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A CHARACTERIZATION OF THE INORGANIC AND AVAILABLE PHOSPHORUS CONTENT OF FOUR SOUTH DAKOTA SOILS

BY

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A thesis submitted
in partial fulfillment of the requirement for the
degree Master of Science, Department of
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and Mechanic Arts

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A CHARACTERIZATION OF THE INORGANIC AND
AVAILABLE PHOSPHORUS CONTENT OF
FOUR SOUTH DAKOTA SOILS

This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

Head of the Major Department

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To my wife Loris much is owed. Her constant encouragement, assistance in the preparation of this manuscript and financial aid made this study possible.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Phosphorus is an element that is becoming increasingly important in South Dakota soils. Although there seems to be a large supply of inorganic phosphorus in these soils, its availability to crops is definitely restricted.

It was thought that a knowledge of the distribution of the different forms of phosphorus over a range of South Dakota soils is a necessary background for further understanding of phosphorus problems in the state. This knowledge should prove valuable in answering the question, are the low values of available phosphorus, as indicated by soil analyses, due to an absolute shortage, or to low availability of that already present?

Interpretation of phosphorus behavior in soils involves some of the most interesting and baffling problems in the realm of soil science. This is generally attributed to the diversity of the type of aggregate in which phosphate ions occur and the variety of associated complexes which affect the solubility of the phosphorus carrier.

Soils have been characterized by determining many parameters such as the pH, the clay content, the cation exchange capacity, and exchangeable bases. Chemical analyses of soils have led to the determination of organic matter, acid, alkali and water soluble phosphorus, iron and aluminum content and a host of other properties. Various forms of soil phosphorus have also been estimated by anion exchange resins and by p^{32} equilibration, as well as other methods. The ultimate value of characterizing the phosphorus of soil depends on its usefulness in evaluating the phosphorus fertility status and interpreting weathering and other processes.

It was the purpose of this research to characterize the South Dakota soils studied as to the amount of phosphorus present as aluminum, iron and calcium phosphate respectively, and to determine the phosphate release patterns of these soils, as indicated by successive leachings.

LITERATURE REVIEW

Because of the dual nature of this investigation, soil phosphorus fractionation and investigation into the available phosphorus content, the author has chosen to present the literature review in three parts: first, a general review; secondly, a review of fractionation from early work to the present; and third, a review of techniques for determining available phosphorus from Truog's first available phosphorus test to the present.

General Review

It has been a little over a century since adsorption of phosphates by soils was first postulated. Likewise, chemical methods of determining available phosphorus in soils were first studied about a century ago. (25) Since the advent of chemistry in the field of soil science the phosphorus chemistry has been studied extensively and nearly continuously.

Way, as cited by Kurtz and Williams (25, 40), in 1850 observed that phosphates were taken from solution by soils. Wild, as also cited by Kurtz and Williams (25, 40), reported that prior to Way's postulation Liebig was aware of phosphate retention by soils and in his later writing is supposed to have discussed this. Apparently he finally agreed that phosphorus as a plant nutrient was important in crop production. As early as 1845, Daubney, as cited by Kurtz (25), studied methods of extracting available phosphorus. Over a century later the task of finding the ideal extractant for plant available phosphorus still remains. As cited by Kurtz (25), Van Bremmelen studied adsorption of available phosphorus in 1888 and Dyer studied extracting available phosphorus in 1894.

Volcker, as cited by Wild (39), in 1863 showed that a sample of clay containing small percentages of calcium carbonate was active in phosphorus sorption. He concluded that this was due to formation of involuble compounds with hydrous oxides of iron and aluminum that were known to be present. A few years later Warington, as cited by Wild (39), reported that the soil with the greatest iron and aluminum content retained the greatest amount of phosphate.

The early 1900's marked the advent of soil phosphorus investigations in the United States. Schreiner and Failyer, as cited by Kurtz (25), reported on phosphorus and potassium fixation in soils. Fraps, Stoddart and Kind, as also cited by Kurtz (25), observed certain phosphorus reactions in soils by 1914. Fraps was among early workers to study the solubility of different phosphate minerals in nitric and sulphuric acids (25).

Burd and Martin in 1923 and Pierre and Parker, as cited by Kurtz (25), in 1927 showed that the concentration of phosphorus in water extract and in the soil solution were of the same relative magnitude and were of the order of less than one ppm (part per million).

In 1916 Alway and Rost (2), working with Nebraska soils, determined there was a steady decrease in total phosphorus from the surface downward. This decrease was independent of the aridity of the climate under which these soils were formed. These samples were taken from across the entire state.

Dean in 1937 (11) studied the distribution of the forms of soil phosphorus and concluded that phosphorus added to acid soils tends to accumulate in alkali soluble forms. Acid conditions give rise to iron and aluminum phosphates; these are the alkali soluble forms. He also concluded that phosphorus added to neutral or calcareous soils tends to accumulate in acid soluble but alkali insoluble forms. Davis (9) in 1943 attributed the retention of phosphate by soils largely to iron and aluminum contained in the soil. He also treated soil with iron and aluminum and found that phosphorus retained by aluminum treated soil was more easily soluble than that retained by the iron treated soil.

Lipps and Chesnin (28) reported that in the Brunizem and Chernozem soils the maximum amount of phosphorus was in the parent material. Above the parent material the phosphorus contents varied with different soils. They attributed the accumulation of acid soluble phosphorus in the surface horizon to redistribution by plants of the rhizosphere. The iron and aluminum phosphates occurred in small quantities. They further stated that the process of soil formation affects the distribution of acid soluble phosphorus and that profile development is accompanied by a decrease in acid soluble phosphorus. (The author presumes an increase in alkali soluble phosphorus since profile development is usually accompanied by increasingly acidic conditions.) Lipps and Chesnin also observed that Brunizem soils are more developed than the Chernozem or Chestnut soils, as indicated by the profile distribution of extractable phosphorus.

Allaway and Rhoades, (1) working on Nebraska soils, found that the percentage of phosphorus soluble in acid was greater in the surface layer of relatively unweathered soils than in surface layers of most highly developed soils. They found that only a small percentage of the phosphorus in the surface of a Keith soil could be dissolved by ammonium flouride. This seems logical. Since the Keith soil is not a highly weathered soil, the alkali soluble forms of phosphorus, which are more highly weathered forms, would be present in only small amounts as compared with the calcium phosphate content or the same forms in more highly weathered soils.

Godfrey and Riecken (17) showed the acid-soluble phosphorus, phosphorus soluble in nearly neutral solutions and alkali-soluble phosphorus to be a function of the position in the profile and to be further related to the degree of profile development. The phosphorus in the A horizon was low in content but approximately equal in acid and alkali media. The B horizon had a preponderance of alkali soluble phosphorus while the C horizon was very high in acid extractable phosphorus. All horizons were low in phosphorus extractable with neutral solutions. This study of Godfrey and Riecken showed that soil weathering tends to change inorganic calcium forms of phosphorus to iron and aluminum forms.

Bhangoo and Smith (4) working on Kansas soils, attempted to relate phosphorus fractions to available phosphorus. They found that the iron and aluminum phosphates were especially significant. Sub-soils where these two types of phosphorus represented two-thirds of the total present had much lower phosphorus availability than did the surface soils where only one-half of the phosphorus existed in these forms. On the other hand a surface soil with only one-third of its phosphorus combined with iron and aluminum had comparatively high availability of its native phosphorus. The quantity of adsorbed phosphorus displaceable by cold .1N HCl did not seem especially important in relation to plant availability.

Chang and Jackson (7), using their own fractionation procedure, determined the inorganic phosphorus amounts in several soils. Results showed the podzolic soils relatively high in iron and aluminum phosphate and low in calcium phosphate, while the reverse was true of soils formed under calcification. Johanessen (23) determined that there was more soil solution phosphate under trees than under grass when the other soil forming factors were kept constant. He explained that this is caused by the difference in phosphate turnover by the two plants. Deeper root penetration and longer growing season enable trees to bring up more phosphate and consequently produce more organic matter.

Cho and Caldwell (8) characterized the inorganic phosphates and found that iron and aluminum predominate in acid soils and the calcium phosphates in calcareous soils. Neutral soils have nearly equal quantities of the three main forms of inorganic phosphate. They used ammonium flouride to extract phosphorus from acid soils because the flouride ion seemed to replace adsorbed phosphorus. Sodium bicarbonate was used to extract phosphorus from the calcareous soils, the theory being that the bicarbonate ion reduces the activity of the calcium ion and thereby increases the solubility of phosphorus. These investigators further stated that the reaction of a soil was not necessarily a good indication of the forms of phosphorus present. Of three soils that had nearly the same pH, the inorganic phosphorus content was quite different.

Nye and Bertheux (30), working on forest soils of the Gold Coast region, found the total phosphorus greatest in the surface horizon and decreasing with depth. The acid soluble phosphorus was found to fall rapidly to a trace in one foot. These results were in contrast to those obtained by Pearson (cited by Nye and Foster (31)) who, working on twelve Iowa soils, determined the acid soluble phosphorus to be low in the lower A and upper B horizons with a marked increase with depth to a maximum in the C horizon. This was explained by greatly reduced weathering in temperate soils.

Fractionation of Soil Phosphorus

For more than a century there have been attempts to fractionate or determine the discrete forms of soil phosphorus and the amounts of these forms. In 1935, Fisher and Thomas (13) developed a rapid method of estimating four forms of inorganic phosphorus: phosphates of calcium, magnesium and manganese were one form; phosphates of iron and aluminum were another form; those adsorbed by hydrous oxides and present in the form of apatite were a third form; by difference they determined the phosphorus present in crystalline forms of iron and aluminum, this being the fourth form. By placing proper values on the phosphorus contained in each group they were able to place twenty-two Maryland soils, representing three provinces, seven series and twelve types in practically identical order of phosphorus requirements as that disclosed by pot tests.

According to Dean (10), Russell grouped phosphorus compounds occurring in soils into: inorganic phosphorus in neutral soils, hydroxy apatite, a calcium phosphate, inorganic phosphorus in acid soils, which were presumably combinations with iron and aluminum oxides and organic phosphorus compounds. Dean, using his own fractionation procedure, showed that, by extracting with sodium hydroxide prior to extracting with an acid, it is possible to divide the phosphorus compounds into three broad groups: organic compounds soluble in sodium hydroxide, inorganic compounds dissolved by extraction with the sodium hydroxide followed by an acid, and insoluble compounds. Dean suggested that sodium hydroxide removed iron and aluminum phosphate, mono- and di-calcium phosphate, and organic phosphate, and that sulphuric acid removed tri-calcium phosphate and apatite. He concluded that the acid soluble phosphorus remaining in the soil after extraction with sodium hydroxide occurred in the apatite form. He also concluded that the largest fraction of the total soil phosphorus was not dissolved by sodium hydroxide or acid extraction. He noted that this fraction was not increased with long continued use of phosphatic fertilizer at Rothamsted.

Ghani, as cited by Wright and Peech (41), modified Dean's procedure by using acetic acid to extract principally mono, di, and tri-calcium phosphates and those combined with iron and aluminum, and sulphuric acid to extract the apatites. Acetic acid was used in order to eliminate interference of soluble exchangeable calcium or magnesium. It was also shown that some phosphate brought into solution is readsorbed by the soil and then extracted with sodium hydroxide. However, this was considered a procedure that gave a good fractionation of the phosphorus compounds present.

Nye and Bertheux (30), working on soils of the Gold Coast, used Williams' fractionation, which is a rapid method and divides the phosphorus into three fractions. Total phosphorus was extracted with acetic acid; the alkali-soluble, inorganic and organic fractions were extracted with sodium hydroxide. The organic fraction was determined by subtracting the inorganic from the total. Using this method they determined that the total phosphorus was greatest in the surface and decreased with depth. The acid soluble phosphorus declined sharply to a mere trace in the surface foot, while the inorganic alkali soluble phosphorus declined more slowly than the acid soluble. Generally speaking, all horizons of all soils were higher in inorganic alkali soluble than in inorganic acid soluble phosphorus.

At the present time the generally accepted method of fractionation procedures is that devised by Chang and Jackson (6). This method is based on the solubility of the discrete forms of inorganic phosphorus in the soil. These forms include aluminum, iron and calcium phosphates as well as the reductant soluble forms, the occluded phosphates. This procedure was the first to differentiate between iron and aluminum phosphate. It employed neutral ammonium flouride to dissolve aluminum phosphate. Sodium hydroxide completely dissolves iron phosphate as well as aluminum phosphate but does not dissolve apatite. Sulphuric acid dissolves apatite completely and aluminum and iron phosphate to a considerable degree; therefore the alkali extractions must precede the acid extractions.

Glen *et al.* (21) modified the fractionation procedure of Chang and Jackson and used ammonium flouride at a pH of 8.5 rather than 7.0. This was the experimentally determined pH where the solubility of iron phosphate was least. This procedure has made possible a fairly accurate account of the inorganic phosphorus constituents of the soil.

Available Soil Phosphorus

Investigators in the field of available soil phosphorus have yet to devise a perfect system to determine plant-available fractions. The research here has followed two main paths: first to find the ideal extracting solution, one that would remove what the plant removes; second, to develop a leaching procedure that would extract the readily available phosphorus, thereby duplicating the pattern of phosphorus release.

Shapiro and Fried (35) reported that soil phosphorus may occur in organic form and as an anion adsorbed to a clay surface. It also may occur adsorbed on the surface of iron and aluminum hydroxides. It may occur as an anion adsorbed by means of a cation bridge to clay, and as precipitates of iron and aluminum. Phosphorus release from precipitated material is governed by solubility product relationships. Adsorbed phosphates are hydrolytically displaced (OH) or displaced by another anion.

Fried and Dean (14) reported that calcium in a system always effected greater retention of phosphate than did sodium. This is an argument in favor of the cation bridge theory. They also reported that surface coatings of iron and aluminum retained large proportions of added phosphorus and that the amount increased with phosphorus concentration.

pH of soils is probably the most widely operating factor influencing the form, abundance and movement of different nutrient elements in soils. Karim and Khan (24), working on East Pakistan soils, reported that sesquioxide-bound phosphorus rose steadily to a pH of 5.6 but that the rate of rise above 5.3 was greater than below 5.3. With an increase in pH to 6.2 the sesquioxide bound phosphorus decreased.

In 1954 Olsen _et al_. (33) reported that sodium bicarbonate was adaptable to rapid routine soil testing procedures. Four criteria of a useful extractant of plant-available phosphorus were postulated: (a) measure all or a definite proportion of the various forms of phosphorus in the same relative amounts as they are adsorbed by plants during the growing season; (b) correlate to a high degree with plant uptake of phosphorus and yield response to added phosphorus over a wide range of soil types; (c) minimize the secondary precipitation and adsorption reactions that may occur during extraction; and (d) be adaptable to rapid routine test measures.

This sodium bicarbonate method consistently gave a high correlation with 'A' values of Fried and Dean, as cited by Olsen _et al_. (33), for all groups of soils where other methods gave lower correlation values. It was compared with earlier methods, including the CO_2 technique and those of Bray and Truog.

The Bray No. 1 method gives low values for extractable phosphorus on highly calcareous soils because secondary precipitation reactions may occur with extractants that increase the hydrogen ion activity because concomitant increase in the calcium ion activity occurs. Increased calcium ion activity usually means more phosphorus fixed as insoluble calcium phosphate. Also the concentration of the acid is insufficient to extract all of the available phosphorus. The Bray No. 2 method increases the acid concentration to compensate for this.

Earlier, Truog (37) in 1930 used .002N sulphuric acid at a pH of 3 as an extracting solution. This concentration was supposed to approximate that in the root zone.

The CO_2 method is affected by two secondary reactions with opposite effects on phosphate solubility when used on calcareous soils. First, there is an increase in solubility caused by a decrease in pH, and secondly, a decrease in solubility when precipitation of calcium phosphate occurs as a result of the increase in calcium ion activity.

The sodium bicarbonate was found to be essentially free from secondary reactions because the bicarbonate ion decreases calcium ion activity by combining with it, thus increasing the solubility of phosphorus that was originally calcium phosphate. This is the common ion effect.

In neutral or acid soils sodium bicarbonate represses calcium ion activity also, but the main effect here is through ionic competition of the HCO_3, CO_3 and OH ions for the phosphate adsorption sites on the surface of the soil particles. According to Kurtz and others, cited by Olsen _et al_. (33), the replacing ability of the bicarbonate ion for phosphate on the soil colloid was greater than the replacing ability of the acetate and sulphate ions.

Miller and Axley (29) determined that extracting two grams of soil with an ammonium flouride-sulphuric acid solution gave the closest correlations with crop responses. The Bray and Kurtz number one and the sodium bicarbonate methods were next in order. They also found that the soil series determined to a large degree the correlation between chemically available phosphorus and crop response.

Saunders (34), working in Southern Rhodesia, used hot .1N sodium hydroxide for extracting available phosphorus from tropical soils. Good correlations were obtained between analytical data and field responses for a variety of soils. Correlations were also obtained between sodium hydroxide soluble phosphates and the optimum application of fertilizer and phosphate required for maize, tobacco and potatoes. This provided the basis for fertilizer recommendations in Southern Rhodesia.

Welch _et_ _al_. (38) compared a hydrochloric acid-sulphuric acid mixture with sodium bicarbonate and with an ammonium flouride-hydrochloric acid mixture and obtained satisfactory results for making fertilizer phosphorus recommendations. Stelly and Recaud (36) reported that an extracting solution of ammonium chloride and hydrochloric acid proved a superior correlation with greenhouse response.

Aslyng as cited in LeMare (27), has shown the chemical potential of monocalcium phosphate in soil or "phosphate potential" expressed by ($\frac{1}{2}$ p Ca + pH_2PO_4) holds promise for temperate soils. LeMare (27) claims this is also an appropriate means of estimating available phosphorus in tropical soils. Nye and Foster (31) reported that a fraction of soil phosphorus exists in a labile pool which will maintain a definite equilibrium potential in the soil solution and that this labile pool is equivalent to the rapidly exchangeable phosphorus.

In an effort to learn more of the available phosphorus supply, a few investigators have attempted successive leaching procedures. Lathwell et al. (26) modified a soil percolator devised by Lees to measure the release of phosphorus by soils. This method employed .005N calcium chloride as a leaching solution. This concentration approximates the electrolytic concentration of the soil solution in most humid regions. This method recycled a small volume of solution through the soil and then through a chloride saturated anion exchange resin. Thus the phosphorus released by the soil was adsorbed by the resin. The resin was then leached with sodium chloride solution and the phosphorus determined. This method was used to compare fertilized and unfertilized soils. This technique reflected the influence of fertilizer treatments on the phosphorus status of these soils. An anion equilibration method was also tried where distilled water and the calcium chloride solution were compared. The water extracted more phosphorus than the solution. Lehr and Van Wesemael as cited by Lathwell et al. (26), showed that the solubility of phosphorus is depressed in the presence of a neutral salt because salts of monovalent cations depress phosphate availability in calcareous soils through an increase in the solubility of calcium.

It may, of course, be argued that water gives a more valid phosphorus measure since the electrolytic concentration of the soil solution will probably be approximated by the time the water has leached through the soil sample. The solution that is approximately equal to the soil solution in electrolytic concentration prior to leaching will be of higher concentration as the leaching proceeds; hence the added electrolyte could increase the depression effect.

Lathwell as cited by LeMare (27), compared his method with the results from Bray, Peech, English, and Fried and Dean. Lathwell's percolation method was highly correlated with 'A' values of Fried and Dean and was also correlated highly with the other methods. Thus the percolation method should provide a reliable technique for evaluating the phosphorus fertility status of widely different soils.

Fried and Shapiro (15) obtained identical results from a continuous leaching procedure and an hourly equilibration with distilled water. They thus were able to plot the phosphorus release pattern of various soils.

In more recent works Friend and Birch (16), working on soils in East Africa, found that out of ten different methods of extracting available phosphorus only hot .1N sodium hydroxide was significantly related to phosphorus response of wheat. Rost, as cited by Hamilton and Lessard (18), found that the lower A and upper B horizons were more deficient in phosphorus than the surface soil. Halstead, as also cited by Hamilton and Lessard (18), found that for most soils the phosphorus supplying power of the surface was considerably greater than the corresponding sub-surface.

MATERIALS AND METHODS

Description of Soils

The four soils used in this study were Moody, Kranzburg, Morton and Keith. These soils were chosen because they represent major croplands from widely separated areas of the state; hence phosphorus content was of utmost importance.

MOODY SILT LOAM

Date: November 21, 1960
Field Name: Moody Silt Loam
Field Classification: Chernozem
Location: Union County
Parent Material: Post-Iowan Loess
Physiography: Near crest of a long slope in gently undulating topography
Relief: Gently undulating
Slope: Convex, approximately 3%
Drainage: Well drained.

A_{1p} horizon 0-6"	Dark grayish brown (10YR4/2 dry) to very dark brown (10YR2/2, moist) noncalcareous silt loam, weak to moderately developed fine granular structure, friable when moist.
B_2 horizon 6-36"	Yellowish brown (10YR5/4 dry) to brown to dark brown (10YR4/3, moist) noncalcareous silt loam, moderately developed prismatic structure, friable when moist.

KRANZBURG SILT LOAM

Date: November 23, 1960
Field Name: Kranzburg Silt Loam
Field Classification: Chernozem
Location: Codington County
Parent Material: Post Tazewell Loess
Physiography: Midway between the crest and valley of a long slope in gently undulating topography.
Relief: Gently undulating
Slope: Convex, approximately 3%
Drainage: Well drained

A_{1p} horizon 0-7"	Very dark gray (10YR3/1 dry) to black (10YR2/1, moist) noncalcareous silt loam, weak fine granules, friable when moist.
B_2 horizon 7-18"	Very dark gray (10YR3/1 dry) to black (10YR2/1, moist) noncalcareous silty clay loam, weak to moderately developed prisms, friable when moist.

MORTON SILT LOAM

Date: November 22, 1960
Field Name: Morton Silt Loam
Field Classification: Chestnut
Location: Ziebach County
Parent Material: Ludlow-Cannonball silts
Physiography: Midway between the crest and valley of a long slope on a very gently undulating landscape.
Relief: Gently undulating
Slope: Convex, approximately 3%
Drainage: Well drained.

A_{1p} horizon 0-4"	Dark grayish brown (10YR4/2, dry) to (10YR2/2, moist) noncalcareous, silt loam, weak fine plates, hard when dry.
B_2 horizon 4-20"	Brown to dark brown (10YR4/3, dry) to dark brown (10YR3/3, moist), noncalcareous silty clay loams, moderately developed prisms, hard when dry.

KEITH SILT LOAM

Date: November 22, 1960
Field Name: Keith Silt Loam
Field Classification: Chestnut
Location: Shannon County
Parent Material: Calcareous loess
Physiography: Along the crest of a small ridge in a gently undulating landscape.
Relief: Undulating to rolling
Slope: Convex, nearly level
Drainage: Well drained

A_{1p} horizon 0-4"	Grayish brown (10YR5/2, dry) to very dark brown (10YR2/2, moist) noncalcareous silt loam, weak fine granules, friable when dry.
B_2 horizon 4-20"	Brown (10YR5/3, dry) to very dark grayish brown (10YR3/2, moist), calcareous silty clay loam, moderate prisms, breaking to fine prisms and blocks, friable when dry.

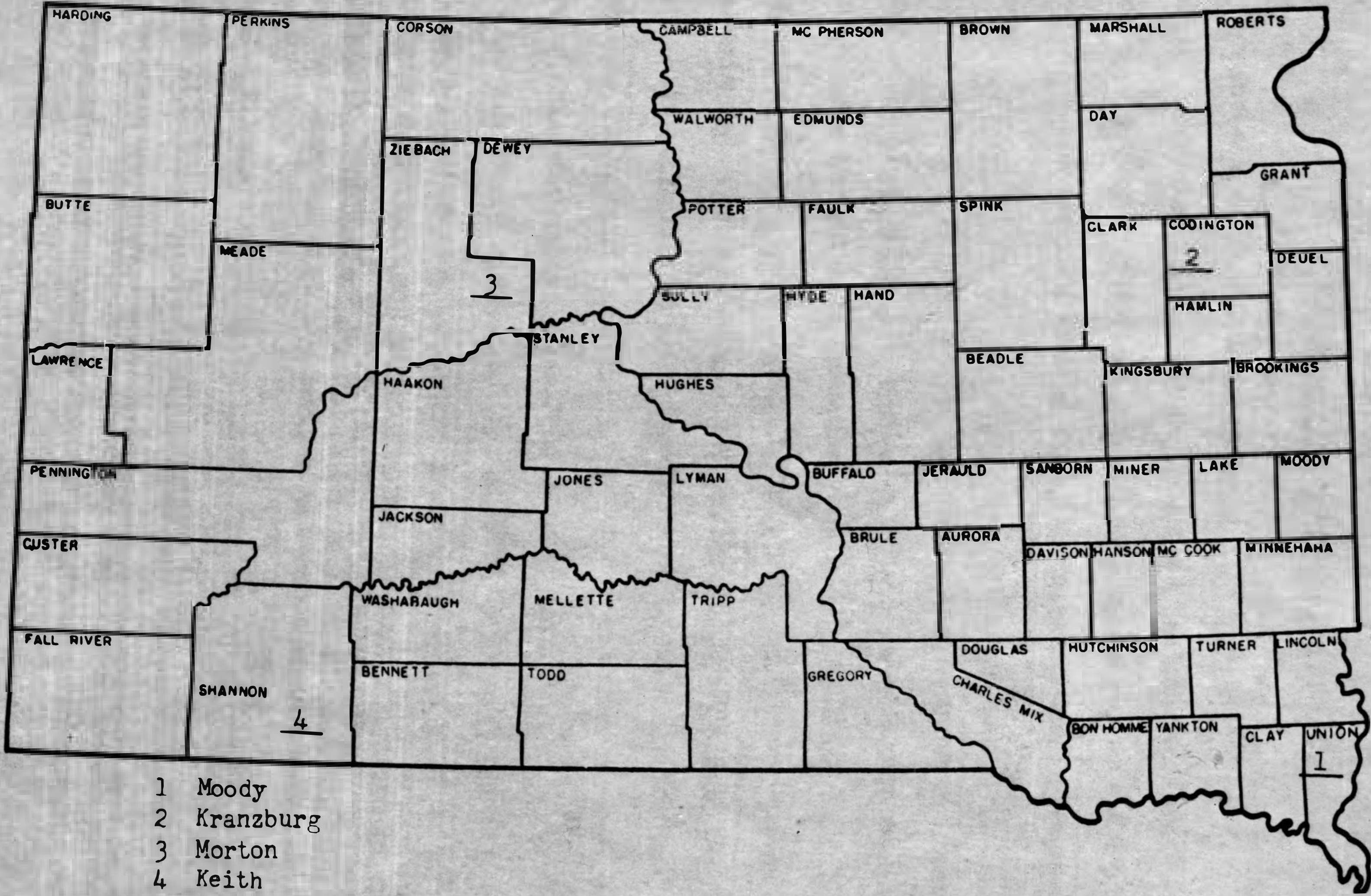
Sampling Procedure

The soil samples were taken the third week in November of 1960. The soil sampling procedure was uniform for all four sites. Three holes were dug in each series sampled; holes ranged from fifty feet to one hundred yards apart and were dug at random. A hole was dug, a slice removed and care taken to have the entire horizon sampled. The samples were placed in polyethylene bags which were placed in paper sacks, sealed and marked. The A and B horizons were sampled, the differentiation between the two being based on color and structure.

The identity of the individual polyethylene bag was maintained right into the laboratory. Chemical studies of each of the forty-eight major samples involved duplicate analysis of each of the three component field samples. Thus each phosphate value in the figures and in Table II is an average of six individual determinations.

The virgin samples were taken as close to the cropland samples as possible and were taken from as nearly similar topographic positions as possible. The profile descriptions compared very favorably. In the case of the Moody the distance was approximately one-fourth mile, while in the case of the Kranzburg the distance was one-half mile. It is not absolutely certain that the Kranzburg virgin sample was a virgin sample. Local inquiry stated that the Kranzburg site had not been plowed or cropped since 1900, if ever; the flora indicated the latter to be the case. The Morton was sampled on opposite sides of a road, and the fields from which the Keith was sampled were separated by a fence. The soil samples were air dried, ground to pass a 35 mm sieve and were stored in the laboratory in ice cream containers.

Figure 1 on the following page shows the location of the sampling sites.



1 Moody
2 Kranzburg
3 Morton
4 Keith

Figure 1. Locations of the sampling sites.

Fractionation Studies

Inorganic phosphates in soil can be classified into four main groups: aluminum phosphate, iron phosphate, calcium phosphates and reductant soluble phosphates or occluded phosphates. The occluded phosphates are highly weathered forms and were not considered in this study.

The Chang and Jackson (6) method of phosphorus fractionation as modified by Glen _et_ _al_. (21) was used in this study. This procedure employs ammonium chloride, ammonium flouride, sodium hydroxide and sulphuric acid to remove available phosphorus, aluminum phosphate, iron phosphate and calcium phosphate respectively. The original paper suggests a ten percent correction factor to be subtracted from the aluminum phosphate and added to the iron phosphate. The author is not certain whether this correction is still applicable after the pH adjustment of the ammonium flouride solution as suggested by Glen _et_ _al_. (21); consequently the ten percent correction factor was not applied in this study.

Preliminary Experiments

Since the amount of various forms of phosphorus is a function of the soil reaction, Table I is included to denote the pH of the soils used.

Table I. The pH by Horizons of each Soil Sample

Soil	A horizon cropped	A horizon virgin	B horizon cropped	B horizon virgin
Moody	5.4	6.2	6.3	7.0
Kranzburg	5.6	6.3	6.2	6.2
Morton	6.0	6.0	6.0	6.3
Keith	7.0	6.4	7.1	6.9

Before proceeding with the fractionation on all soil samples it seemed desirable to run the complete procedure on the same soil sample as directed and to compare the results with those obtained when each extractant was used on a different soil sample. The A horizon of the cropped Kranzburg soil was used. The results of this experiment are presented in Figure 2 on the following page.

Each discrete form of phosphorus was slightly higher in the sample where only the one form was determined as compared with the consecutive fractionation on the same one gram sample. In the case of the aluminum phosphate, equal amounts were obtained from both samples. This is the first measured extraction of the procedure. The iron phosphate extractions varied 1 ppm, from 40 ppm to 39 ppm for the single extractions respectively. The calcium phosphate varied from 176 ppm to 145 ppm, or a difference of 31 ppm in the same manner.

In the directions for the fractionation procedure the initial extracting solution of neutral ammonium chloride was discarded. This step was designed to remove the plant-available phosphorus. It was thought desirable to test for phosphorus in this solution. Both the

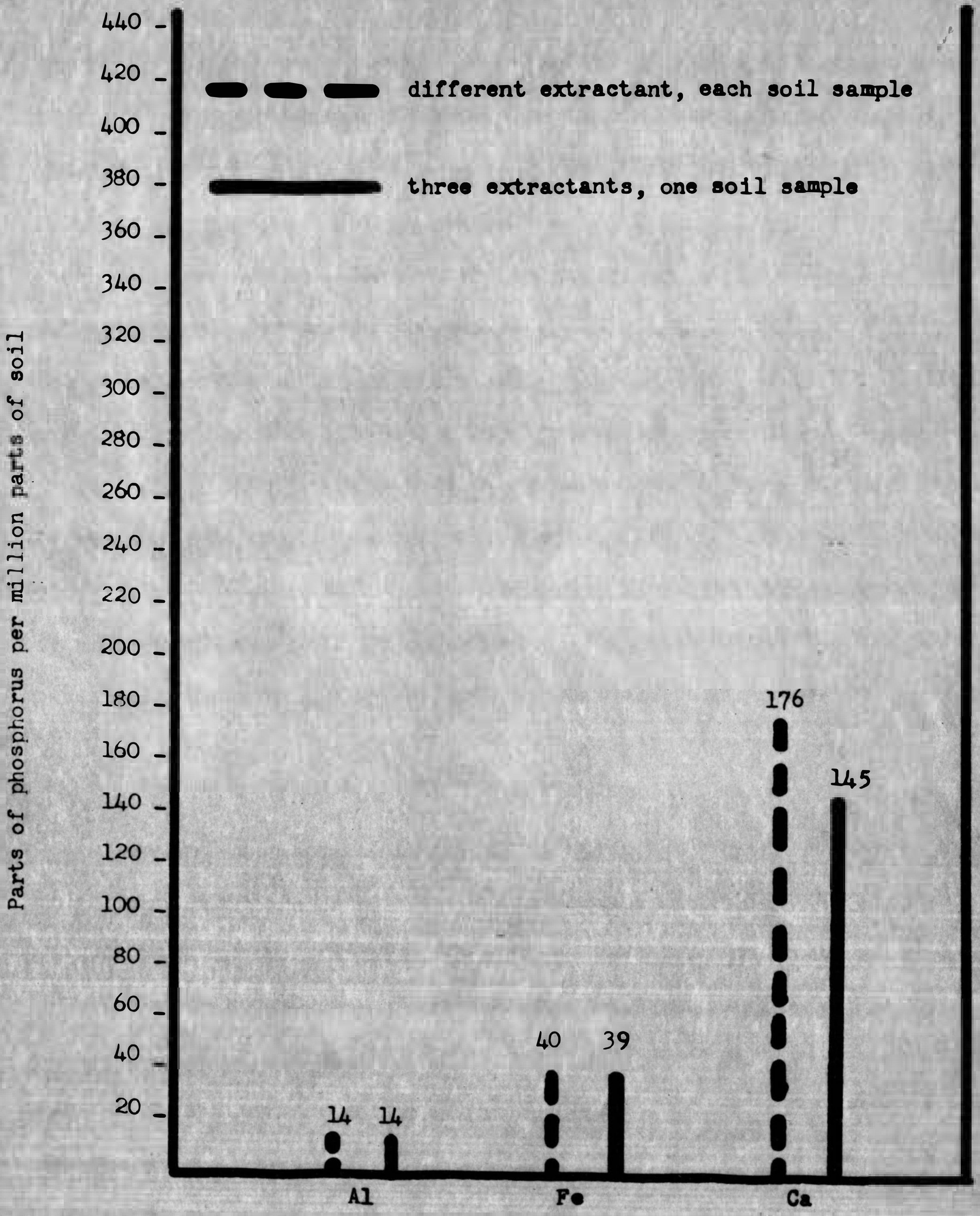


Figure 2. A comparison of phosphorus removed by three extractants on one soil sample and a different soil sample for each extractant.

hydrochloric acid and sulphuric acid systems of color development were used on extract from several soils. At best only a trace of phosphorus was detected; therefore no measurement of phosphorus in this solution is presented in this study.

Another question that arose was the pH of the ammonium flouride extracting solution at the time of phosphorus determination in the extractant. The text, "Soil Chemical Analysis" (22), and the directions for the fractionation procedure, both by Jackson, differed on this point. Again the Kranzburg soil was used and six samples were extracted. On three of the samples the pH was adjusted to 3 with 2N H_2SO_4 prior to phosphorus determination. In the remaining three the phosphorus was determined without prior pH adjustment. The colorimeter readings were practically identical so pH adjustment was deemed unnecessary.

Leaching Studies

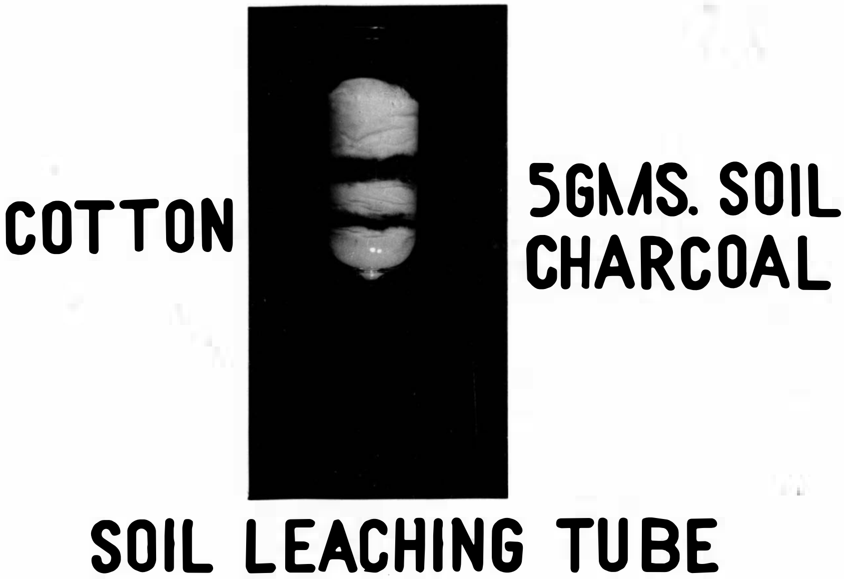
To aid in characterization of the phosphorus content of a soil it is necessary to know both the available phosphorus and the time distribution of its release. The method used was a modification of a successive leaching procedure devised by Fried and Shapiro (15). The method consisted of leaching a five gram sample of soil with a constant head of distilled water, removing successive aliquots and determining the phosphorus in each aliquot.

Preliminary Experiments

Organic matter in the leachate interferred with colorimetric phosphorus determination. Clarification by acid flocculation and centrifugation proved unsuccessful, but filtering the solution with charcoal was effective. However, leaching the soil and filtering the solution proved to be a very time-consuming procedure and so a soil leaching tube was designed that did both in one operation. This tube consisted of a carbon filter tube in which were placed three wads of cotton, one layer of charcoal and one layer of soil in the following sequence: first, a wad of cotton pressed into the bottom of the tube followed by a layer of charcoal, not to exceed one-fourth gram and spread uniformly over the wad of cotton; the charcoal filter was followed by another wad of cotton on which the five gram sample of soil was uniformly spread; this was covered by a third wad of cotton. Figure 3 illustrates the device, along with the apparatus that was built to accomodate six soil leaching tubes operated simultaneously.

There may be some question about using charcoal as a filter because Beaton and Peterson (3) in 1960 reported that charcoal adsorbed phosphorus. To determine the effect of adsorption by charcoal a standard phosphorus solution was leached through a filter after which aliquots of the original solution were compared with aliquots of the leachate. With the instrument that was used no difference in phosphorus concentration was detectable. Bhangoo and Smith (4) also used activated charcoal to remove organic matter coloring when determining available phosphorus.

Fried and Shapiro (15) leached the soil with a constant head of water at the rate of eighty ml per hour and removed forty ml at a time from which an aliquot was taken and the phosphorus determined. This



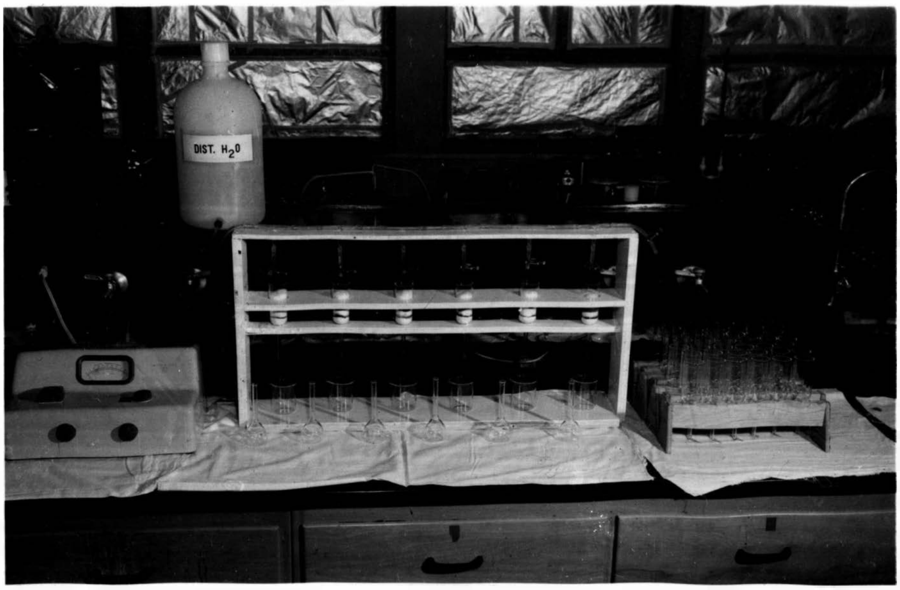


Figure 3. Soil leaching tube and apparatus used in leaching experiments.

was repeated as many as fourteen times and the results plotted on a graph, thus determining the phosphate release pattern of the soil. Once they had completed the initial set of leachings they concluded the experiment.

In the experiment described here an attempt was made to determine the phosphate release pattern of these soils by leaching, incubation, leaching, incubation etc. till the soil had been leached twenty-five times. To determine length and temperature of incubation periods, a set of soil leaching tubes was set up, using the same soil in all tubes. The soils were then leached until 10 forty-ml increments had been leached through the soil. Duplicate tubes were then incubated at room temperature and at 43° C. for periods of six, twelve, eighteen, twenty-four, forty-eight and seventy-two hours. One set of two was allowed to stand at room temperature for several days. It was found that the maximum amount of phosphorus was released after only six hours of incubation at 43° C. Since longer periods of incubation failed to produce any more phosphorus, it was assumed that the equilibrium was reached in this length of time. At room temperature several days were required to reach the same equilibrium.

The soil leaching procedure which was carried out consisted of leaching the soils with a constant head of water at the rate of one drop every two seconds. Forty ml were allowed to pass through, out of which a twenty-five ml aliquot was taken and the rest discarded. In the initial leaching, prior to the first incubation, this was done ten times. The soil was leached five times between incubation periods.

Frequently a complete set of ten or five leachings was not done because in many cases before this point was reached the phosphorus concentration of the leachate was insignificant. When the light transmission in the colorimeter was above 95 percent, it was considered unnecessary to leach the soil any further. Hence, ten times and five times were the maximum number of times the soils were leached.

The sulphuric acid system was used to develop the color in the phosphorus solution. Chang and Jackson (6) used this method in both the acid and alkaline pH ranges. Adjustment of the aliquot to a pH of 3 was found to be unnecessary. Readings were made on a Bausch and Lomb Colorimeter at 660 mu.

EXPERIMENTAL RESULTS

Results of the Fractionation Studies

In this experiment four variables were involved: first, the soil series; second, the cropped versus virgin soil; third, the soil horizon, A versus B; and fourth, the form of phosphorus.

Figure 4 illustrates the amount of phosphorus of each form in the A horizon of each of the cropped soil series. Thus for the Moody, the aluminum phosphate equals 18 ppm, the iron phosphate 47 ppm and the calcium phosphate 102 ppm. The same relationship applies for the Kranzburg, Morton and Keith series. In all soils except the Keith the aluminum phosphate content was the lowest, and in all soils the calcium phosphate far exceeded the other two forms. In the Keith the iron phosphate was the least. These results agree with Alloway and Rhoades (1), who found the acid soluble phosphorus was greater in abundance in the surface horizons of the relatively unweathered soils as compared with the weathered soils. They also concluded that only a small percentage of phosphorus in the surface of the Keith soil series was soluble in ammonium flouride. This was true on all soils in this study, but the Keith had a greater abundance of ammonium flouride soluble phosphorus than did the other three.

Figure 5 compares the forms of phosphorus in the B horizons of these same soils. Here the aluminum phosphate was the form in least supply in all cases while the calcium phosphate was greatest, exceeding that in the A horizon in every case except the Keith. In the extreme

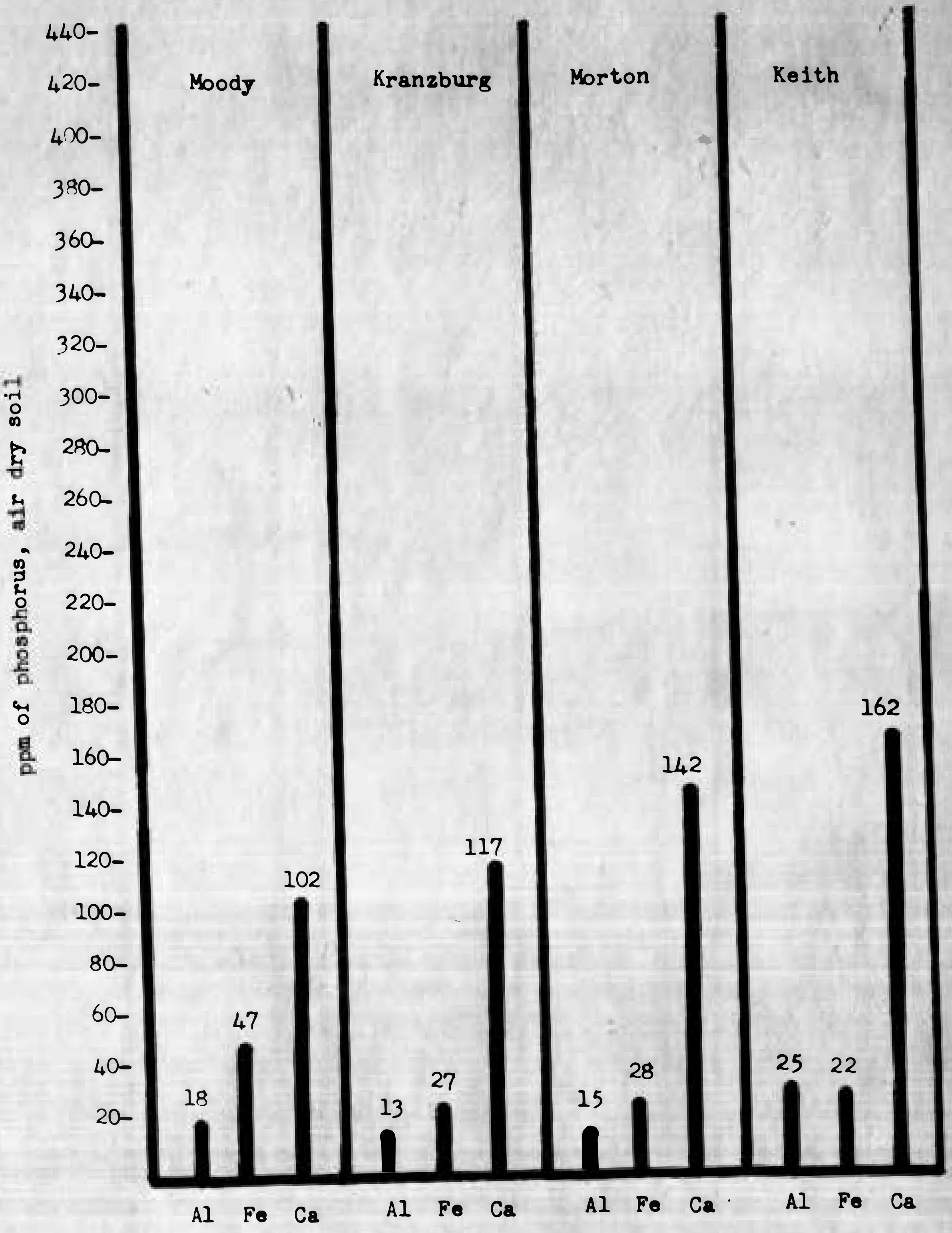


Figure 4. Aluminum, iron and calcium phosphates extracted from the A horizons of four cropped soils.

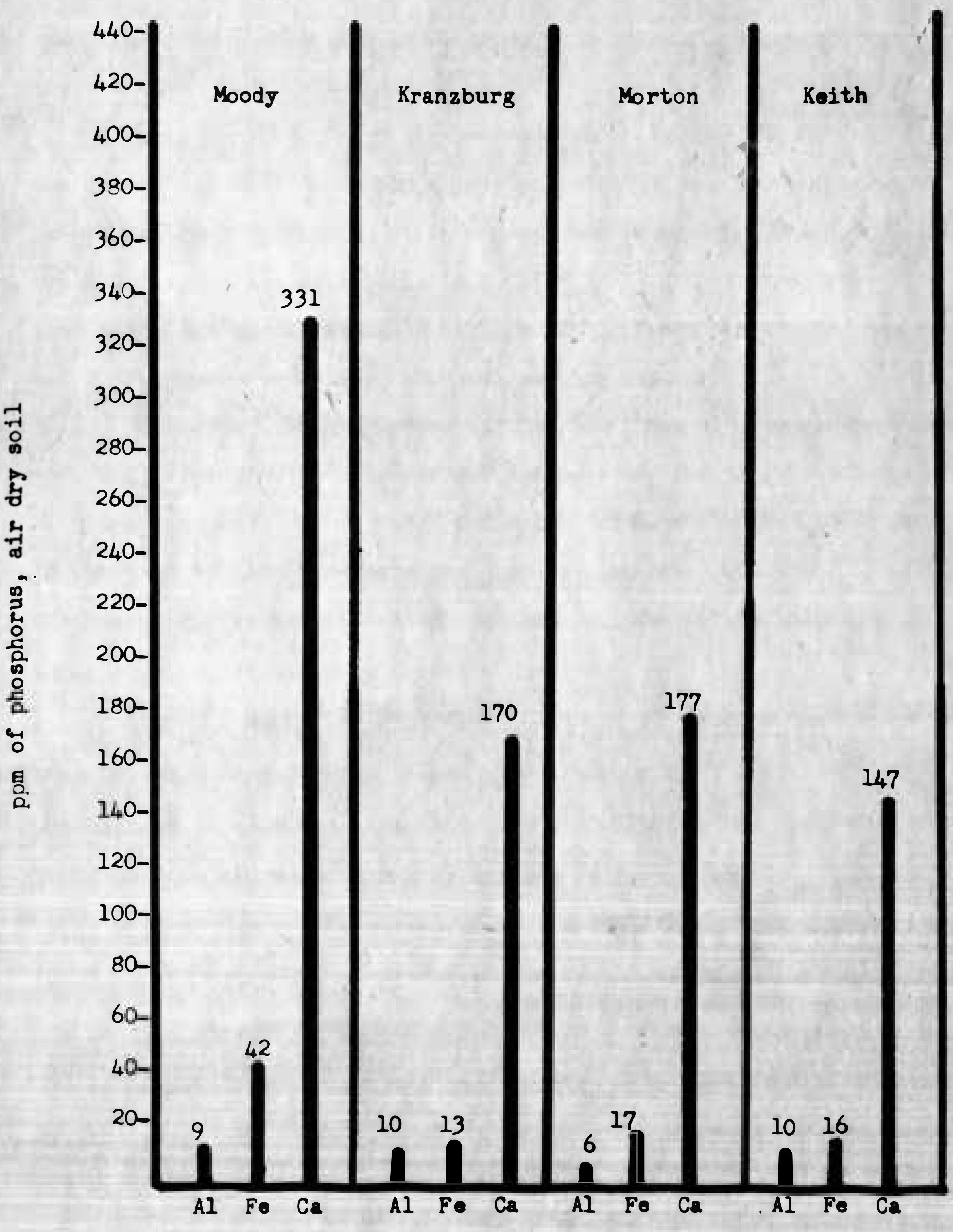


Figure 5. Aluminum, iron and calcium phosphates extracted from the B horizons of four cropped soils.

case, the Moody series had three times more calcium phosphate content in the B horizon than in the A.

These results are in disagreement with Godfrey and Reicken (17), who determined that there was a preponderance of alkali soluble phosphorus in the B horizon in soils of Iowa and Missouri. Chang and Jackson (7) found the calcareous soils to be high in calcium phosphate. In this study the noncalcareous B horizon of the Moody series was the highest in calcium phosphate of all soil samples measured.

In Figure 6 the A horizon results are grouped by compound rather than soil type for the four cropped soils. The Kranzburg was lowest in aluminum phosphate with 13 ppm, while the Keith was high with 25 ppm. In the case of iron phosphate the Moody series was high while the Keith was low. With respect to calcium phosphate, the amount increased in the order of Moody, Kranzburg, Morton and Keith.

Figure 7 compares the various forms of phosphorus in the B horizons of these same cropped soils. The Kranzburg and Keith were equal and highest in aluminum phosphate, while the Morton had the least amount. The eastern soils were both high and low in iron phosphate, the Moody being highest and the Kranzburg lowest in this form. The western South Dakota soils were very nearly equal. Calcium phosphate was highest in the Moody.

Figure 8 compares the A and B horizon for each form of phosphorus of all soils. In every case the aluminum and iron phosphate content was higher in the A horizon than in the B.

Included in this investigation were parallel virgin samples of the soils already discussed. The Moody and Keith samples were taken

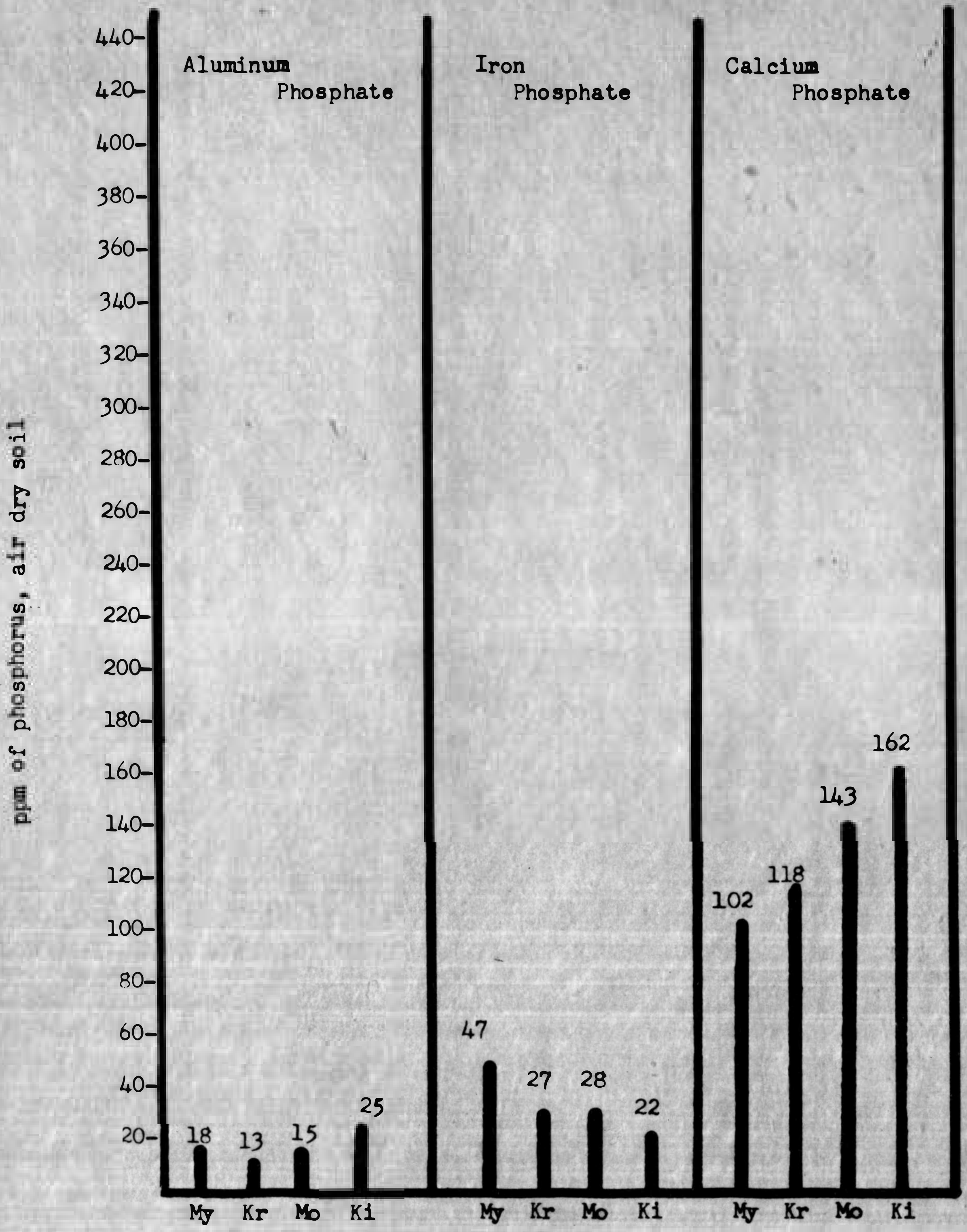


Figure 6. A comparison of the A horizons of the cropped soils with respect to each form of phosphorus.

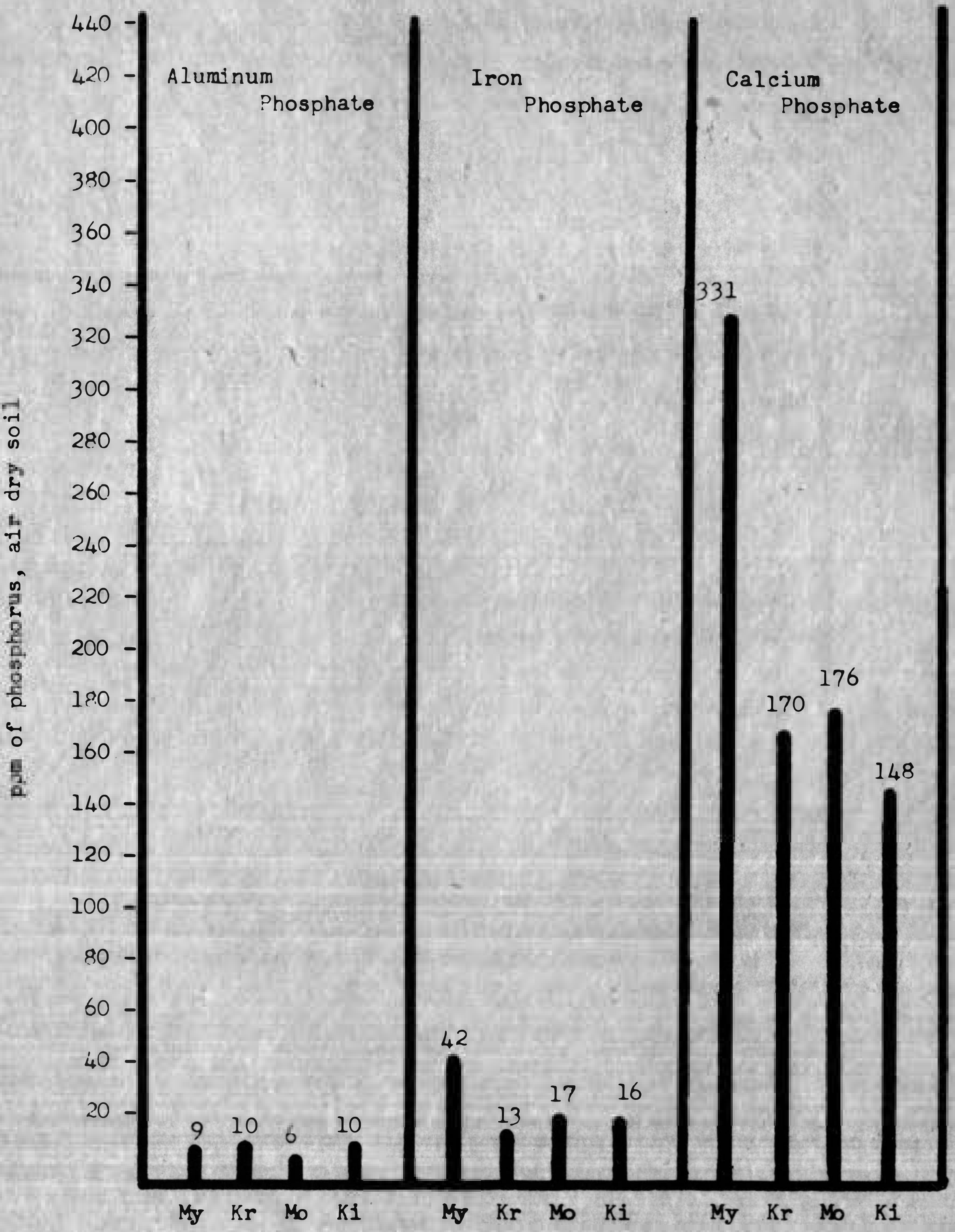


Figure 7. A comparison of the B horizons of the cropped soils with respect to each form of phosphorus.

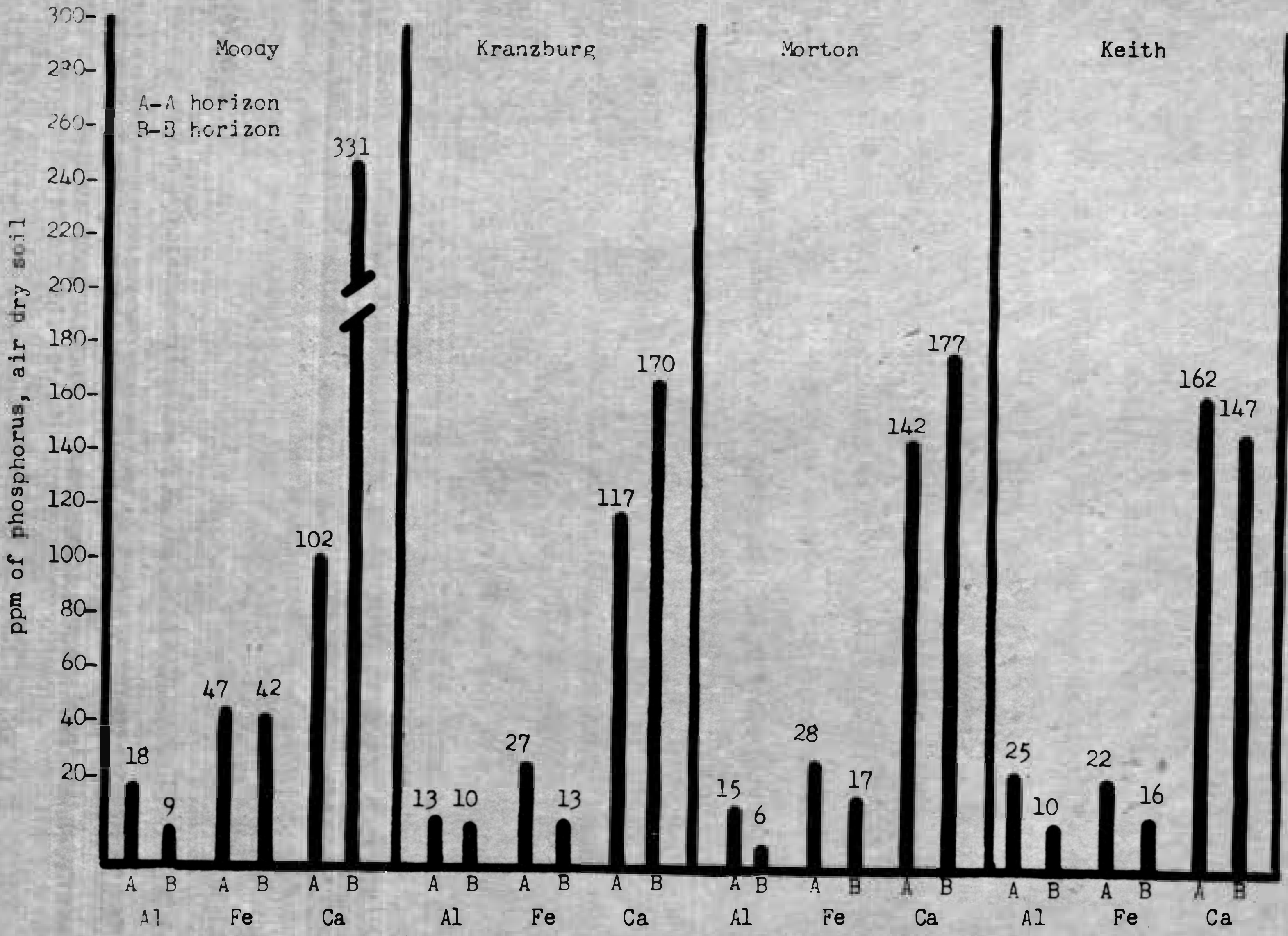


Figure 8. The A and B horizons of four cropped soils compared with respect to each form of phosphorus.

from pastures; the Morton and Kranzburg were taken from haylands. It was intended to compare the cropped and virgin samples to see what cropping has done to the various phosphorus fractions in the soil.

Figures 9 to 13 depict the same information for the virgin samples as those just reviewed gave for the cropped samples.

Figure 9 compares the various forms of phosphorus in the A horizon of each soil. On these virgin soils the aluminum and iron phosphate contents were quite uniform both with each soil and among soils. The calcium phosphates, of course, far exceeded the other forms.

Figure 10 shows the same relationships for the B horizons of the virgin soils. The aluminum phosphate was again the form least in abundance, the iron phosphate content was a little higher, and the calcium phosphate again far exceeded the other forms. The Moody sample was again extremely high in calcium phosphate.

Figure 11 depicts the supply of each form of phosphorus for the virgin samples of the A horizons of all four soils. There is no consistent pattern exhibited. The Moody is lowest in aluminum phosphate, the Kranzburg is highest; the Moody is low in iron phosphate, the Morton is highest; the Kranzburg is lowest in calcium phosphate while the Keith is highest.

Figure 12 illustrates the same relationships for the B horizons of the virgin samples. Aluminum phosphate was low in the Moody series and high in the Keith, iron phosphate was lowest in the Moody and highest in the Morton series, and calcium phosphate was highest in the Moody series and nearly equal in the remaining three representatives.

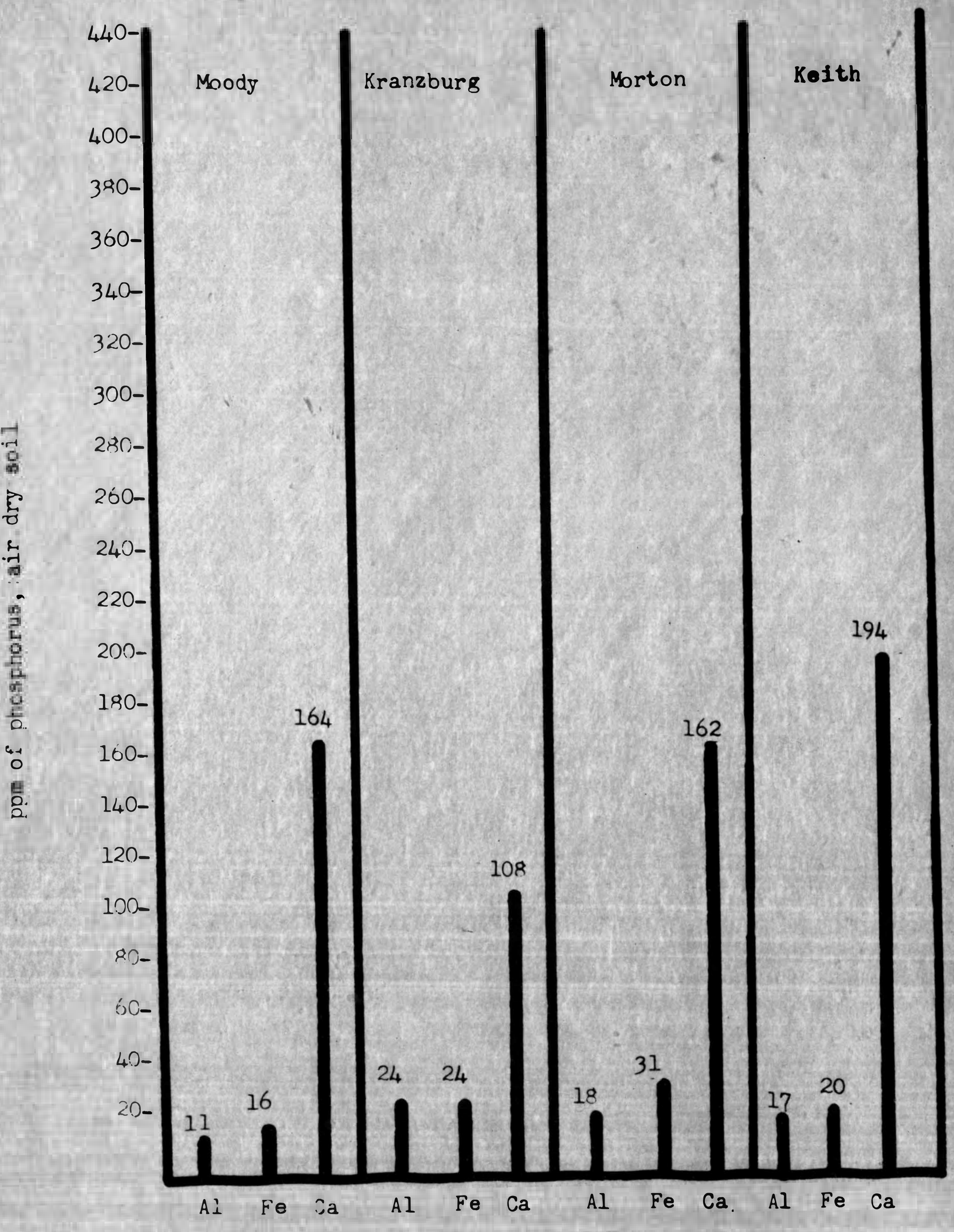


Figure 9. Aluminum, iron and calcium phosphates extracted from the A horizons of four virgin soils.

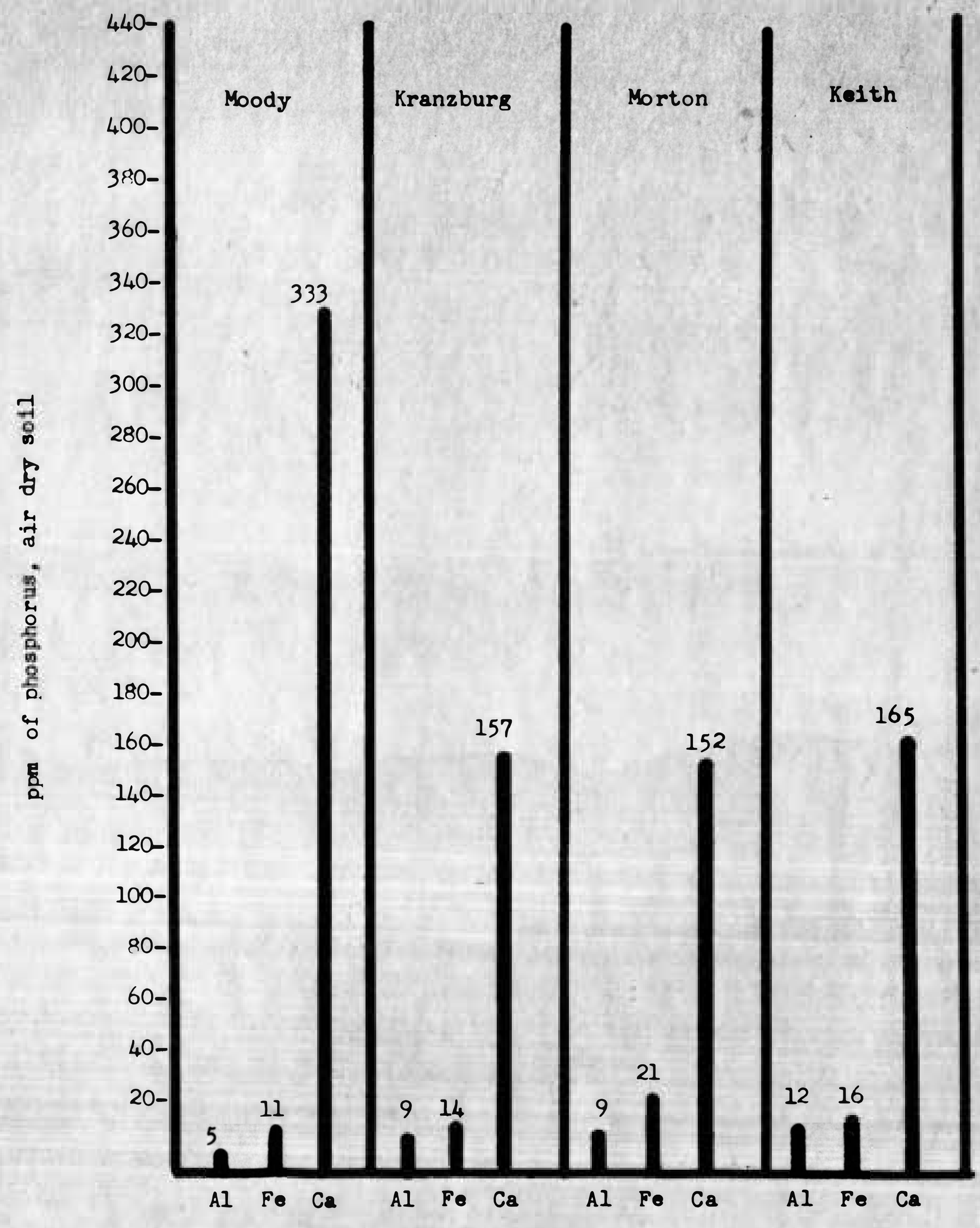


Figure 10. Aluminum, iron and calcium phosphates extracted from the B horizons of four virgin soils.

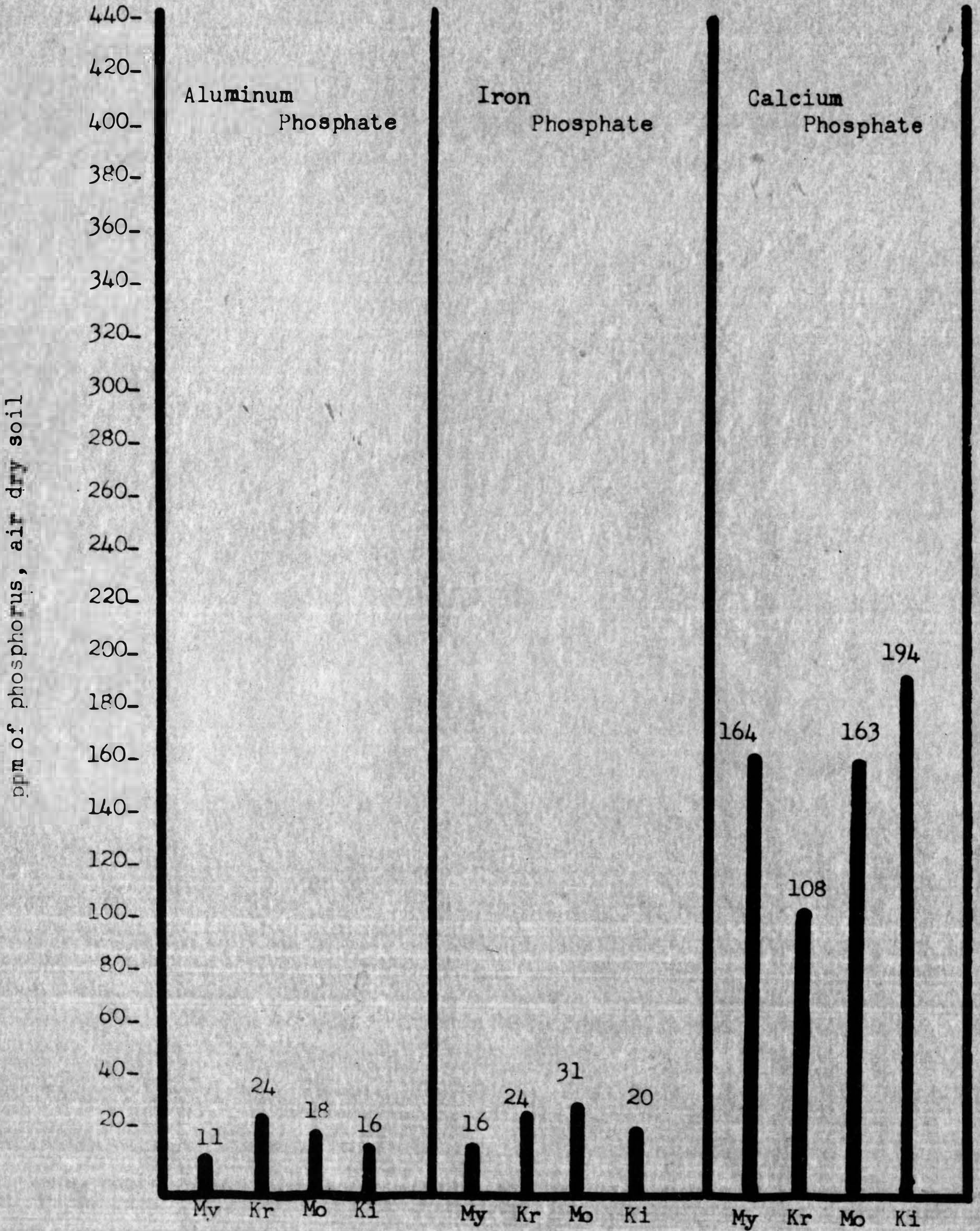


Figure 11. A comparison of the A horizons of the virgin soils with respect to each form of phosphorus.

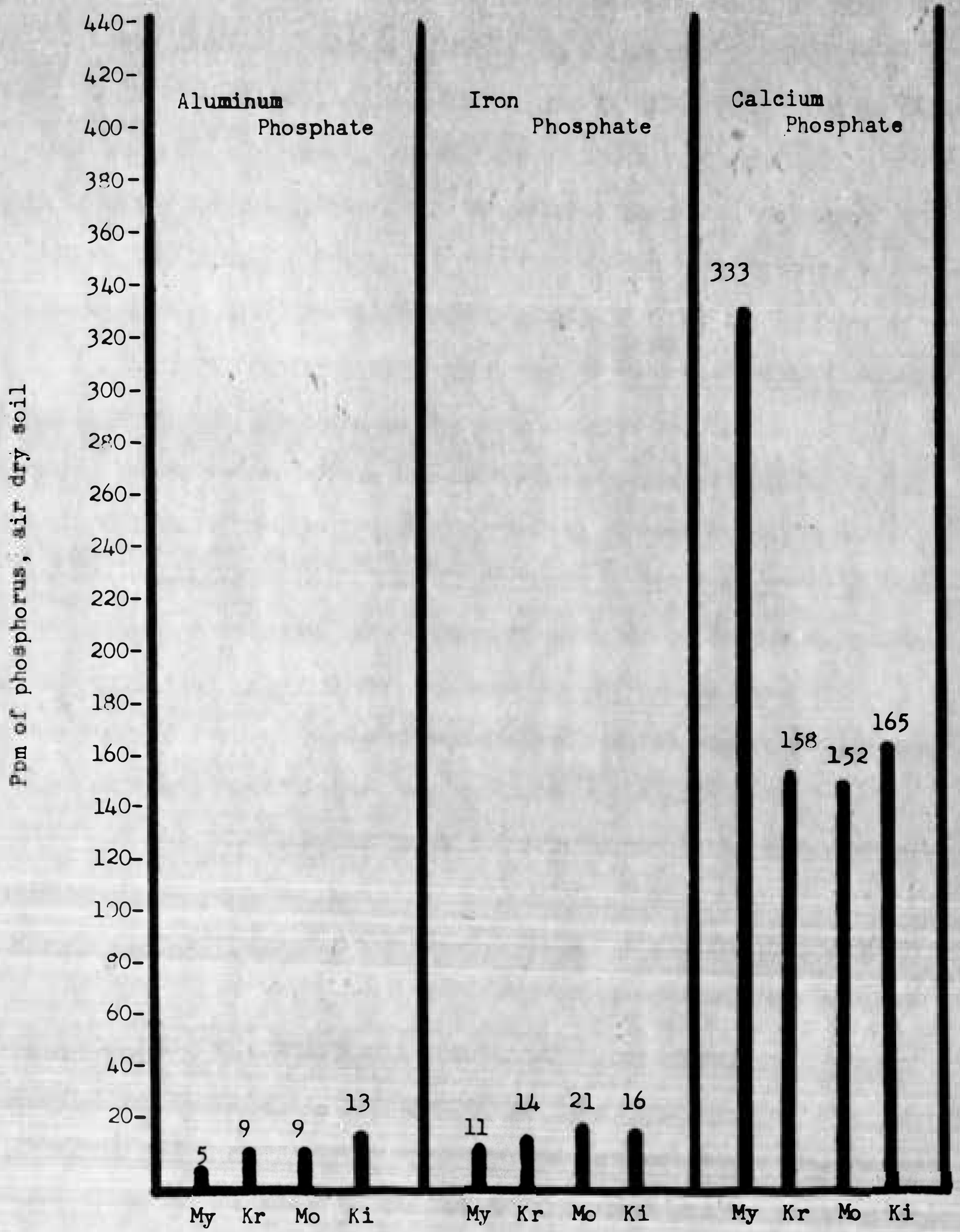


Figure 12. A comparison of the B horizons of the virgin soils with respect to each form of phosphorus.

The phosphate content of the A and B horizons is compared in Figure 13. The aluminum phosphate was low in all cases; the iron phosphate was little higher; the A horizon of the virgin Kranzburg was equal in aluminum and iron phosphate. The calcium phosphate content of the eastern soils was greater in the B horizons, but the situation was reversed in the soils of western South Dakota.

Figure 14 compares the cropped and virgin samples with respect to all forms of phosphorus in the A horizons of all soils. In two soils, the Moody and Keith, the aluminum phosphate was higher in the cropped samples than in the virgin samples. In the remaining two samples the opposite was true. In the case of the iron phosphate the cropped samples were higher in three of the four soils, while the opposite was true in the Morton although the difference was slight. In three out of four cases the virgin samples had the higher calcium phosphate content; the situation was reversed in the Kranzburg.

In the B horizons the eastern South Dakota soils that have been cropped have a greater amount of aluminum phosphate as compared with the virgin samples; in the western South Dakota soils the virgin soils have a greater amount. The cropped sample of Moody has considerably more iron phosphate than its virgin counterpart; the cropped and virgin samples of Kranzburg are nearly equal in this respect; the virgin sample of Morton has a small amount more than the cropped sample while the Keith samples were equal in this respect. Turning to the calcium phosphate, the Moody samples were very nearly equal, the cropped samples were a little more abundant in the Kranzburg and Morton, and the virgin

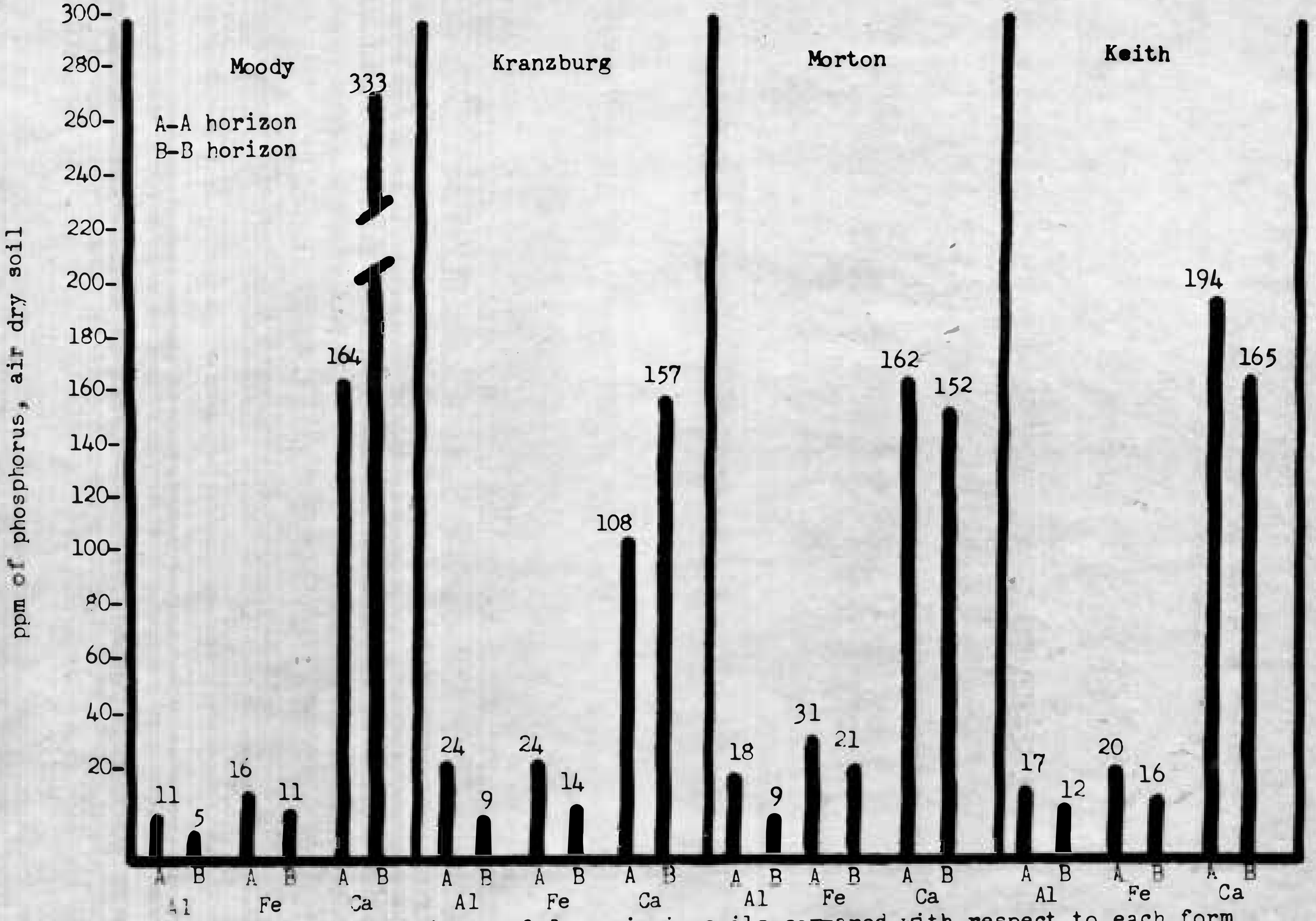


Figure 13. The A and B horizons of four virgin soils compared with respect to each form of phosphorus.

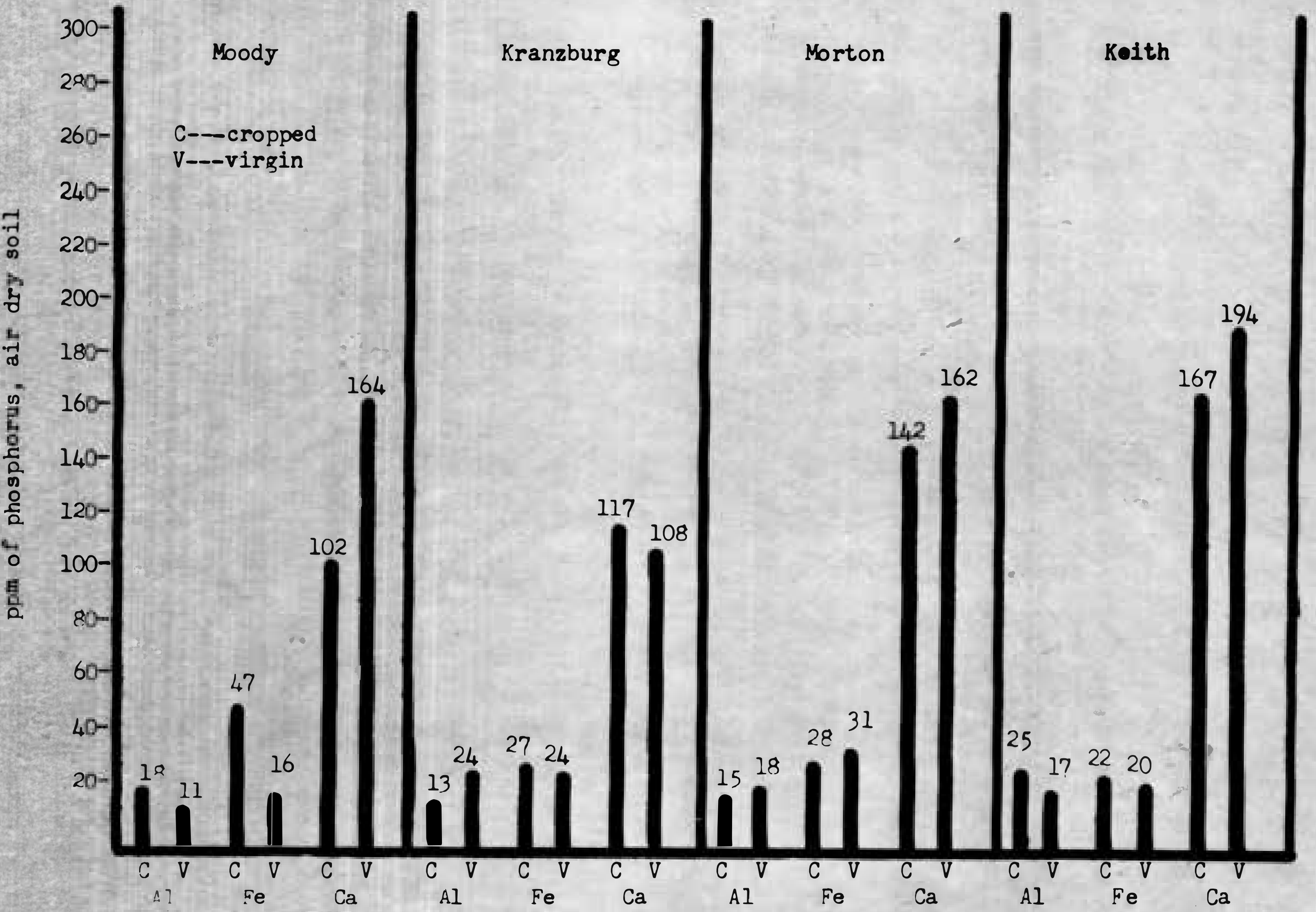


Figure 14. A comparison of the cropped and virgin soils for all forms of phosphorus, A horizon.

sample was slightly higher in the Keith. These are illustrated in Figure 15.

Table II summarizes all the results of the fractionation studies.

Table II. Amounts of the Various Forms of Inorganic Phosphates in Four Soils of South Dakota

Soil Identification	ppm of phosphorus, air dry soil Aluminum Phosphate	 Iron Phosphate	 Calcium Phosphate
Moody, cropped, A horizon	18	47	102
Kranzburg, cropped, A horizon	13	27	117
Morton, cropped, A horizon	15	28	142
Keith, cropped, A horizon	25	22	162
Moody, cropped, B horizon	9	42	331
Kranzburg, cropped, B horizon	10	13	170
Morton, cropped, B horizon	6	17	177
Keith, cropped, B horizon	10	16	147
Moody, virgin, A horizon	11	16	164
Kranzburg, virgin, A horizon	24	24	108
Morton, virgin, A horizon	18	31	162
Keith, virgin, A horizon	17	20	194
Moody, virgin, B horizon	5	11	333
Kranzburg, virgin, B horizon	9	14	157
Morton, virgin, B horizon	9	21	152
Keith, virgin, B horizon	12	16	165

Results of the Leaching Studies

The results of the leaching procedure are presented graphically on the following pages. Figure 16 illustrates the release pattern for the A and B horizons of the cropped Moody soil. After the initial drop the release pattern changed at a slower rate. As would be expected,

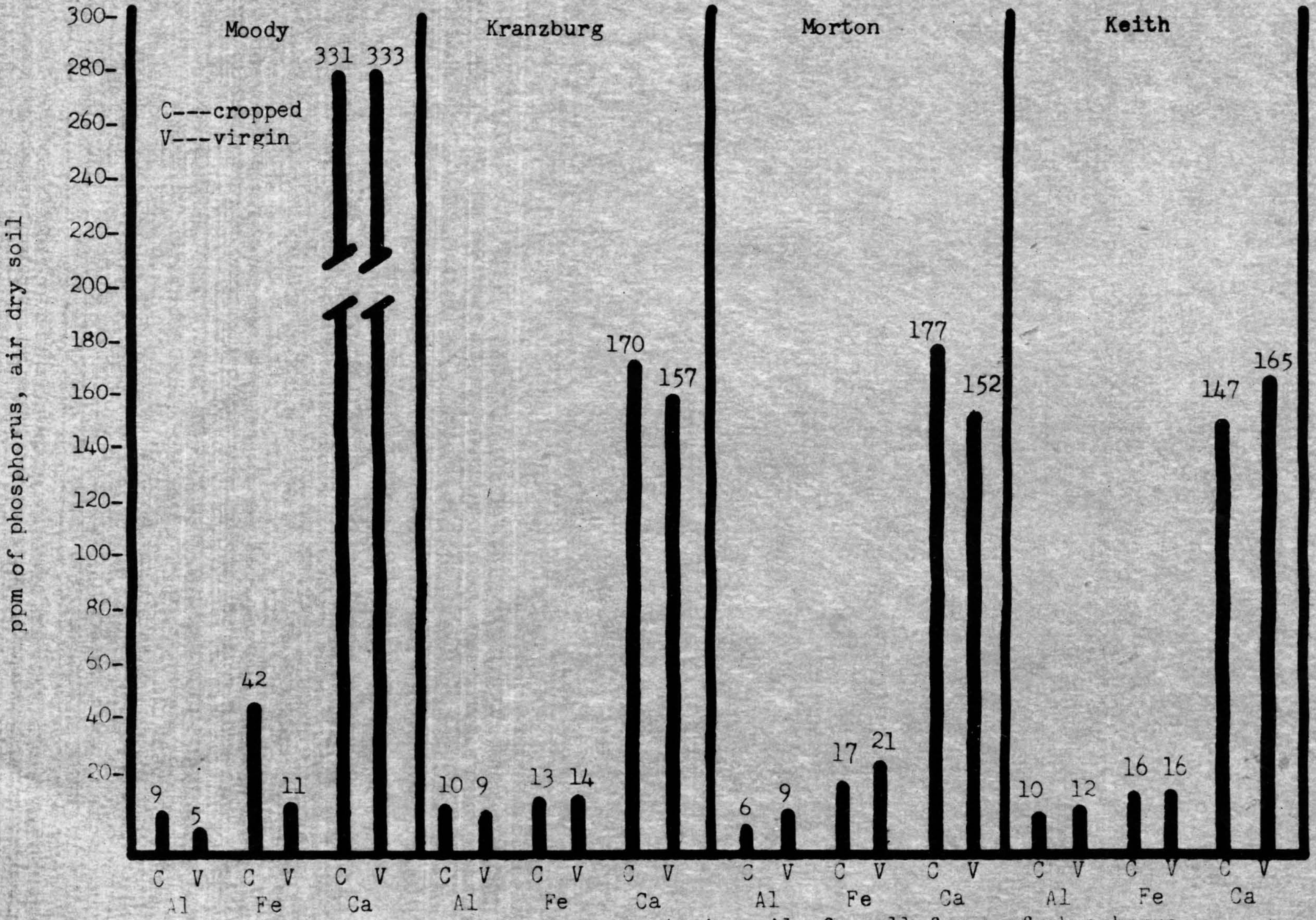


Figure 15. A comparison of the cropped and virgin soils for all forms of phosphorus, B horizon.

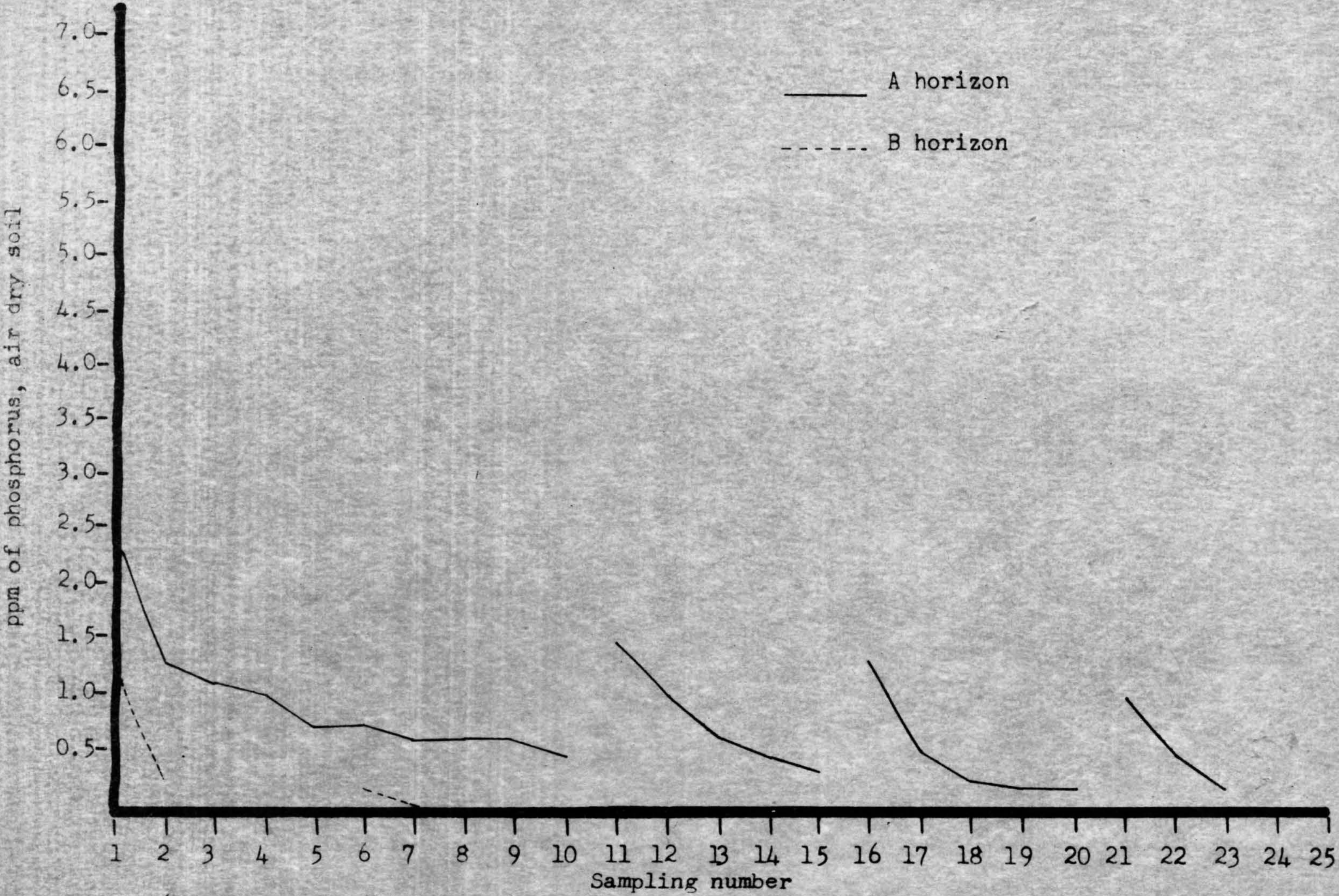


Figure 16. Phosphate release patterns for the A and B horizons of the cropped Moody soil.

the renewal capacity diminished with successive leachings; it was presumed that the ability of the soil to regain phosphorus equilibrium was diminished. Figure 17 presents the same information for the A and B horizons of the cropped Kranzburg soil. Here the A and B horizons possessed the same initial capacity to provide the plant with phosphorus, but the renewal capacity of the B horizon was much lower and did not persist as long. Figure 18 illustrates the same relationship for the two horizons of the Morton soils that have been cropped. The two horizons had a similar capacity to provide the plant with phosphorus initially, but the second leaching on the B horizon produced no measurable amount of phosphorus in the leachate. Some renewal was evidenced after incubation but the capacity again dropped to a trace. Finally, the phosphorus release pattern for the A and B horizons of the Keith series under crop is illustrated in Figure 19. Here the amount of phosphorus available to the plant far exceeds that of the other soils, but dropped off rapidly to become comparable to the other representatives. The B horizon exhibited good available phosphorus supply in the initial leaching but was unable to renew its phosphorus supply. Figure 20 compares the A horizon of all of the cropped soil samples. The most striking feature is, of course, the apparent available phosphorus in the Keith soil, exceeding the others by more than twice. These results agree with Bhangoo and Smith (4) who found that high calcium phosphate is accompanied by high phosphate availability. It should be recalled that the Keith soil that was cropped contained the greatest amount of calcium phosphate of the A horizons in that category. The A horizon

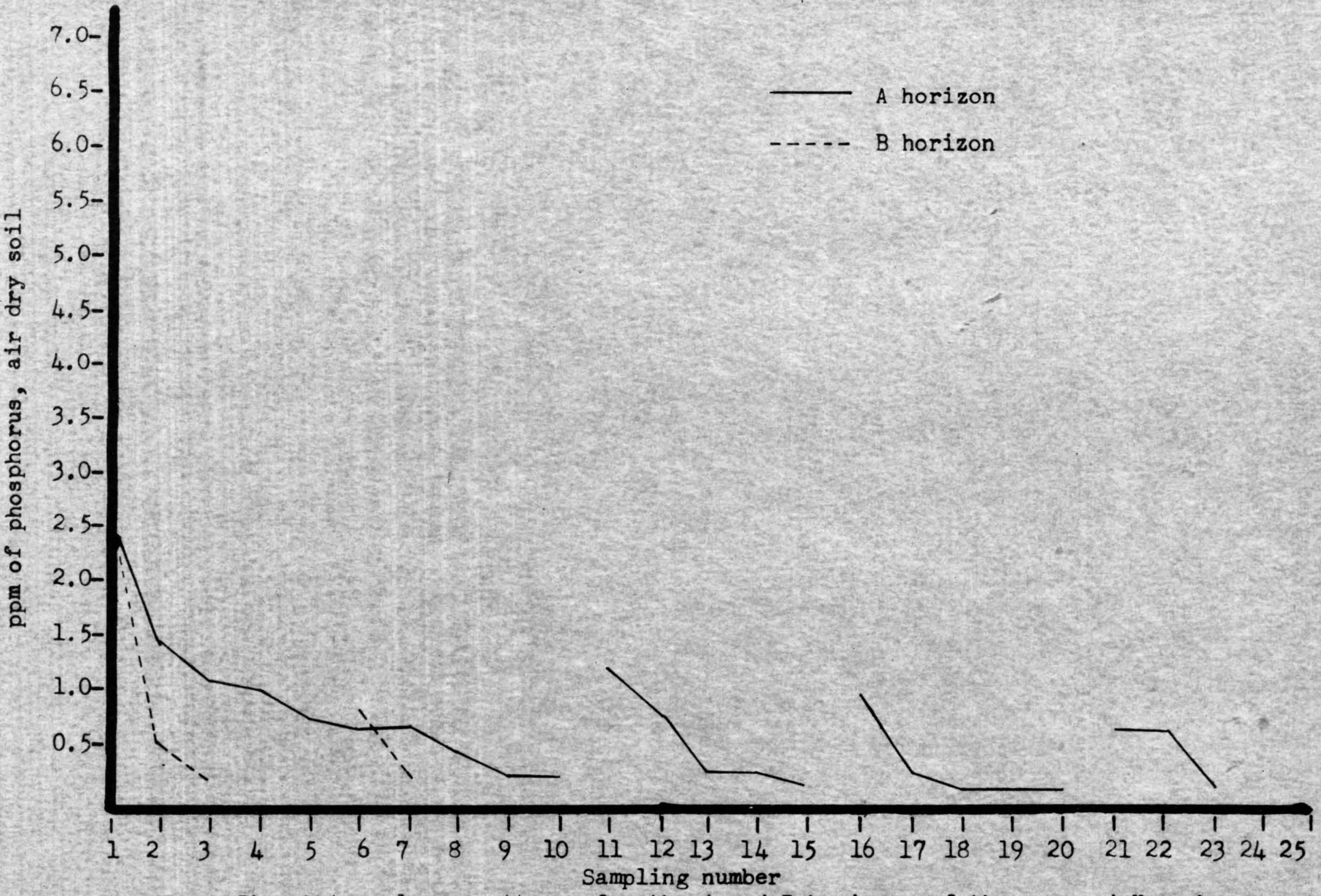


Figure 17. Phosphate release patterns for the A and B horizons of the cropped Kranzburg soil.

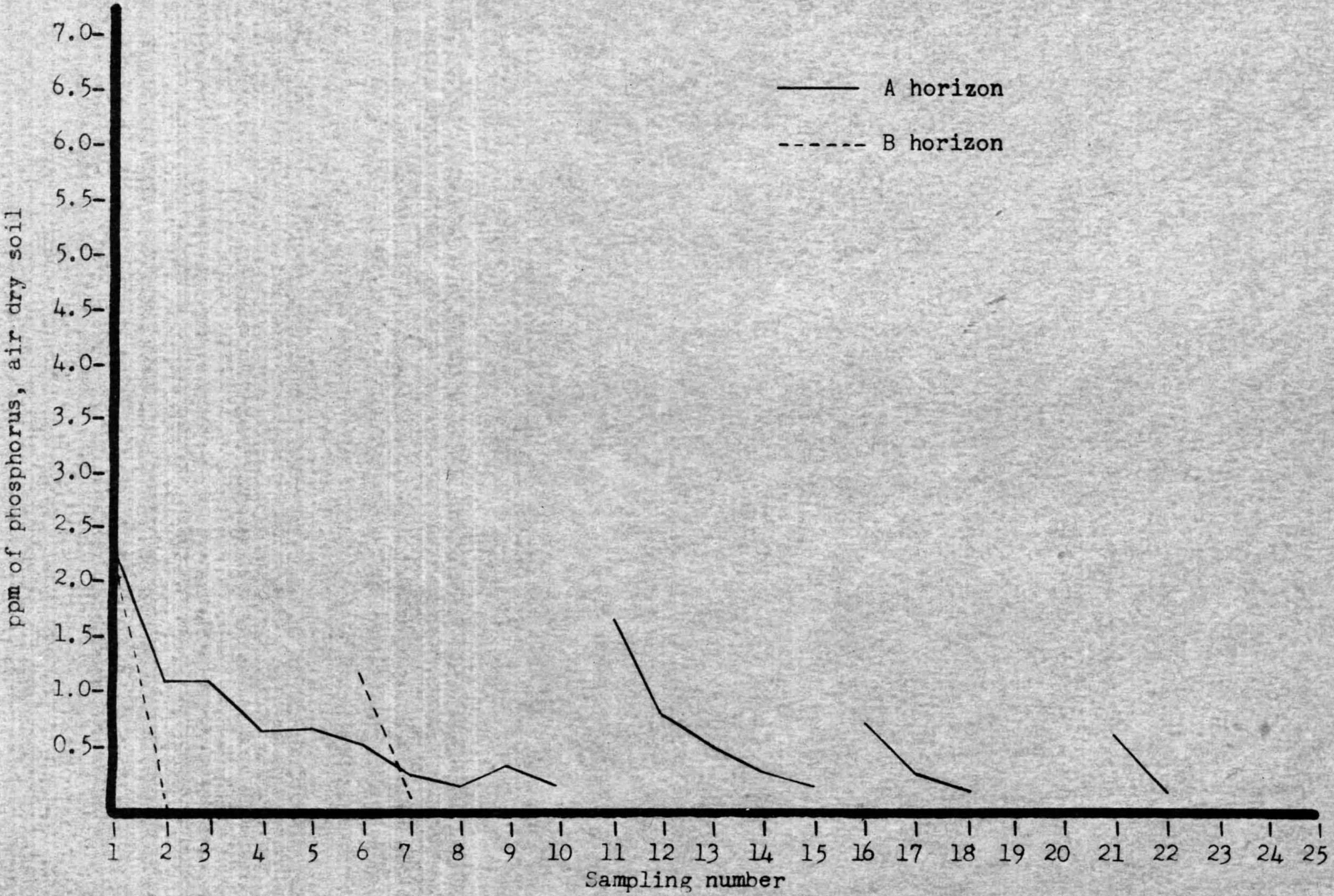


Figure 18. Phosphate release patterns for the A and B horizons of the cropped Morton soil.

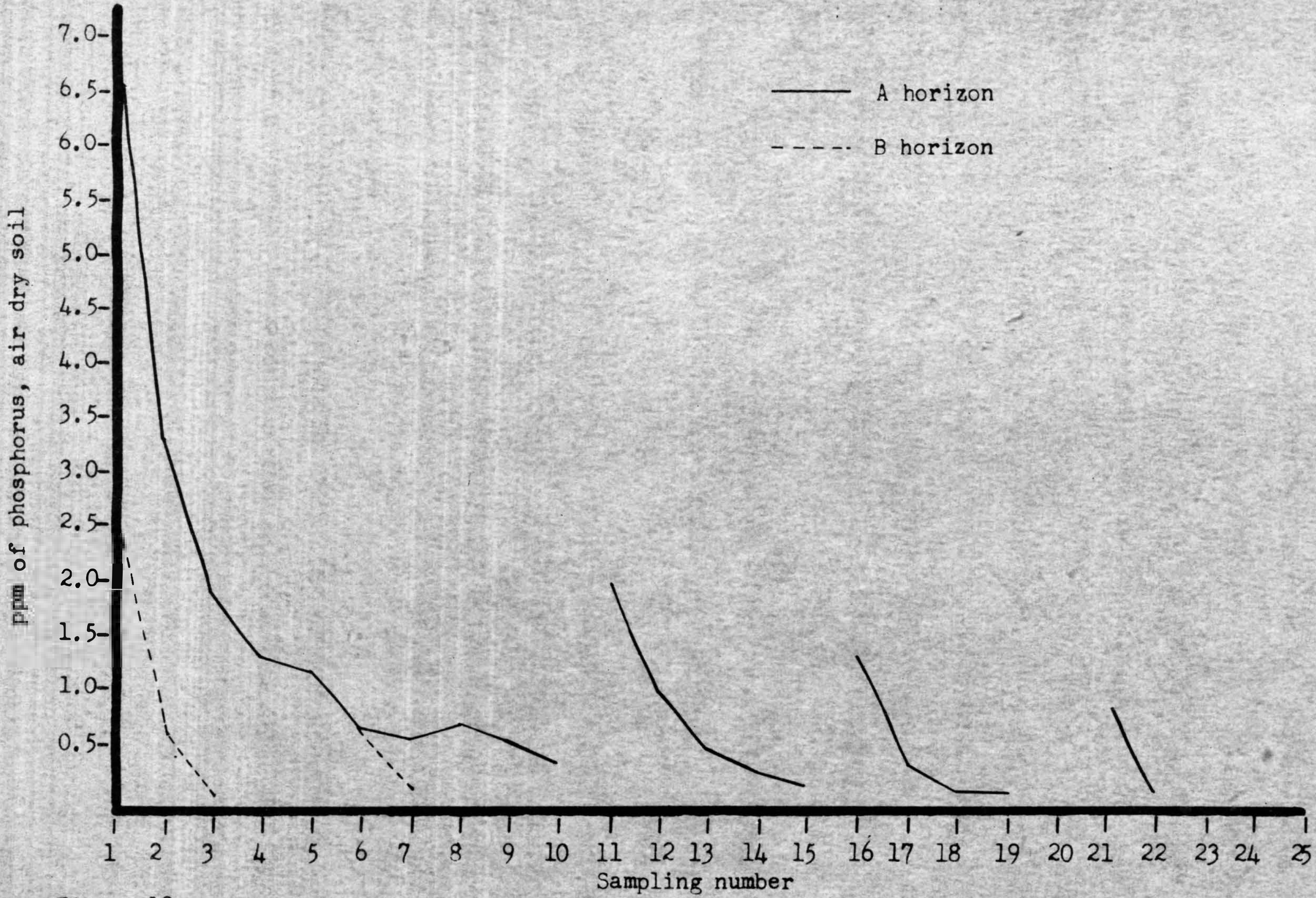


Figure 19. Phosphate release patterns for the A and B horizons of the cropped Keith soil.

of the Keith sample under grass also had the highest calcium phosphate content in this category, but the available phosphorus was less than for the sample under crop. The renewal power of the Keith was superior to others after the first incubation, but after that it was first equalled and finally surpassed by the Moody after the second and third incubations.

The release patterns of the B horizons are exhibited in Figure 21. All were comparatively equal except the Moody which was considerably below the others. It should also be noted that the Morton was completely leached of its phosphorus by the initial leaching prior to incubation.

The studies on the phosphorus supplying capacity of the virgin samples can be illustrated on two graphs. Figure 22 will compare the release patterns for the A horizons of all four soils. All were of approximately the same magnitude initially except the Moody which had much less initial phosphorus supplying power. After the successive incubations the Kranzburg had the greatest power to supply water soluble phosphorus. Figure 23 illustrates the phosphorus supplying power of the B horizons. All were of the same magnitude except the Moody which again was low. It should be pointed out that the B horizon of the Moody far exceeded the others in calcium phosphate, yet the leaching procedure has shown this same horizon to be the poorest provider of plant available phosphorus in every case.

A comparison of the phosphorus release patterns of the same horizon in the cropped and virgin samples is seen in Figures 24 through

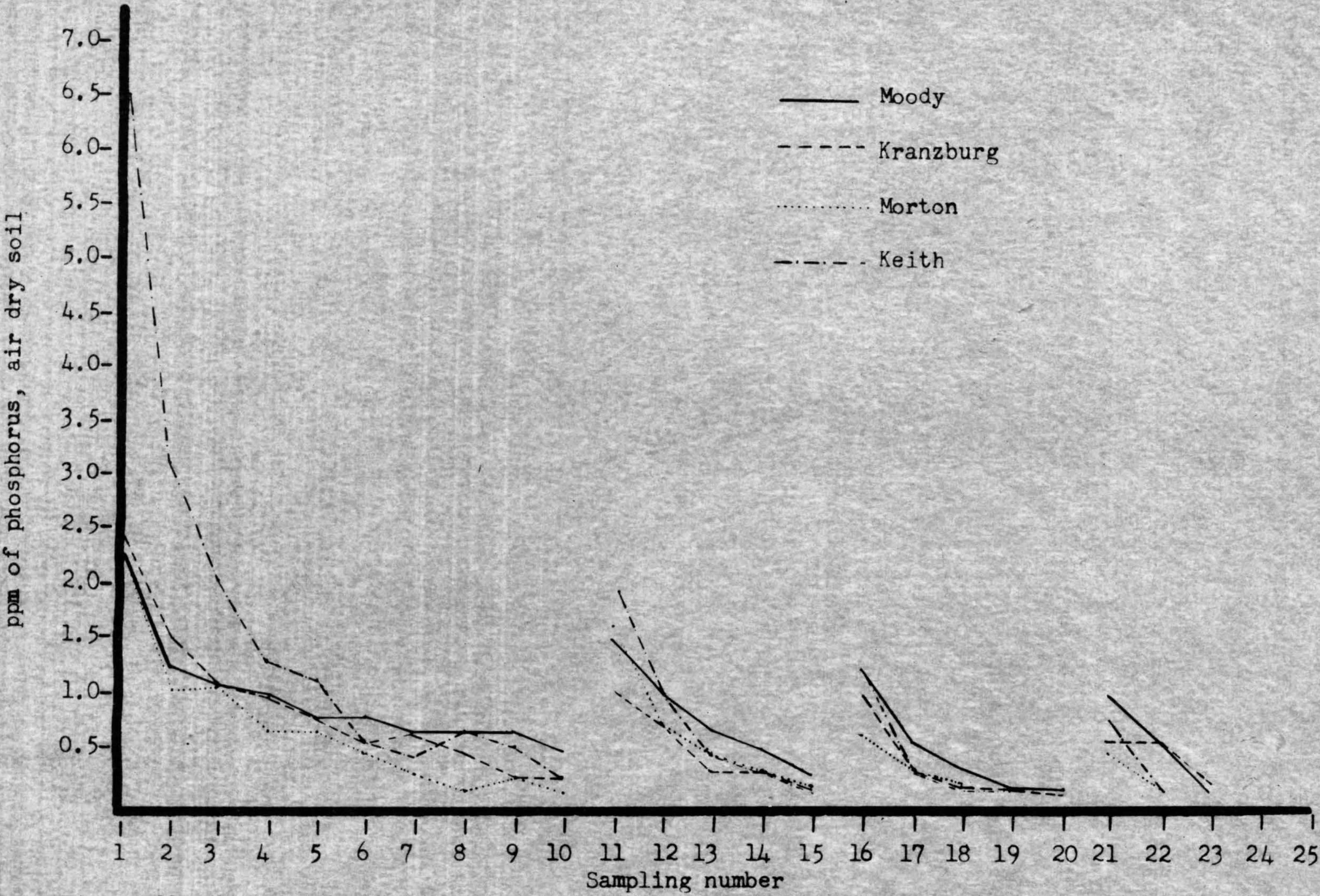


Figure 20. Phosphate release patterns for the A horizons of four cropped soils.

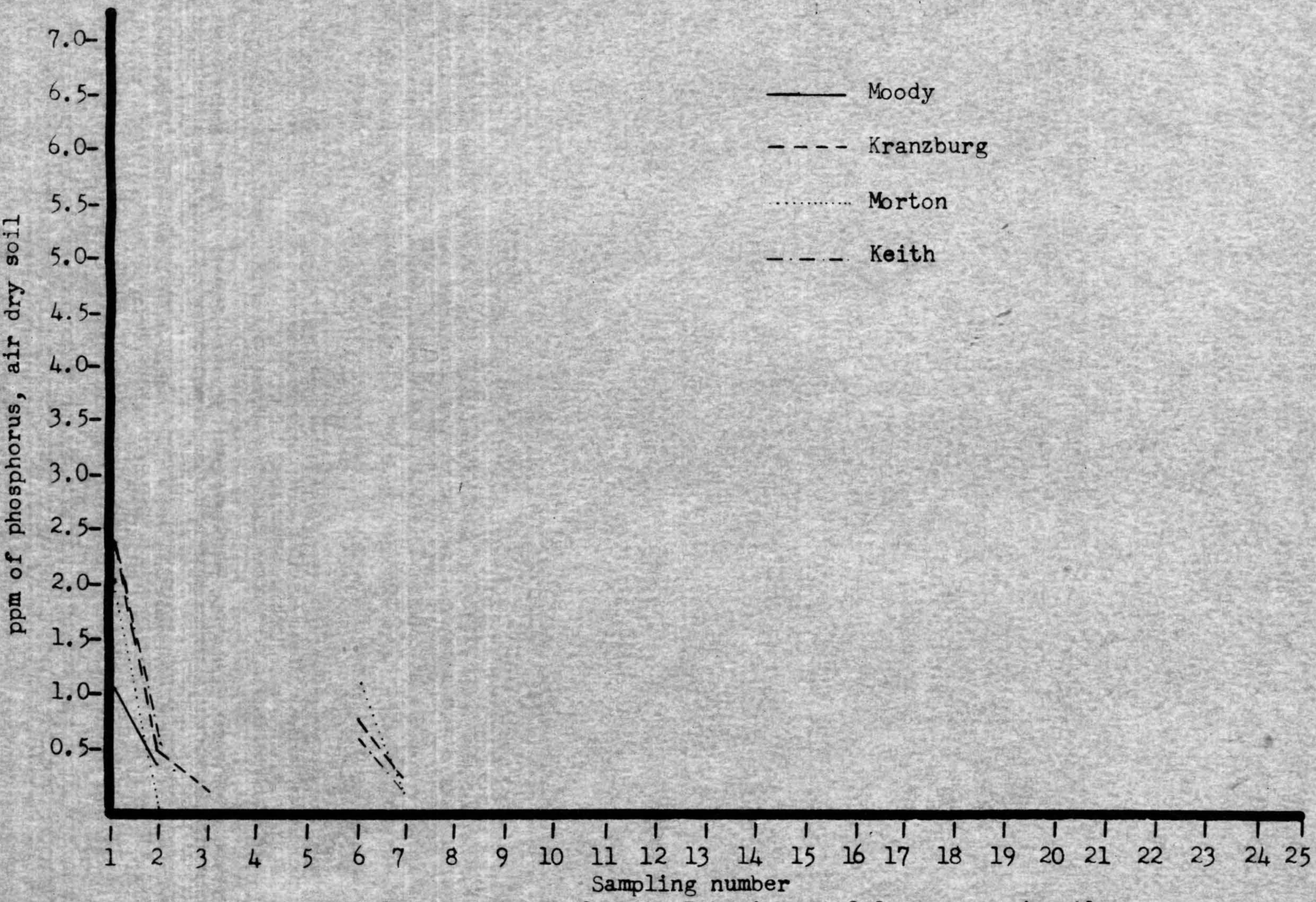


Figure 21. Phosphate release patterns for the B horizons of four cropped soils.

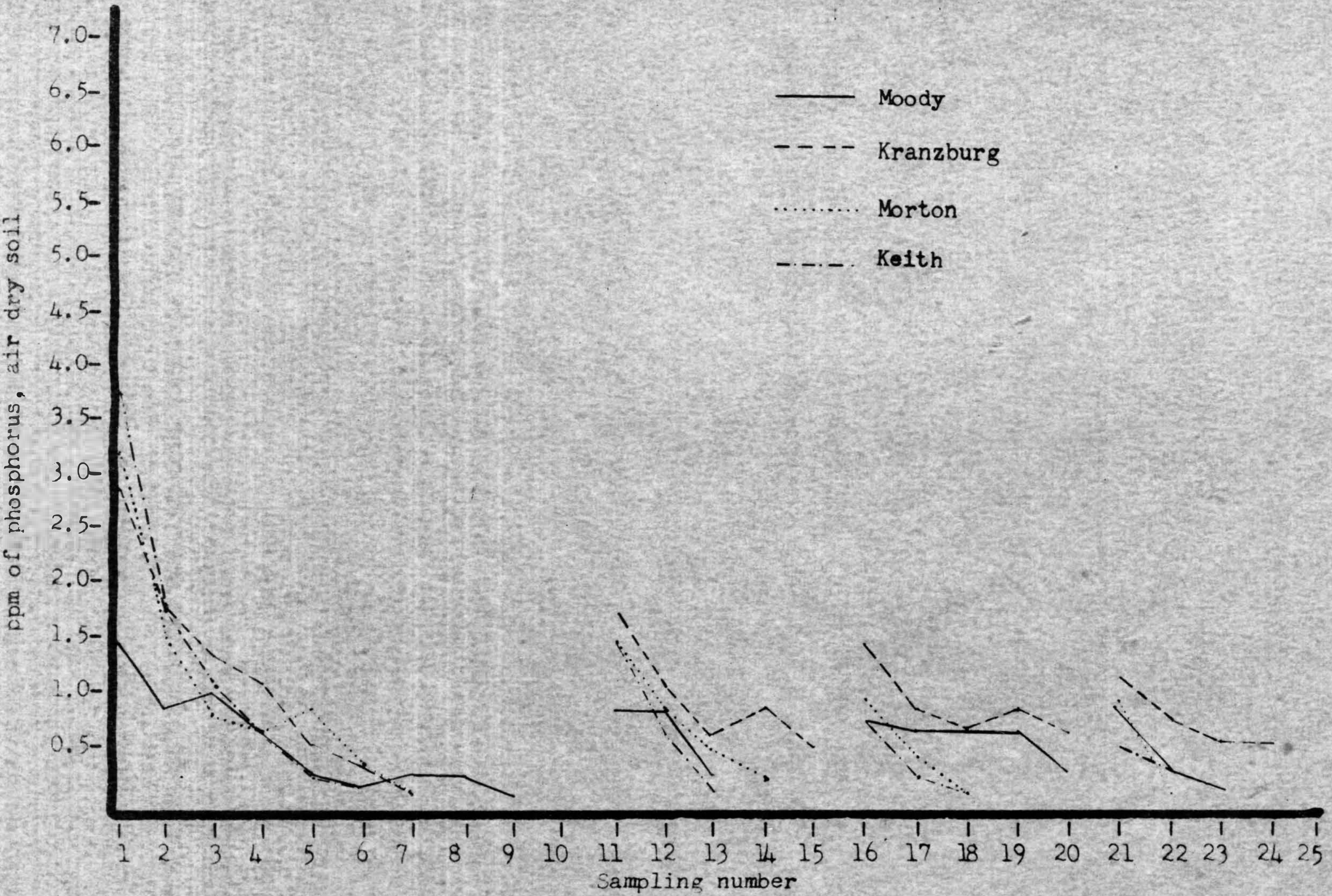


Figure 22. Phosphate release patterns for the A horizons of four virgin soils.

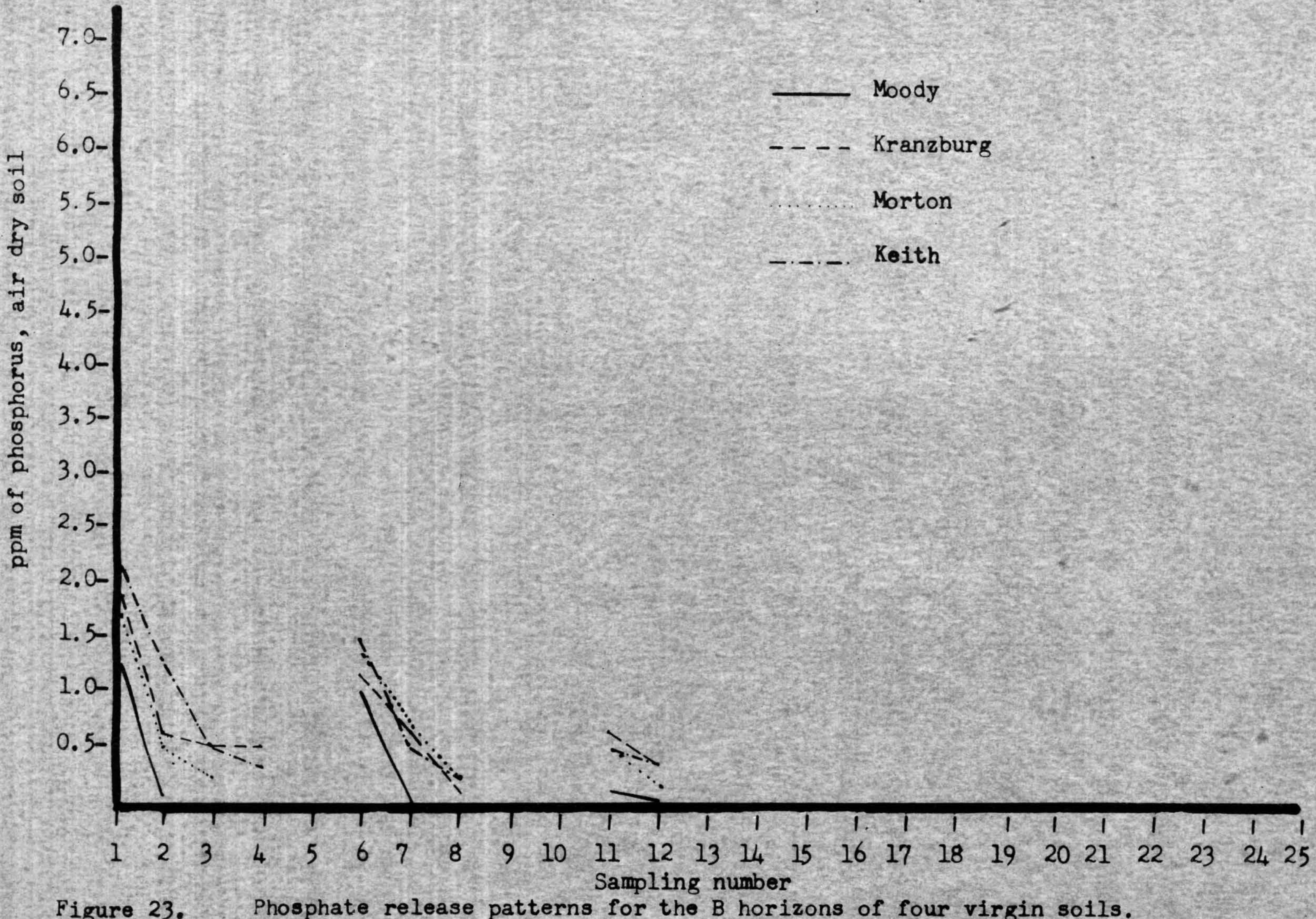


Figure 23. Phosphate release patterns for the B horizons of four virgin soils.

27. The phosphorus supplying power of the cropped Moody is greater than its virgin counterpart, as illustrated in Figure 24. Figure 25 shows the same relationship for the Kranzburg soils, but here the situation is reversed. The virgin sample has the greater supplying power of available phosphorus. The virgin sample of the Morton series generally exhibited a greater supply of water soluble phosphorus than did the cropped counterpart. Only after the initial incubation were they very nearly equal. The Keith series was similar to the Moody in that here again the cropped sample had the greater phosphorus supplying power.

The virgin samples in the B horizons had greater phosphorus supplying power than the cropped samples after the incubation period, although initially there was little difference between cropped and virgin samples. This is illustrated in Figure 28.

A graphic presentation of the complete picture of the phosphorus situation in each soil series is shown in Figures 29 through 32. Cropped and virgin soil results in each series are presented to show independently, and as a comparison, the phosphorus status of these soils.

To illustrate the phosphorus release patterns only the initial leaching after each incubation is reported in the graphs. The B horizons were incubated after five consecutive leachings rather than after ten as in the A horizons. The concentration in ppm for the leaching procedure is on the left hand side of the page, and the scale for the fractionation is on the right hand side. Figure 29 illustrates the inorganic phosphate content and phosphorus release patterns for the

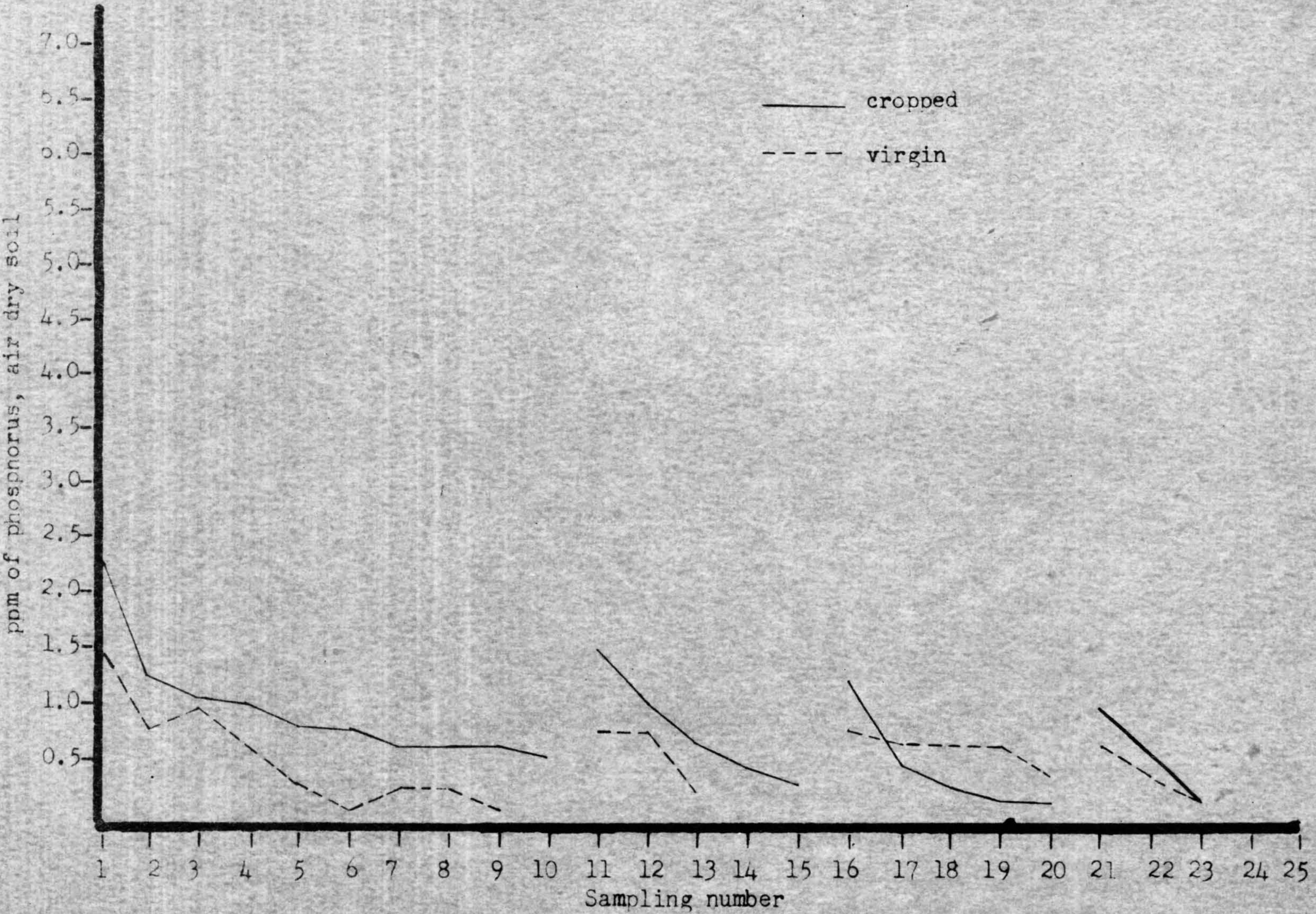


Figure 24. The phosphate release patterns of the A horizon of the cropped and virgin Moody soil.

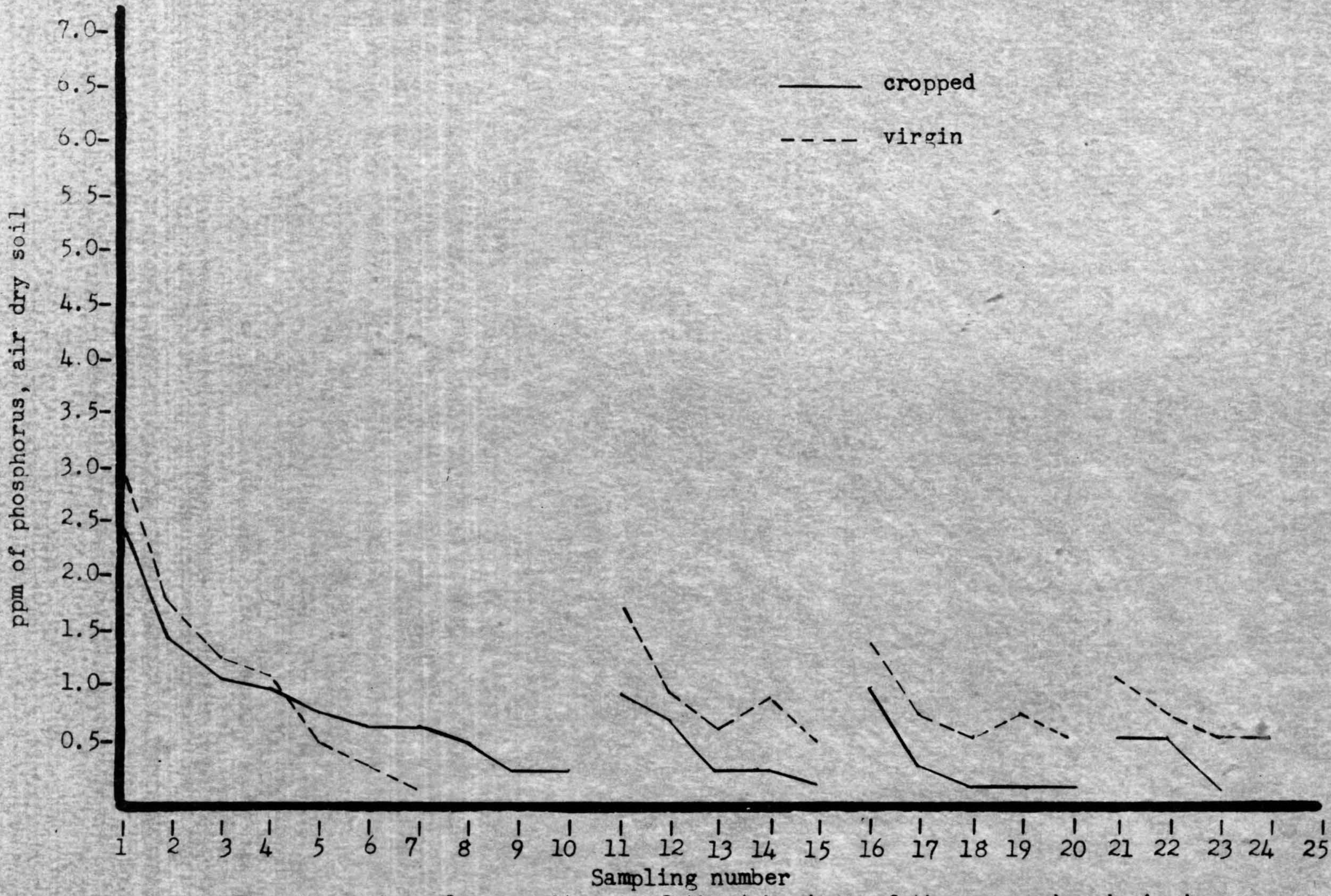


Figure 25. The phosphate release patterns of the A horizon of the cropped and virgin Kranzburg soil.

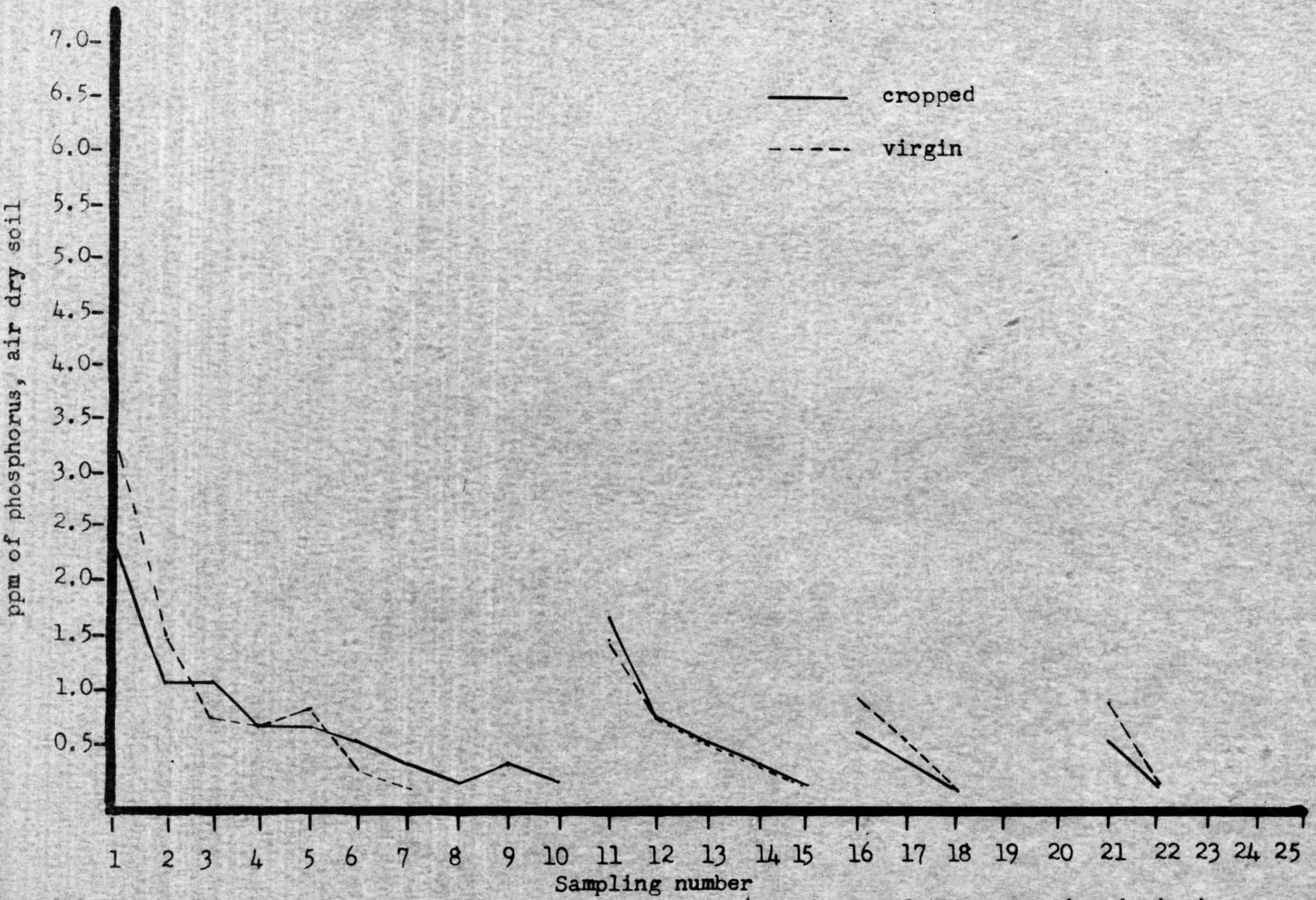


Figure 26. The phosphate release patterns of the A horizons of the cropped and virgin Morton soil.

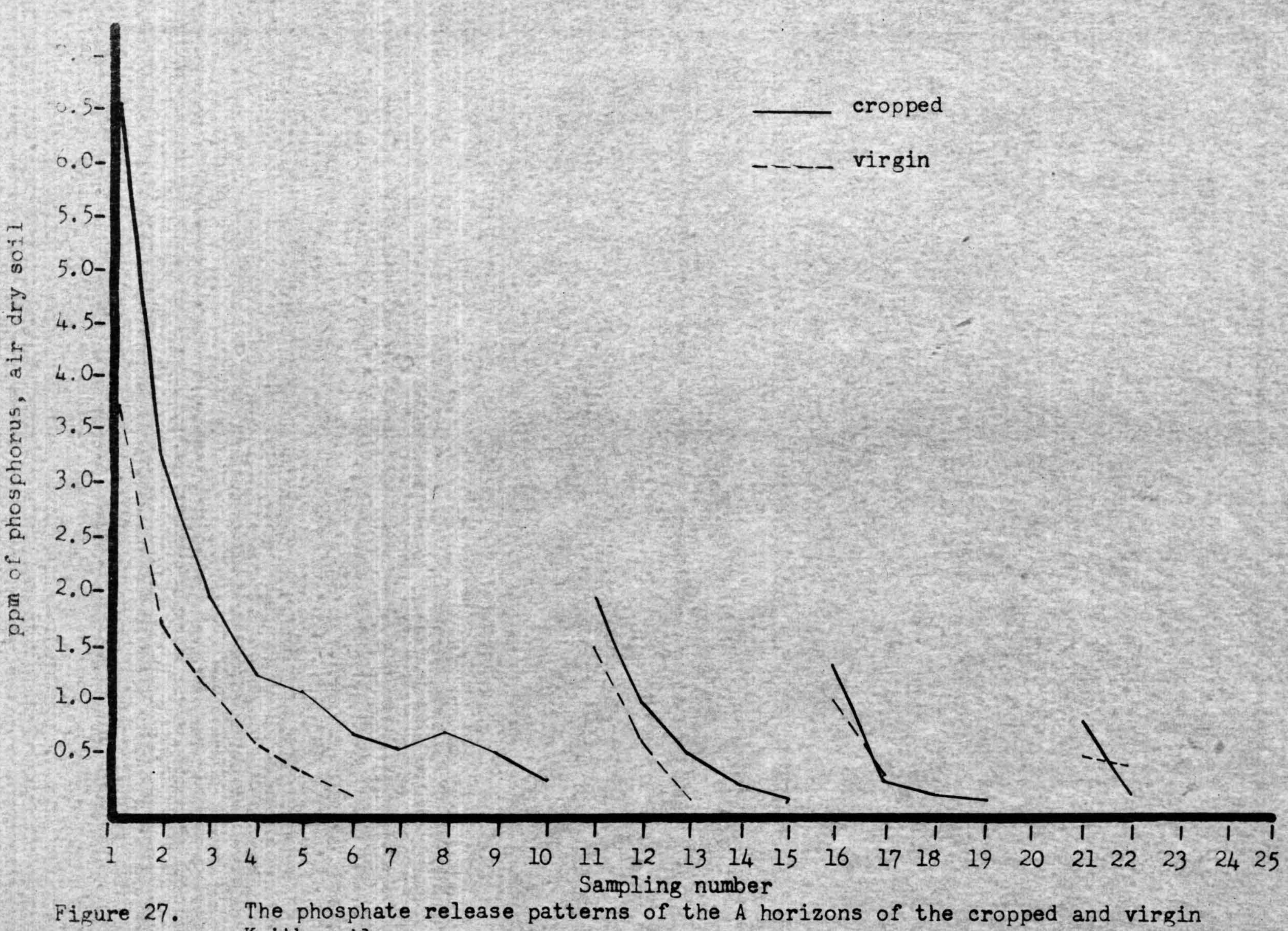


Figure 27. The phosphate release patterns of the A horizons of the cropped and virgin Keith soil.

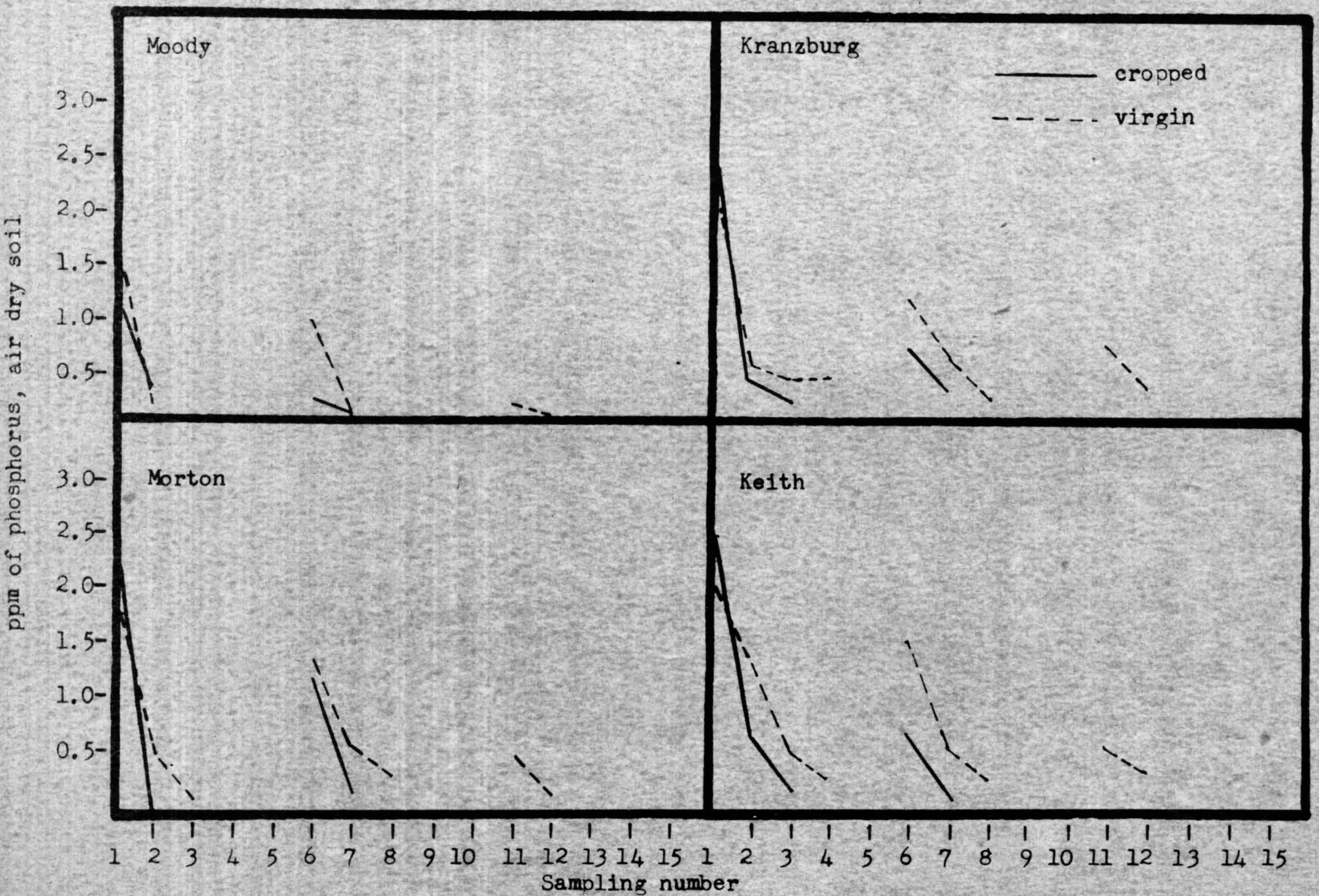


Figure 28. The phosphate release patterns of the B horizons of four soils, cropped and virgin.

virgin and cropped Moody. This graph shows the amount of each form of phosphorus in each horizon and permits comparison of the cropped and virgin samples in this respect. It also illustrates the differences in the phosphate release patterns of both horizons and the cropped and virgin counterparts. Figures 30, 31 and 32 indicate the same for the other three soil representatives of this study.

To corroborate the idea that the leaching procedure is a true measurement of available phosphorus the total phosphorus removed by the initial ten leachings prior to the first incubation and by the total leaching procedure were correlated with the results of the available phosphorus test from the soil testing laboratory. The correlation coefficient was used for this purpose with $r = \Sigma xy / \sqrt{\Sigma x^2 \Sigma y^2}$, with x = the available phosphorus in ppm from the soil testing laboratory and y = the phosphorus in ppm from the leaching procedure. Although the ppm of phosphorus removed by the leaching procedure both in the initial ten leachings and the total leaching procedure were far in excess of that removed by the soil testing laboratory, the complete leaching procedure was more highly correlated than the initial ten leachings. The r value for the complete procedure was 0.788; that for the initial set of leachings was 0.661. Both values were significant at the 1 percent level.

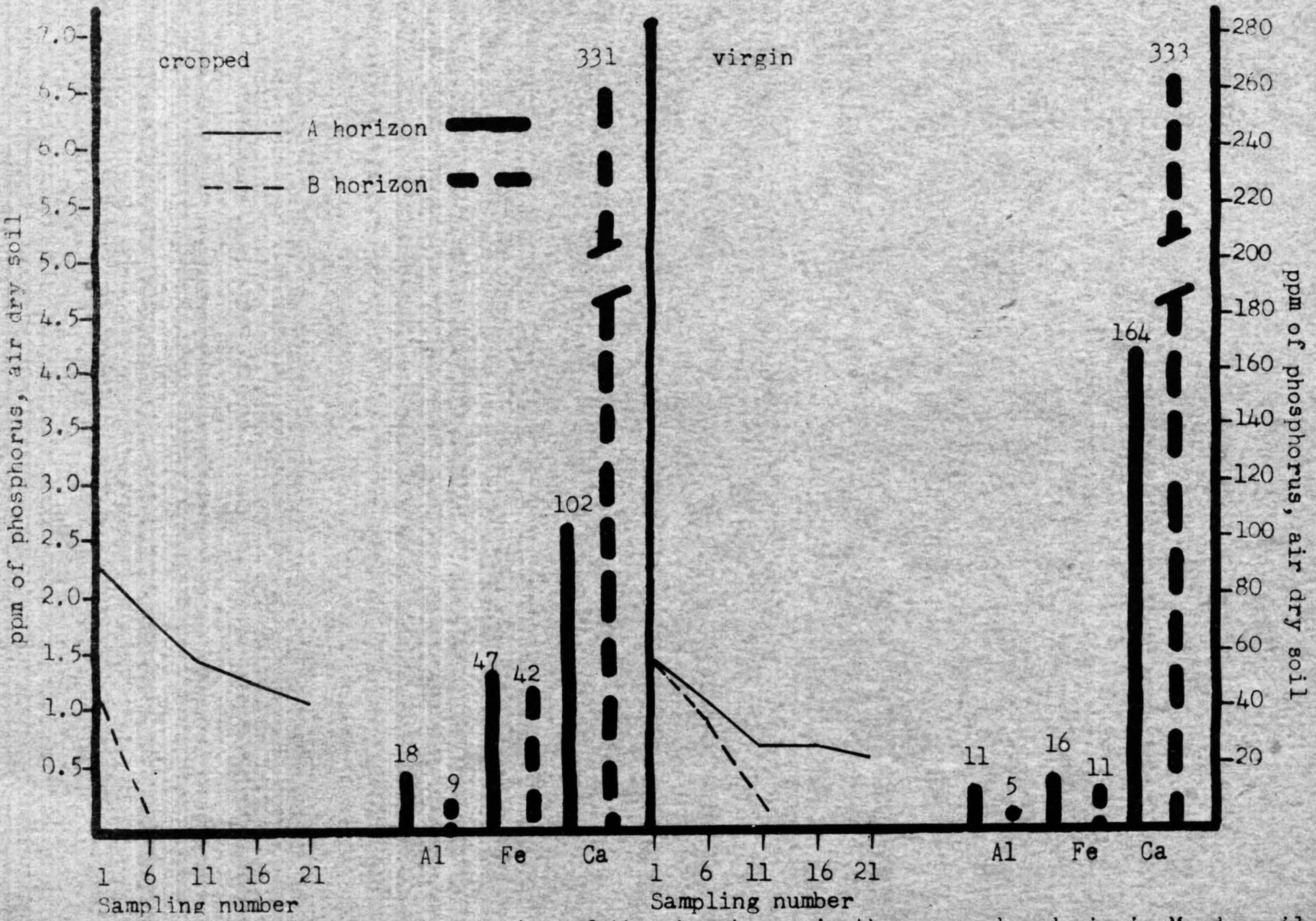


Figure 29. A graphic representation of the phosphorus in the cropped and virgin Moody soil.

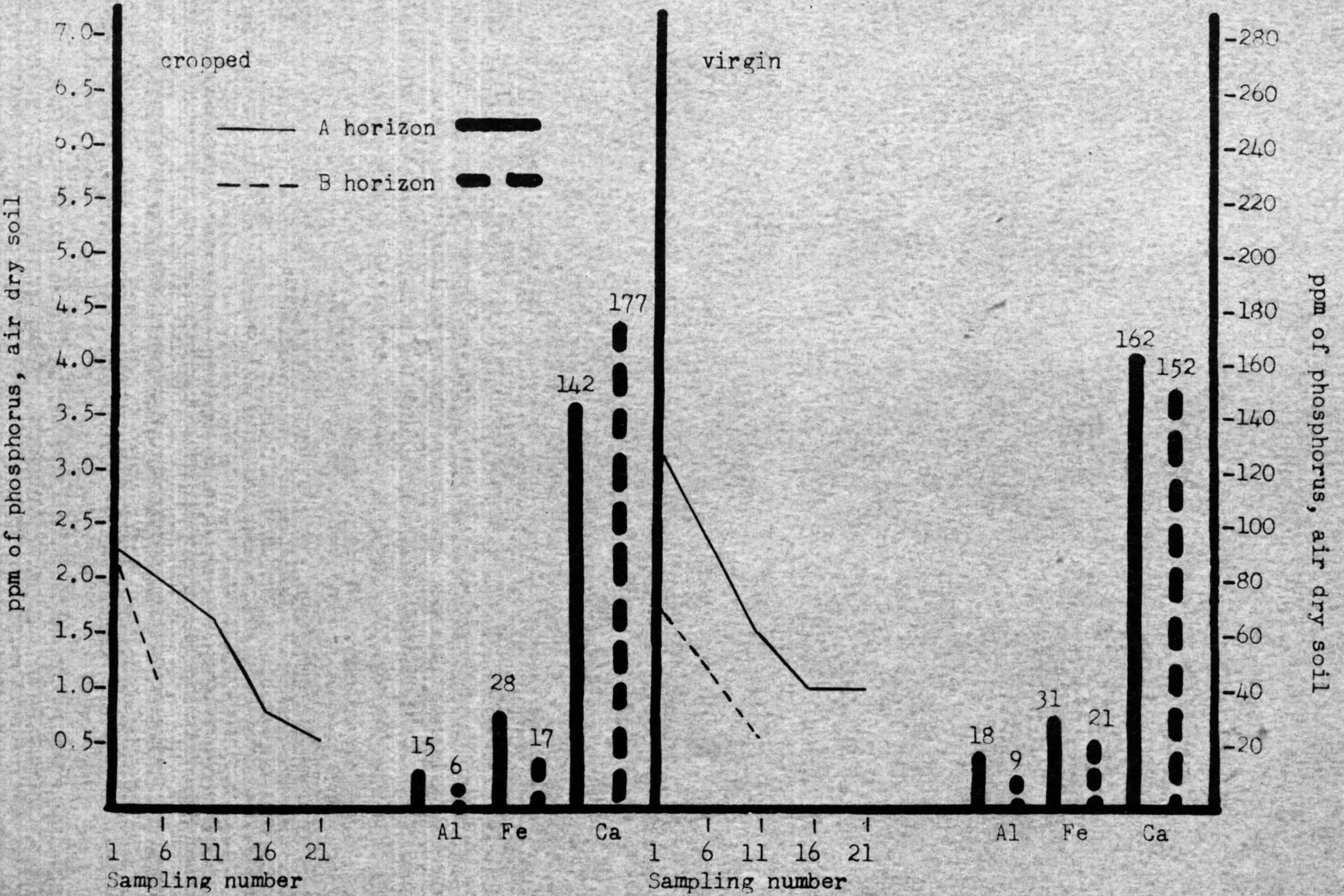


Figure 30. A graphic representation of the phosphorus in the cropped and virgin Kranzburg soil.

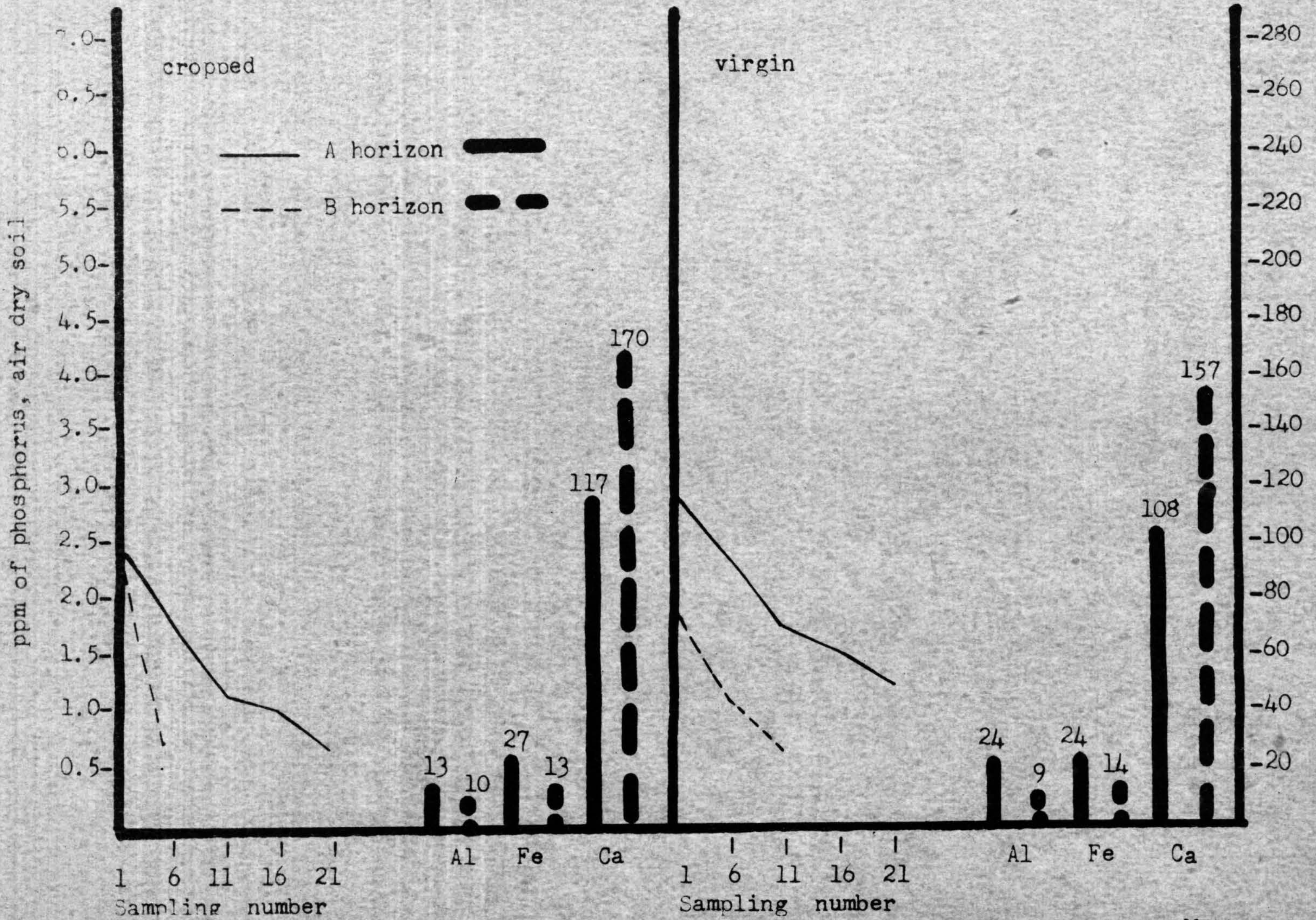


Figure 31. A graphic representation of the phosphorus in the cropped and virgin Morton soil.

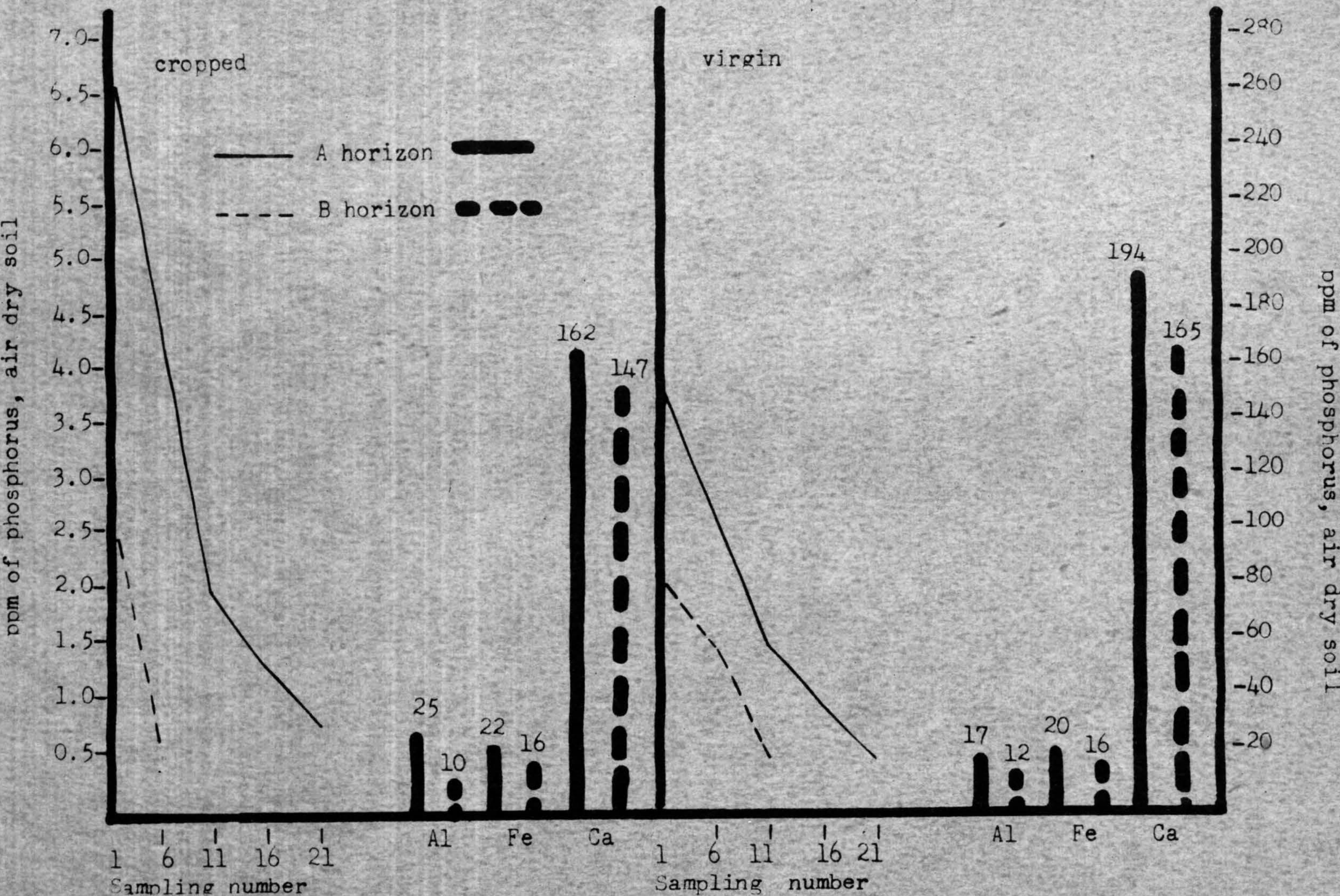


Figure 32. A graphic representation of the phosphorus in the cropped and virgin Keith soil.

DISCUSSION

This work has largely concerned itself with the differences among four soils relative to phosphorus. These differences, while very real, should not obscure the essential similarity of all four soils. All were formed under calcification, under conditions of limited precipitation. Variation in their phosphorus status appears to be a matter of degree.

Rainfall decreases from east to west in South Dakota and so does the soil leaching associated with it. Under weathering it is expected that aluminum and iron will replace calcium in the phosphorus exchange system. To the extent that cropping is itself a form of weathering it would accelerate this trend of replacing calcium with the sesquioxides. This process would be affected by duration and intensity of cropping. Generally Moody soils are cropped more intensively than the Kranzburg, and both of these eastern South Dakota soils more heavily than the two western soils.

With the data available an attempt was made to devise a simple expression for the present inorganic phosphorus status of a soil. Such an expression could involve the amounts in ppm of the various forms of phosphorus present in the order in which they are determined, as:

$$\frac{\text{aluminum phosphate-iron phosphate-calcium phosphate in the A horizon}}{\text{aluminum phosphate-iron phosphate-calcium phosphate in the B horizon}}$$

Using this form, the formulas for the cropped and virgin Moody become

$$\underset{\text{cropped}}{\frac{18-47-102}{9-42-331}} \qquad \underset{\text{virgin}}{\frac{11-16-164}{5-11-333}}$$

This formula illustrates that the cropped soils are higher in the sesquioxide forms of phosphorus than are the virgin samples. The virgin soil is higher than the cropped sample in calcium phosphate in the A horizon, while in the B horizon this form is nearly equal. This formula may be indicative of the fate of phosphorus over a period of many years. Apparently the calcium phosphate is involved in maintaining the equilibrium in the soil system and is probably the source of phosphorus for the increased iron and aluminum forms in the cropped sample.

An attempt was made to include in the expression the available phosphorus as determined by the leaching procedure. It is generally assumed that the virgin soil represents the optimum phosphorus situation for crop production when first tilled, barring the application of phosphate fertilizers. However, this was not the case, for two of the four soils released more water soluble phosphorus from the cropped samples than from the virgin samples. Haas, Grunes and Reichman (19) also found this variability to exist. Practically speaking, this water soluble form of phosphorus is the most important form because it is the form the plants use.

The question naturally arises as to the chemical form of phosphorus removed by the laboratory leaching process. In a preliminary study after the successive leaching procedure was completed the fractionation procedure was used on the leached samples. No consistent depreciation of any form of phosphorus including calcium phosphate resulted. It is presumed that the phosphorus removed by leaching was originally at least partly organic phosphorus transformed to the inorganic form during incubation to maintain the phosphorus equilibrium.

Not included in this investigation were determinations of total and organic phosphorus. These determinations should be included if the study is to be continued. Also the iron and aluminum content of the acid soils as well as the calcium content of the basic soils is important if the fate of applied phosphorus is to be studied. The calcium phosphate fraction needs to be separated into its mono, di and tricalcium phosphate components. The rate of change of calcium phosphate to other forms and the fate of the different forms of applied phosphorus also need attention.

A different approach that also deserves investigation is the phosphate potential formula method of Aslyng (27), which appears in the literature review of this paper.

Future work in this area should involve extreme care in choosing the sampling date. Olsen (32) showed by four different phosphorus tests that plant-available phosphorus is at a low level in the fall, is highest in the early summer, followed by a low level at harvest time. Hence, according to these results the sampling time was incorrect. The author used a Morton sample from the same field separated by only a few feet in the preliminary study and the final investigation. The sample used in the preliminary study was taken in May, while the sample used in the final study was taken in November. The sample taken in early summer was considerably higher in available phosphorus.

The degree of variation in available phosphorus has also been shown by Dodge (12), who sampled one soil every week for two years and another soil every week for one year in an effort to determine the seasonal changes in availability of nitrogen, phosphorus and potassium. Initiating the sampling procedure in November, he found that in one sample the available phosphorus was approximately thirty-five pounds per acre, after which it dropped to slightly over twenty pounds per acre in March. The maximum of thirty-seven pounds per acre occurred in June prior to a sharp drop to eleven pounds per acre at the end of the first year. The maximum available phosphorus supply the second year was twenty pounds and occurred in February, after which it dropped to fifteen pounds in May, reached a new low in July at seven pounds, and leveled off at about eight pounds per acre. The sample on which data are available for one complete year showed a maximum of thirteen pounds in January, a drop followed by a slight rise to nine pounds in April, and a drop to approximately the five pound level for the remainder of the year. This is illustrated in Figure 33. It might be said that these results are the averages of weekly sampling for each month and that the weekly differences were often greater than the average differences from month to month.

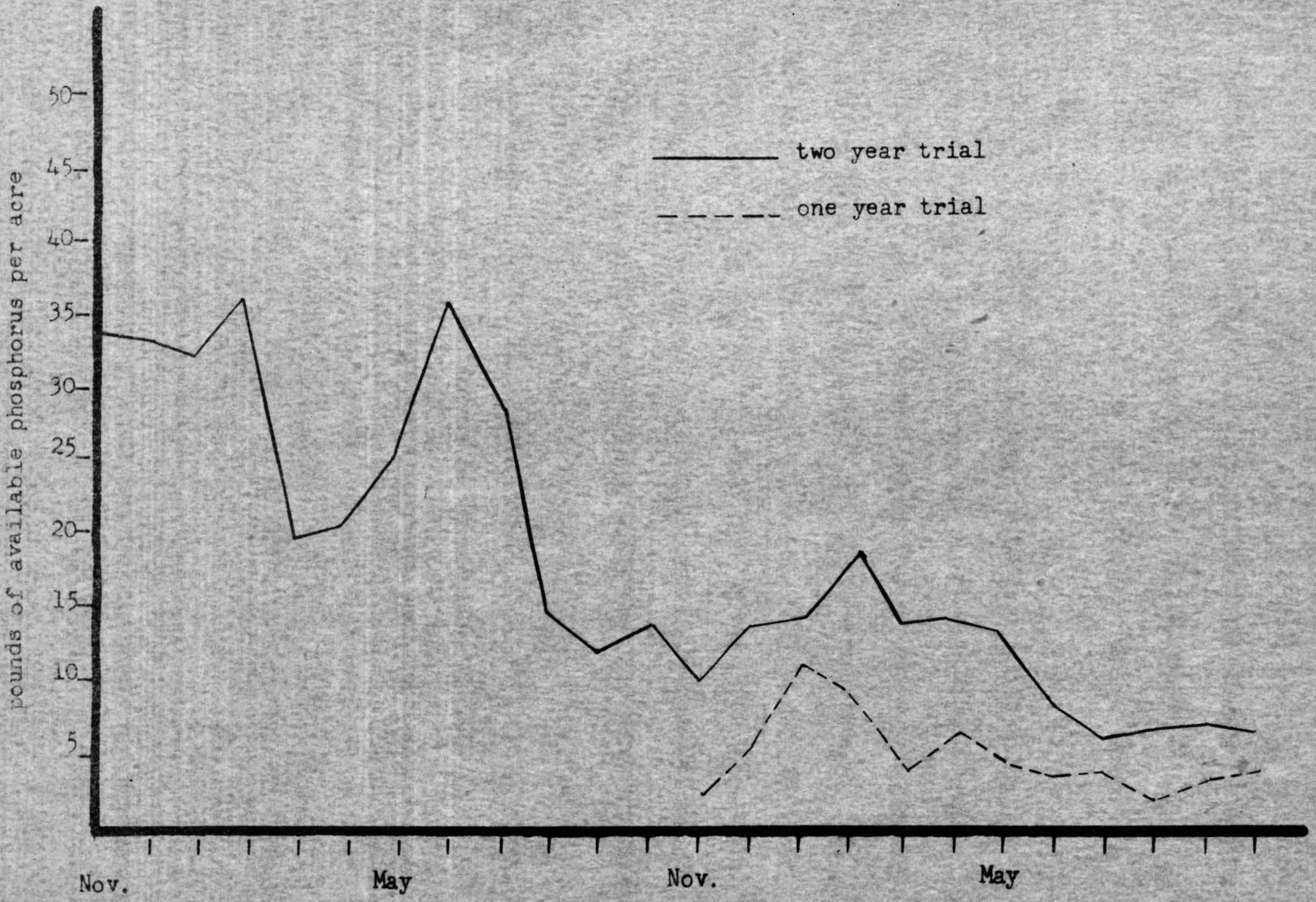


Figure 33. Monthly changes in available phosphorus.

CONCLUSIONS

1. The study of four South Dakota soils, both cropped and virgin, indicates considerable similarities in phosphate status. Aluminum and iron content were low, while calcium content was high (ratio up to 1:10).
2. Cropping tends to shift calcium phosphate to aluminum and iron forms. As might be expected this shift would be more pronounced near the surface. Generally there was a greater change-over in the A horizon than in the B horizon and also in the cropped samples compared to the virgin samples.
3. There was a decrease in the amount of phosphorus in each successive leaching. This may be due to desorption of adsorbed phosphorus rather than a gradual diminishing removal of chemically combined phosphorus.
4. There seemed to be little relation between the phosphorus fractions and the available phosphorus as measured by either the leaching procedure or the available phosphorus test from the soil testing laboratory.
5. There seems to be no indication of a constant ratio between inorganic and water-extractable phosphorus among the four soils examined.
6. By the modified method of Fried and Shapiro, the Moody and Keith soils released more water soluble phosphorus from the cropped samples than they did from the virgin samples. The Kranzburg and Morton soils released more water soluble phosphorus from the virgin samples than they did from the cropped samples.

7. The B horizon of the virgin samples of all four soils released more water-soluble phosphorus than did the B horizon of the cropped samples.
8. The B horizon of cropped soils has considerably less potential to provide the plant with phosphorus than has the A horizon.
9. Two soils with the same initial amount of water-soluble phosphorus may have grossly different release patterns with progressive leaching.
10. The area of "time of sampling" needs further investigation.
11. Low values of water-soluble phosphorus in these soils are due to low desorption rates rather than to low total inorganic phosphorus content.

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