PHOSPHATE STATUS OF OKLAHOMA SOILS AS AFFECTED BY PHOSPHATE APPLICATION AND CROP REMOVAL

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INTRODUCTION

Reactions involving phosphorus are more complex than those involving the other two primary nutrient elements. Most workers agree that aluminum, iron, and calcium phosphates can be formed upon fertilization, but there is considerable disagreement as to the exact compositions and solubilities of these compounds and the extent of their availabilities to plants. Soil factors such as texture, pH, and the amounts and solubilities of iron, aluminum, and calcium compounds influence the formation of phosphate compounds, and must be considered when studying phosphate reactions in soils. Knowledge of phosphate reactions will make accurate fertilizer recommendations possible, since such recommendations can be based on the types, amounts, and availabilities of the various phosphate compounds present and those expected to result from fertilization.

Twenty-five important Oklahoma soils were investigated in this study. The objectives were: 1) to relate phosphate compounds formed as a result of fertilization to soil pH, texture, and reactive aluminum, iron and calcium, 2) to determine the availabilities of soil phosphate compounds to plants, and 3) to compare several soil test extractants for removal of phosphates available to plants grown on specific groups of soils.

CHAPTER II

REVIEW OF LITERATURE

Fixation of Phosphorus by Aluminum and Iron

Various workers have related active aluminum (Al) and iron (Fe) in soils to phosphate (P) fixation. Yuan and Breland (1969) found active Al to correlate better than Fe with the retention of added P. Likewise, Bromfield (1965) concluded tentatively that P sorption was due mainly to active Al, with Fe having only a minor role.

Many workers believe the compounds responsible for P fixation to be amorphous in nature, and have correlated Al and Fe extracted by oxalate with the retention of P. McKeague and Day (1966), and Shukla, et al. (1971) state that oxalate dissolves amorphous Al and Fe compounds, but leaves the crystalline compounds virtually untouched. Williams, et al., (1958) found oxalate-Fe and-Al to be related to P sorption. Ramulu, Pratt and Page (1967) also found the correlation between oxalate-Fe and P fixation to be good and a lesser correlation between dithionite (crystalline + amorphous)-Fe and P fixation.

Yuan (1965) found Al extracted by 0.1 N HCl to be correlated with sorbed P. Tandon (1969) found P and Al extracted by 0.5 N NH_4F to be positively related. Tandon (1970) also found a correlation between NH_4F-Al and P retained as Al-P; this correlation being higher than that between NH_4F-Al and total P retained. He said correlation of Al or Fe with total P retained is not valid because the problem is one of multiple, rather than simple, regression.

Mechanism of Fixation by Aluminum and Iron

There have been varying opinions as to the mechanisms of P fixation and the types of compounds formed. Some workers believe variscite, strengite type compounds to be the ultimate reaction products in soils, while others doubt the existence of such compounds and suggest the major fixation process to be sorption of P onto amorphous Al and Fe oxides and hydroxides.

Raupach (1963) found evidence in favor of sorption of P by Al oxyhydroxide surfaces in soil, and could find no evidence for the existence of variscite in his system.

Hsu and Rennie (1962) found initial fixation of phosphate by Al hydroxide to be primarily an adsorption reaction. The initial fixation was thought to be followed by a slower decomposition-precipitation process. Hsu (1965) believes adsorption to be a special case of precipitation. Al or Fe remains as the constituent of the original phase but reacts with P due to residual forces on the surfaces. Thus, it is the surface-reactive amorphous Al or Fe oxides and hydroxides and not Al^{3+} or Fe^{3+} that are the real factors governing the concentration of P in solution. While the activities of Al^{3+} or Fe^{3+} are negligible at pH 5 or above, there is no such limitation imposed on the surface activities of amorphous Al or Fe compounds. Hsu found no crystallization of Al-P from amorphous compounds in six months and suggested that such crystallization may never take place since surface reactive amorphous compounds are continuously added to the system through the weathering process. Similarly, Colwell (1959) and Chang and Chu (1961) indicate that it is the surface areas and not the amount or activity of the Al or Fe present that determines P fixation.

Bache (1964) explained the mechanism of fixation in terms of "chemisorption". He stated that high-energy chemisorption of small amounts of P by Al and Fe hydrous oxides occurs over a wide pH range without precipitating Al and Fe ions. Contrary to the conclusions of Hsu (1965), Bache thought that with larger amounts of P, Al and Fe ions were precipitated as insoluble P. When the activities of these ions were reduced, increasing additions of P were sorbed at low energy.

There is also considerable evidence for the existence of variscite-strengite type compounds in soils. Haseman, Brown, and Whitt (1950) performed experiments on clay minerals and observed an initial rapid reaction due to the reaction of P with readily available Al and Fe, and a subsequent slower reaction involving Al and Fe released during the decomposition of these minerals. They suggested that P might be fixed in the soil as substituted palmerites and as compounds in the variscite-barrandite-strengite isomorphous series. Wright and Peech (1960) also found some crystalline P mineral of the variscite-strengite isomorphous series to be the ultimate reaction product in acid soils. Coleman, Thorup, and Jackson (1960) observed a correlation between P sorption and exchangeable Al and suggested the formation of a variscite-like compound. However, they believe that sorption could also account for fixation of P in soils containing little exchangeable Al, if large amounts of Fe and Al oxides and hydroxides were present. Lindsay, et al. (1959) believed the immediate reaction products of applied P in acid soils to be much more soluble than variscite, but upon aging the immediate products were slowly transformed into variscite which could coexist with gibbsite. Earlier Low and Black (1947) studied the fixation of P by kaolinite. They hypothesized that kaolinite dissociates into Al and Si ions and that P precipitates the Al ions thereby disturbing the equilibrium and causing the clay to dissolve in accordance with the solubility product principle. Likewise, Hemwall (1957) postulated that P was fixed by clay minerals by reacting with soluble Al, which originated from the exchange sites or from lattice dissociation of the clay minerals, to form a highly insoluble Al-P compound. The reactions followed the solubility product principle and resulted in the formation of variscite. The rate of fixation of P was found to be dependent upon the rate the clay replenished the solution with soluble Al, with lattice dissociated Al the reaction was slow, with exchangeable Al the reaction was rapid. Kittrick and Jackson (1956) also found the formation of P compounds to follow the solubility product principle.

Other aspects of P fixation have been reported. Ahenkorah (1968) concluded that soil organic C, Fe, and their interactions with pH were the dominant factors active in P retention by Ghana soils. Harter (1969) suggested that organic matter is important in the initial bonding of P in soils and proposed that phosphate ions could substitute for hydroxide ions in organic matter. With time some P would be transformed into the less available Fe-and Al-P. Saini and MacLean (1965) also concluded that Al and organic matter had a dominant role in P fixation, but could find no relation to Fe.

Evaluation of the Chang and Jackson Fractionation Procedure

Nearly all workers attempting to quantitatively assess the forms of P in soils use the procedure devised by Chang and Jackson (1957) or some modification of this procedure. Briefly, the original procedure consists of the following steps: 1) removal of loosely bound P by extraction with 1N NH_4Cl for 30 minutes, 2) removal of Al-P by extraction with 0.5N NH_4F for one hour, 3) removal of Fe-P by extraction in 0.1N NaOH for 17 hours, 4) removal of Ca-P by extraction with 0.5N H_2SO_4 for one hour. Reductant-soluble P and occluded-P can also be determined; however most workers studying available P or recovery of fertilizer P choose to disregard these forms since they are thought to form over a period of years and not to be available to plants.

The evaluations and criticisms of this procedure in the fourteen years following its inception have been numerous. The most severe criticism has been the apparent inability of NH_4F to accurately assess the Al-P fraction in fertilized soils. Chang and Jackson (1957) found the measurement to be fairly distinct in unfertilized soils. Even so, they admitted that NH_4F could dissolve some Fe-P and recommended subtracting 10% of the Al-P fraction and adding it to the Fe-P fraction. Fife (1959) believed that P released from aluminum compounds by NH_4F could be resorbed onto Fe compounds causing underestimation of Al-P and subsequent overestimation of Fe-P. He recommended eliminating such sorption by raising the pH of the NH_4F extractant to 8.5. Such a modification has been carried out by most workers. However, Chang and Liaw (1962) discounted the need for such a modification. Since there is some dissolution of Fe-P by neutral NH_4F and also some reprecipitation or sorption of P by Fe during extraction, they said that if the two effects counterbalance each other no modification need be made. Williams, et al. (1971b) found P added in the NH_4F reagent to be removed by lake sediments, and formulated a correction factor based on such removal. Bromfield (1970), however, believed such correction factors to be inadequate.

There are apparently no suitable corrections for the selectivity of NH_4F for Al-P in fertilized soils. Thus, the degree of the error of measurement is unknown, and there are varying opinions as to the accuracy of measurement of the various fractions. Mahapatra and Patrick (1969) stated that NH_4F and NaOH distinguished fairly well between newly synthesized $AlPO_4 \cdot 2H_2O$ and $FePO_4 \cdot 2H_2O$ mixed with the soil. The 10% correction factor of Chang and Jackson (1957) improved their results. Several years before the fractionation procedure was devised Turner and Rice (1952) found 90% of the P adsorbed by Al hydroxide gels to be released with a single 24 hour extraction with NH_4F, and no P to be released from Fe hydroxide gels. They suggested formation of complexes such as $(NH_4)_3FeF_6$ and $(NH_4)_3AlF_6$, the aluminum complex being more stable.

Bromfield (1967a) found the discrimination by NH_4F between phosphated oxides of Fe and Al to be poor. Likewise Yuan, Robertson, and Neller (1960) implied that NH_4F attacks freshly formed Fe-P. With aging, less Fe-P was attacked, perhaps giving a false indication of Fe-P buildup with time. However, Applet and Schalscha (1970) noted a decline in NH_4F-P and an increase in NaOH-P in both phosphated and unphosphated soils, indicating the increase in Fe-P with aging may be real.

Bromfield (1967b) reported dicalcium phosphate to be soluble in NH_4Cl and NH_4F. Since one of the major reaction products of concentrated superphosphate in soils is dicalcium phosphate, such solubility would result in underestimation of Ca-P and a subsequent overestimation of NH_4Cl-P and Al-P. Similarly, Chu and Chang (1966) found surface bonded Ca-P compounds to dissolve almost completely in the NH_4F and NaOH extractants.

In calcareous soils Al-P and Fe-P may be underestimated. According to Williams et al., (1971a) the carbonate ion in $CaCO_3$ may be replaced by the fluoride ion during extraction with NH_4F. The resulting CaF_2 can sorb P causing underestimation of Al-P and Fe-P.

Williams, Syers, and Walker (1967) made extensive modifications of the fractionation procedure to more accurately characterize native P. In addition to NH_4Cl-P, NH_4F-P, reductant soluble-P, and Ca-P, they determined 1st and 2nd NaOH-P, residual organic-P, and residual inorganic-P. Williams and Walker (1969) used this procedure to characterize their "dispersed phosphate" theory. They believed Al and Fe bound P in soils to consist of P ions chemi-sorbed on surfaces occluded wihin the matrices of P-retaining soil components such as gibbsite, goethite, and amorphous alumino-silicates. Inorganic-P was thought to be distributed between the various soil mineral phases in amounts directly related to the P retaining capacity of each phase. They stated the distinction between Al and Fe bound P can only be based on the composition of the mineral species retaining the P, and that such a distinction is not absolute since isomorphous substitution can occur in minerals. On the other hand, Chang and Jackson type procedures imply that the relative amounts of Al-P and Fe-P are influenced by soil maturity and not by soil composition. The conversion of Al-P to Fe-P, for example, would be a consequence of the different solubility products of the two species.

Recovery of Fertilizer Phosphate

In spite of the shortcomings of P fractionation procedures, they have been extensively used to evaluate recovery and availability of added P. Most workers recovered applied fertilizer P in the NH_4Cl, NH_4F, or NaOH fractions. Usually little fertilizer P was recovered as Ca-P (H_2SO_4-P). Chang and Jackson (1958) attributed the lack of recovery of Ca-P from P fertilizers to both crop removal and precipitation of applied P as Al-P and Fe-P. However, they stated that Ca-P (along with Al-P) was more likely to be formed than Fe-P after P application due to the higher activities of Ca and Al ions. Massey, Sheard, and Miller (1970) found 50% of the applied P in the NH_4F fraction and 30% in the NaOH fraction. Similarly Halstead (1967) reported 53% of the applied P was recovered as Al-P and 24% as Fe-P. In neutral soils 28% of the P was recovered as Ca-P.

Laverty and McLean (1961) found P recovered as NH_4Cl-P to increase and P recovered as NaOH-P to decrease with an increase in pH, while NH_4F-P exhibited no change. There was a tendency for Ca-P to increase with pH in both fertilized and unfertilized soils. They used P removed by the Bray #2 extractant as a measure of P fixation and found that their soils fixed 28 to 72% of the applied fertilizer P. Soils fixing 28% of the applied P had nearly 2.5 times as much P fixed as Al-P as compared to Fe-P. Soils fixing 72% of the applied P had nearly twice as much P fixed as Fe-P as compared to Al-P.

Hortenstine (1966) found an increase in Al-P and Fe-P after liming and shaking soils in a 50 ppm P solution. He also found Ca-P to decrease. Alban, Vacharotayan, and Jackson (1964) reported a decrease in P recovered by the H_2SO_4 extractant in both limed and unlimed soils.

Availability of Applied Phosphorus

Several workers have based the availability of the various P forms on results obtained by Chang and Jackson type procedures. Susuki, Lawton, and Doll (1963) proposed that P removed by cropping was derived from Ca-P and Al-P. Grigg (1968) used multiple regression analysis and proposed that yield and relative yield were related to Fe-P, and uptake of P was related to Al-P and Fe-P. Ca-P was related to neither yield nor uptake. Payne and Hanna, (1965) using multiple regression analysis, concluded that Al-P was the main source of plant available P. Fe-P had a greater role in P supply in one soil where it was dominant. Al-Abbas and Barber (1964), also using multiple regression analysis, found Fe-P produced the best correlation with P uptake by the plants. Smith (1965) noted no decline in Fe-P with cropping while there was a significant decline in NH_4Cl-P and Al-P. Fe-P increased in the noncropped soil and he suggested that plants either took up the newly formed Fe-P or competed with Fe compounds for soluble P released from the Al fraction. If the latter was true, he suggested the Al fraction was the major source of available P. Alexander and Robertson (1968) reported both Al-P and Fe-P to be the major sources of available P in their soils. Halstead (1967) found that Al-P gave the best relationship with both percent yield $\left(\frac{\text{Yield without P}}{\text{Yield with P}} \times 100\right)$ and percent P uptake. In unfertilized soils NH_4Cl-P and Al-P decreased while Fe-P and Ca-P increased with cropping.

Shelton and Coleman (1968) found the degree of saturation of the P fixation capacity necessary for maintaining high available P levels to depend upon the relative proportions of Al-P and Fe-P and the rate of conversion of Al-P to Fe-P. Saturation of the P fixation capacity was more efficient in soils that fixed a large amount of applied P as Al-P.

Fassbender, et al. (1968) found P absorption by plants to be correlated with NH_4Cl-P in Central American soils. In the more acid soil group they found no correlation between either Ca-P, Al-P, or Fe-P, and P absorption. They suggested that after exhaustion of NH_4Cl-P no rapid replenishment from other P forms occurs and a severe deficiency develops. Fassbender also said that in soils dominant in Ca-P an adequate supply of P existed, probably due to both Ca-P and Al-P.

Alban, et al. (1964) noted differences between crops in uptake of the various P forms. For clover the uptake sequence was NH_4F-P $>$ H_2SO_4-P $>$ NaOH-P. For oats the sequence was H_2SO_4-P $>$ NH_4F-P with no correlation with NaOH-P. Massey, et al. (1970) also noted differences between crops in the uptake of various forms of P. The uptake of fertilizer P was negatively correlated with NaOH-P, NH_4F-P, and H_2SO_4-P. NH_4Cl-P was correlated with uptake by alfalfa but not bromegrass.

Several workers have applied specific P compounds to soils and studied crop response. Taylor, et al. (1963) found amorphous Al-P to be a moderately effective source of P on acid soils. Crystalline variscite was ineffective. On calcareous soils they found amorphous Al-P, variscite, and potassium and ammonium taranakites to be as effective as monocalcium phosphates. Earlier Taylor, Garney, and Lindsay (1960) found calcium ferric phosphate, potassium taranakite, colloidal Al-P and colloidal Fe-P to be relatively good sources of P, and stated that such forms of P could not be responsible for the "fixation" of P from water soluble fertilizers. Lindsay and DeMent (1961) found colloidal Fe-P to be partially available to plants. Colloidal Fe-P increased in availability during the cropping period, probably because of enlargement of the soil-fertilizer reaction zone. Strengite gave no response on acid soils and was only slightly available on alkaline soils. Juo and Ellis (1968) also found strengite to be unavilable to plants, with variscite being slightly available. They agreed with other workers that colloidal Al-P and Fe-P were good sources of P for plants. Contrary to the results by Lindsay and Dement (1961) they found the availability of colloidal Fe-P to decrease during cropping, and suggested such a decrease to be the result of crystallization. Colloidal Fe-P seemed to crystallize faster than colloidal Al-P since uptake from the latter remained essentially unchanged. Likewise Juo and Ellis (1966) found colloidal Al-P to crystallize more slowly than colloidal Fe-P. They found variscite to be somewhat more available to plants than strengite, probably because of the greater surface area of the former. The sequence of availability of the P compounds in their study was strengite $<$ variscite $\ll$ colloidal Fe-P $\simeq$ colloidal Al-P.

Rather extensive work on P availability was done by Lindsay and Taylor (1960). They separated P sources into those most available and those of only slight availability as follows:

P reaction products most available to plants:

$CaHPO_4 \cdot 2H_2O$

$CaHPO_4$

$CaFe_2(HPO_4)_4 \cdot 5H_2O$

$(NH_4,K)_3Al_5H_6(PO_4)_8 \cdot 3H_2O$

Colloidal Fe- and Al-P

$MgNH_4PO_4 \cdot 6H_2O$

$K_3CaH(PO_4)_2$

$CaH(PO_4)_3 \cdot 3H_2O$

$Ca(NH_4)_2P_2O_7 \cdot H_2O$

$Ca_3(NH_4)_2(P_2O_7)_2 6H_2O$

P reaction products only slightly available to plants:

$KFe_3H_2(PO_4)_6 \cdot 6H_2O$

$FePO_4 \cdot 2H_2O$

$Ca_{10}(PO_4)_6(OH)_2$

$Ca_{10}(PO_4)_6F_2$

$K(Al, Fe)_2(PO_4)_2OH \cdot 2H_2O$

$Ca_2P_2O_7 \cdot 2H_2O$

While most workers agree that certain forms of Al-P and Fe-P are available to plants, there is a difference of opinion as to the availability of Ca-P. Chu and Chang (1966) stated that due to their greater amount of surface-P and specific surface activity, Al-P and Fe-P may be more important sources of P. The low specific surface activity of Ca-P may keep it from being the main source of P even in calcareous soils. Strangely, Chang and Jackson (1958) stated that Ca-P was more available to plants than other forms of P. They said Ca-P was more soluble than other P forms and thus more easily removed by crops. Lehr and Brown (1958) made a petrographic study of calcium phosphate fertilizers. They found crystalline Ca-P bonded to root hairs and suggested contact feeding to be important in P uptake. They found products such as hydroxyapatite, tricalcium phosphate, octacalcium phosphate, and anhydrous dicalcium phosphate to be stable and suggested transformations to other less available products was a relatively slow process.

CHAPTER III

METHODS AND MATERIALS

Twenty-five different soils, representing important soil series in Oklahoma, were collected in the fall of 1969. Each soil was mixed thoroughly, air dried, and crushed to pass a one-quarter inch screen. Fifty-six portions of each soil were weighed into pots, half of the pots receiving 1500 grams, half the pots receiving 750 grams of soil, on an oven dry basis. Fertilizer grade concentrated superphosphate was ground and mixed with the soil to supply four replications of each of seven treatments: 0, 7.5, 15, 30, 60, 90 and 120 ppm P in each size of pot. The two groups of pots were arranged in separate randomized block designs in the greenhouse. The pots containing 1500 grams of soil were planted to Redland X Greenleaf sorghum sudan and watered to field capacity with distilled water on April 28, 1970. The pots containing 750 grams of soil were watered to field capacity on this same date and remained barren throughout the experiment. After emergence the plants were thinned to five plants per pot. The cropped pots were watered when necessary, usually on a daily basis; the noncropped pots were covered and maintained at near field capacity for the entire experiment. The first crop was harvested on May 21, 1970, and the moist and oven dry ($80^{\circ}C$) weights were recorded. The same soils were cropped two more times, the second planting and harvest dates being May 22 and June 18, the third planting and harvest dates being June 23 and July 17, 1970 respectively. Nitrogen, in rates of 100 ppm N as NH_4NO_3 was added with the initial watering and during the growth of each crop. Potassium, in rates of 40 ppm as KCl or K_2SO_4 was added in the initial watering and during growth of the second and third crops.

Core samples of each soil, both cropped and noncropped, were taken at the beginning of the growth period (one week after the initial watering) of the first crop and after each of the three crops were harvested. The noncropped pots were sampled a fifth time after six months had elapsed. The soil samples were air dried, ground, and stored until they could be analyzed.

Soil Analysis

Not all fertilization rates of the soil samples were analyzed for each element studied. The soil samples analyzed and the methods used are given in Table I. The ammonium chloride, ammonium fluoride, sodium hydroxide, and sulfuric acid reagents comprise the Chang and Jackson (1957) fractionation procedure.

The colorimetric procedure using ascorbic acid of Watanabe and Olsen (1965) was used on all P extracts except the NH_4F and $HClO_4$ extracts where the stannous chloride method of Dickman and Bray (1940) and the vanadomolybdophosphoric method of Jackson (1958), respectively, were used. Aluminum and iron were determined using a Perkin Elmer 303 atomic absorption spectrophotometer.

TABLE I

METHODS USED FOR SOIL ANALYSIS

Extractant	Elements Determined	Soil:Solution Ratio	Shaking Time	Rates Analyzed	Sampling Dates	Soils Analyzed	
						Cropped	Noncropped
1 N NH_4Cl[1]	P	1:50	30 min.	0, 15, 90	All	X	X
0.5 N NH_4F(pH8.2)[1]	P	1:50	1 hr.	0, 15, 90	All	X	X
0.1 N NaOH[1]	P	1:50	17 hrs.	0, 15, 90	All	X	X
0.5 N H_2SO_4[1]	P	1:50	1 hr.	0, 15, 90	All	X	X
Bray #1[2]	P	1:20	5 min.	0, 90	All	X	X
0.5 N $NaHCO_3$[3]	P	1:20	30 min.	0	1st	X	
North Carolina[4]	P	1:10	5 min.	0	1st	X	
$HClO_4$[5, 10]	P	-	-				
CDB[6,10]	Al,Fe	-	-				
Oxalate[7,10]	Al,Fe	1:33	1 hr.				
0.1 N HCl[8,10]	Al,Fe	1:10	30 min.				
0.5 N NH_4F(pH8.2)[9,10]	Al	1:50	1 hr.				

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[1] Chang and Jackson (1957)

[2] 0.025 N HCl in 0.03 N NH_4F, Bray and Kurtz(1945)

[3] Olsen (1954)

[4] 0.05 N HCl in 0.025 N H_2SO_4, Melich (1953)

[5] Olsen and Dean (1965)

[6] 0.3 M $Na_3C_6H_5O_7$+1.0M $NaHCO_3$+$Na_2S_2O_4$, Jackson (1956)

[7] 0.2 M $(NH_4)_2C_2O_4$(pH 3.0), McKeague and Day (1966)

[8] Yuan (1965)

[9] Tandon (1969)

[10] Analyses determined on samples as they came from the field.

CHAPTER IV

RESULTS AND DISCUSSION

The soils used in this study and selected properties are given in Table II. For the purposes of discussion the soils are divided into four groups. The classification is basically textural but there is some overlap between groups. The soils could have been classified according to other properties such as pH or P distribution pattern, but with the present classification there are enough similarities and differences within a group to facilitate a logical discussion of P fixation and utilization by plants.

Group 1 includes the sandy loams. The soils exhibit a wide range in pH and P distribution patterns, ranging from the moderately acidic, high P fixing soils such as Bowie and Bates, to the more alkaline, relatively low P fixing soils such as Canadian and Tipton. The soils in group 2 are loams and silt loams. They are neutral or slightly acidic in reaction, with the exceptions of Port and Parsons which are moderately acidic. The soils are generally dominant in Al-P or Fe-P, with Carey and Kingfisher being dominant in Ca-P. The Ca-P contents of these soils do not approach those of the more alkaline soils in group 1. In group 3 are found the heavier textured soils, ranging from silt loams to silty clays, all soils containing more clay than the soils in group 2. The soil reaction ranges from moderately acidic in the case of Waurika to alkaline in the cases of Osage and Foard. All

TABLE II

THE CHEMICAL AND TEXTURAL PROPERTIES OF SOILS STUDIED

						ppm				
Soil	% Sand	% Silt	% Clay	pH (1:1)	CCE (%)	NH_4Cl-P	Al-P	Fe-P	Ca-P	TOTALP ($HClO_4$)
				Group 1						
Bowie s l	54.3	38.2	7.5	5.75	1.1	0.0	6.0	10.9	1.5	132
Bates s l	54.7	36.5	8.8	5.70	1.0	0.0	6.0	10.1	3.7	130
Cobb s l	71.4	16.0	12.6	6.60	0.6	0.0	12.1	16.0	7.5	159
Dill s l	73.0	12.5	14.5	5.95	0.9	4.5	31.7	21.7	35.5	202
St. Paul l	47.1	44.1	8.8	7.35	2.1	7.5	15.7	13.1	197	423
Pratt s l	69.5	23.0	7.5	7.00	1.4	6.4	22.4	16.5	122	313
Canadian s l	64.1	25.8	10.1	7.65	1.5	16.2	19.5	9.4	124	282
Tipton l	50.4	38.2	11.4	7.70	1.7	42.0	44.0	21.3	117	344
				Group 2						
Parsons si l	20.0	66.1	13.9	5.55	0.8	0.0	6.9	24.3	8.6	179
Kirkland l	32.2	48.8	19.0	6.45	1.2	1.5	18.2	42.6	17.5	259
Summit si l	16.4	69.0	14.6	6.45	1.4	0.0	6.4	14.3	13.7	309
Carey l	43.4	40.2	16.4	7.20	1.8	1.5	10.5	12.3	58.8	259
Renfrow l	46.8	40.4	12.8	6.35	1.3	3.0	21.2	41.6	22.0	368
Kingfisher sil	21.9	66.8	11.3	6.00	1.2	2.2	8.6	10.9	40.0	294
Norge l	37.7	49.7	12.6	7.15	1.4	0.7	5.5	14.3	9.0	161
Port l	36.2	46.1	17.7	5.90	1.4	3.7	27.2	46.3	16.2	276
				Group 3						
Waurika si l	13.1	62.8	24.1	5.70	1.4	0.7	20.5	22.5	13.4	244
Hollister si l	12.1	61.1	26.8	6.60	2.0	0.0	24.5	20.8	90.8	332
Osage si c	9.1	48.0	42.9	7.60	2.6	1.5	26.2	29.7	76.4	465
Brewer sicl	12.9	55.2	31.9	6.60	2.7	1.9	41.2	51.6	97.1	448
Lela si c	1.7	54.3	44.0	6.65	2.5	7.1	86.5	102	93.0	745
Foard si l	19.2	56.5	24.3	7.85	2.3	0.0	13.0	10.5	82.0	301
				Group 4						
Ulysses sicl	20.2	51.5	28.3	8.00	5.3	2.2	13.1	3.5	186	418
Miller si cl	3.0	63.9	33.1	7.80	8.9	5.2	32.3	3.5	353	756
San Saba si c	11.3	41.8	46.9	7.85	8.0	9.0	130	21.2	370	918

the soils except Waurika contain moderate amounts of Ca-P. The three soils in group 4 are considered separately because they are calcareous. Because of their calcium carbonate contents they are strongly dominant in Ca-P and are low in Fe-P.

Fixation of Phosphorus by Aluminum and Iron

Table III lists the amounts of Al-P and Fe-P recovered from the 90 ppm P rate on each sampling date and the amounts of Al and Fe extracted. Note that the amounts of the P compounds vary among sampling dates. In Table IV coefficients of determination (r^2) for Al and Fe vs Al-P and Fe-P recovered are listed. These values also vary among sampling dates. It is suggested that the variation in the values of r^2 is caused by the variation in the amounts of the P compounds. The variation in the amounts of the P compounds recovered is due to the instability of such compounds; i.e. by a given date the reactions have not reached a stable equilibrium.

It must be pointed out that the r^2 values are for a linear model. A plot of Al or Fe vs Al-P or Fe-P may not always fit a linear model, and the use of a single model over all sampling dates could also cause variation among the r^2 values. Regardless of whether the variation in the amounts of Al-P or Fe-P formed by different dates is related to the particular model selected or to lack of fit to a correct model, such variation may still be attributed to the lack of establishment of equilibrium by a given date. Therefore, the same linear model is used on each sampling date and the variations in r^2 are attributed to instability or lack of equilibrium of newly formed P compounds.

Observation of the r^2 values in Table IV indicates that the best relation is between oxalate-Fe and Fe-P. Al generally does not account for much of the variation in the amounts of Al-P extracted, the best value being 66.9% for NH_4F-Al for group 1 on the first sampling date.

TABLE III

THE AMOUNTS OF Al AND Fe EXTRACTED FROM THE UNFERTILIZED SOILS VS. THE AMOUNTS OF Al-P AND Fe-P FORMED AT THE 90 ppm FERTILIZATION RATE AS A FUNCTION OF TIME

Soil	Meq/100g Al Extracted in:				ppm Al-P Extracted: Weeks After Application					Meq/100g Fe Extracted in:			ppm Fe-P Extracted: Weeks After Application				
	NH_4F	Oxalate	CDB	HCl	1	4	8	12	26	Oxalate	CDB	HCl	1	4	8	12	26
								Group 1									
Bowie	0.92	1.06	2.23	0.69	44.5	60.8	44.6	44.0	37.3	0.98	6.28	0.022	17.6	19.7	19.0	24.8	23.6
Bates	0.97	1.13	2.44	0.87	42.4	34.5	31.0	30.5	30.6	1.05	7.41	0.029	19.6	24.5	22.7	25.7	25.0
Cobb	1.39	1.53	0.75	0.91	47.9	48.9	47.1	45.9	44.9	0.87	6.20	0.043	18.3	17.2	17.1	20.5	17.9
Dill	0.95	1.46	1.44	0.43	46.0	53.2	59.6	55.2	52.7	0.44	11.04	0.011	6.1	13.3	11.3	7.5	13.4
St.Paul	0.66	1.20	0.74	1.11	23.5	29.1	28.9	31.9	27.2	0.27	7.98	0.009	3.9	8.2	7.7	9.4	10.8
Pratt	0.47	0.53	0.74	0.80	30.5	32.0	31.6	29.0	33.6	0.29	5.98	0.013	6.2	7.4	10.4	6.7	10.3
Canadian	0.79	1.06	0.71	1.02	29.7	29.2	29.0	30.6	28.1	0.26	4.84	0.013	6.9	7.3	6.0	5.2	5.3
Tipton	0.60	1.20	0.88	1.14	23.2	23.3	19.2	25.4	22.2	0.32	4.88	0.020	4.3	3.1	3.5	5.6	4.2
								Group 2									
Parsons	1.00	1.53	2.12	1.02	38.0	35.8	32.8	31.1	27.9	2.87	9.76	0.080	29.9	32.3	37.6	35.7	40.0
Kirkland	0.92	1.33	1.85	0.97	46.6	44.0	31.8	40.1	33.7	1.72	8.70	0.065	21.5	16.7	23.1	29.7	22.2
Summit	1.30	1.86	1.76	1.13	49.6	37.8	43.4	41.0	23.4	3.22	8.02	0.040	31.4	33.3	41.3	41.7	38.4
Carey	1.31	2.06	1.46	1.31	48.5	56.0	57.9	57.6	49.9	0.57	9.00	0.016	11.5	16.5	13.8	15.3	14.5
Renfrow	1.00	1.73	2.15	1.16	45.2	49.3	45.9	46.3	42.0	3.27	9.98	0.066	21.5	28.7	33.1	37.0	39.4
Kingfisher	0.79	1.20	1.04	0.97	36.6	49.0	50.4	45.5	48.0	0.71	6.69	0.013	5.5	7.5	11.2	7.9	10.6
Norge	1.08	1.40	2.08	1.01	49.0	45.1	45.7	51.0	31.8	1.52	11.23	0.043	26.0	25.3	22.9	31.9	25.9
Port	0.66	1.20	2.02	0.81	49.9	43.2	48.6	51.8	40.5	1.05	15.05	0.060	16.8	18.0	12.9	21.1	17.7
								Group 3									
Waurika	1.63	2.13	1.94	1.07	61.7	62.5	68.3	58.2	55.1	1.44	4.39	0.040	15.6	16.0	22.1	17.4	22.0
Hollister	0.89	1.73	1.16	1.38	57.8	58.4	64.6	62.0	56.6	1.04	6.62	0.026	14.4	20.9	9.1	13.0	18.7

TABLE III (Continued)

Soil	Meq/100g Al Extracted in:				ppm Al-P Extracted: Weeks After Application					Meq/100g Fe Extracted in:			ppm Fe-P Extracted: Weeks After Application				
	NH_4F	Oxalate	CDB	HCl	1	4	8	12	26	Oxalate	CDB	HCl	1	4	8	12	26
							Group 3 (Cont'd.)										
Osage	0.95	3.05	1.46	1.90	51.9	62.0	67.6	87.5	69.8	3.12	6.35	0.048	35.7	40.4	45.7	25.1	36.0
Brewer	1.02	2.00	1.39	1.33	56.5	54.6	50.9	58.9	29.0	2.52	6.81	0.101	21.4	20.6	23.6	23.7	21.1
Lela	1.44	2.93	1.66	1.73	81.3	37.6	44.6	81.9	40.6	3.63	6.69	0.082	19.4	8.0	13.0	32.0	30.2
Foard	0.68	2.33	1.44	1.71	38.3	47.0	42.6	43.1	41.4	0.73	8.28	0.013	11.4	14.0	17.3	14.2	10.2

TABLE IV

COEFFICIENTS OF DETERMINATION (r^2) COMPARING Al VS. Al-P, AND Fe VS. Fe-P FORMED AS A FUNCTION OF TIME

Weeks After Application	Al-P Vs. NH_4F Al	Oxalate-Al	CDB-Al	HCl-Al	Fe-P Vs. Oxalate-Fe	CDB-Fe	HCl-Fe
			All Soils				
1	.521	.461	.169	.132	.674	.038	.438
4	.185	.204	.081	.022	.438	.074	.186
8	.245	.325	.025	.058	.606	.018	.258
12	.234	.667	.022	.318	.719	.098	.497
26	.075	.268	.000	.084	.806	.024[1]	.429
			Group 1				
1	.669	.184	.318	.541[1]	.947	.005[1]	.660
4	.387	.126	.241	.608[1]	.887	.091	.339
8	.383	.223	.070	.750[1]	.889	.049	.384
12	.426	.353	.057	.632[1]	.958	.001	.448
26	.381	.201	.029	.724[1]	.878	.084	.290
			Group 2				
1	.106	.099	.130	.017	.640	.018	.425
4	.012	.068	.224[1]	.219	.773	.014	.335
8	.027	.098	.242[1]	.138	.924	.048[1]	.302
12	.007	.034	.063[1]	.053	.828	.006	.452
26	.061	.000	.307[1]	.034	.949	.000[1]	.438
			Group 3				
1	.212	.067	.141	.013[1]	.504	.026[1]	.120
4	.000[1]	.112[1]	.000[1]	.173[1]	.037	.011[1]	.001[1]
8	.058	.021	.010	.118[1]	.166	.034[1]	.011
12	.092	.052	.008	.239	.954	.005[1]	.610
26	.000	.080	.001	.043	.752	.156[1]	.219

[1] Slope of regression line is negative.

There are fair r^2 values in group 1 for HCl-Al after 8 weeks, but the slopes of the regression lines are negative. The reason for an inverse relationship between HCl-Al and Al-P is not known at this time.

The reasons for the lack of a direct relation between Al and Al-P are complex. NH_4F may not fully distinguish between Al-P and Fe-P in fertilized soils (Bromfield, 1965). Also, the extractants used for the removal of Al may not have removed the active Al. As stated previously, the Al-P and Fe-P compounds formed are apparently not at equilibrium. Al-P may be more unstable than Fe-P, since generally good r^2 values were found for Fe vs Fe-P, at least in the case of oxalate-Fe. The best r^2 values for Al were often obtained on the first sampling date, indicating Al is of more importance early in the phosphate fixation process. The first sampling date was one week after the fertilizer was added to the soil, and it is quite possible that an earlier sampling date would have revealed higher r^2 values for Al. Hsu (1964) postulated that Al hydroxide formed in the early stages of his experiment contributed to early rapid fixation of P. He stated that conversion of Al-P to Fe-P was caused by reactive Fe oxides formed during the aging process. The basic difference in Hsu's experiment and the present experiment is that in the present experiment the formation of Al-P and Fe-P is thought to occur because of Al and Fe compounds already present in the soil. P is fixed more rapidly by Al, the conversion to Fe-P occurring as P from the Al compounds reacts with the slower reacting Fe oxides. However, in the present experiment Al and Fe were determined only on the initial samples and the possibility of the formation of Al hydroxides and Fe oxides cannot be discounted entirely.

There is also evidence that Al may be of more importance at high fertilization rates. The ratios of Al-P:Fe-P at each of the three fertilization rates are given in Table V. The ratios generally increase with the fertilization rate, such increases being most pronounced as

TABLE V

THE RATIO OF Al-P TO Fe-P AS A FUNCTION OF THE FERTILIZATION RATE

Weeks After	Rate of Application (ppm P)											
Application	0	15	90	0	15	90	0	15	90	0	15	90
	Dill			Kingfisher			Hollister			Lela		
1	1.21	1.24	2.54	0.57	0.95	2.07	0.93	1.16	2.04	0.85	0.86	1.34
4	1.29	1.43	2.23	0.87	1.17	2.41	0.87	1.09	1.77	0.86	0.88	1.10
8	1.34	1.51	2.55	0.78	1.04	2.14	1.41	1.57	2.55	0.90	1.00	1.11
12	1.70	1.91	2.73	1.09	1.46	2.23	1.31	1.64	2.22	0.86	0.85	1.22
26	1.40	1.51	2.21	1.06	1.25	2.11	1.14	1.28	1.82	0.89	0.85	0.96
	Parsons			Renfrow			Pratt			Osage		
1	0.23	0.37	0.80	0.56	0.65	1.00	1.24	1.65	2.37	0.89	0.87	1.21
4	0.19	0.23	0.73	0.50	0.62	0.96	1.26	1.51	2.30	0.72	0.84	1.28
8	0.21	0.30	0.61	0.50	0.53	0.87	1.01	1.29	2.00	0.97	0.98	1.26
12	0.23	0.30	0.61	0.52	0.60	0.84	1.28	1.72	2.24	0.90	1.04	1.50
26	0.22	0.32	0.51	0.50	0.55	0.78	1.50	1.56	2.10	0.95	1.16	1.50
	Bates			Kirkland			Norge			San Saba		
1	1.03	1.00	1.75	0.58	0.69	1.04	0.49	0.62	1.34	6.70	7.41	7.54
4	0.34	0.54	1.28	0.52	0.63	1.08	0.43	0.53	1.27	6.81	7.20	6.53
8	0.43	0.49	1.25	0.47	0.54	0.82	0.52	0.61	1.36	6.48	6.97	7.25
12	0.39	0.54	1.13	0.46	0.50	0.86	0.40	0.53	1.22	4.38	5.59	6.21
26	0.53	0.57	1.13	0.51	0.53	0.85	0.39	0.55	0.94	5.00	5.64	6.20
	Waurika			Summit			Carey			Tipton		
1	0.90	1.19	2.16	0.59	0.71	1.21	0.99	1.26	2.62	2.06	2.07	2.63
4	0.90	1.14	2.16	0.54	0.54	0.94	0.89	1.06	2.42	2.43	2.47	2.78
8	0.68	0.95	1.99	0.31	0.38	0.85	1.16	1.70	2.76	2.38	2.35	2.56

TABLE V (Continued)

Weeks After Application	Rate of Application (ppm P)											
	0	15	90	0	15	90	0	15	90	0	15	90
	Waurika			Summit			Carey			Tipton		
12	0.87	1.03	1.97	0.52	0.54	0.86	1.12	1.43	2.59	2.12	2.18	2.59
26	0.85	0.98	1.70	0.39	0.43	0.60	1.00	1.42	2.36	2.05	2.15	2.62
	Bowie			Cobb			St. Paul			Foard		
1	0.23	0.14	1.45	0.68	0.91	1.77	1.45	2.13	2.59	1.11	1.70	2.14
4	0.59	0.74	1.84	0.69	0.99	1.87	1.33	1.71	2.31	1.05	1.05	2.26
8	0.46	0.62	1.40	0.81	0.81	1.82	1.35	1.58	2.36	0.94	1.10	1.87
12	0.61	0.62	1.18	0.70	0.85	1.61	1.49	1.59	2.31	1.14	1.14	2.10
26	0.46	0.46	0.95	0.61	0.93	1.71	1.41	1.33	1.97	1.60	1.60	2.39
	Port			Brewer			Canadian			Ulysses		
1	0.53	0.73	1.11	0.85	1.02	1.39	1.26	1.50	2.57	3.84	2.95	5.42
4	0.50	0.63	0.99	0.94	0.90	1.35	1.11	1.51	2.48	3.97	3.66	5.46
8	0.63	0.67	1.15	0.86	0.90	1.25	1.73	1.95	2.68	3.11	3.56	4.88
12	0.59	0.70	1.07	0.87	0.98	1.35	1.75	2.20	2.94	1.91	2.41	3.86
26	0.59	0.59	0.96	0.78	0.79	1.00	1.75	1.43	2.68	2.67	3.16	3.97
	Miller											
1	5.61	6.08	9.19									
4	5.57	6.04	6.98									
8	4.34	4.25	6.97									
12	5.05	4.89	6.21									
26	6.95	5.11	6.91									

the rate is increased from 15 ppm to 90 ppm. At the lower rates there are higher proportions of reactive Fe to P, resulting in a higher percentage of applied P reacting with iron. At the 90 ppm rate, after the more active Fe has reacted, the rate of reaction of P with the slower reacting iron is less than the rate of reaction of P with Al, resulting in a higher ratio of Al-P to Fe-P. Yuan, et al. (1960) offered a somewhat similar explanation. They also found the ratio of Al-P:Fe-P to increase with the application rate. In their soils Al was more plentiful than Fe, and also more ionized, thus there was a greater reaction of P with Al. In the present study Fe was more plentiful than Al, however the Al may have been more active. Reactions in the present experiment may also be similar to those observed by Ramulu and Pratt (1970). They observed that reaction of P with Fe seemed to stop or reach a low level when 25% of the Fe had reacted. This was believed to be caused by formation of Fe-P over the Fe oxide particles so that no more Fe was available to react with P.

Since the r^2 values for Al are low it is difficult to determine which extractant for Al measures the active Al of these soils. NH_4F was used to extract both Al and Al-P. This extractant effectively removes and complexes the Al from Al-P forming a compound such as $(NH_4)_3$-AlF_6. NH_4F also removed Al from Al oxides and hydroxides, the Al removed coming from either active or non-active compounds.

While oxalate and citrate-dithionite-bicarbonate (CDB) are believed to cause dissolution of amorphous and amorphous plus crystalline, Fe oxides and hydroxides, respectively, the same cannot be said of the Al compounds dissolved by these reagents. In Table IV it can be seen that CDB-Fe is always higher than oxalate-Fe, probably confirming that

CDB-Fe includes both crystalline and amorphous (oxalate) Fe. However, oxalate-Al is often higher than CDB-Al indicating a lack of separation of amorphous and crystalline Al compounds by these extractants. The r^2 values for oxalate-Al are generally higher than those for CDB-Al indicating that oxalate-Al may be a more accurate measure of active Al than is CDB-Al. The relation is poor in either case.

The form of Al removed by 0.1N HCl is unknown. Yuan (1965) used 0.1N HCl to measure active Al, but the reagent was of no value in the present study.

The r^2 values for oxalate-Fe vs Fe-P are much better than the values for iron extracted by the other methods, indicating that oxalate dissolves the active Fe compounds and that the active compounds are amorphous in nature. Thus it appears that the primary reaction involving the formation of Fe-P is sorption of phosphate ions onto amorphous Fe oxides and hydroxides. By the end of six months it is possible that some crystalline Fe-P has formed, although the best r^2 values are still for oxalate-Fe. However, crystalline Fe-P formation could involve the dissociation of Fe from amorphous Fe compounds and subsequent precipitation of Fe-P. It is also possible that crystalline Fe-P formation could involve CDB-Fe. The extremely low r^2 values between Fe-P and CDB-Fe may have been caused by the large amounts of CDB present. CDB-Fe:oxalate-Fe ratios of 10 to 20 are common in these soils and considerable CDB-Fe could be involved in reactions with P and leave the values of r^2 virtually unchanged. Such a conclusion is analagous to the general lack of relation between total and available P. In spite of these possibilities the primary reaction between Fe and P appears to be formation of amorphous Fe-P.

When all soils, and groups 2 and 3 soils are considered there is a general increase in the r^2 values for oxalate-Fe vs Fe-P as a function of time. Such an increase indicates that the Fe-P compounds formed approach equilibrium as a function of reaction time, as mentioned previously. In group 2 the increase in the values of r^2 from .640 to .949 between one week and twenty-six weeks is largely due to an increase in the Fe-P contents of Parsons, Summit, and Renfrow. These three soils contain large amounts of oxalate-Fe, resulting in a lengthening of the reaction period. The increase in Fe-P with time in these three soils is reflected in a decrease in the ratios of Al-P:Fe-P as given in Table V. The decrease in Al-P:Fe-P in these soils is also a result of the conversion of Al-P to Fe-P as may be seen in Table III, although the decrease in the ratio for Renfrow is largely due to the increase in Fe-P, since Al-P does not decline consistently.

In group 1 the r^2 values for oxalate-Fe remain fairly constant, explaining a minimum of 87.8% of the variation in Fe-P formed among soils. The amounts of oxalate-Fe in these soils are generally smaller than those in group 2, and there are no soils exhibiting a large change in the amounts of Fe-P formed over the reaction period. Thus, the formation of Fe-P in the soils as a group is nearly complete by the first sampling date, resulting in less change in the values of r^2 than occurred in group 2.

Group 3 exhibits extreme variation in the values of r^2. There are only six soils in this group and less confidence should be placed in the r^2 values. The variation in Fe-P between sampling dates is large, particularly for Hollister, Osage, and Lela, accounting for much of the difference in the values of r^2.

A further relation of oxalate-Fe to Fe-P can be seen by a closer study of Tables III and V. Soils having high or low oxalate-Fe contents exhibit low or high, respectively Al-P:Fe-P ratios. This is particularly true for Parsons, Renfrow, Kirkland, and Summit, which have low ratios of Al-P:Fe-P and for Dill, Pratt, Carey, St. Paul, Canadian, and Tipton which are higher in ratios of Al-P:Fe-P. Many of the other soils approach these extremes.

Whether or not essentially complete ("true" equilibrium is probably never attained) reactions have occurred in the soils in this study cannot be ascertained, since there are no sampling periods between twelve and twenty-six weeks, or after twenty-six weeks. It is unlikely that reactions of the magnitude of those occurring during the six month period will recur, however.

Solubilization of Native Phosphorus and Lack of Recovery of Fertilizer Phosphorus

The recovery of added P in the various forms is shown in Table VI. The values in Table VI were obtained by subtracting the amount of phosphorus for the 0 ppm rate on the first sampling date from the amounts of the 90 ppm rate on each sampling date. P recovered on the remaining four dates reflects changes in native P plus applied P. The amount of P recovered seldom equals the amount applied. When the amount of phosphorus recovered exceeds that applied, significant amounts of P may have been solubilized. Excess recovery or lack of recovery might also reflect random fluctuations in the extraction procedure. Laverty and MacLean (1961) found a range of 95-125% recovery of applied phosphorus and suspected both solubilization and fluctuation. Chang and Chu

TABLE VI

THE RECOVERY OF 90 ppm P APPLIED TO THE EXPERIMENTAL SOILS

Weeks After	Form of P Extracted (ppm)									
Application	NH_4Cl-P	Al-P	Fe-P	Ca-P	Sum	NH_4Cl-P	Al-P	Fe-P	Ca-P	Sum
		Dill					Kingfisher			
1	26.1	46.0	6.1	6.7	84.9	17.8	36.6	5.5	9.2	69.1
4	23.3	53.2	13.3	4.0	93.8	22.1	49.0	7.5	10.2	88.8
8	23.1	59.6	11.3	2.7	96.7	20.2	50.4	11.2	6.5	88.3
12	17.9	55.2	7.5	3.9	84.5	18.3	45.5	7.9	10.3	82.0
26	21.9	52.8	13.4	8.7	96.8	18.8	48.1	10.6	11.8	89.3
		Parsons					Renfrow			
1	2.6	38.0	29.9	9.4	79.9	15.8	45.3	21.6	7.6	90.3
4	4.7	35.8	32.3	7.6	80.4	11.8	49.3	28.7	8.7	98.5
8	5.8	32.8	37.6	8.6	84.8	18.3	45.9	33.1	11.7	10.9
12	3.6	31.1	35.7	6.6	77.0	9.7	46.3	37.0	10.1	103
26	3.2	26.9	39.5	12.9	82.5	13.2	42.1	38.3	11.2	105
		Bates					Kirkland			
1	5.2	42.4	19.5	7.0	74.1	8.1	46.7	21.5	9.2	85.5
4	2.8	34.5	24.5	5.8	67.6	12.7	44.0	16.7	12.5	85.9
8	11.2	31.0	22.7	5.5	70.4	9.4	31.8	23.1	10.2	74.5
12	10.1	30.5	25.7	8.1	74.4	13.6	40.1	29.7	14.2	97.6
26	6.9	30.6	26.0	6.6	70.1	8.8	32.7	22.2	13.6	77.3
		Waurika					Summit			
1	7.7	61.7	15.6	6.6	91.6	7.9	49.6	31.4	11.9	100
4	8.4	62.5	16.0	7.4	94.3	6.2	37.8	33.3	12.2	89.5
8	9.3	68.3	22.1	10.8	110	7.9	43.4	44.8	16.2	112
12	5.6	58.2	17.4	6.3	87.5	6.4	41.0	41.7	16.8	106
26	5.2	55.1	22.0	8.5	90.8	3.0	31.5	38.4	15.7	88.6
		Bowie					Cobb			
1	0.0	44.5	17.7	7.8	70.0	14.7	47.9	18.4	8.3	89.3
4	1.2	60.8	19.7	7.8	89.5	11.7	48.9	17.2	12.5	90.3
8	6.9	44.6	19.0	11.4	81.9	7.9	47.1	17.1	10.6	82.7
12	5.6	44.0	24.8	9.4	83.8	9.3	45.9	20.5	10.5	86.2
26	4.7	33.3	23.6	8.6	70.2	7.2	44.9	17.9	12.7	82.7
		Port					Brewer			
1	19.9	49.9	16.8	8.7	95.3	15.3	56.9	21.4	14.0	108
4	14.7	43.2	18.0	7.0	82.9	13.8	54.6	20.6	9.0	98.0
8	22.4	48.6	12.9	12.1	96.0	12.6	50.9	23.6	11.0	98.1
12	18.4	51.8	21.1	9.7	101	13.1	58.9	23.7	19.0	115
26	16.9	40.5	17.7	12.3	87.4	9.2	29.0	21.1	11.0	70.3
		Hollister					Lela			
1	11.0	57.7	14.4	10.7	93.8	22.0	81.6	19.0	16.1	139
4	12.0	58.4	20.9	9.7	101	1.0	37.6	8.0	5.8	52.4
8	15.4	64.6	9.1	13.7	102	7.3	40.6	30.0	12.1	90.0
12	13.8	62.0	13.0	8.0	96.8	19.5	81.6	32.0	21.1	154
26	10.0	56.5	18.7	12.7	97.9	7.3	40.6	30.0	12.1	90.0

TABLE VI (Continued)

Weeks After Application	Form of P Extracted (ppm)									
	NH_4Cl-P	Al-P	Fe-P	Ca-P	Sum	NH_4Cl-P	Al-P	Fe-P	Ca-P	Sum
			Pratt				Osage			
1	34.8	30.5	6.2	9.0	80.5	11.8	51.9	35.7	18.2	118
4	35.9	32.0	7.4	18.0	93.3	9.1	62.0	40.4	13.6	125
8	36.3	31.6	10.4	17.0	95.3	11.1	67.6	45.7	19.8	144
12	34.6	29.0	6.7	15.0	85.3	13.2	87.5	25.1	26.0	152
26	32.8	33.6	10.3	9.0	85.7	5.0	69.8	36.0	18.7	130
			Norge				San Saba			
1	18.0	49.1	26.1	11.7	104	18.4	42.0	3.3	47.0	111
4	10.4	45.1	25.3	9.6	90.4	17.6	53.0	8.6	54.0	133
8	6.7	45.7	22.9	11.4	86.7	22.0	96.0	11.7	72.0	202
12	12.6	51.0	31.9	12.8	108	15.2	48.0	9.3	51.0	123
26	6.9	31.9	26.0	7.9	72.7	13.1	57.0	10.8	59.0	140
			Carey				Tipton			
1	12.5	48.5	11.5	6.4	78.9	48.4	23.3	4.4	20.0	96.1
4	17.7	56.0	16.5	10.7	100	39.0	23.3	3.1	23.0	88.4
8	12.3	57.9	13.8	6.1	90.1	41.4	19.2	3.5	32.0	96.1
12	14.3	57.6	15.3	7.0	94.2	41.8	25.4	5.6	39.0	112
26	8.3	49.9	14.6	0.4	73.2	37.5	22.3	4.2	30.0	94.0
			St. Paul				Foard			
1	29.5	23.5	3.9	-1.0	55.9	32.5	38.2	11.5	11.0	93.2
4	11.7	29.1	8.2	9.0	58.0	30.8	47.0	14.0	15.1	107
8	30.9	28.9	7.7	4.0	71.5	24.3	42.6	17.3	16.0	100
12	27.4	31.9	9.4	9.0	77.7	24.1	43.1	14.2	21.2	103
26	21.0	27.2	10.8	10.0	69.0	20.7	41.4	10.3	27.1	99.5
			Canadian				Ulysses			
1	40.3	29.7	6.9	15.0	91.9	29.2	41.8	6.8	33.0	111
4	35.0	29.2	7.3	10.0	81.5	32.8	49.9	8.2	25.0	116
8	30.9	29.0	6.0	18.0	83.9	30.1	48.7	9.3	40.0	128
12	33.7	30.6	5.2	14.0	83.5	31.3	53.1	13.7	29.0	127
26	29.3	28.1	5.4	14.0	76.8	15.9	37.7	9.4	20.0	83.0
			Miller							
1	41.9	49.6	2.9	24.0	118					
4	25.4	38.1	4.2	23.0	90.7					
8	27.0	46.4	5.4	47.0	125					
12	18.3	36.2	5.2	30.0	89.7					
26	20.7	44.9	5.5	41.0	112					

(1961) reported both a lack of recovery and excess recovery of applied phosphorus. In a later study Volk and McLean (1963) used ^{32}P and found that fertilizer phosphorus did indeed have an effect on native phosphorus. The studies by Lindsay, et al. (1959) which demonstrated solubilization of Fe and Al compounds by the triple point solution (reaction of concentrated superphosphate with water to form the system $CaO\text{-}H_2O\text{-}P_2O_5$) is well known. Further work by MacKenzie and Cambell (1963) showed that the triple point solution could act on silicate clays, causing decreases in Al and Fe in the clay minerals. In the present study the relatively low fertilization rates may tend to rule out the solubilization of native Al- and Fe-P in amounts necessary to account for more than a few ppm. Excess recovery of more than five or six ppm should not be entirely discounted, however.

In the present study a significant amount of the variation in P recovered is probably due to random fluctuation. However, trends can be observed in some of the soils, particularly when observing lack of recovery of added P. Three of the soils which fix large amounts of P, Parsons, Bates and Bowie, exhibit a marked lack of recovery of applied P on all sampling dates. In Parsons this P might be some form of Fe-P not soluble in NaOH or H_2SO_4. Occluded-P was not determined in this study since it was thought the formation of such P would take a longer period of time. However, the lack of recovery of P from Parsons and other soils, particularly those having high P fixing capacities, may indicate formation of occluded-P. It should also be noted that lack of recovery occurred at six months in several of the soils in addition to those mentioned above. Cobb, Brewer, Norge, Carey, Canadian, and Ulysses exhibit a lack of recovery of applied P at six months. Due to the variation in P removed from these and other soils the data in Table VI is far from conclusive. However, the possibility of formation of occluded-P or some other unknown form of P not soluble in the extracting reagents does exist.

The Yield of Sorghum-Sudan

The yields of sorghum-sudan vs P application rate for each of the three crops are given in Table VII. The increase in yield with added P are obvious, the responses being functions of the properties of the individual soils. In many soils a reduction in yield occurred by the second or third crop, probably due to depletion of readily available P. Some soils exhibit an increased yield of the second or third crop over previous crops.

Crop Removal of Phosphorus and Changes in Phosphorus Fractions as a Function of Time

Figures 1-25 are plots of the amounts of NH_4Cl-P, Al-P, Fe-P and Ca-P measured vs. time for both the cropped and noncropped soils. The soils were sampled at the beginning of each crop and after the third crop. The noncropped soils were also sampled at the end of six months. These sampling dates correspond to one, four, eight, twelve, and twenty-six weeks after the application of P. It was not possible to sample both the cropped and noncropped soils on the same day. Thus there are differences in the amounts of P extracted from some of the cropped and noncropped soils on the first sampling date.

A discussion of each group of soils follows.

TABLE VII

THE YIELD OF SORGHUM SUDAN

		Grams of Forage Harvest No.						Grams of Forage Harvest No.			
Soil	ppm P Applied	1	2	3	Sum	Soil	ppm P Applied	1	2	3	Sum
Bowie	0	0.6	1.4	0.5	2.5	Pratt	0	2.9	3.8	6.2	12.9
	7.5	1.6	1.0	0.3	2.9		7.5	3.6	4.2	8.8	16.6
	15	2.7	0.8	0.4	3.9		15	4.2	5.5	9.0	18.7
	30	4.9	1.5	1.8	8.2		30	5.5	7.4	8.9	21.8
	60	6.5	2.4	5.3	14.2		60	7.1	7.1	9.0	23.2
	90	8.7	4.2	5.5	18.4		90	8.0	7.2	9.1	24.3
	120	7.9	5.3	5.7	18.9		120	8.1	8.8	8.1	25.0
Bates	0	0.7	2.4	2.6	5.7	Canadian	0	1.5	1.9	2.5	5.9
	7.5	1.7	3.1	3.0	7.8		7.5	2.6	2.4	2.9	7.9
	15	3.2	3.1	3.9	10.2		15	3.0	3.1	3.3	9.4
	30	5.6	4.1	5.2	14.9		30	4.6	3.6	4.2	12.4
	60	8.6	5.5	4.8	18.9		60	5.9	4.6	6.3	16.8
	90	9.3	6.2	5.1	20.6		90	7.8	5.5	6.1	19.4
	120	10.5	8.0	5.7	24.2		120	7.8	5.9	5.9	19.6
Cobb	0	0.5	3.0	2.3	5.8	Tipton	0	2.3	5.4	9.4	17.1
	7.5	1.6	2.7	2.2	6.5		7.5	2.7	5.8	9.1	17.6
	15	2.1	3.0	3.5	8.6		15	3.1	5.5	7.5	16.1
	30	4.0	4.8	5.3	14.1		30	4.2	6.7	6.5	17.4
	60	6.1	7.1	5.1	18.3		60	6.1	7.3	6.4	19.8
	90	8.9	7.2	4.5	20.6		90	6.9	7.9	5.9	20.7
	120	7.9	8.7	4.9	21.5		120	7.3	8.9	6.0	22.2
	0	5.7	5.9	7.1	18.7		0	0.5	1.1	0.5	2.1
	7.5	7.4	7.4	6.1	20.9		7.5	0.9	3.0	1.3	5.2

TABLE VII (Continued)

		Grams of Forage						Grams of Forage			
	ppm P	Harvest No.					ppm P	Harvest No.			
Soil	Applied	1	2	3	Sum	Soil	Applied	1	2	3	Sum
	15	7.3	6.8	6.5	20.6		15	1.4	3.8	1.8	7.0
Dill	30	8.1	8.4	6.7	23.2	Parsons	30	2.3	4.6	3.6	10.5
	60	8.6	7.9	7.0	23.5		60	4.9	5.7	5.1	15.7
	90	10.1	9.4	6.8	26.3		90	5.7	6.8	5.1	17.6
	120	10.5	9.2	7.0	26.7		120	6.9	8.5	5.0	20.4
	0	2.6	3.2	4.2	10.0		0	2.7	6.4	4.2	13.3
	7.5	3.0	3.5	4.2	10.7		7.5	6.1	5.6	4.4	16.1
	15	3.5	3.8	5.5	12.8		15	6.0	5.5	4.6	16.1
St. Paul	30	5.5	5.3	6.3	17.1	Kirkland	30	7.6	7.8	4.6	20.0
	60	6.1	5.0	6.3	17.4		60	8.2	8.0	5.9	22.1
	90	7.4	7.9	5.7	21.0		90	9.9	7.7	6.3	23.9
	120	7.6	8.4	5.8	21.8		120	10.2	10.3	6.1	26.6
	0	1.0	2.3	3.1	6.5		0	6.3	6.8	3.4	16.5
	7.5	2.0	2.8	4.2	9.0		7.5	7.1	6.5	3.5	17.1
	15	3.1	3.0	4.9	11.0		15	7.1	6.9	4.2	18.2
Summit	30	6.1	4.1	6.2	16.4	Port	30	8.1	7.8	4.3	20.2
	60	8.8	8.9	6.4	24.1		60	8.6	8.7	4.3	21.6
	90	10.4	10.3	6.5	27.2		90	9.0	9.7	5.3	24.0
	120	9.3	11.1	6.0	26.4		120	9.5	8.9	5.0	23.4
	0	0.7	2.6	0.7	4.0		0	2.2	5.3	5.1	12.6
	7.5	1.8	3.2	0.9	5.9		7.5	3.3	4.2	5.7	13.2
	15	3.1	3.2	1.2	7.5		15	5.2	4.3	6.4	15.9
Carey	30	4.6	4.2	3.0	11.8	Waurika	30	6.4	5.6	6.1	18.1
	60	7.4	7.2	5.5	20.1		60	8.5	8.5	5.7	22.7

TABLE VII (Continued)

		Grams of Forage						Grams of Forage			
	ppm P	Harvest No.					ppm P	Harvest No.			
Soil	Applied	1	2	3	Sum	Soil	Applied	1	2	3	Sum
	90	9.0	8.8	6.0	23.8		90	9.2	10.9	5.6	25.7
	120	8.9	10.3	5.8	25.0		120	10.4	11.0	5.3	26.7
Renfrow	0	6.4	3.8	7.0	17.2	Hollister	0	3.8	4.5	5.0	13.3
	7.5	7.4	4.3	7.5	19.2		7.5	5.2	5.1	7.2	17.5
	15	7.7	7.1	6.9	21.7		15	5.9	5.3	6.9	18.1
	30	8.6	7.4	7.7	23.7		30	7.3	8.2	6.5	22.0
	60	10.8	8.1	7.5	26.4		60	9.2	7.9	6.8	23.9
	90	11.6	10.7	7.8	30.1		90	9.8	9.4	6.2	25.4
	120	10.9	10.2	8.2	29.3		120	10.5	9.4	6.4	26.3
Kingfisher	0	1.5	4.5	4.0	10.0	Osage	0	2.9	7.9	3.9	14.7
	7.5	3.3	5.9	3.9	13.1		7.5	3.9	7.8	3.7	15.4
	15	5.8	6.6	5.0	17.4		15	4.2	9.4	3.4	17.0
	30	8.5	8.7	5.6	22.8		30	6.5	8.1	3.4	18.0
	60	8.9	11.9	7.5	28.3		60	8.6	7.7	3.8	20.1
	90	10.3	12.4	7.2	29.9		90	9.6	7.9	4.7	22.2
	120	10.7	12.8	7.5	31.0		120	10.4	7.4	4.4	22.2
Norge	0	0.5	1.1	0.6	2.2	Brewer	0	6.8	4.4	7.8	19.0
	7.5	1.1	1.9	0.7	3.7		7.5	7.0	4.7	8.1	19.8
	15	1.8	2.9	1.4	6.1		15	6.9	6.3	6.1	19.3
	30	3.5	4.4	2.4	10.3		30	7.3	5.8	6.0	19.1
	60	7.4	6.5	3.4	17.3		60	8.5	6.7	6.0	21.2
	90	8.8	7.4	4.4	20.6		90	9.5	6.8	5.3	21.6
	120	9.6	7.6	5.6	22.8		120	9.7	8.9	5.1	23.7

TABLE VII (Continued)

		Grams of Forage						Grams of Forage			
	ppm P	Harvest No.					ppm P	Harvest No.			
Soil	Applied	1	2	3	Sum	Soil	Applied	1	2	3	Sum
Lela	0	7.7	12.1	5.8	25.6	Foard	0	0.7	1.1	0.5	2.3
	7.5	9.5	13.0	6.3	28.8		7.5	2.0	1.4	0.8	4.2
	15	8.4	11.8	6.9	27.1		15	2.7	1.7	1.5	5.9
	30	8.9	12.2	6.3	27.4		30	4.7	2.0	2.3	10.0
	60	9.5	11.9	6.3	27.7		60	7.3	3.5	6.5	17.3
	90	10.7	11.9	6.1	28.7		90	8.7	5.2	6.7	20.6
	120	9.7	11.8	6.7	28.2		120	9.7	5.6	6.5	21.8
Ulysses	0	0.5	1.8	2.0	4.3	Miller	0	1.5	3.6	2.6	7.7
	7.5	0.9	2.2	2.3	5.4		7.5	3.3	3.0	2.1	8.4
	15	1.7	3.8	2.2	7.8		15	5.3	3.5	3.8	12.6
	30	3.6	3.5	4.0	11.1		30	7.8	2.6	4.0	14.4
	60	6.5	3.4	5.8	15.7		60	9.7	5.9	4.5	20.1
	90	7.1	4.4	5.3	16.8		90	10.4	7.6	4.7	22.7
	120	7.7	4.9	5.6	18.2		120	11.7	7.4	5.2	24.3
San Saba	0	4.0	7.1	5.6	16.7						
	7.5	4.7	5.3	4.7	14.7						
	15	5.0	6.4	6.2	17.6						
	30	6.0	7.3	6.2	19.5						
	60	6.9	6.3	6.8	20.0						
	90	7.9	8.0	6.3	22.2						
	120	8.5	7.6	6.0	22.1						

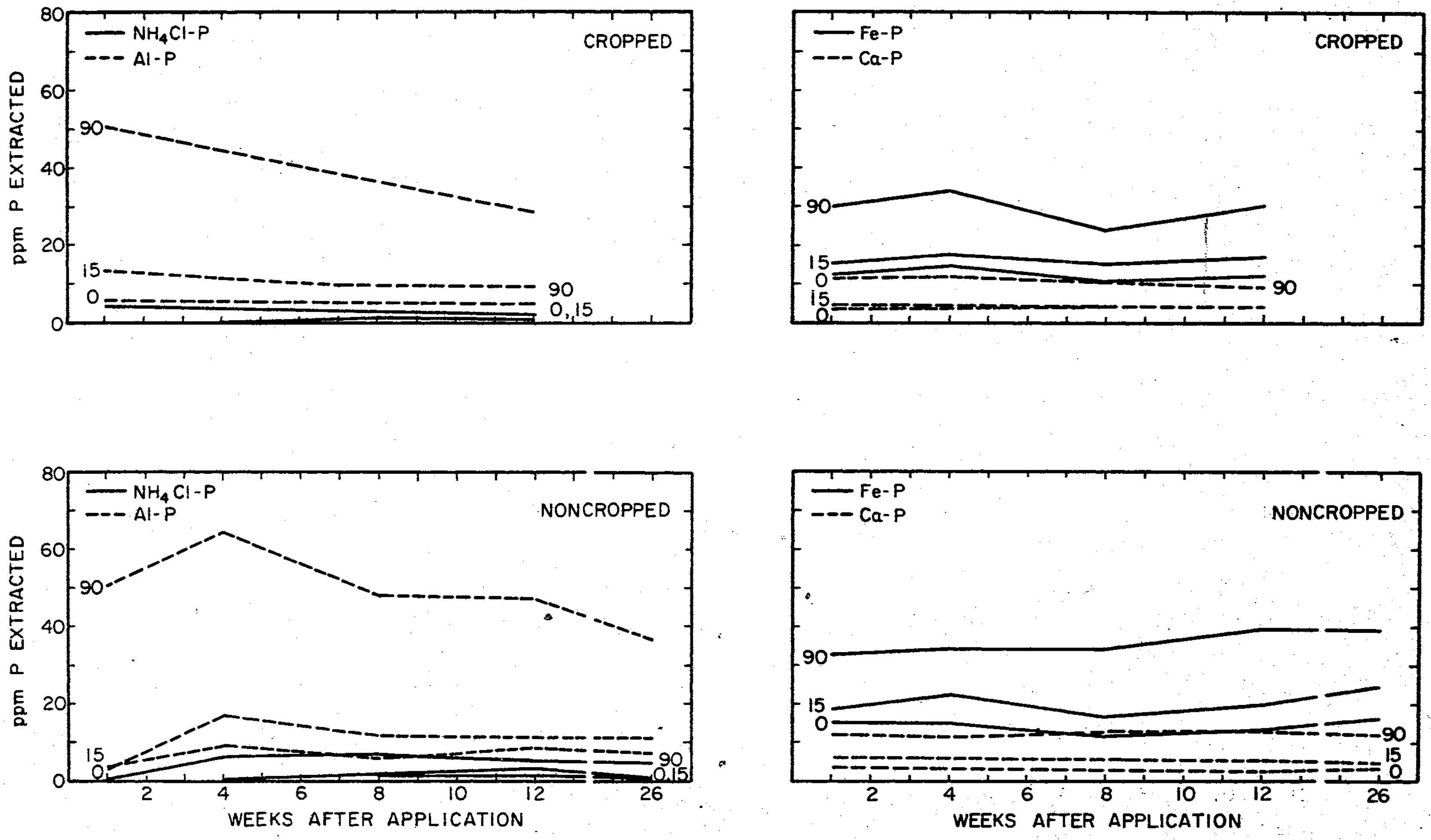

Figure 1. The Phosphate Fractions Removed from Bowie Sandy Loam as a Function of Time, Both Cropped and Noncropped.

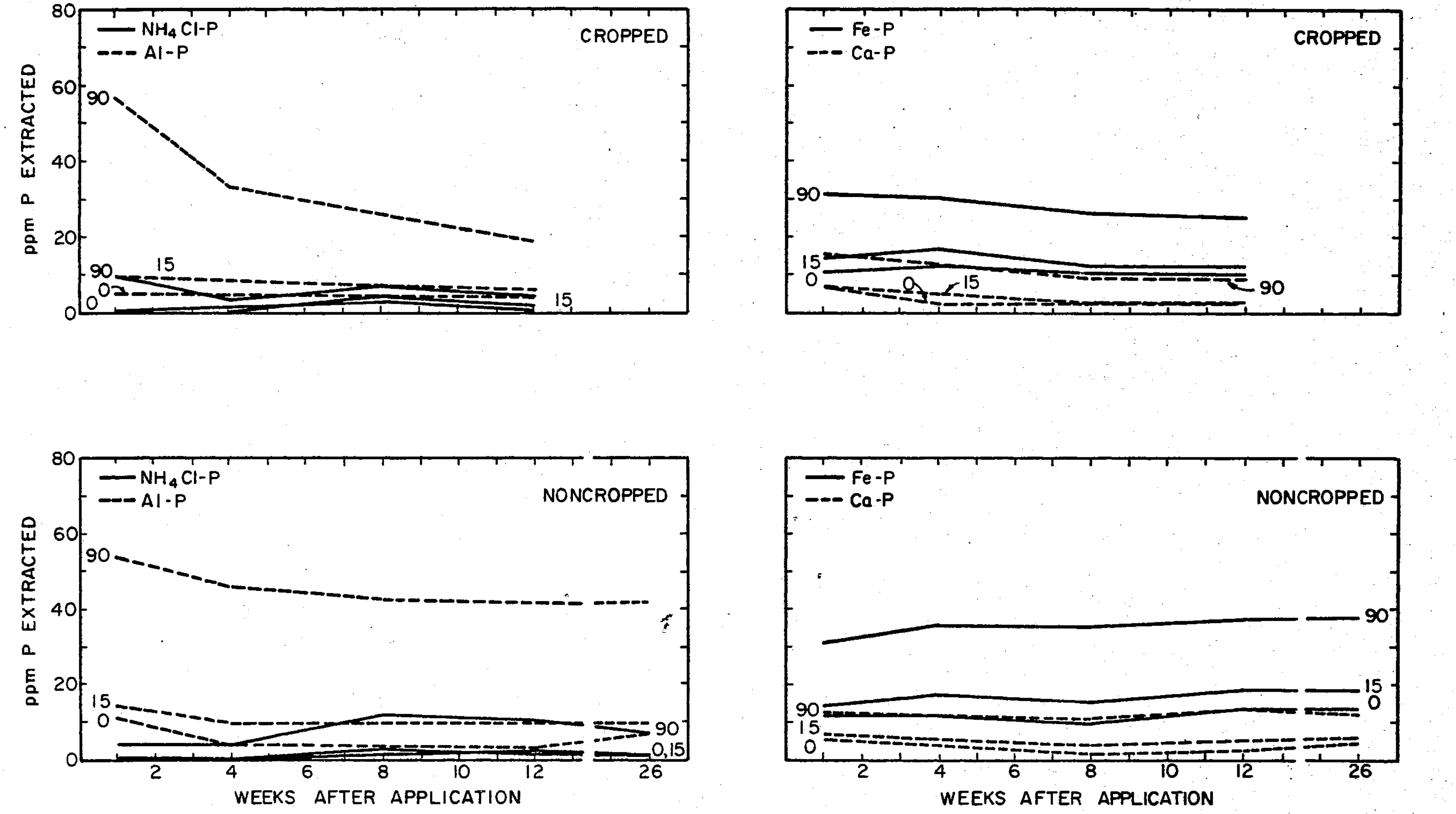

Figure 2. The Phosphate Fractions Removed from Bates Sandy Loam as a Function of Time, Both Cropped and Noncropped.

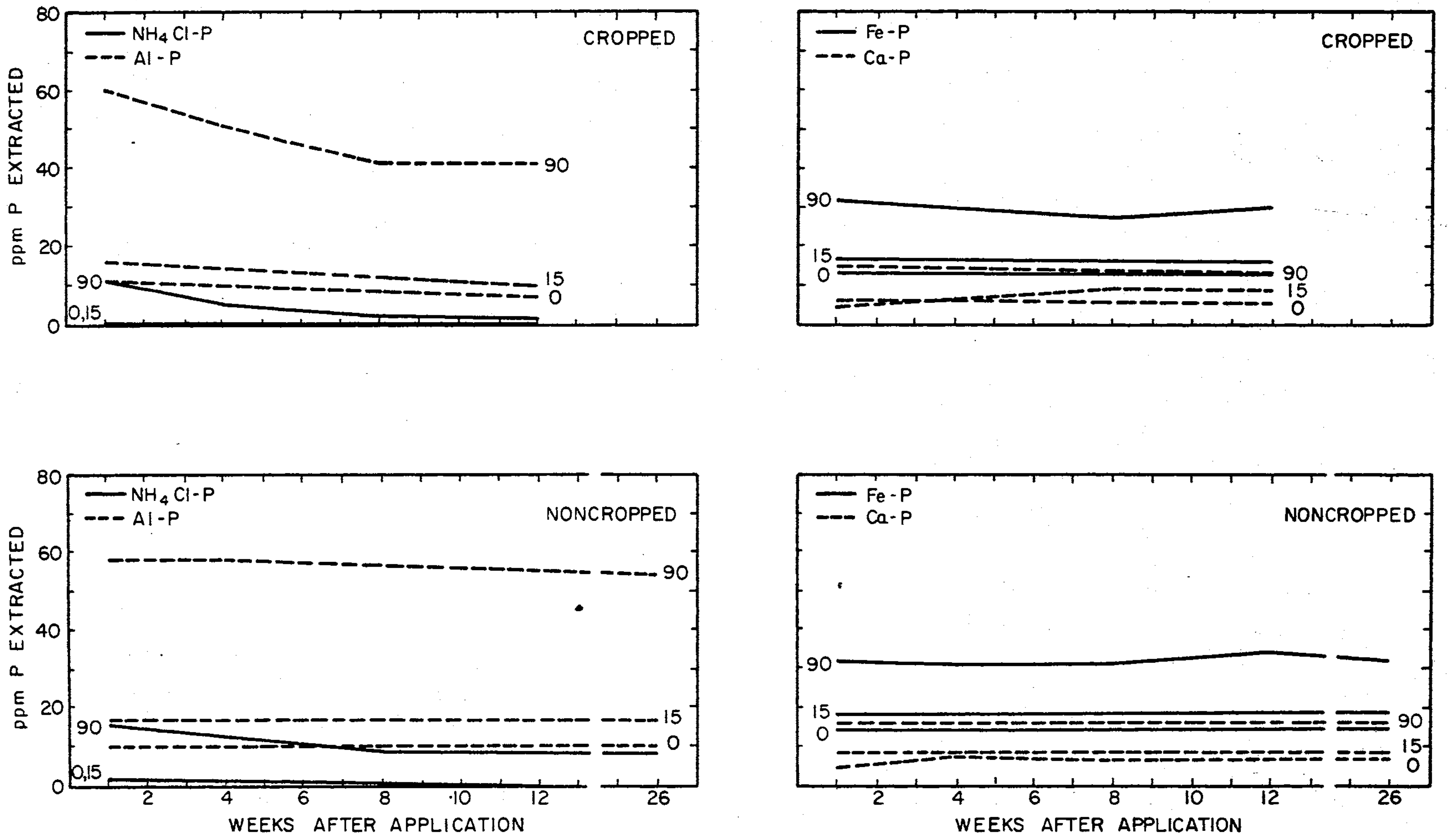

Figure 3. The Phosphate Fractions Removed from Cobb Sandy Loam as a Function of Time, Both Cropped and Noncropped.

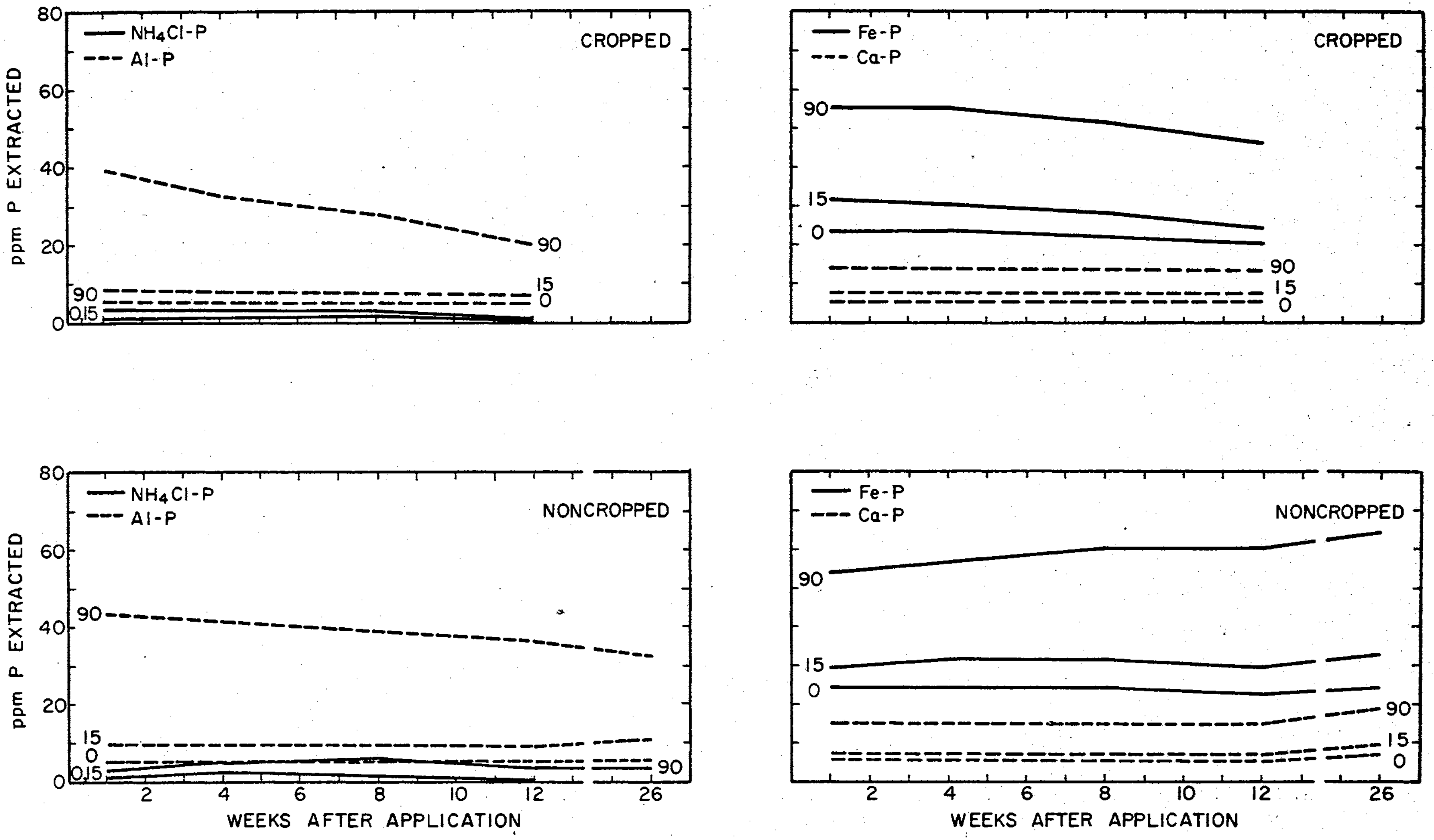

Figure 4. The Phosphate Fractions Removed from Parsons Silt Loam as a Function of Time, Both Cropped and Noncropped.

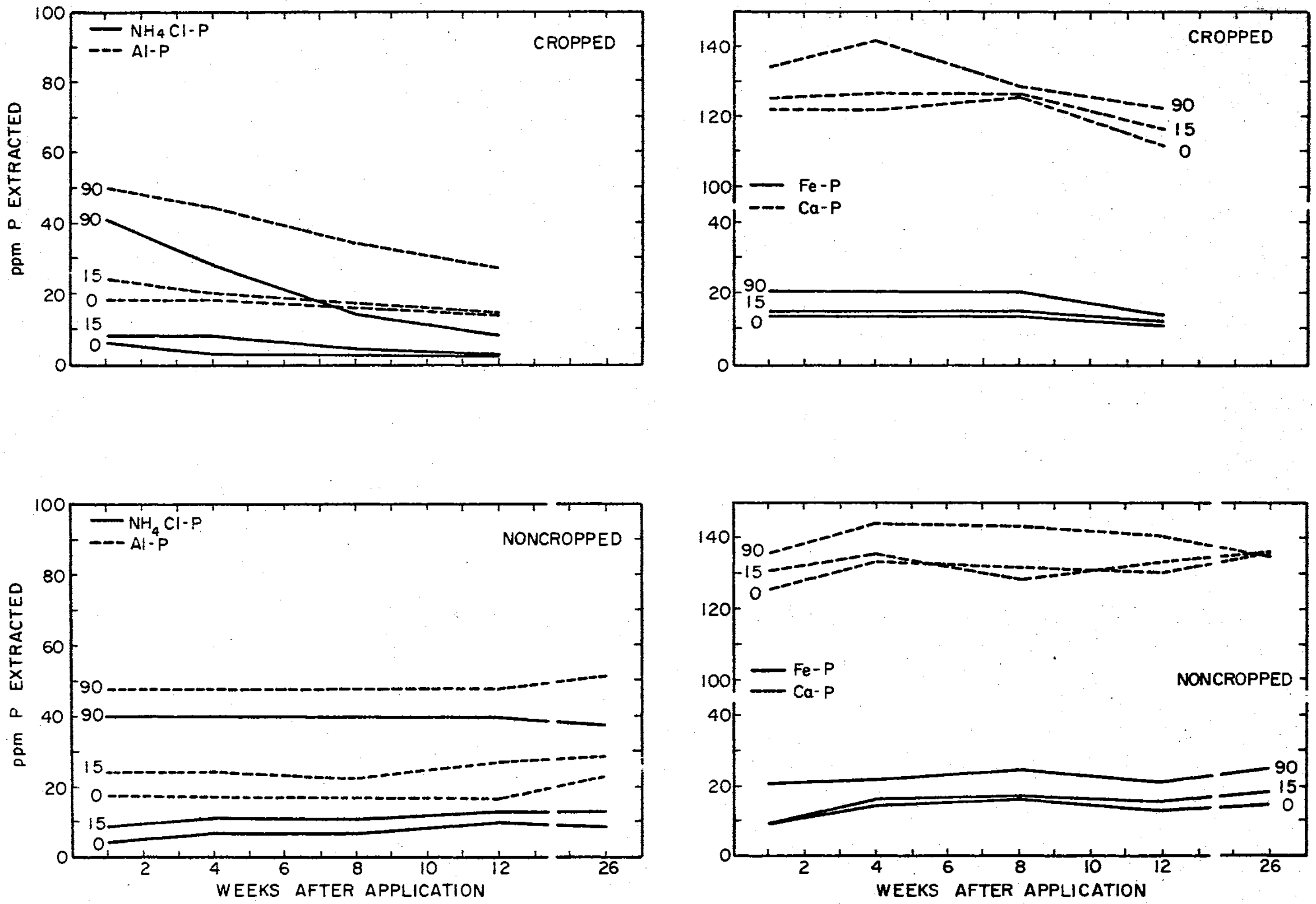

Figure 5. The Phosphate Fractions Removed from Pratt Sandy Loam as a Function of Time, Both Cropped and Noncropped.

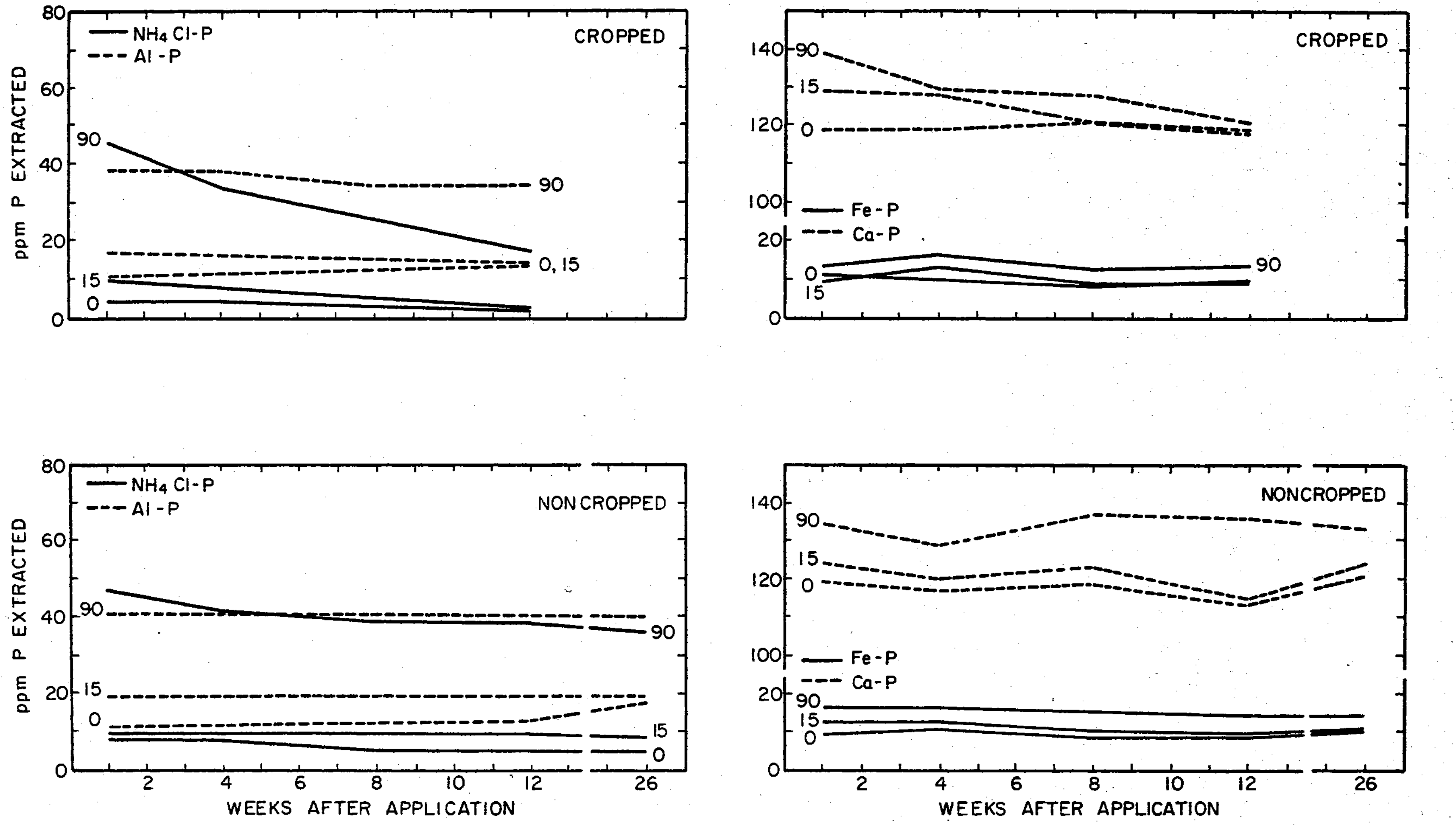

Figure 6. The Phosphate Fractions Removed from Canadian Sandy Loam as a Function of Time, Both Cropped and Noncropped.

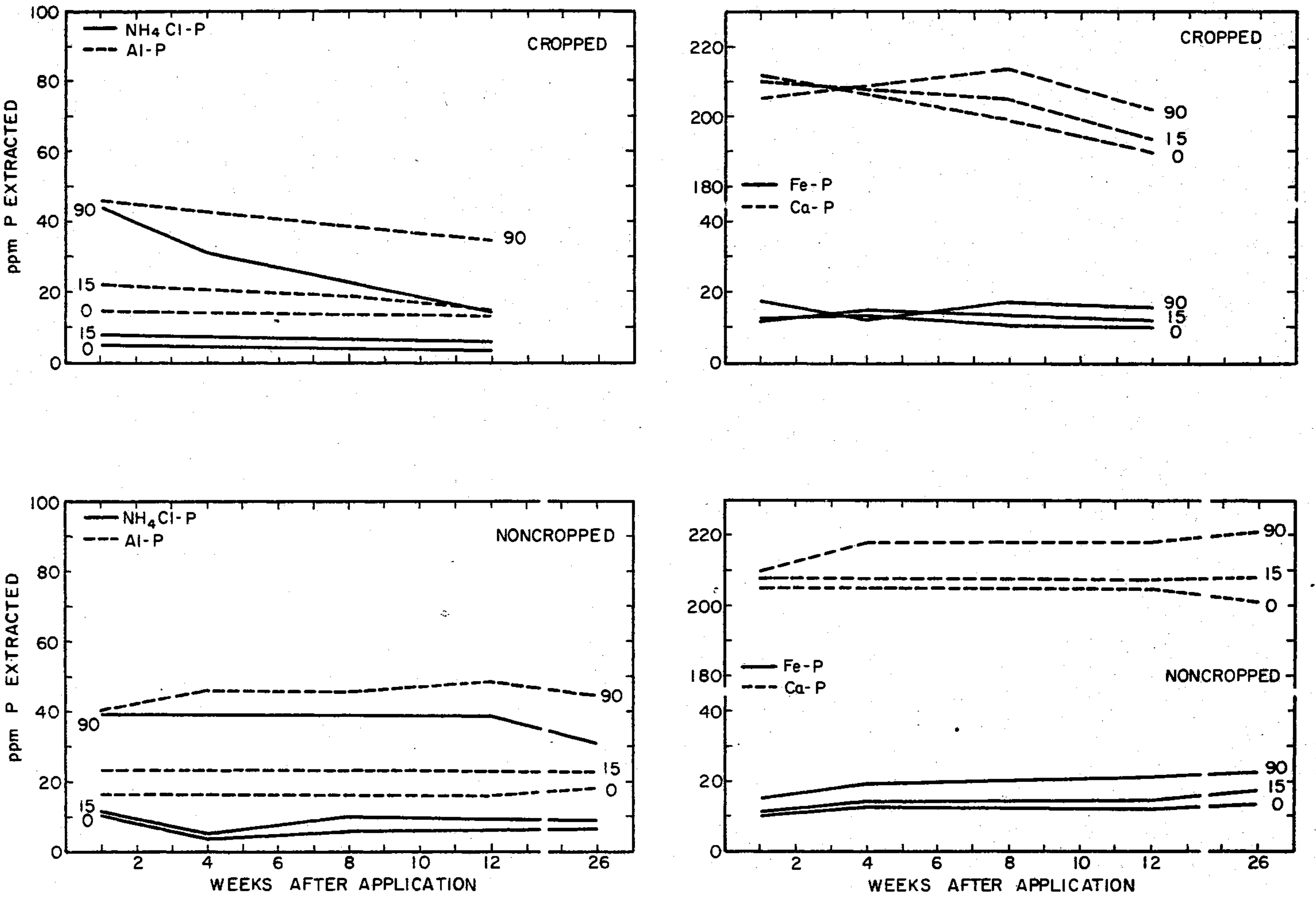

Figure 7. The Phosphate Fractions Removed from St. Paul Loam as a Function of Time, Both Cropped and Noncropped.

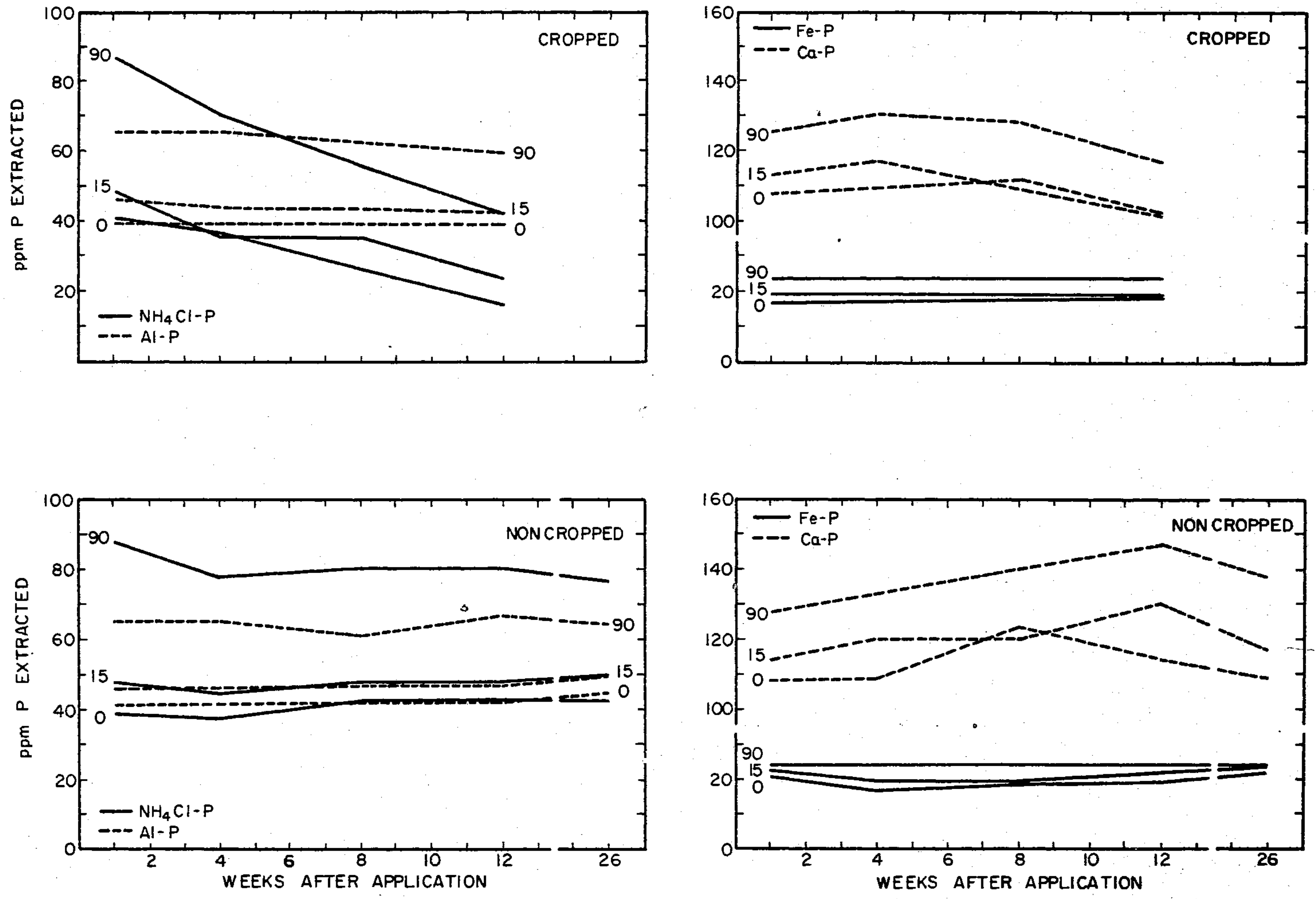

Figure 8. The Phosphate Fractions Removed from Tipton Loam as a Function of Time, Both Cropped and Noncropped.

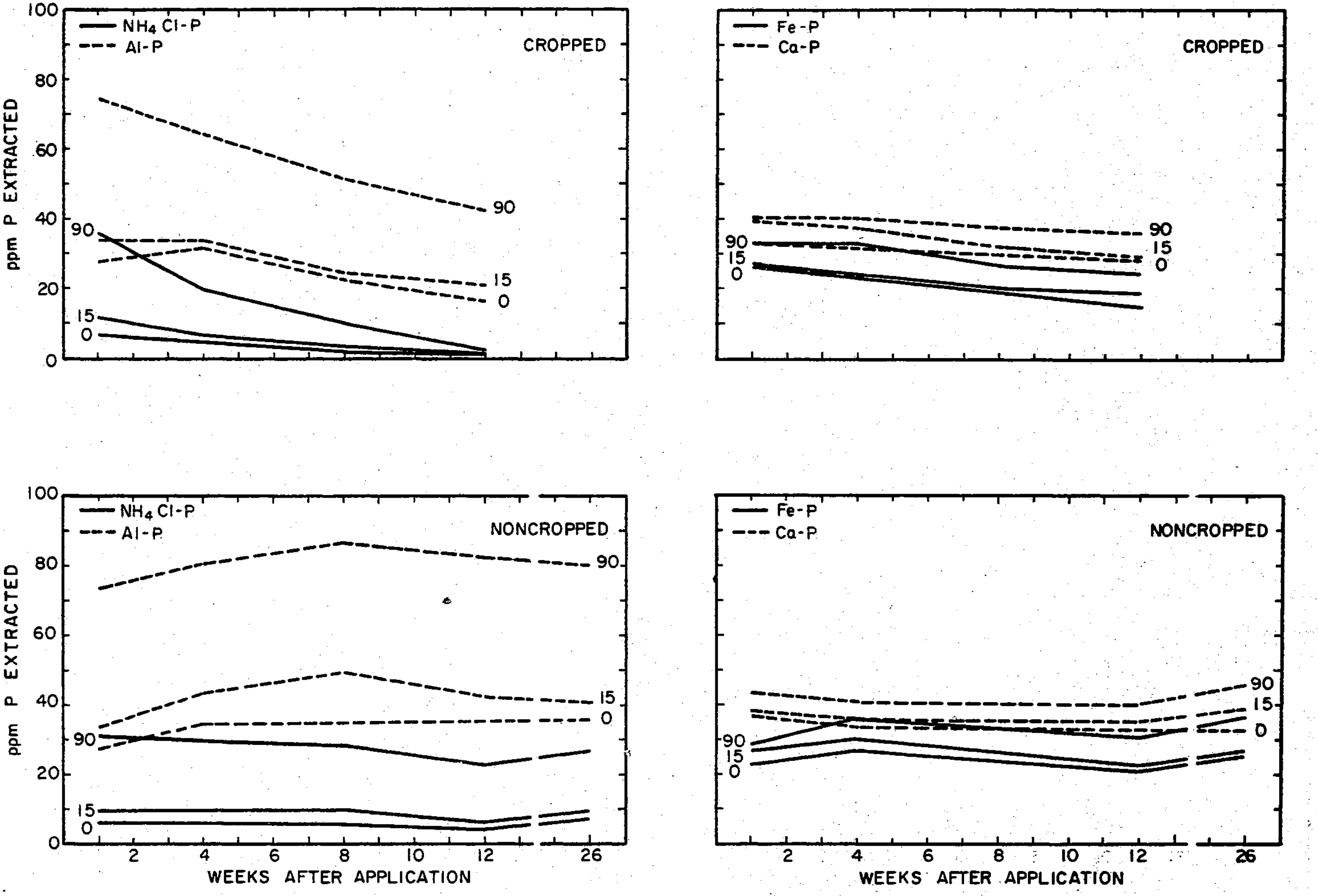

Figure 9. The Phosphate Fractions Removed from Dill Sandy Loam as a Function of Time, Both Cropped and Noncropped.

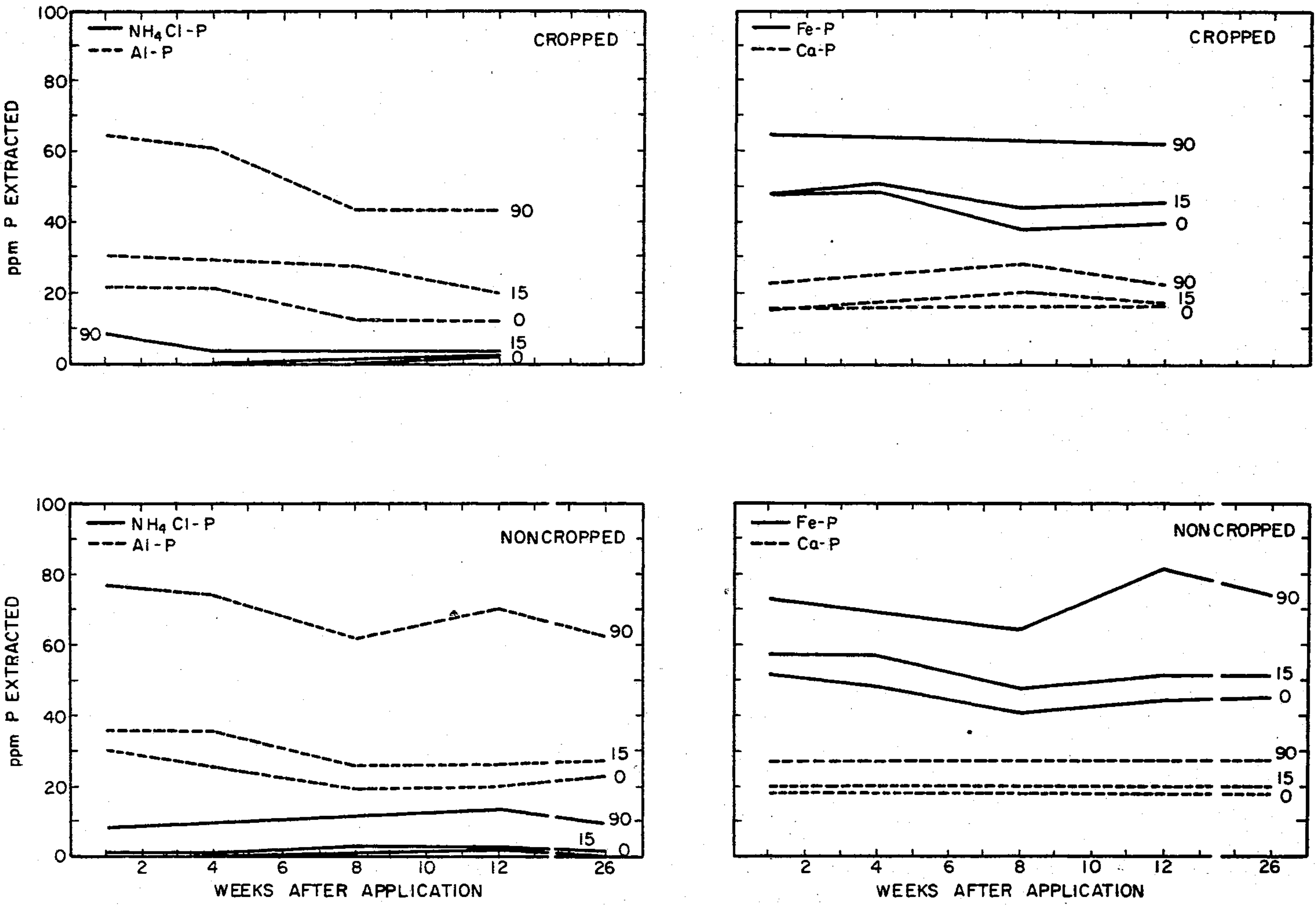

Figure 10. The Phosphate Fractions Removed from Kirkland Loam as a Function of Time, Both Cropped and Noncropped.

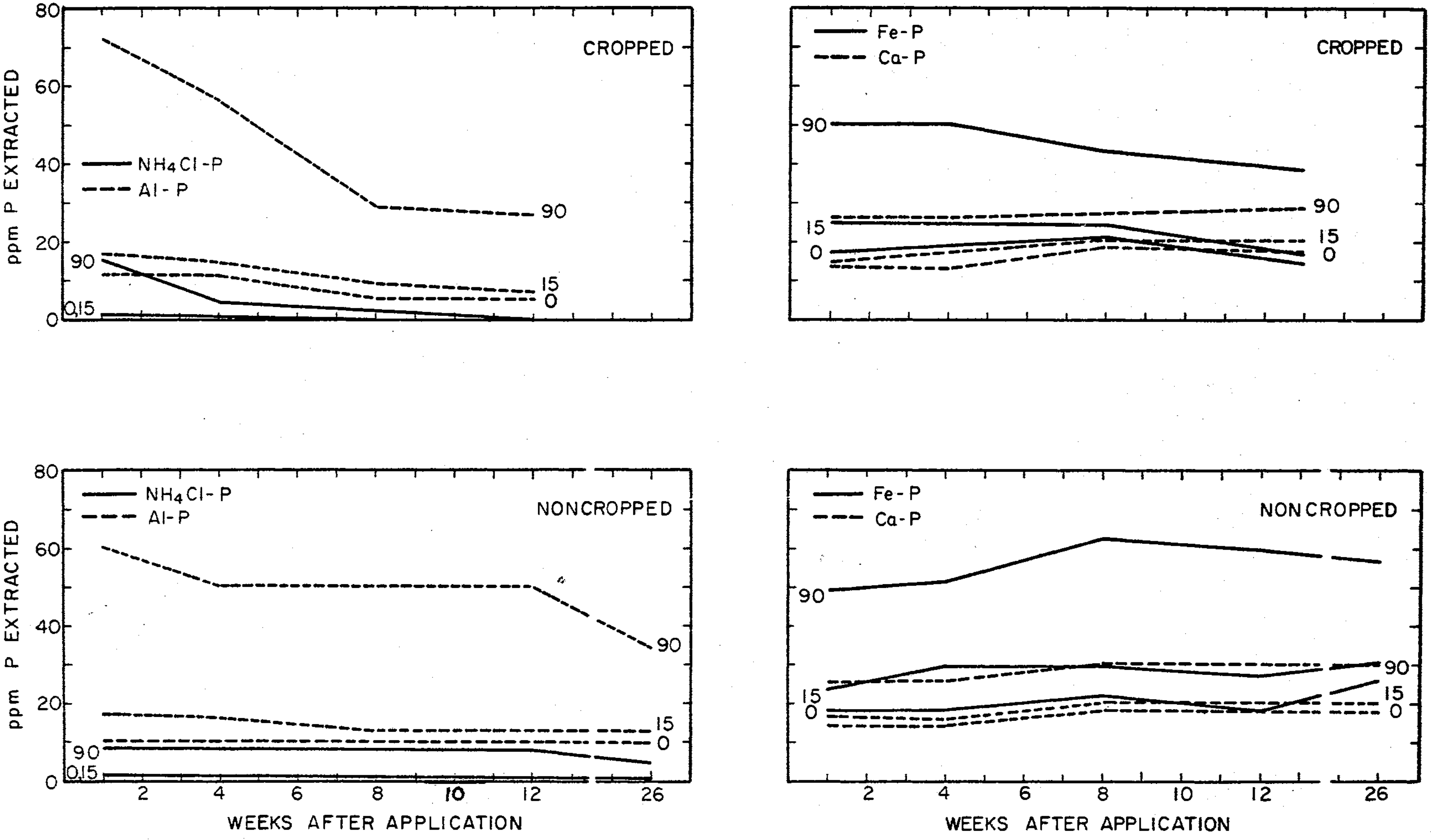

Figure 11. The Phosphate Fractions Removed from Summit Silt Loam as a Function of Time, Both Cropped and Noncropped.

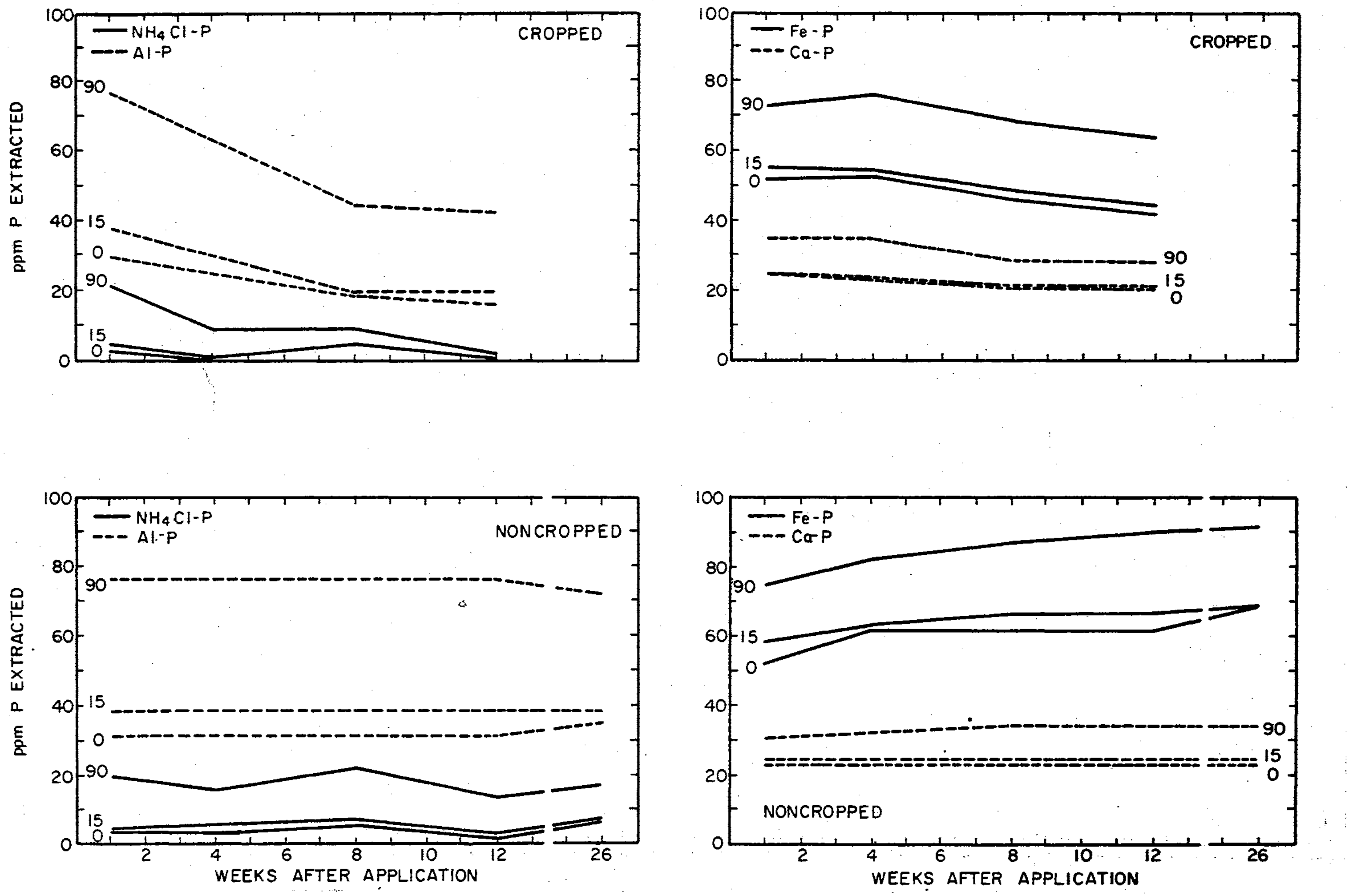

Figure 12. The Phosphate Fractions Removed from Renfrow Loam as a Function of Time, Both Cropped and Noncropped.

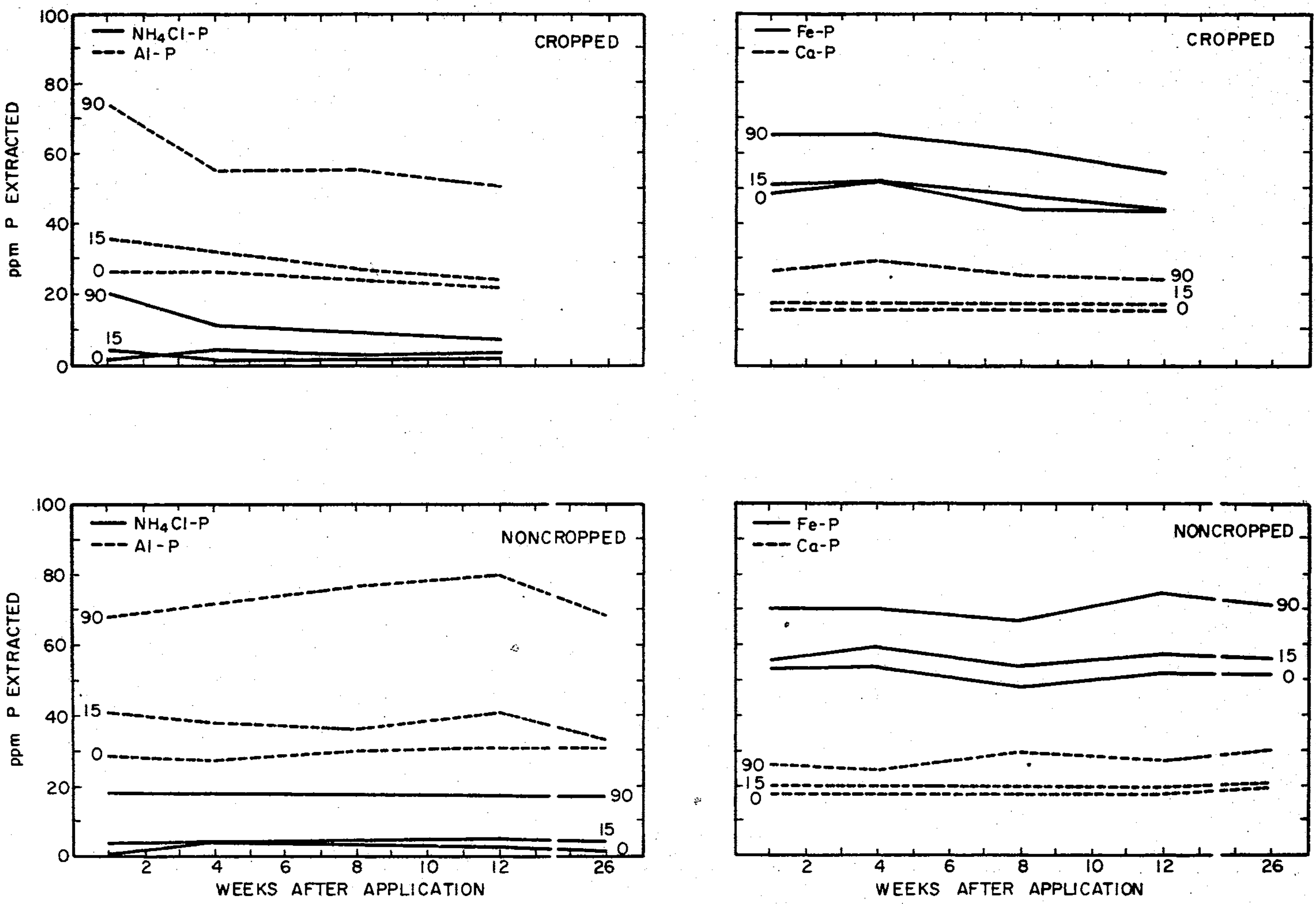

Figure 13. The Phosphate Fractions Removed from Port Loam as a Function of Time, Both Cropped and Noncropped.

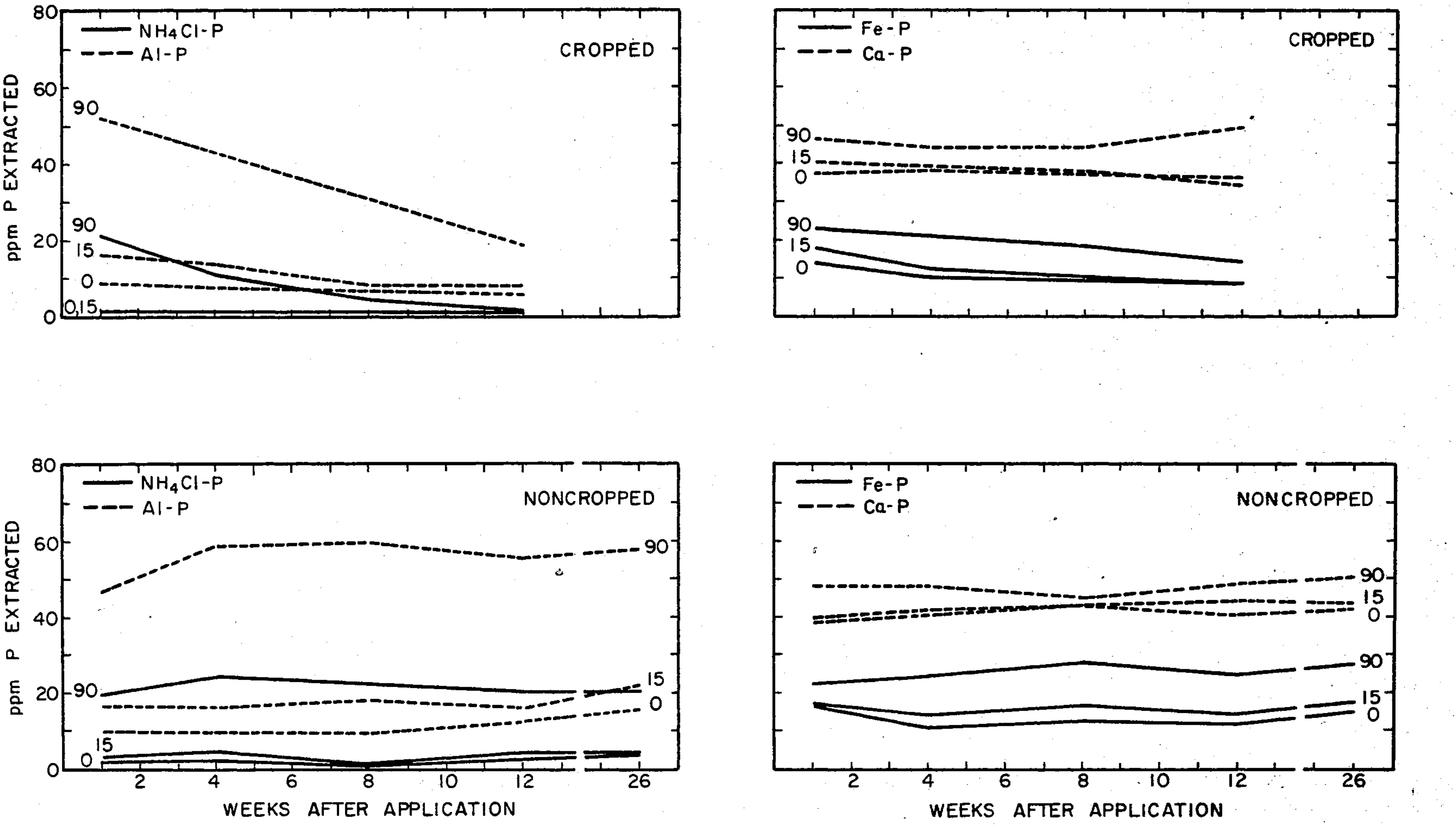

Figure 14. The Phosphate Fractions Removed from Kingfisher Silt Loam as a Function of Time, Both Cropped and Noncropped.

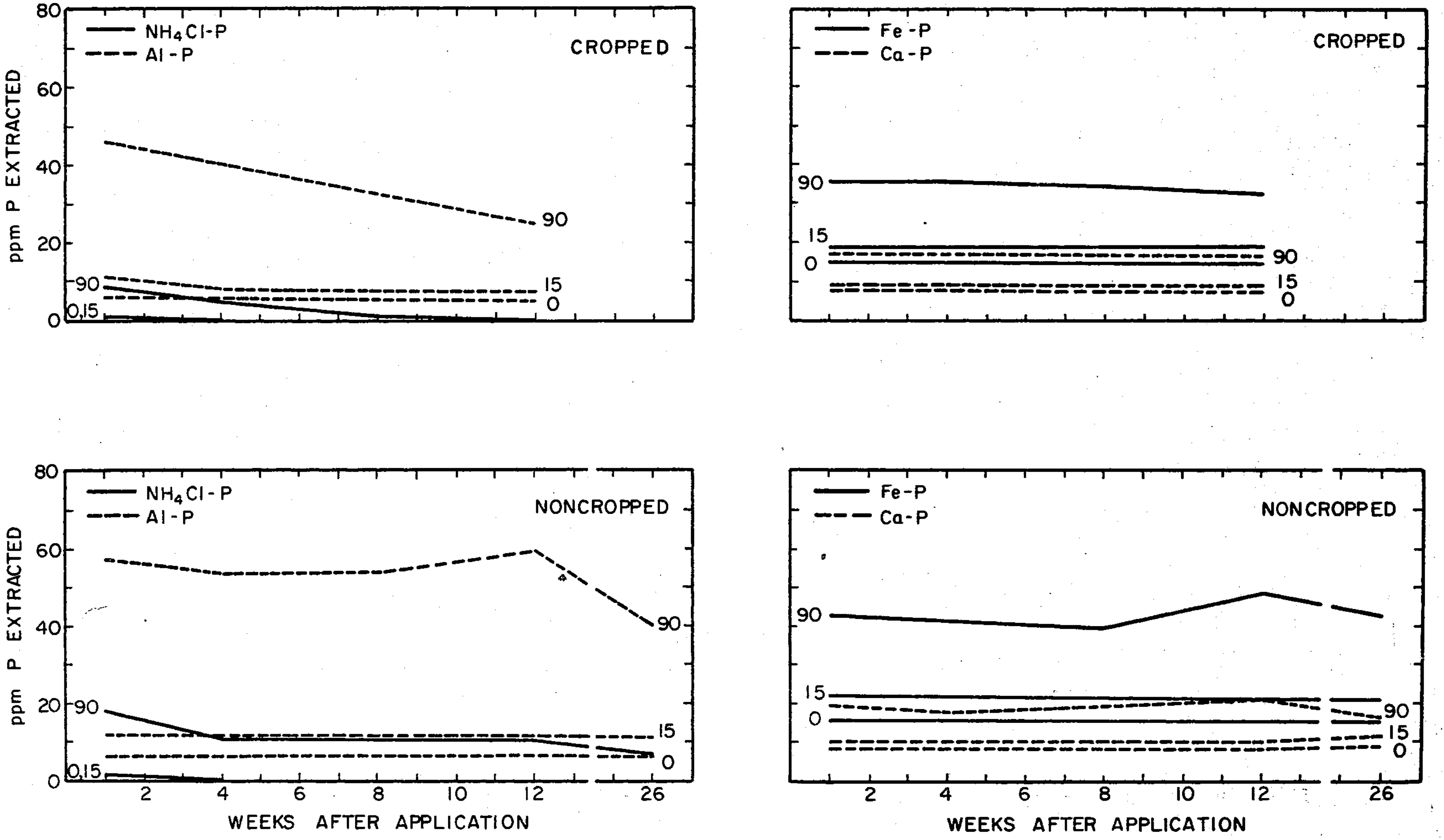

Figure 15. The Phosphate Fractions Removed from Norge Loam as a Function of Time, Both Cropped and Noncropped.

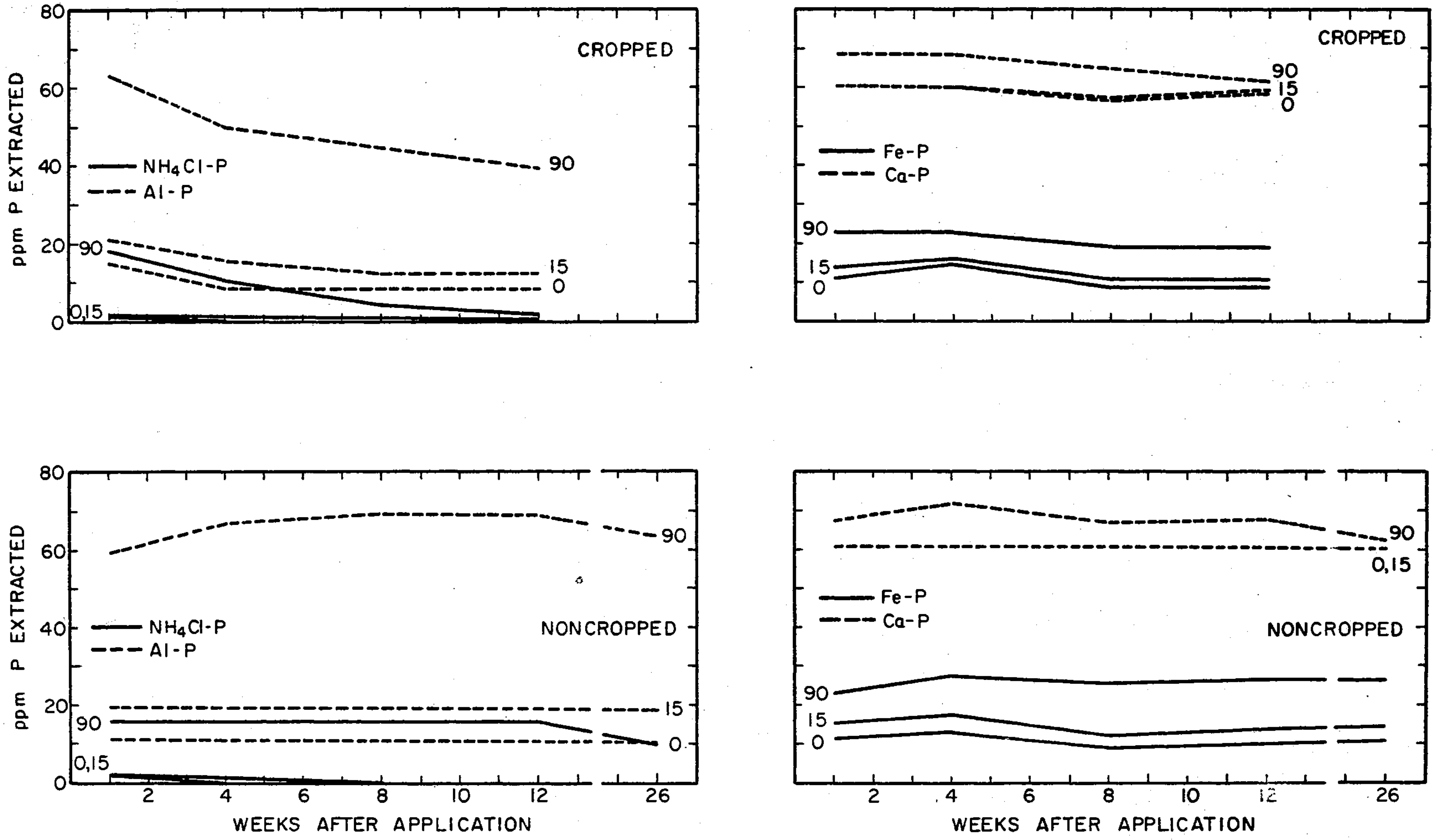

Figure 16. The Phosphate Fractions Removed from Carey Loam as a Function of Time, Both Cropped and Noncropped.

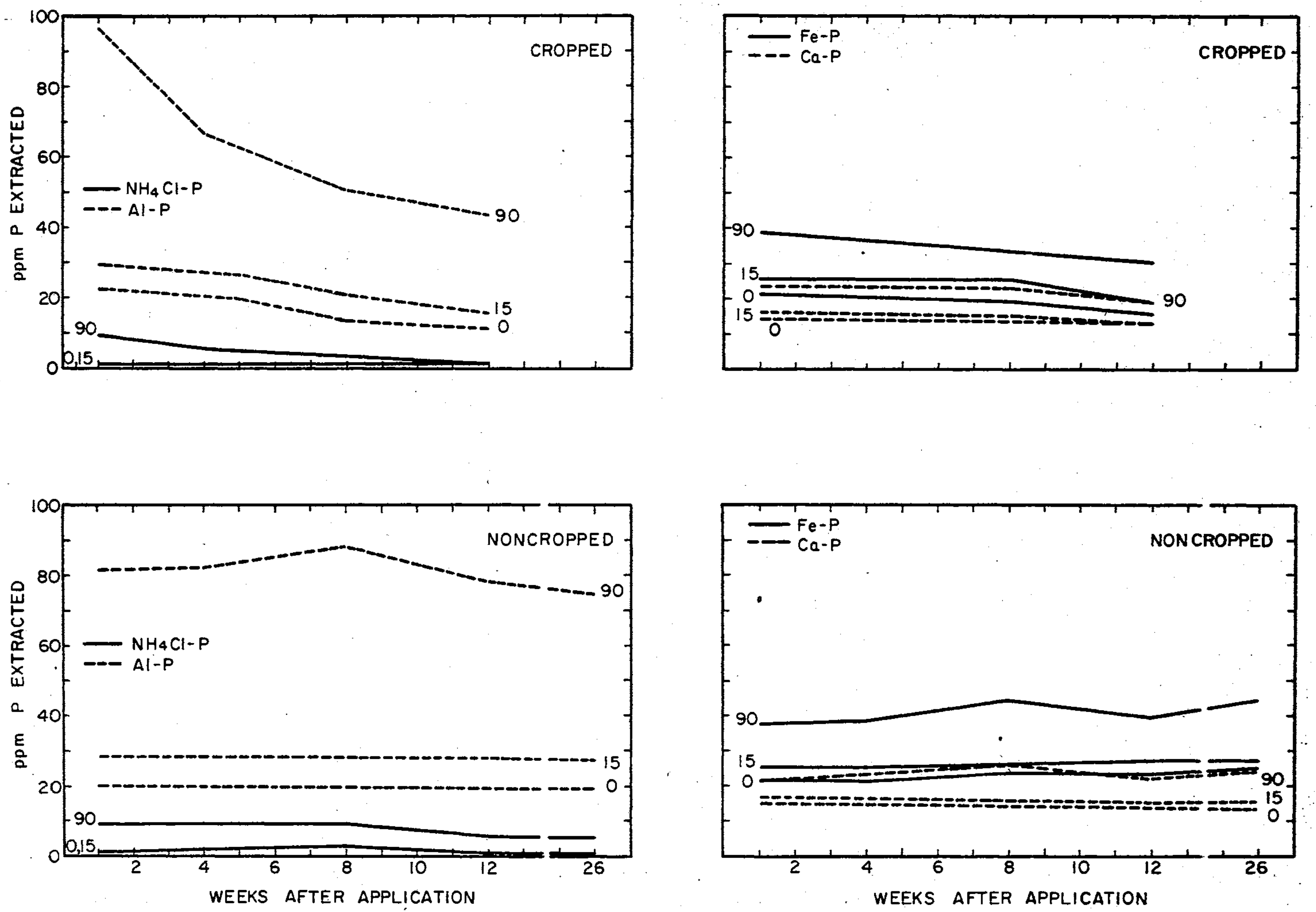

Figure 17. The Phosphate Fractions Removed from Waurika Silt Loam as a Function of Time, Both Cropped and Noncropped.

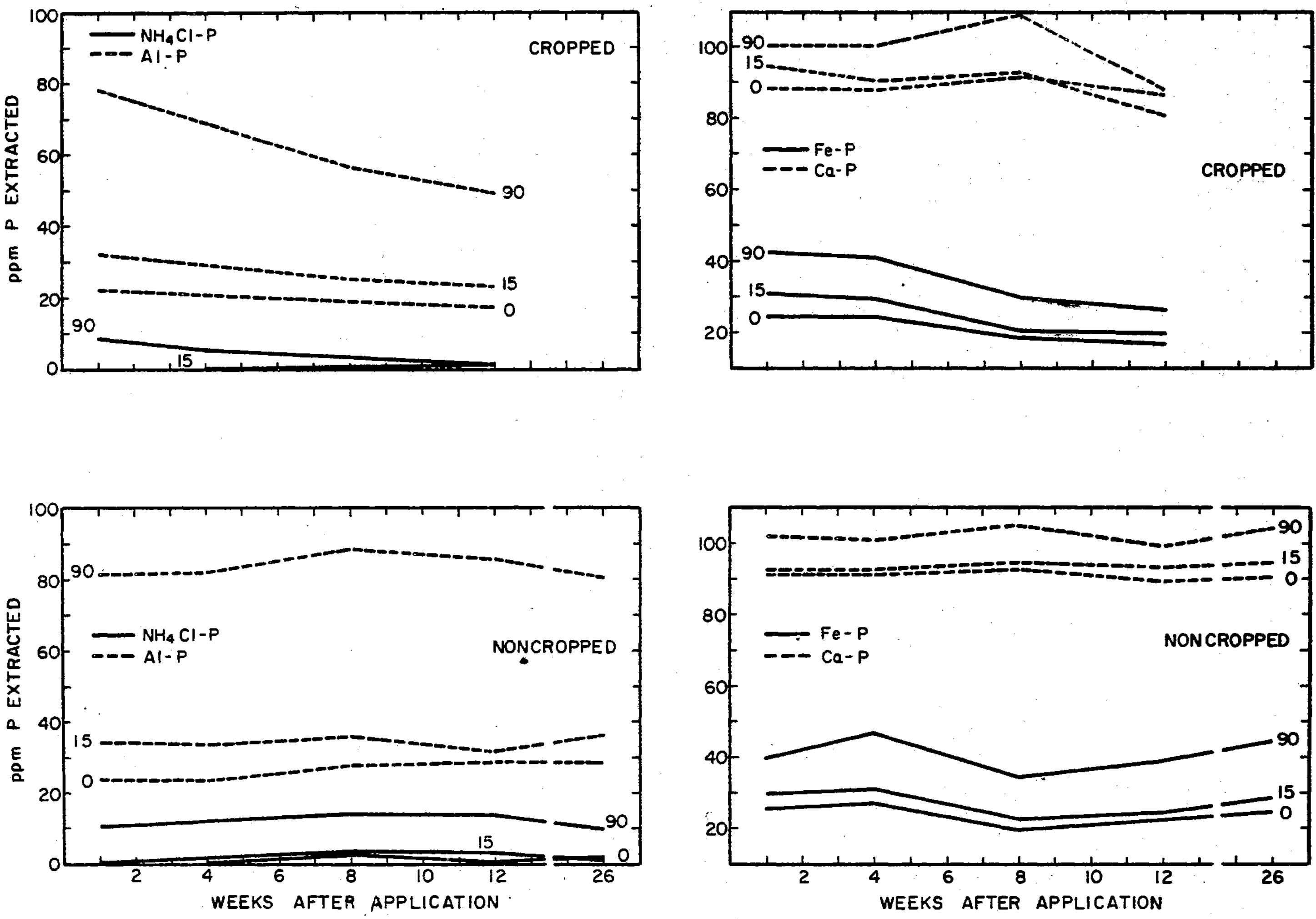

Figure 18. The Phosphate Fractions Removed from Hollister Silt Loam as a Function of Time, Both Cropped and Noncropped.

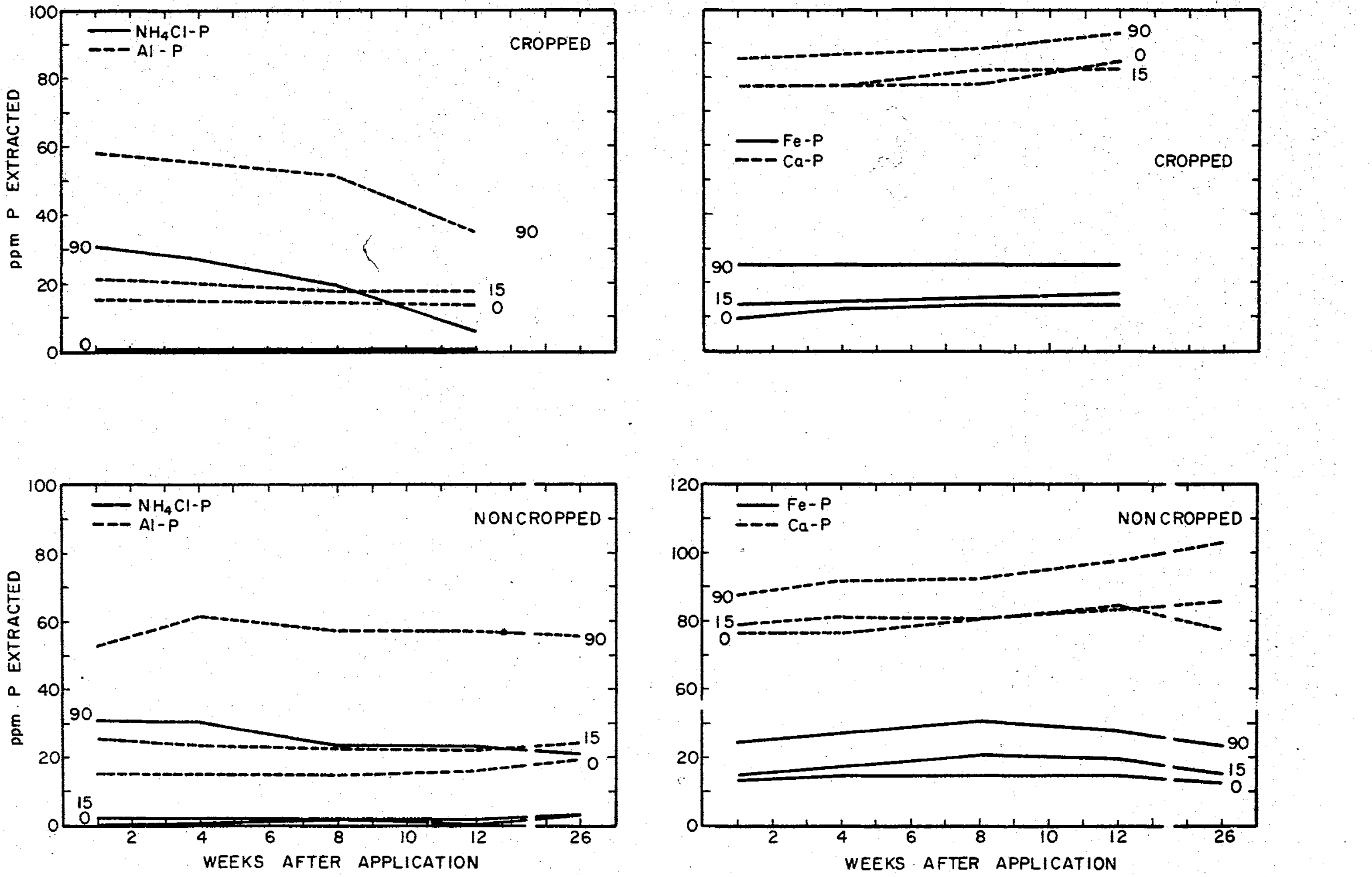

Figure 19. The Phosphate Fractions Removed from Foard Silt Loam as a Function of Time, Both Cropped and Noncropped.

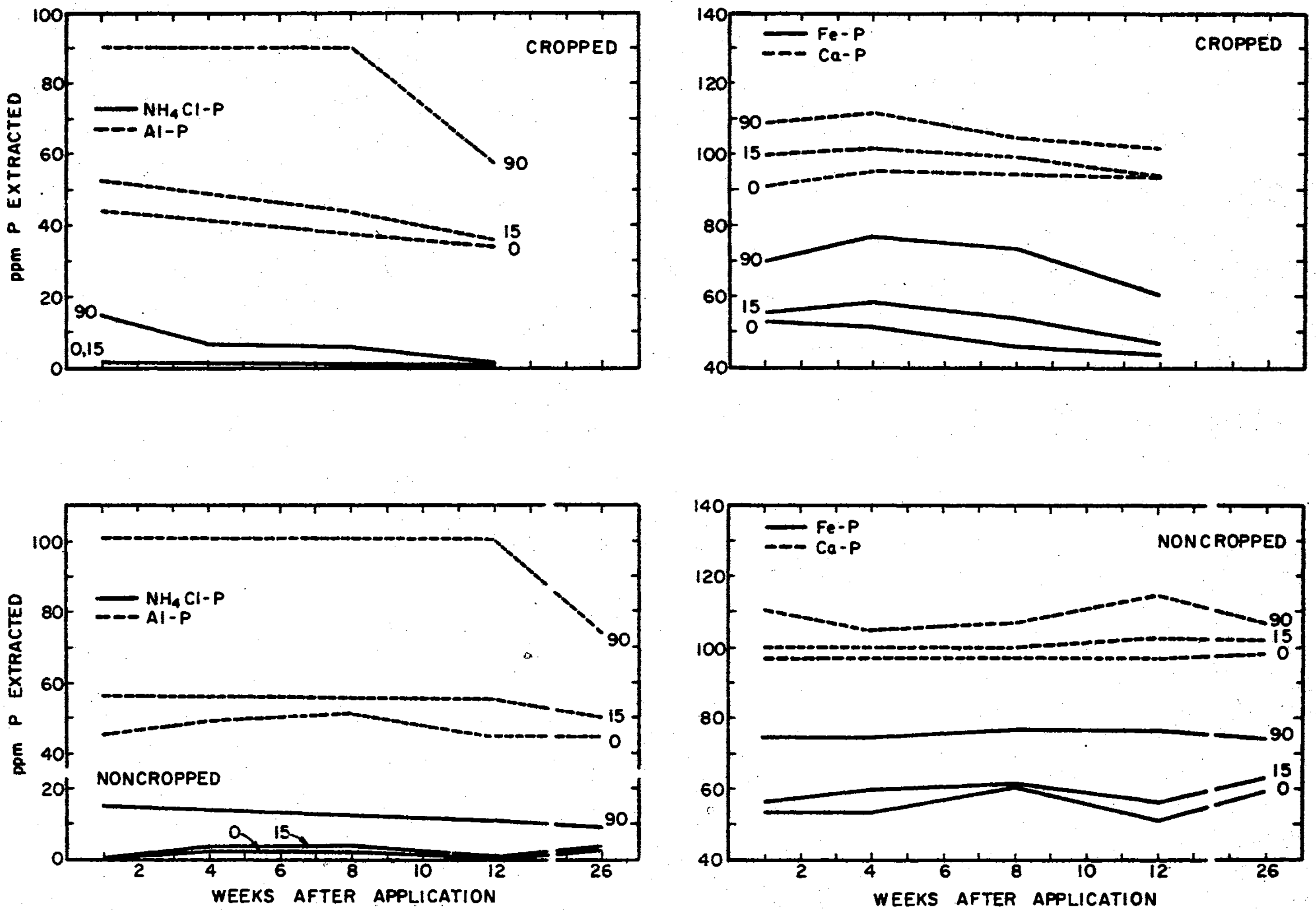

Figure 20. The Phosphate Fractions Removed from Brewer Silty Clay Loam as a Function of Time, Both Cropped and Noncropped.

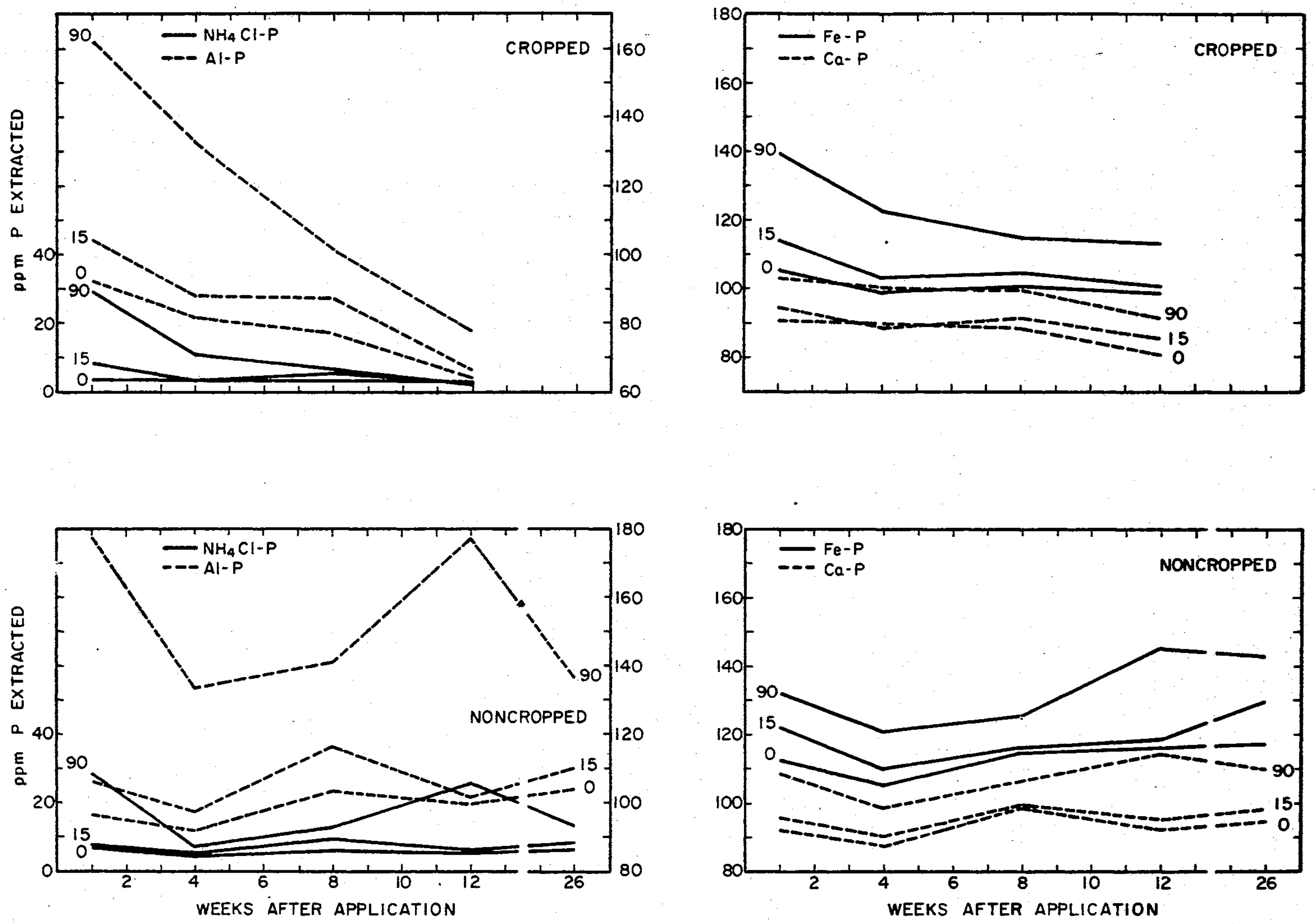

Figure 21. The Phosphate Fractions Removed from Lela Silty Clay as a Function of Time, Both Cropped and Noncropped.

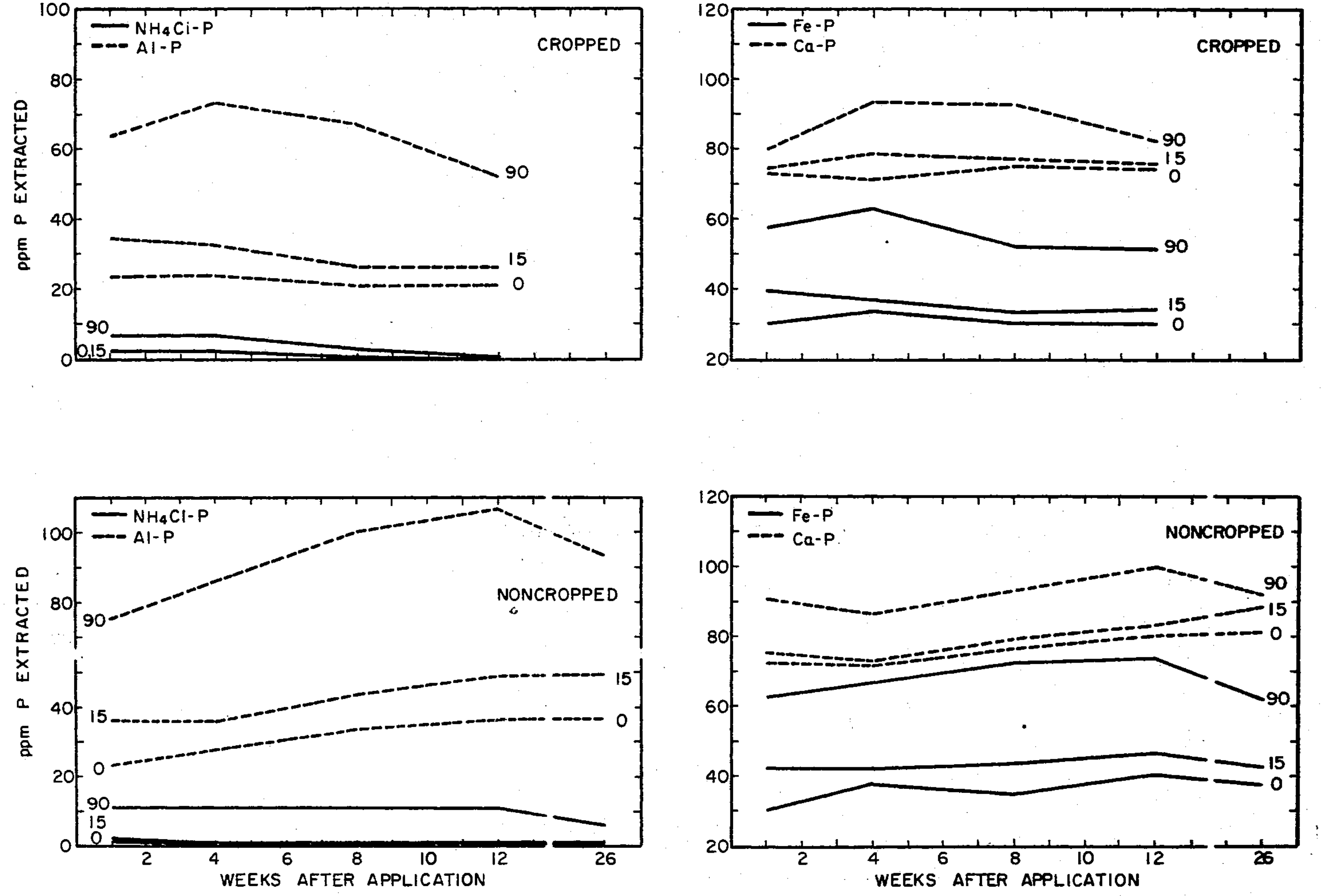

Figure 22. The Phosphate Fractions Removed from Osage Silty Clay as a Function of Time, Both Cropped and Noncropped.

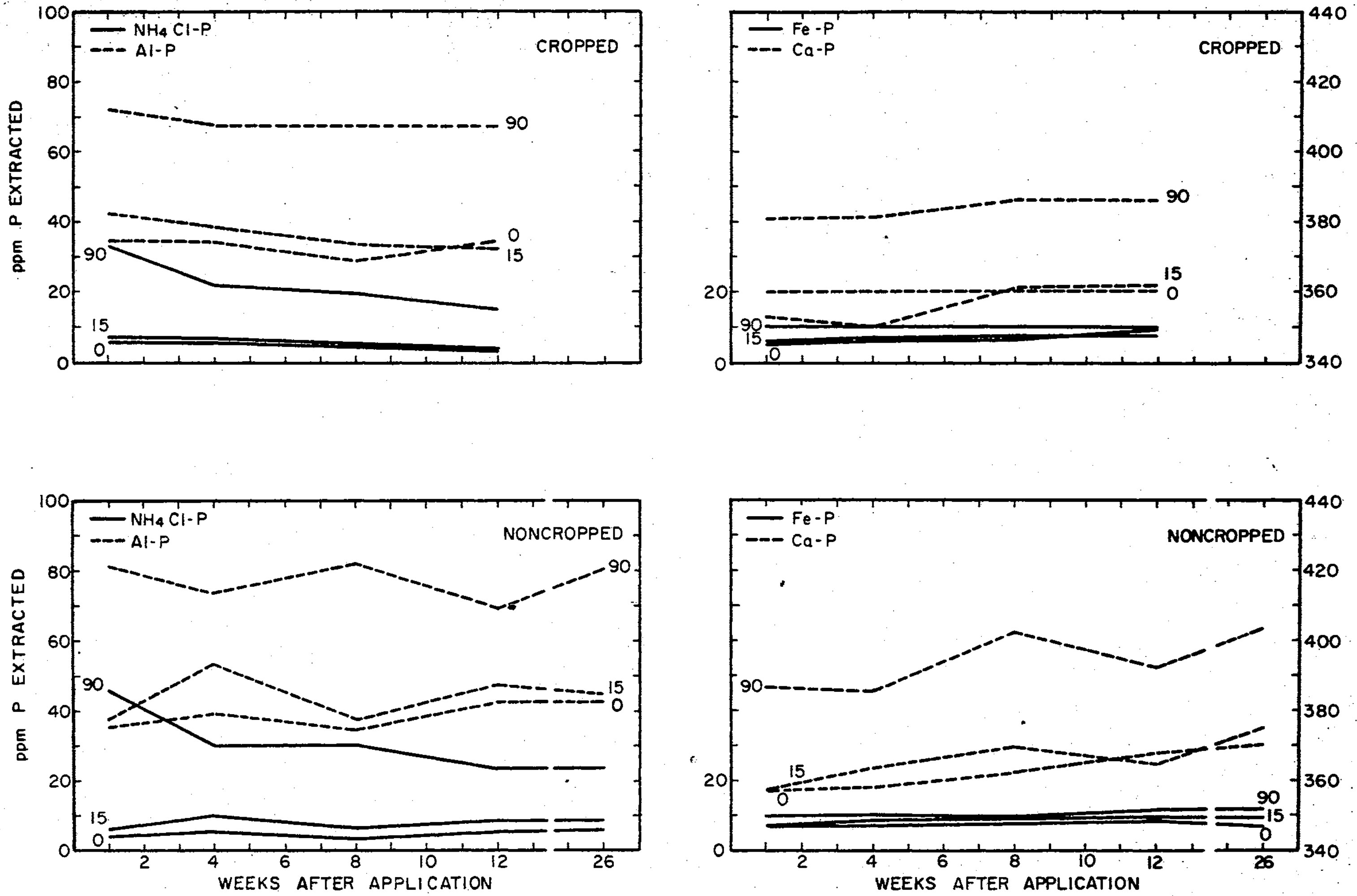

Figure 23. The Phosphate Fractions Removed from Miller Silty Clay Loam as a Function of Time, Both Cropped and Noncropped.

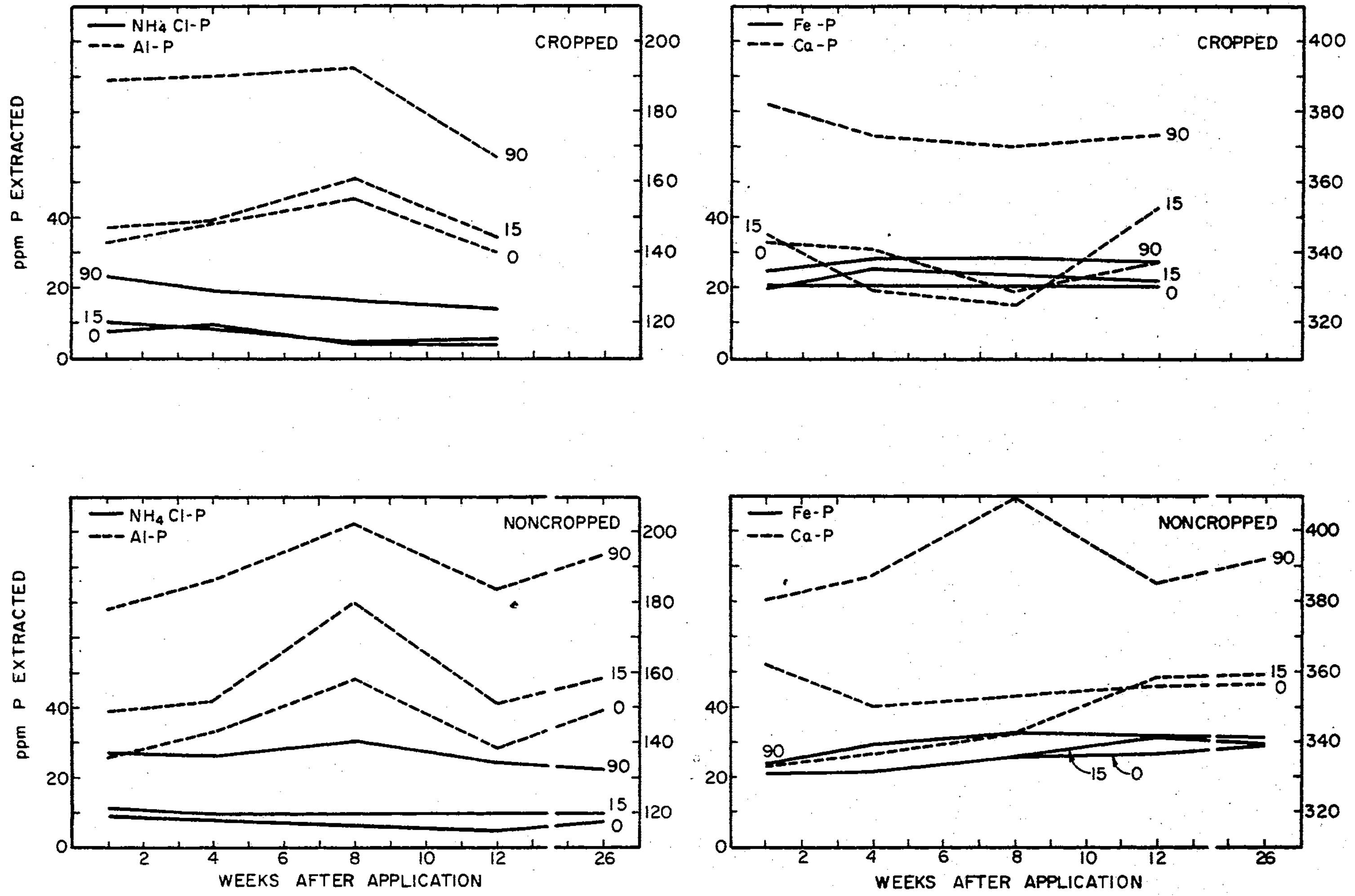

Figure 24. The Phosphate Fractions Removed from San Saba Silty Clay as a Function of Time, Both Cropped and Noncropped.

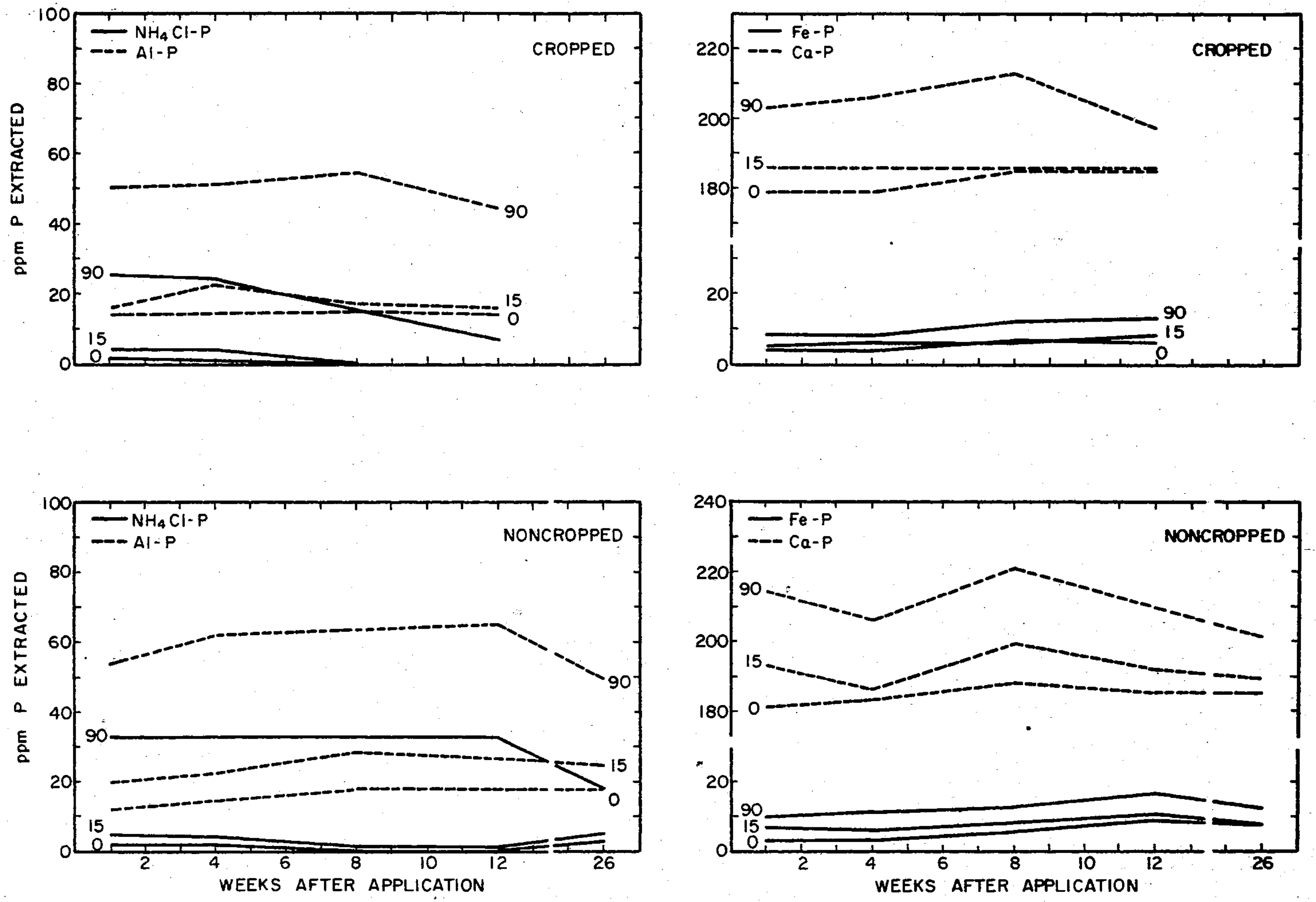

Figure 25. The Phosphate Fractions Removed from Ulysses Silty Clay Loam as a Function of Time, Both Cropped and Noncropped.

Group 1

For the purposes of discussion the soils in this group can be divided into two subgroups. In one subgroup are the more acidic soils Bowie, Bates, Cobb, and Parsons. Parsons was classed as a group 2 soil in previous sections, but seems to fit better in terms of P utilization in group 1. In the other subgroup are the more alkaline soils Pratt, Canadian, St. Paul and Tipton, along with an acidic soil, Dill. Dill is included in the latter subgroup because of its relatively low P fixation, i.e. more P is recovered in the NH_4Cl fraction.

Bowie, Bates, Cobb, and Parsons, Figures 1, 2, 3, 4, are low in NH_4Cl-P and have Al-P as their major source of available P as evidenced by the decline of Al-P with cropping. Al-P also declines in the noncropped soils as a function of time, but the decline is less in magnitude. There are also declines in Fe-P in Parsons and Bates with cropping. Taken by themselves these declines are small compared to the decline in Al-P. However, Fe-P in the noncropped soils is increasing, with a simultaneous decline in Al-P. The lack of an increase in Fe-P in the cropped soils can be interpreted to mean that the newly formed Fe-P is removed by plants. It is also possible that the plants removed P dissociating from the Al compounds before it could be fixed by Fe compounds. The latter explanation was also given by Smith (1965) who reported similar results. There are, then, two possible sources of available P in these soils: 1) Al-P, particularly newly formed Al-P, and 2) Newly formed Fe-P. P dissociating from Al compounds could also be fixed by Fe in the absence of plants. With reference to 2), native Fe-P is probably too insoluble to be of much benefit to plants.

Pratt, Canadian, St. Paul, and Tipton (Figures 5, 6, 7 and 8) have

Ca-P as their dominant phosphate form. These soils, and Dill (Figure 9), are high in NH_4Cl-P and thus exhibit relatively low P fixation characteristics. NH_4Cl-P is apparently nearly 100% available. The NH_4Cl-P content of Dill is depleted nearly to the level of the zero fertilization rate as a result of cropping, and would probably be depleted to this level in the other soils with further cropping. In some of the soils there is often greater usage of NH_4Cl-P than Al-P. This is particularly obvious in Canadian and Tipton soils (Figures 6 and 8) and to a lesser extent in the Pratt and St. Paul soils (Figures 5 and 7). In the noncropped soils NH_4Cl-P does not decline appreciably, indicating that this fraction is probably stable enough to avoid fixation for periods in excess of six months.

There is little evidence of Fe-P utilization by crops grown on the four alkaline soils. The acid soil, Dill, does exhibit a decline in Fe-P by cropping but a decline also occurs in the noncropped soil. The decline is more consistent in the cropped soil, indicating probable usage of Fe-P by plants grown on Dill.

Pratt, Canadian, St. Paul and Tipton (Figures 5, 6, 7 and 8) exhibit some evidence of Ca-P utilization by plants. Such evidence should be viewed with caution, however, due to the fact that there was considerable variation between replications. For example the crossing of the Ca-P curves of St. Paul (Figure 7) between the first and second sampling dates probably is due to the variation between replications being as large as the difference between rates. It is best to observe the overall pattern of change in Ca-P in these four soils and not emphasize specific, particularly small, values of change. Dill (Figure 9) exhibits a decline in Ca-P at the 15 ppm rate in the cropped soil but the decline does not occur to the same extent at 90 ppm. There was probably enough NH_4Cl-P and Al-P present at the 90 ppm rate to satisfy the needs of the plant. It can be concluded that there is an overall pattern of Ca-P usage in this subgroup of soils but the absolute magnitude of such usage is uncertain.

Group 2

Figures 10 through 16 illustrate changes in the P contents of this group of soils. Rather clear evidence of Al-P usage, and to a lesser extent, Fe-P usage is noted in all soils with the exception of Kirkland (Figure 10). The changes in the amounts of Al-P in Kirkland are about the same in both the cropped and noncropped soils, the difference being an increase in the noncropped soil during the third cropping period, indicating possible Al-P usage by the third crop. The lack of any obvious pattern of P utilization during earlier cropping periods is not easily explained. The values of Bray-P (Figure 40, page 85) decline as a function of cropping so there was definite measurable removal of available P. It was difficult to obtain reproducible results for the various fractions in Kirkland and it is possible that the correct values were not obtained.

Two of the soils, Summit and Renfrow (Figures 11 and 12), exhibit a marked decline in Al-P usage by the third crop. A lesser yield of the third crop (Table VII) indicates the readily available phosphorus has been depleted. Port (Figure 13) also exhibits a decline in utilization of Al-P, however Al-P is increasing under the noncropped condition so apparently crops grown on Port are utilizing this newly formed Al-P.

Summit, Renfrow, Port, and Kingfisher (Figures 11, 12, 13, and 14) exhibit clear indications of crop removal of Fe-P. In addition Fe-P increases under noncropped conditions in Summit and Renfrow indicating removal of P by plants before it is fixed by Fe as discussed for the soils in group 1.

There is enough NH_4Cl-P present in most of the soils to have an effect on yield, particularly the yield of the first crop. Kirkland and Norge (Figures 10 and 15) had less than 10 ppm NH_4Cl-P present at the beginning of the first crop, thus NH_4Cl-P was only of limited importance in these two soils.

Ca-P is only of limited importance in most of these soils. Renfrow and Carey (Figures 12 and 16) do exhibit a slight decline in Ca-P with cropping.

Group 3

Graphs of the P contents of group 3 soils are shown in Figures 17 through 22. Al-P in Waurika (Figure 17) declines considerably with cropping, particularly during the first and second crops. The decline in Al-P also occurs to a greater extent at the lower fertilization rate than it does in the other soils. Substantially less Al-P was utilized by the third crop at 90 ppm than by the previous two crops and is reflected in a lesser yield of the third crop (Table VII). The third crop on Hollister (Figure 18) also exhibits a smaller response to P than previous crops but the decrease in utilization of Al-P is not as marked as in the case of Waurika, possibly becuase of the somewhat lower yield of the previous crops. However, the decline in Fe-P is much greater in Hollister than in Waurika. Also, Ca-P declines markedly during the third cropping period. The combination of Al-P, Fe-P and Ca-P utilization by the third crop of Hollister should have resulted in a greater yield. It is possible that some other factor limited growth.

Brewer, being relatively high in native P, did not exhibit as good a yield response (Table VII) as some soils. Also, there was apparently an unknown limiting factor since yields were not as good at the higher fertilization rates as on some soils, particularly when the third crop is considered. Conversely, Al-P does not decline consistently until the third crop, as evidenced in Figure 20. The decline in Al-P may reflect fixation in the form of some insoluble Al compound, since a similar decline occurred by six months in the noncropped soils. Perhaps wetting and drying hastened the fixation process in the cropped soil. The decline during the third cropping period also occurred in the case of Fe-P in the cropped soil but no decline had occurred by six months in the noncropped soil.

Lela is one of the four soils in the study having a high clay content. At least partially because of the clay content, available phosphorus is high. A significant response to applied P for the first crop occurred but a much lesser response occurred during succeeding crops (Table VII). The variability of P, particularly Al-P, from date to date is very large in the noncropped soil as evidenced in Figure 21. This may be due to inadequate mixing of soil and fertilizer resulting in a large sampling error. However, a rather large fluctuation also occurs in the check soils, which have no mixing error. Also, the pattern of decline, particularly at 90 ppm, of Al-P in the cropped soil is uniform, and is probably a fair indication of the results expected if proper mixing did occur. The decline in Al-P with cropping is very large and occurred to a considerable extent even when no phosphorus was applied. Considerable NH_4Cl-P is formed at 90 ppm; this fraction is depleted rapidly during the first crop. There is considerable decline in Fe-P with cropping, although the fluctuation from date to date in the noncropped soils casts some doubt on the utilization of Fe-P. The statements given above for Al-P can also be applied to Fe-P, however.

In spite of variations between dates in the amounts of phosphorus extracted, the uptake of large amounts of phosphorus from Lela is obvious. The yield of the second crop (Table VII), was much greater at all fertilization rates than the yield of the first crop, perhaps indicating increased availability of P. The second crop apparently depleted the available P since a large reduction in the yield of the third crop occurred.

Osage (Figure 22) has about the same clay content as Lela, but otherwise the soils are dissimilar. Osage is an alkaline soil and has Ca-P as its dominant phosphate form. The amount of native NH_4Cl-P is very low and the amount of NH_4Cl-P is increased only slightly after fertilization. Osage is higher in native Fe-P than the other alkaline soils, and considerable Fe-P is formed in the fertilized soil. The higher amounts of Fe-P in Osage are probably functions of both iron and clay content.

Osage does not exhibit a large decline in Al-P with cropping. Conversely Al-P increases during the first cropping period at 90 ppm in both the cropped and noncropped soils. During the latter two crops the increase in Al-P continues in the non-cropped soil and declines in the cropped soil, indicating substantial uptake of Al-P. The same pattern is true for Fe-P, but to a lesser degree. The pattern for Ca-P is basically similar to that of Al-P, except during the first cropping period when Ca-P declines.

Group 4

The three soils in this group, Miller, San Saba, and Ulysses (Figures 23, 24 and 25) are calcareous. The basic difference in the phosphate distribution pattern of these soils and non-calcareous soils is the large amount of Ca-P present due to precipitation of P onto $CaCO_3$, and the lack of formation of Fe-P due to the lack of reactive Fe.

Unlike most soils these soils do not exhibit a clear pattern of decline of Al-P with cropping. All three soils contain enough NH_4Cl-P after fertilization to be of benefit to plants and this is the only fraction that undergoes a consistent decline.

The yields of all crops from San Saba and Ulysses (Table VII) are small compared to the yields on some of the other soils, and the utilization of NH_4Cl-P could have been adequate for the smaller yields obtained. The substantial yield of the first crop from Miller probably can be accounted for by the decline in NH_4Cl-P and Al-P during this period. The yields of the second, and particularly the third crop were small, resulting in no change in Al-P and only a small change in NH_4Cl-P.

General Discussion

The preceding results indicate that NH_4Cl-P, Al-P, and to a lesser extent Fe-P and Ca-P are sources of phosphorus for plants. However the situation is complicated by several factors. One is the apparent inability of NH_4F to accurately distinguish between Al-P and Fe-P in fertilized soils. Newly formed Al-P in soils is probably quantitatively removed by NH_4F, but the amount of newly formed Fe-P soluble in NH_4F is unknown. According to Bromfield (1965) NH_4F is of little value in determining the amount of Al-P in fertilized soils. The low r^2 values obtained between Al and Al-P (Table IV) indicate further that NH_4F may not be selective for Al-P. Further evidence might be seen in Table VI which lists the amounts of each form of P recovered. In many cases the amounts of P recovered as Al-P appears to be disproportionally large. However, r^2 values for oxalate-Fe vs Fe-P are generally quite good, indicating an accurate measurement of the Fe-P fraction.

In many of the soils the amounts of Ca-P recovered were small, particularly in some of the more alkaline soils such as Canadian, St. Paul, Pratt and Foard, in which Ca-P might be expected to persist for long periods of time. It is known that dicalcium phosphate ($CaHPO_4$) is soluble in the extractant for loosely bound P, NH_4Cl (Bromfield, 1965). $CaHPO_4$ is a major reaction product when concentrated superphosphate is applied to soils, and can persist for considerable periods of time (Hinman, Beaton, and Read, 1962; Strong and Racz, 1970; Lehr, Brown and Brown, 1959; Ramulu and Pratt, 1970). Solubility of $CaHPO_4$ in NH_4Cl could account for the lack of recovery of applied P as Ca-P. Further it is also possible that such P might react with Al and Fe compounds during the extraction with NH_4Cl causing over-estimation of Al-P and Fe-P. It is quite probable that such reactions took place when the P fractionation procedure was utilized in this study. However, the extent of such reactions is not known. In Table VI (and also in the graphs of phosphorus extracted vs. time discussed previously) it can be seen that in many soils NH_4Cl-P does not decline appreciably over twelve weeks, and often only slightly by six months. It seems that if the NH_4Cl fraction included $CaHPO_4$, NH_4Cl-P would show a decline with time, simply through precipitation of compounds such as octacalcium phosphate, or through reactions of $CaHPO_4$ with Al and Fe to form P compounds not soluble in NH_4Cl. Although $CaHPO_4$ can persist in soils for long periods of time, the workers who measured such persistence used larger quantities of fertilizer per volume of soil than were used in this study. Therefore, $CaHPO_4$ may not have persisted for as long a period of time in this study as it did in other studies. The stability of NH_4Cl-P may indicate either lack of persistence of $CaHPO_4$, or lack of solubility of $CaHPO_4$ in soils in NH_4Cl. If either is true then perhaps Chang and Jackson type procedures can be considered to be fair indications of P reactions and utilization in soils. Clarification can only occur through research.

Changes in the Amounts of Bray-P as a Function of Time

In Figures 26 through 50 are graphs of Bray-P (P soluble in the Bray #1 extractant) vs. time in both the cropped and noncropped soils at the 0 ppm and 90 ppm rates. Generally the changes in Bray-P with time reflect changes in the NH_4Cl-P plus Al-P fractions (note the

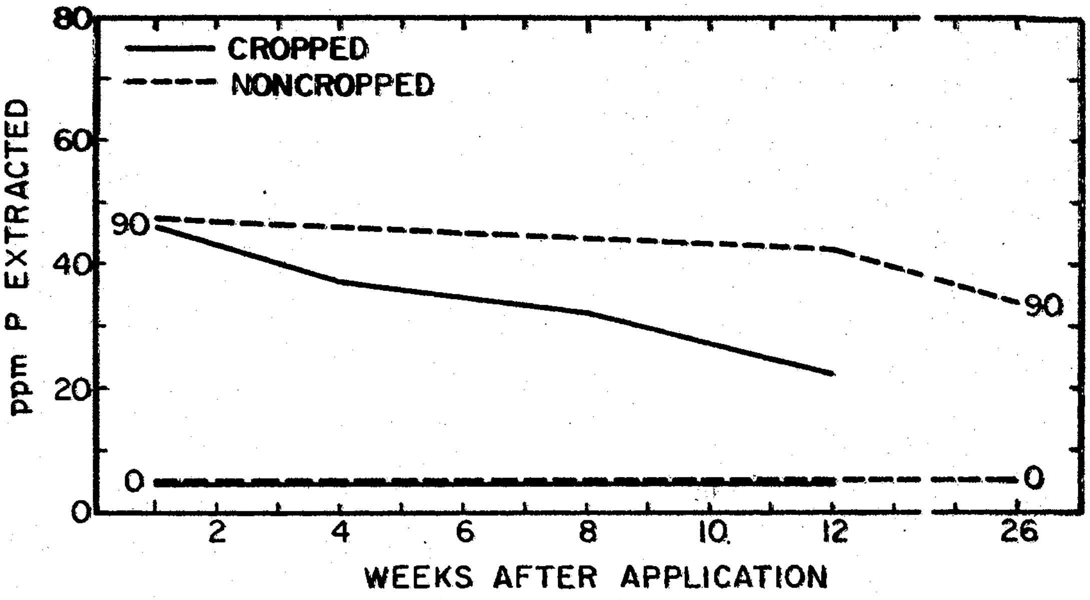

Figure 26. The Amounts of Bray-P Extracted from Parsons Silt Loam as a Function of Time, Both Cropped and Noncropped.

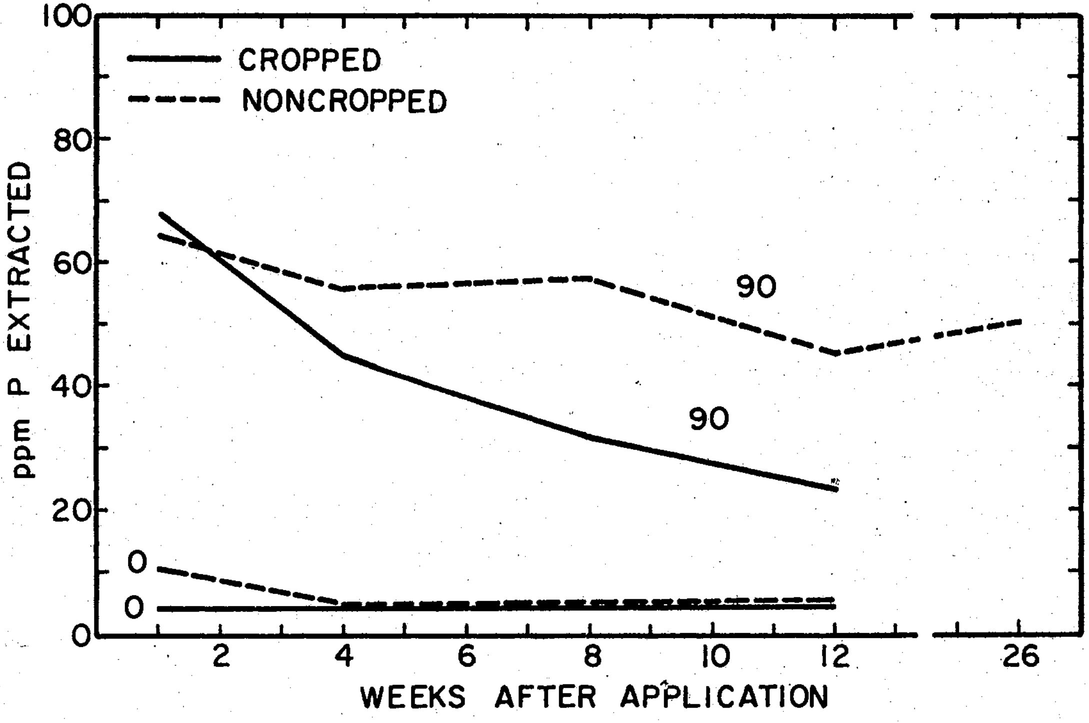

Figure 27. The Amounts of Bray-P Extracted from Bates Sandy Loam as a Function of Time, Both Cropped and Noncropped

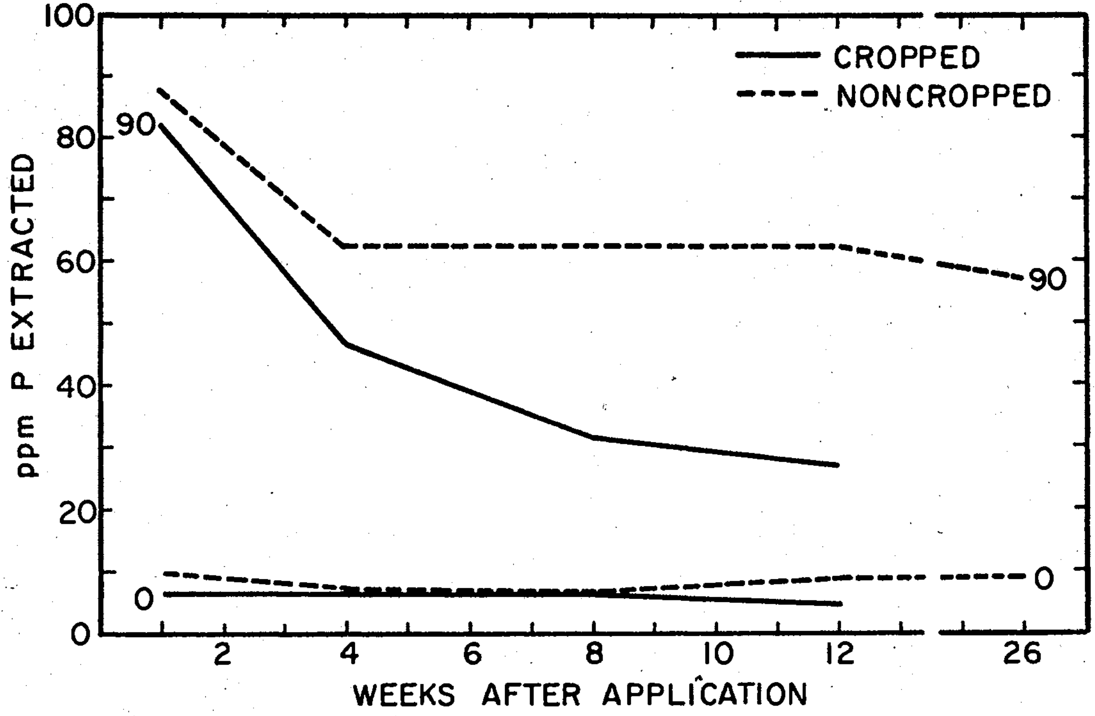

Figure 28. The Amounts of Bray-P Extracted from Summit Silt Loam as a Function of Time, Both Cropped and Noncropped.

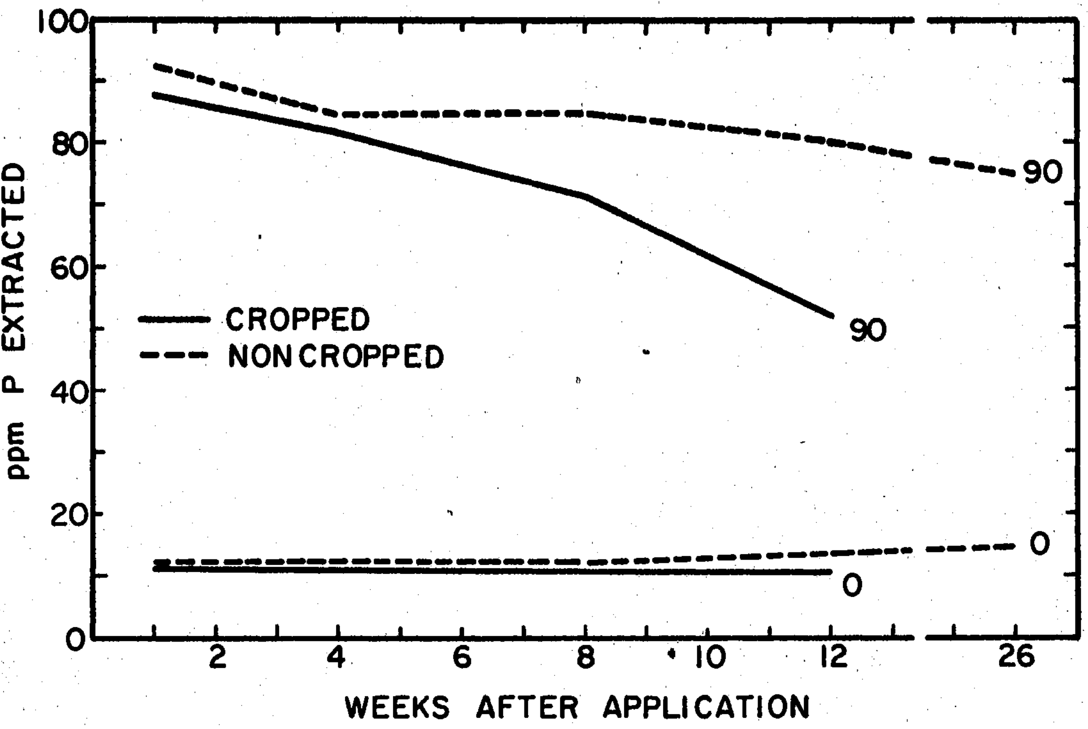

Figure 29. The Amounts of Bray-P Extracted from Foard Silt Loam as a Function of Time, Both Cropped and Noncropped.

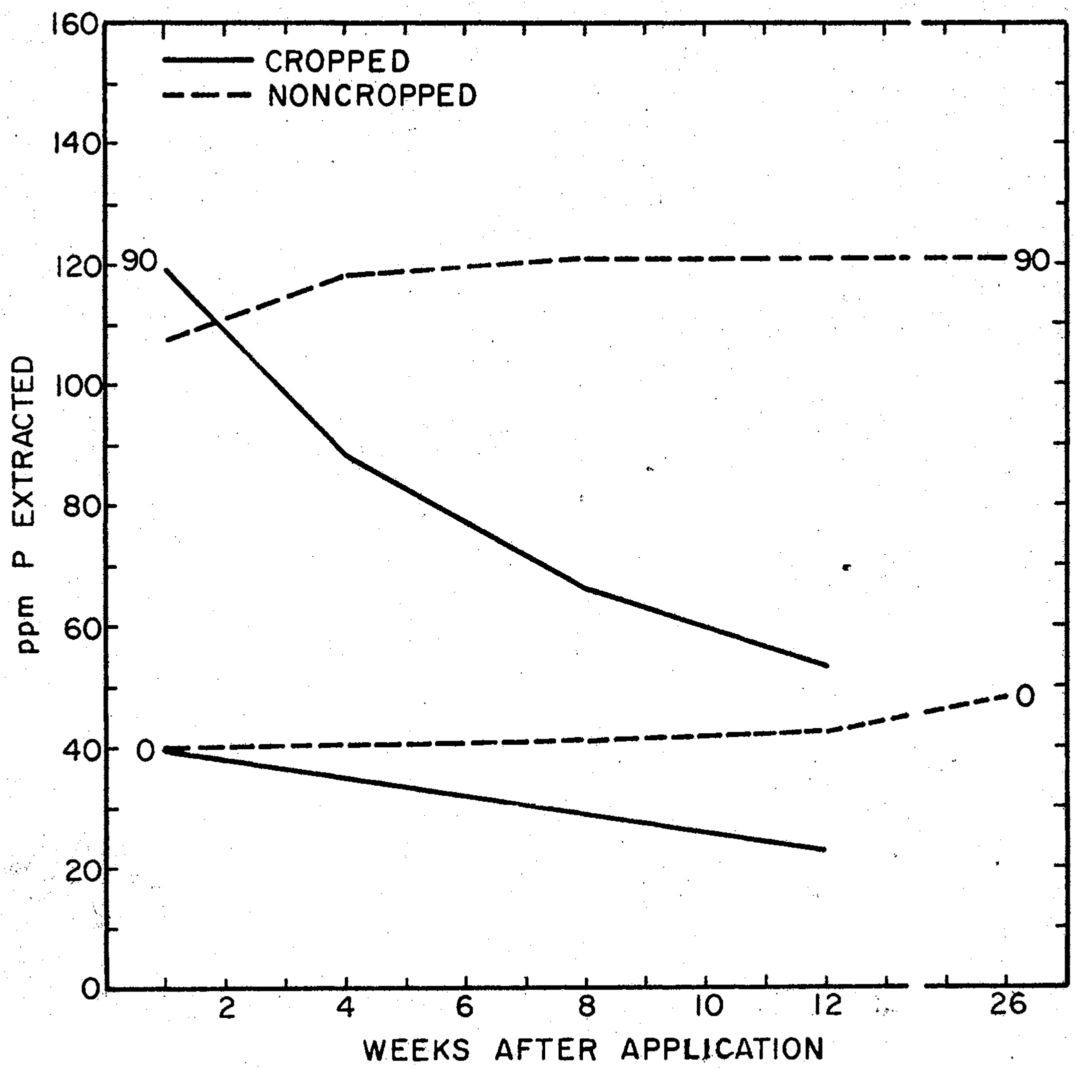

Figure 30. The Amounts of Bray-P Extracted from Dill Sandy Loam as a Function of Time, Both Cropped and Noncropped.

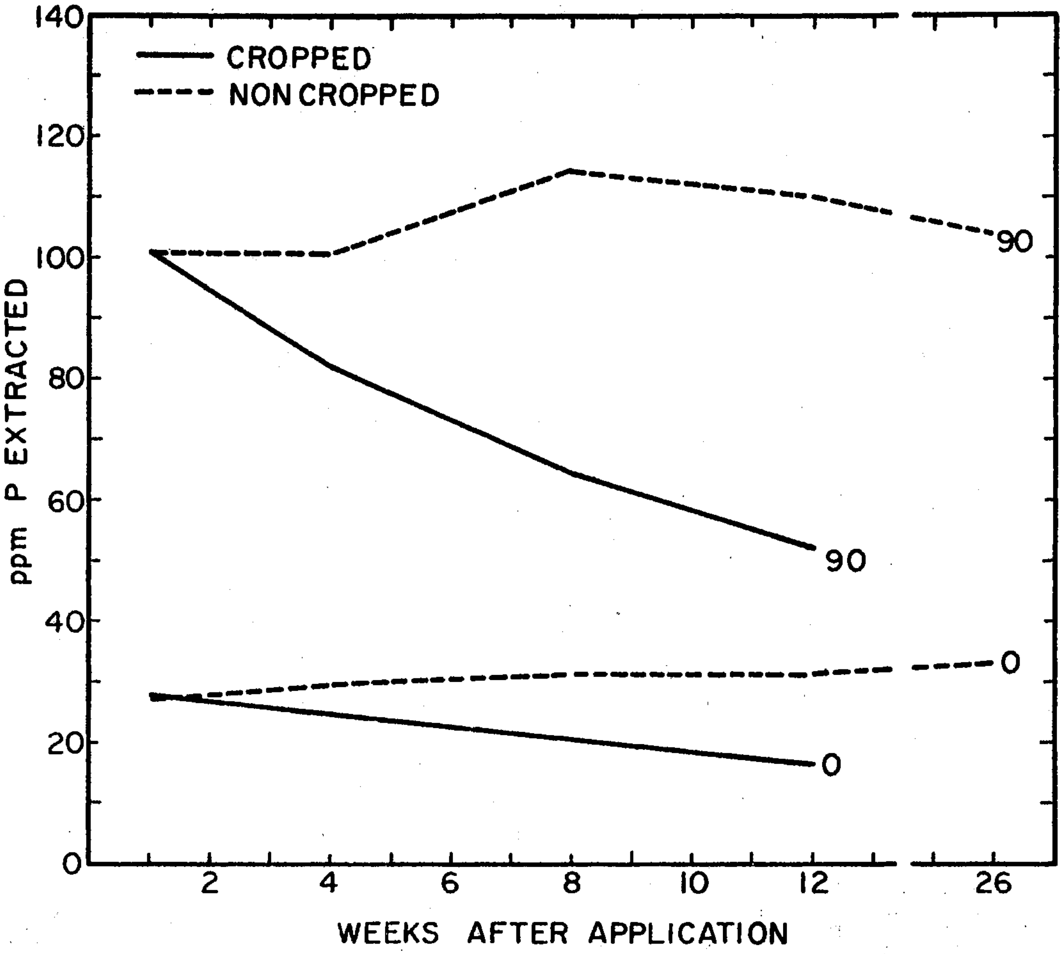

Figure 31. The Amounts of Bray-P Extracted from Holister Silt Loam as a Function of Time, Both Cropped and Noncropped.

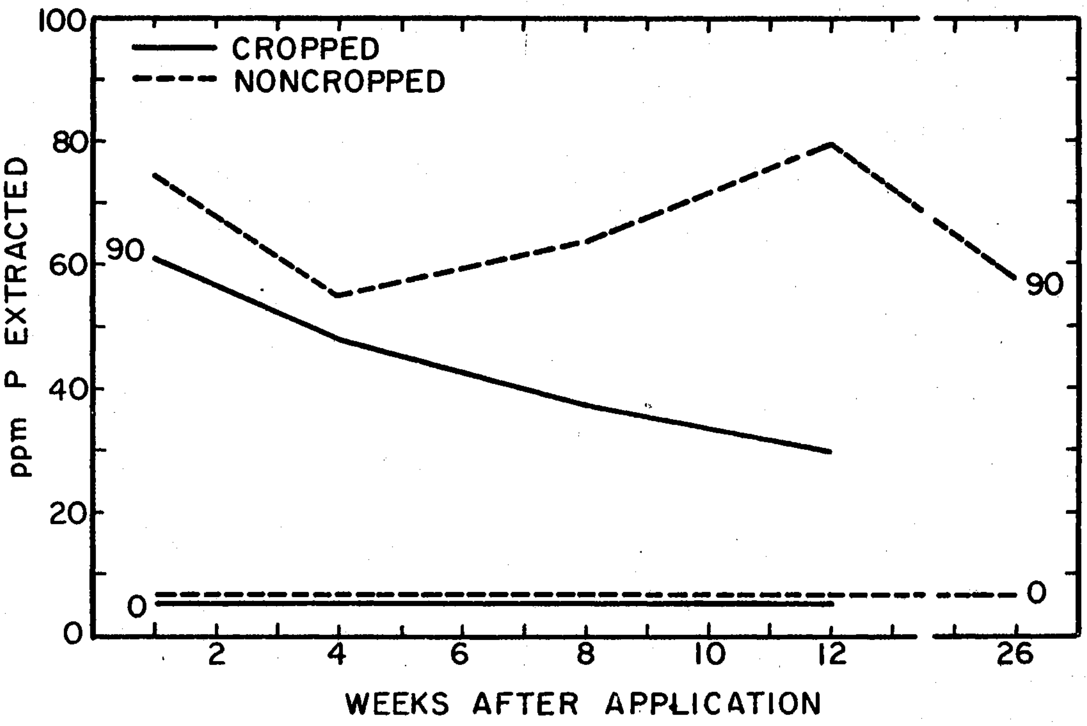

Figure 32. The Amounts of Bray-P Extracted from Norge Loam as a Function of Time, Both Cropped and Noncropped.

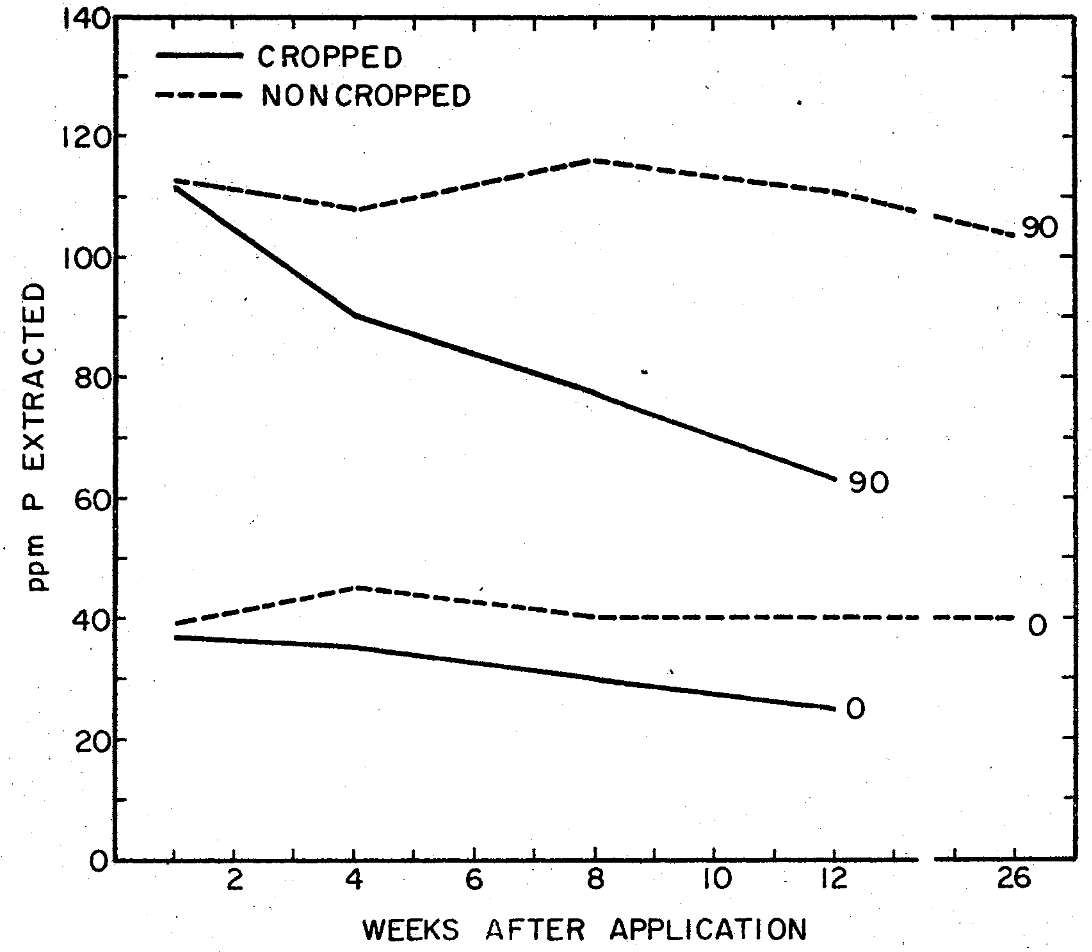

Figure 33. The Amounts of Bray-P Extracted from Port Loam as a Function of Time, Both Cropped and Noncropped.

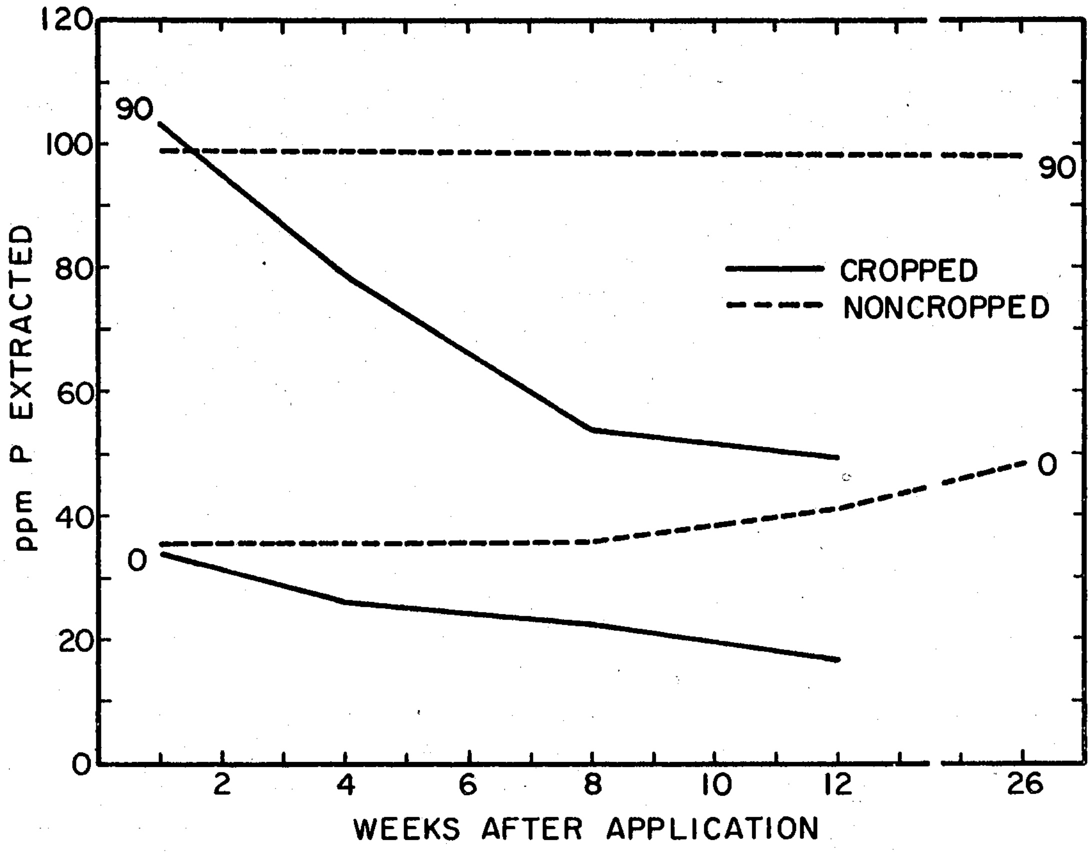

Figure 34. The Amounts of Bray-P Extracted From Renfrow Loam as a Function of Time, Both Cropped and Noncropped.

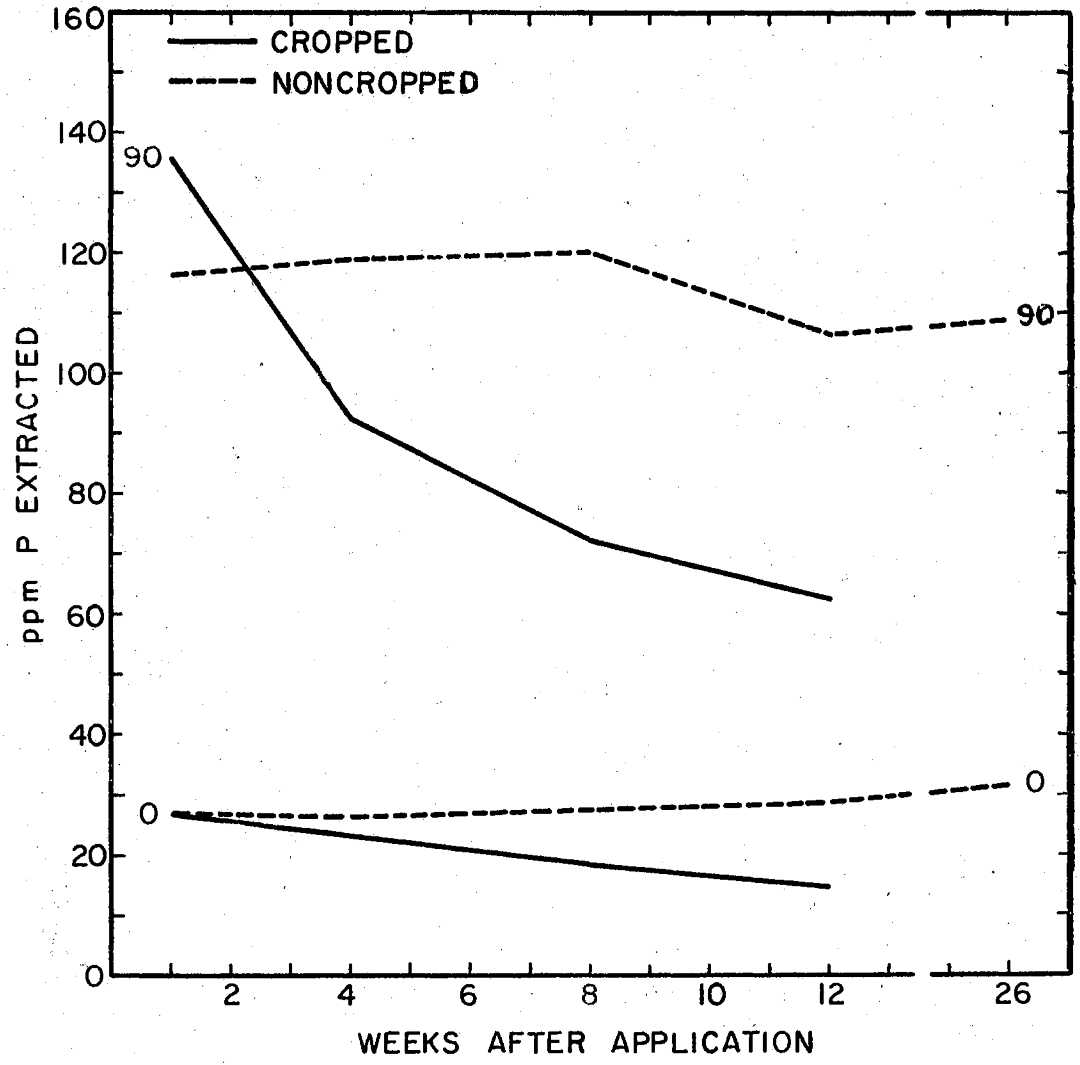

Figure 35. The Amounts of Bray-P Extracted from Waurika Silt Loam as a Function of Time, Both Cropped and Noncropped.

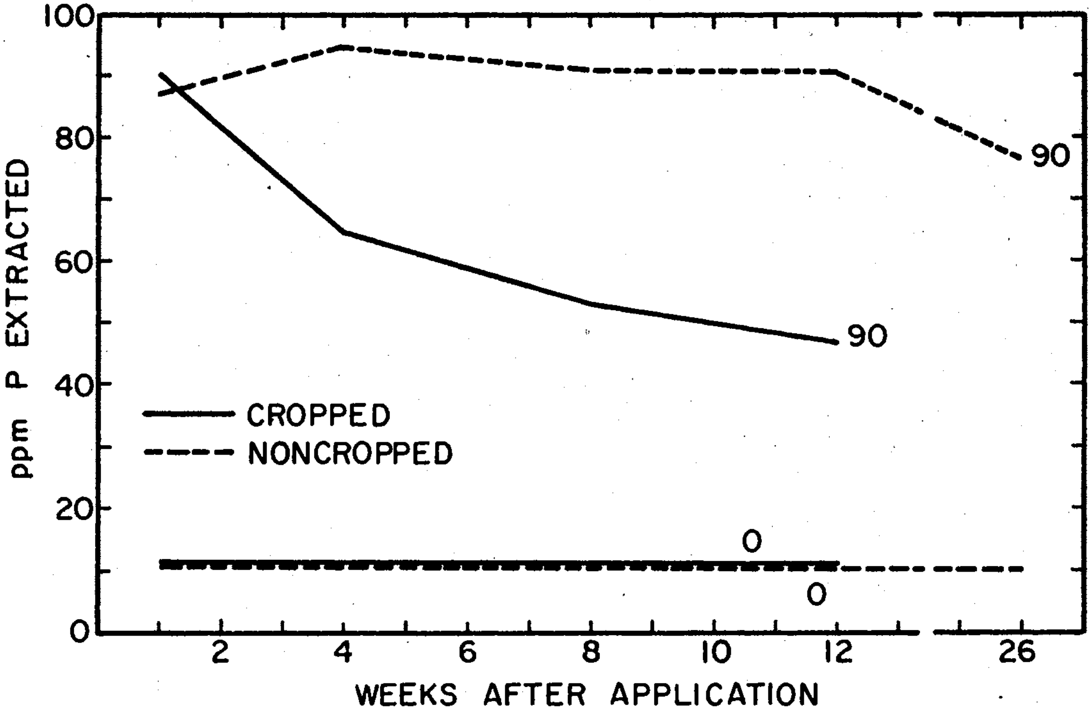

Figure 36. The Amounts of Bray-P Extracted from Carey Loam as a Function of Time, Both Cropped and Noncropped.

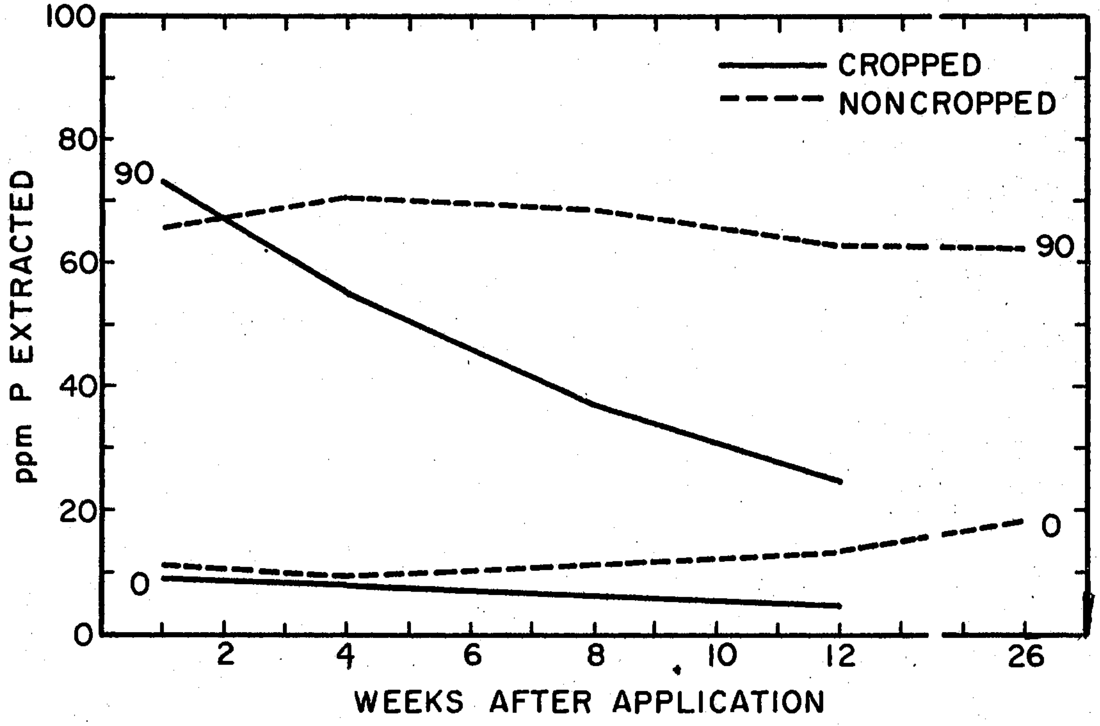

Figure 37. The Amounts of Bray-P Extracted from Kingfisher Silt Loam as a Function of Time, Both Cropped and Noncropped.

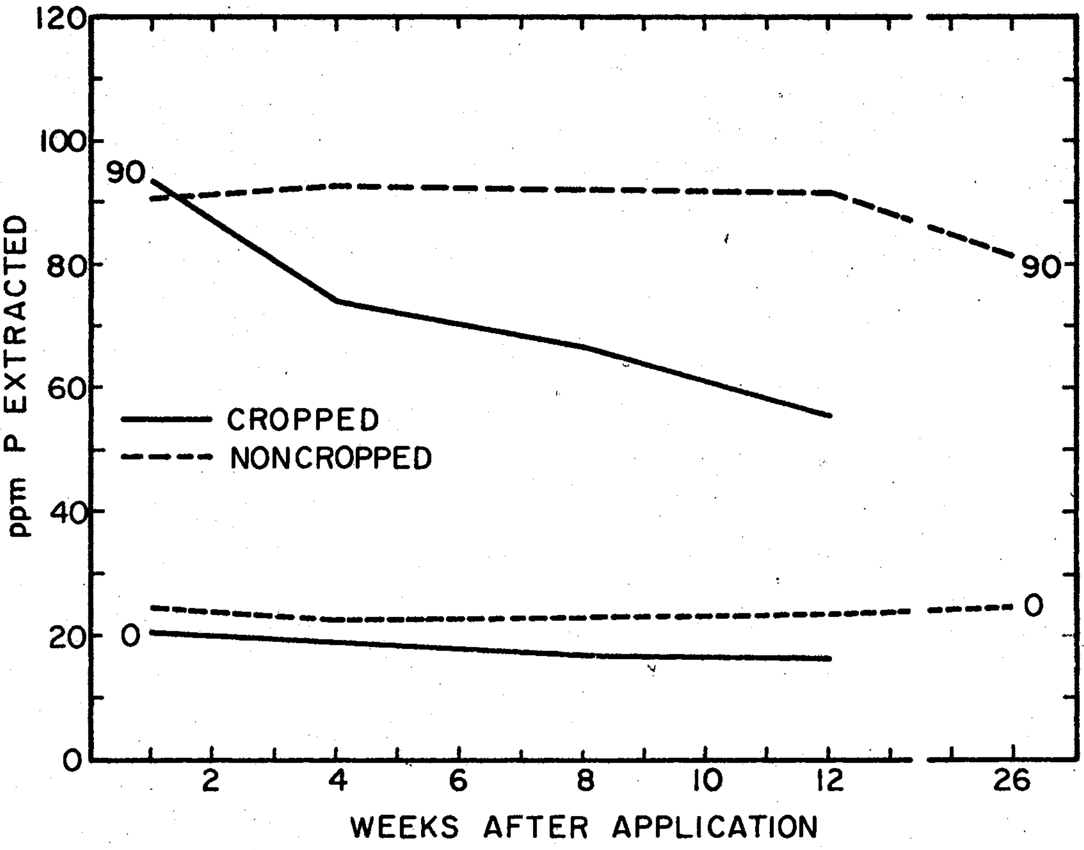

Figure 38. The Amounts of Bray-P Extracted from St. Paul Loam as a Function of Time, Both Cropped and Noncropped.

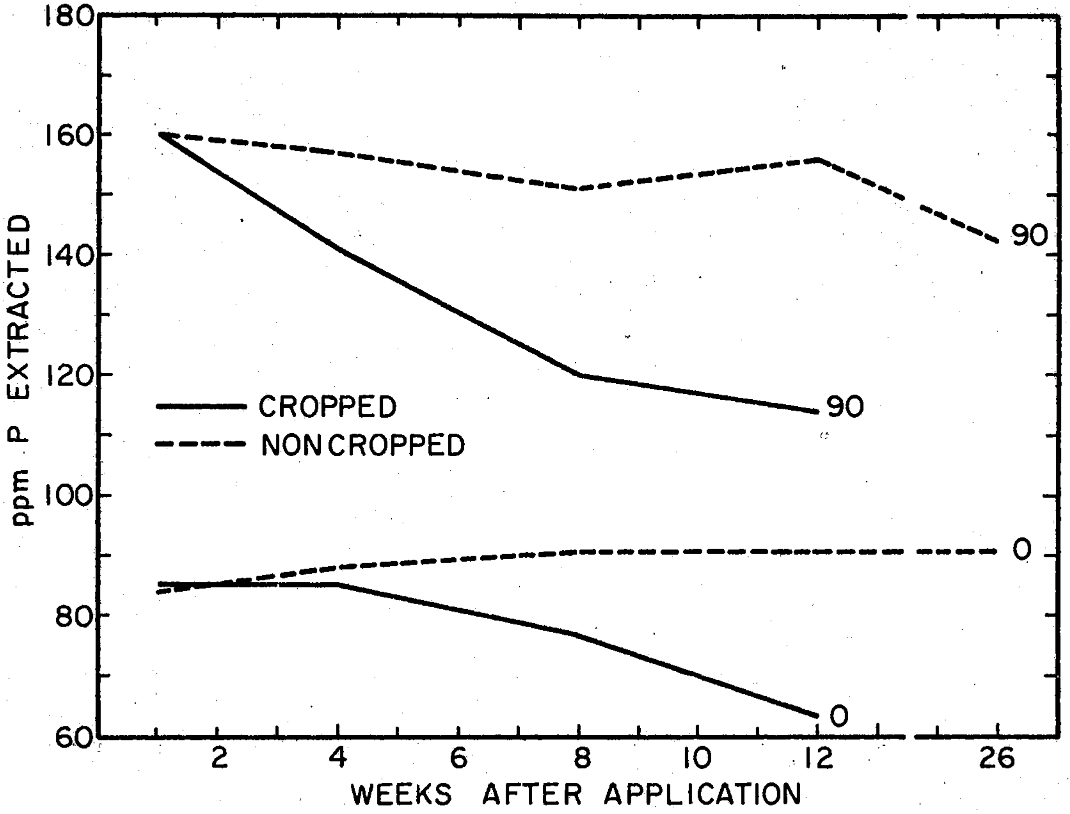

Figure 39. The Amounts of Bray-P Extracted from Tipton Loam as a Function of Time, Both Cropped and Noncropped.

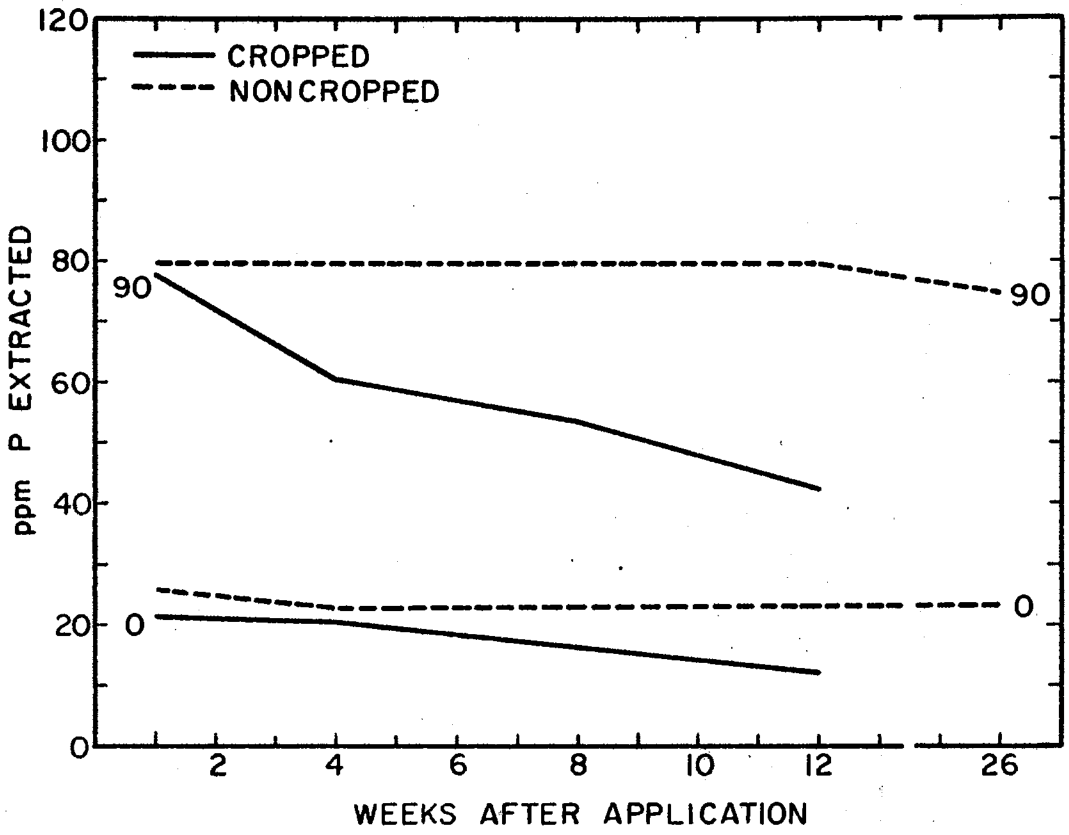

Figure 40. The Amounts of Bray-P Extracted From Kirkland Loam as a Function of Time, Both Cropped and Noncropped.

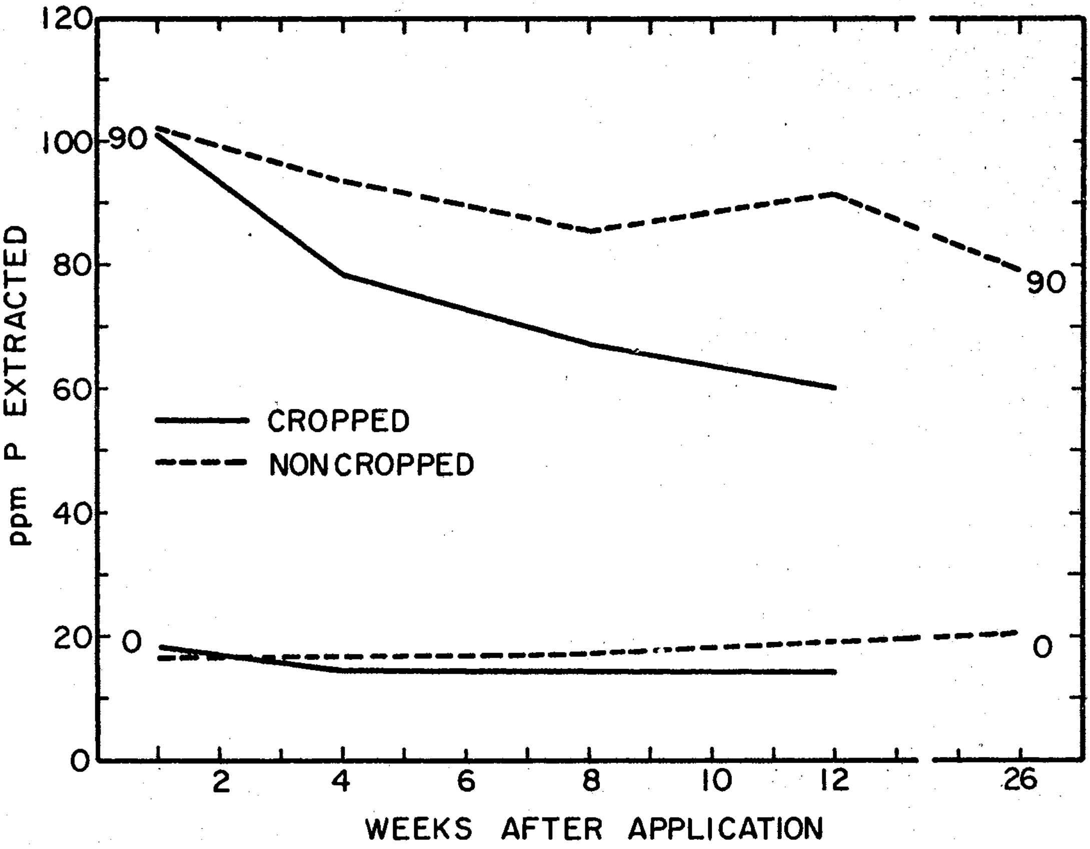

Figure 41. The Amounts of Bray-P Extracted from Canadian Sandy Loam as a Function of Time, Both Cropped and Noncropped.

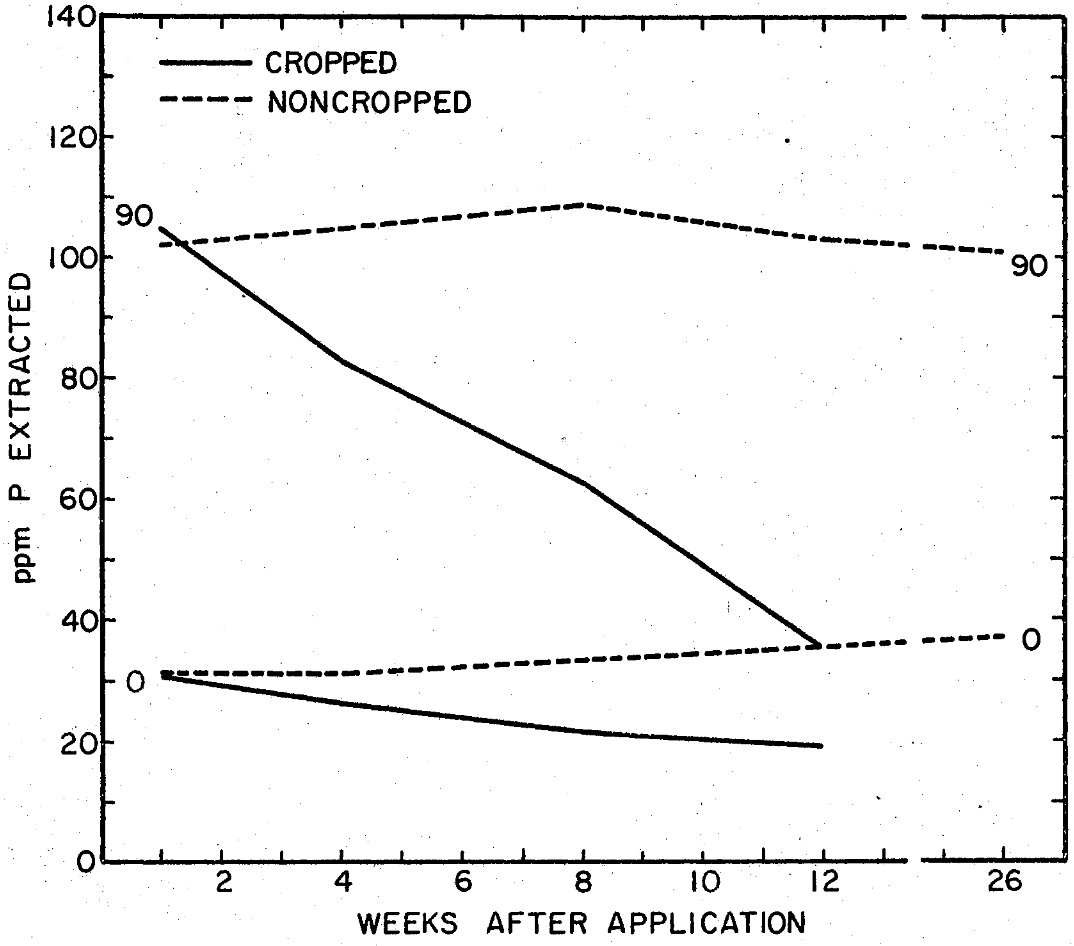

Figure 42. The Amounts of Bray-P Extracted from Pratt Sandy Loam as a Function of Time, Both Cropped and Noncropped.

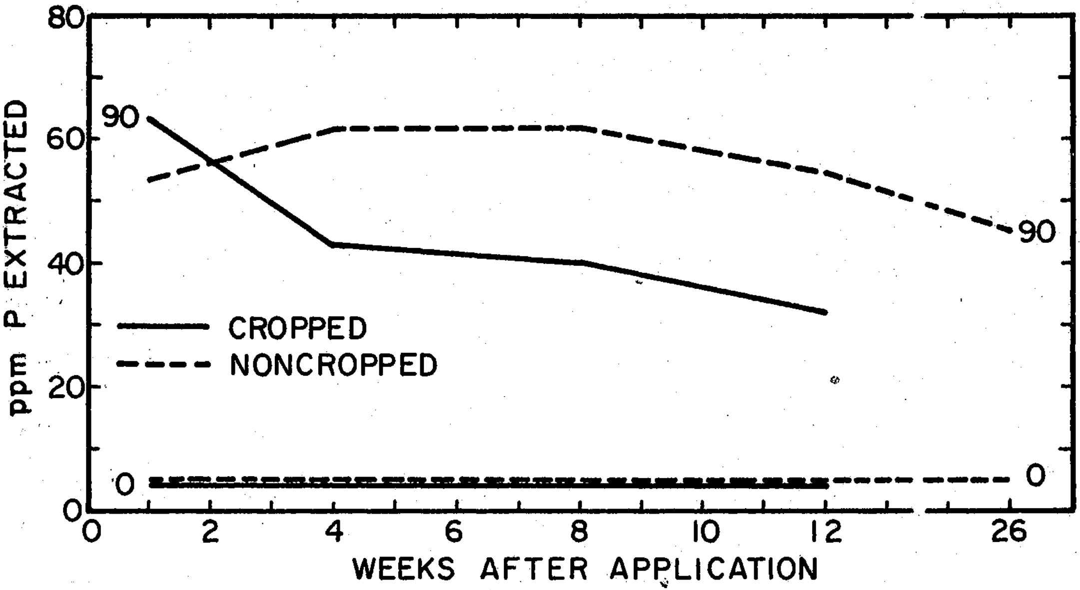

Figure 43. The Amounts of Bray-P Extracted from Bowie Sandy Loam as a Function of Time, Both Cropped and Noncropped.

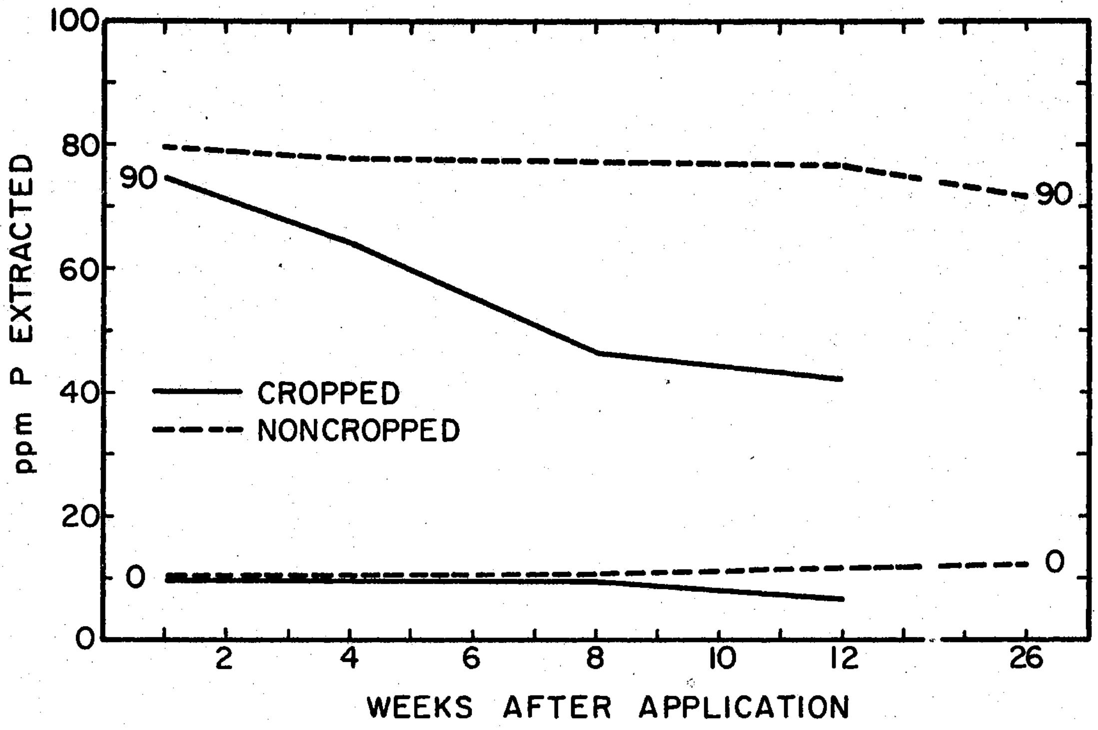

Figure 44. The Amounts of Bray-P Extracted from Cobb Sandy Loam as a Function of Time, Both Cropped and Noncropped.

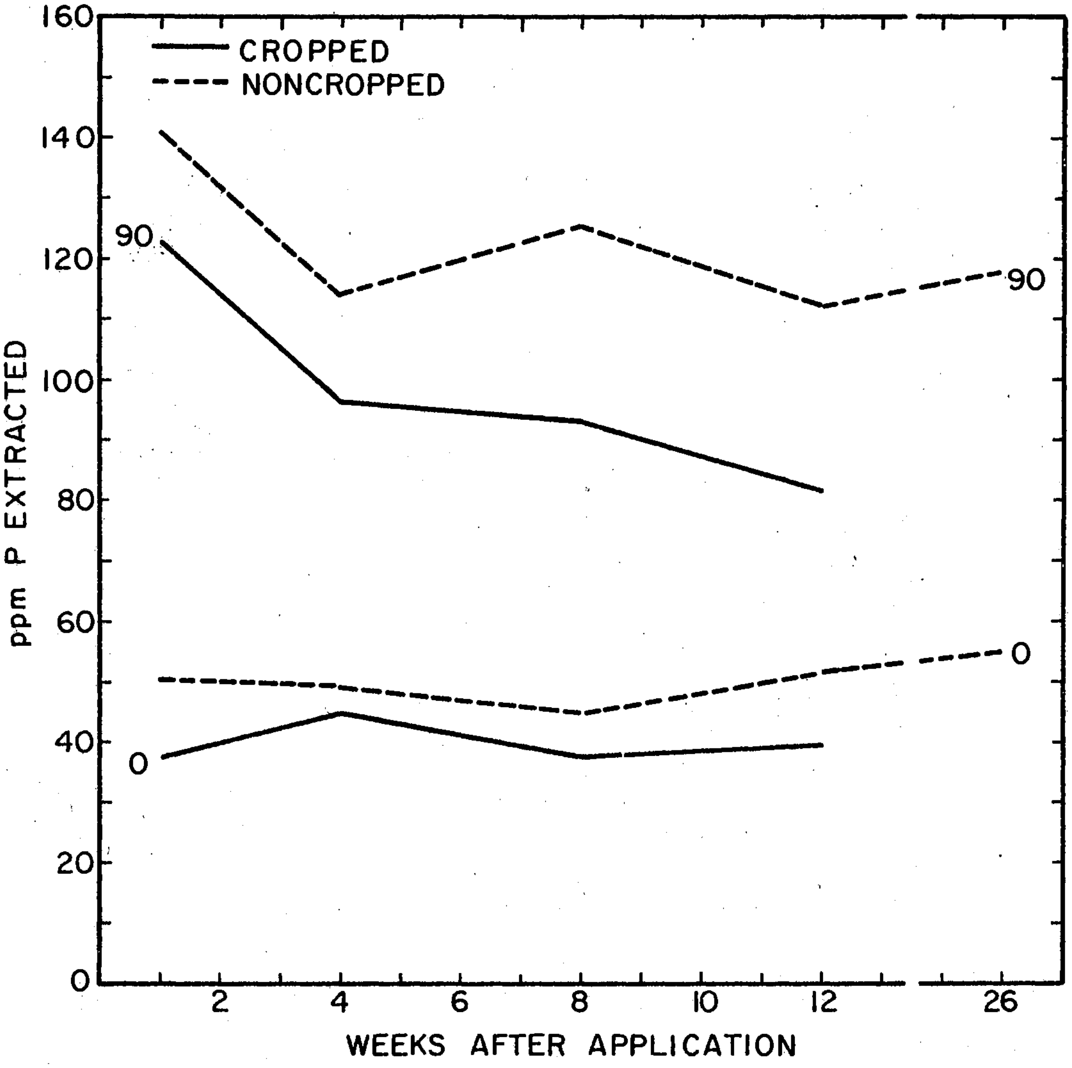

Figure 45. The Amounts of Bray-P Extracted from Miller Silty Clay Loam as a Function of Time, Both Cropped and Noncropped.

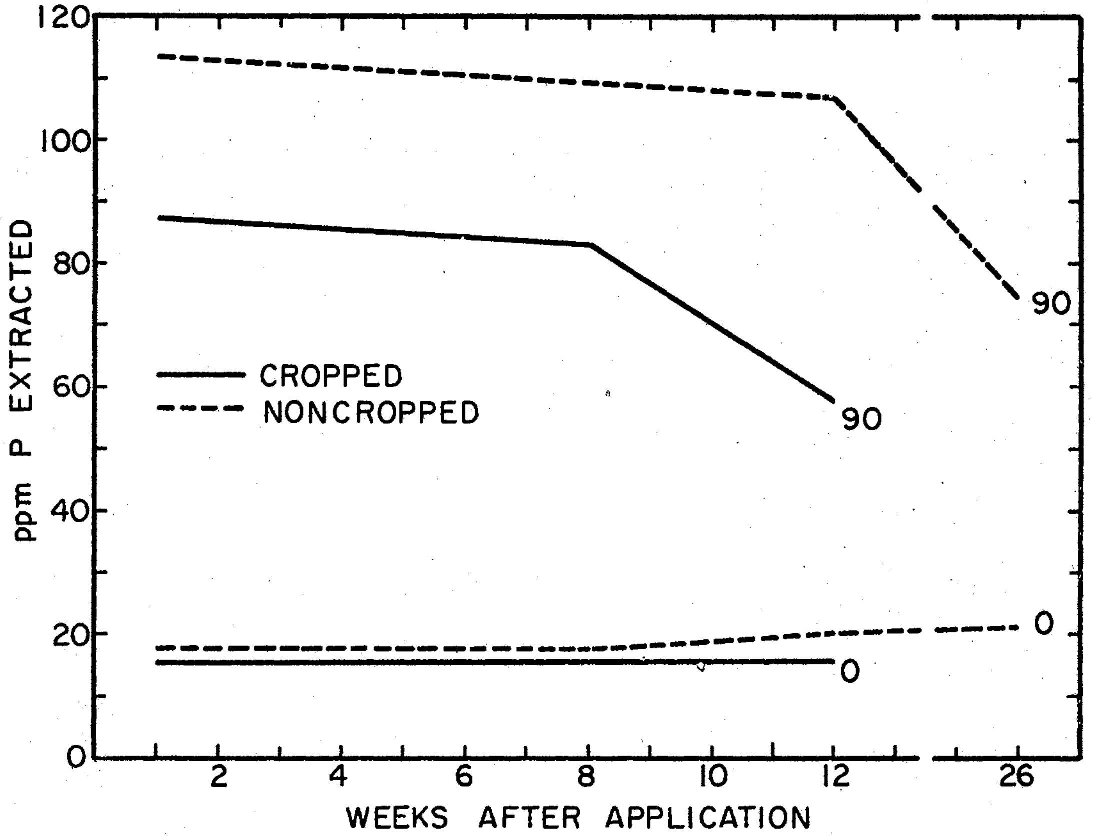

Figure 46. The Amounts of Bray-P Extracted from Ulysses Silty Clay Loam as a Function of Time, Both Cropped and Noncropped.

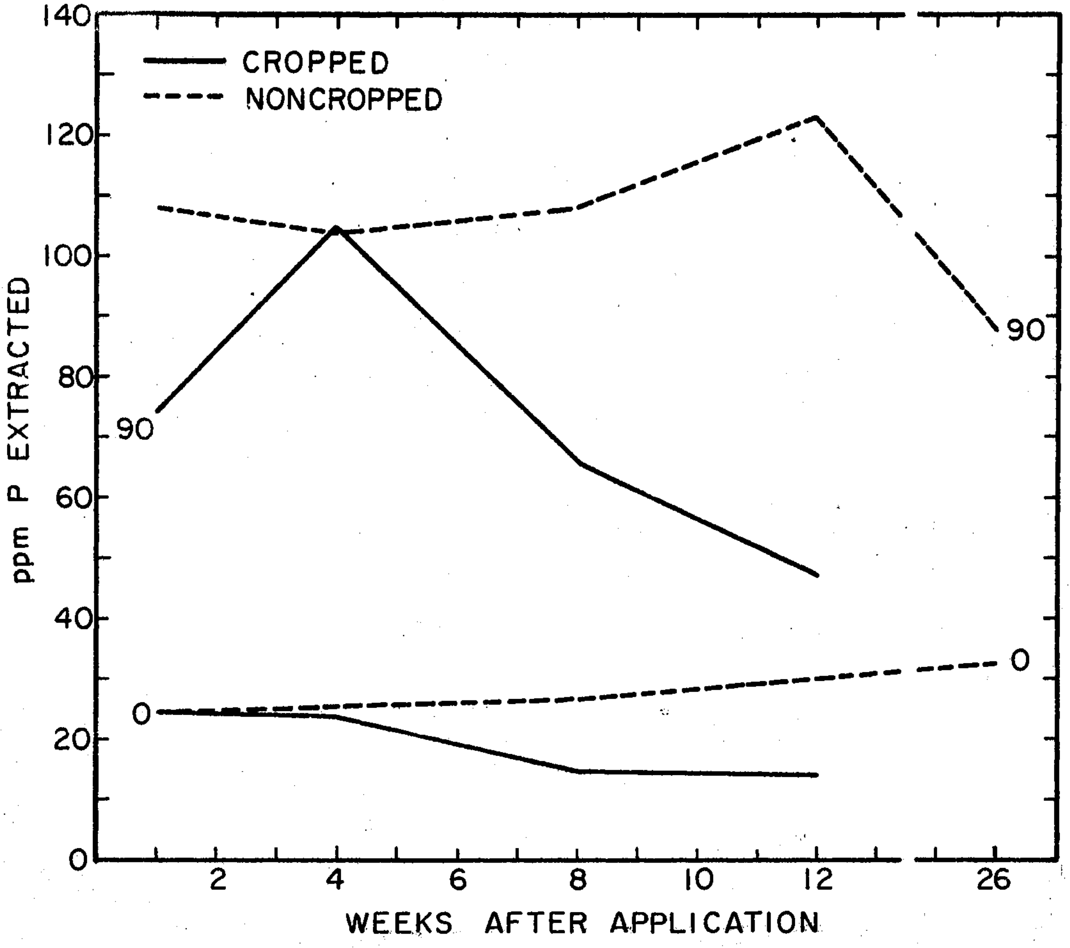

Figure 47. The Amounts of Bray-P Extracted from Osage Silty Clay as a Function of Time, Both Cropped and Noncropped.

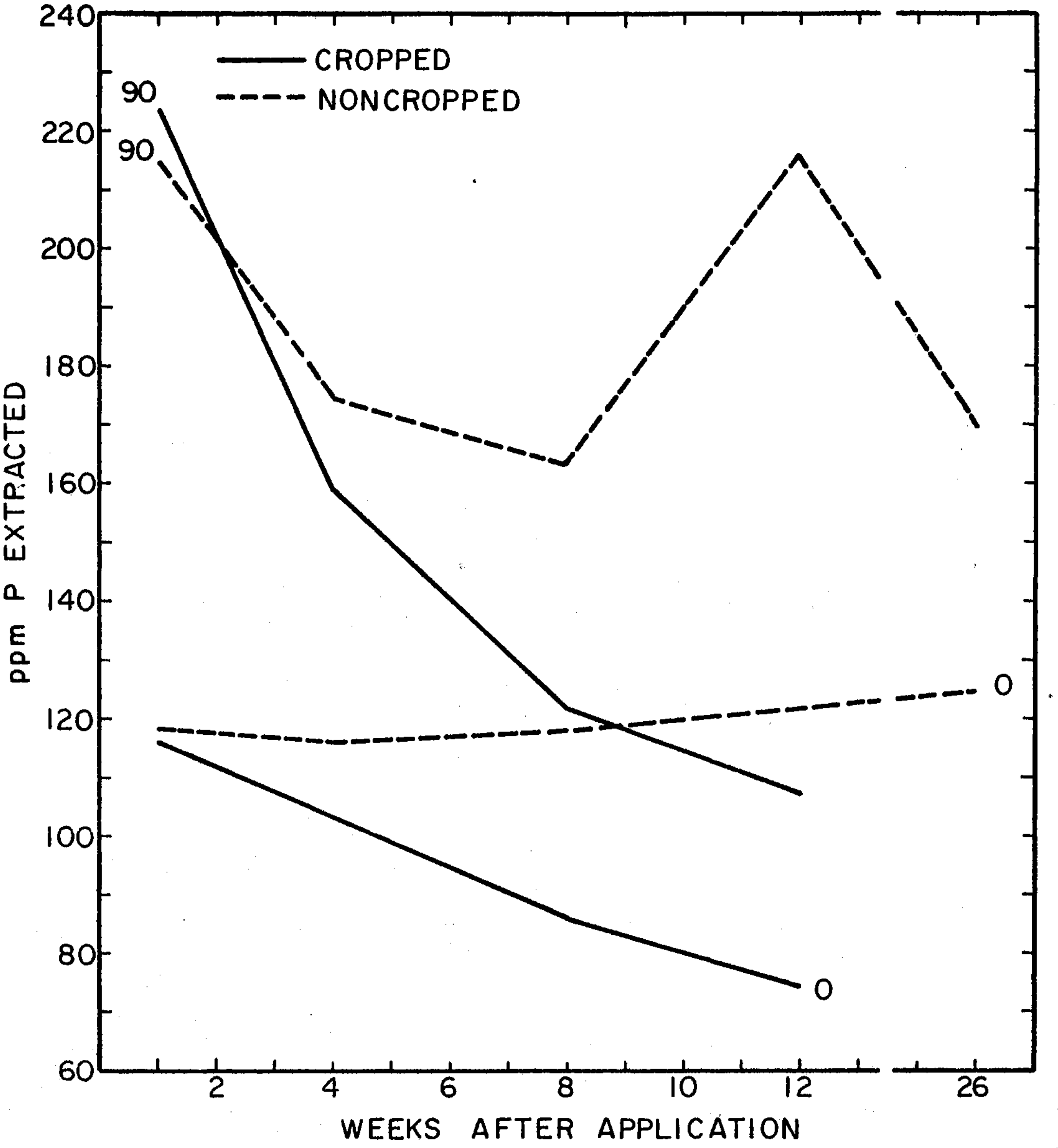

Figure 48. The Amounts of Bray-P Extracted from Lela Silty Clay as a Function of Time, Both Cropped and Noncropped.

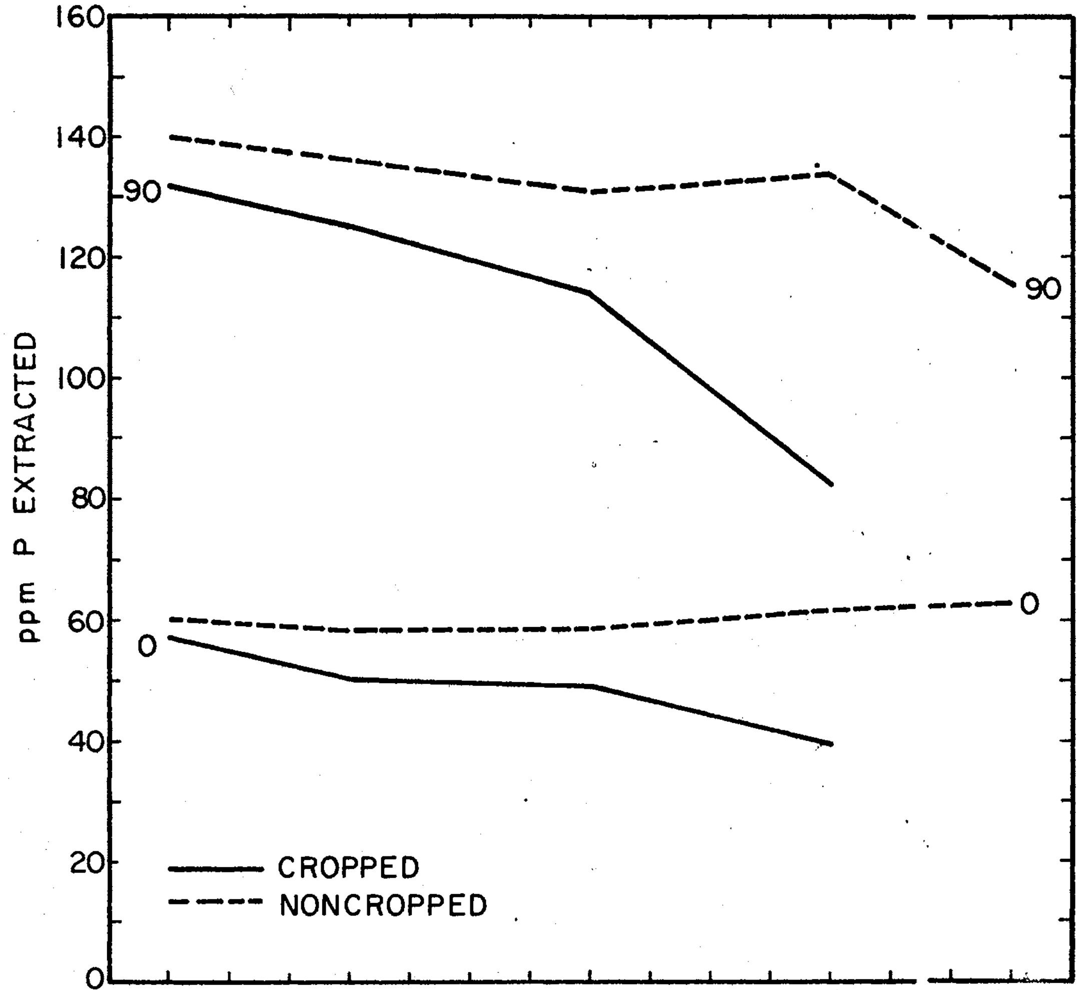

Figure 49. The Amounts of Bray-P Extracted from Brewer Silty Clay Loam as a Function of Time, Both Cropped and Noncropped.

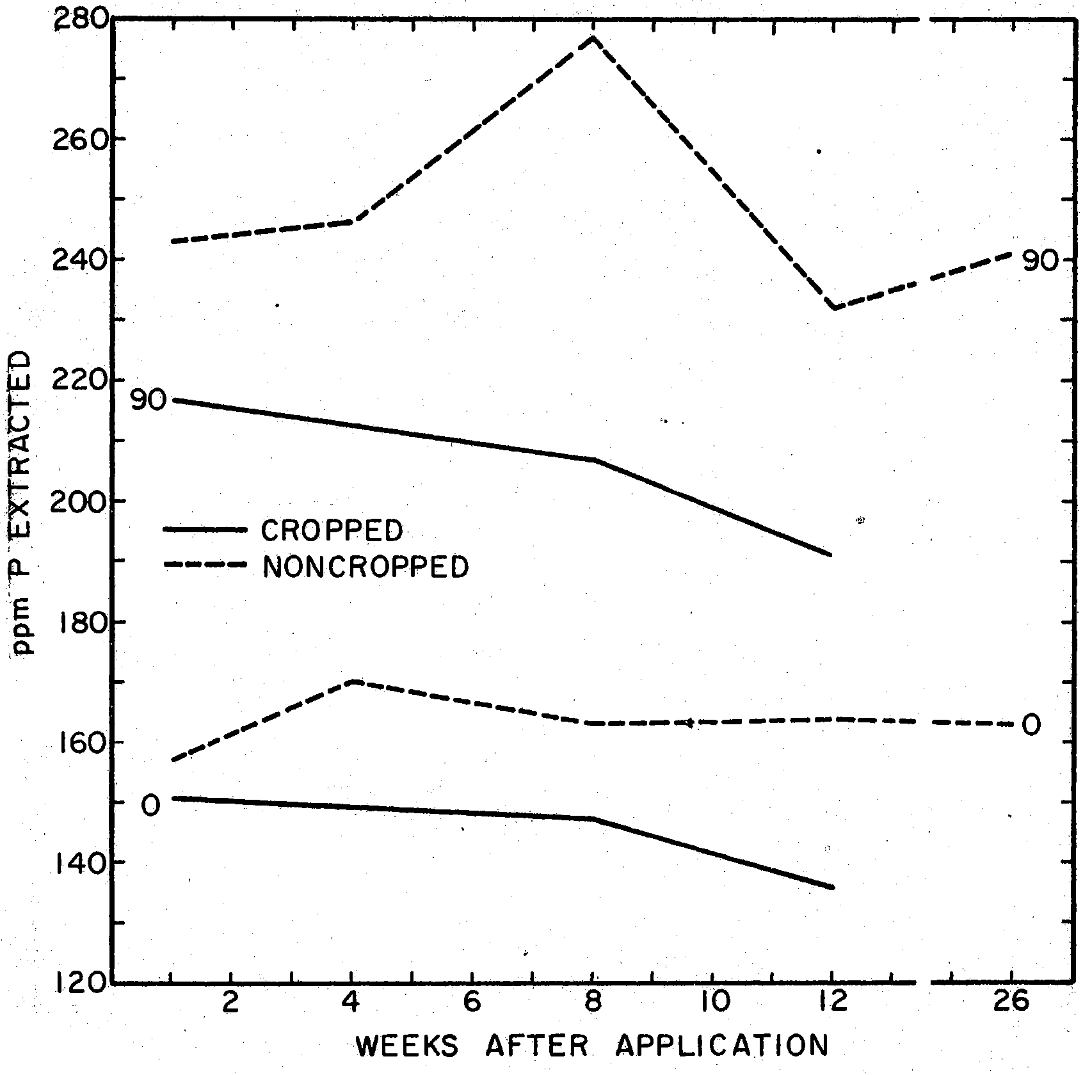

Figure 50. The Amounts of Bray-P Extracted from San Saba Silty Clay as a Function of Time, Both Cropped and Noncropped.

value of r^2 in Table VIII). Declines of Bray-P in the cropped soils indicate that it is a measure of available P.

In many of the noncropped soils there is little change in Bray-P as a function of time. The lack of change indicates that much of the fixation of P as Bray-P occurred during the one week prior to the first sampling in most soils. The rapid fixation of P was followed by a much slower period of fixation in several of the soils, however, as evidenced by either increases or decreases in Bray-P. In some of the high P-fixing soils, notably Parsons, Bates, and Summit, (Figures 26, 27 and 28) there are declines in Bray-P with time. These soils contain appreciable amounts of oxalate-Fe (Table III) and the decline is probably due to fixation of phosphorus as Fe-P not soluble in the Bray reagent.

The decline in Bray-P in Foard (Figure 29) probably reflects fixation of Ca-P since this fraction is increasing as evidenced in Figure 19. Such a decline in Bray-P and an increase in Ca-P is evidence that the fluoride ion of the Bray reagent suppresses some of the more insoluble forms of Ca-P.

A notable increase in Bray-P occurs in a few soils. In Dill (Figure 30) the increase is probably due to formation of Al-P as evidenced in Figure 9. The change of Bray-P in Hollister (Figure 31) is similar to the changes in Al-P, NH_4Cl-P and Ca-P, with the change in Fe-P being nearly opposite to that of Bray-P. The peculiar pattern of Bray-P in Norge (Figure 32) appears to be related to changes in NH_4Cl-P, Al-P, and Fe-P but the change in Bray-P is considerably in excess of the sum of the changes of these fractions. The initial decline of Bray-P in Norge is an indication that the initial fixation

TABLE VIII

COEFFICIENTS OF DETERMINATION (r^2) COMPARING AVAILABLE P AND YIELD OF SORGHUM SUDAN, AND CORRELATION COEFFICIENTS (r) COMPARING AVAILABLE P AS MEASURED IN SEVERAL EXTRACTANTS

	r^2			r		
Extractant	1st Crop	1st & 2nd Crop	1st, 2nd & 3rd Crops	$NaHCO_3$	North Carolina	NH_4Cl-P + Al-P
Bray[1]	.872	.745	.808	.954	.537	.986
North Carolina[1]	.202	.241	.319			.425
$NaHCO_3$[1]	.884	.788	.805		.363	.922
Bray[2]	.908	.910	.902	.998	.984	.998
North Carolina[2]	.828	.901	.933			.985
$NaHCO_3$[2]	.933	.923	.887		.984	.947
Bray[3]	.947	.611	.766	.911	.625	.956
North Carolina[3]	.129	.190	.430			-.024
$NaHCO_3$[3]	.912	.676	.743		.554	.940

[1] r^2 and r values are for all soils as a group.

[2] r^2 and r values are for those soils having Al-P or Fe-P as the dominant form of P.

[3] r^2 and r values are for those soils having Ca-P as the dominant form of P.

had not reached completion by the first sampling. Similar declines were noted in a previous study (Norwood, 1969) in several soils. In that same study Bray-P also increased following the initial decline. The difference in reactions between the two studies were caused by factors which remain unknown.

Extraction of Available Phosphorus from Soils and Its Relation to Yield

In Table IX are listed the amounts of NH_4Cl-P + Al-P, Bray-P, North Carolina-P and $NaHCO_3$-P extracted from each of the 25 soils. The soils are divided into two groups according to their phosphate distribution patterns. In Table VIII are listed correlation coefficients (r) and coefficients of determination (r^2) comparing P extracted by the various extractants and yield of sorghum sudan. It was necessary to omit certain soils from some of the comparisons; reasons for omission are listed in the footnotes.

The amounts of phosphorus removed by the Bray reagent have been found to be related to the Al-P fraction (Pratt and Garber, 1964; Tripathi, et al., 1970; Martens, et al., 1969; Grigg, 1965, 1968; Susuki, et al., 1963), and the results of the present study confirm this relationship. In most soils the amounts of phosphorus extracted by the Bray reagent are nearly equal to the sum of NH_4Cl-P and Al-P (Table IX). An r value of .986 is obtained between Bray-P and NH_4Cl-P + Al-P when all soils are considered (Table VIII). Since NH_4Cl-P and Al-P are the phosphate forms most available to plants, the validity of Bray-P as an accurate measure of available P is strengthened.

$NaHCO_3$ removes considerably less P from soils than does Bray but the r value of .954 between P extracted by those two reagents indicates that the forms of P are quite similar. Similar r^2 values are obtained when these reagents are used to predict yields. $NaHCO_3$ can probably be used without modification to extract P from calcareous soils, while the Bray reagent can be partially neutralized by $CaCO_3$, necessitating an increase in the soil:solution ratio (Smith, Ellis, and Grava, 1957;

TABLE IX

THE AMOUNTS OF AVAILABLE PHOSPHORUS MEASURED IN SEVERAL EXTRACTANTS

	Form of P (ppm)			
Soil	NH_4Cl-P + Al-P	Bray P	North Carolina P	$NaHCO_3$ P
		Al-P or Fe-P Dominant		
Parsons	6.24	4.62	3.02	2.04
Norge	6.75	5.50	5.12	1.90
Bowie	5.50	3.75	2.85	1.70
Bates	3.69	4.50	4.17	2.30
Cobb	11.12	9.80	10.15	4.70
Kingfisher	10.06	9.15	29.65	3.10
Waurika	23.59	26.70	24.00	11.10
Kirkland	20.77	21.15	26.85	11.40
Port	30.78	37.45	40.60	19.60
Renfrow	32.28	34.15	37.57	16.90
Dill	34.12	39.05	49.27	18.90
Lela	96.67	116.0[1]	157.0[1]	61.10[1]
Summit	11.50	6.45	13.45	3.80
		Ca-P Dominant		
Foard	12.50	12.50	65.82	6.40
Carey	16.30	11.42	44.70	4.80
Ulysses	15.17	12.33[3]	58.33	4.80
Canadian	14.99	18.35	85.45	6.50
Miller	40.37	34.00[3]	20.40[1]	9.10
St. Paul	20.61	20.30	133.0	6.10
Pratt	24.72	30.80	90.72	12.20
Hollister	22.20	27.80	84.20	14.10
Osage	23.68	24.30	82.80	13.50
San Saba	150.0	105.0[2]	34.50[2]	57.30[1]
Tipton	80.32	85.25[1]	173.0[1]	22.10[1]
Brewer	45.76	57.40	104.0	28.80

[1] Omitted from calculations because of high available P.

[2] Omitted from calculations because of high available P and calcareous nature of the soil.

[3] Omitted from calculations because of calcareous nature of the soil.

Randall and Grava, 1971). The main effect of $NaHCO_3$ in calcareous soils is to decrease the Ca^{2+} activity, which in turn increases the solubility of P (Olsen, et al., 1954). The effect of the fluoride ion of the Bray reagent in calcareous soils is to repress the solubility of forms of Ca-P that are of low availability to plants (Smith, et al., 1957). Randall and Grava (1971) found that the fluoride ion could be deactivated by calcium: $Ca^{2+} + 2F \rightleftharpoons CaF_2$, and is further reason to widen the soil:solution ratio when extracting P from calcareous soils.

According to Olsen, et al., (1954) the main effect of $NaHCO_3$ on acid and neutral soils is probably competition of HCO_3^-, CO_3^{2-}, and OH^- ions for P sorbed on the surface of soil particles. In acid soils the fluoride ion of the Bray reagent effectively complexes Al, releasing P ions to the solution. The fluoride ion also replaces sorbed P ions (Bray, 1945).

In spite of differences in the actions of the Bray reagent and $NaHCO_3$ the similar r^2 values obtained when P extracted is related to yield indicates that the reagents are equally satisfactory for estimating available P.

The North Carolina extractant should not be used to extract available P from soils containing appreciable Ca-P. The reagent does not distinguish between available and unavailable forms of Ca-P. Unlike the Bray reagent it contains no anion to repress the solubility of unavailable Ca-P. Any appreciable amount of Ca-P will cause an overestimation of available P when using the North Carolina method. Examples of soils containing such amounts of Ca-P are Kingfisher and Carey which contain only moderate amounts of Ca-P (Table I) yet exhibit high values of North Carolina-P, particularly when compared to Bray-P. On the other hand North Carolina-P appears to be entirely adequate for the extraction of available P from acid or neutral soils that do not contain appreciable Ca-P. It extracts amounts of P from such soils comparable to the amounts extracted by the Bray reagent.

CHAPTER V

SUMMARY AND CONCLUSIONS

In order to characterize their P status a study was made of the reactions and availability of P in 25 Oklahoma soils. The following conclusions were reached:

1. Fe extracted by oxalate was found to be related to newly formed Fe-P. It was concluded that the major form of P fixation by Fe in these soils was sorption of P onto amorphous Fe oxides or hydroxides. A good relation between Al and newly formed Al-P was not found. The reasons for the lack of a relation were not determined with certainty but it was assumed that either; 1) the active Al was not measured, 2) newly-formed Al-P could not be accurately determined, or 3) the Al-P compounds formed were too unstable to be related to Al at any one time. It was suspected that Al might have been important early in the fixation process since r^2 values were higher on the first sampling date than on later sampling dates. On the other hand the relation between oxalate-Fe and Fe-P tended to improve with time, indicating slow formation of Fe-P and conversion of Al-P to Fe-P in certain soils. Al was thought to have a greater role in P fixation at higher fertilization rates as evidenced in the increase in the ratios of Al-P:Fe-P with increasing rates of fertilization.

2. It was postulated that the acidifying effect of concentrated superphosphate in soils may have been responsible for recovery of P

in excess of that applied. It was also found that applied P could be converted to forms not soluble in any of the reagents used in the P fractionation procedure.

3. All forms of P, as determined by the Chang and Jackson fractionation procedure, were found to be at least partially available to plants grown on certain soils. NH_4Cl-P was found to be nearly 100% available, but was not formed to a large extent in soils of high P fixing capacity. Al-P was found to be a major source of P in all soils; Fe-P was utilized to a much lesser extent. The status of Ca-P was found to be in doubt. Generally not much depletion of Ca-P was measured as a result of cropping, but this could have been due to solubility of $CaHPO_4$ in NH_4Cl, the first extractant in the fractionation procedure. The extent of the persistence and resulting period of availability of $CaHPO_4$ in soils could not be determined, nor could the extent of its solubility in NH_4Cl. The possibility of the conversion of $CaHPO_4$ to Al-P and Fe-P during the extraction with NH_4Cl was also considered. However, based on the stability of NH_4Cl-P in noncropped soils (lack of conversion of NH_4Cl-P to forms of P not soluble in NH_4Cl) it was tentatively concluded that the fractionation procedure may have provided a reasonable estimate of Ca-P in fertilized soils; however, the issue remains in doubt.

4. Changes in Bray-P as a function of time and cropping generally followed changes in NH_4Cl-P plus Al-P. In some soils correlations of Bray-P with Fe-P and Ca-P were found. In most of the noncropped soils there was essentially no change in Bray-P with time, indicating rapid fixation of applied P as Bray-P by the first sampling date.

5. Bray-P, North Carolina-P, and $NaHCO_3$-P were all found to be

good estimates of available P, with certain limitations. Bray-P was a good estimate of available P in all soils regardless of the P distribution pattern, with the exception of calcareous soils. Widening the soil:solution ratio would probably adapt the Bray reagent to calcareous soils. $NaHCO_3$ can be used without modification for the extraction of available P from all soils, and is a near equivalent of Bray. The North Carolina method is a near equivalent of Bray and $NaHCO_3$ when used on soils which do not contain appreciable amounts of Ca-P. When used on soils containing even moderate amounts of Ca-P the North Carolina method overestimated available P.

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