The movement of phosphoric acid and triple superphosphate in soils
by Willis B Johnston

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University
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Abstract:
Laboratory leaching studies on four different soils were made to compare the movement of phosphorus when applied as phosphoric acid and as triple superphosphate. Applications of both fertilizers were made at a rate of 200 pounds P2O5 per acre, following which, the soils were either analyzed for phosphorus or leached with eight six-inch applications of Bozeman tap water. Total phosphorus and available phosphorus were then determined on the soils and total phosphorus was determined on the leachates in order to determine how much phosphorus had been leached out of the soil.

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Approved:

P. C. Gaines
Head, Major Department

Leon H. Johnson
Chairman, Examining Committee

J. A. Nelson
Dean, Graduate Division

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ABSTRACT

Laboratory leaching studies on four different soils were made to compare the movement of phosphorus when applied as phosphoric acid and as triple superphosphate. Applications of both fertilizers were made at a rate of 200 pounds P_2O_5 per acre, following which, the soils were either analyzed for phosphorus or leached with eight six-inch applications of Bozeman tap water. Total phosphorus and available phosphorus were then determined on the soils and total phosphorus was determined on the leachates in order to determine how much phosphorus had been leached out of the soil.

INTRODUCTION

The problems connected with the fixation, availability, and penetration of phosphorus in the soil have been attacked from various viewpoints by many investigators. The literature available on these subjects is indeed voluminous. No attempt will be made to present a review of the literature on phosphorus availability and fixation, but, rather, the discussion will be confined to a review of that work dealing directly with the movement and penetration of phosphorus. Because of the vast number of relationships existing, fixation and availability of phosphorus cannot be ignored when dealing with problems concerning its movement and penetration. For a cursory review of the work on availability and fixation reference is made to Ford (1933), Ravikovitch (1934), Stout (1939), Midgley (1940), Kelley and Midgley (1943), Perkins and King (1943) (1944) (1945), and Burd (1948).

The problem of the penetration of phosphorus is a very important one because, in order for the plant to absorb it, the phosphorus must be positionally located somewhere near the root zone. Thus if the phosphorus remains on the surface of the soil it will not be of much use to the plant, while on the other hand, if it penetrates through the soil out of reach of the roots it will again be inaccessible to the plant.

Most of the work on the availability, fixation, and penetration of phosphorus in the soil has been done on the orthophosphates. The majority of the investigations on the problem of phosphorus movement have shown that inorganic phosphorus fertilizers are rather quickly immobilized when they come into contact with the soil. The extent to which immobilization

occurs is, of course, dependent upon the kind of soil and the presence or absence of various salts. Acidic soils containing iron and aluminum tend to fix phosphorus in difficulty available forms, such as $FePO_4$ and $Al_2(OH)_3PO_4$. Calcareous soils tend to fix phosphorus in the form of $Ca_3(PO_4)_2$.

Heck (1934) proposed three groups of fixed phosphorus, terming them (a) readily available phosphorus ($Ca_3(PO_4)_2$), (b) moderately available phosphorus ($AlPO_4$), and (c) difficulty available phosphorus ($FePO_4$, $Al_2(OH)_3PO_4$, $Fe_2(OH)_3PO_4$. He based this grouping upon the solubilities of the above compounds in 0.002N H_2SO_4 buffered to pH 3 with K_2SO_4. In calcareous soils, however, $Ca_3(PO_4)_2$ is generally conceded to be more difficulty available than Heck indicates.

In penetration studies Heck found that the greatest penetration of phosphorus occurs in soils which are neutral or slightly acid in reaction.

The work of Alway and Rost (1916) showed that in the surface foot of prairie soils, there was a steady decrease in phosphorus from the surface inch downward, indicating at least some movement of the phosphorus in these soils. However, the majority of the phosphorus was concentrated in the surface two inches.

Hockensmith, Gardner, and Kezer (1933) found very little movement of phosphorus when applied as superphosphate, in calcareous soils. In a soil nine inches deep most of the phosphorus remained in the surface three inches. Since the fertilizer was incorporated with the surface two inches of soil only slight downward movement was indicated. (Superphosphate is monocalcium phosphate containing gypsum. The gypsum is formed in the man-

ufacture of superphosphate when raw rock phosphate is treated with sulfuric acid.)

On the other hand, Robinson and Jones (1927), working with North Welsh soils with a high degree of base saturation, found considerable penetration of phosphorus. After a ten-year period, soils which had been treated with basic slag at the rate of 200 lbs. P_2O_5 per acre did not differ in phosphorus content in the surface eighteen inches from non-treated soils, indicating a relatively complete removal of the applied phosphorus by the leaching processes.

Doak (1933) claims that phosphorus penetrates best when it is applied heavily and at infrequent intervals. The explanation of this may be that the heavy applications tend to saturate the fixing potential of the soil, thus allowing the excess phosphorus to penetrate.

Beater (1938) studied the movement of superphosphate in a dark heavy loam and in a light sandy loam and observed little or notpenetration in either soil below the surface inch. Irrigation tended to prolong phosphorus availability.

In studies of the movement of superphosphate in soils, Neller (1946) was able to recover 79.1% of the applied phosphorus in the leachates from Leon fine sand. From sandy loams, however, he was able to recover only a trace to 1.6% of the applied phosphorus.

The foregoing work raises a very pertinent question. How do the various forms of phosphorus fertilizers compare in their abilities to penetrate the soil? A great deal of work has been done by various investigators in an attempt to answer this question.

Midgley, (1927), in an investigation into the movement and fixation of phosphates in relation to permanent pasture fertilization, compared the penetrations of superphosphate, ammonium phosphate, potassium phosphate, and sodium phosphate by leaching studies. Using Miami silt loam he found that the respective recoveries of phosphorus were 3.9%, 96.5%, 22%, and 22%. With Carrington silt loam he found 0.0%, 88.1%, 3.3% and 3.4% recoveries respectively. These are all percentages of the original application. It is seen that the penetration of superphosphate was very poor in both soils.

Stephenson and Chapman (1931) found that in light to medium soils, there was appreciable penetration through the surface foot, while in heavy soils little or no penetration was observed. They also found that when manure was added alone or when manure and superphosphate were added, the amount of penetration increased. It is probable that the phosphorus accurring in manure is in the form of organic phosphorus compounds and its greater penetration may be explained on the basis of the work done by Spencer and Stewart (1934) who compared the penetrations of organic phosphates to those of inorganic phosphates. The phosphates compared were calcium glycero phosphate, calcium glyco phosphate, calcium sorbityl phosphate, calcium glucose phosphate, triple superphosphate, meta-phosphoric acid, Ammo-Phos. B. (phosphorus fertilizer manufactured by the American Cyanamid Company) and di-sodium phosphate. (Triple superphosphate is monocalcium phosphate containing no gypsum. Raw phosphate rock is treated with sulfuric acid and the gypsum is filtered off. More rock phosphate is treated with the resulting phosphoric acid. This results in a higher

phosphorus content than is contained in superphosphate.) These phosphates were placed on the surface of 405 gram portions of soil through which were leached three successive eight-inch columns of water. The percentage recoveries for the organic phosphates were 75.0%, 79.13%, 89.97%, and 94.81% respectively, while for the inorganic phosphates the respective percentage recoveries were 0.67%, 4.28%, 6.30%, and 11.51%. Thus it is seen that organic phosphates penetrated very readily and were not fixed in appreciable quantities.

Brown (1935) compared the penetration of rock phosphate to that of superphosphate. He showed that biennial surface applications of superphosphate penetrated not more than three inches while rock phosphate applied in the same manner penetrated more than seven inches. However, plant responses showed superphosphate to be the more efficient fertilizer.

Gilligan (1941) found that superphosphate penetrated better than metaphosphates. He also studied the effects of alternate wetting and drying of soils on the availability of these fertilizers. Alternate wetting and drying decreased the availability of superphosphate while it increased the availability of metaphosphates.

MacIntire, Shaw, and Robinson (1949) investigated the migrations of phosphorus from soils treated with $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(PO_3)_2$, H_3PO_4, $NH_4H_2PO_4$, and $(NH_4)_2HPO_4$. Movement was observed in all cases. Their conclusions were that the type of fertilizer which would be most mobile depended to a great extent upon the type of soil. Phosphorus incorporated in the acidic state, such as H_3PO_4, was more efficient in soils of adequate calcium supply.

In the past few years phosphoric acid has had some use as a phosphatic fertilizer. The phosphorus content of the acid being higher than any other common fertilizer, has made it possible to ship phosphoric acid at a lower cost per unit of phosphorus. This has tended to be a factor in favor of the use of the acid as a fertilizer. It also lends itself to uniform field distribution by application in irrigation water. Because of its liquid form it might be expected to better penetrate the soil.

The results of the experiments cited on the different forms of phosphatic fertilizers and their abilities to penetrate the soil are somewhat contradictory. Consequently, it was thought advisable to compare the movement and penetration of the liquid with a widely used solid form. Leaching experiments were carried out on four different surface soils, two of which had shown a definite response to phosphate fertilization, and two which had not responded to this treatment. The movement of phosphorus was determined by a conventional analytical method and also by the use of radioactive phosphorus.

EXPERIMENTAL WORK

Apparatus for Leaching: The apparatus used in this investigation was built by the author in this laboratory. Sketches of this equipment are shown in Fig. 1. The leaching tubes were made of lucite tubing. Each tube was one foot in length with an inside diameter of 2 3/8" and an outside diameter of 2 3/4". The bottoms of the tubes were made of sheet lucite cut into discs 2 3/4" in diameter. Each disc was then placed in a metal turning lathe and three concentric grooves were cut in the face of the disc. Four grooves were then cut at right angles to the concentric grooves. These grooves facilitated the drainage of solution from the bottom of the tube. Through the center of each disc was bored a 9/16" hole, into which a 10 mm. glass delivery tube was fitted with a number one rubber stopper. Each disc was then cemented to one end of a lucite tube with lucite cement, made by dissolving lucite shavings in acetone. These tubes proved to be very successful because they took a great deal of shock without being damaged.

Another necessary item was some type of a deflector which would deflect the solution being poured into the tube so that it would not disturb the surface of the soil. A disc of lucite very slightly less than 2 3/8" in diameter was cut. Through this disc were drilled about 75 holes 1/32" in diameter. These holes were countersunk on the side that was to receive the water being poured on the soil. This disc was cemented to a rod of lucite two feet in length and 7/16" in diameter. This rod served both as a handle in the manipulation of the deflector and as an instrument with which to remove the soil from the lucite tubes.

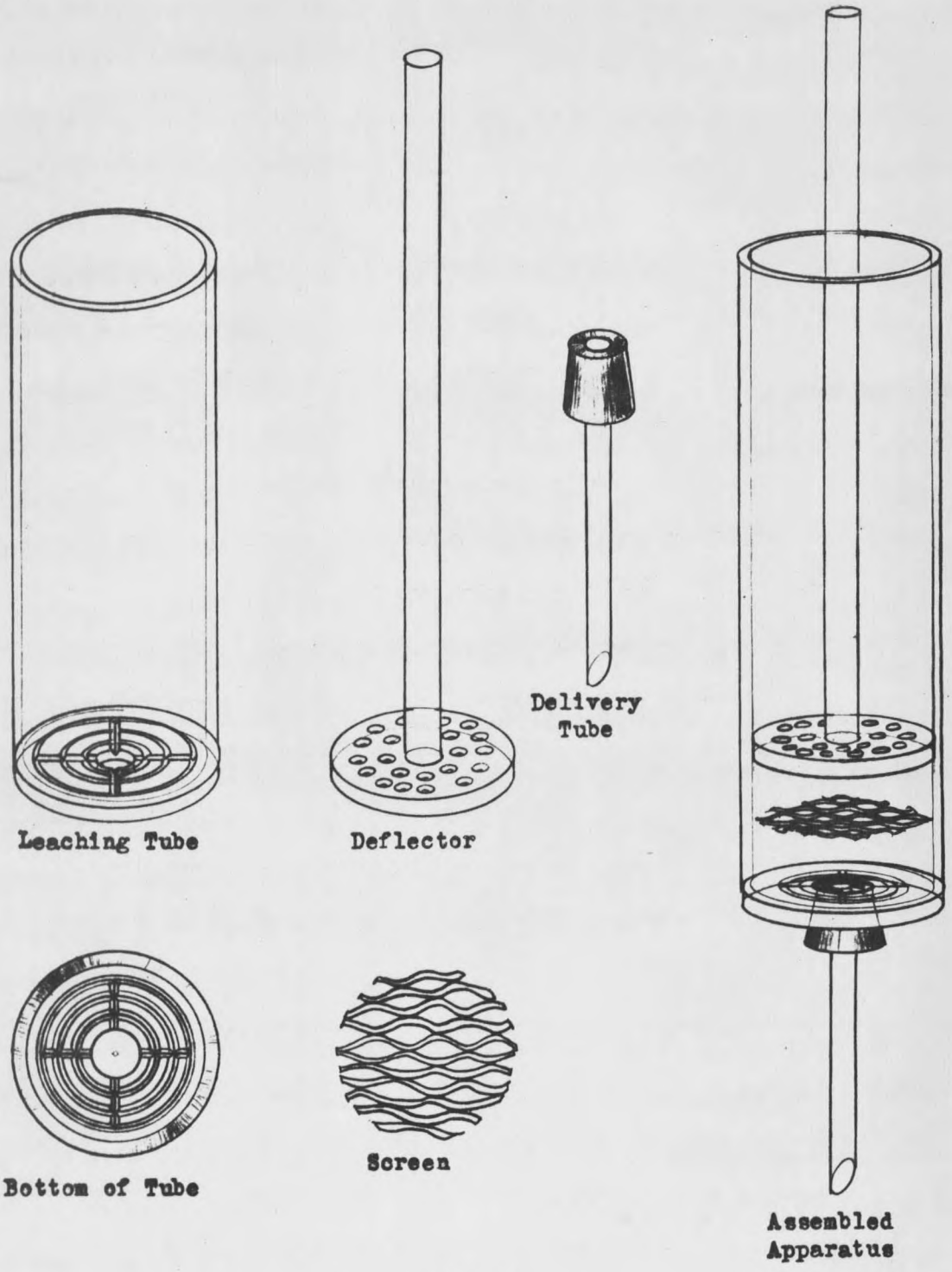


Fig. 1
Leaching Apparatus

A metal screen was necessary to form a rigid base upon which to place an S and S No. 597 filter paper. Metal lathing, pounded flat and cut to fit into the leaching tube, was used for this purpose.

Preparation of Samples: The soils used were first thoroughly air dried and mixed on a large canvas. They were then ground to pass a 2 mm. seive after which they were mixed again. Each soil was then analyzed for total and available phosphorus.

Samples of 200 grams were weighed out for the leaching studies. In preliminary investigations, it was found that if the samples were put in the leaching tubes dry and then packed, it was very difficult to duplicate leaching rates. In order to overcome this difficulty, it was decided to try sprinkling some tap water on the soil before placing and packing it in the leaching tube. Accordingly the soil was brought to a friable state by sprinkling it and mixing the water throughout the sample by kneading it with the hands. In order to insure homogeneity, soil 95 had to be tempered for about forty-eight hours after the water had been added. The preceding method was successful in attaining leaching rates duplicating on the average within five to fifteen ml. per hour.

Once a sample had thus been prepared, it was poured into the leaching tube through a funnel made by removing the bottom of a 1000 ml. volumetric flask. The leaching tube was then dropped from the height of 1 1/2" fifty times in order to pack the soil uniformly. This packing resulted in a soil column about three inches long. Immediately following this step the soil was leached with the appropriate solution.

Treatments:

Series A - Thosphoric acid (Mallinckrodt analytical reagent - assay 85% H_3PO_4) equivalent to 27.695 mg. of phosphorus was added to the soils in the leaching tubes. This is equivalent to 200 lbs. P_2O_5 per acre, calculated on the basis of the acreage in a cross-section of the leaching tube. This was calculated to be 6.98×10^{-7} acres. The total volume of phosphoric acid solution was 430 ml. made up with tap water. This volume gives a six-inch column of solution over the soil at the outset of leaching.

It was felt that tap water should be used in this investigation rather than distilled water because the tap water, containing about 116 ppm. total hardness as well as other ions, would more nearly duplicate irrigation water.

These leachates, hereafter referred to as the P-leachates, were collected in 600 ml. lipless tall form beakers. When the entire solution had leached through the soil, a period of twelve to fifteen hours was allowed for the soil to drain. The total time consumed from the commencement of leaching until the soil was either leached again or removed from the tube, was about twenty-four hours. When this period of time had elapsed the soils were removed from the tubes, cut longitudinally into four approximately equal sections, numbered one through four, (number one being the surface section, two and three being the middle sections, and four being the bottom section) and allowed to thoroughly air dry. The sections were then ground, mixed separately, ashed, and analyzed for total phosphorus. Total

phosphorus was also run on the leachates.

Series D - The samples in series D were treated exactly as those in series A except that after the collection of the P-leachate the soils were removed from the tubes and allowed to dry without being sectioned. The samples were ground as before, mixed thoroughly with water as outlined in the sections on preparation of the sample and, in the same way, replaced in the tubes. Subsequently the soils were leached with eight six-inch applications of tap water designated as H_2O-1 leachate, H_2O-2 leachate, etc. Approximately twenty-four hours elapsed between each successive application. All the leachates were collected in 600 ml. beakers and analyzed for total phosphorus. The soils were removed from the tubes, sectioned, dried, and ground. These samples were analyzed for total phosphorus and available phosphorus.

Series F - The samples in this series were treated exactly as those of series A except that triple superphosphate (hereafter referred to as TSP) was applied in place of the phosphoric acid. In applying the TSP, a sample was weighed out containing 27.695 mg. phosphorus and worked into the surface of the soil, after which 430 ml. of tap water were applied.

Series G - These samples were treated exactly as those in series D except that TSP was applied in place of phosphoric acid.

Series H - No phosphorus was added to the soild in this series. These samples were leached with eight six-inch applications of tap water. Due to lack of time the soil samples were not analyzed, but

leachates H_2O-1, H_2O-4, H_2O-5, and H_2O-8 were analyzed for total phosphorus. The phosphorus levels in leachates H_2O-4, H_2O-5, and H_2O-8 were so low that the results obtained were at best estimations. In addition to this, the phosphorus levels in these three leachates were practically the same. Consequently, determinations were not made on leachates H_2O-2, H_2O-3, H_2O-6, and H_2O-7 because it was assumed that the phosphorus levels in these leachates would be very low and of the same order as those of the preceding leachates in this series.

Series K - The samples in this series were treated with phosphoric acid at the same rate as those in series A. However, the acid was labeled with radioactive phosphorus. The work was done in the laboratory of the Holter Research Foundation, Helena, Montana.

Due to lack of time and equipment several modifications in procedure were necessary. Unlike the samples in series D and G, and samples in series K were not removed from the tubes prior to the application of the first six inches of water. Instead the samples were left in the tubes and leached with eight six-inch applications of Bozeman tap water.

The soils were not analyzed because of the lack of a hood which could carry away the radioactive dusts produced by grinding.

Methods of Analysis: In determining total phosphorus the soil samples and leachates were ashed according to the following procedure. One gram samples of soil or 100 ml. aliquots of leaching solutions were transferred into 300 ml. Berzelius beakers to which were added 20 ml. concen-

trated nitric acid, 10 ml. concentrated perchloric acid, and 1 ml. concentrated sulfuric acid. The mixtures were boiled on a hot plate until oxidation was complete. They were then evaporated on a steam plate until only sulfuric acid remained.

The ashed residues were extracted with boiling water and filtered through Whatman No. 2 filter paper into 100 ml. volumetric flasks. The solutions were cooled to room temperature, made to volume, appropriately aliquoted, and analyzed for phosphorus.

In all cases except series K phosphorus was determined colorimetrically by the method of Allen (1940), using 10 N. sulfuric acid in place of 10 N. perchloric acid. The Coleman Spectrophotometer model 11, set at 650 millimicrons, was used in all colorimetric determinations.

The activities of the leachates of series K were determined using a Geiger counter and a dipping tube. Particular care was taken to keep the counting geometry constant. Thirty ml. aliquots of the leachates were transferred to tygon tubes, into which the Geiger tube was placed. The distance the Geiger tube was submerged was kept constant. A 30 ml. aliquot of the original leaching solution was run as a reference standard.

Available phosphorus was determined by a carbonic acid extraction method. Ten grams of air dry soil were placed into a 200 ml. round bottom flask, to which were added 100 ml. of distilled water. Carbon dioxide was then bubbled through the suspension, with occasional shaking, for 30 minutes. The suspension was filtered through Whatman No. 3 paper and phosphorus determined colorimatrically on an aliquot. This method is similar to the one described by Ensminger and Larson (1944) with the excep-

tion that they bubbled carbon dioxide through the suspension for 20 minutes.

pH measurements were made using a Beckman pH meter employing the glass electrode, and conductance measurements with the Solu-Bridge Soil Tester model RD-26.

RESULTS AND DISCUSSION

The soils selected for this study were given the following laboratory designations: 88A, 89, 90, and 95. Descriptive data on these soils appear in Table I. Soils 88A and 90 are highly calcareous while 95 is moderately calcareous. Soil 89 is non-calcareous. Sample 88A was taken from the George Rauser farm at Toston, Montana; 89 is a typical Gallatin Valley sample, taken near Bozeman, Montana; 90 was taken from the Taylor McNiven farm in the Shields River Valley in Montana, and 95 was taken from Plot K - V - 22 of the Huntley Branch of the Montana Agricultural Experiment Station at Huntley, Montana. This soil has been in continuous sugar beets since 1912 and was labeled as one of the most phosphorus deficient soils ever received by the Soil and Fertilizer Laboratory BPISAE at Beltsville, Maryland. Soils 88A, 89, and 90 were all taken off of phosphate fertilizer check plots.

Based upon plant responses to phosphorus fertilization, soils 88A and 89 are classed as non-deficient with respect to phosphorus, while soils 90 and 95 are deficient. The textures of these soils are silt loam, silty clay loam, silt loam, and silty clay respectively.

The results of some of the series are tabulated in Tables II through V. Some of this data and that from other series is presented graphically in Fig. 2 through 14.

It should be noted that triplicate leaching tests were made in series A and D, while duplicate leaching tests were made in series E, G, H, and K. The change from triplications to duplications was made in order to bring the number of samples that had to be analyzed to a more reasonable

figure. Justification for this is apparent from Figs. 2 through 5. In these figures, curves of the same color represent replications of the leaching process on the same soil. It will be noted that the internal precision in all cases is reasonably good.

Table I

Description of Soils

Soil No.	Phosphorus Status	Texture	K X 10^3 [1]	pH [2]	Total P_3 [3]	Available $P_{3,4}$ [4]
88A	Not deficient	Silt loam	1.20	7.7	716	3.2
89	Not deficient	Silt clay loam	0.44	6.8	934	6.6
90	Deficient	Silt loam	0.92	7.9	805	1.9
95	Deficient	Silt clay	0.84	7.8	508	2.0

1. Determined on saturation extracts from the soils: Measure of conductance.
2. Determined on saturated pastes of the soils.
3. Phosphorus values expressed in parts per million.
4. Carbon dioxide extraction.

The results obtained by leaching the untreated soils with eight six-inch applications of tap water are depicted in Fig. 5, series H. It was thought advisable to carry out this experiment in order to find out how much native phosphorus could be removed from the soils under these conditions. It will be noted that the amounts of native phosphorus removed were very small compared with the phosphorus removed by the leaching processes from the fertilizer treated soils, shown in Fig. 1 through 4. It has been assumed that all of the phosphorus removed from the treated soils was added phosphorus. The calculations of the percentage recoveriess in all series have been based on this assumption. This assumption is not entirely valid for any series except series K where radioactive phosphorus

was used.

Table II

Phosphorus Recovery[1]

Soil No.	P_2	Per Cent P. Recovered in Each Leachate 1	2	3	4	5	6	7	8	Total Per Cent P. Available[4]
					Series D - Phosphoric Acid					
88A	1.1	17.0	13.8	9.6	7.7	5.2	3.7	2.9	2.2	63.2
89	2.1[2]	7.0	7.4	5.1	4.0	3.6	2.8	2.5	1.9	36.3
90	0.5	11.9	7.4	5.0	3.7	2.0	1.5	1.2	1.2	34.6
95	10.8	13.4	7.9	5.3	4.8	4.1	3.2	2.7	2.4	54.6
					Series K - Phosphoric Acid Labeled with P^{32}					
88A	Not used.									
89	0.4	3.0	4.2	3.2	2.6	2.0	1.5	1.2	1.1	19.3
90	0.3	12.6	10.1	6.4	3.6	2.5	1.9	1.7	1.4	40.4
95	0.1	10.0	8.0	6.2	4.1	2.9	2.1	1.7	1.4	36.6
					Series G - Triple Superphosphate					
88A	8.2	13.2	11.1	8.1	6.1	4.7	3.6	2.8	2.2	60.1
89	16.1	4.5	5.1	4.2	3.1	2.4	2.0	1.6	1.5	40.5
90	25.1	4.4	4.5	3.8	2.5	2.0	1.5	1.0	0.8	45.7
95	36.7	5.1	3.7	3.0	2.5	2.2	2.0	1.8	1.6	58.7

1. Average results from replications.
2. Leachate from original fertilizer application.
3. Numbers refer to successive water leachates.
4. "Available" here means that this phosphorus would presumably be available to a plant since it is water-soluble phosphorus. Represents the sum of nine leachings.

In the case of series K, the assumption is entirely valid because all of the phosphorus measured radiactively in the leachates represents only added phosphorus. In all series there is the possibility that added phosphorus may have exchanged with native phosphorus or that some native phosphorus was leached out of the soil. The latter would manifest itself in apparent higher recoveries in all series where the commonly used chemical analyses were applied. The fact that the results in series H, Fig. 5,

were so low justifies to some extent this assumption.

The curves presented in Fig. 2 and 4 which represent the results from series D and K respectively show that as far as the shapes of the curves are concerned the results of the chemical method compare well with those of the tracer method. It will be noted, however, that there are quite wide differences in the actual magnitudes of the phosphorus content of the leachates, particularly with regard to soils 89 and 95. No tracer work was carried out on soil 88A. A comparison of the data representing series D and K in Table II indicates that the total per cent recoveries of phosphorus in series D, soils 89, 90, and 95 were 36.3, 34.6, and 54.6 respectively, while the recovery of added P. for the same soils in series K were 19.3, 40.4, and 36.6. There is little difference in the total per cent recovery in the case of soil 90 in the two series, while the differences appearing in soils 89 and 95 are 17% and 18% respectively.

The explanation for this probably lies in the fact that in series K the soils were not removed from the leaching tubes before the application of the first six inches of water as they were in series D. It is probable that the complete mixing of the soils between the fertilizer application and the first water leaching is the decisive factor. This mixing effected a redistribution of the phosphorus in the soil in series D so that at the onset of water leaching the phosphorus was distributed evenly throughout the soil. In series K, however, the distribution of phosphorus in the soil prior to the first water leaching was not uniform. This may be seen by observing the concentration of phosphorus in each soil layer as depicted in Fig. 9, series A, which, in treatment partly duplicates series K.

That is, the soils in series A were leached only with the original phosphoric acid application and were then sectioned and analyzed for total phosphorus. Series K soils should then exhibit approximately the same vertical distribution of phosphorus as those of series A when the first water application is made. The curves in Fig. 9 show higher concentrations of phosphorus in levels one and two than are present in levels three and four. This would indicate that in series K the phosphorus would have to be moved farther in order to be leached out of the soil. This would result in a lower recovery of the applied phosphorus in the leachate. The fact that soil 90 shows no great differences may be due to the fact that there is a more uniform distribution of phosphorus in the first three levels of the soil column, following the P-leaching, than there is in the case of soils 89 and 95, Fig. 9. It must be noted that some of the differences in the recovery of phosphorus between series D and K might be attributed to native phosphorus appearing the leachates. This would, of course, cause an apparent decrease in recovery in series K, when compared with series D, since native phosphorus would not be measured radioactively.

It will be noted that the P-leachates of soil 95, series D, Fig. 2, are considerably higher in phosphorus than corresponding leachates in series K, Fig. 4. It will be remembered that the soils in series D were treated with phosphoric acid while those in series K were treated with phosphoric acid labeled with P^{32}. In a check leaching, similar in all respects to series K exept that P^{32} was not used, the average recovery of phosphorus in the P-leachates of soil 95 was 3.3 parts per million.

This corresponds more closely to a recovery of less than one part per million for soil 95 in series K than it does to an average recovery of 15.2 parts per million in series D. The high phosphorus content of the P-leachate of soil 95, series D, may have been caused by some channeling due to the fact that this soil is a clay and was very difficult to pack uniformly in the tube.

An examination of Figs. 2 and 4, where data from series D and K are graphed, shows that the movement of phosphorus, as evidenced by the concentration of phosphorus in the various leachates, was different for each of the four soils studied. Any attempt to explain these differences must take into account many factors such as the phosphorus status, the texture, the lime content, and the mineral form predominating in the soil. As for the mineral forms comprising these soils, little can be said, since only soil 95 has been mineralogically analyzed. This soil is predominantly a montmorillonite type. According to Stout (1939) montmorillonite has a relatively low phosphorus fixing capacity, which in part explains the relatively high recovery of water-soluble phosphorus from this silty clay soil. However, no comparison may be made here with the other soils since the mineralogical data is not available.

If these soils are considered solely on the basis of their textures, one would expect the greatest movement of phosphorus in soils 88A and 90, with 89 coming next, followed by 95. An examination of the results tabulated in Table II indicate that this is not the case. If, on the other hand, the soils are considered on the basis of soil status alone, one might expect soils 88A and 89 to evidence greater phosphorus movement

followed by 90 and 95. This assumption might be explained on the basis of the definitions of deficient and non-deficient soils. A plant growing on a non-deficient soil does not respond to phosphate fertilization while one growing on a deficient soil responds to added phosphorus. The reason the plant growing on the non-deficient soil does not respond is that it is getting enough phosphorus from the soil to satisfy its needs. It might be reasoned from this that the phosphorus fixing factors in the non-deficient soils are more or less saturated so that any added phosphorus should move through a soil of this type quite readily. The opposite line of reasoning would apply to the deficient soils. The factor of the deficiency or non-deficiency is apparently not the only one at work in the retention of phosphorus in these soils. This is clearly indicated by the data in Table II.

If these soils are considered on the basis of their lime content it would be expected that a greater movement of phosphorus would be found in soil 89, than in the other three soils, since it is the only soil which contains no lime. Examination of the data shows, however, that it shares the distinction of having the lowest phosphorus movement along with soil 90.

It is evident from the foregoing discussion that the movement of phosphorus in soil is governed by many factors. The extent of the movement will depend upon which of these factors or combination of factors is dominant in the soil. It is seen that the actual sequence of decreasing phosphorus movement as indicated by the total percentage recoveries is 88A, 95, 89, 90. For practical purposes soils 89 and 90 may be considered to have the same ability to fix phosphorus, although the mechanism by which

the phosphorus is fixed may be very different in the two soils. It seems reasonable to expect a relatively greater movement of phosphorus in soil 88A because it is a silt loam, is non-deficient, and is lower in lime than soil 90. It would be expected that the movement of phosphorus in soil 95 would be relatively low since this soil is a silty clay and has a history of phosphorus deficiency. However, in this soil the factors accounting for retardation of phosphorus movement were in part offset by the relatively low lime content and the presence of montmorillonite as the basic clay mineral in this soil. The fact that soil 89 is a silty clay loam apparently overshadows the lack of lime and the effect of its deficiency status. Soil 90, on the other hand, is the highest in lime and is also deficient. Apparently the two factors have a greater combined effect than its texture.

In comparing the data from series D and G, Figs. 2 and 3, it is seen that the shapes of the curves representing the treatments with phosphoric acid differ quite radically from those representing treatments with TSP. It will be remembered that series D and G treatments were identical except that phosphoric acid was applied in series D while TSP was applied in series G. The differences existing between these two treatments are also depicted in Table II. It will be noted that the greatest difference lies in the very high phosphorus content of the P-leachate in the case of series G, followed by an abrupt drop in the water soluble phosphorus content of the H_2O-1 leachates. It will be noted that the average per cent recoveries for the P-leachates in series D are 1.1, 2.1, 0.5, and 10.8 while for series G they are 8.2, 16.1, 25.1, and 36.7. Following the H_2O-1

leachates the curves in the two series are quite similar, showing a gradual decrease in phosphorus content of the succeeding leachates except for a slight increase in the H_2O-2 leachate in the case of soils 89 and 90 in series G and in increase in 89 in series D.

It will be noted that although the curves representing soil 88A are similar in both series, the P-leachate of soil 88A in series G is significantly higher in phosphorus than the corresponding R-leachate of this soil in series D. In addition, the H_2O-1 leachate of soil 88A, series G, is much lower in phosphorus.

It was recognized that this high level of phosphorus in the P-leachates of series G, particularly in the cases of soils 89, 90, and 95, might be due to channeling. However, the fact that the P-leachates of series E fairly well duplicated those of series G rules out this possibility. The average per cent recoveries for the P-leachates of series E are: 88A - 13.1; 89 - 14.4; 90 --21.2; and 95 - 37.2; while for series G the per cent recoveries are 8.2, 16.1, 25.1, and 36.7 respectively.

A comparison of the data recorded in Table II shows that in series D the total percentages of added phosphorus recovered from soils 88A, 89, 90, and 95 are 63.2, 36.3, 34.6, and 54.6 respectively, while in series G the percentages are 60.1, 40.5, 45.7, 58.7. Thus it is seen that the differences in the total amount of phosphorus leached from the same soils in the two series were not large.

The great differences existing in the curves representing the soils treated with phosphoric acid and those treated with TSP certainly warrant an explanation. However, a satisfactory explanation of this phenomonon is

very difficult. It was thought that the differences might be explained on the basis of the differences in pH of the two original leaching solutions. It could be reasoned that in the case of the phosphoric acid, sufficient hydrogen ion in excess of that existing in a similar solution of TSP would tend to free more calcium in the soil, which could then temporarily, at least, tie up significant quantities of phosphorus, giving rise to the low phosphorus content of the P-leachates in series D. This explanation, however, does not hold since the pH of the acid leaching solution is 4.9 while that of the TSP leaching solution is about 5.5. The corresponding hydrogen ion concentrations are 13×10^{-6} and 3.1×10^{-6} moles per liter respectively. Thus, the acid leaching solution contains only about four times as much hydrogen ion as the TSP leaching solution. It is very difficult to postulate that this small amount of hydrogen ion could account for the great differences in the phosphorus content of the leachates in these two series. Another item of interest in this respect is the fact that both original leaching solutions show very little buffering capacity and therefore, in neither case could the original leaching solution be expected to remain at an acid pH for any appreciable length of time. One would assume that upon contact with the well buffered soil, the solution would immediately lose its acidic characteristic. The fact that the corresponding leachates in both series exhibit essentially the same pH values further strengthens this viewpoint. Comparison of these pH values may be made from Table III.

It was also postulated that the differences might be explained on the basis of difference in method of solution of the two fertilizers. That is;

Table III

pH of Leachates

Series D_1 and G_2

Leachates	Soil 88A		Soil 89		Soil 90		Soil 95	
	H_3PO_4*	TSP**	H_3PO_4	TSP	H_3PO_4	TSP	H_3PO_4	TSP
P	7.2	7.5	6.8	6.8	7.8	7.0	7.1	7.3
	8.1	8.1	6.7	7.2	7.0	7.0	7.0	7.4
	7.2		6.8		7.0		7.0	
H_2O-1	7.6	7.1	7.3	7.4	7.1	7.1	6.9	6.7
	8.0	6.7	7.3	7.4	7.3	7.3	6.9	7.3
	7.7		7.3		7.2		7.1	
H_2O-2	8.0	7.8	7.4	7.8	7.2	7.8	7.1	8.1
	8.0	7.9	7.1	6.9	7.4	8.0	7.0	8.2
	8.0		7.3		7.3		7.3	
H_2O-3	7.8	7.9	7.4	6.8	7.6	7.6	7.6	7.7
	7.8	7.9	7.4	6.7	7.9	7.8	7.4	7.7
	7.8		7.3		7.8		7.0	
H_2O-4	7.8	7.4	7.3	7.7	7.9	7.9	7.2	8.1
	7.8	7.7	7.5	7.4	7.8	8.0	7.4	8.1
	7.8		7.4		7.7		7.1	
H_2O-5	7.8	7.6	7.5	7.6	8.2	7.6	7.3	7.3
	8.1	7.3	7.5	7.8	7.5	8.0	7.8	7.4
	7.3		7.5		8.3		7.2	
H_2O-6	7.2	7.9	7.2	8.1	7.6	8.1	7.4	7.9
	7.6	7.9	7.9	8.0	7.5	8.1	7.1	8.0
	7.2		7.7		8.0		7.1	
H_2O-7	7.9	7.7	7.3	7.9	7.8	7.6	6.5	7.6
	7.8	7.9	7.4	7.6	7.7	7.7	7.0	7.6
	7.8		7.5		7.7		8.2	
H_2O-8	7.4	7.6	7.8	8.0	8.0	6.7	7.8	8.1
	7.4	7.6	7.3	6.8	7.7	7.2	7.1	7.8
	7.5		8.1		7.7		7.4	

1. Data represents triplicate leachings.
2. Data represents duplicate leachings.

* Series D

** Series G

the phosphoric acid constituted a homogeneous solution when it was placed on the soil while the TSP was worked into the surface of the soil and then six inches of water was applied. Now, in the case of the TSP, homogeneity did not exist with respect to the six inches of water. The TSP was being dissolved gradually as each increment of water came into contact with it. It would be expected that when the first increment of water comes in contact with the TSP the resulting pH should be quite low. This was established in an ideal situation by placing the same weight of TSP as used in these experiments on a filter paper in a Buchner funnel and pouring tap water on the TSP. Successive 25 ml. portions were collected and their pH values determined. These values appear in duplicate in Table IV. It is seen that the pH of the first 25 ml. portion is about 4.7 and the values increase to about the fourth or fifth portion where they more or less level off.

Table IV

pH Values of 25 ml. Portions of Tap Water Filtered Through TSP*

Successive Portions	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
pH	4.6	6.6	7.2	7.3	7.6	7.6	7.4	7.6	7.7	7.7	7.9	7.9	7.8	7.9	7.8	7.8	7.6
pH	4.8	6.7	7.9	8.1	8.1	8.1	8.1	8.1	8.1	8.2	8.1	8.1	8.1	8.1	8.2	8.0	8.1

*Total of 425 ml. of tap water leached through 0.1493 grams TSP.

It was thought that possibly the low pH, existing when the water first comes in contact with the TSP, might increase the solubility of phosphorus in the soil giving rise to the high concentrations of phosphorus in the

P-leachates of series G. This theory also runs into the objection that in the soil these relatively low pH values will exist for such a short period of time that they should have little effect on the results obtained. Indeed, it is improbable, due to the low buffering capacity of these TSP solutions, that these low pH values exist at all in contact with the well buffered soil.

The phenomenon might also be explained on the basis of the differences in the intimacy of contact of the two fertilizers with the soil. It seems probable that in the case of the TSP, less intimate contact was established between the fertilizer and the soil particles. It is possible that phosphorus dissolved at a particular point by the water might not diffuse throughout the soil solution, thus not coming in contact with all of the soil particles. On the other hand, the phosphoric acid leaching solution is homogeneous when it is applied to the soil and must therefore come in more intimate contact with all the soil particles, giving the soil a better chance of fixing the phosphorus. This might account for the low values of phosphorus in the P-leachates of series D and the relatively high values of these leachates in series G.

The results of soil leaching in series D and H are shown graphically in Figs. 6 and 7. Comparisons are made of the amounts of phosphorus removed from the soil by leaching with the amount added in the treatment, the total native phosphorus in the soil, the total phosphorus in the soil after leaching with four acre feet of water, and the total phosphorus in the soil after the fertilizer treatment. Addition of the phosphorus removed by leaching to the phosphorus remaining in the soil after leaching

Table V

Results of Calculations* Using Data From Figs. 6 and 7

Soil No.	88A	89	90	95
	Series D - Phosphoric Acid			
1. P. removed by leaching.	90	50	50	75
2. P. remaining in soil after leaching with 4 acre feet of water	7740	1035	980	565
3. Sum of 1 and 2.	830	1085	1030	640
4. P. remaining in the soil after fertilizer treatment.	865	1259	1085	640
5. Per cent difference between 3 and 4.	4	14	5	0
	Series G - TSP			
1. P. removed by leaching.	85	55	65	80
2. P. remaining in soil after leaching with 4 acre feet of water.	685	1015	975	555
3. Sum of 1 and 2.	770	1070	1040	635
4. P. remaining in the soil after fertilizer treatment.	885	1145	1080	635
5. Per cent difference between 3 and 4.	10	7	4	0

* All phosphorus values calculated in parts per million.

should be equal to the total phosphorus in the soil after the fertilizer treatment. This should also give some indication of the precision attained in this work. The results of these calculations for both series D and G are shown in Table V.

A graphical representation of the relation of the phosphorus removed by leaching to the available phosphorus left in the soil after leaching was completed, is depicted in Fig. 8, series D and G. The available phosphorus was determined on the soils by the carbon dioxide extraction method described earlier in this paper. These values are an average of the available phosphorus found in the four soil layers analyzed. It will be noted that in every case except soil 89 the amount of available phosphorus still remaining in the soil is greater in series D. This is to be expected because, in general, more phosphorus was leached out of the TSP treated soils of series G. It will also be noted that the available phosphorus left in the soil after the leaching processes were completed was higher in the cases of the non-deficient soils 88A and 89. That the available phosphorus in all the soils in both series was higher after the leaching processes than the available phosphorus in the untreated soils may be seen by comparing the available phosphorus data in Table I with that in Fig. 8.

It was felt, when work on this problem was started, that some valuable information as to the vertical distribution of phosphorus in the soil might be obtained by analyzing four approximately equal vertical layers of the soil. The relative distribution of total phosphorus in the soils treated with acid (series A) and with TSP (series E), immediately after the fertilizer application, is represented by Figs. 9 and 10. As may be

seen, the curves seem to indicate a general accumulation of phosphorus in layers one and two in series A. The data from series # indicate a general accumulation of phosphorus in layer one followed by a general leveling out of the phosphorus concentration in the succeeding levels.

Fig. 11 and 12 show the vertical distribution of total phosphorus in the soil after the fertilizer treatment was followed by eight six-inch applications of leaching water. In general the phosphorus concentrations in both series D and G have tended to level out and approach a common value. A very slight tendency toward a higher concentration in the fourth layer is shown, although it probably has no significance.

The vertical distribution of available phosphorus in the soil levels of series D and G is depicted in Fig. 13 and 14. In the case of the available phosphorus there seems to be a tendency for the phosphorus concentration to be highest in the lowest level. This is to be expected, since if any phosphorus in the soil is going to show evidence of movement it should be the available phosphorus. It will again be noted that the available phosphorus in each level of the non-deficient soils is noticeably higher.

The foregoing discussion leads to a very obvious question. What fertilizer is the more efficient, phosporic acid or TSP? According to MacIntire et al (1947) phosphoric acid was slightly less effective than Wilson Dam superphosphate (actually a triple superphosphate since it contains 42.5% available P_2O_5). His results were based upon the response in rye grass and red clover to the two phosphatic fertilizers.

In making any statements as to which of these two fertilizers is the

better, it must be remembered that the work cited in this paper was carried out on disturbed soil samples and only four soils were studied. In addition to this only surface soil samples were used so that any effects the subsoil might have upon phosphorus movement would not be shown here.

It is possible that both the crop and soil should be taken into consideration in choosing between the two fertilizers. Perhaps the use of a mixture of the two fertilizers would be the most efficient.

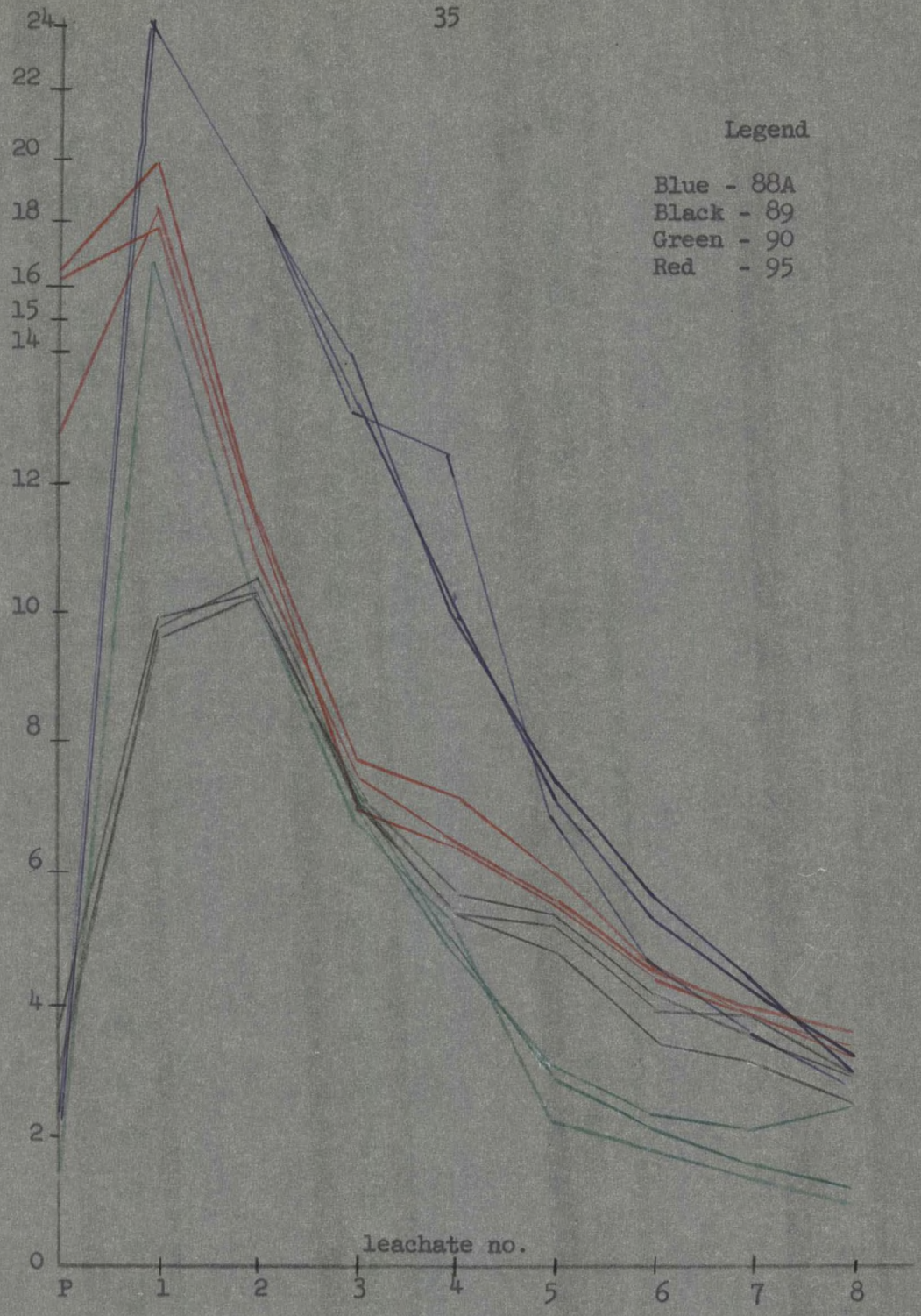


Fig. 2
Series D
Ppm. P. in Leachates vs. Leachate Number.
10 mm. = 1 Ppm. to 14 Ppm.- 5 mm. = 1 Ppm. above 14 Ppm.

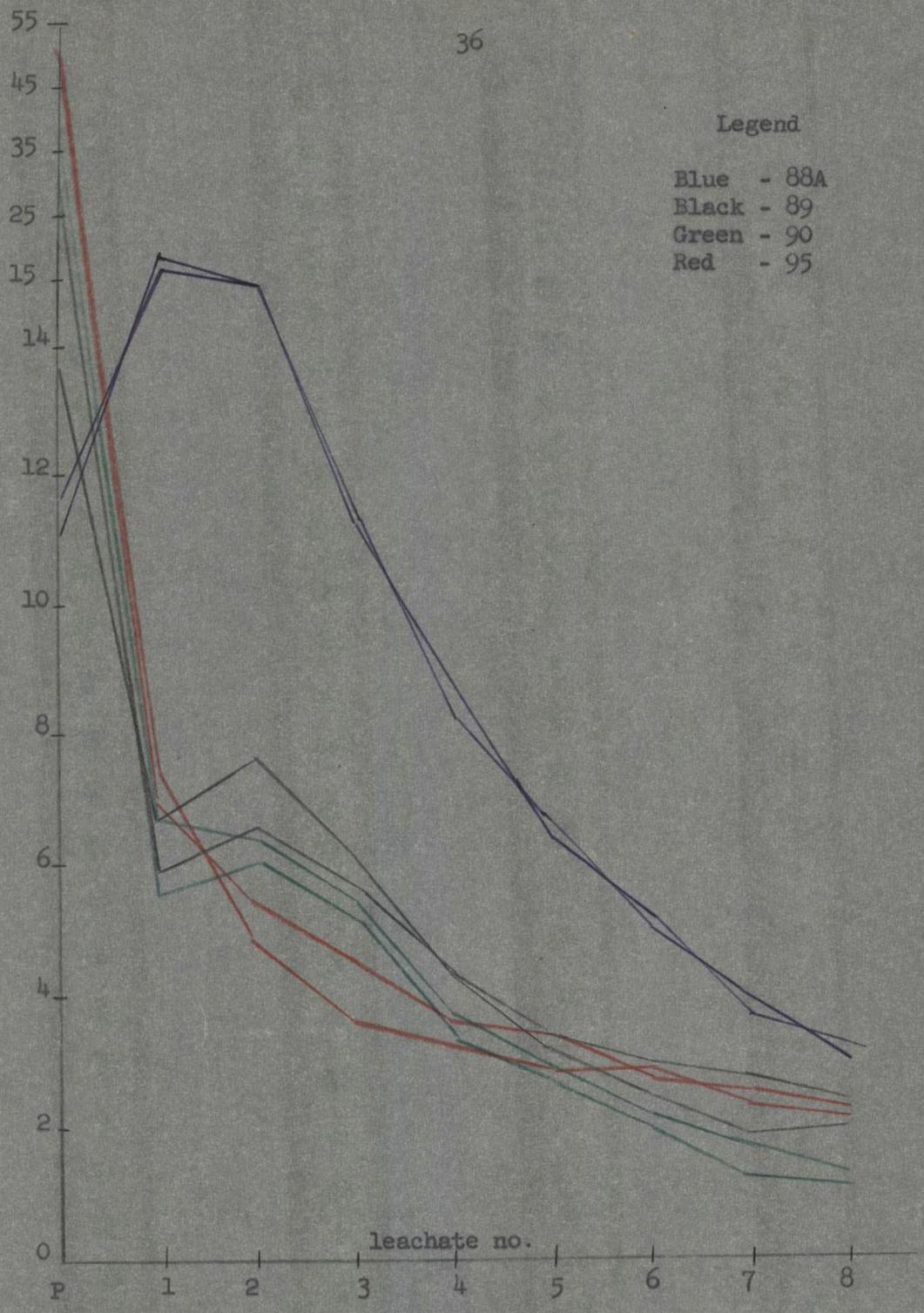


Fig. 3
Series G
Ppm. P. in Leachates vs. Leachate Number.
10 mm. = 1 Ppm. to 15 Ppm. = 1 mm. = 1 Ppm. above 15 Ppm.

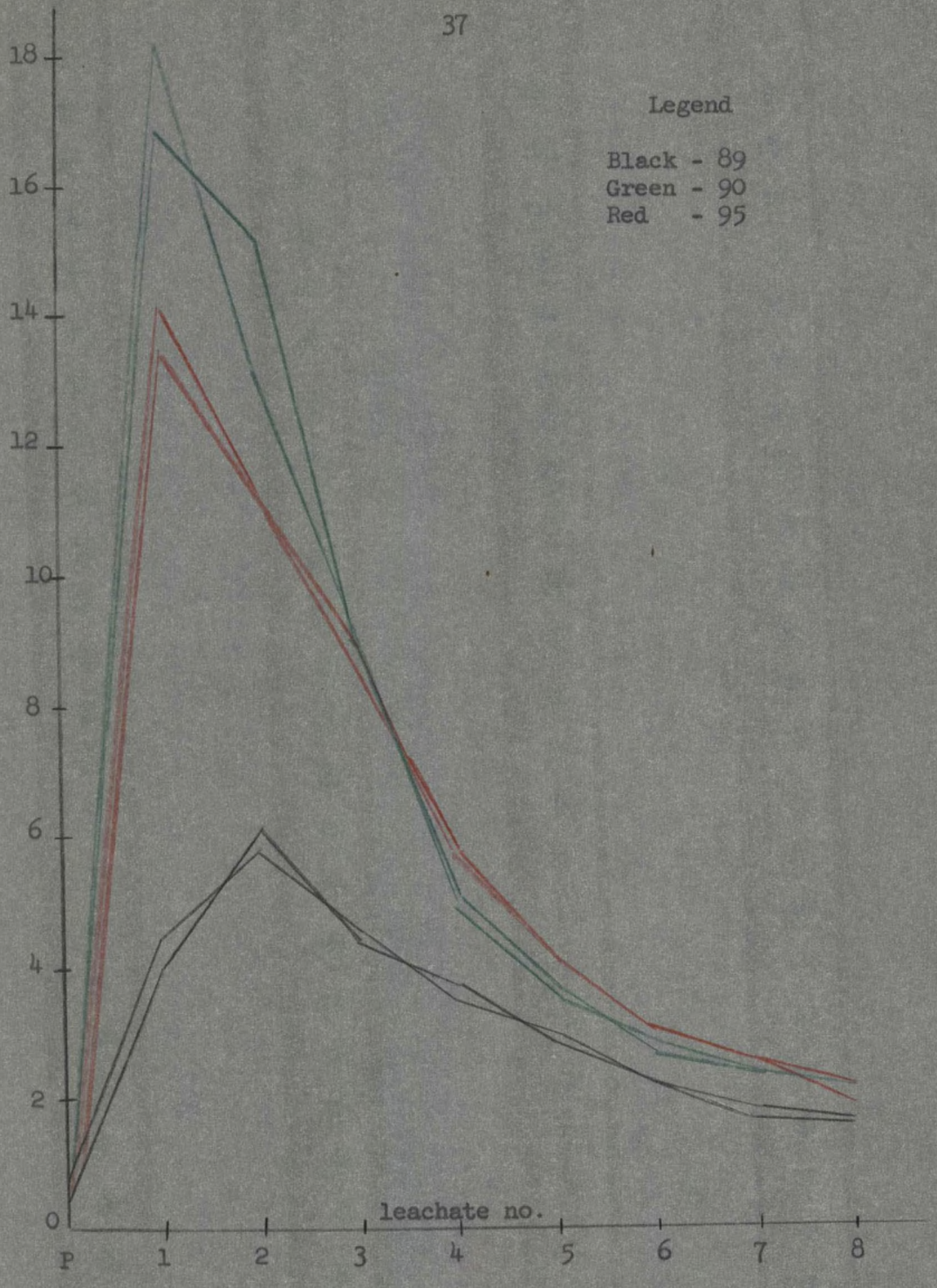


Fig. 4
Series K
Ppm. P. in Leachates vs. Leachate Number.

Legend

Blue - 88A
Black - 89
Green - 90
Red - 95

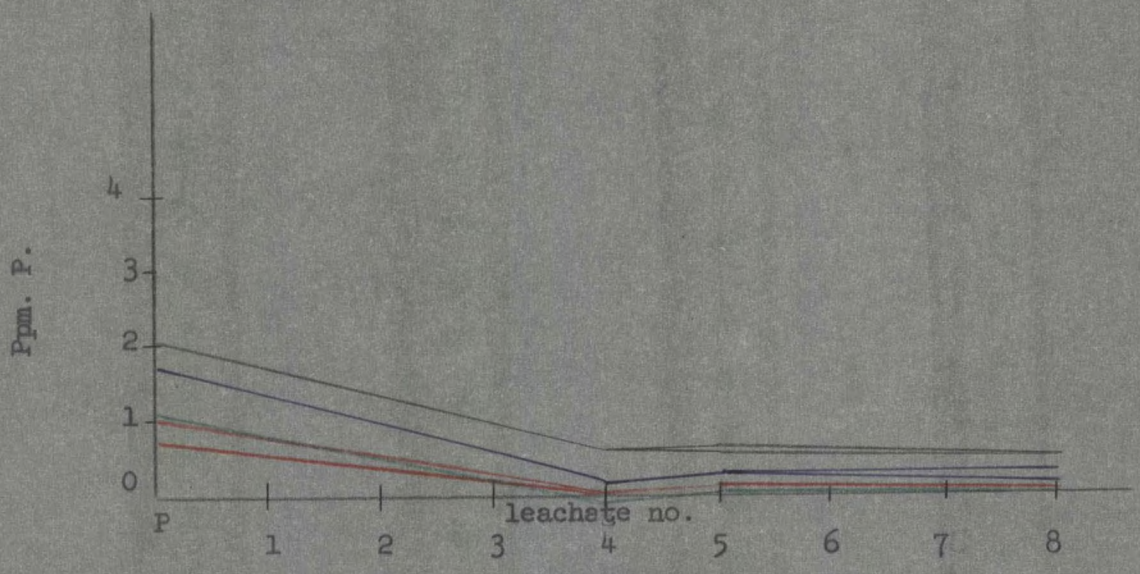


Fig. 5
Series H
Ppm. P. in Leachates vs. Leachate Number.

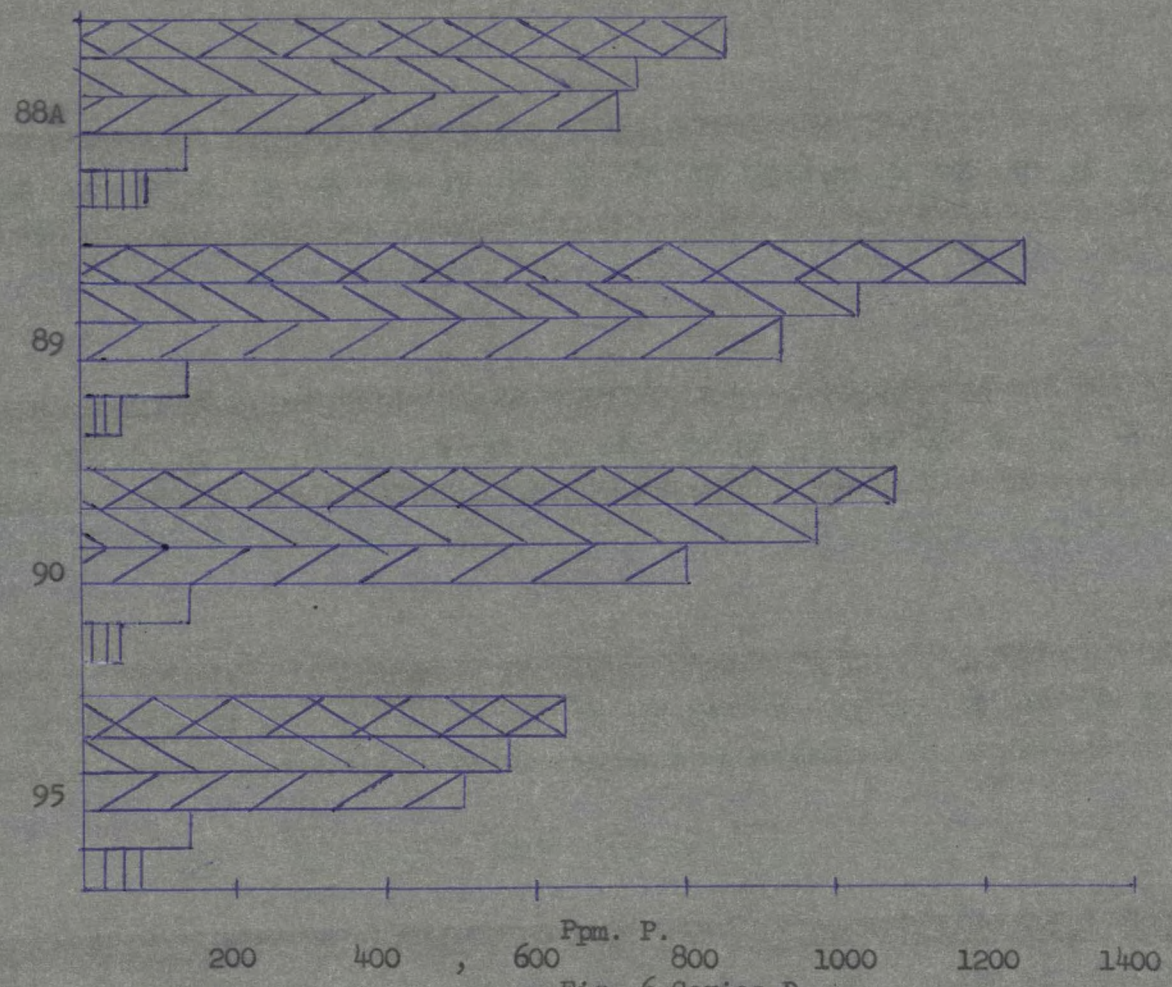


Fig. 6 Series D

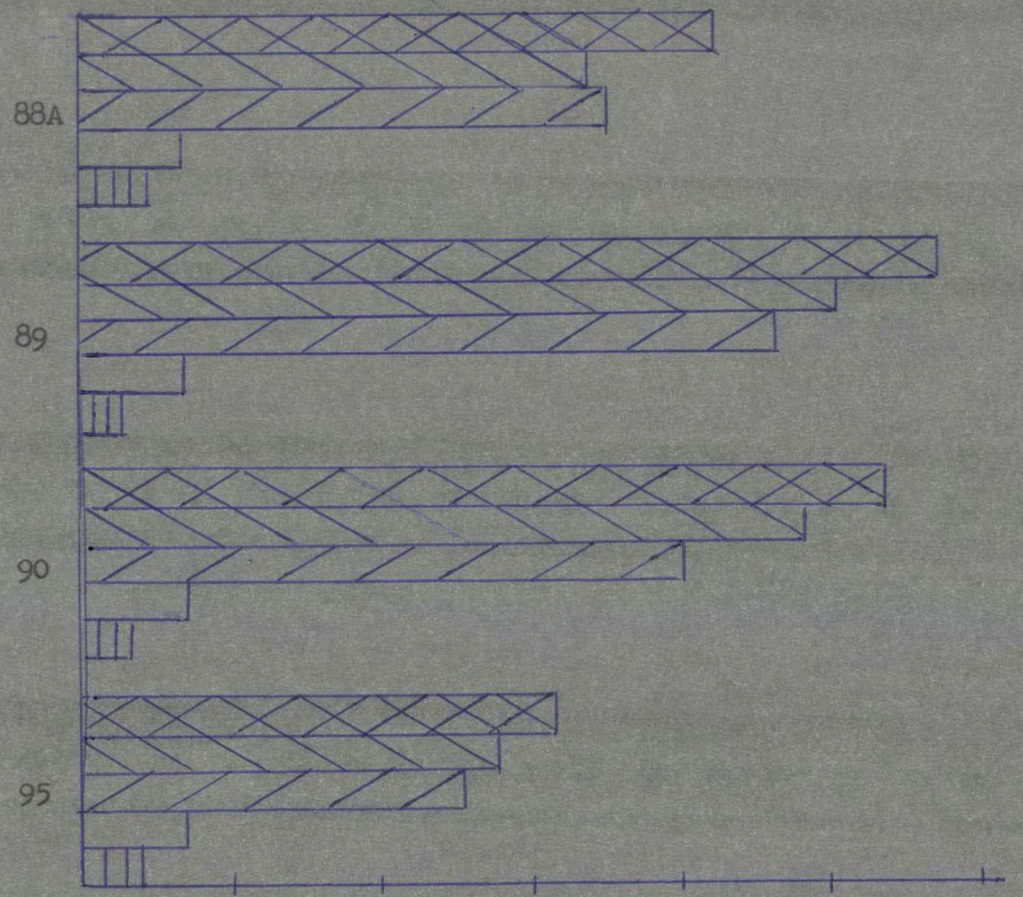


Fig. 7 Series G

Total P. in Soil after Fertilizer Application
Total P. in Soil after Leaching Completed.
Total P. Originally in Soil.
P. Added in Fertilizer Application.
P. Removed by Complete Leaching Process.

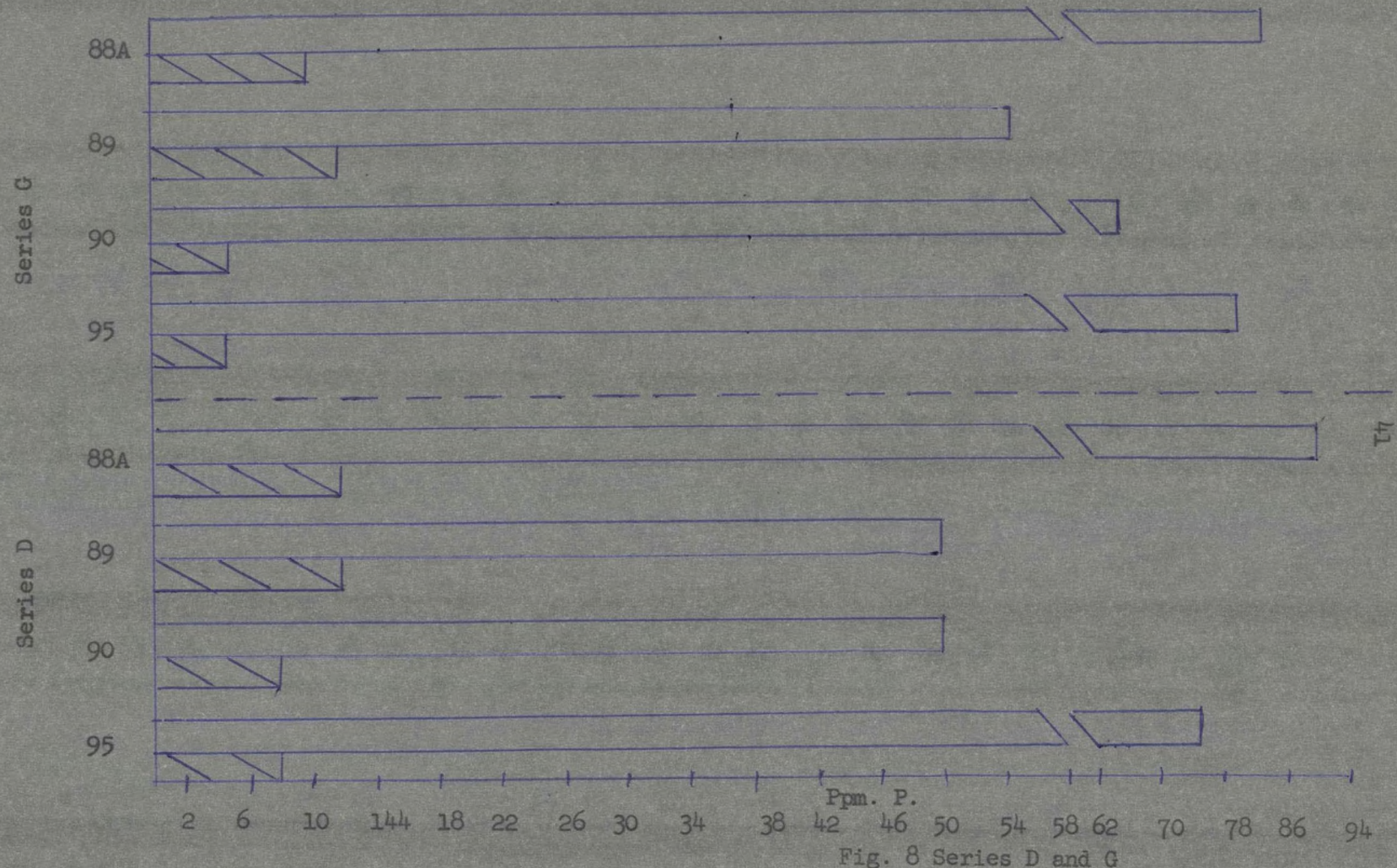


Fig. 8 Series D and G

P. Removed from Soil by Complete Leaching Process.
Available P. Remaining in Soil after Leaching Completed.
5 mm. = 2 Ppm. to 58 Ppm. - 5 mm. = 4 Ppm. above 58 Ppm.

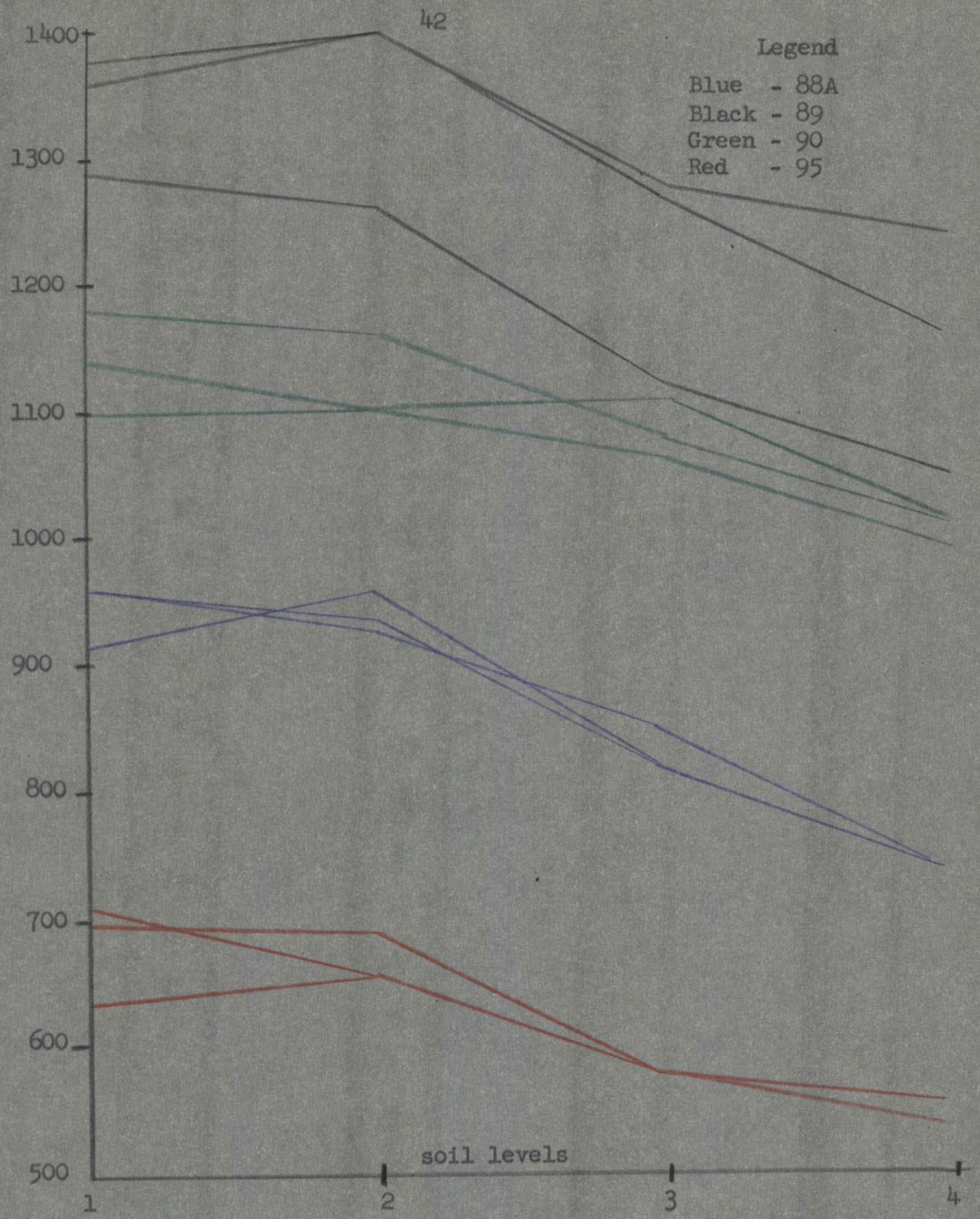


Fig. 9
Series A
Ppm. P. in Soil Sevels vs. Soil Levels.

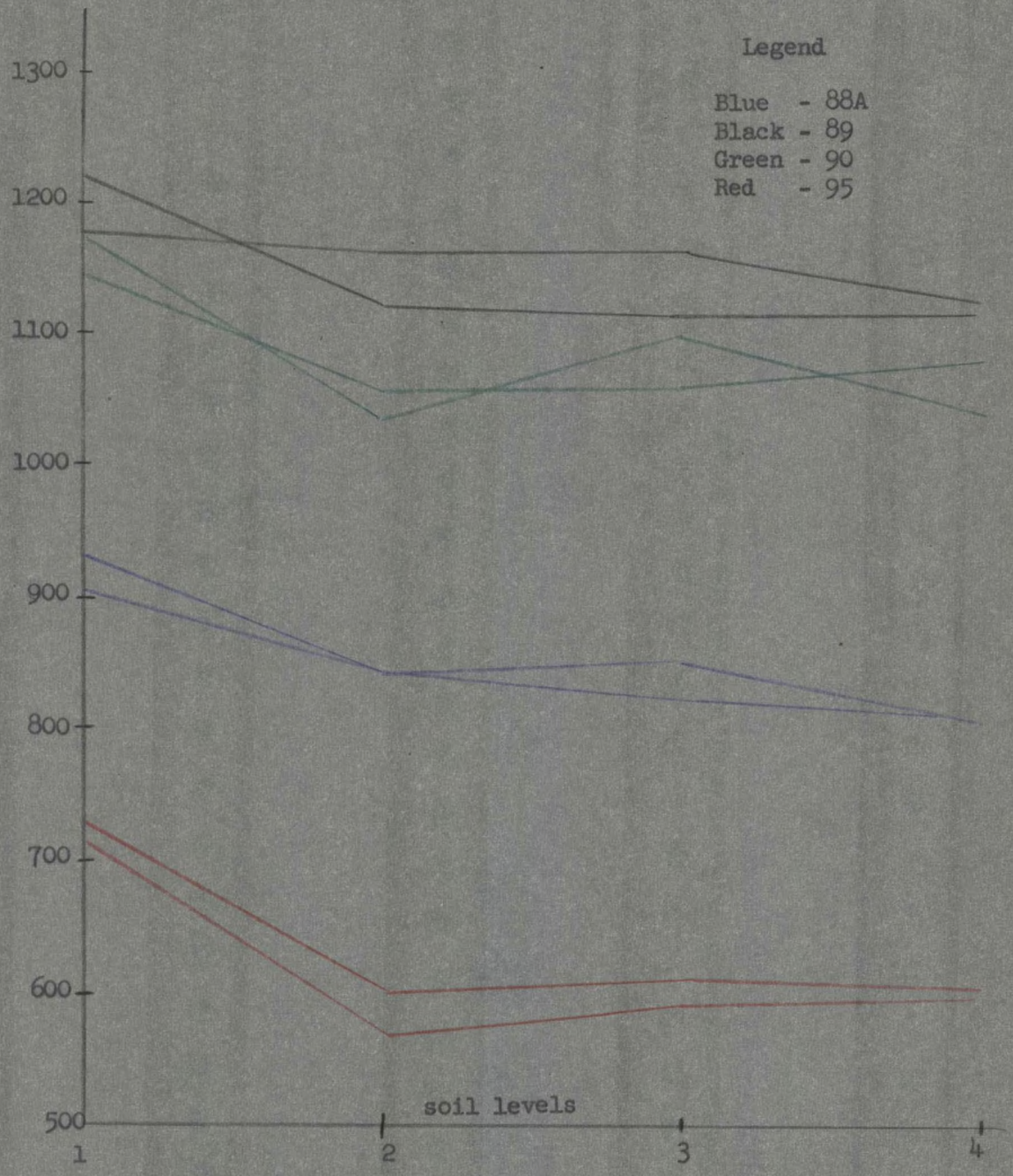


Fig. 10
Series E
Ppm. P. in Soil Levels vs. Soil Levels.

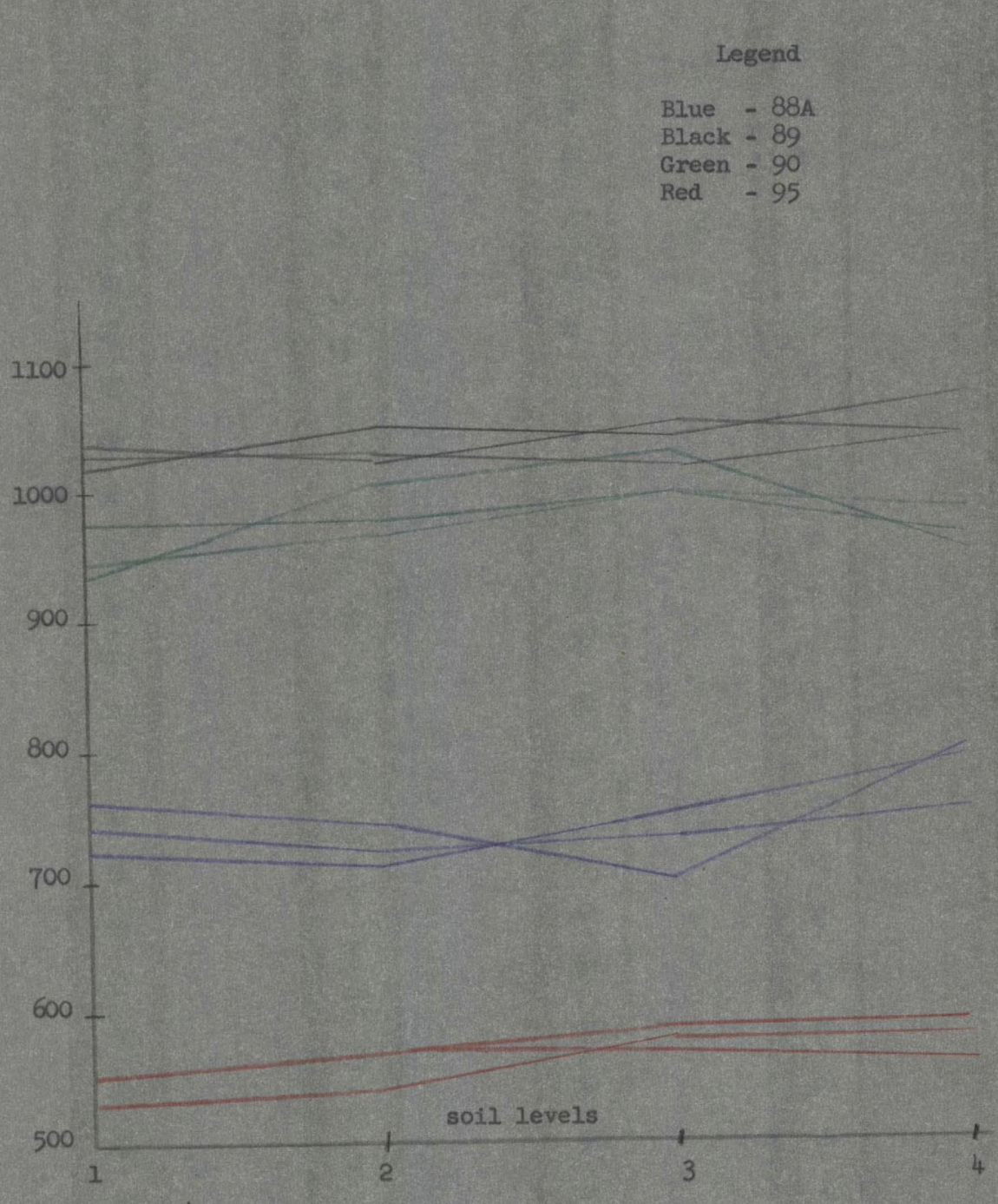


Fig. 11
Series D
Ppm. P. in Soil Levels vs. Soil Levels.

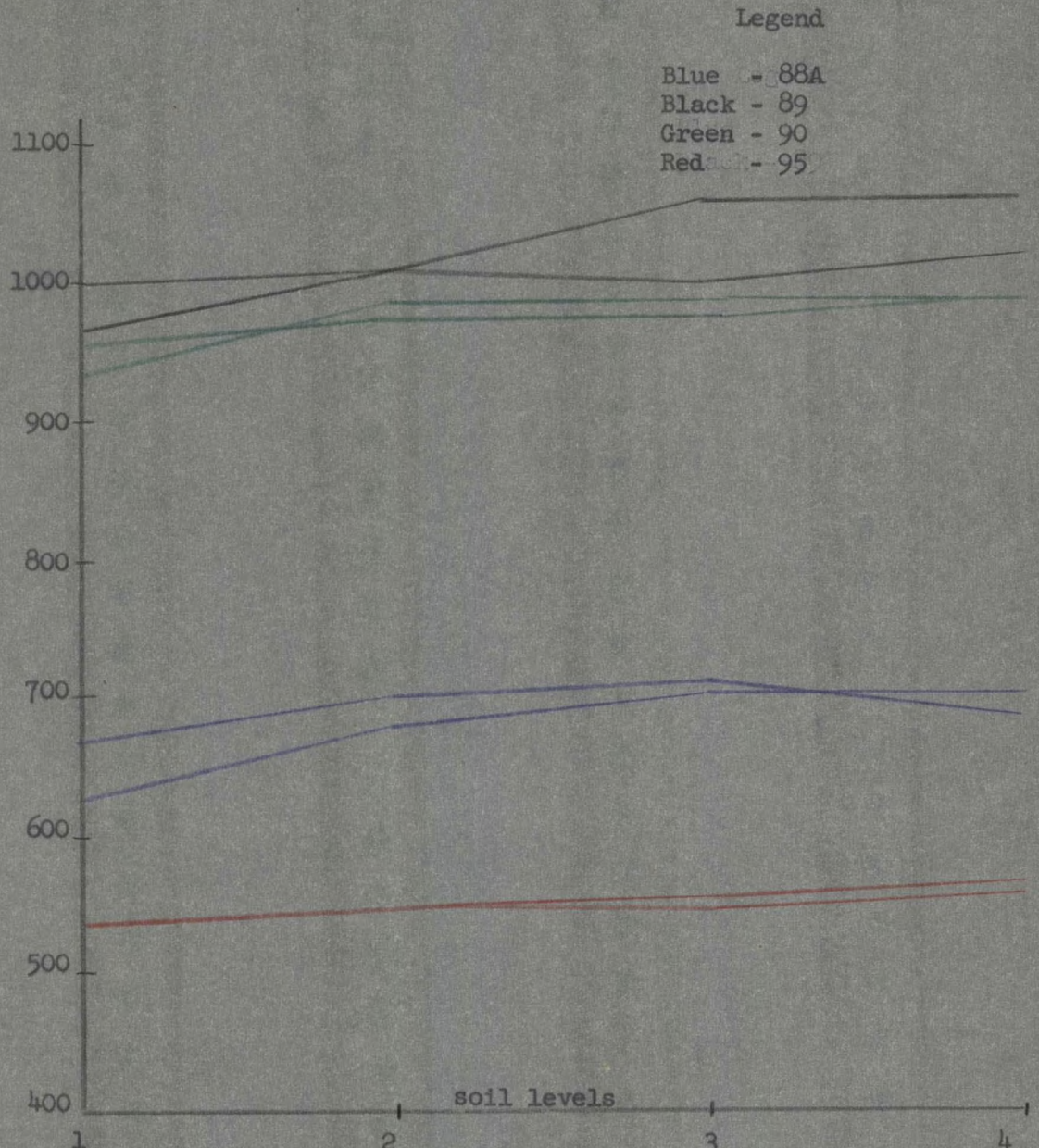


Fig. 12
Series G
Ppm. P. in Soil Levels vs. Soil Levels.

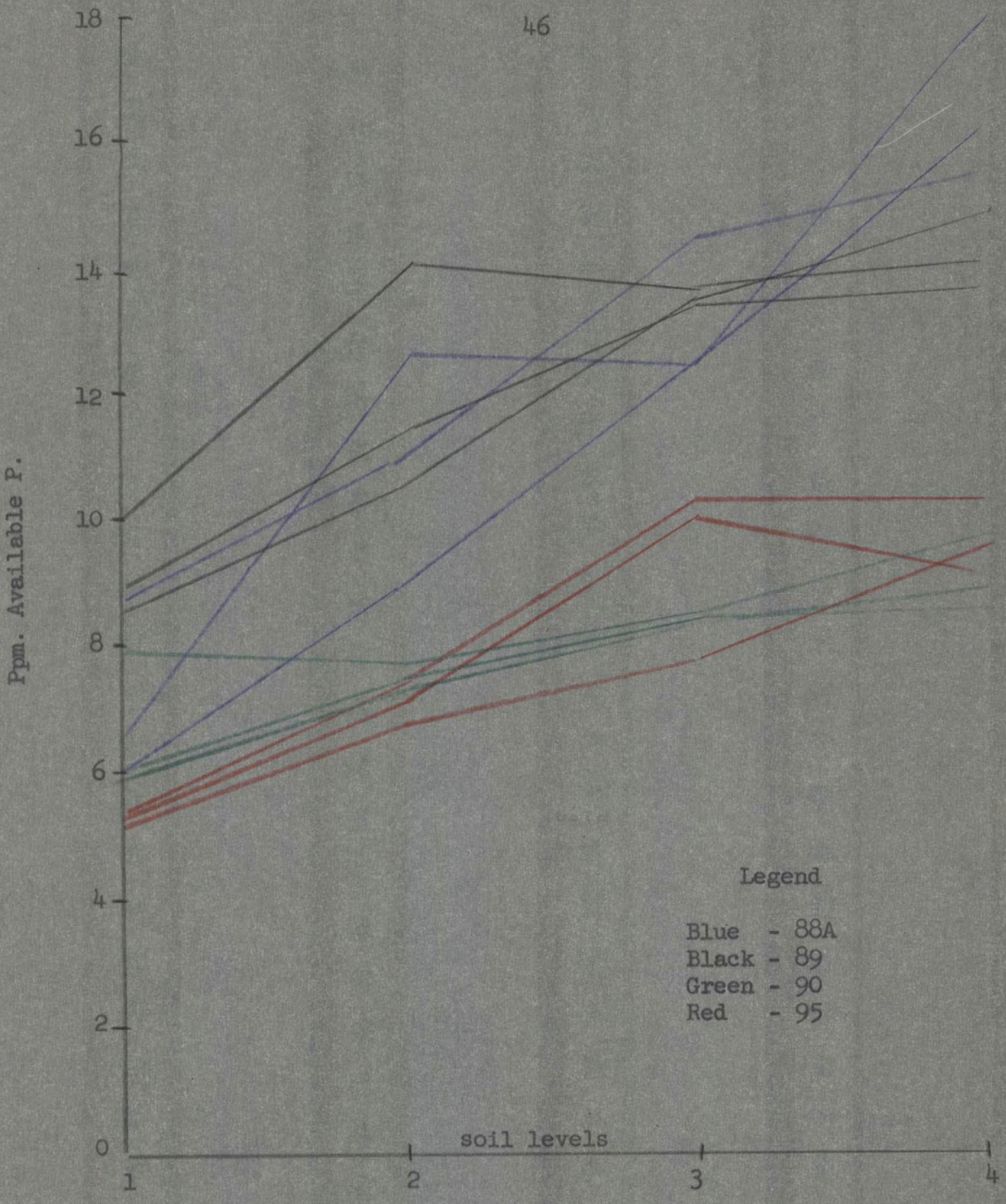


Fig. 13
Series D
Ppm. P. in Soil Levels vs. Soil Levels.

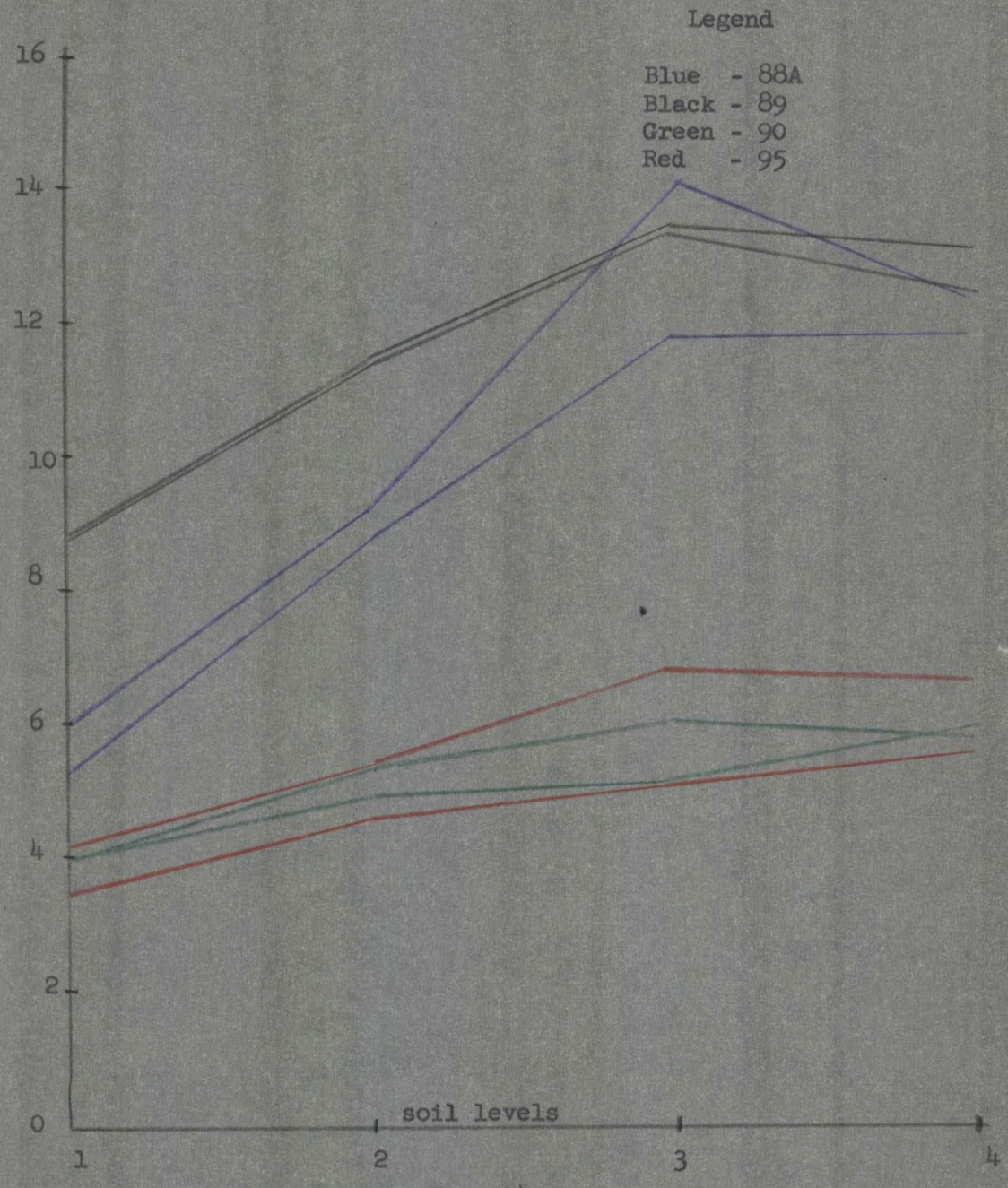


Fig. 14
Series G
Ppm. P. in Soil Levels vs. Soil Levels.

SUMMARY

In leaching experiments the movement of phosphorus when applied as triple superphosphate and phosphoric acid to four different soils was studied. It was found that during the process of fertilizer application, much greater movement of the added phosphorus occurred in the case of the triple superphosphate. Three hypotheses were advanced in an attempt to explain this phenomonon, but considerably more work is necessary before it can be satisfactorily explained.

After the fertilizer applications had been followed by eight successive six-inch applications of tap water, the total amount of phosphorus recovered in the leachates did not differ greatly between the two fertilizers.

On the basis of the leachate analyses appreciable amounts of added phosphorus were leached through the soil columns.

There was some indication that phosphorus tended to concentrate in the surface of the soil during the fertilizer applications and that available phosphorus concentrated in the lower levels of the soil after the water leaching was completed.

On the basis of the data presented here, there is no justification in coming to any conclusion as to which fertilizer is more efficient from the standpoint of phosphorus penetration and movement.

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BIBLIOGRAPHY

Allen, L., Biochemical J., 34, (2) 858 (1940).

Alway, F. J. and Rost, C. C., Soil Sci., 2, 493 (1916).

Beater, B. E., Soil Sci., 46, 453 (1938).

Brown, L. A., Soil Sci., 39, 277 (1935).

Burd, J. S., Soil Sci., 65, 227 (1948).

Doak, B. W., New Zealand J. Sci. Tech., 15, 155 (1933). C. A. 28:5548.

Ensminger, L. E. and Larson, H. W. E., Soil Sci., 58, 253 (1944).

Ford, M. C., J. Am. Soc. Agron., 25, 134 (1933).

Gilligan, G. M., Del. Agr. Exp. Sta. Bull., 229, 3 (1941).

Heck, A. F., Soil Sci., 37, 343 (1934).

Hockensmith, R. D., Gardner, R., and Kezer, A., Soil Sci., 36, 35 (1933).

Kelley, J. B. and Midgley, A. R., Soil Sci., 55, 167 (1943).

MacIntire, W. H., Winterberg, S. H., Clements, L. B., and Johnson, H. S., J. Am. Soc. Agron., 39, 971 (1947).

MacIntire, W. H., Shaw, W. M., and Robinson, B., Soil Sci., 67, 377 (1949).

Midgley, A. R., J. Am. Soc. Agron., 23, 788 (1927).

Midgley, A. R., Soil Sci. Soc. Am. Proc., 5, 24 (1940).

Neller, J. R., Soil Sci. Soc. Am. Proc., 11, 227 (1946).

Perkins, A. T. and King, H. H., Soil Sci. Soc. Am. Proc., 8, 154 (1943).

Perkins, A. T. and King, H. H., Soil Sci., 58, 243 (1944).

Perkins, A. T. and King, H. H., Soil Sci. Soc. Am. Proc., 9, 61 (1944).

Perkins, A. T., Soil Sci. Soc. Am. Proc., 10, 102 (1945).

Ravikovitch, S., Soil Sci., 38, 219 (1934).

Robinson, G. W. and Jones, A. O., J. Agr. Sci., 17, 94 (1927).

Spencer, V. E. and Stewart, R., Soil Sci., 38, 65 (1934).

Stephenson, R. E. and Chapman, H. D., J. Am. Soc. Agron., 23, 759 (1931).

Stout, P. R., Soil Sci. Soc. Am. Proc., 4, 177 (1939).

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