described many well defined podzol profiles in this area.

In the podzolization process, as described by Robinson (71), rain-water, after first percolating through a layer of organic matter, leaches the iron and aluminum from the surface mineral soil ( $A_2$  horizon) and deposits it in a lower (B) horizon. The manner of deposition of the iron and the forms in which it exists in the B horizon are not clearly understood. The iron and aluminum may be in combination with humus, silica, or bases, and some of it may exist as free adventitious sesquioxides. Aarnio (1) found that humus materials, in solution from the organic layer, caused a reduction of the iron and that it passed to the lower horizons in the ferrous form. Dana (10) states that ferrous carbonate forms limonite on oxidation. There is then the possibility that some of the iron in Vermont soils may exist in the forms suggested by Ford.

Lunt (47) has given the average percentages of sesquioxides in the horizons of three strongly podzolized profiles from Cherry Mountain, New Hampshire,  $\text{Fe}_2\text{O}_3$  increasing from 1.58 percent in the  $A_2$  horizon to 5.40 percent in the  $B_1$  and 4.82 percent in the  $B_2$  horizon, while the average content in the parent material was 2.96 percent.



If, as Hall and Vogel (34) state, the percentage of iron and aluminum in a soil is indicative of its power for fixing phosphates into unavailable forms and if some of this iron and aluminum exists as the sesquioxides, as is suggested by Ford, the B horizons of a podzol may be expected to fix large amounts of phosphorus.

The comparative phosphorus fixing power of several different horizons was determined in the laboratory. Samples of well developed podzol profiles were secured from five localities. Most of the profiles were found at comparatively high elevations and on quite light soils. A good example of this type of profile is shown in plate 3.

The method developed by Heck (38) at the Wisconsin station was used in determining their fixing powers. The dried samples were passed through a 40-mesh sieve. To one gram of sifted soil was added 450 parts per million of phosphorus and 25 c.c. of water, and this was boiled slowly in a flask until nearly dry and the residue then evaporated to complete dryness. A similar procedure was carried out without the addition of extraneous phosphorus. The available phosphorus in the treated and untreated samples was determined by the Truog colorimetric method. The amount present in the untreated was subtracted from that in the treated sample, thus enabling the computation of the amount of added phosphate that had become fixed by the soil. The fixation by the horizons of each profile appears in table 7.

TABLE 7.—PHOSPHORUS FIXATION IN PODZOL PROFILES

Horizon of profile	Mgs. fixed by profiles from different localities				
	Breadloaf Mountain	Barton	Lyndon	Troy	Mount Mansfield
A <sub>2</sub>	0.199	0.066	0.000	0.170	0.098
B <sub>2</sub>	0.365	0.432	0.300	0.438	0.441
C	0.337	0.396	0.290	....	....

The B horizon (zone of iron and aluminum accumulation) fixes much more phosphorus than does the A horizon (zone from which iron and aluminum have been removed). The C horizon or parent material exerts an intermediate fixing power.

Phosphorus fixation by the Breadloaf profile was also determined by a laboratory plant method. Thirty rye seedlings were grown on 200 grams of soil from each horizon, lime, potash and nitrogen being added in amounts sufficient to supply plant needs while superphosphate was added at the rate of 600 pounds per acre. The phosphate recovery was 100 percent on the A<sub>1</sub> horizon, 52.4 percent on the A<sub>2</sub> horizon,

while on the B<sub>1</sub> and B<sub>2</sub> horizons less was recovered than was added in the seeds.

Clearly both chemical analysis and plant growth show that the zone of iron and aluminum accumulation in the profile is where pronounced fixation occurs. It must be remembered, however, that these results were obtained on well developed profiles. On podzolic soils, where the process is less complete, presumably the differences in fixation by the horizons would be less marked.

Robinson (71) states that on soils under cultivation the horizons within reach of the tillage implements may all be confounded. In deforested areas the profile may be truncated by erosion, the present surface soil being the former B horizon. Such conditions would seem quite possible on the podzolized soils of Vermont in view of the fact that the organic layer tends to decompose and disappear with cultivation. The silica layer, being quite shallow, would then become mixed with the B horizon by tillage, or, indeed, become completely lost by erosion, especially on the steep slopes. Evidences of this degree of erosion may be seen in some sections of Vermont. For example, plate 4 shows pasture erosion at a point where the horizons have been removed down to the parent material. The presence of the B horizon in the surface soils of this area would cause them to become very active fixation agencies and the application of phosphates under such circumstances would be of doubtful expediency.

Lateritic soils have been regarded as high fixers of phosphorus. The phosphate fixing powers of two semi-lateritic soils from Florida were compared with those of several Vermont podzolic soils. The amount of phosphorus fixed by each, according to the Heck method, is shown in table 8. Apparently Vermont podzolic soils fix as much phosphorus as do some lateritic soils.

TABLE 8.—COMPARATIVE PHOSPHORUS FIXING POWER OF PODZOLIC AND LATERITIC SOILS

Soil	Mgs. phosphate fixed	Percentage phosphate fixed	Soil	Mgs. phosphate fixed	Percentage phosphate fixed
B <sub>2</sub> horizon of podzol.	0.444	88.8	Hollis sandy loam....	0.398	79.6
Hermon fine sand....	0.442	88.4	Hermon sandy loam..	0.320	64.
*Gainesville clay.....	0.413	82.6	Addison clay .....	0.268	53.6
Blanford sandy loam.	0.410	82.	*Norfolk deep sand..	0.255	51.

\* Semi-lateritic soils obtained from the Florida Experiment Station.

These results have been confirmed by Heck (38). Samples of four Vermont soils were sent to him and he found that the Hollis and Hermon soils fixed as much phosphorus as the laterite soils which

he examined. Indeed, the Hermon, Hollis, and a Pittsfield loam stood well above the common soils of other sections of this country in their powers of phosphorus fixation. Heck feels that his method quite closely approximates the phosphorus fixation which actually takes place under field conditions. If the amount thus fixed by such soils is calculated to superphosphate, it assumes the proportions of five to six tons per acre. When the possibility of so much fixation exists, plant recoveries of only 10 to 20 percent of a 600-pound application are to be expected.

Definite iron and aluminum compounds in these Vermont soils have not been identified and, consequently, their rôle in phosphate fixation has not been actually demonstrated. However, from the evidence presented in literature and the data obtained on fixation in the podzol profiles, it seems reasonable to assume that in the main phosphate fixation in these soils is brought about by iron and aluminum. In order to eliminate the complex conditions encountered in soils, fixation studies were conducted with pure minerals and prepared compounds of these two elements. The fixing power of minerals from several sources and of several iron salts precipitated with calcium carbonate are given in table 9.

TABLE 9.—PHOSPHORUS FIXATION BY IRON AND ALUMINUM COMPOUNDS

	Milligrams of phosphorus fixed per gram		Milligrams of phosphorus fixed per gram
Bog ore (Pa.) ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ )	2.7	Hematite ( $\text{Fe}_2\text{O}_3$ )	none
Bauxite (Tenn.) ( $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ )	1.8	Ferric nitrate (pptd.)	7.
Goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )	1.4	Ferric sulphate (pptd.)	3.8
Limonite (Ala.) ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ )	1.1	Ferric hydroxide (pptd.)	2.1
Diaspore (Mo.) ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )	0.5		

Most of these minerals fixed relatively large amounts of phosphorus, but hematite—as has been pointed out by other observers—fixed none whatever. The freshly precipitated iron salts exhibited very high fixing powers. Since these compounds are held to exist in many soils, the significance of these results seems obvious. Their presence, in amounts considerably less than most soil analyses show, could account for all of the phosphate fixation ordinarily occurring in many soils.

#### METHODS OF OVERCOMING FIXATION

Several methods of delaying or overcoming phosphate fixation have been suggested. The effect of the more important means, such

as time and rate of application, the use of silica and silicates, of organic matter, and of lime were studied.

*Effect of Time and Rate of Application.*—Some writers have held that the extent of fixation may be lessened if the phosphate is applied in small annual dosages rather than in larger ones to last for a period of years. In order to determine the relation of frequency of application to pasture yields, field plot studies were conducted on three soils using three sources of phosphorus. The three-year results are shown below.

TABLE 10.—INFLUENCE OF THE FREQUENCY OF SURFACE APPLICATIONS OF THREE PHOSPHATES ON YIELDS OF PASTURAGE. EXPRESSED AS PERCENTAGE INCREASES OVER CHECKS (THREE-YEAR AVERAGE)

Pounds per acre	Superphosphate		Ammophos		Sodium phosphate	
	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed
Waterbury						
600 once .....	88.7	33.7	86.3	50.3	104.	61.9
200 three times ....	75.7	27.4	61.3	47.9	95.5	72.8
Middlebury						
600 once .....	124.8	103.8	125.8	94.4	115.2	105.8
200 three times ....	104.6	92.4	90.5	89.	122.3	114.4
Brandon						
600 once .....	....	76.1	....	106.8	....	78.3
200 three times ....	....	93.6	....	85.2	....	104.5

Apparently the influence of frequency of applications of phosphate varies somewhat with the material used. The increased yields which resulted from the application of 600 pounds the first year were greatest on all plots treated with Ammophos and on all but one of those on which superphosphate was sown. However, the results were practically reversed when sodium phosphate was used. Liming gave very marked responses on all soils, particularly on those where the fertilizer was used at the 600-pound rate. The results secured with sodium phosphate are in agreement with the findings of Gericke (27) who states that soluble phosphates should be applied regularly; those secured with the other two can best be explained by Spillman's (83) assertion that the absorptive power of the soil must be satisfied before increased yields can be expected.

*Effect of Silica and Silicates.*—The low phosphate fixation by the silica layer of podzol profiles in previous fixation studies as well as a review of the literature, led to the belief that silicates might be effective in overcoming fixation. A greenhouse pot trial was conducted on the

Hermon soil for the purpose of studying the influence of calcium silicate on phosphate recovery and plant growth. Superphosphate at the rate of 400 pounds and rock phosphate at the rate of 600 pounds per acre were added to 5,500 grams of soil in two-gallon crock jars. Lime and calcium silicate were applied separately at rates equivalent to the lime requirement of the soil. The pots were seeded to turnips and the crops harvested after two months' growth. The yields and phosphoric acid contents of the plants are given in table 11. A comparison of the plant responses on the rock phosphate series is also shown in plate 5.

TABLE 11.—EFFECT OF CALCIUM SILICATE AND CALCIUM CARBONATE ON YIELD OF TURNIPS AND ON PHOSPHORUS RECOVERY

	Yield in gms.	Mgs. $P_2O_5$ in plants	Percentage $P_2O_5$ in plants
Rock phosphate .....	3.5	7.7	0.22
Rock phosphate and calcium silicate.	11.1	93.02	0.84
Rock phosphate and calcium carbonate .....	8.2	71.34	0.87
Superphosphate .....	4.	22.	0.55
Superphosphate and calcium silicate.	13.5	117.45	0.87
Superphosphate and calcium carbonate	10.5	80.75	0.77

The applications of calcium silicate increased phosphorus recovery to quite a marked degree when either rock phosphate or superphosphate were used. Since in the amounts used both calcium silicate and calcium carbonate possess equivalent acid-neutralizing powers and calcium contents, the increments from these two factors might be expected to be identical which, however, was not the fact. The larger yields obtained when calcium silicate was applied may, therefore, be attributed to the influence of its silica content.

In a somewhat similar trial an attempt was made to study its influence on phosphate recovery in an Addison clay soil to which 1.25 percent of freshly precipitated iron oxide was added. This was used because of its known powers to fix phosphorus. Increased yields and greater phosphate recovery by rape plants on both rock and superphosphate followed the use of calcium silicate. The response of the plants to the treatments on the rock phosphate series is shown in plate 6.

Other workers have observed this beneficial influence of silica on plant growth and phosphate recovery but they disagree as to the rôle which silica plays. One group, including Gaarder (21), Fisher (18), Nemec (64), Reiffenberg (70), Lemmerman, et al. (45), Kappen and Bollenbeck (43), and Gile and Smith (28), consider that it acts

primarily to increase the availability of, or to release, phosphorus. On the other hand Thomas (87) and Butkevich (7) explain its action by the Gibbs-Donan equilibrium, stating that the presence of the non-permeable silica ion allows plants to feed on smaller concentrations of phosphate. However, Pfeiffer (69) advances yet another theory, claiming that the silica replaces the phosphate in inorganic combinations in the plant.

Laboratory trials were instituted in order to throw light upon the action of silica in increasing phosphate recovery. In one case 250 parts per million of soluble silica as potassium silicate were added to the soil. The amount of water soluble silica removed from solution and its influence on phosphate recovery in the soil was determined. The regular fixation procedure was followed, using 400 parts per million of phosphorus. The results on six soils are given in table 12.

TABLE 12.—INFLUENCE OF ADDITION OF SILICA ON PHOSPHATE RECOVERIES IN SOILS

Soils	Silica fixed (parts per million)	Parts per million of phosphorus recovered		Soils	Silica fixed (parts per million)	Parts per million of phosphorus recovered	
		Normal soil	Silica-treated soil			Normal soil	Silica-treated soil
Hollis sandy loam...	94	26	44	Blanford sandy loam	40	30	30
Hermon fine sand...	100	10	16	Dutchess loam .....	30	40	80
Pittsfield sandy loam.	80	105	185	B <sub>2</sub> horizon of podzol.	50	35	55

Apparently soils may fix quite large amounts of silica and its presence in the soil increases phosphatic availability. Its function in this case is thought to be partially to deactivate the soil fixing compounds.

The influence of silica on the fixation of phosphate by bog ore (limonite) was also determined. To one gram of bog ore was added 25 milligrams of silicic acid and 4.75 milligrams of soluble phosphorus as anhydrous phosphoric acid. To another gram of bog ore only the phosphorus was added. Its fixation (Heck's method) was 31 percent in the silica treated sample and 84.2 percent in the untreated sample. Apparently the silica partially overcame the fixing power of the limonite. Similar trials using other iron compounds and aluminum fixing materials gave like results. Undoubtedly increased plant yields following the use of silica or some of its compounds can be attributed, in part at least, to the increased phosphate availability brought about by deactivation of the sesquioxides.

It may be possible, if an economical process can be developed, to produce commercial phospho-silicate fertilizers. Some phosphate-silicate mixtures prepared in the laboratory were found to be much less subject to fixation than were the common phosphates.

*Effect of Organic Matter.*—The fact that organic phosphates were found to penetrate readily in soil led to the belief that organic matter may be effective in deactivating the iron and aluminum fixing materials. A study of the influence of a humus material on phosphate fixation by bog ore was conducted in the laboratory. It was extracted from a muck soil with dilute sodium hydroxide precipitated with hydrochloric acid, washed and, finally, electro-dialyzed to remove the electrolytes. When 0.25 of a gram was added to a gram of bog ore the amount of phosphorus fixed was reduced by 40 percent. Similar trials with freshly precipitated iron and aluminum hydroxides gave like results. It would seem that humus is capable of deactivating the iron and aluminum compounds and thus reducing phosphate fixation.

*Effect of Lime.*—Liming increased the yields and phosphate recoveries by plants in both field and pot data, as shown in tables 10 and 11. It is thought that lime may function in three ways to increase phosphate recoveries. It may deactivate the iron and aluminum compounds; it may precipitate the soluble phosphates as tri-calcium phosphate, thus preventing reaction with iron and aluminum; and, by improving the general vigor of the plants, it may induce them to assimilate phosphorus. Preliminary laboratory studies indicate that lime may often actually increase the fixing power of iron and aluminum compounds, but conclusive evidence is lacking. Other studies of liming in relation to superphosphate fertilization show by pot yields on four soils that the best results were obtained when lime was sown one year in advance of the application of the phosphate.

#### SUMMARY

Studies were made of the penetration and fixation of phosphates in Vermont soils. The trials included:

- (A) Field plot studies of three phosphatic fertilizers.
- (B) Greenhouse studies of plant response from several phosphatic fertilizers and from two ways of applying superphosphate.
- (C) Studies of the comparative movement of different phosphates and the influence of various fertilizer salts on the penetration of superphosphate under controlled laboratory conditions.

(D) Chemical studies of phosphate fixation by soils and by iron and aluminum compounds.

(E) Plant and chemical studies on methods of overcoming phosphate fixation.

Field studies with super-, ammonium and sodium phosphates indicate that phosphate penetration is a problem of minor importance under field conditions in Vermont. However, laboratory results seem to show that superphosphate penetrates slowly in soils.

Penetration of superphosphate may be enhanced by certain materials, such as the sulphate and nitrate salts of sodium, potassium, ammonium and magnesium.

Sodium, ammonium, and certain organic phosphates penetrate more quickly in soils than does superphosphate.

Exposure of a phosphate to relatively large amounts of soil, a situation observed in cases of deep penetration, results in enhanced fixation.

Vermont soils are comparatively high fixers of phosphorus. Their fixing power in some cases was equal to that of lateritic soils. Their ability to fix a phosphate is explained by the presence of much of the B horizon in the surface soil, due to the loss of a considerable portion of the A horizon through cultivation and erosion.

The B horizon (zone of iron and aluminum accumulation) of podzolized soils has the ability to fix large amounts of phosphorus. Phosphate fixation in such soils is thought to be brought about chiefly by iron and aluminum compounds.

Certain hydrated oxides and precipitated salts of iron and aluminum fix large amounts of phosphorus.

Certain silicates and minerals, when applied to soils, reduce their fixing power.

Organic matter (e.g., specially prepared humus) also reduces fixation.

Liming increases the ability of a crop to recover phosphorus. However, chemical studies indicate that liming may sometimes increase fixation.

The influence of frequency of application on phosphate recovery was found to vary with the form of phosphatic fertilizer used. Recovery from sodium phosphate was greater when small and frequent applications were made, but recovery from superphosphate and Ammophos was greater when large and less frequent applications were made.



## BIBLIOGRAPHY

1. Aarnio, B. Experimental Investigations on the Question of Precipitation of Iron in Podsol Soils. (Trans. title) *Internat. Mitt. Bodenk.*, 3, 1913, 2-3: pp. 131-140. Abs. in *Exp. Sta. Rcd.*, 30:216 (1914).
2. Arie, J. Red Soils and Phosphatic Manuring. *Bul. Agr. (Sao Paolo)* 15 ser., 6-7: pp. 535-555. Abs. in *Exp. Sta. Rcd.*, 35:725 (1914).
3. Arrhenius, O. Clay as an Ampholyte. *Jour. Amer. Chem. Soc.*, 44: pp. 521-524 (1922).
4. Austin, R. H. Some Reactions between Mono-calcium Phosphate and Soils. *Soil Sci.*, 24: pp. 263-269 (1928).
5. Buie, T. S. The Effect Various Soil and Plant Factors have Upon the Availability of Phosphatic Fertilizers. *Amer. Fert.*, 75:9 (1931).
6. Burgess, J. L. The Relative Availability of Acid Phosphate and the Native Soil Phosphates in the Presence of Pulverized Limestone. II. Future of the Agricultural Lime Industry. *N. C. Dept. Agr., Bul. 41, 3.* Abs. in *Exp. Sta. Rcd.*, 43:26 (1920).
7. Butkevich, V. V. The Rôle of the Donan Membrane Equilibrium in Osmotic processes in the living cell. *Biochem.* 2, 161: pp. 468-487. Abs. in *Chem. Abs.*, 20:924 (1925).
8. Comber, N. M. The Rôle of the Electronegative Ions in the Reactions between Soils and Electrolytes. *Trans. Faraday Soc.*, 20: pp. 567-572 (1924).
9. Crawley, J. T. Fixation of Phosphoric Acid in the Soil. *Jour. Amer. Chem. Soc.*, 24: pp. 1114-1119 (1902).
10. Dana, E. S. *A Textbook of Mineralogy* (p. 433.) John Wiley & Sons, New York (1921).
11. Das, S. An Improved Method for the Determination of Available Phosphoric Acid of Soils. *Soil Sci.*, 30: pp. 33-48 (1930).
12. Doughty, J. L. Fixation of Phosphate by Peat Soil. *Soil Sci.*, 29: pp. 23-35 (1930).
13. Dreyspring, C., Krugel, C., and Doerell, E. G. Phosphoric Acid Content and Reaction Conditions of Soils in Various Countries. *Superphosphate*, 2: pp. 221-230 (1929).
14. Duchon, F. Explanation of the Yield-Increasing Action of Colloidal Silica in Sand Cultures Deficient in Phosphoric Acid (trans. title) *Ztschr. Pflanzenernahr. U. Dungung*, 4, 5, *Wiss.*, pp. 316-325; Abs. in *Chem. Abs.*, 19:3557 (1925).
15. Egorov, M. A. Phosphate Applications and their Influence on Chernozem: IV. The Reversion of Phosphoric Acid in Soils. *Kharkov Exp. Sta., U. S. S. R. Trans. Soil Sci.*, 25:463-472.
16. Ellenberger, H. B., Newlander, J. A., and Jones, C. H. Yield and Composition of Pasture Grass. *Vermont Sta., Bul. 295* (1929).
17. Fisher, E. A. The Phenomena of Absorption in Soils: A Critical Discussion of the Hypothesis Put Forward. *Trans. Faraday Soc.*, 17: pp. 305-316 (1922).
18. ———. A Preliminary Note on the Effect of Sodium Silicate in Increasing the Yield of Barley. *Jour. Agr. Sci.*, 19: pp. 132-139 (1929).
19. Ford, M. C. The Nature of Phosphate Fixation in Soils. *Jour. Amer. Soc. Agron.*, 25: pp. 134-144 (1933).
20. ———. The Distribution, Availability, and Nature of the Phosphates in Certain Kentucky Soils. *Jour. Amer. Soc. Agron.*, 24: pp. 395-410 (1932).
21. Gaarder, T. Fixation of Phosphoric Acid in Soils. *Medd. Vestlandets Forstl. Forsoksstat*, 14: pp. 1-140. Abs. in *Chem. Abs.* 24:5408 (1930).
22. Gaither, E. W. Effect of Lime Upon the Solubility of Soil Constituents. *Jour. Indus. and Eng. Chem.*, 2: pp. 315-316 (1910).
23. Ganssen, R. Laws of Solubility of Phosphates and Potash in Mineral Soils. *Mitt. Lab. Preusz. Geol. Landesanst.*, 9. Abs. in *Chem. Abs.* 25:3113 (1929).
24. Gehring, A. Action of Various Phosphatic Manures. *Das Superphosphat* 8: pp. 109-111. Abs. in *British Chem. Abs. B.*, 1932:1046 (1932).
25. Gericke, S. Mobility of Phosphoric Acid in Soils. *Z. Pflanz Dung.*, 27A: pp. 144-162. Abs. in *British Chem. Abs. B.*, 1932:201 (1932).

26. ———. Der Einfluss hoher Kalkgaben auf die Wurzellöslichkeit der Nährstoffe Kali und Phosphorsäure im Boden. Fortschr., Landw. 2 (12): pp. 381-384. Abs. in Biol. Abs., 3:21010 (1928).
27. ———. Distribution of Phosphoric Acid in the Soil and Extent to which it can be Assimilated by Plants. Superphosphate, 1:58 (1928).
28. Gile, P. I., and Smith, J. G. Colloidal Silica and the Efficiency of Phosphates. Jour. Agr. Rsch., 31: pp. 247-260 (1925).
29. Gosh, J. C., and Bhattacharyya, P. B. Removal of Ions from Solutions of Calcium Dihydrogen Phosphate by Treatment with Hydrous Gels of Alumina, Silica, and their Mixtures. Soil Sci., 29: pp. 311-322 (1929).
30. Gracanic, M. The Effect of Sodium Nitrate and Ammonium Sulphate on the Availability of Soil Potash and Soil Phosphoric Acid. Z. Pflanzenernähr. Dungung U. Bodenk, 9B: pp. 300-309. Abs. in Chem. Abs., 25: 2229 (1930).
31. Greaves, J. E., and Carter E. G. The Action of Some Common Soil Amendments. Soil Sci., 7: pp. 121-160 (1925).
32. Greenhill, A. W. The Availability of Phosphatic Fertilizers as Shown by an Examination of the Soil Solution and of Plant Growth. Jour. Agr. Sci., 20: pp. 559-572. Abs. in Exp. Sta. Rcd., 64:425 (1930).
33. Hall, A. D., and Morison, C. G. T. The Function of Silica in the Nutrition of Cereals. I. Proc. Roy. Soc. (London), Ser. B., 77, No. B 520; pp. 455-477. Abs. in Exp. Sta. Rcd., 18:125 (1906).
34. Hall, T. D., and Vogel, J. C. Reversion of Acid Phosphate in Acid Soils. Soil Sci., 15:367-369 (1923).
35. Harper, H. J. A Study of the Secondary Effects of Hill Fertilization. Ia. Sta., Rsch. Bul. 87 (1925).
36. Harrison, W. H., and Das, S. Retention of Soluble Phosphates in Calcareous and Noncalcareous Soils. India Dept. Agr., Chem. Sec., 5, No. 9: pp. 195-236. Abs. in Exp. Sta. Rcd., 46:121 (1921).
37. Heck, A. F., and Truog, E. The Nature of Phosphate Fixation in Soils. Abs. of papers presented at 24th annual meeting Amer. Soc. Agron., p. 29 (1931).
38. Heck, A. F. (Private Communication), (1932).
39. Hock, A. Silico-superphosphate. Superphosphate, 7: pp. 174-176. Abs. in Chem. Abs. 25:5494 (1931).
40. Hopkins, C. G. Soil Fertility and Permanent Agriculture, pp. 363-378. Ginn & Company, Boston (1910).
41. Jensen, C. A. Effect of Decomposing Organic Matter on the Solubility of Certain Inorganic Constituents of the Soil. Jour. Agr. Rsch., 9: pp. 253-268 (1917).
42. Jones, C. H. Method for the Lime Requirements of Soils. Jour. Assoc. Off. Agr. Chem., 1: pp. 353-362 (1915).
43. Kappen, H., and Bollenbeck, K. Importance of Forms of Acidity in Soil for Dissolving Difficulty Soluble Phosphates. (Trans. title) Ztschr. Pflanzenernähr. U. Dungung, 4, No. 1-2, Wiss. pp. 1-12. Abs. in Exp. Sta. Rcd., 54:214 (1925).
44. Kellogg, C. E. Magnesium: A Possible Key to the Phosphorus Problem in Certain Semi-arid Soils. Jour. Amer. Soc., Agron., 23: p. 494 (1931).
45. Lemmerman, O., Weissmann, H., and Sammet, K. Investigations on the Cause of the Yield-increasing Action of Silica. (Trans. title) Ztschr. Pflanzenernähr. U. Dungung, 4, No. 5, Wiss: pp. 265-315. Abs. in Exp. Sta. Rcd., 54:218-219 (1925).
46. Loew, O. The Effect of Calcium upon Physiological Function of Magnesium. Ernähr. Pflanze, 27: pp. 97-101; 121-122. Abs. in Chem. Abs. 25:5498 (1931).
47. Lunt, H. A. Profile Characteristics of New England Forest Soils. Conn. Sta. Bul. 342 (1932).
48. Marais, J. S. The Comparative Value of Insoluble Mineral Phosphates of Aluminum, Iron, and Calcium. Soil Sci., 13; pp. 355-410 (1921).
49. Martin, F. J., and Doyne, H. C. Laterite and Lateritic Soils in Sierra Leone. Jour. Agr. Sci., 20: pp. 135-143. (1930).
50. Marbut, C. F. Symposium on "Soil Organic Matter and Green Manuring." 1. Relation of Soil Type to Organic Matter. Jour. Amer. Soc. Agron., 21: pp. 943-950 (1929).

51. Mattson, S. The Electrokinetic and Chemical Behavior of the Alumino-Silicates. *Soil Sci.*, 25: pp. 289-311 (1927).
52. ———. The Laws of Soil Colloidal Behavior: III. Isoelectric Precipitates. *Soil Sci.*, 30: pp. 459-495 (1930).
53. McGeorge, W. T. The Influence of Silica. Lime and Soil Reaction upon the Availability of Phosphates in Highly Ferruginous Soils. *Soil Sci.*, 17: pp. 463-468 (1924).
54. McGeorge, W. T., and Breazeale, J. F. The Relation of Phosphate Availability, Soil Permeability, and Carbon Dioxide to the Fertility of Calcareous Soils. *Ariz. Sta., Tech. Bul.* 36 (1931).
55. ———. Phosphate Solubility Studies on Some Unproductive Calcareous Soils. *Ariz. Sta., Tech. Bul.* 35 (1931).
56. ———. Studies on Iron, Aluminum, and Organic Phosphates and Phosphate Fixation in Calcareous Soils. *Ariz. Sta., Tech. Bul.* 40 (1932).
57. Meyer, A. H. Phosphorus Fixing Compounds in the Soil. *Science*, 71: p. 461 (1930).
58. ———. Necessity of Organic Matter for the Maintenance of an Available Supply of Phosphorus in the Soil. *Science*, 73: p. 702 (1932).
59. Midgley, A. R. The Movement and Fixation of Phosphates in Relation to Permanent Pasture Fertilization. *Jour. Amer. Soc. Agron.*, 23: pp. 788-798 (1931).
60. Miller, P. R., and Randall, R. O. Fertilization and Management of Addison County Pastures. *Vt. Ext. Serv. et al.*; pamph. (1932).
61. Miller, P. R., and Aronson, H. A. Fertilization and Management of the Pasture and Hay Crops in Washington County. *Vt. Ext. Serv. et al.*; pamph. (1932).
62. Nagaoka, M. On the Action of Various Insoluble Phosphates Upon Rice Plants. *Bul. Col. Agr. Tokyo Univ.*, 6, No. 3: pp. 215-261. Abs. in *Exp. Sta. Rcd.*, 16:555 (1904).
63. Nehring, K., and Keller, A. Influence of (Soil) Reaction on the Phosphoric Acid Intake from Various Phosphate Fertilizers. *Z. Pflanz. Dung.*, 11B: pp. 257-273. Abs. in *Brit. Chem. Abs.-B.* 1932:782 (1932).
64. Nemeč, A. Determination des Besoins des Sols en Acide Phosphorique d'Après la Silicie Soluble. *Compt. Rend. Acad. Sci.*, 186 (16): pp. 1060-1062. Abs. in *Biol. Abs.*, 3:2609 (1928).
65. Nemeč, A. A Contribution to the Evaluation of Requirements for Fertilizing Soils with Phosphorus. *Vestník Ustr. Jednoty Reparo Csl.*, 11:277; *Listy cukr. Var.*, 49, No. 4 *Rozhledy*: 1. Abs. in *Chem. Abs.*, 25:2508 (1930).
66. Niklas, H., Schropp, W., and Hock, A. Manurial Experiments with Silicophosphate. *Arch. Pflanzenbau*, 9: pp. 470-495. Abs. in *Brit. Chem. Abs.-B.* 1932:163 (1932).
67. Overseth, O. E. Movement of Fertilizers in Carrington Loam. *Jour. Amer. Soc. Agron.*, 25: pp. 202-216 (1933).
68. Parker, F. W., and Tidmore, J. W. The Influence of Lime and Phosphatic Fertilizers on the Phosphorus Content of the Soil Solution and of Soil Extracts. *Soil Sci.*, 21: pp. 425-441 (1925).
69. Pfeiffer, Th. The Possibility of a Partial Replacement of Phosphoric Acid by Silicic Acid in Plants. *Mitt. Deut. Landw.-ges.*, 38: pp. 196-198. Abs. in *Chem. Abs.*, 17:3069 (1923).
70. Reifenberg, A. The Influence of Colloidal Silicic Acid on the Assimilation of Phosphoric Acid and Crude Phosphates. *Z. Pflanzenernahr. Dungung u. Bodenk.*, 17A: pp. 1-11. Abs. in *Chem. Abs.*, 24:5917. (1930).
71. Robinson, G. W. Soils—Their Origin, Constitution, and Classification (pp. 6, 66, 199-223). D. Van Nostrand Co., New York (1932).
72. Roszman, C. A. Retention of Phosphorus by Soil Colloids. *Soil Sci.*, 24: pp. 465-474 (1927).
73. Russell, E. J., and Prescott, J. A. The Reaction Between Dilute Acids and Phosphorus Compounds of the Soil. *Jour. Agr. Sci.*, 8: pp. 65-110. (1916).
74. Scarseth, G. D. Morphological Greenhouse and Chemical Studies of the Black Belt Soils of Alabama. *Ala. Sta., Bul.* 237 (1932).
75. Schmitt, L. Contribution to the question of Mobility of Phosphoric Acid in Soil. *Das Superphosphat*, 7: pp. 54-58. Abs. in *Chem. Abs.*, 25:3758 (1931).

76. Schollenberger, G. J. Silica and Silicates in Relation to Plant Growth and Composition. *Soil Sci.*, 14: 347-362 (1922).
77. Schreiner, O. Organic Phosphorus in Soils. *Jour. Amer. Soc. Agron.*, 15: pp. 117-124 (1923).
78. Schulze, B. On the Influence of Liming on the Availability of Phosphoric Acid in Commercial Fertilizers. *Fuhling's Landw. Ztg.*, 53 (5), pp. 186-188; (6), pp. 216-222; (7), pp. 261-265. *Abs. in Exp. Sta. Rcd.*, 16:32 (1904).
79. Sen, J. The Retention of Soluble Phosphate in Calcareous and Non-calcareous Soils. *Agr. Rsch. Inst. Pusa, Sci. Rpt.*, pp. 35-39. *Abs. in Exp. Sta. Rcd.*, 45:331 (1919).
80. Simmermacher, W. The Action of Calcium Carbonate in the Fertilizing of Oats with Monocalcium and Dicalcium Phosphate. *Landw. Vers. Stat.*, 77, No. 5-6; pp. 441-471. *Abs. in Exp. Sta. Rcd.*, 27:726 (1912).
81. Simon, R. H. The Effect of Phosphate and Lime Upon the Rate Curve of Solubility of Phosphorus from a Wooster Silt Loam Soil. *Soil Sci.*, 29: 71-78 (1930).
82. Spencer, V. E., and Stewart, R. Soil-penetrating Phosphates. Reprint from *Jour. Amer. Soc., Agron.*, 23: p. 27 (1931).
83. Spillman, W. J. Measuring Absorbed Phosphates and Nitrogen. *Science*, 73: pp. 215-216 (1931).
84. Spurway, C. H. Some Factors Influencing the Solubility of Phosphorus in Soil-acid Phosphate Mixtures. *Soil Sci.*, 19; pp. 399-405 (1925).
85. Starkey, E. B., and Gordon, N. E. Influence of Hydrogen-ion Concentration on the Adsorption of Plant Food by Soil Colloids. *Soil Sci.*, 14; pp. 449-457 (1922).
86. Teakle, L. J. H. Phosphate in the Soil Solution as Affected by Reaction and Cation Concentrations. *Soil Sci.*, 25:143 (1928).
87. Thomas, W. The Effect of Colloidal Silica on the Absorption of Phosphoric Acid by Plants. *Science*, 71: pp. 422-423 (1930).
88. Truog, E. The Utilization of Phosphates by Agricultural Crops, Including a New Theory Regarding the Feeding Power of Plants. *Wis. Sta., Rsch. Bul.* 41 (1916).
89. ———. The Determination of Readily Available Phosphorus of Soils. *Jour. Amer. Soc. Agron.*, 22: pp. 874-882. (1930).
90. ———. Available Calcium and Magnesium in Relation to Phosphate Utilization. *Jour. Amer. Soc. Agron.*, 23: p. 1055 (1931).
91. Truog, E., and Parker, F. W. Lime Maintains Availability of Phosphorus. *Wis. Sta., Bul.* 323: pp. 55-56 (1920).
92. Van Alstine, E. The Movement of Plant Food Within the Soil. *Soil Sci.*, 6: pp. 281-308 (1918).
93. Van Alstine, E., and Cook, T. D. Fertilizing Rutland County Pastures *Vt. Ext. Serv. et al.*; pamph. (1931).
94. Vanstone, E. Available Phosphorus in Soils. *Jour. Agr. Sci.*, 15: pp. 460-465 (1925).
95. Weidmann, A. G. Some Factors Involved in Studying Fixation of Phosphorus by Soils. *Soil Sci.*, 26: p. 281.
96. Westhauser, F., and Zielstorff, W. The Influence of Applications of Lime and Magnesia on Phosphate Fertilizing. *Landw. Vers. Stat.*, 65: pp. 441-447. *Abs. in Exp. Sta. Rcd.*, 18:1029. (1907).
97. Whiting, A. L., and Heck, A. F. The Assimilation of Phosphorus from Phytin by Oats. *Soil Sci.*, 22: pp. 477-493 (1926).
98. Wojtysiak, M. Fixation of Phosphoric Acid in Certain Soil Types. *Roez. Nauk. Roln. Les.*, 27: pp. 65-136, *Chem. Zentr.*, 2884. *Abs. in Brit. Chem. Abs.-B*, 1932:1046 (1932).
99. Wolkoff, M. Relative Availability of the Phosphorus of Raw Rock and Acid Phosphate in Soils. *Soil Sci.*, 17: pp. 39-56 (1924).