PHOSPHORUS AND POTASSIUM AS INFLUENCED BY ONE ANOTHER AND CALCIUM IN REFERENCE TO THEIR AVAILABILITY IN MARYLAND SOILS.

By

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INTRODUCTION

In 1839-1840, Justus Von Liebig demonstrated that treating animal bones with sulfuric acid increased their fertilizer value. Shortly thereafter, Sir John B. Lawes started to manufacture superphosphate. This was the beginning of the manufacture of commercial fertilizer, an industry which has so developed that it now supplied the farmers of the United States with approximately two and a quarter million tons of phosphoric acid and one and one tenth million tons of potash in the form of commercial fertilizers. When these fertilizers are applied, they are usually in a mixed form; certainly, interactions between these applied fertilizer elements could occur in the soil.

Though the soil phosphorus and potash problems have been studied for years by many investigators, little work on the influence of potash on phosphorus availability or the influence of phosphorus on the availability of potassium has been published. However, in 1940 Eriksson in Sweden (24) studied the influence of potassium on phosphate treatment in relation to the yield of grain. He reported that there was often a reduction in the yield of grain when muriate of potash was applied with superphosphate. This reduction was eliminated by applying larger quantities of phosphate. The purpose of the work reported in this paper was to investigate the interaction of applied phosphorus and applied potassium in reference to their chemical availability in some Maryland soils. The influence of calcium on phosphorus and potassium availability was also considered.

REVIEW OF LITERATURE

Numerous soil phosphorus studies have been conducted since Lawes' original experiment at Rothamested in 1842. As a result the literature on this subject is quite voluminous so only some of the work pertinent to this paper will be reviewed in the following sections; namely, retention of phosphorus by iron and aluminum; exchangeable phosphorus; retention of phosphorus by calcium; influence of pH on phosphorus retention, influence of organic matter and silica on phosphorus availability, influence of liming and fertilizer materials on phosphorus availability, penetration of phosphorus in soils, and the influence of phosphorus on exchangeable cations.

RETENTION OF PHOSPHORUS BY IRON AND ALUMINUM

It has been widely accepted that iron, and aluminum either in solution or as hydrated oxides, are considered to be one of the principal agents responsible for retention of phosphate in acid soils (4, 14, 21, 25, 26, 27, 33, 34, 41, 58, 65, 72). Maximum phosphate fixation is known to occur in very acid soils where iron and aluminum are most active, moreover the isoelectric point for the precipitation of iron by phosphorus occurs at approximately pH of 3 and that for aluminum at pH 4 (16, 70, 71). Kelly and Midgely (37) reported that the fixation of soluble phosphate in most soils is due to a considerable amount of iron oxide distributed as a film over individual soil particles especially in "the lateritic and podzolic soils (B-horizons)". Studies of Allison and Scarseth (2), Chandler (10), Toth (73), and Metzger (46) have shown that the treatments of colloids or soils to remove the freeiron oxides substantially reduces phosphorus retention. This has been supported by Ghani and Islam (26) in 1946, who found that more than 90% of the fixed phosphorus was recovered as iron and aluminum phosphates. That phosphorus combined with iron in the soil is held more tenaceously than that with aluminum was shown by Davis (17). Scarseth and Tidmore (62) and Giles (27) indicate that the fixing power of soil colloides varies inversely as the ratio $\frac{SiO_2}{R_2O_3}$ of the colloid. On the other hand, Davis (16) reported that the formation of iron and aluminum phosphates that were insoluble in Truog extract was not the major form of fixation at soil reaction above pH 4.5. Stout (68) contended that the type of clay mineral largely determines the amount of phosphate retained by soils. In general, these conclusions support the contention that in soils of pH 5 or less the phosphorus retention is primarily due to the formation of insoluble phosphate compounds containing iron and aluminum.

EXCHANGEABLE PHOSPHORUS

Dean and Rubins (22) consider that phosphorus adsorption is due to an exchange between certain hydroxyl ions of the clay minerals or hydrous oxides and the phosphate ions in solution in accordance with the following reaction:

$$\underset{\text{Soil surface}}{XOH} + \underset{\text{Solution}}{H_2PO_4} \rightleftharpoons \underset{\text{Soil surface}}{XH_2PO_4} + \underset{\text{Solution}}{OH^-}$$

Other investigators (9, 13, 14, 38, 54, 55, 56, 60) have arrived at the same conclusion in that the anion exchange of clay minerals is an effective agent for the removal of soluble phosphate from the soil solution. Kelly and Midgley (37) indicated that phosphate fixation is an exchange of phosphate ions for the exposed hydroxyl ions and that the dehydration and the removal of hydroxyl ions by high temperatures greatly reduced the phosphate fixing capacity of soils and of hydrated iron oxides. However, Stout (68) pointed out that it is difficult to distinguish between fixation by adsorption and chemical precipitation. He reported that the crystal structure of kaolinite changed to a new crystal structure after fixing phosphate. This belief is supported indirectly by Low and Black (41), and Toth (72) who give evidence of silica release from clays accompanying phosphorus retentions.

RETENTION OF PHOSPHATES BY CALCIUM

One of the major forms in which phosphorus may be retained by soils is calcium phosphate according to Allison (1) Barbier et al (3) and Davis (19). Heck (31) explained this phenomena in the following statement, "The predomination form in which soluble phosphate is fixed in the soil depends much upon the relative abundance in the soil of different materials capable of fixing phosphorus. If the ratio of active calcium to active iron and aluminum is high, the fixation will be largely in the calcium form, and the fixed phosphorus will be readily available. If the reverse is true, the fixation will be largely as the iron and aluminum compounds of phosphorus, which are difficulty available." However, in some instances where calcium salts are abundant and soil pH is high some apatite-like minerals may occur. McGeorge et al (44) report the formation of carbonato-apatite $\left[3\ Ca_3 - (PO_4)_2 . CaCO_3\right]$ and hydroxyl-apatite $\left[3\ Ca_3\ (PO_4)_2 . Ca(OH)_2\right]$ as a contributing factor to low phosphate availability in calcareous alkaline soils.

INFLUENCE OF pH ON PHOSPHORUS RETENTION

Bradfield et al (6) postulated that the ability of soils to retain phosphate ions over a wide range of reactions and concentrations is due to at least three distinct although overlapping mechanisms. At pH 2 to 5 the retention is due chiefly to the gradual dissolution of iron and aluminum and their reprecipitation as phosphates. At pH 4.5 to 7.5, phosphates are fixed on the surface of clay particles, and at pH 6 to 10 phosphate is precipitated by divalent cations if present. Hibbard (34) concluded that pH is the most important factor for phosphorus solubility, since phosphates of calcium and magnesium becomes easily soluble below pH 7, whereas, Fe and Al phosphates are not much dissolved above pH 3. Troug (75) stated that "at pH 6.5, lime is sufficiently abundant and available to keep a considerable portion of phosphorus in the form of calcium phosphate which is soluble in carbonic acid, and hence readily available to crops. This holds for both the phosphorus naturally present in soils and that applied in the form of manures and fertilisers. When lime is present or added in amounts so as to raise pH beyond 7.5, then the influence on phosphate availability gradually becomes less favorable, although this is usually not serious until the pH goes beyond 8 and there is present 2 to 3% and more of free calcium carbonate." Then he added, "As the pH goes up to 8.5 and higher a tendency should develop for the formation of sodium phosphate, which being soluble, would be readily available for plant use."

INFLUENCE OF ORGANIC MATTER AND SILICA ON PHOSPHORUS AVAILABILITY

The presence of certain organic anions produced in the soil reduced greatly the amount of phosphate fixed by iron and aluminum (69, 70) and it has been found that organic matter made phosphates more available for plant use (11, 46, 61).

Gile and Smith (28), Pierre and Browning (52) and Chapman (11) have concluded that silica gel produced an increase in water soluble phosphate. Scarseth (61) indicated that silicate ion replaced adsorbed phosphate by soils and thus made it available.

INFLUENCE OF LIMING AND FERTILIZER MATERIALS ON PHOSPHORUS AVAILABILITY

Lime applied to acid soils seems to help increase the availability of native soil phosphorus (48, 66). MacIntire and Hatcher (42) and others (20) found that phosphorus uptake from applied superphosphate by plants was increased by liming. Davis (16) reported that the readily available phosphorus as measured by Truog's method and by CO_2 - saturated water was increased by liming. Truog (75) concludes that for general farming, acid soils should be limed to pH 6.5 where phosphorus is most available for plant use and he stated: "In fact, if lime produced no other benefit than its favorable influence on phosphate availability, it would usually pay to use it." On the other hand, excessive liming caused a decrease of phosphorus availability (52). This may be explained by the formation of tricalcium and fluorophosphates according to MacIntire and Hatcher (43). Exchangeable calcium, as indicated by Allison (1) and Davis (19), is an important factor in retaining appreciable amounts of phosphate in acid soil probably in the form H_2PO_4-Ca-Micelle and that this form of phosphate may be the most available form to plants (1). Heck (31) explains the practical importance of these views with the following excerpt: "The Miami silt loam apparently contains relatively little active iron or aluminum and not more than a trace of calcium carbonate. With these factors balanced in this way, this soil is almost ideal for the active use of soluble phosphates. There is very little difficulty available phosphate formed and there is sufficient exchangeable calcium to prevent excess leaching, and at the same time, not enough calcium carbonate to hold the phosphate in the immediate surface soil. As a result, a good positional fixation is obtained."

Perkins (51), studying the affect of various mixtures of cations with phosphate on phosphate retention, found with increasing cationic concentrations soil phosphate retention was increased whether single or mixed cations were used. Hock (32) stated that "a low degree of base saturation tends to give a soil a greater capacity for fixing phosphorus in a difficulty available form than if the soil is more fully saturated with bases." Ravikovitch (57), working on the influence of exchangeable cations on the availability of phosphate in soils, found that the degree of PO_4 availability is influenced greatly by the kind of cations present in the soil. His results indicated that the effectiveness of the various exchangeable cations in the liberation of the adsorbed PO_4 could be arranged by the following order: $Na > K > NH_4 > H > Mg > Ca$, whereas these cations could arranged in the reverse order in their effectiveness of PO_4 adsorption by the soil.

Lohse and Ruhnke (40) have studied the influence of different fertilizer salts incorporated with mono- and di-calcium phosphate upon phosphorus solubility and noted that in every case dicalcium phosphate in soil was more soluable than monocalcium phosphate when an acid solution of potassium acid sulfate was used as the extractant. However, Hibbard (34) showed by using Troug's extract, that dicalcium phosphate was frequently fixed more tenaceously than monocalcium phosphate, and he concluded that "the relative fixing power of different soils is different for different salts, thus indicating that the most effective salt for one soil may not be the best for a different soil". Collings (15) and Jones (36) pointed out that ammonium salts and muriate of potash increased the availability of rock phosphate. Bauer (5) in 1920 reported that sodium nitrate had no appreciable influence on the availability of rock phosphate, while Liebig in 1865 (39) showed that sodium nitrate increased the solubility of calcium phosphate. Greaves and Crater (29) in 1919, stated that sodium, magnesium and potassium chlorides have little, if any, direct effect on the phosphate solubility. Wheeting (76), in 1925, recorded that mono-calcium phosphate was not influenced by any treatment. However, Eriksson (24) in 1940, in Sweden, studied the influence of potassium fertilization upon the fixation of phosphorus in Swedish soils. He concluded from the results of his pot experiments that potassium fertilizers applications caused a decrease in the available phosphorus in soils relatively rich in sesquoxides. This was so marked that barley plants grown under these conditions exhibited symptoms of phosphorus deficiency which could be overcome through increased application of phosphorus. He also studied these soils by shaking them with phosphorus solutions containing various amounts of KCl for 302 hours. His findings showed that the solubility of phosphate decreased as the addition of potassium chloride increased. He assumed that iron and aluminum compounds were activated by the addition of potassium chloride and caused more phosphorus fixation. To determine whether this was an important factor in field production, he analyzed 450 grain experiments and found when potassium was added with phosphorus, potassium caused a reduction in crop yield in 45% of the cases as compared to phosphorus fertilizers application alone. Haseman et al. (30) reported that phosphate might be fixed in acid soils that contained potassium, ammonium or sodium as minerals similar to palmerite, variscite or strengite. He stated that "the rapid fixation is believed to result from a combination of phosphate ions with superficial ions of Al, Fe that are held in the extremities of the lattice or by exchangeable attachments on both the clays and hydrous oxides of Fe and Al. The product of this reaction initially is relatively soluble and presumably is readily available to plants, but its solubility decreases gradually, probably as a result of crystallization and partial dehydration to form phosphate similar to palmerite, variscite, or strengite."

PENETRATION OF PHOSPHORUS IN SOILS

Measurement of penetration of phosphorus in soil has been used as an index of fixation. Midgley (47), Stephenson and Chapman (67) found a varying penetration in the field depending upon the kind of soil, the amount of applied phosphorus and the manner of its application. Their field observation indicated that little or no penetration took place with heavy soils, but with light textured soils appreciable movement might occur.

Heck (31) stated that "either active calcium, iron or aluminum inhibits the downward movement of phosphorus in soils in proportion to the amount present and inversely proportional to the solubilities of their compounds with phosphorus." Whereas, Sell and Olson (64) reported that top dressing soils with limestone was found to increase the penetration of available phosphorus.

Patton (49) in 1911, pointed out that more phosphorus can be leached from the soil when weak solutions of salts: KCl, K_2SO_4, KNO_3, or K_2CO_3 are passed through the soil, than can be obtained with distilled water. Brown (8) found that when rock phosphate was applied with ammonium sulfate or sodium nitrate, the penetration of phosphorus in the soil was more rapid than was superphosphate if applied with the same nitrogen carriers. Midgely (47), working on the influence of different fertilizer materials on the downward movement of superphosphate, reported that potassium and ammonium sulfate checked the movement of phosphate, while sodium nitrate greatly increased it. He reasoned the action of these salts is caused by potassium and ammonium being more active than sodium in replacing calcium from the exchange complex, and the displaced calcium formed more difficulty soluble tri-calcium phosphate.

THE INFLUENCE OF PHOSPHORUS ON EXCHANGEABLE CATIONS

The total cation exchange capacity was found to be increased by the addition of phosphates to the soils (18, 46, 53, 72). This amount of increase in total base exchange as indicated by Davis (18) and Prince and Toth (53) was dependent upon the amount of phosphate added. This might be explained on the basis that the added phosphate increased the acidoid - basoid ratio of the soil colloids (53, 12).

Wood and De Turk (77) and Hoover (35) showed that both the exchangeable potassium and the fixed potassium were greater in soils that had been treated with potassium phosphate than in those treated with potassium chloride. This increase in replaceable potassium might be explained by the PO_4- linkage as pointed out by De Turk et al. (23).

MATERIALS AND METHODS

Soil Samples. The soils selected for this investigation are representative of the important agricultural areas of the State of Maryland and differed widely in soil profile characteristics. Nine soils were chosen: three of them, Collington, Beltsville, and Sassafras from the Coastal Plain, and the others, Chester, Myersville, Conowingo, Montalto, Penn, and Hagerstown, from the Piedmont Plateau. These soils were derived from the following materials:

Collington fine sandy loam was derived from green sand or glauconitic material.

Beltsville silt loam was developed from beds of unconsolidated silts and sands (often containing some gravel) mostly on remnants of Pliocene terraces.

Sassafras sandy loam was developed from unconsolidated sand of Coastal Plain.

Chester silt loam was derived from the weathered products of gneiss mica schist and granites.

Conowingo silt loam was derived from the weathered products of serpentine.

Myersville silt loam was developed from the weathered products of green schist.

Montalto clay loam was developed from the weathered products of basic rocks such as diorite, diabase, gabbro, and rocks locally called "iron stone".

Penn silt loam was derived from the weathered products of weak red or purplish red sandstones and shales of the Triassic Age.

Hagerstown silt loam was derived from the weathered products of massive hard limestones.

For the purpose of this investigation, individual soil samples were taken at a zero to six inch depth from each of the nine different Maryland soil series. For further statistical study, six of the nine soil series, namely; Collington, Beltsville, Chester, Conowingo, Penn, and Myersville were selected. Each of these was sampled at five more locations. These locations, for one soil series, were quite far apart. However, they were usually within a radius of five miles. The general location of each soil series where samples were obtained is given in Table 1.

Table 1

Location of Sampling Areas in Maryland

Soil Name	Location
Collington fine sandy loam	Woodmore
Beltsville silt loam	Beltsville
Sassafras sandy loam	Federalsburg (Eastern Shore)
Chester silt loam	Hunting Hill (3 miles NW of Rockville)
Conowingo silt loam	Gaithersburg
Myersville silt loam	5 miles NW of Frederick
Montalto silt loam	5 miles NE of Baltimore
Penn silt loam	Poolesville
Hagerstown silt loam	Beaver Creek (5 miles SE of Hagerstown)

Leaching Procedure:

These samples were air dried and passed through a 2 mm. screen. Each was spread on a heavy brown wrapping paper, and with constant mixing, water was applied with an atomizer until there was no dust left on the paper. After this treatment, the soil was placed in a closed jar for twelve hours to permit further equilibriations.

Three glass funnels were used to build a column as shown in Fig. 1.

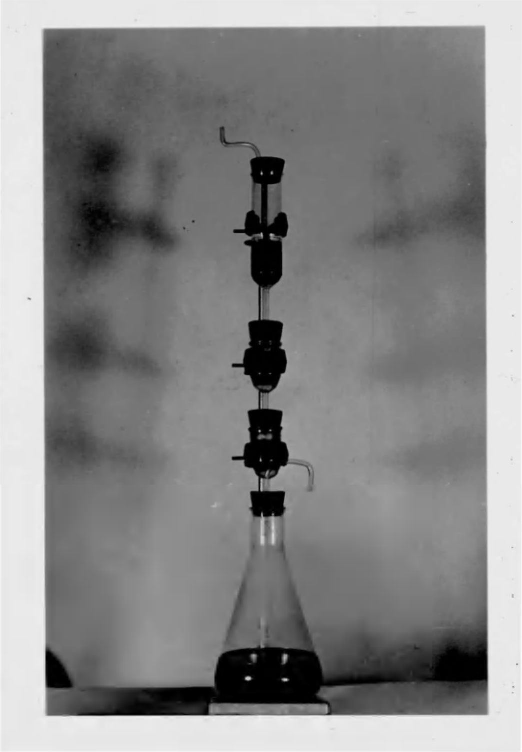


Fig. 1. The Three Funnel Column Used for Leaching the Soils.

These cylindrical funnels were fitted with a fritted glass disc at the bottom, and the cylinder was 1 3/8 inches in diameter and 1 7/8 inches in length with the exception of the top funnel which had the same diameter but was five inches long.

To keep the soil uniform in each funnel, small portions of the sample were placed individually around the side and in the middle of each funnel until a thirty gram portion of the nearly dry soil from the closed glass jars had been added. A uniform weight was used to pack the soil in the funnels and then the soil surface was covered by glass wool. The stem of each funnel was fitted with a rubber stopper and connected to the funnel below. Then a 1000 ml. flask was connected to the bottom of each column to receive the leachate. The soil was placed in this type of a column to facilitate percolation, and to permit accurate sampling of the soil at various depths.

Each soil was treated by adding to the soil in the top of the column, salts dissolved in 20 ml. of distilled water. The salts used in these treatments are given in Table 2. The amount of salts applied to each column was two milliequivalents of each cation added and 61.96 milligrams of phosphorus.

Table 2

Treatments Applied to Soil Columns of Each Soil Series

Column Number	First Treatment Followed by 20" of H_2O	Second Treatment Followed by 20" of H_2O
1	$Ca(H_2PO_4)_2.H_2O$	None
2	KH_2PO_4	None
3	$KCl + Ca(H_2PO_4)_2.H_2O$	None
4	KCl	$Ca(H_2PO_4)_2.H_2O$
5	$Ca(NO_3)_2.4H_2O$	$Ca(H_2PO_4)_2.H_2O$
6	$MgSO_4.7H_2O$	$Ca(H_2PO_4)_2.H_2O$
7	$NaNO_3$	$Ca(H_2PO_4)_2.H_2O$
8	HCl	$Ca(H_2PO_4)_2.H_2O$

In each case, after adding the salt solutions, the columns were permitted to stand overnight. They were then leached with twenty inches of distilled water. In the case of two treatments, the process was repeated. After the last addition of water, they were permitted to drain for twenty-four hours. Then the columns were placed in an oven at 50° C until the soil was dry.

Methods of Analysis:

Available phosphorus was determined by Troug's method. Four grams of soil were extracted with 400 ml. of 0.002 N sulfuric acid. The extracted phosphorus was determined colorimetically by the method of Zinzade (78) as modified by Peech et al. (50) by use of Beckman's spectrophotometer.

Total phosphorus was determined according to Bray's method (7) as modified by Rubins (59). One gram of 60 mesh oven dry soil sample was digested with twenty millimeters of 72 per cent perchloric acid in a 70 ml. florence flask until colorless. Then the resulting solution was made up to 250 ml. and a 10 ml. aliquot was transferred to a 50 ml. volumetric flask until colorless. The reaction was adjusted with 5 per cent sodium carbonate and 1 N sulfuric acid to colorless with quinaldine red indicator. Then the molybdenum blue color was developed by the method of Zinzade (78) as modified by Peech et al. (50). The transmittancy was measured using a 660 mu filter with the Beckman spectrophotometer.

Exchangeable potassium was determined by leaching ten grams of soil samples with 150 ml. of 1 N ammonium acetate solution according to Schollenberger's method (63). These leachates were then taken to dryness on the hot plate and the residues were treated with 9 ml. of concentrated nitric acid and heated for five minutes. Then 3 ml. of 72 per cent perchloric acid was added and heated until dense white fumes first appeared. After cooling, they were transferred to 200 ml. volumetric flasks and 20 ml. of 1000 p.p.m. of lithium sulfate was added. They were then brought to volume with distilled water and the potassium was determined by flame photometry with a Perkin Elmer instrument.

The pH of a 1:1 soil water suspension was measured with a Beckman pH meter using the glass electrode.

RESULTS

Available phosphorus pertains to those forms of phosphorus in soils which are usable by plants, and since those forms of phosphorus are very important for plant growth, a study has been made in the laboratory to determine the available phosphorus as influenced by the elements calcium, magnesium, potassium, sodium and hydrogen. These data are given in Tables 3, 4 and 5. To aid in explaining the results obtained, parts of these tables have been presented in a simplified form as shown in Tables 6 and 7.

Influence of Calcium and Potassium on Phosphorus Availability.

The concentration of available phosphorus in the first inch of soil could well effect the growth of seedling plants as well as larger plants. In this phase of the experiment where the same concentrations of elements were applied to the surface inch of the various soils, phosphorus availability in this layer was greatly influenced by both the soil minerals and the type of treatment. However, in a lower layer, the phosphorus availability was determined not only by reaction within this layer, but by the reaction of the applied elements with the upper layer of soil as well. Table 6 and Figures 2 to 10 show phosphorus availability, as effected by calcium and potassium in the first inch of soil when treated with 61.96 milligrams of phosphorus and then leached with twenty inches of distilled water.

But with two exceptions, Hagerstown silt loam and Montalto clay loam, the data show that the greatest phosphorus availability occurred in the first inch of soil in which the exchangeable calcium was first increased by treating the soils with calcium nitrate before the mono-calcium

Table 3

The Influence of Calcium and Potassium in Combination with the Applied Phosphate* Upon Available and Total Phosphorus in Nine Maryland Soils.

Soil	pH	Phosphorus per Inch Depth of Untreated Soil.		Depth in Inches	Treatments + 20" H_2O					
					$Ca(H_2PO_4)_2 \cdot H_2O$		KH_2PO_4		$KCl + Ca(H_2PO_4)_2 \cdot H_2O$	
		Available P	Total P		Available P	Total P	Available P	Total P	Available P	Total P
		mg.	mg.		mg.	mg.	mg.	mg.	mg.	mg.
Chester	5.75	0.96	23.49	0 - 1	9.10	48.60	5.56	41.85	6.69	45.22
				1 - 2	4.75	35.10	3.70	32.40	3.51	33.75
				2 - 3	3.27	32.94	3.99	33.75	2.59	33.75
Collington	5.18	0.77	17.01	0 - 1	7.72	30.24	3.53	28.35	6.10	29.03
				1 - 2	2.78	21.60	1.92	21.60	1.89	18.90
				2 - 3	2.46	21.60	2.16	20.79	2.45	19.98
Conowingo	4.50	0.19	8.77	0 - 1	4.94	40.50	2.32	33.75	3.07	20.35
				1 - 2	2.75	24.30	2.62	22.95	2.32	17.55
				2 - 3	1.92	18.90	1.78	23.49	1.99	16.74
Penn	4.85	0.35	12.15	0 - 1	8.32	33.75	4.32	27.00	4.32	24.84
				1 - 2	4.40	21.60	3.16	22.95	2.26	20.25
				2 - 3	5.40	24.84	3.62	23.49	1.89	18.90
Montalto	5.70	0.54	25.65	0 - 1	11.34	56.70	7.10	49.95	9.18	53.33
				1 - 2	5.76	40.50	3.86	37.80	3.56	37.80
				2 - 3	3.13	35.10	3.24	33.75	3.51	33.75

*61.96 mg. of phosphorus were applied.

Table 3 (Continued)

The Influence of Calcium and Potassium in Combination with the Applied Phosphate* Upon Available and Total Phosphorus in Nine Maryland Soils.

Soil	pH	Phosphorus per Inch Depth of Untreated Soil.		Depth in Inches	Treatments + 20" H_2O					
					$Ca(H_2PO_4)_2.H_2O$		KH_2PO_4		$KCl+Ca(H_2PO_4)_2.H_2O$	
		Available P mg.	Total P mg.		Available P mg.	Total P mg.	Available P mg.	Total P mg.	Available P mg.	Total P mg.
Myersville	5.45	0.31	33.75	0 - 1	6.20	57.40	4.61	54.00	4.86	49.95
				1 - 2	3.76	49.95	3.40	51.30	3.24	43.20
				2 - 3	2.27	43.20	2.62	37.80	2.48	43.20
Beltsville	5.10	0.23	12.83	0 - 1	7.34	36.45	5.07	31.05	6.48	32.40
				1 - 2	5.18	26.33	3.24	23.49	3.24	23.63
				2 - 3	3.51	21.60	3.53	24.30	2.86	20.25
Hagerstown	6.10	0.19	14.17	0 - 1	6.91	31.05	3.86	20.79	5.94	28.76
				1 - 2	5.29	28.35	2.62	17.55	2.48	20.25
				2 - 3	3.13	20.25	3.40	20.25	2.26	19.17
Sassafras	4.70	0.66	7.15	0 - 1	2.70	9.72	3.40	11.34	2.80	14.18
				1 - 2	3.51	13.50	1.62	9.45	2.91	13.50
				2 - 3	1.84	13.50	1.84	10.80	1.73	12.15

* 61.96 mg. of phosphorus were applied.

Table 4

Influence of Potassium and Sodium Applications Prior to Mono-Calcium Phosphate* Treatment on the Available and Total Phosphorus in Nine Soils.

Soil	pH	Phosphorus per Inch Depth of Untreated Soils		Depth in Inches	1st Treatment + 20" H_2O 2nd Treatment + 20" H_2O			
					1st KCl 2nd $Ca(H_2PO_4)_2.H_2O$		1st NaCl 2nd $Ca(H_2PO_4)_2.H_2O$	
		Available P mg.	Total P mg.		Available P mg.	Total P mg.	Available mg.	Total P mg.
Chester	5.75	0.96	23.49	0 - 1 1 - 2 2 - 3	6.93 5.21 3.61	40.50 36.45 35.10	8.32 3.94 3.86	41.85 37.80 33.75
Collington	5.10	0.77	17.01	0 - 1 1 - 2 2 - 3	3.08 5.09 5.01	25.65 29.70 27.54	4.62 4.05 2.97	30.24 24.30 20.79
Conowingo	4.50	0.19	3.77	0 - 1 1 - 2 2 - 3	3.06 2.32 1.99	45.90 27.00 18.90	3.54 1.99 1.46	40.50 27.00 18.90
Penn	4.05	0.35	12.15	0 - 1 1 - 2 2 - 3	5.23 5.56 3.16	27.00 27.00 21.60	6.64 5.56 4.59	31.05 27.54 27.00
Montalto	5.70	0.54	25.65	0 - 1 1 - 2 2 - 3	6.94 7.25 2.21	56.70 54.00 20.35	5.69 8.64 2.70	47.25 52.65 35.10

* 61.96 mg. of phosphorus were applied.

Table 4 (Continued)

Influence of Potassium and Sodium Applications Prior to Mono-Calcium Phosphate* Treatment on the Available and Total Phosphorus in Nine Soils.

Soil	pH	Phosphorus per Inch Depth of Untreated Soils		Depth in Inches	1st Treatment + 20" H_2O 2nd Treatment + 20" H_2O			
					1st KCl 2nd $Ca(H_2PO_4)_2 \cdot H_2O$		1st NaCl 2nd $Ca(H_2PO_4)_2 \cdot H_2O$	
		Available P mg.	Total P mg.		Available P mg.	Total P mg.	Available P mg.	Total P mg.
Myersville	5.45	0.31	23.75	0 - 1	5.40	56.70	-	-
				1 - 2	6.32	60.75	-	-
				2 - 3	3.85	51.30	-	-
Beltsville	5.10	0.23	12.83	0 - 1	6.75	41.85	6.39	39.15
				1 - 2	4.47	25.65	3.86	27.54
				2 - 3	2.16	22.14	3.40	22.95
Hagerstown	6.10	0.29	14.17	0 - 1	6.32	33.75	-	-
				1 - 2	5.85	31.05	-	-
				2 - 3	4.21	25.65	-	-
Sassafras	4.70	0.66	7.15	0 - 1	2.85	10.80	2.70	14.85
				1 - 2	3.31	14.04	3.24	13.50
				2 - 3	4.32	16.20	3.13	13.50

* 61.96 mg. of phosphorus were applied.

Table 5

Influence of Calcium, Magnesium and Hydrogen Applications Prior to Mono-Calcium Phosphate* Treatment on the Available and Total Phosphorus in Nine Soils.

Soil	pH	Phosphorus per Inch Depth of Untreated Soils		Depth in Inches	1st Treatment + 20" H_2O 2nd Treatment + 20" H_2O					
					1st $Ca(NO_3)_2.4H_2O$ 2nd $Ca(H_2PO_4)_2.H_2O$		1st $MgSO_4.7H_2O$ 2nd $Ca(H_2PO_4)_2.H_2O$		1st HCl 2nd $Ca(H_2PO_4)_2.H_2O$	
		Available P mg.	Total P mg.		Available P mg.	Total P mg.	Available P mg.	Total P mg.	Available P mg.	Total P mg.
Chester	5.75	0.96	23.49	0 - 1	10.13	45.90	8.02	43.20	5.86	43.20
				1 - 2	3.94	33.75	2.62	30.24	2.62	30.24
				2 - 3	3.08	32.40	2.22	31.05	2.62	31.05
Collington	5.18	0.77	17.01	0 - 1	9.03	35.10	6.71	33.75	4.93	27.54
				1 - 2	2.48	22.95	2.62	18.90	3.08	18.90
				2 - 3	2.32	21.60	1.93	16.74	2.62	21.60
Conowingo	4.50	0.19	8.77	0 - 1	5.25	41.05	2.81	42.52	3.24	37.80
				1 - 2	3.54	31.05	2.59	32.40	3.02	31.05
				2 - 3	1.69	20.25	1.18	20.25	2.37	22.95
Penn	4.85	0.35	12.15	0 - 1	9.10	33.75	9.25	35.10	4.18	25.65
				1 - 2	3.55	18.90	3.39	20.25	8.37	31.05
				2 - 3	2.93	18.90	2.31	16.74	3.32	20.25
Montalto	5.70	0.54	25.65	0 - 1	10.80	63.45	8.64	56.70	6.32	60.75
				1 - 2	3.55	36.45	3.69	37.80	3.24	35.10
				2 - 3	2.62	33.75	2.53	32.40	2.62	31.05

* 61.96 mg. of phosphorus were applied.

Table 5 (Continued)

Influence of Calcium, Magnesium and Hydrogen Applications Prior to Mono-Calcium Phosphate* Treatment on the Available and Total Phosphorus in Nine Soils.

Soil	pH	Phosphorus per Inch Depth of Untreated Soils		Depth in Inches	1st Treatment + 20" H_2O 2nd Treatment + 20" H_2O 1st $Ca(NO_3)_2.4H_2O$ 2nd $Ca(H_2PO_4)_2.H_2O$		1st $MgSO_4.7H_2O$ 2nd $Ca(H_2PO_4)_2.H_2O$		1st HCl 2nd $Ca(H_2PO_4)_2.H_2O$	
		Available P	Total P		Available P	Total P	Available P	Total P	Available P	Total P
		mg.	mg.		mg.	mg.	mg.	mg.	mg.	mg.
Myersville	5.45	0.31	33.75	0 - 1	8.94	69.39	6.32	60.75	6.48	55.35
				1 - 2	4.47	55.35	5.56	54.00	2.16	45.90
				2 - 3	2.62	40.50	2.16	45.90	2.37	40.50
Beltsville	5.10	0.23	12.83	0 - 1	8.10	41.85	8.17	36.45	6.94	33.75
				1 - 2	2.70	22.95	2.00	18.90	3.85	24.30
				2 - 3	2.16	20.79	3.54	18.90	2.23	20.25
Hagerstown	6.10	0.19	14.17	0 - 1	6.17	29.70	6.94	33.75	5.24	31.05
				1 - 2	4.93	24.30	3.08	22.95	3.85	24.30
				2 - 3	4.16	22.95	2.16	18.90	2.46	24.18
Sassafras	4.70	0.66	7.15	0 - 1	4.01	13.50	2.80	14.85	3.00	12.69
				1 - 2	3.55	14.18	3.24	17.55	2.62	9.45
				2 - 3	2.47	12.83	2.70	10.80	1.62	[illegible]

* 61.96 mg. of phosphorus were applied.

Table 6

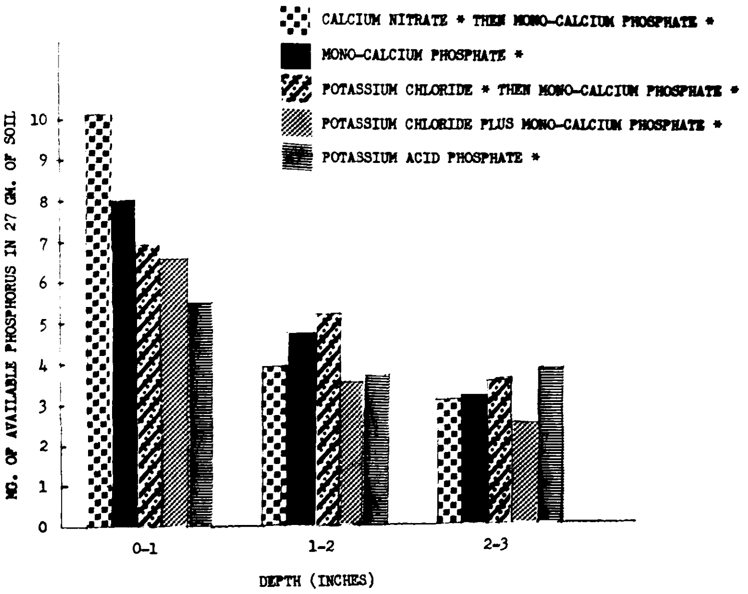
Available Phosphorus as Influenced by Calcium and Potassium in the First Inch of Nine Soils When 61.96 mg. of Phosphorus were Applied.

Soil	Treatments + 20" H_2O			First Treatment + 20" H_2O Second Treatment + 20" H_2O	
	$Ca(H_2PO_4)_2.H_2O$	KH_2PO_4	$KCl+Ca(H_2PO_4)_2.H_2O$	1. KCl 2. $Ca(H_2PO_4)_2.H_2O$	1. $Ca(NO_3)_2.4H_2O$ 2. $Ca(H_2PO_4)_2.H_2O$
	mg.	mg.	mg.	mg.	mg.
Chester	8.10	5.56	6.69	6.93	10.13
Collington	7.72	3.53	6.10	7.08	9.03
Conowingo	4.94	2.32	3.07	3.86	5.25
Penn	8.32	4.32	4.32	5.23	9.10
Montalto	11.34	7.10	9.18	6.94	10.80
Myersville	6.80	4.61	4.86	5.40	8.94
Beltsville	7.34	5.07	6.48	6.75	8.10
Hagerstown	6.91	3.86	5.94	6.32	6.17
Sassafras	2.70	3.40	2.80	2.85	4.01

Table 7

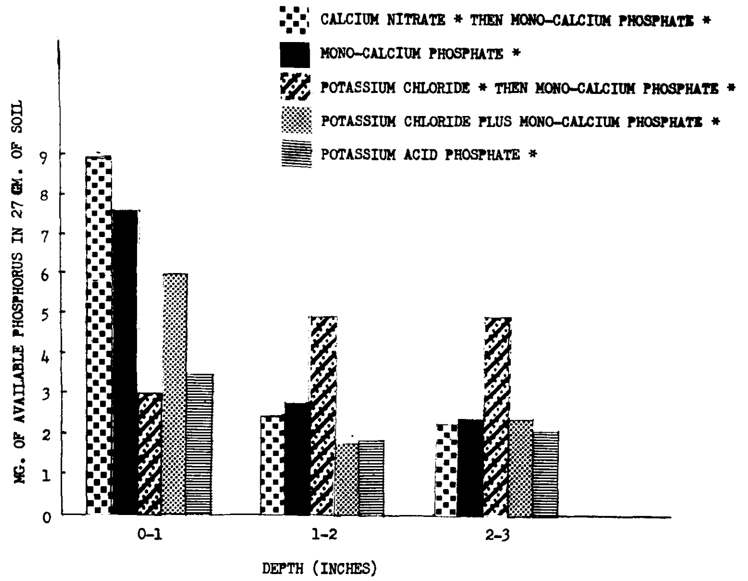
Available Phosphorus as Influenced by Calcium and Potassium in the First Three Inches of Nine Soils When 61.96 mg. of Phosphorus were Applied.

Soil	Treatments + 20" H_2O			First Treatment + 20" H_2O Second Treatment + 20" H_2O	
	$Ca(H_2PO_4)_2.H_2O$	H_3PO_4	$KCl+Ca(H_2PO_4)_2.H_2O$	1. KCl 2. $Ca(H_2PO_4)_2.H_2O$	1. $Ca(NO_3)_2.4H_2O$ 2. $Ca(H_2PO_4)_2.H_2O$
	mg.	mg.	mg.	mg.	mg.
Chester	16.12	13.25	12.79	15.75	17.15
Collington	12.96	7.61	10.44	13.18	13.83
Conowingo	9.61	6.72	7.38	8.17	10.48
Penn	18.12	11.10	8.47	13.95	15.58
Montalto	20.23	14.20	16.25	16.40	16.97
Myersville	12.85	10.63	10.58	15.57	16.03
Beltsville	16.03	11.84	12.58	13.38	12.96
Hagerstown	15.33	9.88	10.68	16.18	15.26
Sassafras	8.05	6.36	7.44	10.48	10.03



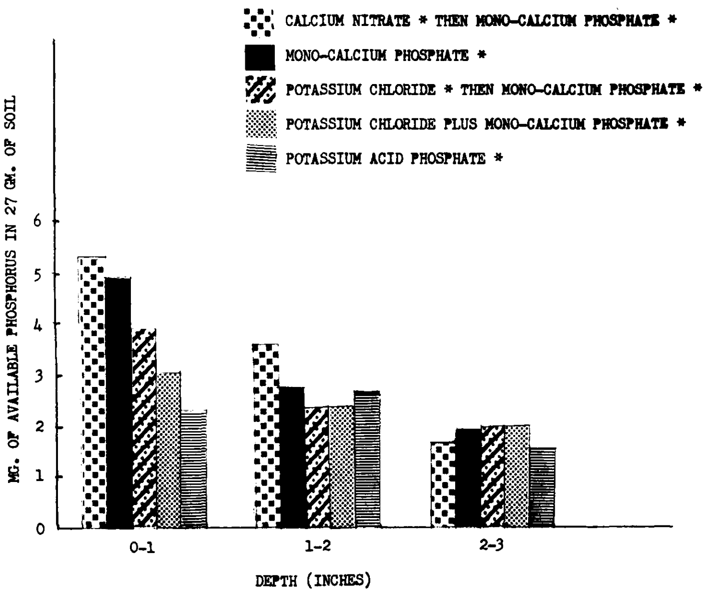
*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 2. Available Phosphorus as Influenced by Calcium and Potassium in Chester Silt Loam when 61.96 mg. of Phosphorus were Applied.



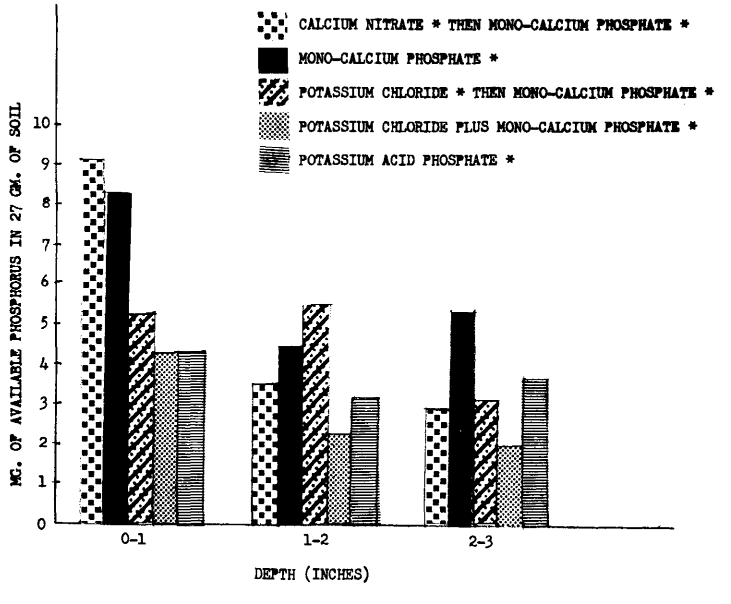
*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 3. Available Phosphorus as Influenced by Calcium and Potassium in Collington fine sandy loam when 61.96 mg. of Phosphorus were Applied.



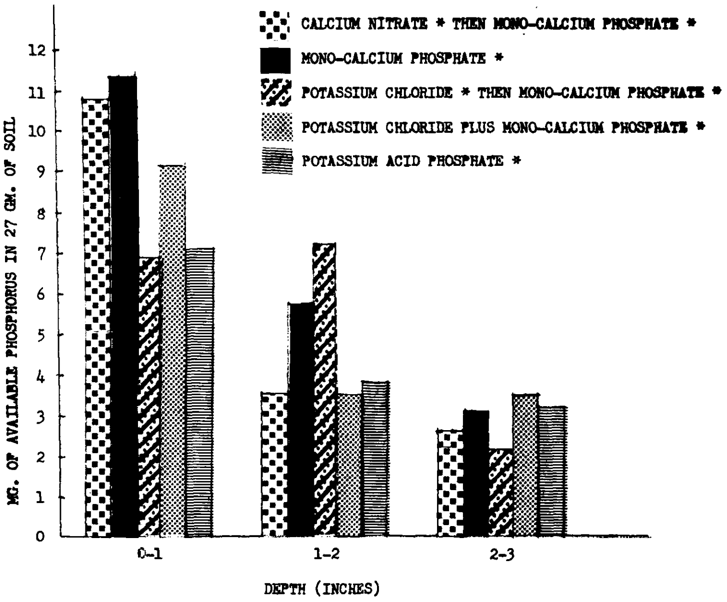
*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 4. Available Phosphorus as Influenced by Calcium and Potassium in Conowingo silt loam when 61.96 mg. of Phosphorus were Applied.



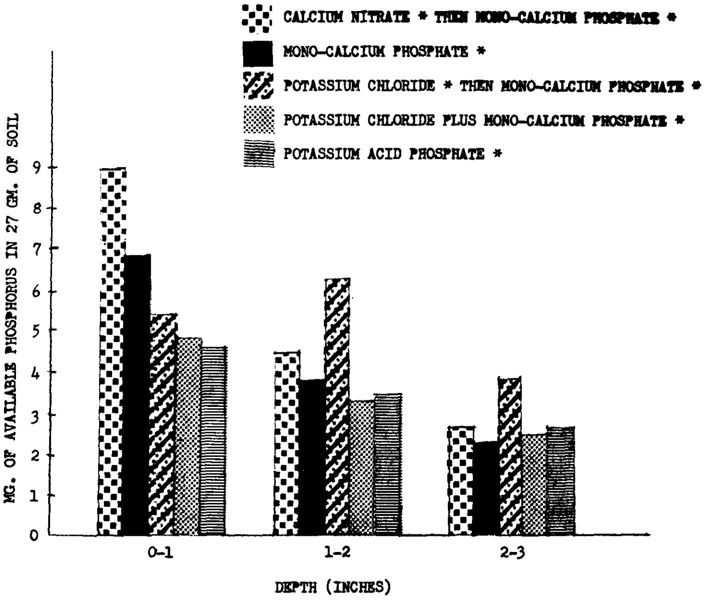
*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 5. Available Phosphorus as Influenced by Calcium and Potassium in Penn silt loam when 61.96 mg. of Phosphorus were Applied.



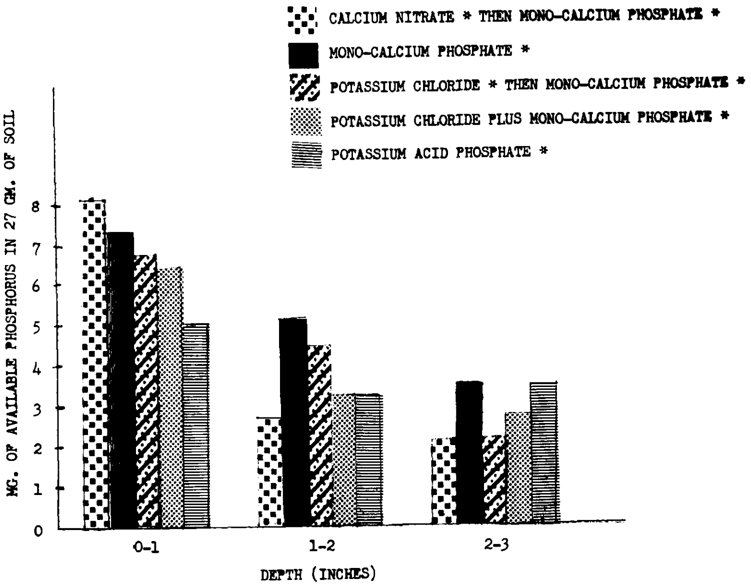
*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 6. Available Phosphorus as Influenced by Calcium and Potassium in Montalto clay loam when 61.96 mg. of Phosphorus were Applied.



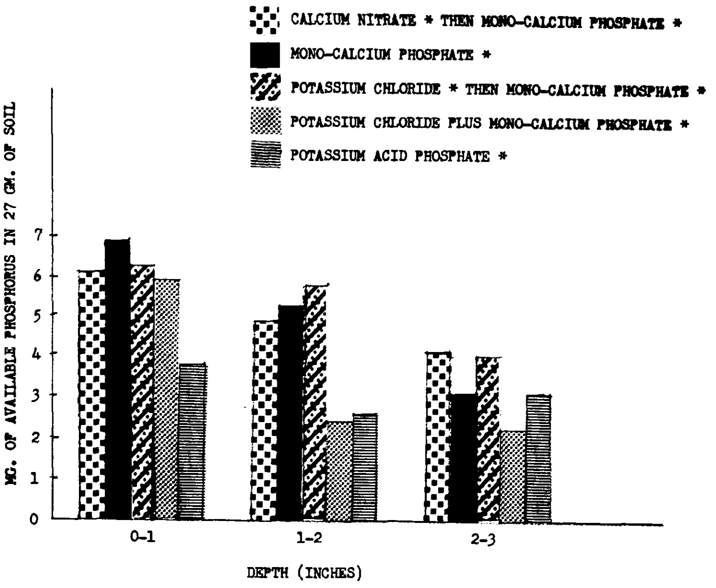
*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 7. Available Phosphorus as Influenced by Calcium and Potassium in Myersville silt loam when 61.96 mg. of Phosphorus were Applied.



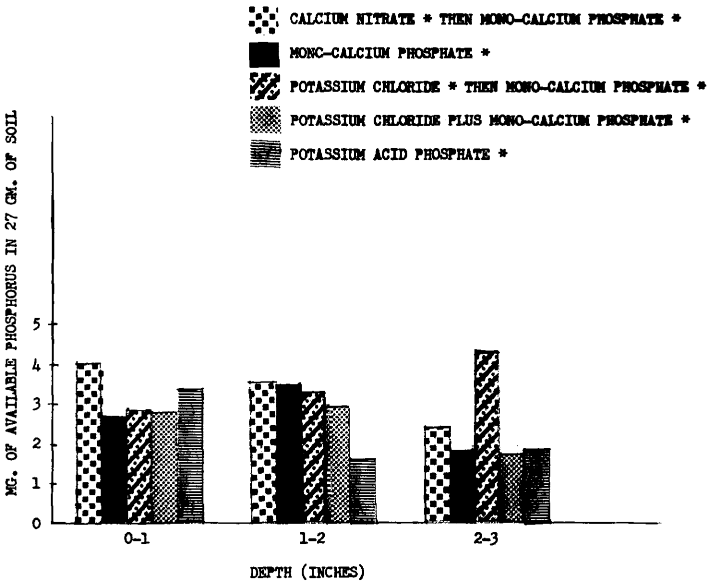
*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 8. Available Phosphorus as Influenced by Calcium and Potassium in Beltsville silt loam when 61.96 mg. of Phosphorus were Applied.



*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 9. Available Phosphorus as Influenced by Calcium and Potassium in Hagerstown silt loam when 61.96 mg. of Phosphorus were Applied.



*Each asterisk indicates that the soil was leached with 20 inches of distilled water 15 hours after the salt application.

Figure 10. Available Phosphorus as Influenced by Calcium and Potassium in Sassafras sandy loam when 61.96 mg. of Phosphorus were Applied.

phosphate treatment. On the other hand, if the treatment consisting of only monocalcium phosphate is taken as the standard, there was a reduction in Troug available phosphorus in eight out of nine soils whenever potassium was applied. In the second inch of these soil columns the same type of reduction was observed for two of the three potassium treatments; namely, KH_2PO_4 or KCl with $Ca(H_2PO_4)_2 \cdot H_2O$. However, when KCl was applied before $Ca(H_2PO_4)_2 \cdot H_2O$, available phosphorus was greater in this layer than that found with $Ca(H_2PO_4)_2 \cdot H_2O$, treatment in six out of nine soils.

It is noteworthy that in most cases the available phosphorus decreased as the depth was increased; consequently, phosphorus availability in the third inch was the lowest.

If the three inch layers of soil are considered as a single layer, it is evident from the data in Table 7 that the striking difference found in the first inch of the soils are no longer present. However, in most cases where the potassium-phosphorus treatments are compared to the calcium-phosphorus treatments the tendency for the reduction of phosphorus availability by potassium still occurs. Also, the data show that KH_2PO_4 and $KCl+Ca(H_2PO_4)_2 \cdot H_2O$ in general react similarly.

To study this potassium reaction over a range of concentrations, one inch layers of Collington fine sandy loam were treated with different rates of mono-calcium phosphate, potassium acid phosphate, and mono-calcium phosphate plus two milliequivalents of potassium chloride (potassium chloride was kept constant for all rates). Results are given in Figure 11; and, in Table 8, are converted to pounds per acre. The Figure shows that the application of potassium to this soil always

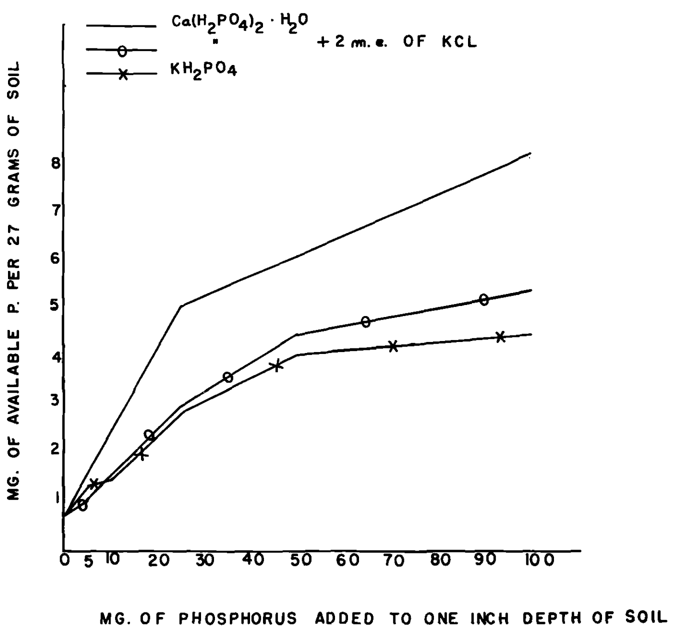


Figure 11. Available Phosphorus as Influenced by Calcium and Potassium in the First Inch of Collington fine sandy loam when Increasing Applications of Phosphates were made.

Table 8

Available Phosphorus as Influenced by Calcium and Potassium in the First Inch of Collington fine sandy loam when Increasing Applications of Phosphates were made.

Treatments	Equivalent Amounts of P_2O_5 added	Equivalent Amounts of K_2O added	Available Phosphorus in the top inch
	Pounds per Acre	Pounds per Acre	P_2O_5 Found per Acre
$Ca(H_2PO_4)_2 \cdot H_2O$	140.30	——*	43.49
$Ca(H_2PO_4)_2 \cdot H_2O + KCL$	140.30	1142	28.15
KH_2PO_4	140.30	92.16	37.95
$Ca(H_2PO_4)_2 \cdot H_2O$	280.60	——*	67.24
$Ca(H_2PO_4)_2 \cdot H_2O + KCL$	280.60	1142	43.34
KH_2PO_4	280.60	184.32	41.21
$Ca(H_2PO_4)_2 \cdot H_2O$	701.50	——*	143.15
$Ca(H_2PO_4)_2 \cdot H_2O + KCL$	701.50	1142	84.55
KH_2PO_4	701.50	460.80	80.23
$Ca(H_2PO_4)_2 \cdot H_2O$	1403.0	——*	173.51
$Ca(H_2PO_4)_2 \cdot H_2O + KCL$	1403.0	1142	127.97
KH_2PO_4	1403.0	921.60	114.91
$Ca(H_2PO_4)_2 \cdot H_2O$	2806.0	——*	229.98
$Ca(H_2PO_4)_2 \cdot H_2O + KCL$	2806.0	1142	151.80
KH_2PO_4	2806.0	1843.2	125.77

* No Potassium added.

resulted in a reduction in the amount of available phosphorus. It also appears that the calcium of the mono-calcium phosphate aids in keeping the available phosphorus high in the soil. This is suggested by the three following points: first, the soil treated with mono-calcium phosphate always contained more available phosphorus; second, when large amounts of potassium are present in relation to mono-calcium phosphate such as indicated in the initial addition on the mono-calcium phosphate plus two milliequivalents of potassium chloride curve (Figure 11), the smallest amount of available phosphorus was present in the soil; third, when phosphorus is added with potassium in the form of potassium acid phosphate and no calcium, the available phosphorus was usually reduced more than the other two treatments especially with increasing amounts of potassium.

Influence of Calcium and Potassium on Phosphorus in the Leachate.

The determination of phosphorus in the leachate aids in the study of phosphorus retention as the phosphorus present in the leachate obviously cannot appear in the soil. To study phosphorus leaching, the leachates of the nine soils were analyzed. These data are given in Table 9. These data show the leaching of phosphorus was, in general, reduced to a minimum when the soils were treated with potassium chloride followed by monocalcium phosphate. However, treatments of potassium, as potassium acid phosphate, or potassium chloride with the mono-calcium phosphate usually resulted in increased leaching of phosphorus. Here again, the close agreement in the interactions of the two treatments; namely, potassium acid phosphate and potassium chloride with mono-calcium phosphate in the soils still occurs.

Increasing the exchangeable calcium by the addition of calcium nitrate before the mono-calcium phosphate treatment caused the phosphorus to be retained by the soil, and in general resulted in decreased leaching of phosphorus. This suggests that the increase in the amount of exchangeable calcium present in these soils is responsible for the additional phosphorus retention as well as the decrease in the leachate. This observation might be explained as follows: If the intraplanar surface exchange of the clay minerals has sufficient calcium present this calcium could enter into a reaction with the added mono-calcium phosphate in the

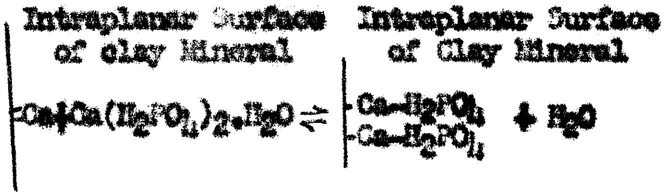
Table 9

Phosphorus Leached from the Three Inches of Soil After Applications of Phosphates Involving Calcium and Potassium.

Soils	$Ca(H_2PO_4)_2.H_2O$	$Ca(NO_3)_2.4H_2O$ then $Ca(H_2PO_4)_2.H_2O$	KH_2PO_4	KCL plus $Ca(H_2PO_4)_2.H_2O$	KCL then $Ca(H_2PO_4)_2.H_2O$
	Mg.	Mg.	Mg.	Mg.	Mg.
Hagerstown	24.30	23.00	30.6	27.45	5.52
Myersville	19.35	5.76	18.00	22.5	2.76
Conowingo	5.4	0.18	16.2	19.20	0.0
Montalto	2.7	2.18	8.91	6.75	1.10
Beltsville	15.3	10.58	21.6	19.80	11.04
Collington	10.5	34.22	47.70	41.40	33.12
Chester	15.90	18.40	23.40	23.40	22.08
Penn	35.30	27.60	34.20	37.20	20.24
Sassafras	40.10	44.04	47.70	40.10	44.10

* 61.96 mg. of phosphorus were applied to the soil and leached with 20 inches of distilled water.

following possible manner:



$$\left|-\mathrm{Ca} + \mathrm{Ca(H_2PO_4)_2 \cdot H_2O} \rightleftharpoons \right| \begin{array}{l} -\mathrm{Ca{-}H_2PO_4} \\ -\mathrm{Ca{-}H_2PO_4} \end{array} + \mathrm{H_2O}$$

Davis (19) pointed out that phosphate might occur in the form of H_2PO_4 - Ca - micelle and that this form of phosphate is probably most available for plant use (1). If this is true, the farming practice of adding calcium to acid soils would seem to be not only advisable for the purpose of neutralizing the soil acidity, but also for the purpose of increasing phosphorus retention and availability.

On the other hand, in this experiment, when sufficient soluble potassium is present, the mobility of the applied phosphorus is increased as in the case of the treatments KH_2PO_4 and KCl plus $Ca(H_2PO_4)_2 \cdot H_2O$. This was indicated by reduced available phosphorus and increased amounts of phosphorus in the leachate. Therefore, where phosphorus is needed at lower depths in the soils, the addition of potassium chloride with monocalcium phosphate might be recommended.

<u>Influence of Calcium and Potassium on Phosphorus Fixation.</u>

Fixed phosphorus is that part retained by soils in an unavailable or relatively unavailable form to plants. Consequently, the study of the relative ability of the different kinds of soils, as influenced by different fertilizer elements, is an important factor in assessing the fertility status of the soil. Phosphorus fixation by soils has been determined by a variety of methods. One of those methods is measuring the decrease in concentration of aqueous phosphate solutions equilibrated with soils without taking into account that a part of the phosphorus taken up from solution will be available in the soil. Other workers used available phosphorus as an index of phosphorus fixation without giving any consideration to that phosphorus in the leachate. In these two instances, no attempt was made to define the nature of the combination between soil and soluble phosphate, and it has been argued that such methods of studying phosphorus fixation do not give adequate information. In this investigation, both available phosphorus and phosphorus found in the leachate are considered simultaneously.

To determine the amount of phosphorus fixed due to the effect of treatment, the following method has been used: first, the amount of available phosphorus in the check treatment is subtracted from the available phosphorus present in the treated soil. This difference is added to the phosphorus in the leachate, and the sum is the total amount of the applied phosphorus that has not been fixed in the soil. Subtracting this figure from the applied phosphorus gives the phosphorus fixed by the soil. Dividing this by the amount applied, times 100 gives the percentage of fixation. This method is shown in the following example:

(1) 16.12 mg. of available P in treated soil.
- 2.88 mg. of available P in untreated soil.
13.24 mg. of available P due to treatment.

(2) 13.24 mg. of available P due to treatment.
+18.90 mg. of P in leachate
32.14 mg. P not fixed by the soil.

(3) 61.96 mg. of P applied to soil.
- 34.14 mg. P not fixed by the soil.
29.82 mg. of P fixed.

(4) $\frac{\text{29.82 mg. of P fixed X 100}}{\text{61.96 mg. P applied to soil.}}$ = 48.13% P fixed.

By comparing the results from different treatments in Table 10, it can be ascertained to what degree the fixation occurred. These data show

Table 10

Influence of Calcium and Potassium on the Fixation of the Applied Phosphorus*.

Soils	Treatments + 20" H_2O			First Treatment + 20" H_2O Second Treatment + 20" H_2O	
	$Ca(H_2PO_4)_2 \cdot H_2O$	KH_2PO_4	$KCl + Ca(H_2PO_4)_2 \cdot H_2O$	1st. $Ca(NO_3)_2 \cdot 4H_2O$ 2nd $Ca(H_2PO_4)_2 \cdot H_2O$	1st KCl 2nd $Ca(H_2PO_4)_2 \cdot H_2O$
	%	%	%	%	%
Hagerstown	36.96	35.59	37.38	39.17	65.89
Conowingo	76.69	63.93	57.05	83.57	87.73
Myersville	49.53	55.29	48.11	66.72	71.92
Beltsville	50.55	47.14	48.85	59.12	61.70
Montalto	65.61	65.32	65.49	70.22	74.37
Collington	17.45	14.46	20.06	26.18	29.00
Penn	47.76	28.58	27.02	32.01	46.52
Chester	48.13	45.49	46.24	47.27	43.59
Sassafras	25.48	15.13	26.47	15.93	15.01

* 61.96 mg. of phosphorus were applied.

that the greatest fixation occurred in six of nine Maryland soils, when they were treated with potassium chloride before the mono-calcium phosphate treatment. These soils were Hagerstown, Conowingo, Myersville, Beltsville, Montalto and Collington.

This indicates that potassium chloride fertilizer used in this manner may cause increased fixation of the applied phosphorus. This increased fixation in the presence of potassium might be explained by the formation of variscite type minerals as pointed out by Haseman et al. (30). However, when potassium was added with mono-calcium phosphate or as potassium acid phosphate little or no increase in fixation occurred; in fact, fixation was noticeably decreased in Penn and Conowingo when compared to mono-calcium phosphate.

Increasing the exchangeable calcium by the addition of calcium nitrate, caused some phosphorus fixation in Conowingo, Myersville, Beltsville and Montalto soils, but in Penn and Sassafras soils this treatment reduced the fixation.

From the results, one can arrange these Maryland soils according to their fixing power for any one treatment. For mono-calcium phosphate, the order would be Conowingo > Montalto > Beltsville > Myersville > Chester > Penn > Hagerstown > Sassafras > Collington.

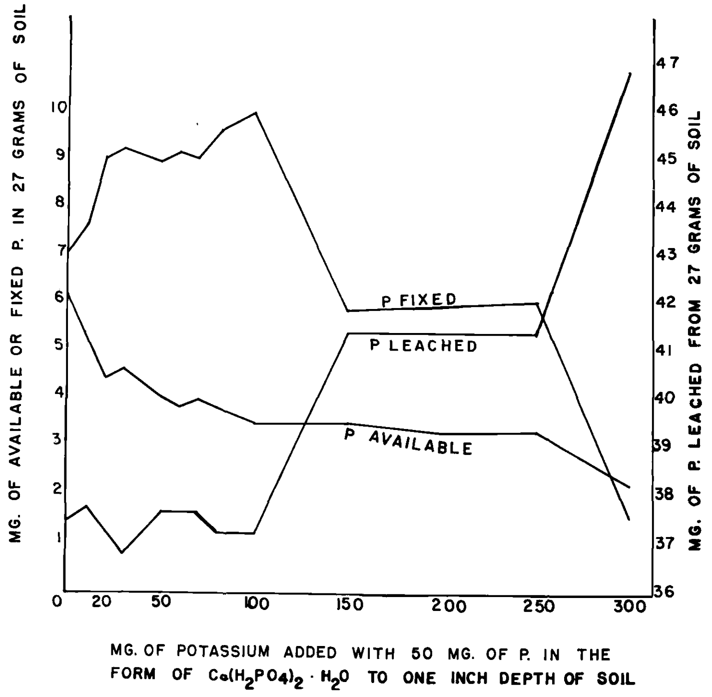
In another experiment, the influence of varying amounts of potassium (KCl) on a constant amount of applied phosphorus (50 mg. as $Ca(H_2PO_4)_2.H_2O$) to one inch depth of Collington fine sandy loam soil was studied. These results are shown in Table 11 and Figure 12.

It would appear from the figure there are two major levels of phosphorus fixation in this soil: a high level which occurs between approximately 20 to 100 mg. of added potassium and a second lower level of

Table 11

Available, Fixed and Leached Phosphorus in the First Inch of Collington fine sandy loam as Influenced by Successive Increments of Potassium when 50 mg. of Phosphorus were Applied.

Amount of K Added with 50 mg. of P	Available P in One Inch Depth of Soil	Amount of P in the Leachate	Amount of P Fixed in One Inch Depth of Soil	% of P Fixed
mg.	mg.	mg.	mg.	mg.
0	6.17	37.50	7.10	14.20
10	5.4	37.72	7.65	15.30
20	4.45	37.26	9.06	18.12
30	4.72	36.80	9.25	18.50
50	4.05	37.72	9.00	18.00
60	3.86	37.72	9.19	18.38
70	3.99	37.72	9.06	18.12
80	3.86	37.26	9.65	18.30
100	3.51	37.26	10.00	20.00
150	3.53	41.40	5.84	11.68
200	3.32	41.40	6.05	12.10
250	3.32	41.40	6.05	12.10
300	2.24	46.90	1.61	3.22



MG. OF POTASSIUM ADDED WITH 50 MG. OF P. IN THE FORM OF $Ca(H_2PO_4)_2 \cdot H_2O$ TO ONE INCH DEPTH OF SOIL

Figure 12. Available, Fixed and Leached Phosphorus in the First Inch of Collington fine sandy loam as Influenced by Successive Increments of Potassium when 50 mg. of Phosphorus were Applied.

of fixation occurring between 150 to 250. It is obvious that the amount of phosphorus leached is almost inversely proportional to the amount of phosphorus fixed, or in other words, the more fixed, the less leached. The available phosphorus in the soil was decreased as the amount of added potassium was increased. This available phosphorus was reduced to almost half with the addition of 100 mg. of potassium and to almost one third with the addition of 300 mg. of potassium.

Influence of Magnesium, Sodium, and Hydrogen on Phosphorus Availability.

It has been previously indicated that the $Ca(NO_3)_2.4H_2O$ treatment followed by mono-calcium phosphate usually results in the highest amount of available phosphorus in the first inch of the soils. If the soil is treated with $MgSO_4.7H_2O$ instead of $Ca(NO_3)_2.4H_2O$, as shown in Table 5, the available phosphorus is usually slightly less. However, when NaCl is substituted for the $Ca(NO_3)_2.4H_2O$, the available phosphorus in the soil is reduced still further and when HCl is substituted for $Ca(NO_3)_2.4H_2O$, the available phosphorus in the first inch of soil may be either increased or decreased when compared to NaCl, but when compared to $Ca(NO_3)_2.4H_2O$, it is always less (Tables 4 and 5).

Phosphorus Fixation as Influenced by Magnesium, Sodium and Hydrogen Treatments:

The fixation of the phosphorus of mono-calcium phosphate as influenced by NaCl, $MgSO_4.7H_2O$ or HCl in soils, is given in Table 12. This fixation was usually increased by the addition of Hydrochloric acid. However, Magnesium sulfate seemed to reduce fixation in the case of Chester, Penn and Sassafras. Sodium Chloride also seemed to reduce the amount of fixed phosphorus in Penn, Sassafras, and Conowingo.

Table 12

Influence of Magnesium and Sodium on the Fixation of the Applied Phosphorus*.

Soils	Treatments + 20" H_2O	1st Treatment + 20" H_2O 2nd Treatment + 20" H_2O		
	$Ca(H_2PO_4)_2 \cdot H_2O$ %	$MgSO_4 \cdot 7H_2O$ then $Ca(H_2PO_4)_2 \cdot H_2O$ %	NaCl then $Ca(H_2PO_4)_2 \cdot H_2O$ %	HCl then $Ca(H_2PO_4)_2 \cdot H_2O$ %
Collington	17.45	30.36	39.65	34.62
Myersville	49.53	74.39	-	65.91
Hagerstown	36.96	42.66	-	71.89
Beltsville	59.95	53.00	62.01	[illegible]9.31
Montalto	65.61	70.92	70.55	74.05
Conowingo	76.69	88.49	73.31	82.54
Chester	48.13	45.28	54.87	54.07
Penn	47.76	30.96	46.39	44.90
Sassafras	25.48	22.27	12.83	24.69

* 61.96 mg. of phosphorus were applied.

Statistical Determination of Variation Due to Treatment and Soil Series.

After the previous series of tests were completed, it was necessary to determine the variations between soil series and different treatments. For this reason, six samples of each soil series were treated with 61.96 mg. of phosphorus in one of the three forms: $Ca(H_2PO_4)_2 \cdot H_2O$, KH_2PO_4 and KCl plus 2 m.e. of KCl. To reduce the number of analysis only a one inch layer of soil was treated according to the general procedure. The soils were then analysed for available phosphorus and these results are presented in Table 13.

They show in almost every case that potassium caused a reduction in the availability of applied phosphorus when compared to the mono-calcium phosphate. This reduction was greater when soils were treated with KH_2PO_4 than when those treated with $Ca(H_2PO_4)_2 \cdot H_2O$ + 2 m.e. of KCl.

The difference due to treatments was found to be significant at 1% level. The summary of the statistical analysis (Table 14) shows that the different soil series may respond differently to similar treatments and this difference in response was found to be highly significant as well as the interaction between treatments and soil series.

Table 13

Available Phosphorus as Influenced by Treatment in the First Inch of Six Soil Series Each of Which was Sampled at Six Different Locations

oil Series	TREATMENTS																	
	$Ca(H_2PO_4)_2.H_2O$						$Ca(H_2PO_4)_2.H_2O+2m.e.$ of KCl						KH_2PO_4					
	1 mg.	2 mg.	3 mg.	4 mg.	5 mg.	6 mg.	1 mg.	2 mg.	3 mg.	4 mg.	5 mg.	6 mg.	1 mg.	2 mg.	3 mg.	4 mg.	5 mg.	6 mg.
Collington	6.16	7.29	9.10	8.10	9.18	7.72	3.99	4.43	8.85	7.13	7.29	6.10	2.54	3.45	5.94	3.40	4.43	3.53
Myersville	9.59	11.63	13.77	7.29	7.56	6.80	8.64	11.47	9.72	6.48	5.53	4.86	6.75	7.02	6.34	2.43	2.43	4.61
Beltsville	4.86	5.94	4.75	5.72	6.91	7.34	4.64	5.07	4.69	5.18	6.50	6.48	2.91	3.18	2.70	1.67	5.13	5.07
Conowingo	3.56	3.56	4.75	4.86	4.11	4.94	2.75	2.75	3.99	4.53	3.56	3.07	1.10	1.13	1.94	3.24	1.08	2.32
Chester	9.99	9.05	9.99	11.07	8.91	8.10	9.31	8.64	9.85	10.26	7.02	6.69	5.80	4.99	5.40	6.88	4.32	5.56
Penn	2.77	4.86	4.32	8.64	8.10	8.32	3.13	4.10	3.99	7.66	7.56	4.32	1.99	2.70	2.64	4.75	4.05	4.32

* 61.96 mg. of phosphorus were applied.

Table 14

Available Phsophorus in the First Inch of Six Soils
As Influenced by Treatments.

Soil Series	Treatments			Average Available P for Soil Series
	$Ca(H_2PO_4)_2.H_2O$	$Ca(H_2PO_4)_2.H_2O$ + 2 m.e. KCl	KH_2PO_4	
	mg./inch soil	mg./inch soil	mg./ in.soil	mg./inch soil
Collington	7.79	6.29	3.88	6.05
Myersville	10.61	7.78-	4.93	7.77
Beltsville	5.92	5.44	3.44	4.93
Conowingo	4.29	3.44	1.80	3.18
Chester	9.65	8.63	5.49	7.92
Penn	6.17	5.13	3.41	4.90
Average Available P for Treatments	7.44	6.12	3.83	———

L.S.D. (5% point) between treatments = 0.45
L.S.D. (5% point) between soil series = 1.94
L.S.D. (5% point) for treatments X soil series interactions = 1.10.

Exchangeable Potassium as Influenced by Phosphorus.

Since exchangeable potassium may be influenced by phosphorus, it was necessary to study the reaction between these two elements in the soil. In this section of the study the influence of 61.96 mg. phosphorus on the exchangeable and leached potassium was investigated. These results are given in Tables 15 and 16.

The data show that applications of 2 m.e. of KH_2PO_4 usually resulted in more exchangeable potassium in the soils than similar amounts of potassium either as KCl or KCl plus $Ca(H_2PO_4)_2 \cdot H_2O$.

De Turk et al. (23) reasoned that KH_2PO_4 increased the exchangeable potassium because of the PO_4- linkage. When KCl was added with mono-calcium phosphate simultaneously, the exchangeable potassium in the first inch of the soils was seldom increased as much as that in the second and third inch. Leachate results (Table 16) showed that the greatest amount of potassium came from soils treated with KCl plus $Ca(H_2PO_4)_2 \cdot H_2O$ and the smallest amounts were derived from soils treated with KH_2PO_4.

To further study this potassium reaction, one inch layers of Collington fine sandy loam were treated with different rates of $Ca(H_2PO_4)_2 \cdot H_2O$ + 2 m.e. of KCl (KCl was kept constant for all rates). The application of mono-calcium phosphate always resulted in a reduction of exchangeable potassium in the soil as shown in Table 17 and Figure 13. As the mono-calcium phosphate applications were increased, the exchangeable potassium was reduced, as would be expected in cation exchange.

Table 15

Exchangeable Potassium in Nine Soils as Influenced by Phosphorus and Calcium when 2 m.e. of Potassium were Applied.

Soil	Soil Depth In (Inches)	Treatments KCl	$NH_4H_2PO_4$	$KCl+Ca(H_2PO_4)_2 \cdot H_2O$
		mg.	mg.	mg.
Chester	0 - 1	29.70	28.35	21.12
	1 - 2	18.55	29.02	22.95
	2 - 3	20.92	25.65	22.95
Collington	0 - 1	24.98	24.30	8.42
	1 - 2	18.90	21.60	14.17
	2 - 3	14.85	16.20	14.85
Penn	0 - 1	17.87	23.22	6.75
	1 - 2	14.58	21.60	11.47
	2 - 3	13.50	20.25	14.85
Conowingo	0 - 1	17.87	28.35	11.12
	1 - 2	17.87	25.65	13.82
	2 - 3	13.50	12.83	10.80
Beltsville	0 - 1	24.08	27.00	15.85
	1 - 2	19.58	23.62	19.58
	2 - 3	17.87	16.88	19.85
Myersville	0 - 1	24.30	22.95	17.39
	1 - 2	16.20	17.82	18.55
	2 - 3	9.45	9.73	20.92
Montalto	0 - 1	23.95	31.46	12.83
	1 - 2	19.58	26.33	26.33
	2 - 3	17.87	22.28	22.95
Sassafras	0 - 1	3.24	4.05	2.70
	1 - 2	3.24	4.05	2.70
	2 - 3	2.97	4.05	2.70
Hagerstown	0 - 1	—	16.88	10.80
	1 - 2	—	16.88	16.20
	2 - 3	—	16.88	17.59

Table 16

Influence of Treatment on Exchangeable and Leached Potassium of a Three Inch Layer of Nine Soils.

Soil	Potassium	Treatments KCl	 KH_2PO_4	 $(KCl + Ca(H_2PO_4)_2 \cdot H_2O)$
		Mg.	Mg.	Mg.
Chester	Exchangeable	69.17	83.02	67.02
	Leached	31.95	29.25	61.20
Collington	Exchangeable	58.73	62.13	37.44
	Leached	29.70	31.05	57.15
Penn	Exchangeable	45.95	65.07	33.07
	Leached	54.0	39.15	70.20
Conowingo	Exchangeable	49.24	66.83	35.74
	Leached	35.55	13.95	45.45
Beltsville	Exchangeable	61.48	67.50	55.11
	Leached	28.8	19.35	38.7
Myersville	Exchangeable	49.95	50.50	56.06
	Leached	8.10	10.35	24.75
Montalto	Exchangeable	61.40	80.07	62.11
	Leached	31.95	20.25	37.60
Sassafras	Exchangeable	9.45	12.15	8.10
	Leached	75.50	72.0	73.50
Hagerstown	Exchangeable		50.64	44.59
	Leached		30.15	45.00

Table 17

Exchangeable Potassium in the First Inch of Collington fine sandy loam as Influenced by Successive Increments of Mono-calcium Phosphate in Combination with 2 m.e. of Potassium Chloride.

Phosphorus Added with 2 m.e. of KCl	Exchangeable Potassium
mg.	mg.
0	24.90
5	24.30
10	23.27
25	13.23
50	11.79
100	9.09

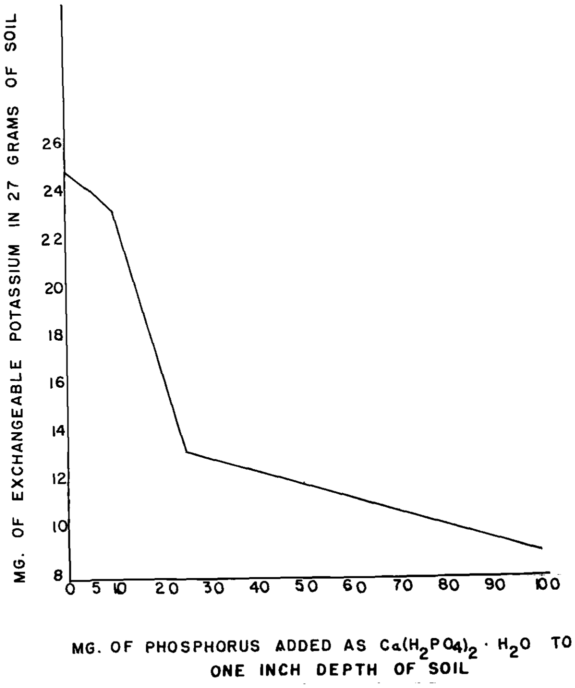


Figure 13. Exchangeable Potassium in the First Inch of Collington fine sandy loam as Influenced by Successive Increments of Mono-calcium Phosphate in Combination with 2 m.e. of Potassium Chloride.

It has been shown when potassium chloride was added to a soil, the leaching of potassium is not nearly as great as when it was added with mono-calcium phosphate. The data given in Table 18 and 19 show that a similar behaviour occurs with calcium nitrate. This emphasizes that the increase in leaching of potassium chloride when combined with mono-calcium phosphate is primarily a base exchange reaction.

Table 18

The Influence of Calcium in Fertilizers Upon the Exchangeable Potassium.

Soil	Depth (Inches)	TREATMENTS			
		KH_2PO_4*	KH_2PO_4 plus $Ca(NO_3)_2 \cdot 4H_2O$*	1st KH_2PO_4* 2nd $Ca(NO_3)_2 \cdot 4H_2O$*	1st $Ca(NO_3)_2 \cdot 4H_2O$* 2nd KH_2PO_4*
		mg.	mg.	mg.	mg.
Collington	0 - 1	22.95	13.50	7.76	19.57
	1 - 2	19.58	16.20	9.45	20.92
Penn	0 - 1	23.63	9.45	7.08	20.92
	1 - 2	20.25	13.50	9.11	18.58
Conowingo	0 - 1	26.95	9.45	6.75	22.27
	1 - 2	23.28	16.54	10.12	17.55
Montalto	0 - 1	31.39	23.62	8.44	24.30
	1 - 2	25.45	23.62	13.84	25.31

* Indicates that the soil was leached with 20 inches of distilled water after salt application.

Table 19

The Influence of Calcium in Fertilizers Upon the Amount of Potassium Leached From the First Two Inches of Four Soils.

Soil	TREATMENTS			
	KH_2PO_4*	KH_2PO_4 Plus $Ca(NO_3)_2 \cdot 4H_2O$*	1st KH_2PO_4* 2nd $Ca(NO_3)_2 \cdot 4H_2O$*	1st $Ca(NO_3)_2 \cdot 4H_2O$* 2nd KH_2PO_4*
	Mg.	Mg.	Mg.	Mg.
Collington	40.95	56.25	73.60	46.92
Penn	53.00	68.40	85.56	53.36
Conowingo	30.15	53.55	69.00	34.04
Montalto	36.00	43.20	73.60	40.48

* Indicates that the soil was leached with 20 inches of distilled water after salt application.

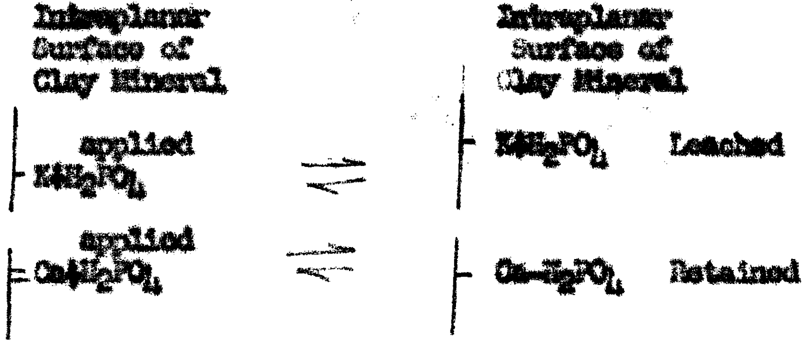
DISCUSSION

Increasing the exchangeable calcium present in these soils is often responsible for additional phosphorus retention as well as the decrease in the amount of phosphorus in the leachate. In one case, the increase of available phosphorus was as much as 32% when the calcium of the base exchange complex was increased by the addition of calcium nitrate prior to the mono-calcium phosphate application. This observation might be explained as follows: If the intraplanar surface exchange of the clay minerals has sufficient calcium present, this calcium would enter into a reaction with the added mono-calcium phosphate in the following manner:

$$\left|\begin{array}{l}\text{Intraplanar surface}\\ \text{of clay mineral}\\ = Ca + Ca(H_2PO_4)_2 \cdot H_2O\end{array}\right. \rightleftharpoons \left|\begin{array}{l}\text{Intraplanar surface}\\ \text{of clay mineral}\\ - Ca-H_2PO_4\\ - Ca-H_2PO_4\end{array}\right. + H_2O$$

Davis (19) pointed out that phosphate might occur in the form of H_2PO_4Ca - micelle, and this form of phosphate is probably most available for plant use (1). If this is true, the farming practice of adding calcium to acid soils would seem to be not only advisable for the purpose of neutralizing the soil acidity, but also for the purpose of increasing phosphorus retention and availability.

On the other hand in this experiment, when sufficient potassium is used as a treatment, the mobility of the applied phosphorus is increased as in the case of potassium acid phosphate or potassium chloride plus mono-calcium phosphate. This was indicated by smaller quantities of available phosphorus in the soil and increased amounts in the leachate. In Collington fine sandy loam when an application was made equivalent to 1738 pounds of P_2O_5 per acre, the amount of available phosphorus was found to be 217 pounds of P_2O_5 per acre in the top inch. This amount of available phosphorus was reduced to 171 pounds of P_2O_5 when potassium chloride equivalent to 1142 pounds of K_2O per acre was applied with the phosphate. When potassium acid phosphate containing 1738 pounds of P_2O_5 per acre was used in place of mono-calcium phosphate the available phosphorus was reduced to 99 pounds in the top inch. Furthermore, when the same amount of applied potassium (1142 pounds of K_2O per acre) had been used with smaller amounts of phosphorus the reaction still occurred, (Table 8). Even when smaller amounts such as 184 pounds of K_2O per acre had been applied to the Collington soil with 280 pounds of P_2O_5 per acre the available phosphorus was still reduced from 67 to 41 pounds of P_2O_5 per acre in the top inch, or in other words the reduction was almost 39%. This observation might be explained as follows: The ion $[H_2PO_4]$ of the applied phosphate can only attach itself to the clay colloid through the medium of polyvalent cations. This reaction would be impossible with potassium as it is a monovalent cation. Additions of potassium to soils usually result in the reduction of exchangeable calcium and an increase in exchangeable potassium. Therefore, some of the calcium, which is a partial cause for this type of phosphorus retention, has been removed and the result is that more of the applied phosphorus may be leached. The following equation is a schematic representation of this theory:



Of course, phosphorus is also held in the soil on the anion exchange as indicated by Dean and Rubins (22) or by a reaction between hydrated Fe, Al and the applied phosphorus as shown by others (37).

Not only does potassium cause phosphorus leaching when sizable quantities of potassium are added with the phosphorus, but it also causes fixation of phosphorus when smaller quantities of potassium are added in relation to the applied amount of phosphorus (Figure 12). This has certainly led to confusion in interpreting properly the results of many field experiments in which phosphorus and potassium were involved. The reduction of the applied soluble phosphorus by increasing potassium fertilizer application to barley plants grown in pots and field experiments was pointed out by Eriksson in Sweden(24). He failed in these experiments to determine the phosphorus that was leached, so he did not know whether this reduction was due to fixation or leaching. However, he attributed it all to fixation, assuming that iron and aluminum compounds were activated by the addition of potassium chloride which resulted in greater phosphorus fixation.

CONCLUSIONS

A study of the interaction of applied phosphorus and applied potassium in reference to their availability in nine Maryland soils was conducted in the laboratory. The nine soils chosen for this experiment were located in prominent agricultural areas and represent diversified soil conditions.

The general conclusions reached for the soils studied in this investigation can be briefly stated as follows:

(1) The available phosphorus in a three inch layer of soils was frequently greater when phosphorus as mono-calcium phosphate was applied without a potassium application for the nine soils.

(2) A study of a comparison of mono-calcium phosphate with either potassium chloride plus mono-calcium phosphate or potassium acid phosphate showed that available phosphorus in a one inch layer of six soils was reduced whenever potassium was applied. These results were found to be highly significant for treatments, soil series, and interactions between soil series and treatments.

(3) Potassium chloride plus mono-calcium phosphate or potassium acid phosphate resulted in more leaching of phosphorus from the three inches layers than did treatments of mono-calcium phosphate.

(4) Phosphate fixation was increased to a maximum in this study in six out of nine soils when potassium in the exchange complex was first increased by the addition of potassium chloride before the mono-calcium phosphate treatment.

(5) Phosphate fixation in a one inch layer of Collington fine sandy loam,could be separated into three phases. Firstly, a rapid increase in fixation to a relative maximum by adding quantities less than 20 mg. of potassium (293 pounds of K_2O per acre), secondly, maximum fixation over wide range of potash additions, and thirdly, increase leaching of phosphorus and reduction of the fixed phosphorus by applying quantities greater than 1464 pounds of K_2O per acre.

(6) Increasing exchangeable calcium of the soils tended to increase phosphorus availability as well as retention.

(7) Calcium in fertilizers applied with or after potassium chloride resulted in the downward movement of potassium. On the other hand, calcium had little influence on potassium movement when it was applied and leached with water previous to the potassium applications.

(8) Exchangeable potassium was greater in soils that had been treated with potassium acid phosphate than in those treated with similar quantities of potassium chloride or potassium chloride plus mono-calcium phosphate.

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