

PHOSPHORUS AVAILABILITY, SOLUBILITY AND EXTRACTABILITY
AS AFFECTED BY AMOUNT AND FREQUENCY OF APPLICATION
AND TIME OF INCUBATION

by

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ABSTRACT

This study was conducted to determine the relative efficiencies of a single-large application of phosphorus versus small-frequent applications. One hundred ppm P as MCP and DCPD and 50 ppm P as MCP and DCPD were thoroughly mixed with the soil to represent single-large applications whereas 5, 10 and 20 ppm P as MCP were added as a band treatment prior to seeding of each barley crop to represent frequent small applications. Six successive crops were grown in the growth chamber. Yield and soil analyses were used to evaluate the supply of phosphorus from the various treatments.

Dry matter yields, for the first two crops, were higher for the single-large applications than for the frequent-small applications and declined in the order: 100 ppm P as MCP or DCPD > 20 ppm P as MCP > 50 ppm P as MCP or DCPD > 10 ppm P band > 5 ppm P band > control. Yields for crops 3 to 6 were higher for the frequent-small applications than for the single-large applications and declined in the order: 20 ppm P band > 10 ppm P band > 100 ppm P as MCP or DCPD > 5 ppm P band = 50 ppm as MCP or DCPD.

Phosphorus content of plants grown with the single-large applications were much higher than for plants treated with frequent-small applications for crops 1 and 2. However, for crops 4, 5 and 6, percent phosphorus in plants treated with smaller but frequent applications of phosphorus were equal to or greater than plants treated with single-large applications of phosphorus.

Uptake and percent recovery of applied phosphorus declined with cropping for the single-large applications of phosphorus. In contrast, uptake and percent recovery of applied phosphorus remained relatively constant with cropping for the frequent-small applications, particularly for crops 2 to 6 inclusive. The greatest total uptake and percent recoveries occurred when 50 or 100 ppm P were added. These higher recoveries, however, were not reflected in yield increases.

NaHCO_3 -extractable phosphorus decreased rapidly with time for the single-large applications of phosphorus, whereas the banded treatments maintained extractable phosphorus levels at relatively constant levels. NaHCO_3 -extractable P concentrations were greatest for the single-large applications of phosphorus for crops 1 and 2, but declined to values less than that for the 10 and 20 ppm banded treatments for crops 5 and 6.

Results of solubility studies showed that the largest phosphorus application had the highest initial P solubility. Phosphorus solubility decreased with cropping for the single-large applications of phosphorus. Soil treated with frequent small dressings of phosphorus had higher solubilities of P after the first two to three crops than soils with the single-large applications of phosphorus.

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LIST OF ABBREVIATIONS

P -	phosphate
MCP -	monocalcium phosphate (Ca(H ₂ PO ₄) ₂)
DCPD -	dicalcium phosphate dihydrate (CaHPO ₄ ·2H ₂ O)
DCPA -	dicalcium phosphate anhydrous (CaHPO ₄)
DMPT -	dimagnesium phosphate trihydrate (MgHPO ₄ ·3H ₂ O)
TMP -	trimagnesium phosphate (Mg ₃ (PO ₄) ₂)
MKP -	monopotassium phosphate (KH ₂ PO ₄)
OCP -	octacalcium phosphate (Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O)
H.A. -	hydroxyapatite (Ca ₁₀ (PO ₄) ₆ (OH) ₂)

I INTRODUCTION

The central points of studies in soil chemistry has always been the relations existing between the solid and liquid phases of the soil. These relations determine the concentration of different elements in the soil solution essential for plant growth and the capacity of the soil to supply a sufficient quantity for high yields. The soil solution contains many cations and anions. The dynamics or kinetics of the solid liquid system is not as simple as may be indicated by a reaction such as $P_{\text{solid}} \rightleftharpoons P_{\text{liquid}}$. Many environmental factors and soil properties affect the equilibrium. The major portion of phosphorus fertilizers added to soils enters the solid phase either as adsorbed or precipitated phosphorus. All the reaction products formed by precipitation, or adsorption will change with time to less soluble forms. An equilibrium is maintained, however, between solid and solution phases. This equilibrium changes with time.

Although the fate of phosphorus in soils is relatively well known, conflicting reports were found in the literature on the long-term availability of added phosphorus. Some authors have suggested that a single-large application of phosphorus applied infrequently was as effective in increasing yields as were annual but smaller applications when equivalent amounts of phosphorus were added over a period of time. Other authors stated that annual applications were much superior to infrequent but large applications in increasing yields. This study was conducted to determine the relative efficiencies of a single-large

application of phosphorus versus small-frequent applications. The study was conducted in the growth chamber using pots. Plant growth studies and soil analysis such as solubility studies and NaHCO_3 -extractable phosphorus were used to evaluate the supply of phosphorus from the various times and methods of phosphorus application.

REVIEW OF LITERATURE

(1) Rate of Reaction of Phosphorus With Soil

The reaction rate of phosphorus with soil minerals is a function of phosphate concentration and the total amount reacted is a function of time (Russell and Prescott 1916). Kittrick and Jackson (1955) found the phosphate reaction rate for several soils to be very rapid immediately after phosphorus application and to decrease to lower values in a matter of minutes. The rate of reaction with an acid soil with phosphorus after three minutes contact was two hundred and twenty tonnes of super phosphate per hectare per hour but after one month the rate of reaction had fallen to about one kg per hectare per hour. Tamimi et al. (1968) found that one-fifth of the ammonium phosphate added, reacted within the first two hours of contact with the soil. Following this period, the reaction rate slowed down considerably. It reached a low rate after eight hours of contact.

It has been postulated that the high initial rate of reaction of phosphate in acidic soils is due to phosphorus reacting with readily available aluminum and iron ions, while the subsequent slower rate is due to the reaction of phosphate with aluminum and iron released from decomposing clay minerals (Haseman et al. 1950; Kittrick and Jackson 1956).

The term slow reaction or slow fixation is usually used to describe the processes which cause the slow decline in the concentration of phosphate in soil solution. Munns and Fox (1976) mixed dissolved phosphate with a surface soil sample and followed the decline in

solution phosphate concentration for 200 to 300 days. They found the slow fixation reaction followed first order kinetics with respect to phosphate concentration in the soil solution.

Lindsay et al. (1962) investigated the reaction rate in a Hartsells soil after treatment with monoammonium phosphate. They had different periods of contact between soil and fertilizer prior to filtration, and found that increasing the reaction time decreased the quantity of precipitate formed in the filtrate. Kittrick and Jackson (1955) concluded that due to adequate reactive ions in this soil, the initial reaction rate increased with phosphate concentration. The lower reaction rate of phosphate in soil with increasing time of contact indicated depletion of reactive soil ions.

An exponential rate of loss of labile P was suggested by Larsen et al. (1965). In the pH range of 5.5 to 7.5 they found the half-lives of labile phosphorus in their mineral soils to vary from 1 to 6 years; the more rapid loss being associated with soils of higher pH. Eanes et al. (1965) suggested that the formation of pure hydroxylapatite caused a spontaneous autocatalytic change from initial amorphous products to well crystalline materials. Thus, the exponential curve for loss of labile phosphorus was probably due to this spontaneous change occurring at random in the isolated spots where labile amorphous phosphorus compounds had been formed from the added phosphorus compounds.

It has been observed that the level of addition of phosphate did not affect the proportion converted to a form which was not extracted by arsenate (Barrow 1974a), nor the proportion which did not equilibrate with isotopically labelled phosphate (Barrow 1974b). In this respect

the conversion to the ineffective form followed first-order reaction kinetics with respect to phosphate. However for first order reaction kinetics plots of the logarithm of residual effectiveness vs. time should be linear (Glasston 1964). This was not observed by Barrow (1974b). He suggested that the observed effects of time and temperature on phosphate converted to ineffective forms can be described by the following equation:-

$$d\alpha/dt = K(1-\alpha)^n$$

where:

α is the proportion of phosphate converted into an ineffective form,

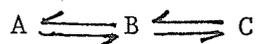
K is the rate constant (proportional to $\text{Exp}(-E/RT)$),

E is analogous to the energy of activation,

T is temperature in K° ,

t is time, and the value of n was about 3.

He showed that the decrease in effectiveness of phosphate fertilizer is very rapid in warm moist soil. He also found a three-fold decrease in the rate of effectiveness for each 10° increase in temperature. Barrow and Shaw (1975) reported that when the temperature was changed during incubation, the rate of reaction changed to a value appropriate to the new temperature. They represented all reactions of soil phosphate as a three compartment system:



where A represents phosphate in the soil solution. Its concentration is determined by the concentration of adsorbed phosphate in compartment B

according to an adsorption isotherm. C represents phosphate which has been converted into a form which is not in direct equilibrium with compartment A. They postulated that the transfer from compartment B to C could be described by an equation similar to that which described the transformation of phosphate from an effective to an ineffective form for plant growth (Barrow 1974b). This equation was combined with an adsorption isotherm relationship to develop an equation to describe the effect of time and temperature on the concentration of phosphate in solution. The equation developed is shown below:

$$\ln X_t = K + B_1 \ln P - B_2 \ln t + B_3/T$$

where:

χ is the concentration of P in solution,

k is reaction rate, t is time, T is temperature in K°

$K = 1/b_2 \ln(m/a) - b_1/b_2 \ln(A/b_1)$,

$B_1 = 1/b_2$, $B_2 = b_1/b_2$ and $B_3 = b_1 E/b_2 R$

$b_1 = 1/(n-1)$

$a_1 b_2$ are constants for any given soil,

E is analogous to the energy of activation,

R is the gas constant and P is amount of phosphorus added.

The equation stated that the logarithm of the solution concentration of phosphate would be a linear function of (1) the logarithm of the concentration of phosphate added (2) the reciprocal of temperature, and (3) the logarithm of time.

The review of literature on rate of reaction of phosphorus in soil indicates that phosphorus applied to soils is rapidly removed

from soil solution after dissolution of the fertilizer granule. This initial rapid reaction decreases with time to very slow reaction rates. The review of literature also shows that the rates of reaction vary with soil type and environmental factors.

The rates of reaction are important in assessing plant availability of applied phosphate. Since the amounts of phosphorus in soil solution are greatest immediately after phosphate application and then decrease with time, the availability of phosphorus to plants is likely to be greatest immediately after phosphorus application and then decrease with time.

(2) Adsorption Reactions of Phosphorus in Soil

Adsorption is a very important phenomenon in the chemistry of soil phosphorus and is one mechanism which determines the phosphorus concentration in soil solution. Soils adsorb added phosphate in amounts which depend on amounts of calcium carbonate in calcareous soils (Hemwall 1957; Larsen and Widdowson 1970), soil pH, exchangeable aluminum, free iron oxide, organic matter and clay content of soils.

(a) Phosphate adsorption in acid soils

The surfaces that are active in phosphate sorption contain aluminum and ferric ions. They may be active by having a part of their positive charge neutralized by the negative charge on the clay or humic surfaces and part by the phosphate anions; the aluminum may be at the broken edge of the clay sheet, or the active aluminum and iron may be present as surface films of their hydroxides (Russell 1973). It has not been simple to determine the relative importance of these various processes for holding phosphate in any particular soil because of lack of methods for distinguishing between them.

Rajan (1975) found that at concentrations of less than 600 μ moles P/g soil, phosphate is adsorbed by ligand exchange. At concentrations greater than 500 μ moles P/g soil, however, other mechanisms were also involved. These were:

- i) disruption of aluminum polymers
- ii) displacement of clay structural silica.

The displacement of structural silica by phosphate occurred because of the stronger bonding of aluminum with phosphate than with silicate

(Mattson 1931). Also, both phosphate and silicate are tetrahedrons of similar size. The ionic radius of Si^{4+} is 0.42 \AA and that of P^{5+} is 0.35 \AA .

The relationship between amount of phosphate adsorbed or released and time has often been described by a first order kinetic equation (Fried et al. 1957; Larsen et al. 1965; Larsen and Probert 1968) or a series of exponential terms (Amer et al. 1955; Arambarri and Talibudeen 1957). Kuo and Lotse (1972), proposed a second-order kinetic equation, based on a simple physical model, to describe phosphate adsorption which fits the Langmuir adsorption isotherm.

The relation between the amount of phosphate a soil will adsorb from a phosphate solution and the concentration of the phosphate left in the solution is known as the adsorption isotherm. Constant temperature is essential because the relationship is temperature dependent (Russell, 1973). The determination of adsorption isotherms is one of the most useful experimental procedures in the study of the interaction of phosphate with soils. Several models have been used to describe anion adsorption, with most workers favoring the Langmuir model which is described by the following equation:-

$$\theta = \frac{Kc}{1+Kc}$$

where

c = solution concentration,

θ = x/x_m

x = amount of ion adsorbed

X_m = the sorption maximum

K is a constant related to the adsorption energy.

In the Langmuir model, derived for the adsorption of gases onto solid surfaces, it is assumed that adsorption is restricted to a monolayer and that the energy of adsorption does not vary with the surface coverage. The equation can be written in the linear form:-

$$\frac{c}{x} = \frac{c}{x_M} + \frac{1}{Kx_M}$$

The equation has been used to calculate the constants for soil phosphate data (Olsen and Watanabe 1957) but this was possible only by covering the concentration range to $0.5 \times 10^{-4}M$ to $5 \times 10^{-4}M$, over which the Langmuir plot was approximately linear. Over wider concentration ranges plots were curved. This was also found by Gunary (1970). This curvature indicates that the bonding energy is not in fact constant over a wide concentration range and that there is no well defined adsorption maximum. A possible reason for this is that sorbed phosphate migrates to sub-surface layers.

Low and Black (1947) and Low and Black (1950) using $10^{-4} M$ phosphate solution, found adsorption to be consistent with a Freundlich adsorption isotherm. They suggested exchange with surface hydroxyl groups and silicate tetrahedra in the kaolinite crystals as a mechanism for the initial rapid adsorption of phosphate, and subsequent recrystallization of the surface phosphate to aluminum phosphate for the slow uptake of phosphate from solution. They concluded that adsorption was a chemisorption and that the reaction was between the phosphate and the surface hydroxyl ions of the clay mineral.

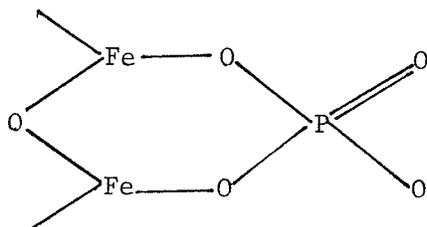
Pissarides et al. (1968) used three different clay minerals previously saturated with various mono and divalent cations. They showed:

- i) phosphorus retention data conformed to the Langmuir isotherm.
- ii) the values of the phosphorus adsorption maxima were a function both of the type of clay and saturating cations.
- iii) phosphorus was retained by adsorption on the surface of the clay minerals, most likely on the edge surfaces.

Adsorption isotherm studies demonstrated the need for distinction between the relatively strong bonding of adsorbed phosphate ions (specific adsorption), and the relatively much weaker bonding by other types of anions such as Cl^- and NO_3^- (non specific adsorption).

Phosphate adsorption changes the surface charge towards more negative values, in contrast to the behavior of chloride and nitrate. Because of these differences it was postulated that phosphate coordinates with Fe^{3+} ions, giving a strong bond owing to close approach of the opposite charges. Whilst non specifically adsorbed anions did not enter Fe^{3+} coordination, giving a much weaker bond owing to separation by one or more water molecules (Hingston et al. 1967, 1968, 1972).

This model was further developed by P^{32} isotope exchange studies, showing a relatively very slow rate of exchange which was attributed to involvement of two Fe^{3+} ions for each phosphate ion in a binuclear rather than mono nuclear coordination (Atkinson et al. 1972). Infrared spectroscopic studies have provided direct evidence for binuclear, $\text{Fe-O-P(O}_2\text{)-O-Fe}$, bonding such as



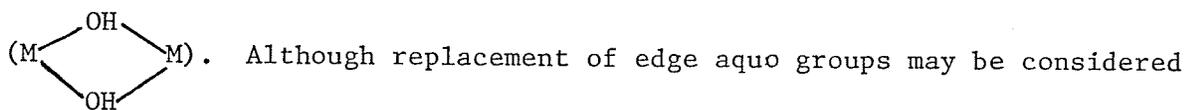
. This bonding involves the coordination of the phosphate ions to two Fe^{3+} ions on the goethite surface (Atkinson et al. 1974). Other infrared studies have shown that the spectral bands due to hydroxide ions singly coordinated to Fe^{3+} on goethite surface are lost when phosphate is adsorbed (Russell et al. 1974). Parfitt et al. (1975) by using infrared spectroscopic techniques found that two surface hydroxyl ions (or water molecules) are replaced by one phosphate ion, resulting in a binuclear surface complex of the same type suggested by Atkinson et al. (1972). This coordination structure was suggested for phosphate adsorption on the surfaces of goethite, hematite, lepidocite, β -ferric hydroxide, and amorphous ferric hydroxide gel.

Tandon (1969) studied the relation between fluoride extractable aluminum in soil and fluoride-extractable phosphate. He found a linear relationship which supported the hypothesis that small additions of P resulted in a stronger bonding between P and Al than larger additions. This suggests that the greater the amount of P added the greater will be the variation in the distance between phosphate ions and the retention site thus resulting in P-Al bonds of varying strengths.

Colwell (1959) studied the phosphate retention characteristics of several amorphous and crystalline compounds of aluminum and found

that the relative values for phosphate retention by precipitated hydrated aluminum hydroxide (amorphous) and neutral gibbsite (crystalline) were 7.34% and 0.05%, respectively, of the weight of the hydroxides. He concluded, that the greater degree of phosphate retention by amorphous aluminum hydroxide was due to its greater degree of hydration and surface area (smaller particle size). A sample of amorphous aluminum hydroxide was shown to retain 137 times more monophosphate than crystalline aluminum hydroxide (Gorbunov 1959).

Perrott et al. (1974) stated that although the iron (III)-hydroxy surface adsorbed more phosphate than the aluminum-hydroxy surface, the shape of the isotherms were similar with the change in slope between 10^{-6} and 10^{-5} M. Two linear regions were obtained which could be interpreted as two separate Freundlich isotherms indicating different sorption sites or mechanism operating above and below this concentration. Two separate sites for ligand exchange in iron (III) and aluminum hydroxypolymers at low phosphate concentration would be the edge hydroxyl or aquo groups (M-OH, M-OH₂) and structural bridging groups



as a simple adsorption reaction, replacement of the structural bridging hydroxyl groups would eventually break the hydroxypolymers into smaller units leading to their dissolution and perhaps precipitation of basic phosphate at higher phosphate concentrations.

Soils differ in their capacity of retaining phosphate in the adsorbed phase due to their different physico chemical and mineralogical

composition (Deb and Datta 1966). Vanolphen (1963) hypothesized that clays possess, in addition to the double layer due to the negative charge on the planer surfaces, a positive double layer at the edge surfaces which may be capable of adsorbing anions even at neutral pH values. Edge adsorption of anions by clays has been demonstrated by electron-optical techniques. The adsorption of anions can be greatly reduced as a result of an extensive cationic atmosphere at the edge sites (Russell 1973).

Pissarides et al. (1968) proposed that the abnormally high adsorption maximum obtained with the K-illite-phosphorus system can be attributed to the interlayer adsorption of K during dehydration with ethanol and drying. K fixation leads to a decrease in the negative charge on the clay and causes a concentration of the diffuse double layer and a corresponding increase of phosphate ion activity at the vicinity of the clay surface.

Barrow (1974c) found that previous additions of phosphate to a soil reduced the soils ability to adsorb phosphate. His result indicated that some (but not necessarily all) of the phosphate which had been changed into a form which was no longer isotopically exchangeable within 24 hr remained on the adsorption sites thus effectively blocking them from further reaction with phosphate.

Muljadi et al. (1966) found that there are three regions in phosphate adsorption by soil which they related to the affinity of phosphate for at least three energetically different sites. They are:

Region I - at phosphate concentrations $< 1 \times 10^{-4}M$. In this region adsorption takes place on sites with a very high affinity

for phosphate. The adsorption sites of this region were originally thought to be Al ions associated with exchangeable cation sites, the aluminum ions being derived from the edge surface of the crystals (Cashen 1959).

Region II - at phosphate concentrations of approximately 10^{-4} M. The reaction sites responsible for adsorption in this region are considered to be similar to region (I).

Region III - at phosphate concentrations from 10^{-3} to 10^{-1} M. The adsorption in this region was associated with some part of the clay surface which is less crystalline than the bulk minerals.

Hingston et al. (1968) found that phosphorus availability increased after application of silica and attributed the increase in availability to the competition between phosphate and SiO_2 on adsorption sites in the kaolinite fraction of the soil. The role of silica seems to be omitted by several other workers dealing with the mechanism of phosphate adsorption on kaolinite.

With pH expected to be one of the most important factors determining phosphate sorptivity, its role in a mixed population of soils is evidently masked by variations in other soil properties. William et al. (1958), Ahenkorah (1968) and Lopez-Hernandez and Burnham (1974a) have all failed to show a significant correlation between phosphate sorptivity and pH. Lopez-Hernandez and Burnham (1974b) found the correlation between pH and phosphate retention was not significant for a group of mixed soils but a group of pedologically similar soils

differing mainly in pH gave a highly significant ($p = 0.001$) decrease in retention with increasing pH. They found the highest phosphate adsorption occurred at the lowest pH (4.45). They attributed the effect of pH on phosphate adsorption to the alteration in the activity of aluminum upon pH change.

The adsorption of P at a pH of 7.15, even though there was no exchangeable aluminum at this pH, was due to the presence of surface-active iron and aluminum hydroxides and the formation of calcium phosphate. Obihar and Russell (1972) found that the adsorption envelope of phosphate, as described by Hingston et al. (1967, 1968), reached a maximum at low pH values for soils known to have high affinities for phosphate.

Deb and Datta (1967a) found that at a pH of 4.0, the higher activity of Fe and Al accompanied by development of a positive charge on soil colloids caused a higher retention of the ambient solution phosphate. The decrease in activity of Fe and Al and the comparative inactivity of the positive spots on colloidal surfaces are the main factors responsible for the low retention of P at higher pH. The effectiveness of associating anions changes with change of pH of the ambient solution.

Anions play a very significant role in the adsorption of phosphorus in soil. Swenson et al. (1949) and Struthers and Sieling (1950) suggested that organic anions form stable complexes with active iron and aluminum and experimental evidence presented by them seems to be conclusive. Dean and Rubins (1947) have demonstrated that organic

anions are not adsorbed to any considerable extent through anion exchange reactions.

Organic phosphorus compounds play a significant role in the phosphate regime of a soil. According to Williams et al. (1958) the relative amount of phosphorus associated with organic matter varies quite widely and very frequently represents not less than half the total amount of phosphorus in the upper soil horizons. Sinah (1971) observed that stable undissociable organo metallic phosphates were formed only when humic and fulvic acids contained complexed iron or aluminum. Wild (1950) pointed out that phosphorus adsorption by organic matter was negligible and any adsorption that occurred was due to the cations associated with organic matter. Fox and Kampruth (1971) studied phosphate adsorption in organic acid soils and high organic matter sand and found that these kinds of soils had very high capacities to adsorb phosphate. However the adsorbed phosphorus was very soluble.

Appelt et al. (1975) found that the adsorption of simple organic anions that are specifically adsorbed block to some extent the adsorption sites for non specifically adsorbed anions such as chloride and/or nitrate. But, organic anions did not compete for or block adsorption sites for phosphate anions, because of the much higher affinity of phosphates for the adsorption sites in the volcanic-ash derived soil being used.

The role of organic matter in phosphate sorption, therefore is a dual one; either it can sorb phosphate as shown by the positive correlations

between adsorption and organic matter content reported by a number of investigators such as William (1960) or else block potential phosphate sites on inorganic particles. The existence of decreasing sorptivity by competition between phosphate and organic anions has been demonstrated by Dalton et al. (1952).

b) Phosphate adsorption in calcareous soils

The chemistry of calcareous soils is dominated by soil carbonates and calcium and magnesium ions which may react with phosphate. Chang and Jackson (1957) have estimated that 95% of the phosphorus contained in calcareous subsoils is in the calcium form.

Calcium carbonate is one of the most surface-active constituents of calcareous soils. Talibudeen and Arambarri (1964) used a Ca^{45} isotope exchange procedure to measure CaCO_3 specific surface areas and found that these ranged from 20 to 51 M^2/g of CaCO_3 in soils containing from 7 to 81% CaCO_3 . Holford and Mattingly (1975) found an inverse linear relationship between specific surface area and percent CaCO_3 for soils with more than 12% CaCO_3 , but the relationship was hyperbolic below 12%

Cole et al. (1953) indicated that phosphate adsorption followed the Langmuir isotherm up to 9 mg P/l, at which concentration there was evidence of precipitation, probably of DCPD. Kuo and Lotse (1972) found that phosphate sorption by CaCO_3 showed two different types of behaviour depending on the concentration of phosphate in solution. At low initial phosphate concentrations, 0.5, 1, 2, 3, 4, and 5 ppm, and a reaction time of 24 hours, the adsorption data fitted the Langmuir isotherm. This indicated that phosphate adsorbed by CaCO_3 at low concentrations

forms a monolayer on the surface. They also hypothesized that in a water suspension of CaCO_3 crystallites, oxygen atoms of water molecules, bicarbonate ions, and hydroxyl ions may fill the vacant coordinate positions of exposed surface Ca^{2+} ions. The phosphate ions may replace adsorbed water molecules, bicarbonate ions, and hydroxyl ions. The drastic change in the $\frac{C}{x}$ value of the Langmuir plot between 5 and 10 ppm initial phosphate concentration was thought to be caused by precipitation of dicalcium phosphate.

Griffin and Jurinak (1973) described adsorption isotherms of phosphate on calcite by a two region Langmuir isotherm equation. The break in the slope of Langmuir plot was found to correspond closely to the division between OCP and HA. Stumm and Morgan (1970) reported that the initial adsorption of phosphate takes place on a limited number of specific surface sites. As adsorption proceeds, site coverage increases to the extent that lateral interaction occurs between the adsorbed ions. Lateral interaction produces doublets, triplets and eventually surface clusters of phosphate ions. These clusters serve as centers from which spontaneous crystal growth can occur. Qualitatively, the function of the specific adsorption sites on calcite is to reduce the activation energy required to form the critical phosphate clusters which are the necessary precursors for the nucleation of calcium phosphates crystals. This interpretation of the phosphate adsorption data is corroborated by the electron microscope studies of Stumm and Leckie (1970) who showed that exposure of calcite crystals to phosphate solutions resulted in nucleation of hydroxylapatite on widely separated surface sites.

Griffin and Jurinak (1974) studied the kinetics of phosphate

interaction with calcite in order to obtain kinetic data at short reaction times and also to verify if the phosphate reaction was a surface mediated or strictly a precipitation type of reaction. They found the reaction was surface mediated since when no calcite was present, the concentration of solution phosphate remained essentially constant during the entire four-hour reaction period. Whereas, the phosphorus concentration in the samples containing calcite fell rapidly to low values within 20-30 minutes after the initiation of the reaction.

Griffin and Jurinak (1974) reported that temperature dependence of the adsorption reaction was in the range from 0 C to 40 C. The higher temperatures increase the reaction rate while the lower temperature markedly decrease the approach toward equilibrium.

One of the important variables which affect phosphorus sorption studies is the ionic composition, both species and concentration of the solution. Ryden and Syers (1975a) found phosphate sorption was highest from 10^{-2} M Ca and lowest from water. Also they found that above a final phosphate concentration of 0.1 μ g P/ml, the amounts of phosphate sorbed from 10^{-2} M Ca were between 1.5 and 2.5 times greater than those sorbed from water. Ryden and Syers (1975b) reported that an increase in ionic strength enhanced phosphate sorption during 40 hours but the species of cation also influenced the amount of P sorbed.

The effect of Ca on P adsorption was not due to bulk precipitation of di- or octa-calcium phosphate. The solubility products of these salts as found by Helyar et al. (1976a) were not exceeded even in the most concentrated solutions. They postulated that Ca increases adsorption because it complexes with adjacent adsorbed phosphate ions,

reducing the repulsion force between them. The fact that Mg, K, and Na do not affect adsorption, whereas Ca does have an affect, suggests specific association between Ca and the adsorbed phosphate. Helyar (1976b) reported that divalent cations with a radius near 1.0 \AA increased the adsorption of phosphate by gibbsite. Ca, Cd, and Sr which increased adsorption have a crystal ionic radii of 0.99, 0.99, and 1.13 \AA , respectively, (Pauling 1948), while ineffective cations, Mg, Zn, Na, and K have a radii of 0.66, 0.74 0.95 and 1.33 \AA , respectively.

In summary the reactivity of CaCO_3 in soils depends on the specific surface area of the carbonate and hence on its total surface area. Adsorption on calcium carbonate and limestone has been found to follow a Langmuir isotherm up to 9 mg at which concentration there was precipitation, probably as DCPD. The adsorption of phosphate on CaCO_3 is kinetic and much phosphate is adsorbed rapidly on the surface as a monolayer, though the amount adsorbed and the equilibrium concentrations of phosphate vary with the surface area of the CaCO_3 used. Griffin and Jurinak (1973) obtained two distinct linear sections (region I and II) to their isotherms for phosphate adsorption on calcite and believed the reactions responsible were i) adsorption at various sites on the surfaces, (ii) multi-layer adsorption, and iii) nucleation of calcium phosphate.

(3) Precipitation of phosphorus in soil

The number of precipitates formed between soil and applied phosphorus is large and the chemistry governing transformations between the different forms is extremely complex. The soil phase contains Fe^{3+} , Al^{3+} , Ca^{2+} , Mg^{2+} , K^{+} , NH_4^{+} , H^{+} , OH^{-} , and F^{-} and must be considered as potential reactants with phosphate. Whether or not phosphate containing these ions precipitate, will depend to a large extent upon the activities of these ions in solution.

a) Precipitation of phosphorus in acid soils

In acid soil systems, phosphorus is known to form relatively insoluble compounds of iron and aluminum (Ghani and Islam 1946). Kittrick and Jackson (1955) proposed a dissolution-precipitation mechanism for the retention of phosphate by hydrous oxides and clay minerals. This was the replacement of structural bridging hydroxy groups followed by the breaking of the hydroxy polymers into smaller units leading to their dissolution and precipitation of basic phosphates. Hemwall (1957), using solubility-product criteria, showed that aluminum ions dissociating from the clay lattice could precipitate phosphorus in the form of variscite at a pH 4. Wild (1953) reported that the Al-ions replaced by cations may precipitate with the phosphate ions, either in equilibrium solution or in the diffuse double layer; the activity of the phosphate ions in both the equilibrium solution or in the diffuse double layer was determined by the concentration and charge of added cations.

Chu et al. (1962) found; 1) a single curvilinear relationship

for all soils studied, between soil pH and the amount of Al-phosphate formed. 2) The pH vs. Fe-phosphate relationships tended to separate on the basis of soil-free Fe content, more Fe-phosphate being formed with higher Fe contents. 3) The Fe-P/Al-P ratio apparently increased with time.

Taylor and Gurney (1965a) reported that when acidic calcium phosphate solutions were reacted with aluminum hydroxide in the presence of little potassium, all the potassium was precipitated as taranakite $K_3Al_5H_6(PO_4)_8 \cdot 18H_2O$; phosphate was also precipitated as aluminum and calcium aluminum phosphates. In the presence of sufficient potassium, however, the precipitation of phosphate was governed by the initial composition of the solution; as much as 25% of the phosphate was precipitated as dicalcium phosphate and most of the rest was precipitated as taranakite. They also found that goethite was much less reactive than gibbsite, both being more reactive than clay minerals.

In a continuation of studies of phosphate-soil reactions, Taylor and Gurney (1965b) used soil clays extracted from Davidson clay loam and from Nipe clay as phosphate precipitants. These clays contained 23 to 39% Al_2O_3 and Fe_2O_3 . The changes in composition of the solutions in contact with clays were dominated by the precipitation of phosphate by aluminum as potassium taranakite. The reactions observed with two soil clays were those predicted from similar studies of the precipitation of phosphate by mixtures of pure aluminum hydroxide and iron oxide and the results could be applied in the interpretation of fertilizer reactions in the soil.

Phosphate ions have been reported to enhance the decomposition of clay minerals at low pH values. For instance, Black (1941, 1942) observed the gradual dissolution of aluminum from kaolinite in concentrated acid phosphate solution (0.1-1.0 M) and attributed it to lattice disruption by substitution of phosphate ions for internal hydroxyl groups in kaolinite. Dipak et al. (1977), reported that MCP caused a progressive dissolution of soil constituents which resulted in the formation of a colloidal amorphous iron-aluminum phosphate compounds.

Kittrick and Jackson (1954, 1955) investigated the effect of 1.0 M phosphate solutions on kaolinite at 90 C and demonstrated the presence of a variscite-like compound. In experiments designed to simulate the conditions in soil surrounding a dissolving granule of MCP, Lindsay and Stephenson (1959) successively extracted dry soil with triple point solutions. They showed that the solutions dissolved appreciable amounts of iron, aluminum, manganese and calcium from the soil yielding filtrates which readily precipitated iron, aluminum and calcium phosphate. Low and Black (1947) hypothesized that phosphate induced decomposition of kaolinite, but only when the adsorbed H_2PO_4^- ions made a significant contribution to the H^+ ion activity in the bathing solution.

b) Precipitation of phosphorus in calcareous soils.

In base saturated and calcareous soils the cations Ca and Mg dominate the soil solution and thus are the major reactants with P. When MCP hydrolyzes in a basic soil, the usual initial residues of DCP are left behind,

and the dissolved phosphate is rapidly precipitated throughout the surrounding soil - much of it as DCPD and DCPA (Leher et al. 1959). Racz and Soper (1967) found DCPD and DMPT to be initial reaction products of pelleted MKP added to neutral and calcareous Manitoba soils. Hinman et al. (1962) found DCPD and DCPA to be the dominant reaction products when MCP was added to a Saskatchewan calcareous soil.

Strong and Racz (1970) incubated four soils with different Ca and Mg contents with KH_2PO_4 or K_2HPO_4 pellets for 1, 3, 6, 9, 12 and 15 months. They found six calcium and magnesium phosphates, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, $\text{Ca}_3\text{Mg}_3(\text{PO}_4)_3$ and $\text{Ca}_4\text{P}_2\text{O}_7$, formed in the soils.

Eanes et al. (1965) showed that Ca-phosphates precipitated from solution undergoes aging, changing from an amorphous to a more crystalline form. They showed X-ray diffraction patterns exhibited increased peak height with time. Griffin and Journak (1973) indicated that the processes of adsorption and heterogeneous nucleation are inseparable when describing phosphate interaction with calcite. The kinetics of the nucleation-crystal formation interaction is probably the reason hydroxylapatite is not found in natural systems as often as may be expected even though it is the thermodynamically stable form of calcium phosphate.

Bouldin et al. (1960) reported that as the time required for dissolution was increased, the quantity of DCPA formed increased. They also found that the addition of CaCO_3 to MCP increased the amount of

phosphorus in the residues to about 92% of the added P and OCP and DCPD were the predominant phosphate phases.

Brown and Leher (1959) found that the fraction of the phosphate left at the granule site of dissolved MCP as DCP or DCPD was governed by the relation:

$F = (1-R)/(2-R)$ where R is the mole ratio of $\text{CaO}/\text{P}_2\text{O}_5$ in the composite solution removed from the granule, and can be determined experimentally or estimated from the phase rule data for the system; $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$.

Webber and Mattingly (1970) found the changes in $\frac{1}{2} \text{pCa} + \text{pH}_2\text{PO}_4$ and $\text{pH}-\frac{1}{2} \text{pCa}$ that occurred when MCP was added to the soil were consistent with slow precipitation of the added phosphate as OCP. Amer and Ramy (1971) reported the formation of OCP after reaction of KH_2PO_4 with CaCO_3 . By isotopic exchange measurements they confirmed the presence of OCP, when the amount of P retained exceeded 44 μmoles per gram CaCO_3 .

c) Changes in reaction product with time

The reaction products formed upon phosphate fertilizer addition are metastable and with time will change into more insoluble compounds. Transformation of phosphorus applied to soil is generally thought to occur as a complex series of multistep kinetic reactions (Talibudeen 1974; Mattingly 1975). Chang and Chu, (1961) reported that as time elapses, the calcium and aluminum phosphates formed in acid soils change gradually to less soluble iron phosphate according to solubility product principles.

Mandal and Chatterjee (1972) studied the transformation of applied

water soluble phosphate in six latosolic low land rice soils. They found the transformation into Al-P and Fe-P to be directly related to the quantity of these inorganic forms of phosphate already present in the soils. They also found that transformation into Ca-P was low in all the soils, ranging from 6-12% of the added amount for the different soils. About 10 to 30% of the added phosphorus transformed into reductant soluble iron phosphate.

Mandal and Das (1970) in acid low land rice soils found the magnitude of transformation of the added phosphorus into insoluble aluminum phosphate in different soils was closely related to their Al_2O_3 content. In a soil with 23% Al_2O_3 as much as 44% of the added phosphorus was transformed into Al-P. They also found the maximum fixation as aluminum phosphate occurred within the first week.

Taylor et al. (1963) incubated acidic phosphate-soil reaction products with an acid soil for 10 months and found that $\text{H}_3\text{KFe}_3(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$ was relatively more stable and was present at the end of incubation period. Juo and Ellis (1968), in pure systems, found that colloidal iron phosphates crystallized to form strengite, while colloidal Al-phosphate formed variscite. The amorphous forms of iron and aluminum phosphate were relatively good sources of P for plants grown on acid soils, whereas the crystallized forms of iron and aluminum were virtually unavailable (Taylor et al. 1963; Juo and Ellis 1968). Lindsay and Dement (1961) and Taylor et al. (1963) also found that synthetic, colloidal Al-P and Fe-P were relatively good sources of P for plants while variscite and strengite were almost completely unavailable when applied to acid soils.

Subbaro and Ellis (1975) found that ammonium polyphosphates slowly disappeared and transformed into $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 25 \text{H}_2\text{O}$ after 28 weeks. They also found the reaction product, $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ in the saturated-solution extracts. Adding the orthophosphate to the slightly acid soil resulted in magnesium orthophosphate as a reaction product: $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ was identified after 16 weeks, and $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ was found after 28 weeks.

In calcareous soils, the initial reaction products such as DCPD change to less soluble calcium phosphates. Lehr and Brown (1958) found that DCPD changed to OCP and colloidal apatite in a period of four months. Larsen and Widdowsen (1970) stated that although CaHPO_4 may initially be formed when soluble phosphate is added to a calcareous soil it is not stable in the soil and will be converted to less soluble calcium phosphates and ultimately end up as the least soluble form, (fluorapatite). DCPD in calcareous soils is unstable at pH values above 6.38, and initially hydrolyzes to OCP (Moreno et al. 1960). Lehr et al. (1959) indicated that the transformation of phosphorus to OCP and apatite in basic soils proves they are more stable under these conditions than their precursor DCPD.

Abdou and Larsen (1964) developed a radioactive tracer method for measuring the solubility of sparingly soluble phosphates in soil and found that powdered DCP was totally converted to other forms in a soil of pH 6.5 incubated for one day at 25C. They also found the rate of conversion was dependent on the moisture content of the soil and the authors took this as further evidence for diffusion being the rate

controlling process. They also found that hydroxyapatite persisted unchanged in the soil for eight weeks.

Bell and Black (1970) found that DCPD changed to OCP in 4 weeks in soils having pH values above 7.9 and in 44 weeks in soils having pH values above 6.9 but below 7.9.

Talibudeen (1958) found that the labile phosphorus from MCP added to a calcareous soil decreased by one-third over a period of three months. Strong and Racz (1970) treated 4 soils, which were saturated with different amounts of Ca and Mg, with MKP and DKP and incubated them for 1, 3, 6, 9, 12 and 15 months. DCPD that formed in all soils gradually changed to OCP. DMPT persisted for periods of 5 months but there was evidence that some of the DMPT changed to $Mg_3(PO_4)_2 \cdot 22H_2O$. Larsen et al. (1964) found that granules of DCPD were recovered apparently unchanged 26 months after application to soils of varying textures in pots stored in the open. However, all the DCPD had disappeared after 37 months of incubation.

The review of literature indicates that initial reaction products of soluble phosphates in base saturated or carbonated soils change to more basic calcium and/or magnesium phosphates. DCPD changes to OCP and then eventually to HA. DMPT changes to the less soluble TMP. These reactions affect the long-term availability of applied phosphorus. Since the relatively soluble initial reaction products change to less soluble forms with time, plant availability of applied phosphorus will also decrease with time.

(4) Solubility of phosphorus in soils

Solubility of phosphate in the soil is influenced by many factors, but generally it is low under all conditions. The factors, favoring solubility are as follows:

1. A good supply of readily decomposable organic matter;
2. A pH between 6.5 and 7.5;
3. A high level of phosphorus;
4. A substantial level of soil moisture;
5. A high silica:sesquioxide ratio.

(a) Solubility of native phosphorus compounds

Solubility of phosphorus minerals in virgin soils is very low. However, the concentration of phosphorus in soil solution remains relatively constant with cropping. Level of phosphorus in soil solution will be maintained by the dissolution of phosphorus minerals, desorption of adsorbed phosphorus and mineralization of organic phosphorus (Larsen and Sutton, 1963; Vaidyanathan and Talibudeen, 1965).

Hydroxyapatite is considered to be the source of native soil phosphorus and the ultimate reaction product of added phosphate in base saturated and calcareous soils (Larsen, 1967), and thus the soil solution P concentration should be in equilibrium with that of HA. However, phosphate solubility in virgin soils deviate from that of pure HA. Jenson (1971) found that soils with pH values above 6.3, were super saturated with respect to hydroxyapatite, while those have pH values below 6.4 were under saturated. Larsen (1966) reported that it is not easy to prove under what conditions hydroxyapatite controls the

solubility of phosphate in the soil solution because:

1. solubility depends on whether HA is being precipitated or dissolved.
2. the surface of the crystal may possess an isoelectric point, which implies that an electric double layer outside the surface is either enriched in calcium ions or in phosphate anions, depending on whether the pH of the solution is above or below this point. The solution appears to be supersaturated with respect to HA if the pH is above the isoelectric point, and under saturated if below the isoelectric point.

Ulrich and Khanna (1968) found that for soils with a pH above about 6.5, the H_2PO_4^- concentration in the soil solution was controlled by the solubility of a calcium phosphate more soluble than hydroxyapatite but less soluble than octacalcium phosphate. They also found that if the soil is more acid than about pH 4 in a 0.01 M CaCl_2 solution, the H_2PO_4^- concentration was controlled by an aluminum phosphate more soluble than variscite but less soluble than amorphous aluminum phosphate. Thus the solubility of phosphorus is related to the pH of the soil. Alkaline soils usually have a solubility-pH curve similar to that of apatite, while acid soil usually have a solubility-pH curve similar to that of iron or aluminum phosphate.

In acid soils Al-P and Fe-P, such as variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) are generally believed to be the predominating ultimate end-product of inorganic phosphorus formed during soil genesis and by fertilization. Cole and Jackson (1951) determined the solution equilibria for variscite, which is one of the least soluble phosphorus

compounds and found it has a minimum solubility at pH 4, corresponding to a solubility product of $K_{sp} = 2.8 \times 10^{-29}$ when formulated as $(Al)(OH)^2(H_2PO_4) = K$. Lindsay et al. (1959) found that the pK is 30.5 at 25C. Chang and Jackson (1957) showed that for iron phosphate the corresponding pK values were about 34 to 35 for dissolution and 33 for precipitation. Variscite gave pK values of 24.7 to 28.4 for dissolution.

(b) Solubility of added phosphorus

The composition of the solution produced by dissolution of a single salt is reproducible and usually easily determined. When dissolution is incongruent, such as that of MCP in water, the situation is more complex, but still relatively simple in comparison with the dissolution of complex mixtures of salts, particularly when the solution is continuously removed. The dissolution of the mixture is governed by the combination of the solubilities of the individual salts and their rates of solution.

Lehr et al. (1959) found that MCP hydrolyzed in water with precipitation of DCPD which persisted even after 7 months of incubation. Moreno et al. (1960) used phosphate equilibria to study the chemical reaction of DCPD in soils. They equilibrated soil-water suspensions with different amounts of DCPD in 10 days at low DCPD levels. At higher levels of DCPD all indications were that DCPD persisted throughout the experiment of 60 days. These studies indicate that soil solution P concentration are in equilibrium with DCPD when this phosphate is added to soil or formed as a result of soluble phosphate additions.

Hagin and Hadas (1962) found that the solubility of phosphate was higher than that of OCP and increased beyond that of CaHPO_4 with increasing additions of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and attributed this to lack of phosphate equilibrium. Clark and Peech (1955) found a phosphate solubility less than that of hydroxyapatite after adding KH_2PO_4 and storing the mixtures moist for 5 months. Lindsay et al. (1959) reported that the solubility of reaction products decreased gradually upon aging.

Racz and Soper (1970) found the solubility of phosphate approximated that of DCPD and/or DMPT when KH_2PO_4 , H_3PO_4 and K_2HPO_4 were added to 4 Manitoba soils.

It has been suggested that the rate of dissolution of DCPD in soil is controlled by the rate of diffusion of dissolved material from the surface of the solid. The rate of dissolution of granular DCP should therefore be much slower than that of powdered DCP. Granules of DCP have been recovered after 3 to 6 months contact with cropped soil (Bouldin and Sample, 1957), and after 26 months in uncropped soil (Laresen et al. 1964). Probert and Larsen (1970a) found that the release of phosphate from the sample of DCP with the smallest particle size was rapid and was virtually complete in 30 days. The recovery of phosphate from the coarsest DCP increased throughout the period, while the results for the samples with intermediate particle size were within these two extremes. Murrmann and Peech (1969) found that 30 to 70% of the powdered DCP dissolved in 108 hours.

Sree Rumula and Pratt (1970) studied the effect of preheating, wetting and drying and of anaerobic conditions with and without additions of

organic matter on the dissolution of DCPD in three soils using phase equilibria. They found slightly higher rates of dissolution of DCPD in samples that had been wetted and dried. They also found that DCPD had dissolved completely at the 0.25 g of DCPD rate within 30 days in the wetting and drying treatments, whereas DCPD still persisted in the standard treatments at the same level of application. They also found that organic matter added to anaerobic samples increased the rate of the dissolution of DCPD added to soils.

Bache (1965) found the solubility of imperfect crystalline or amorphous Al- and Fe-phosphates was higher than that of the corresponding perfect crystalline compounds. This indicates that the iron and aluminum amorphous phosphates initially formed when acidic soils are phosphated will maintain a higher P concentration in soil solution than the crystalline forms which form after the soils are incubated for a long period of time.

Beaton et al. (1965) found that differences in the concentration of water-soluble P among various P fertilizers decreased with increases in time of reaction with soil. At the end of 56 days very little differences among MKP, DAP, and MCP were evident. The differences between these 3 sources and DCPD narrowed appreciably after 56 days of reaction with soil. The conclusion from these studies was that, the reaction products of various P sources for a given soil become nearly alike with time.

Temperature might be expected to affect P dissolution in 2 ways:-

1. Increase the diffusion coefficients of phosphate and calcium ions in the soil solution.

2. Increase the concentrations of calcium and phosphate in the moisture film adjacent to the DCP particles and so provide a higher concentration gradient for diffusion. Both effects will tend to increase the rate of dissolution.

Hinman et al. (1962) found significantly more water soluble P was extracted following reaction of MCP with soil at 5 C than when the reaction took place at either 16 or 27 C. The greatest release was obtained from the 60 bar moisture tension treatment at 5 C. Robinson (1942) obtained greater uptake of P from MCP treated soil when the soil was incubated prior to planting at 3 C than when it was incubated at 15 C or 45 C. Beaton et al. (1965) found that the rate of water-soluble phosphate fertilizer dissolution decreased markedly as temperature increased. For each 15 degree increase in temperature there was about a 33% reduction in concentration of water soluble P.

Huffman et al. (1960) studied the chemical and kinetic aspects of three possible soil phosphates; calcium ferric phosphate ($\text{H}_4\text{CaFe}_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$), strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), and colloidal ferric phosphate and found none of these materials dissolved congruently in phosphoric acid solutions of pH 3 and 4, in water, or in ammonium hydroxide solutions. They also found that strengite and colloidal ferric phosphate dissolved readily in the stable triple point solution of the system $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$, the probable immediate environment of a granule of MCP in the soil.

Solubility of added phosphorus is usually high relative to solubility of native forms immediately following phosphate application. Decreases in phosphate solubility with time occur. Rate of decrease

is a function of soil properties and environmental factors. However, it can be stated, without exception, that the chemical extractability or solubility of applied P is greatest immediately after phosphate application.

5) Availability of native and applied phosphorus

The importance of phosphate compounds in the soil and those added to it depend on their ability to keep the



equilibrium in amounts adequate for good plant growth. This ability depends on the physical and chemical properties of the phosphate compounds and as well the soil.

Plants take their phosphorus needs from the small amount in soil solution. The equilibrium between $\overset{x}{P}$ solution and labile P is usually maintained during crop growth. However, the equilibrium state between labile and non labile phosphorus takes a long time to re-establish when labile P is diminished. Thus labile phosphorus is not likely to contribute much phosphorus to plants over a period as short as one growing season. The supply of phosphorus to the plant then depends directly on the concentration in soil solution and indirectly on soil factors which maintain this.

Phosphate reaction products are less soluble than their precursor and hence less efficient for plant use. Since the initial reaction products of added soluble phosphate change to less soluble forms with time, the plant availability of applied phosphorus decreases with time of reaction. Anderson et al. (1961) and Larsen and Gunary (1964) noted a reduction in yield and uptake of phosphate by ryegrass as reaction time was increased. Allen et al. (1954) reported that a 70% reduction in availability of monosodium phosphate following contact with soil for 7 months.

Massey et al. (1970) found that after one week of incubation the amount of fertilizer phosphorus removed by H₂O dropped from 17 to 10 mg P/g of soil, a reduction of 40%. They also found that phosphorus uptake by alfalfa and bromegrass was reduced at least one-third after 9 weeks of MCP reaction with soil. Terman et al. (1960) found that the uptake of fertilizer phosphorus by oats decreased by 25% after a reaction period of 6 months.

Mattingly and Penny (1968) found yields of ryegrass from plots with no phosphate did not differ from plots treated with either superphosphate or dicalcium phosphate 19 weeks prior to cropping.

Devin et al. (1968) found the availability of super phosphate, as determined by 1% acetic acid, was high immediately after application but after 3 years of soil contact the availability, compared with freshly applied superphosphate, was only about 10% in a sandy soil with a pH of 4.7, 25% in sandy clay soil of pH 5.7, and 34% in sandy clay loam soil of pH 6.5. Findlay (1973), using Brady and Fox sandy loam soils which were not phosphated, found soil phosphorus levels declined slowly but consistently over a 4 year period. An annual addition of 19.6 kg/ha of phosphorus increased the phosphorus levels and reduced the rate of decline, while the application of larger amounts of phosphorus, 39.1 and 58.7 kg/ha phosphorus annually, increased the phosphorus level in the soil at all locations. Steele (1975) investigated the changes in phosphate availability and forms over a 12 month period after superphosphate application to a pasture on Foxton black sand and Pukepuke brown

sandy loam soils. He found 39 and 13% of 250 g/m² and 500 g/m² applied to Foxton and Pukepuke soils, respectively, were lost from the upper 5 cm of soil. Values for P availability fell rapidly with time.

Bailey et al. (1977) using chernozemic soils, found NaHCO₃-extractable phosphorus levels in soils phosphated with 100 kg P/ha as super-phosphate decreased to about 8 kg P/ha after 8 years of cropping which was considered to be inadequate for crop production. Peeck and Macdonald (1965) found that after 7 years of continuous phosphorus application available soil phosphorus was extremely high. After application of P was discontinued, soil P declined rapidly but a highly significant residual effect still remained after 8 years of no further phosphorus application. They also found that the rate of decline of both soil and applied P was more rapid during the first 2 years than during the next 6 years.

Olsen et al. (1954) reported on an evaluation of the availability of phosphates on some western calcareous soils in Montana. They found that efficiency of use of added phosphate was more strongly influenced by the initial level of available phosphorus than by soil type, soil texture, or CaCO₃ content of the soil used.

LeMare (1968) found that dressings of 900 kg/ha or less of triple superphosphate was converted to a very insoluble form approximating that of variscite within two years after application to an acid Buganda clay loam soil. Application of 1800 kg/ha provided a much greater phosphate concentration two years after its application, and the soil appeared to be super saturated with respect to variscite.

Larsen et al. (1965) added superphosphate in quantities equivalent to 0, 245 and 490 kg P/ha to 24 sites in Britain and followed the decline of phosphorus with time using radioactive orthophosphate and a technique in which growing plants were used to measure the extent of isotopic dilution of the added ^{32}P . Half life, the time required for the increase in labile phosphorus as a result of fertilization to decrease to one-half the original level, varied from 1 to 6 years.

As shown by the work cited previously, the value of residual phosphorus to crops differs considerably among soils, presumably because of differences in rate and extent to which the added phosphorus is converted to forms of low solubility. Variation in availability of residual phosphorus fertilizer may be due to several factors:-

1. The type of reaction products formed;
2. The initial level of phosphorus in the soils;
3. The capacity of the soil to adsorb phosphate;
4. The rate of phosphate applied.

The experiments on residual phosphorus have shown accumulations of available phosphorus occur when soils are phosphated over a period of time. Yong et al. (1966) reported on a 40 year study in which 13 ppm of P was applied to a moderately calcareous soil every 4th year.

NaHCO_3 extractable P increased more than two-fold over a period of 40 years. Spratt and McCurdy (1966) studied a highly calcareous soil and found that phosphorus rates had to exceed 13 ppm P annually before an appreciable accumulation of available phosphorus occurred. Ridley and Hedlin (1962) reported increases in available phosphorus when 17 ppm phosphorus was applied once every 4 years for 38 years.

Kampruth (1967) using an acid, high iron P-fixing soil, indicated that a long period of time was required for applied phosphorus to become plant unavailable. A large initial application enhanced the available P in the soil for at least 9 years as measured by corn growth. Stanberry et al. (1955) reported residual effects lasting 2 to 4 years, as measured by A-values and NaHCO_3 -extractable phosphorus, following moderate to heavy applications of phosphorus. Read et al. (1973) studied chernozomic soils and concluded that wheat would not respond to additional phosphorus until available phosphorus from residual plus indigenous sources in the soil had declined to a level represented by approximately 10 ppm of NaHCO_3 -extractable phosphorus in the surface 15 cm of the soil. This was confirmed with greenhouse studies; after application of 100 kg P/ha it took five crops of oats and barley alternatively to decrease the levels of NaHCO_3 -extractable phosphorus to 10 ppm. Application of 400 kg P/ha supported 19 crops.

In contrast to the above studies, Kohn (1974) found that superphosphate applied to one crop had no residual effect on subsequent crops. Halm (1972) found that the application of 20 kg P/ha as superphosphate without fertilizer nitrogen to a very deficient heavy clay chernozemic soil produced no initial or residual yield response for native grassland, but did result in a 25% increase in grain yield of wheat grown on an adjacent recently cultivated site.

Values of 5 to 25% recovery of applied phosphorus was reported by Mitchell (1957) and Olsen and Flowerday (1971) for small amounts of phosphorus applied with the seed. Hunter et al. (1961) found that residual crop yield response ceased to be measured when about 35% of

he applied phosphorus had been removed by the crops. This point also coincided with a reduction in levels of NaHCO_3 -extractable phosphorus in top soil to less than $10 \mu\text{g P/g}$ soil.

Piper and Vries (1964) investigated the residual effects of superphosphate on a red brown earth naturally deficient in phosphate by means of field experiments, pot trials, and chemical extraction. They found in a field on a site where 2744 kg of superphosphate per ha had been previously applied over a period of 23 years that crops in a wheat-barley-fallow rotation could be grown only for 5 years before a response developed to superphosphate applied at 5.24 or 10.47 P/ha. They suggested soils which have received a generous application of superphosphate in the past should be fertilized annually with an application of P sufficient to replace the average amount of P removed by each crop. They also found that the amount of P removed per crop declined severely over the entire period of the experiment.

Arndt and McIntyre (1963) studied the initial and residual effects of superphosphate and rock phosphate with sorghum on a lateritic red soil and found that residual effects from 112 kg of superphosphate/ha were practically exhausted by the seventh year. The residues from higher rates, 224 and 560 kg/ha of superphosphate and 225 kg/ha of rock phosphate, were still effective but yield increases were not significant. For superphosphate the residual value left after one year was 50% of the initial value and after 7 years it was only 8%. They suggested that regular annual dressings of 112 to 225 kg/ha of superphosphate would give in the long run at least 80% of the sorghum production possible of that with phosphate being present in totally



adequate amounts.

Mattingly (1968) compared the residual value of 6 cumulative annual dressings of superphosphate versus a single large application of superphosphate applied once. He found a single-large application to be better than annual application for the first 2 years and less effective in the last 3 years. NaHCO_3 -extractable phosphate increased during the first 5 years on plots given superphosphate annually, but began to decrease in the third year on plots given a single large application.

Ridley and Tayakepisuthe (1974) found that NaHCO_3 -extractable phosphate increased with rate of P application but it declined with time after application because of crop utilization and soil reaction. Giskin et al. (1972) indicated that freshly applied phosphorus had a greater influence on both yield and phosphate uptake than residual phosphate.

Residual phosphorus that remains in the soil is changed to forms that do not contribute directly to the supply of phosphorus for plants. Mattingly (1958) found that, of the increase in soil phosphorus content resulting from fertilization of 3 soils with superphosphate for about 100 years, about two-thirds was non labile as measured by isotopic dilution-plant uptake tests, and about one-third was in the labile fraction from which the phosphorus was used by plants.

The increase in availability of phosphorus from accumulated residues of previous phosphate applications may be too small to be significant if the quantities applied have been small. In instances where heavy applications have been made the increase may be great enough to reduce

substantially the current need for fertilizer.

Dissolution, precipitation-transformation, and adsorption are the reactions which occur when phosphorus is added to a soil. The rate of each reaction depends primarily upon the amount of P added, while the amount and type of products formed will depend on the period of time which has elapsed after addition and the physical and chemical properties of both the fertilizer and the soil. All the products formed are less soluble and in turn less available to plant uptake with time. Thus, it appears that phosphating soils on annual basis with moderate amounts of phosphorus are likely to result in greater average yields than a single-large application applied infrequently when similar amounts of P are used over a period of time.

III MATERIALS AND METHODS

(I) Soil

A Neuenberg (gleyed carbonated Rego Black) very fine sandy loam soil was used. Soil was obtained from the 0 to 15-cm depth, air dried, ground to pass through a 2 mm seive, and very well mixed (Table 1).

(?) Analytical methods

1. Soil pH. The pH of soil samples or solutions was determined electrometrically by the use of a standard combination glass-calomel electrode. A soil: distilled water ratio of 1:10 was used for solubility studies. The pH of the supernatant above the soil was measured. A 1:1 soil paste was used for determining the pH in characterizing the soil.

2. Electrical conductivity. The electrical conductivity of a 1:1 water to soil paste was determined with a Radiometer conductivity meter equipped with a standard conductivity cell.

3. Soil organic matter. Soil organic matter was determined according to the method of Walkley and Black (1934), as described by Allison (1965) except that the titration was performed potentiometrically using an automatic titrator.

4. CaCO_3 . The manometric quantitative method as outlined by Skinner et al. (1959) was used to determine the amount of inorganic carbonates in the soil.

5. Nitrate-N. Nitrate-N in the soil sample was determined by the conventional diazotization-coupling reaction. Nitrate-nitrogen

TABLE 1. Some Characteristics of Soil Used.

pH (1:1 soil-water paste)	7.8
EC (1:1 soil-water paste) (mmoles/cm)	0.92
Organic matter (%)	2.52
NO ₃ -N content (ppm)	59
NH ₄ OAC-extractable K (ppm)	216
NaHCO ₃ -extractable P (ppm)	11.2
Water-soluble Ca (ppm)	15
Water-soluble Mg (ppm)	12
% CaCO ₃	4.36

was extracted by shaking 2.5 gram soil with 50 ml of 0.5 M NaHCO_3 at a pH of 8.5. A 10 ml aliquot of the extract was treated with copper and hydrazine to reduce nitrate to nitrite. The nitrite was treated with sulfanilamide and the resultant salt reacted with n-1-naphthyl-ethylene-diamine-dihydrochloride to form the colored azo compound.

6. Exchangeable K - Exchangeable K was estimated by shaking one part of soil with 20 parts of 1.0 N NH_4OAc solution containing 250 ppm Li for one hour. The suspensions were filtered and the concentration of K in the filtrate measured using a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

7. Phosphorus - NaHCO_3 extractable phosphorus was determined as outlined by Olsen (1954). Five grams of air dried soil was shaken with 100 ml of 0.5 M NaHCO_3 at a pH 8.5 for 30 minutes in the presence of 1.0 g charcoal in 250 ml Erlenmyer flasks. The suspensions were filtered and the concentration of P in the filtrates determined as described by Murphy and Riley (1962).

8. Calcium and magnesium in solution - Calcium and magnesium in solution were determined by adding 2.5 ml of a 2500 ppm LiNO_3 solution to 1.0 ml of extract, diluting the solution to a volume of 25 ml and aspirating the solution into a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

9. Water content at field capacity. Water content of the soil at field capacity was determined as follows: Soil, sieved through a 2 mm sieve, was placed into 400 ml beakers and sufficient water added to wet the surface one-half of the soil. The samples were enclosed in

polyethylene bags and allowed to equilibrate for several days.

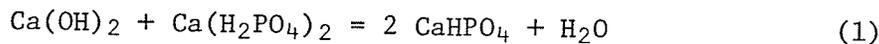
Soil samples were then taken above the wetted front, weighed and placed in preweighed 100 ml beakers. The samples were placed in an oven at 100 C for 24 hours, removed, cooled and reweighed. The percent moisture, expressed on an oven dry basis, was then calculated.

10. Plant analysis - Phosphorus concentration of the plant tissues was determined as follows: - One gram of milled dry matter was placed into microkjeldahl flask. Five ml of concentrated HNO_3 and 2.5 ml of 70% HClO_4 were added to each sample. The plant material was digested by boiling the mixture until the solution completely cleared. The digest was diluted to 100 ml with distilled water. The phosphorus concentration was determined colorimetrically. For samples where the yield was less than one gram, 0.5 gram of sample and one-half the quantity of acid given above were used.

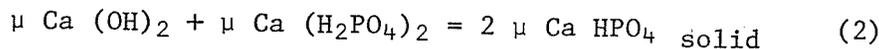
(3) Solubility of phosphorus

Solubility of phosphorus in soil samples was determined as described by Racz and Soper (1970). Ten grams of soil were shaken in 100 ml water for 24 hours at $25 \pm 1^\circ\text{C}$. The pH of the suspensions were measured after the shaking period and then the suspensions filtered. The calcium and magnesium concentrations of the filtrate were determined by atomic absorption spectrometry. The phosphorus concentration was determined as described previously.

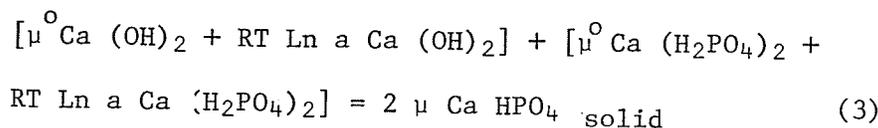
The solubility of phosphorus in soils can be expressed by the mutually interdependent variables, pH, calcium concentration, and the concentrations of the three orthophosphate species, H_2PO_4^- , $\text{HPO}_4^{=}$, and $\text{PO}_4^{=}$ (Cole and Olsen 1959). The solubility of each crystalline calcium phosphate can be represented on a two co-ordinate diagram provided all the constituent ions are included as co-ordinates. The phosphate species are related to one another in a definite way by their dissociation constants and by the H^+ ion activity. Thus, if the H^+ ion activity is included as a co-ordinate, it is necessary to calculate the activity of only one of the phosphate species. The solubilities of the calcium phosphates can be represented on a two co-ordinate diagram in terms of the activities of the compounds, $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ which represent the molecular species for the phosphates and are assumed to be in solution. The co-ordinates of the solubility diagram are derived as follows: Using DCPD, as an example, a balanced equation can be written for the equilibrium formation of solid DCPD from the molecular species $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$:-



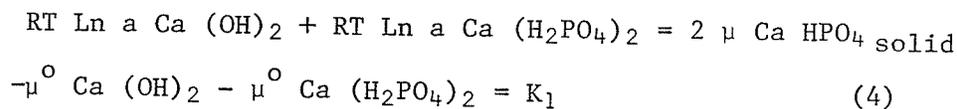
Expressing this equation in terms of chemical potentials, assuming that the chemical potential of water is constant and the solution dilute.



and



Rearranging the above equation results in the following equation:



substitution of $a_{\text{Ca}^{++}} \cdot a_{\text{OH}^-}^2$ for $a_{\text{Ca (OH)}_2}$ and of $a_{\text{Ca}^{++}} \cdot a_{\text{H}_2\text{PO}_4^-}$ for $a_{\text{Ca (H}_2\text{PO}_4)_2}$ into equation (4) and dividing by 2.303 RT results in the following equation:

$$\text{Log } a_{\text{Ca}^{++}} \cdot a_{\text{OH}^-}^2 + \text{Log } a_{\text{Ca}^{++}} \cdot a_{\text{H}_2\text{PO}_4^-} = K_2 \quad (4)$$

where

$$K_2 = \frac{2 \mu \text{Ca HPO}_4 \text{ solid} - \mu^\circ \text{Ca (OH)}_2 - \mu^\circ \text{Ca (H}_2\text{PO}_4)_2}{2.303 RT} \quad (5)$$

The above equation can be rewritten as:

$$(\text{pCa} + 2 \text{pOH}) + (\text{pCa} + 2 \text{pH}_2\text{PO}_4) = -K_2 \quad (6)$$

where the terms pCa, pOH, and pH₂PO₄ represent the negative logarithm of the activities of the respective ions. Substituting (14-pH) for pOH and dividing equation (6) by -2 gives:-

$$[\text{pH} - \frac{1}{2} \text{pCa}] - [\text{pH}_2\text{PO}_4 + \frac{1}{2} \text{pCa}] = K_3 \quad \text{where } K_3 = -K_2$$

The terms $(\text{pH} - \frac{1}{2} \text{pCa})$ and $(\text{pH}_2\text{PO}_4 + \frac{1}{2} \text{pCa})$ are known as the "lime

potential" and "phosphate potential", respectively, and are the two co-ordinates of the solubility diagram.

Similar equations relating the lime and phosphate potential can be developed for octacalcium phosphate,

$$5[\text{pH} - \frac{1}{2} \text{pCa}] - 3 [\text{pH}_2\text{PO}_4 + \frac{1}{2} \text{pCa}] = K \text{ for OCP,}$$

and for hydroxy apatite,

$$7[\text{pH} - \frac{1}{2} \text{pCa}] - 3 [\text{pH}_2\text{PO}_4 + \frac{1}{2} \text{pCa}] = K.$$

The values for "K" can be established experimentally by measuring the lime and phosphate potentials of the pure phosphate compounds in distilled water. The values of K relating the lime and phosphate potentials for DCPD, OCP, HA, are 0.66 for DCPD (Russell 1973), 9.93 for OCP (Moreno et al. 1960) and 14.7 for HA (Clark, 1955).

The solubility diagrams can be used to establish the existence of certain solid phase phosphates in soils. The position of a solubility value on the diagram indicates the solid phase phosphate governing the concentration of phosphorus in the soil solution. For example, if a solubility value was close to the DCPD isotherm, it is probable that DCPD is present in the soil and controlling the phosphorus concentration in the soil solution. This, however, does not mean that OCP and/or HA were not present in the soil, but that the most soluble solid phase phosphate in the soil was DCPD.

The activities of the calcium and H_2PO_4 ions and the lime and phosphate potentials of soil extracts were calculated as described by Racz and Soper (1970). The pH of the extracts studied was between 7.7 and 8.2, thus the total phosphorus concentration,

$$[Pt] = [H_2PO_4^-] + [HPO_4^{=}] + [M HPO_4], \quad (1)$$

Where $H_2PO_4^-$ and $HPO_4^{=}$ are phosphate ions in solution and $MHPO_4$ a soluble complex of calcium or magnesium with HPO_4 (Chaughtai et al. 1968; Taylor et al. 1963). The dissociation constant, K_d of the $CaHPO_4$ and $MgHPO_4$ complex has been found to be 1.75×10^{-3} (Chaughtai et al. 1968; Moreno et al. 1960) and 1.24×10^{-3} (Taylor et al. 1963), respectively. A mean value of 1.50×10^{-3} was used when both Ca, and Mg were present in solution. Substitution of activities for concentrations,

$$\frac{(M^{2+})(HPO_4^{=})}{K_d} \text{ for } [MHPO_4] \text{ and } \frac{(H^+)(HPO_4^{=})}{K_2} \text{ for } [H_2PO_4^-]$$

into Equation (1) results in the following expression:-

$$[PT] = (HPO_4^{=}) \left[\frac{(M^{2+})}{K_d} + \frac{(H^+)}{f^- K_2} + \frac{1}{f^{2-}} \right] \quad (2)$$

where (M^{2+}) represents calcium plus magnesium, f^- the activity coefficient of the $H_2PO_4^-$ ion, f^{2-} the activity coefficient of $HPO_4^{=}$ ion, K_2 the second dissociation constant of phosphoric acid, the brackets concentrations and the parentheses activities. The total calcium plus magnesium in solution,

$$[M_T^{2+}] = [M^{2+}] + [MHPO_4] \quad (3)$$

Where $[M^{2+}]$ represents the concentration of calcium plus magnesium in solution and $MHPO_4$ the soluble complex of calcium or magnesium with $HPO_4^{=}$.

Thus,

$$[M_T^{2+}] = \frac{(M^{2+})}{f^{2+}} + \frac{(M^{2+})(HPO_4^{=})}{K_d} \quad (4)$$

and

$$(M^{2+}) = \frac{[M_T^{2+}]}{\left\{ \frac{1}{f^{2+}} + \frac{(HPO_4^-)}{K_d} \right\}} \quad (5)$$

where f^2 represents the activity coefficient of calcium and/or Mg substitution of the expression derived for (M^{2+}) in equation (5) into equation (2) results in the following quadratic equation by which the HPO_4^- ion activity was calculated

$$(HPO_4^-)^2 \left[(H^+) f^{2-} + f^- K_2 \right] + (HPO_4^-) \left[-[P_T] f^- K_2 f^{2-} + [M_T^{2+}] f^- K_2 f^{2-} + \frac{K_d}{f^{2+}} ((H^+) f^{2-} + f^- K_2) \right] - \frac{[P_T] K_d f^- K_2 f^{2-}}{f^{2+}} = 0 \quad (6)$$

The calcium or magnesium ion activity was obtained from the following quadratic equation derived by substituting the expression for $(HPO_4^-)^-$ derived from equation (2) into equation (5)

$$(M^{2+})^2 \left[f^- K_2 f^{2-} \right] + (M^{2+}) \left[(H^+) K_d f^{2-} + K_d f^- K_2 + [P_T] f^{2+} f^- K_2 f^{2-} - [M_T^{2+}] f^{2+} f^- K_2 f^{2-} \right] - [M_T^{2+}] \left[f^{2+} (H^+) K_d f^{2-} + f^{2+} K_d f^- K_2 \right] = 0$$

The activity coefficients, f , were calculated from the Debye-Hückel equation, $\log_{10} f = \frac{-AZ^2\sqrt{\mu}}{1 + B a_i \sqrt{\mu}}$, (Maron and Prutton 1959) which gives the activity coefficient of the ion as a function of the total ionic strength of the solution. A and B are constants depending on the solvent used. For water, at 25C, the values used were 0.51 and 0.33×10^8 respectively. Z represents the valency of the ion, and a_i the mean ionic diameter. Values used for diameter were: H_2PO_4 , $4A^{\circ}$; H_2PO_4 , $4A^{\circ}$; Ca, $6A^{\circ}$ and Mg $8^{\circ}A$ (Maron and Prutton 1959). The ionic strength was calculated from the expression: $\mu = \frac{1}{2} \sum C_i Z_i^2$ (Maron and Prutton 1959) where Z_i

represents the valencies of the respective ions, and C_i the concentrations of these ions.

The ionic activities were calculated by a series of successive approximations, first assuming no association of ions in solution and then correcting for complexing until a constant value for the ion activity was obtained. The values for pCa , and $pHPO_4$ were then calculated by taking the negative logarithm of the ion activities. The values for pH_2PO_4 were obtained from the expression

$$pH_2PO_4 = pHPO_4 - pK_2 + pH$$

where pK_2 represents the second dissociation constant of phosphoric acid.

(4) Plant growth studies

Polyethylene pots were cleaned, dried and weighed. To each of 64 pots, 2500 gram air dried soil was added. Eight pots were assigned to each treatment. The treatments, in addition to a control (no phosphorus added), were 5, 10, 20 ppm P as MCP added as a band 5 cm below the soil surface, 50 and 100 ppm P as MCP and 50 and 100 ppm P as DCPD mixed with the entire volume of soil within each pot.

One hundred ppm of K as K_2SO_4 was added to each pot before seeding. One hundred ppm of N as NH_4NO_3 was added to each pot before seeding and at the second and fourth week after emergence.

Barley was used as a test crop. Twelve seeds were placed in each pot and thinned to eight plants after emergence. The pots were placed in a completely randomized design in the growth chamber (Model PG 36, Controlled Environments Ltd., Winnipeg, Manitoba, Canada). The temperature was adjusted to 20C during the 16-hour light period and to 16C during the 8-hour dark period. The relative humidity was adjusted to 50% during the light period and to 80% during the dark period. The light intensity was 500-550 micro Einsteins/ M^2 S at plant canopy height.

Soils were watered to field capacity by daily additions of distilled water. The pots were rotated on the growth bench to eliminate the possibility of variation arising from differences in environment inside the growth chamber.

The plants were grown for seven weeks (heading stage), then the aerial parts were harvested 2 cm above the soil surfaces. The yield

from each pot on an oven dried weight basis was obtained. The plant samples were ground using a Wiley Mill and the phosphorus content of the tissue determined.

After harvest, the soil from each pot was removed. Root crowns were removed and the soil mixed and repotted. One pot of soil (one replicate) of each treatment was saved for soil analysis. Treatments in which the phosphorus was banded, 5, 10 and 20 ppm P as MCP were applied as described before. No additional phosphorus was added to pots treated with 50 and 100 ppm P as MCP and DCPD. Seeding, care of pots, fertilization with nitrogen and potassium and harvesting were as described for the first crop. A total of five crops were taken using the above procedures. Number of replicates for the 1st, 2nd, 3rd, 4th and 5th crops were 8, 7, 6, 5 and 4, respectively. A sixth crop using three replicates and without any phosphorus being added to any treatment was also grown. All other procedures used were as described previously. This cropping and fertilizer phosphorus addition sequence was selected in order to compare the long-term effects of a single large application of phosphorus versus small frequent additions on plant growth.

RESULTS AND DISCUSSION

(1) Yield

Yield of barley without phosphorus fertilizer for the first crop was much less than when phosphate fertilizer was applied (Table 2). This indicates the level of plant available phosphorus in this soil was very low and the soil would not support good plant growth without phosphorus. Application of 5 ppm P as MCP in a band increased yields about three-fold above that without added phosphorus. Increases in the amount of P added in a band above 5 ppm P increased yields above that with 5 ppm P as MCP. Application of phosphorus in amounts exceeding 20 ppm, 50 and 100 ppm P as MCP or DCPD mixed with the soil, did not increase yields above that with 20 ppm P band except when 100 ppm P as MCP was mixed with the soil.

Figure 1 shows that 20 ppm P as MCP in a band produced yields nearly equal to that of much higher amounts mixed with the soil for crop 1.

Dry matter yields for the second crop for all treatments were less than that for the first crop. The yield for soil treated with 100 ppm P as MCP was significantly higher than other treatments except for the 100 ppm P as DCPD treatment. Addition of 5 ppm P as MCP had little or no effect on the yield. However, addition of 10 ppm P as MCP doubled the yield when compared to that of the untreated soil. Yields with 20 ppm P as MCP in a band was significantly higher than with 50 ppm P broadcast as MCP or DCPD and slightly lower than with 100 ppm P as DCPD.

TABLE 2. Yield of Dry Matter as Affected by Time and Method of Phosphorus Application (g).

<u>Treatment</u>	<u>Crop Number</u> ¹						<u>average</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u> ²	
Control	5.09e ³	4.83e	1.89g	1.54e	0.78f	0.54e	2.44
5 ppm P(MCP)	16.11d	5.87e	5.17f	4.86d	4.08d	1.52ed	6.92
10 ppm P(MCP)	17.29c	9.03d	9.39d	9.54b	8.24b	2.90cb	9.40
20 ppm P(MCP)	18.80b	17.38b	14.24a	13.52a	14.48a	8.9a	14.55
50 ppm P(MCP)	19.13ba	11.39c	7.73e	4.47d	2.13e	1.55ed	7.73
100 ppm P(MCP)	19.51a	19.59a	10.82c	8.85cb	5.40c	2.84cb	11.17
50 ppm P(DCPD)	19.21ba	10.27dc	7.5 e	4.33d	2.16e	1.90dc	7.56
100 ppm P(DCPD)	18.64b	18.10ba	12.24b	7.93c	5.26c	3.34b	10.92

¹ The yield for each treatment represents an average of eight replicates for Crop No. 1. No. of replicates for each treatment was reduced by one for each successive crop.

² Phosphorus was not added.

³ Duncans Multiple Range Test - Treatment means for each crop followed by the same letter are not significantly different at P = 0.05.

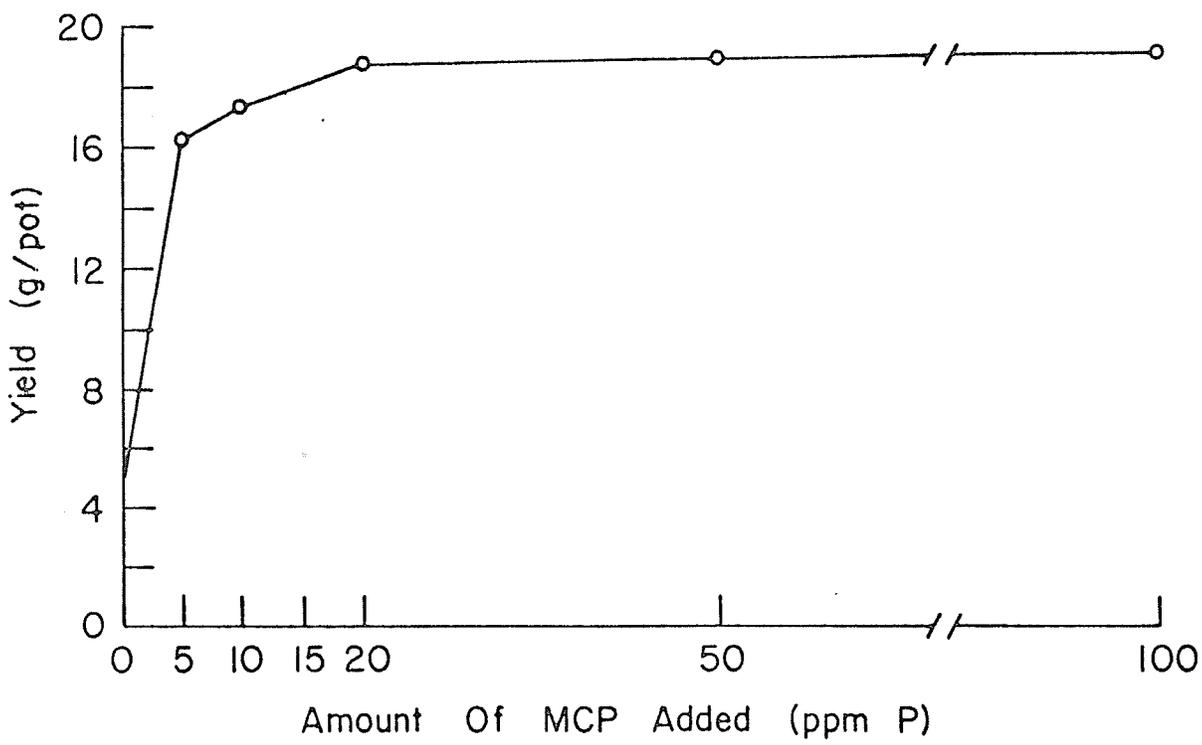


Fig.1 Yield Of Barley As Affected By Amount Of MCP Added.

Dry matter yields of the third crop for most treatments were lower than for the second crop. Yield on the untreated soil was the lowest whereas the yield when 20 ppm P as MCP was banded was the highest. Yields with 50 ppm P as MCP and DCPD were much less than that with 10 or 20 ppm P as MCP. Also, yields with 20 ppm P as MCP were significantly higher than with 100 ppm P as DCPD or MCP applied once. These results are in accordance with those of Mattingly (1968) who reported that residues of large amounts of applied P were significantly more effective than annual dressings for the first two years and less effective in the last three years. However, the results are in contrast with those of Clare and Caldwell (1972) who showed that a large-single application of 109.11 kg P per ha was as effective as annual applications of one-fifth the amount, and appeared to be sufficient to satisfy the requirements of five successive cereals following grass on a chalky boulder clay of the Hanslope soil series.

The results of the fourth crop showed that the yield on the untreated soil (control) was significantly lower than any other treatment. The yield with 5 ppm P as MCP was slightly higher than with 50 ppm P as MCP or DCPD. The yield with 10 ppm P as MCP was higher than with 100 ppm P as MCP and DCPD. Yield with 20 ppm P as MCP was significantly higher than any other treatment. Thus, the single-large applications of P were much less effective in increasing yields than adding P frequently but at much smaller amounts.

Results of the fifth crop show that the yield with 20 ppm P as MCP was significantly higher than for all other treatments. The

yield with 10 ppm P as MCP was higher than that of 50 ppm P as MCP, 50 ppm P as DCPD, 100 ppm P as MCP and 100 ppm P as DCPD. Yields with MCP and DCPD were the same for equal amounts added.

The sixth crop, in which no phosphorus was added to any treatment, indicates that the residual effects of 10 and 20 ppm P as MCP added frequently were usually greater than for the single-large applications of 50 and 100 ppm P as DCPD or MCP, respectively (i.e.), the yields of dry matter were higher with small frequent applications than with a single-large application when equal amounts of P were added.

The average yields obtained for the six crops clearly demonstrate that greater average yields will occur with small-frequent P applications than with a single-large application when equal amounts of P are added over a period of time.

Declines in yields were noted with cropping even when 20 ppm P was applied to each crop. This is evident when one compares yields of crops 1 and 2 with crops 3, 4, and 5 when 10 and 20 ppm P as MCP was added. This decline in yield may have been due to a decline in other plant available nutrients in the soil. If yields could have been maintained at levels such as for crops 1 and 2, it is likely the differences between treatments for crop 3, 4 and 5 may have been even larger than noted for the present study.

(2) Percent P in plant tissue

The percentage of phosphorus in plant tissues for the control treatment was high for crop 1 but declined with cropping to very low levels for crop 6 (Table 3). The high concentration of P in the tissues for crop 1 on the control may be due to the very low yield coupled with an inadequate P supply from the soil at early stages of plant growth. High P percentages were also found in the plant tissues of soils treated with a single large application of P. This is a result of luxury consumption of phosphorus which occurred in the first crop. The percent of P in plant tissues from the control, 50 ppm P as MCP and DCPD and 100 ppm P as MCP and DCPD steadily decreased with cropping. This decrease in percent P was probably a result of a continuous depletion of phosphorus by plant uptake and to fixation of phosphorus by the soil with time. The percent P in plant tissues remained relatively constant with cropping when 5, 10 and 20 ppm P as MCP were added.

Phosphorus content of plants treated with 50 and 100 ppm P as MCP and DCPD were much higher than phosphorus contents of plants treated with 5, 10 and 20 ppm P as MCP for crops 1 and 2. However, for crops 4, 5 and 6 percent phosphorus in plants treated with the smaller but frequent applications of phosphorus were equal to or greater than plants treated with a single-large application of phosphorus.

The average phosphorus content of plant tissues for all treatments indicates that the average percent phosphorus in plants was

TABLE 3. Percent of Phosphorus in Plant Tissue.

<u>Treatment</u>	<u>Crop Number</u>						<u>Average</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u> ¹	
Control	0.31	0.17	0.13	0.11	0.10	0.06	0.15
5 ppm P(MCP)	0.13	0.16	0.16	0.14	0.14	0.14	0.15
10 ppm P(MCP)	0.14	0.15	0.12	0.12	0.14	0.17	0.14
20 ppm P(MCP)	0.17	0.13	0.13	0.14	0.15	0.15	0.15
50 ppm P(MCP)	0.28	0.18	0.16	0.14	0.12	0.11	0.17
100 ppm P(MCP)	0.40	0.21	0.17	0.12	0.13	0.12	0.19
50 ppm P(DCDP)	0.30	0.19	0.15	0.15	0.13	0.12	0.17
100 ppm P(DCPD)	0.44	0.21	0.16	0.13	0.13	0.13	0.20

¹Phosphorus was not added.

greater for the single-large applications than for the small-frequent applications of P. The higher average for the single-large application is a result of the very high P levels in crop 1 and 2 in which luxury consumption of added phosphorus occurred.

(3) Uptake of phosphorus

Uptake of phosphorus by barley for all crops is presented in Table 4. Phosphorus uptake increased with increases in the amount of added phosphorus. The amount of P uptake decreased with cropping except for the crops treated with 10, 20 ppm P as MCP. The highest uptake occurred in the first crop. This was due to crop 1 yields being greater than yields of the other crops and the high plant availability of phosphorus in treatments receiving a single-large application of phosphorus.

P uptake from 100 ppm P as DCPD was similar to that from 100 ppm P as MCP and P uptake from 50 ppm P as DCPD was similar to that of 50 ppm P as MCP. This indicates that these forms of phosphorus in powder form behaved very similarly in the soil. Uptake increased with amount of phosphorus applied for crop 1, the highest P uptake values were noted in the soil treated with 50 and 100 ppm P as MCP or DCPD. The high uptake values for these crops were due mainly to increases in P contents of the tissue as yield did not increase appreciably when more than 20 ppm P was added.

P uptake for all treatments was lower for the second crop than for the first crop. P uptake were greatest for the 100 ppm P treatments and decreased in the order 100 ppm P as DCPD or MCP mixed >20 ppm P as MCP band >50 ppm P as MCP or DCPD >10 ppm P as MCP band >5 ppm P as MCP band >control. P uptakes for DCPD and MCP were similar when similar amounts of P were added.

P uptake for the 20 ppm P as MCP treatment was slightly higher

Table 4. Uptake of Phosphorus (mg/pot).

<u>Treatments</u>	<u>Crop Number</u>						<u>Total</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6*</u>	
Control	15.8	8.0	2.5	1.8	0.8	0.3	29.2
5 ppm P as MCP	20.8	9.1	8.3	6.5	5.7	2.1	52.5
10 ppm P as MCP	24.9	13.4	11.4	11.2	12.0	4.8	77.7
20 ppm P as MCP	32.7	26.0	19.1	18.1	21.9	13.4	131.2
50 ppm P as MCP	53.7	19.7	12.5	6.3	2.6	1.8	99.0
100 ppm P as MCP	77.7	40.2	17.8	10.6	7.2	3.5	157.0
50 ppm P as DCPD	57.8	18.9	10.8	6.2	2.8	2.4	98.9
100 ppm P as DCPD	81.6	34.9	18.9	10.4	6.7	4.4	156.9

*Phosphorus was not added.

than for any other treatments for crop 3. The yields with 20 ppm P as MCP was also greater than for any other treatment. Thus P uptakes suggest that the single-large applications were superior to freshly added phosphorus in P uptake for the first two crops but were not as effective as the smaller but frequent application for crop 3.

For the fourth crop the 20 ppm P as MCP applied in a band was much superior to adding a single-large application of 100 ppm P. Ten ppm P as MCP in a band was also more effective than either 100 ppm P as MCP or DCPD, while 5 ppm P as MCP was slightly more effective than either 50 ppm MCP or DCPD. Yields also showed this trend. The 10 ppm P as MCP treatment did not increase yields or P uptake to optimal levels. Thus, this amount of P was not sufficient to meet plants needs and the accumulation of residual P from the preceeding crops was very low. This is in agreement with findings of Spratt and McCurdy (1966) who showed that on a calcareous soil, phosphorus rates had to exceed 13 ppm P annually before any appreciable accumulation of available phosphorus occurred.

P uptake in the 5th and 6th crop was also greater for 10 and 20 ppm P as MCP banded than for the single-large applications of P.

P uptake for the control declined with cropping and decreased to very low amounts for the sixth crop. Dry matter yeilds also showed a steady decrease with cropping.

Total P uptake by the six crops was greater for the single-large applications of P than for the banded treatments when equivalent

quantities were applied.

Thus total P uptake of the six crops did not correlate well with total yields. This is due to luxury consumption of phosphorus for crops 1 and 2 for soils treated with 50 and 100 ppm P as DCPD or MCP.

(4) Percent recovery of applied phosphorus

Table 5 and Figures 2 and 3 shows the percent recovery of applied P for all crops grown. Percent recovery by the first crop decreased with increases in amount of P applied. The reduction in percent utilization with increases in amount added were due to limitations of the plants requirements for phosphorus. Recoveries by all crops were similar for DCPD and MCP.

Percent recovery decreased for the 50 ppm Pas MCP and DCPD and the 100 ppm Pas MCP, and DCPD with cropping. The highest percent P recovery on these treatments was for the first crop and the lowest recovery was reported for the 6th crop. Sharp decreases in percent P recovery occurred for the second crop for the 50 and 100 ppm P treated soils. This was probably due to conversion of the applied phosphorus to less available forms and to depletion of phosphorus by plant uptake. Percent recoveries of about 1.5 to 6% were found for these treatments for crops 3 to 6 inclusive.

Percent recoveries for the banded treatment for crops 1 to 5 remained relatively constant with cropping and usually varied from about 30 to 40 percent.

The greatest total recoveries (recoveries by six crops) occurred when 50 and 100 ppm P were added once. These high recoveries, however, were not reflected in yield increases.

TABLE 5. Percent Recovery of Applied Phosphorus¹

Treatment	<u>Crop Number</u>						<u>Total</u> ²
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6*</u>	
5 ppm P(MCP)	40.00	8.80	46.40	37.60	39.2	14.40	37.28
10 ppm P(MCP)	36.40	21.60	35.60	37.60	44.80	18.00	38.80
20 ppm P(MCP)	33.80	36.00	33.20	32.60	42.20	26.20	40.08
50 ppm P(MCP)	30.32	9.400	8.00	3.60	1.40	1.20	55.84
100 ppm P(MCP)	24.80	12.90	6.12	3.50	2.60	1.28	51.12
50 ppm P(DCDP)	33.60	8.70	6.60	3.50	1.60	1.68	55.76
100 ppm P(DCPD)	26.30	10.80	6.60	3.40	2.40	1.64	51.08

* Phosphorus was not added.

¹ Percent Recovery = $\frac{\text{P Uptake with P added} - \text{P Uptake without P}}{\text{Amount of P added}} \times 100$

² Total recovery was calculated using total P uptake values for all six crops shown in Table 4.

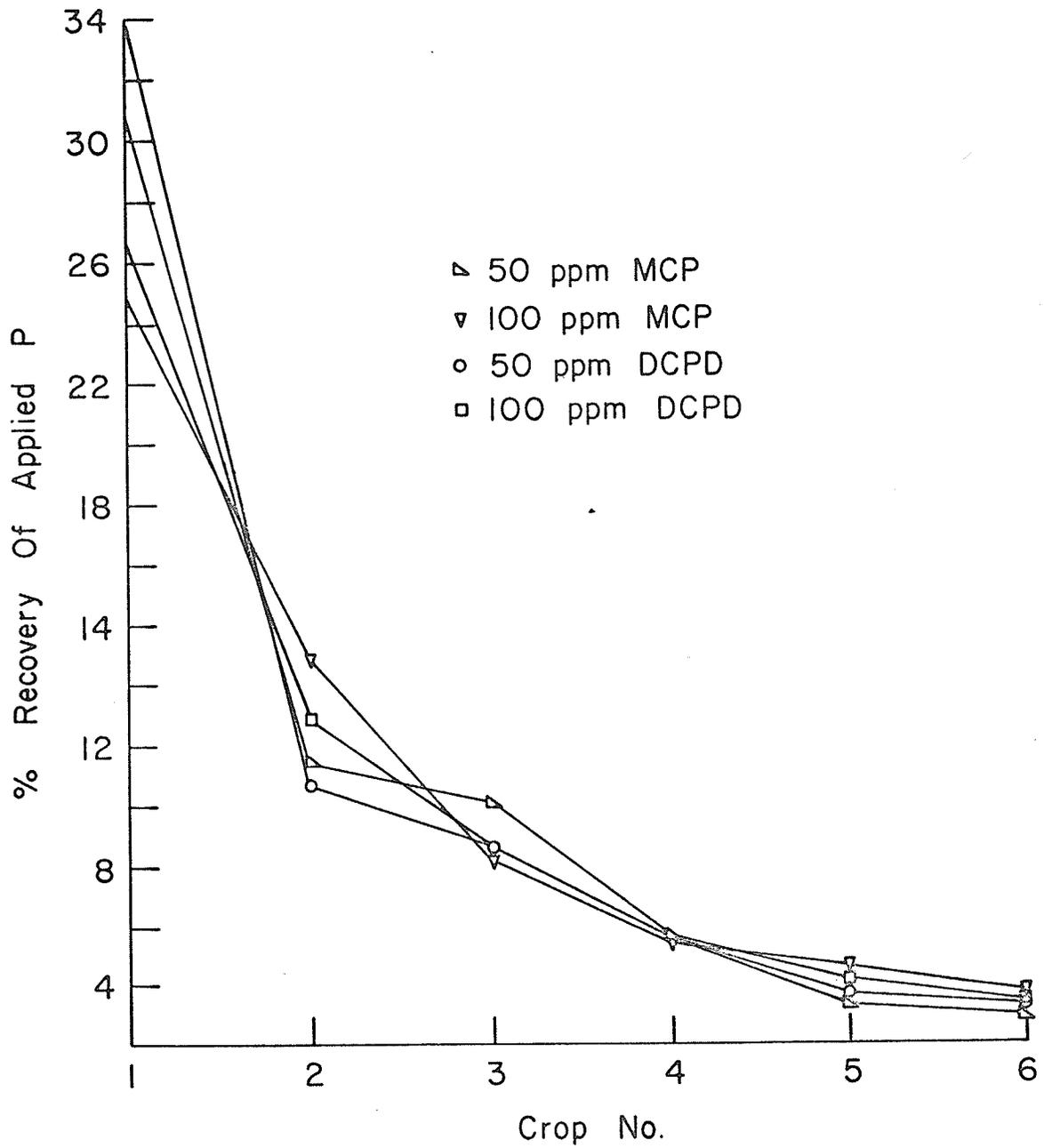


Fig. 2 Percent Recovery Of Applied Phosphorus. (Broadcast)

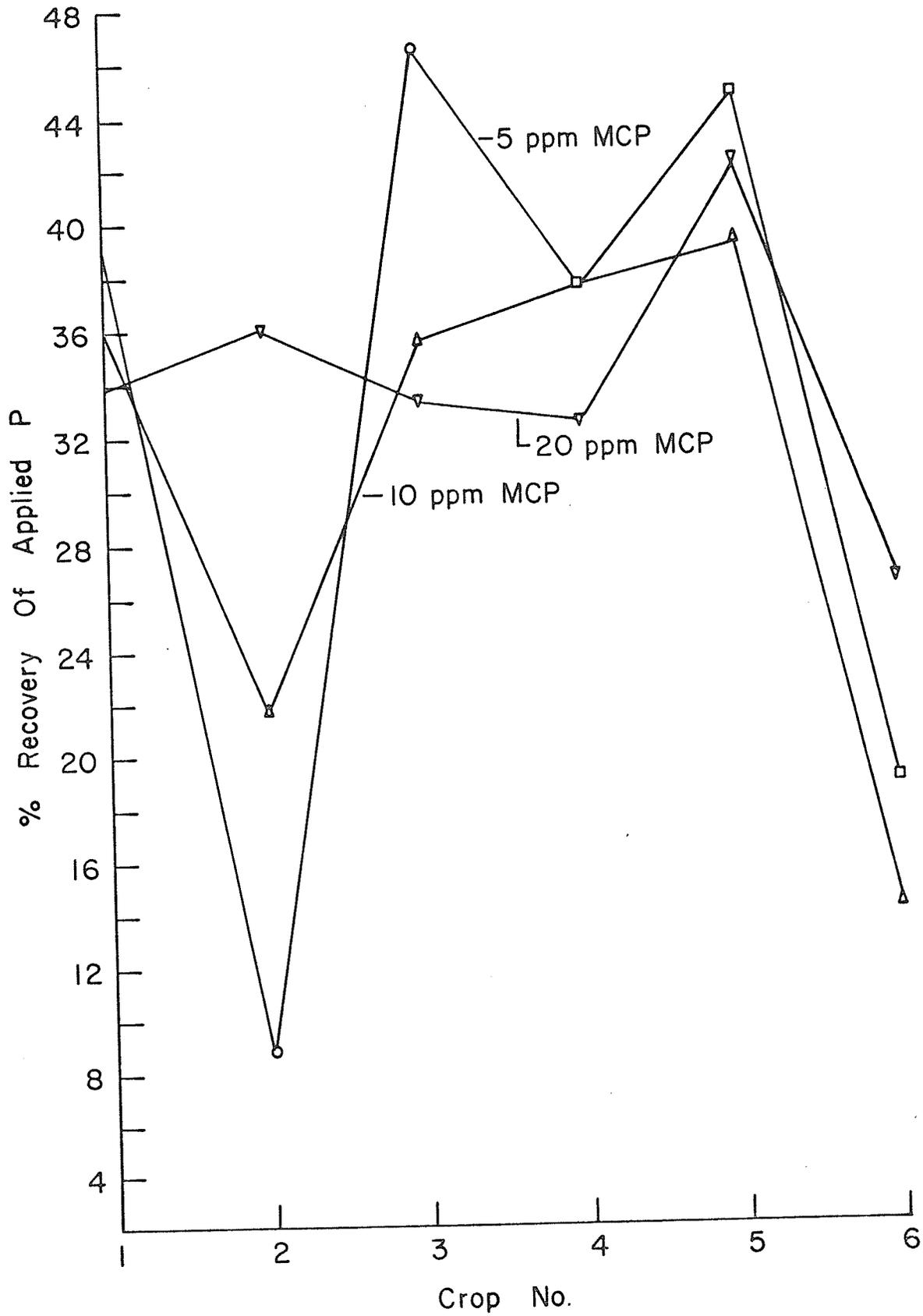


Fig. 3 Percent Recovery Of Applied Phosphorus. (Banded)

(5) NaHCO_3 - Extractable Phosphorus

The amounts of phosphorus extracted were greatest immediately after the P was applied (Table 6 and Figure 4). The amounts of P extracted increased with increases in the amount of phosphorus added for crops 1 to 3. (i.e.) Fifty and 100 ppm P as MCP or DCPD gave higher extractable P contents than the banded treatments for crops 1 to 3. However, for crop 4, extractable-P content for the 10 and 20 ppm P as MCP banded treatments were about equal to the single-large application of P. For crops 5 and 6 the extractable content of the 10 and 20 ppm P banded treatments were higher than for the single large application of P.

NaHCO_3 -extractable P decreased rapidly with time for the single-large applications of P (Figure 4), whereas the 10 and 20 ppm banded treatments maintained extractable-P levels at relatively constant levels.

The data obtained for extractions on the 0 time samples confirms findings by Kittrick and Jackson (1955 and 1959) and Barrow (1974a,b) that phosphate reacts very rapidly after addition to the soil with elements in soil solution and with different soil constituents.

The decrease in extractable P with time for the single large-applications of P was probably due to plant uptake and phosphorus reaction with the soil. Ridley and Tayakesiuthe (1974) reported decreases in NaHCO_3 -extractable P with time due to crop utilization and soil reaction. The lowest reduction in NaHCO_3 -extractable P was for the control while the greatest reduction was for the 100 ppm P as MCP and DCPD treatments.

TABLE 6. NaHCO_3 -Extractable Phosphorus [ppm-P].

<u>Treatment</u>	<u>Crop Number</u>						
	<u>0 time</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6*</u>
Control	11.2	7.5	7.0	8.7	5.0	4.4	3.6
5ppm P(MCP)	13.7	8.0	9.0	9.5	7.5	5.0	5.9
10 ppm P(MCP)	15.9	9.0	9.5	12.0	11.6	11.0	9.9
20 ppm P(MCP)	19.3	12.0	10.4	13.0	16.0	13.0	12.4
50 ppm P(MCP)	38.0	19.0	13.3	14.0	7.5	6.0	6.7
100 ppm P(MCP)	69.0	36.0	26.5	20.0	18.0	9.0	9.1
50 ppm P(DCPD)	39.0	18.0	13.0	13.0	7.5	6.0	7.5
100 ppm P(DCPD)	71.0	38.0	26.5	22.0	18.0	9.0	9.9

*phosphorus was not added.

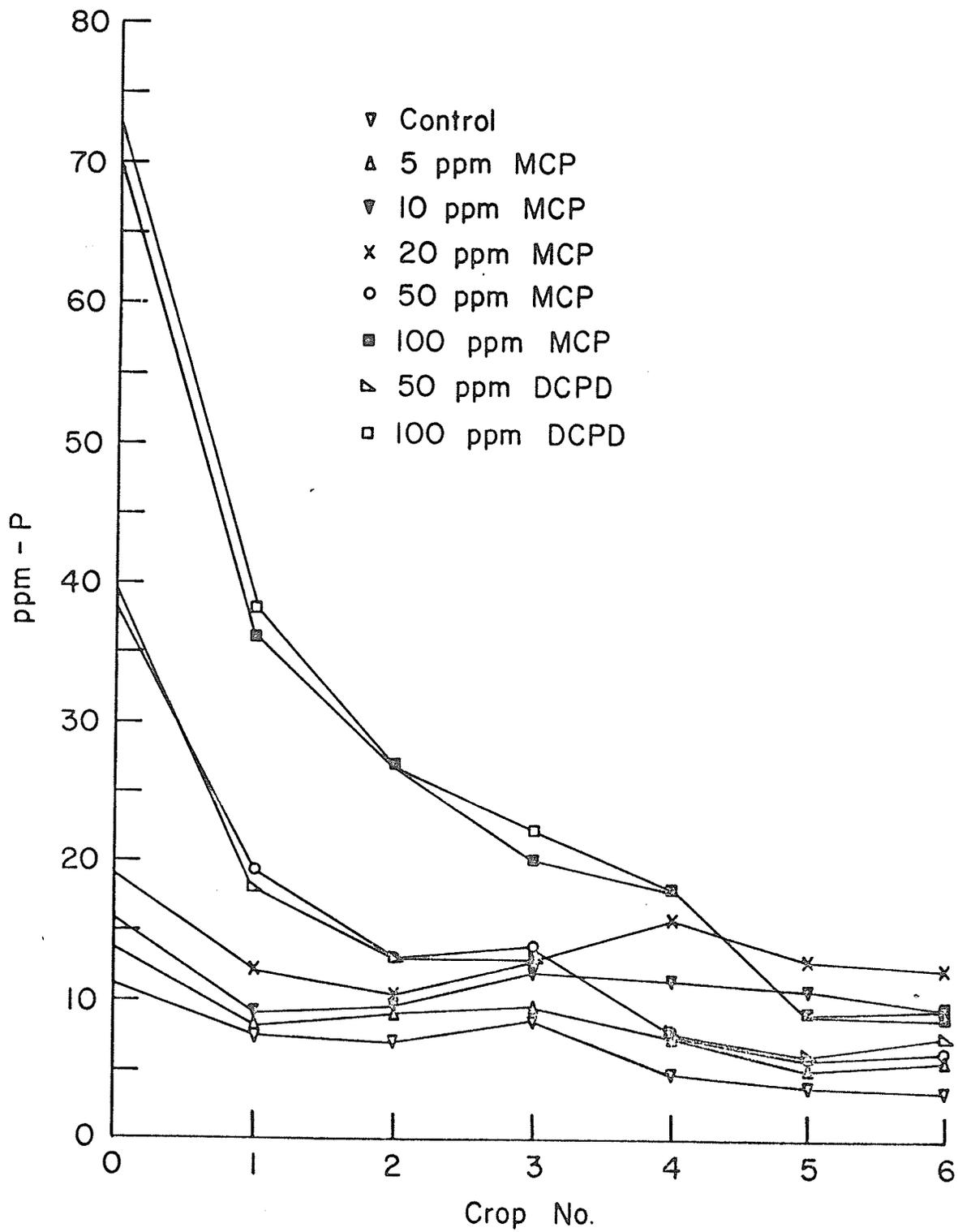


Fig. 4 NaHCO_3 Extractable P Concentration.

The extractability of phosphorus applied as MCP and DCPD were similar. Correlations between NaHCO_3 -extractable P and yield of the various crops for the single-large application of P appears to be a good one, (i.e.) yields declined as NaHCO_3 -extractable P contents declined. It is also interesting to note that yields for the 20 ppm P band were greater than for the 50 ppm P and 100 ppm P treatments for crops 2 and 4, respectively. Thus, yields were not at an optimum when NaHCO_3 -extractable P levels decreased below about 20 to 25 ppm P.

(6) Solubility of phosphorus in soils

The pH values for all soils tended to decrease with cropping (Table 7). These decreases in pH were small and generally pH values after the first crop varied from 7.7 to about 7.9. The slight decrease in pH may have been due to increases in the partial pressure of CO₂ in the soils with cropping.

Calcium and magnesium concentrations increased with cropping. The highest values were noted for the fifth crop and for treatments with the lower average yields. The increase in Ca and Mg concentrations with cropping was probably due to the additions of K⁺ as a fertilizer. Since K was added to each crop in excess of the plant needs, the added K replaced Ca and Mg ions from the exchange sites when not utilized by the plant. Adding phosphate fertilizer generally decreased Ca and Mg in solution. This was due to the greater yields with applied phosphorus. This would result in less K in the soil to displace Ca and Mg from exchange sites.

The solubility of phosphorus in the untreated soil was between that of OCP and HA at zero time and approximated that of HA for crop 6 (Table 7 and Figure 5). This indicated that a phosphate compound with a solubility close to HA, governed the concentration of phosphorus in the soil solution.

Solubility of phosphorus in soils treated with 5 ppm P as MCP was only slightly greater than for the untreated soil (Figure 6). Solubilities were between that of OCP and HA.

Addition of 10 ppm P as MCP increased the solubility of P in the soil prior to cropping (Figure 7). Immediately after application,

a solubility close to that of OCP was obtained indicating that OCP was probably controlling the phosphorus concentration in soil solution at this time. The solubility of P decreased with cropping. Although solubility of P in the soil with this treatment was greater than for the control or with 5 ppm P as MCP, solubilities of P were not great and were between that of HA and OCP.

Solubility of P in soils treated with 20 ppm P as MCP followed the trends outlined for the 10 ppm P treatment, with the exception that solubilities were usually slightly greater than with 10 ppm P (Figure 8).

Phosphorus solubility in soils treated with 50 and 100 ppm P as MCP were similar (Figures 9 to 12). The highest phosphorus solubility values were obtained at time of P application, and were close to the OCP isotherm. Solubilities of phosphorus for these treatments immediately after P application and for crops one and two were greater than with 20 ppm P as MCP. However, for crop 4 and particularly for crop 5 the solubilities of P in the soils were very low, approximating that of HA and very close to values obtained for the untreated soil.

In summary, these studies indicated the following:

1. The largest P application had the highest initial P solubility.
2. Phosphorus solubility decreased with cropping for the single large-applications of phosphorus. The solubilities approximated that of HA after 5 crops were grown.
3. After the first two crops, soils with frequent small dressing of phosphorus had higher solubilities of P than soils with the single-large application of phosphorus.

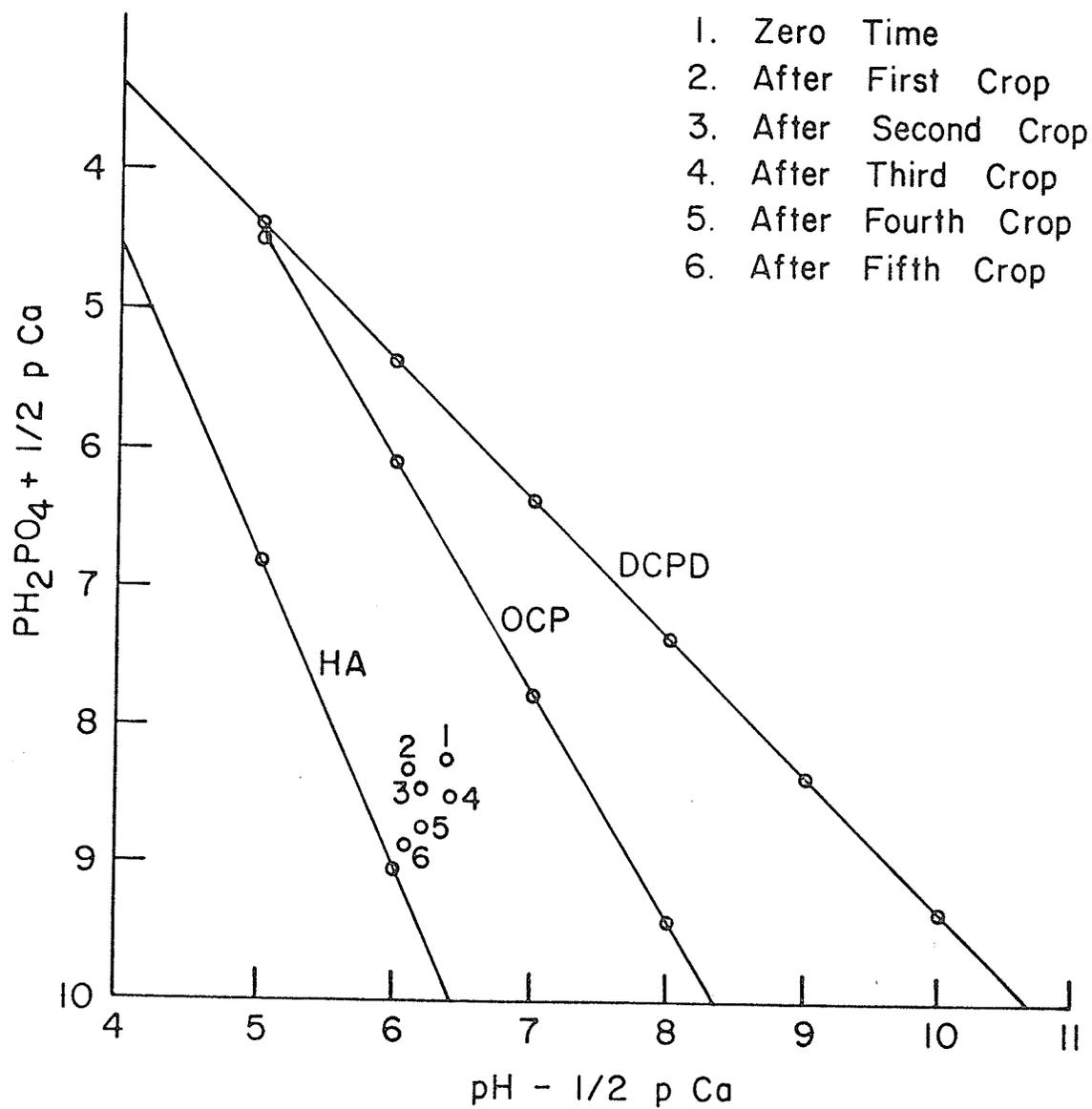


Fig. 5 Solubility Of P In Untreated Soil As Affected By Cropping.

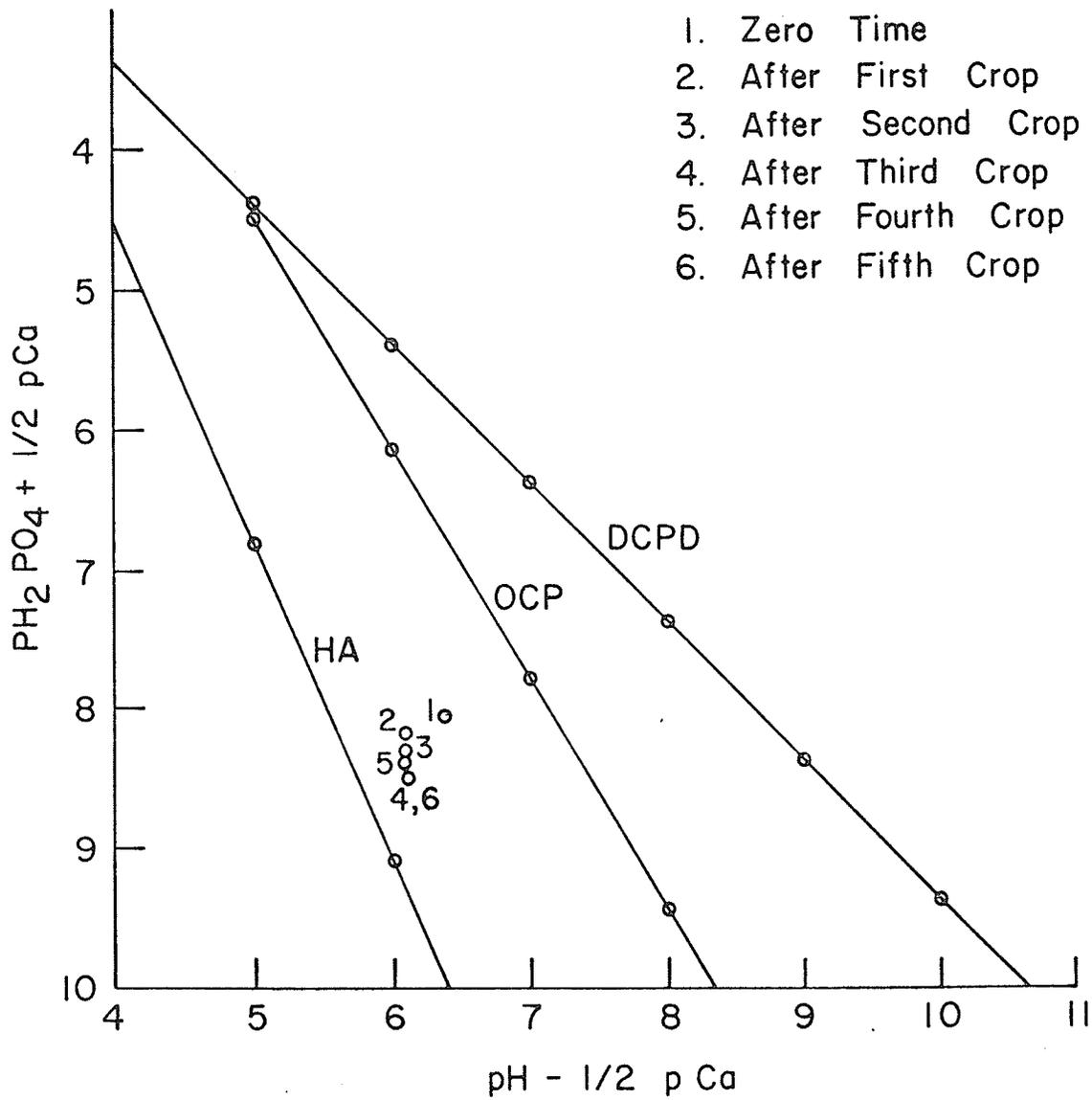


Fig. 6 Solubility Of P In Soil Treated With 5 ppm P As MCP As Affected By Cropping.

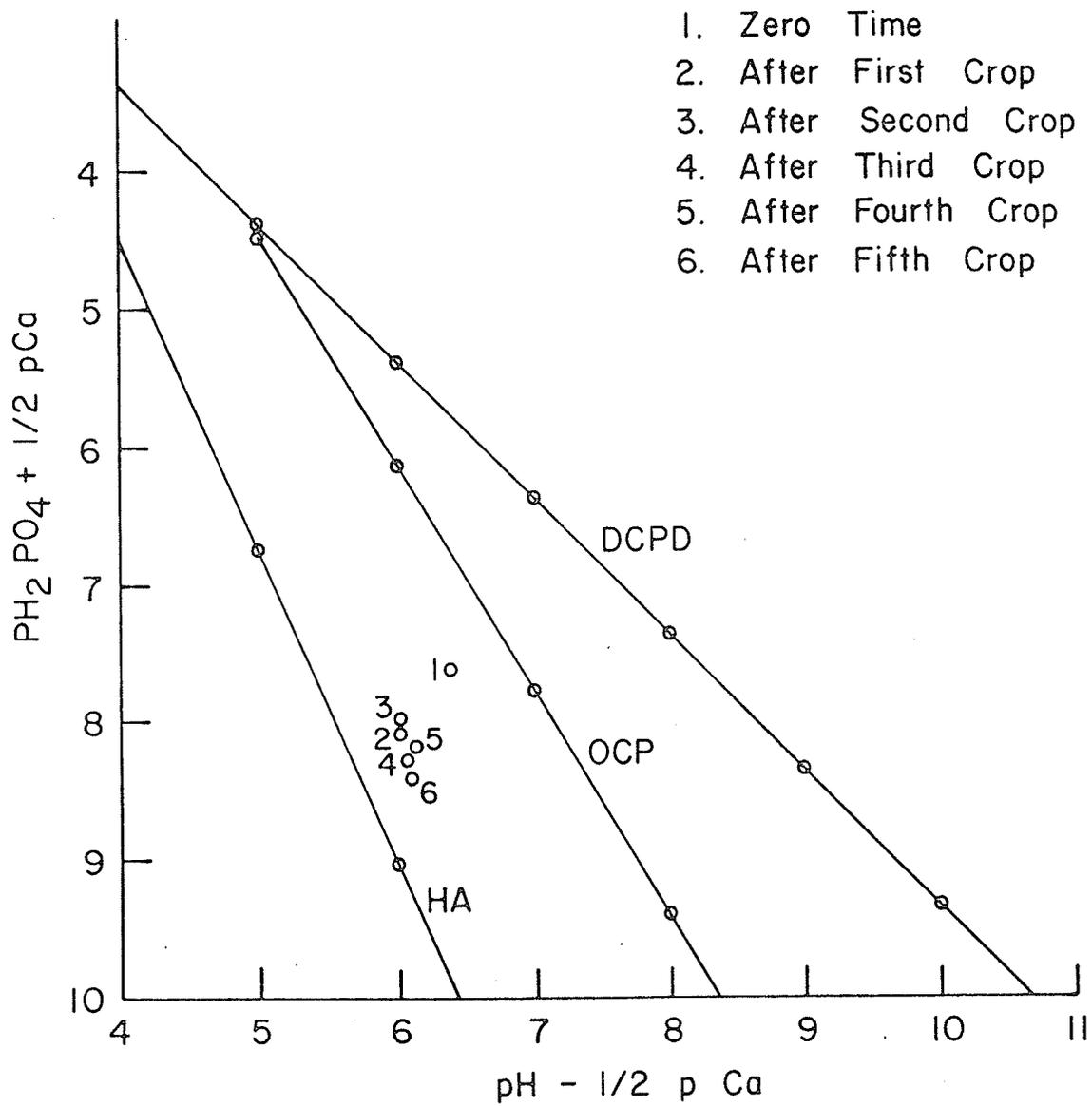


Fig. 7 Solubility Of P In Soil Treated With 10 ppm P As MCP As Affected By Cropping.

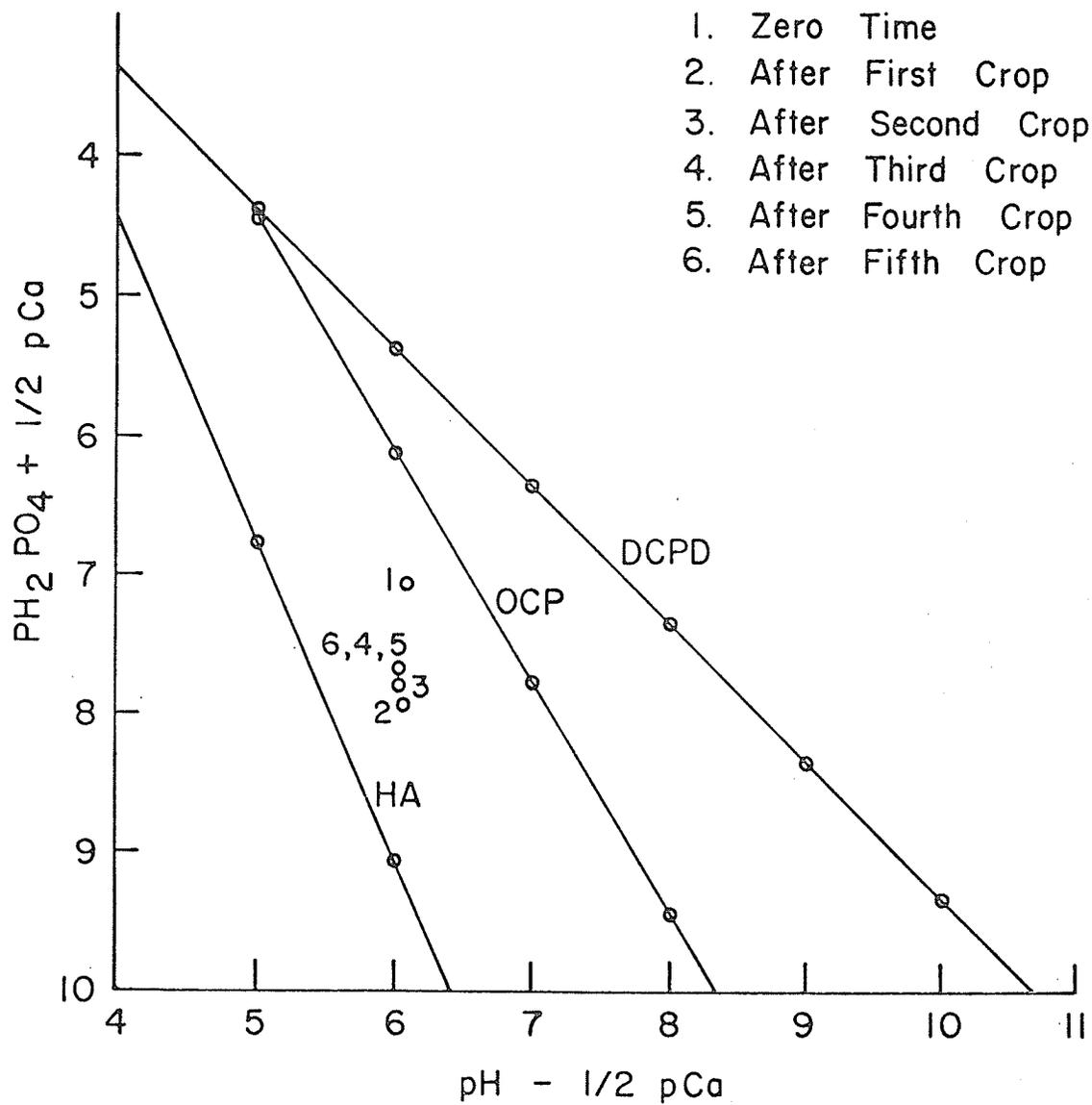


Fig. 8 Solubility Of P In Soil Treated With 20 ppm P As MCP As Affected By Cropping.

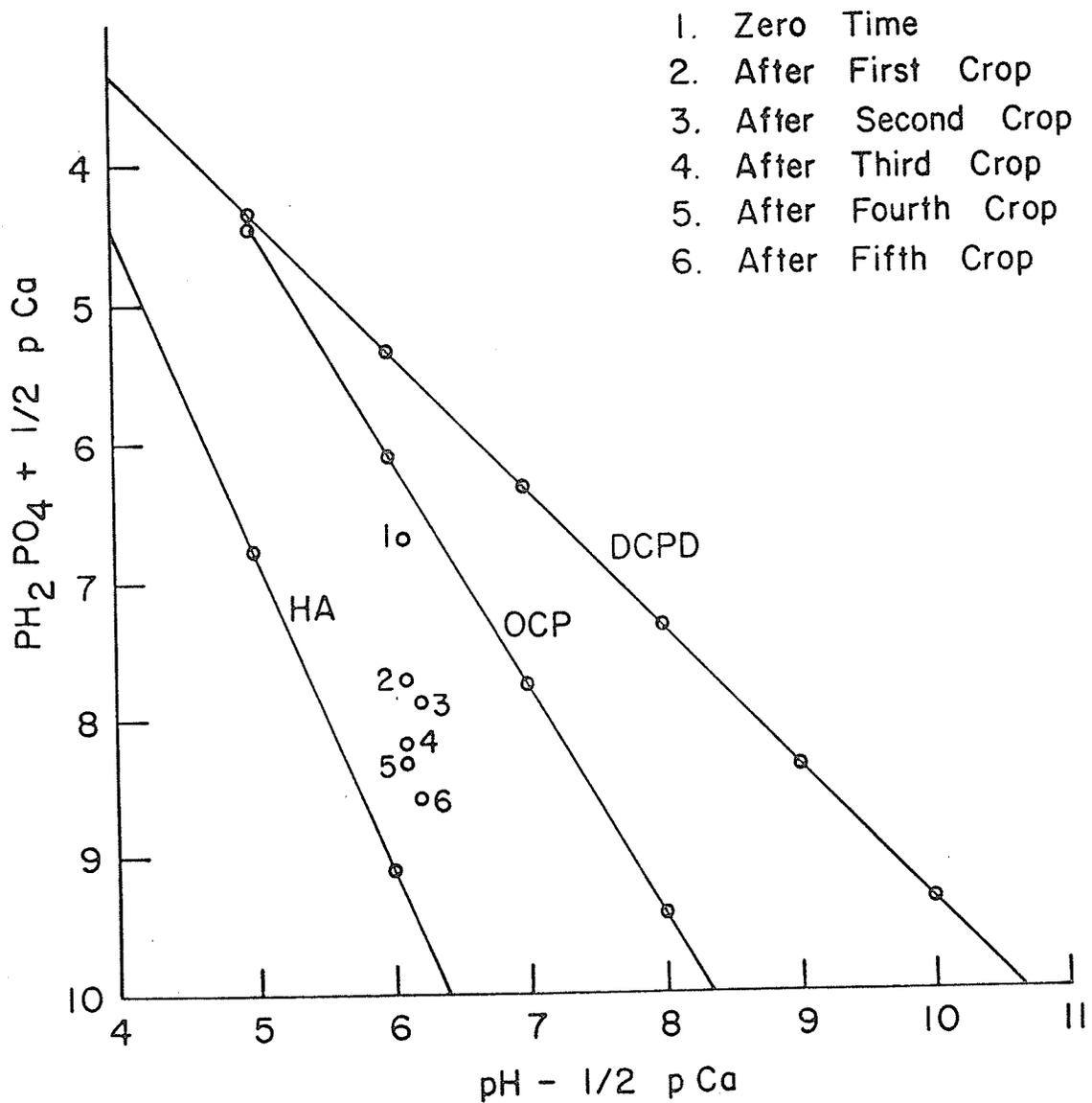


Fig. 9 Solubility Of P In Soil Treated With 50 ppm P As MCP As Affected By Cropping.

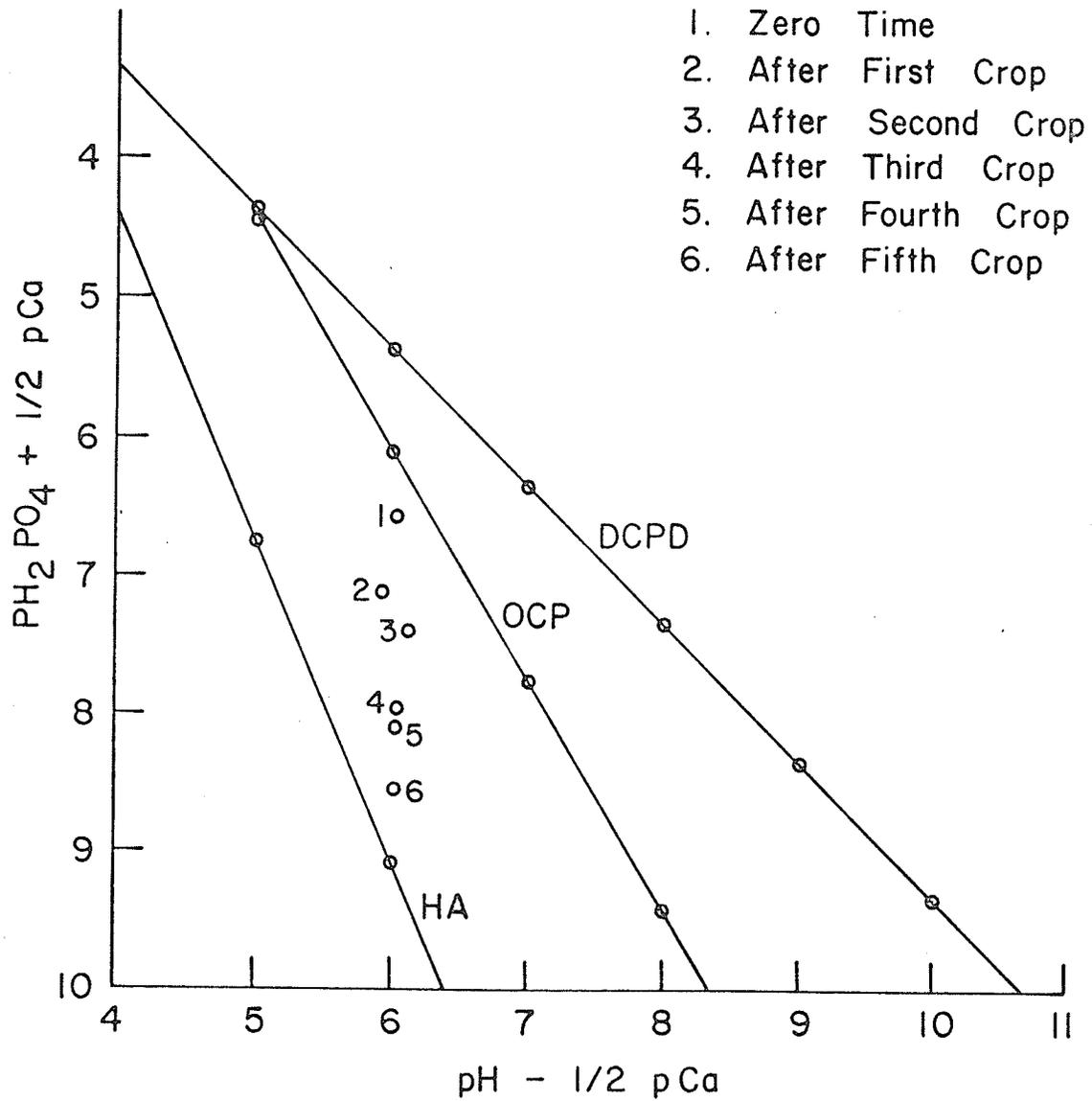


Fig.10 Solubility Of P In Soil Treated With 100 ppm P As MCP As Affected By Cropping.

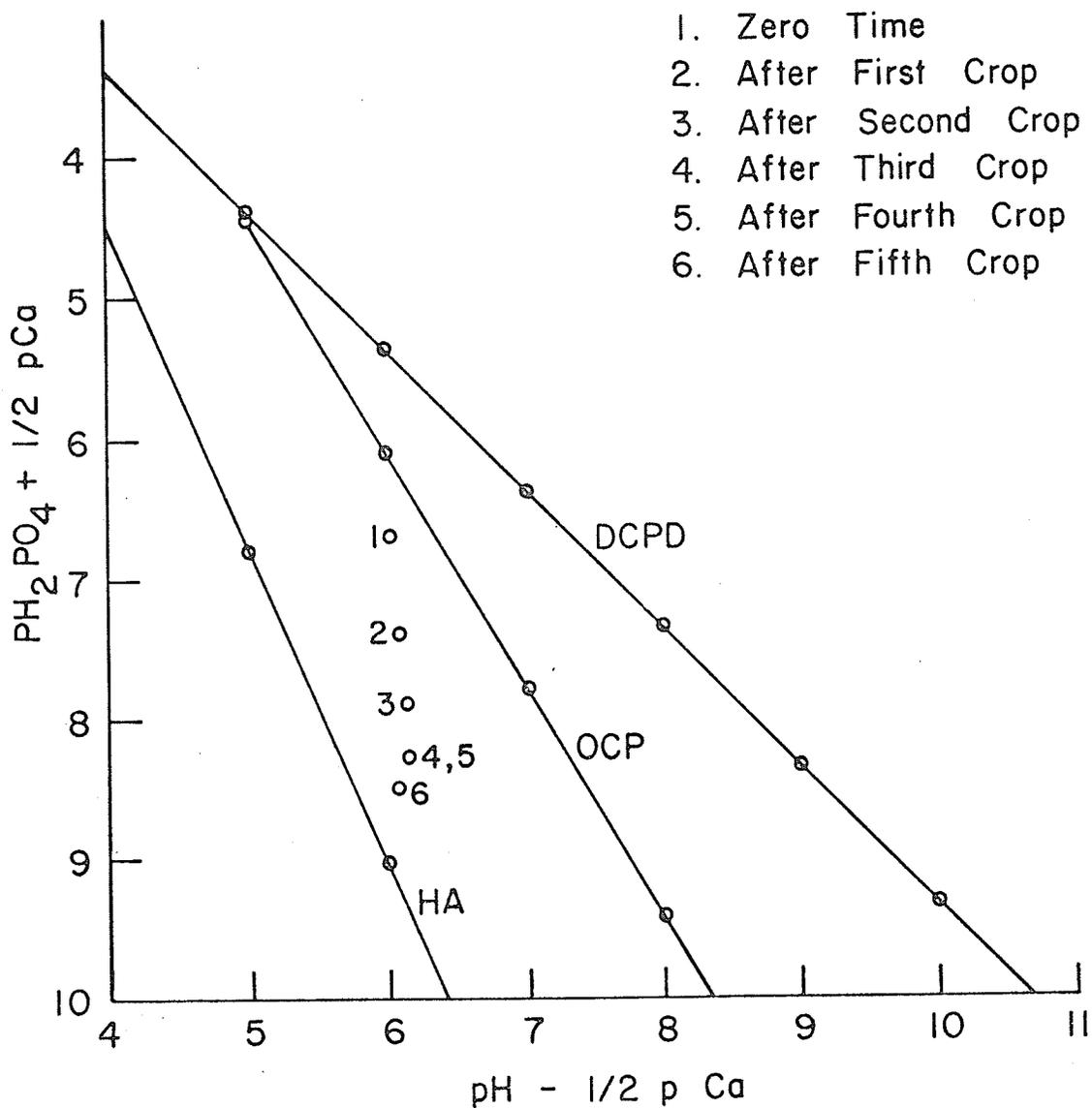


Fig.II Solubility Of P In Soil Treated With 50 ppm P As DCPD As Affected By Cropping.

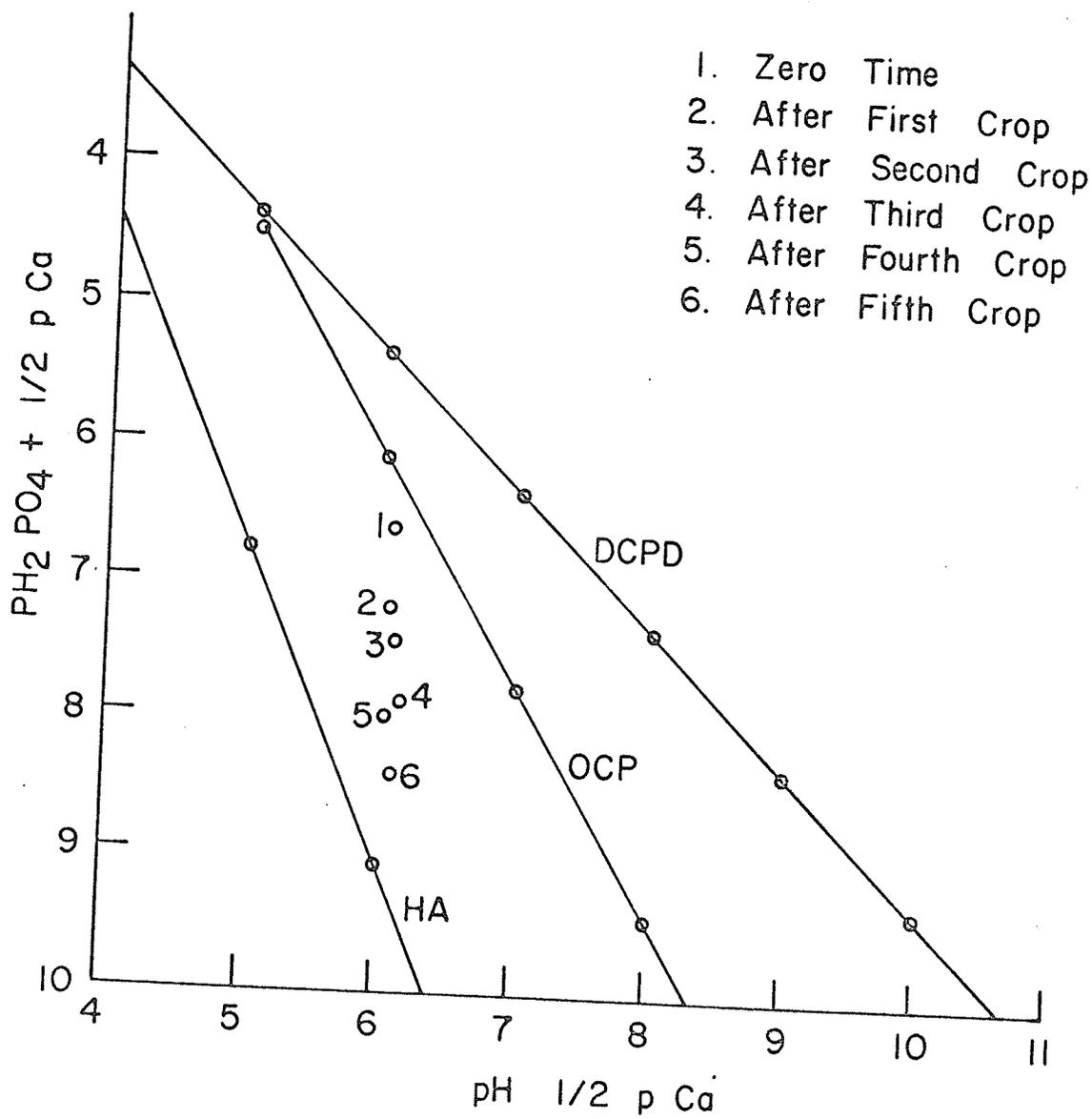


Fig. 12 Solubility Of P In Soil Treated With 100 ppm P As DCPD As Affected By Cropping.

TABLE 7. Ionic concentrations and activities, and lime and phosphate potentials for soils.

10^{-6}	pH	[Ca] $\times 10^{-4}M$	[Mg] $\times 10^{-4}M$	[P] $\times 10^{-6}M$	$\frac{1}{2}pCa$	pH_2PO_4	$pH - \frac{1}{2}pCa$	$pH_2PO_4 + \frac{1}{2}pCa$
Control								
<u>0 Time</u>	8.2	3.743	4.936	4.70	1.758	6.587	6.442	8.345
<u>1st Crop</u>	7.9	3.992	5.347	2.33	1.745	6.627	6.115	8.372
<u>2nd Crop</u>	7.8	7.485	9.255	1.16	1.620	6.927	6.180	8.547
<u>3rd Crop</u>	7.8	9.980	10.49	1.06	1.563	6.999	6.237	8.562
<u>4th Crop</u>	7.7	13.85	13.57	0.47	1.499	7.323	6.200	8.822
<u>5th Crop</u>	7.7	19.96	17.87	0.35	1.429	7.514	6.271	8.943
5 ppm Pas MCF								
<u>0 Time</u>	8.2	3.743	4.936	9.10	1.758	6.300	6.442	8.058
<u>1st Crop</u>	7.9	3.493	4.730	3.51	1.771	6.432	6.129	8.203
<u>2nd Crop</u>	7.8	4.366	5.528	2.33	1.726	6.546	6.074	8.272
<u>3rd Crop</u>	7.8	7.111	9.049	1.18	1.631	6.912	6.169	8.543
<u>4th Crop</u>	7.7	9.980	10.49	1.12	1.563	6.922	6.137	8.485
<u>5th Crop</u>	7.7	11.35	10.49	0.94	1.537	6.975	6.163	8.512

TABLE 7 Continued...

	pH	[Ca] X10 ⁻⁴ M	[Mg] X10 ⁻⁴ M	[P] X10 ⁻⁶ M	$\frac{1}{2}$ pCa	pH ₂ PO ₄	pH- $\frac{1}{2}$ pCa	pH ₂ PO ₄ + $\frac{1}{2}$ pCa
10 ppm Pas MCP								
<u>0 Time</u>	8.2	3.743	4.936	21.462	1.759	5.927	6.441	7.686
<u>1st Crop</u>	7.8	3.493	4.730	3.5080	1.771	6.345	6.029	8.116
<u>2nd Crop</u>	7.8	4.366	5.528	3.508	1.726	6.368	6.074	8.094
<u>3rd Crop</u>	7.8	5.364	7.609	1.921	1.687	6.667	6.113	8.354
<u>4th Crop</u>	7.7	8.234	9.050	1.921	1.601	6.624	6.099	8.225
<u>5th Crop</u>	7.7	8.608	9.049	1.182	1.591	6.839	6.109	8.430
20 ppm Pas MCP								
<u>0 Time</u>	7.9	3.493	4.936	47.861	1.775	5.299	6.125	7.074
<u>1st Crop</u>	7.8	3.244	3.908	17.373	1.785	6.201	6.015	7.986
<u>2nd Crop</u>	7.8	3.867	4.730	5.908	1.750	6.123	6.05	7.873
<u>3rd Crop</u>	7.7	5.364	5.964	5.141	1.684	6.134	6.052	7.818
<u>4th Crop</u>	7.7	6.113	7.198	5.430	1.659	6.132	6.041	7.791
<u>5th Crop</u>	7.7	5.614	6.170	4.292	1.675	6.217	6.025	7.892

TABLE 7 Continued...

	pH	[Ca] X 10 ⁻⁴ M	[Mg] X 10 ⁻⁴ M	[P] X 10 ⁻⁶ M	$\frac{1}{2}pCa$	pH ₂ PO ₄	pH- $\frac{1}{2}pCa$	pH ₂ PO ₄ + $\frac{1}{2}pCa$
50 ppm Pas MCP								
<u>0 Time</u>	7.8	3.493	4.730	89.445	1.777	4.936	6.023	6.713
<u>1st Crop</u>	7.9	3.992	5.141	9.604	1.745	6.008	6.105	7.753
<u>2nd Crop</u>	7.9	4.366	5.347	5.908	1.726	6.227	6.174	7.953
<u>3rd Crop</u>	7.8	5.614	6.992	2.427	1.677	6.561	6.123	8.238
<u>4th Crop</u>	7.7	9.980	10.490	1.425	1.563	6.783	6.137	8.346
<u>5th Crop</u>	7.7	13.600	11.1100	.465	1.495	7.191	6.205	8.686
100 ppm Pas MCP								
<u>0 Time</u>	7.8	3.493	4.730	127.702	1.780	4.780	6.02	6.56
<u>1st Crop</u>	7.8	2.994	3.291	34.683	1.802	5.319	5.998	7.121
<u>2nd Crop</u>	7.9	3.992	5.141	17.373	1.745	5.750	6.155	7.495
<u>3rd Crop</u>	7.8	5.364	6.581	4.300	1.686	6.305	6.114	7.991
<u>4th Crop</u>	7.7	7.485	7.815	2.814	1.618	6.439	6.082	8.057
<u>5th Crop</u>	7.7	5.740	9.872	1.061	1.676	6.866	6.024	8.542

TABLE 7 Continued...

	pH	[Ca] X10 ⁻⁴ M	[Mg] X10 ⁻⁴ M	[P] X10 ⁻⁶ M	$\frac{1}{2}$ pCa	pH ₂ PO ₄	pH- $\frac{1}{2}$ pCa	pH ₂ PO ₄ + $\frac{1}{2}$ pCa
50 ppm Pas DCPD								
<u>0 Time</u>	7.8	3.618	4.936	68.862	1.769	5.054	6.031	6.823
<u>1st Crop</u>	7.9	3.493	3.908	17.373	1.77	5.725	6.13	7.495
<u>2nd Crop</u>	7.9	3.992	4.936	4.702	1.744	6.227	6.156	7.971
<u>3rd Crop</u>	7.8	6.362	7.609	1.921	1.652	6.678	6.148	8.330
<u>4th Crop</u>	7.7	9.481	9.872	1.425	1.573	6.773	6.127	8.346
<u>5th Crop</u>	7.7	7.111	12.340	7.702	1.635	6.952	6.065	8.587
100 ppm Pas DGPD								
<u>0 Time</u>	7.8	3.493	4.730	99.23	1.778	4.887	6.022	6.665
<u>1st Crop</u>	7.9	2.994	3.291	31.611	1.841	5.438	6.059	7.279
<u>2nd Crop</u>	7.8	3.992	4.936	14.725	1.745	5.731	6.055	7.476
<u>3rd Crop</u>	7.8	5.364	5.964	5.141	1.684	6.220	6.116	7.904
<u>4th Crop</u>	7.7	7.111	7.609	3.028	1.629	6.376	6.071	8.005
<u>5th Crop</u>	7.7	5.364	9.049	1.425	1.689	6.725	6.011	8.414

Figure 13 illustrates the change in phosphate potential ($\text{pH}_2\text{PO}_4 + \frac{1}{2} \text{pCa}$) with cropping for the five crops grown. The phosphate potential for the control treatment increased linearly from about 8.2 to 9.0 with cropping. Phosphate potentials for untreated soils were greater than for any other treatment. Application of 5 ppm P as MCP decreased phosphate potentials compared to the untreated soil, but were generally greater than for any other treatment except after crop 5 where the phosphate potential was less than for the 50 ppm P as MCP or DCPD treatments. Phosphate potentials for the 5 ppm P treatment varied between 8.0 and 8.5 with cropping.

Phosphate potentials varied from 7.7 to 8.3 when 10 ppm P as MCP was added. These values are much lower than for 5 ppm P as MCP and control treatment. Phosphate potentials when 10 ppm P was added was similar to that of the 50 ppm P as MCP treatment after two crops. After five crops the P potential was lower than that for the 50 and 100 ppm P as MCP or DCPD treatments. This indicates the 10 ppm P as MCP treatment usually maintained higher phosphate concentrations in soil solution than the 50 ppm P treatments.

The lowest phosphate potentials, after five crops were grown, were obtained when 20 ppm P as MCP added. Phosphate potentials for this treatment increased for crop 1 but decreased from this value for crop 2 to 5. The phosphate potential for this treatment was less than for the 50 or 100 ppm P treatments after 3 to 5 crops were grown. This indicates that the 20 ppm treatment maintained the highest

phosphate concentration in soil solution.

The phosphate potentials for 50 ppm P as MCP and DCPD were similar. Addition of 100 ppm P as MCP and DCPD also resulted in similar phosphate potentials. Phosphate potentials for the 50 ppm P treatments were greater than that of 100 ppm P treatments. Phosphate potentials with these treatments were low initially but increased almost linearly with cropping. Phosphate potentials for these treatments increased to values greater than for the 10 and 20 ppm P as MCP treatments for crops 4 and 5.

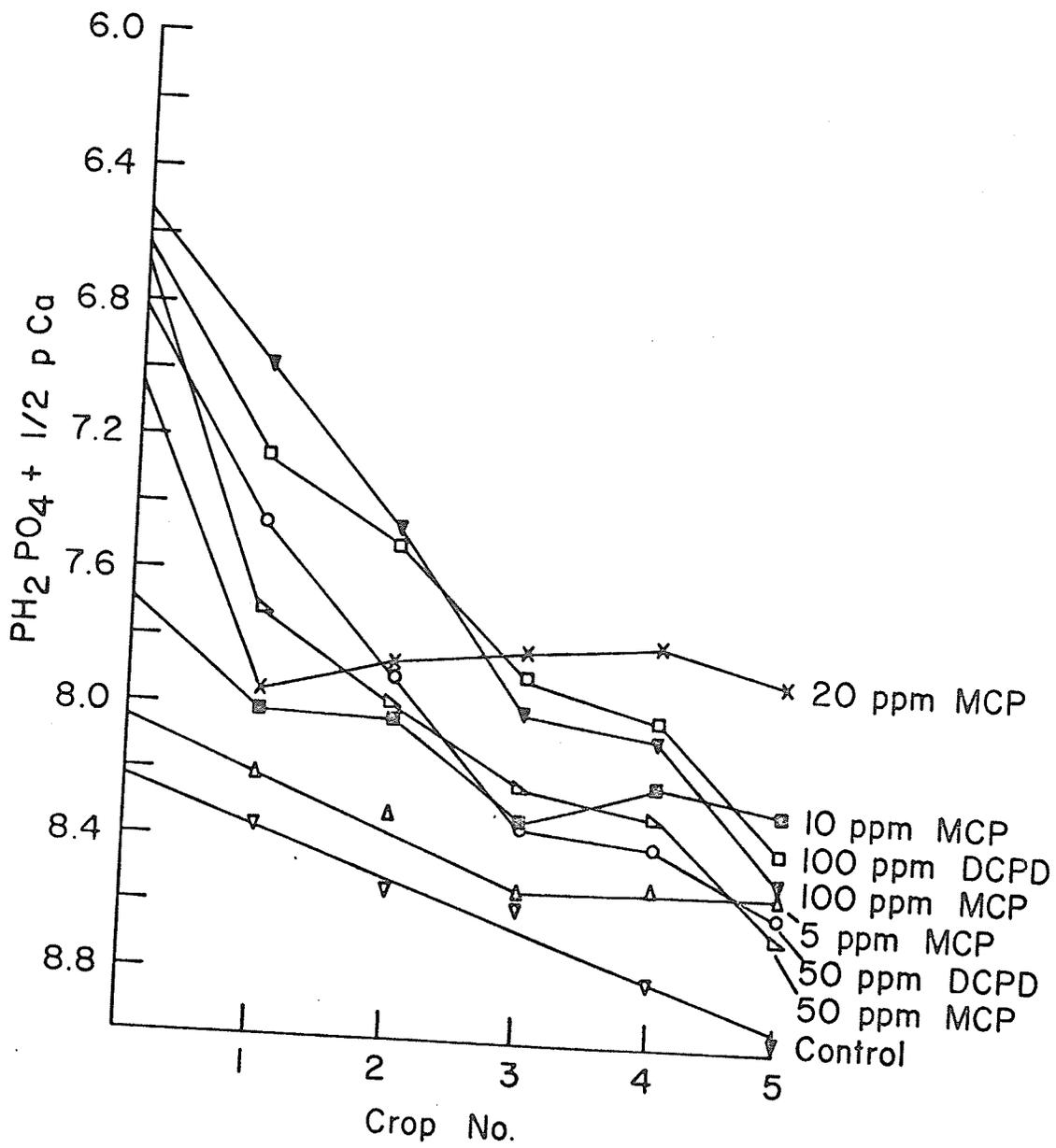


Fig. 13 Phosphate Potential As Affected By Cropping.

SUMMARY AND CONCLUSIONS

The concentration of phosphorus in soil solution of most Manitoba soils is unusually inadequate to supply the phosphorus needs of most crops grown and fertilizer phosphorus has to be added for optimum yields. Some authors have suggested that a single-large application of phosphorus applied infrequently was as effective in increasing yields as were annual but smaller applications when equivalent amounts of phosphorus were added over a period of time. Other authors stated that annual applications were superior to the infrequent large applications. This study was conducted to determine the relative efficiencies of a single-large application of phosphorus versus small-frequent applications.

One hundred ppm P as MCP or DCPD and 50 ppm P as MCP or DCPD were thoroughly mixed with the soil to represent single-large applications whereas 5, 10 and 20 ppm P as MCP were added as a band treatment prior to seeding of each barley crop to represent frequent-small applications. Six crops were grown, yield and soil analysis (NaHCO_3 -extractable P and Solubility Studies) were used to evaluate the supply of phosphorus from the various treatments.

Yields of barley were increased by phosphorus application. Yields for crops 1 and 2 generally declined in the order: 100 ppm P as MCP or DCPD > 20 ppm P band > 50 ppm P as MCP or DCPD > 10 ppm P band > 5 ppm P band > control. Yields for crops 3 to 6 decreased in the order: 20 ppm P band > 10 ppm P band > 100 ppm P as MCP or DCPD > 5 ppm P band ~ 50 ppm P as MCP or DCPD. The average yields, average of all crops grown, were greater for the small-frequent applications than for the single-large applications when equivalent quantities of P were added.

Phosphorus content of plants treated with 50 and 100 ppm P as MCP or DCPD were much higher than the phosphorus content of plants treated with 5, 10 and 20 ppm P as MCP for crops 1 and 2. However, for crops 4, 5 and 6 percent phosphorus in plants treated with the smaller but frequent applications of phosphorus were equal to or greater than plants treated with single-large applications of phosphorus. The average percent phosphorus in plant tissue, average of all 6 crops, was greater for the single-large applications than for the small-frequent application of P. The higher average for the single-large application was due to very high phosphorus levels in crop 1 and 2 in which luxury consumption of added phosphorus occurred.

Uptake and percent recovery of applied phosphorus declined with cropping for the single-large applications of phosphorus. In contrast, uptake and percent recovery of applied phosphorus remained relatively constant with cropping for the frequent-small applications, particularly for crops 2 to 6 inclusive. The greatest total uptake and percent recoveries of applied phosphorus occurred when 50 and 100 ppm P were applied. These higher recoveries, however, were not reflected in yield increases.

NaHCO_3 -extractable phosphorus decreased rapidly with time for the single-large applications of phosphorus - whereas the banded treatments maintained extractable phosphorus levels at relatively constant levels. NaHCO_3 -extractable phosphorus contents were greatest for the single large applications of phosphorus for crop 1 and 2 but declined to values less than that for the 10 and 20 ppm banded treatments for crops 5 and 6.

Determination of the solubility of phosphorus in the soils as a function of cropping showed the following: the largest phosphorus application had the highest initial P solubility. Phosphorus solubility decreased with cropping for the single-large application of phosphorus. The solubilities approximated that of HA after 5 crops were grown, after the first two to three crops, soils with frequent-small dressings of phosphorus had higher solubilities of P than soils with the single-large applications of phosphorus.

In summary, these investigations show that small-frequent applications of phosphorus are considerably superior to single-large applications of phosphorus in increasing yields when equivalent amounts of phosphorus are applied over a period of time. The small-frequent applications also maintained a sufficiently higher enough concentration of phosphorus in soil solution for all crops whereas the single-large application maintained high concentration of P in soil solution only for crops 1 and 2.

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