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Characterization of residual phosphorus in some Michigan soils

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**CHARACTERIZATION OF RESIDUAL PHOSPHORUS
IN SOME MICHIGAN SOILS**

By

Olusegun Adedayo Yerokun

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Crop and Soil Sciences

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ABSTRACT

CHARACTERIZATION OF RESIDUAL PHOSPHORUS IN SOME MICHIGAN SOILS

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Olusegun Adedayo Yerokun

When phosphorus (P) is applied to the soil it undergoes reactions that render it more stable. Therefore only a fraction of annual P application is removed by plants. Cultural practices have resulted in an accumulation of high levels of P residue in some areas of intensive agriculture. It was of interest to know the effectively available portion of this residue.

Selected extractants - Bray P1, Bray P2, Olsen, AER, and CaCl_2 were evaluated in a greenhouse study in relation to plant dry matter yield and P uptake, on 10 Michigan soils with various levels of residual soil P. This group of heterogenous soils varied in pH from 5.6 to 7.8. Furthermore, the chemical nature of P in these soils was determined by the solubility product principle.

The amount of P extracted on each soil varied with extractant but was highest with the Bray tests. In this case a soil:solution ratio of 1:20 for the Bray P1 extracted P similar to Bray P2 (1:8) except on a calcareous Charity clay soil when more P was extracted by the latter method. Generally the Bray method was more effective in detecting the soil testing low in P.

Plant dry matter yield over ten consecutive 5-week crops was only weakly correlated with soil tests, and soil characteristics as well as plant physiological adjustments were found to have influenced this observation. The Olsen, AER, and CaCl_2 tests were better correlated with P uptake on this group of heterogenous soils. When the soils were separated by relative buffering capacity and P release mechanism it was found that the Bray tests were affected more, as correlations were improved.

A mass balance comparison of P uptake with change in soil tests showed that the effectively available P was under estimated for the soils, except a Montcalm sandy loam soil. In this case it appeared that unavailable P was being extracted by the Bray tests. Generally the Bray P1 (1:20) and Bray P2 (1:8) more closely predicted plant P uptake from the soils. Furthermore, the uptake from some uncultivated soils suggested that organic-P contributions were significant. The results of the solubility study showed that Al-P and Ca-P were important sources of P to plants, however, the high levels of residual P in some soils increased the contributions from adsorbed P.

DEDICATION

To my family.

With love to my Wife, Dellia Judith

The wind beneath my wings.

With affection to my Daughter, Gbadero Aweni II

The essence of my hopes and aspirations.

In honor of my dear Mother, Gbadero Aweni I

The essence of my joy and struggle.

In dear and loving memory of my Father, Simeon Alabi

The pillar of my determination and a

Monument of unageing intellect.

Who taught me to

Follow Knowledge like a sinking star

To the utmost bounds of human thought.

ACKNOWLEDGEMENTS

Dr. Donald R Christenson served as my program and thesis adviser throughout my graduate study. I am most indebted to him for his understanding and support. The members of my advisory committee were Drs. Boyd Ellis, Norman Good, Bernard Knezek, and Darryl Warncke. I thank them for their time and critical review of my program.

I am grateful to the many people who helped me in the course of my project.

I thank my Sisters and Brothers for their interest in my goals and encouragement of my pursuits. The patience and strength shown by my Mother through my years away from home eased the burden on my mind. Though saddened that my Father was not present to witness my progress through this path that he set me off on, I rejoice in sharing with him the attainment of this milestone.

My work could not have been completed without the selfless support of my Wife. She as much as I, has earned this.

Saving the best and most for last, I give ceaseless praise and thanks to God Almighty who has made everything possible by the breath of life.

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INTRODUCTION

The importance of phosphorus (P) in crop production is well documented. Therefore it is common practice for farmers to include P in their annual fertilizer management programs. As early as 1841, Leibig suggested that "it must be borne in mind that as a practice of arable farming, what is taken from the soil must be returned to it in full measure." Because P applied to the soil regresses into unavailable forms (Larsen et al., 1965), annual applications in excess of plant requirements are usually supplied in order to fulfill plant growth capacities. Nonetheless, it is known that P from previous applications (residual P) can become available in subsequent years. This raises the question of its importance as an integral of production programs. Can residual P by itself sustain a season of production at the current levels?

The practice of continuous fertilization has resulted in an establishment of high P levels in many regions of intensive agriculture (Table 1). This can bring about concerns about soil nutrient imbalances as well as for the environment (leaching and eutrophication), especially in a state such as Michigan with many game and recreational inland waters. On the other hand, such residual P may be as effective as fresh P applications for crop production (Mattingly, 1971). When this is not so, residual P is nonetheless valuable, affecting the soil physical properties (Biswas et al., 1970; Lutz and Haque, 1975). The nature of

Table 1. Median phosphorus levels for Michigan for soil samples tested at the MSU Soil Testing Laboratory⁺.

Year	Number of Samples	P ^F
		-mg/kg-
1962	6,792	12
1963	10,397	12
1964	14,172	15
1966	15,021	18
1967	13,753	17
1968	18,668	16
1969	14,063	20
1970	12,216	22
1971	12,323	26
1972	12,139	27
1973	14,140	29
1974	24,446	32
1975	19,263	34
1976	27,207	34
1977	29,953	35
1979	24,755	48
1980	24,319	54
1981	27,574	49
1982	24,631	50
1983	29,580	52
1984	24,886	54
1985	22,038	53

⁺Source: Michigan State University Soil Testing Laboratory.

^FBray-P1, 1:8, soil:solution attraction.

residual soil P has been of interest but not of concern. There is no indication of urgent considerations of the mobilization of residual soil P. This may be because of the availability of high quality P minerals at economical price.

The prediction of the availability and plant use of residual P on high P testing soils is not now well understood. Yet this knowledge is imperative to economically manage the rising soil P levels. Recent observations (Table 2) have indicated a lack of response to further P applications to more of these soils. Excessive fertilization can only result in P uptake by plant without acceptable gains in dry matter yield. This has prompted some agronomic and economic concerns. Furthermore, the energy and raw materials used in commercial fertilizer production are limited resources and must not be wasted.

Whereas chemical soil test methods have been used to estimate the amount of P that can become available to crops, these are sometimes questionable. A reliable soil test should extract the P fractions which are well correlated with the P removed by plants. For a single method, this may be adequate on similar soils but inconsistent on soils of differing properties. Moreover, these tests may not reflect the chemical and microbial transformations that contribute to P equilibrium and plant uptake. Beringer (1985) has suggested that soil test interpretations and applications be reviewed to suit the current levels of high fertility. In the continuing effort to determine the amount of P that can be supplied by the residual fraction, some agronomists have resorted to exhaustive and relative cropping. The one set back to this approach is that it is retrospective. In order to use any parameter of soil P, it

Table 2. Effect of applied phosphorus and potassium on yield of corn grain in a long term study conducted on a Conover loam, 1973-1983.

Fertilizer ^a Applied		Year										Average
P ₂ O ₅	K ₂ O	1973	1974	1975	1976	1977	1978	1979	1980	1981	1983	
--lb/acre--		-----bu/acre-----										
0	0	124	175	139	150	182	183	160	190	175	179	166
0	150	128	171	142	151	173	178	156	187	178	176	164
50	150	125	179	138	158	180	169	155	192	178	170	164
100	150	122	176	147	147	178	180	166	190	186	180	167
b	150	123	168	157	159	165	182	157	196	170	175	165
100	0	125	173	147	158	158	179	151	191	175	177	164
100	75	123	177	144	160	171	177	152	190	185	175	165
50	c	124	177	135	151	176	178	154	190	171	181	164
LSD (5%)		NS ^d										NS ^e

^aAnnual application except b and c below.

^b150 lb P₂O₅/acre applied in 1973, 1976, 1979 and 1982; none in other years.

^c225 lb K₂O/acre applied in 1973, 1976, 1979 and 1982; none in other years.

^dYear x treatment interaction.

^eComparison of treatment averages.

Source: Christenson and Vitosh (1984).

should be able to foretell and account for the variation in yield of and uptake by plants grown on soils of varying P levels.

The following study was conducted to: 1. Evaluate the availability and plant use of residual soil P. 2. Monitor some transformations of residual soil P.

CHAPTER 1

AVAILABILITY OF RESIDUAL SOIL PHOSPHORUS

INTRODUCTION

Frequent use of inorganic fertilizers is an integral part of current intensive production programs. Of particular attention are the macro-nutrients. The nature of P is such that only a fraction of that applied in a single season is available for plant use. A portion of the remainder can become available for plant use in subsequent seasons. This accumulating P fraction is available residual P.

Soil characteristics influence the behavior of P. For this reason soils need to be treated differently in terms of P management. Soil test methods evolved out of the need to know the magnitude of plant available nutrients. Because of the heterogeneity of soils and the possible interferences with P extractants, there is no one universal test applicable. This further complicates the interpretations of soil test results. Therefore, attempts have been made to exhaustively remove P from soils with plants and relate these to soil test results.

In Michigan where increasing P levels can become of concern, it was of interest to examine the potentials of these soils and soil test performance. The following study was undertaken to: 1. Study P levels in soils with varying fertilization histories. 2. Determine the effect of cropping on P levels in soils. 3. Examine the relationship between P

levels and plant performance. 4. Examine the influence of soil factors on plant P use.

LITERATURE REVIEW

Russell (1977) proposed a nutrient dynamics model (Fig 1) that could serve to illustrate the fate of P fertilizers. This model suggests that following plant removal and loss from the system, of P, there remains a pool of plant available P residue. If no further nutrient input is made it would be expected that plants can obtain some nutrition from this pool. Available residual soil P does not remain constant because slow reactions render it unavailable in time (Barrow, 1974). Many factors interact to partition the P supply into the different pools. Some of these are discussed below.

The P removed in agricultural products depends on the kinds of products exported and cultivation practices. In Australia, Gifford et al. (1975) reported that an average of less than 20% of annual P application is removed in the same year. Larsen (1974) estimated 10% for Denmark, and Davis (1962) put the figure at 25% for the U.S. Various characteristics of plants influence their ability to use soil P. Some of these are rooting patterns, root physiology (Johnston and Olsen, 1972; McLachlan, 1976), and plant age (Barrow and Campbell, 1972).

Phosphorus losses such as by leaching and erosion are usually small, in the vicinity of 2% (Schumann et al., 1973). However, on sandy soils with low buffering capacities and low water retention, it could be high exceeding 80% (Neller et al., 1951).

Immobilization reactions between soil and fertilizer reduce the residual value of soil P. These reactions are principally those of adsorption, precipitation and fixation. In the final analysis, the soil type and characteristics play an important part in the magnitude of P

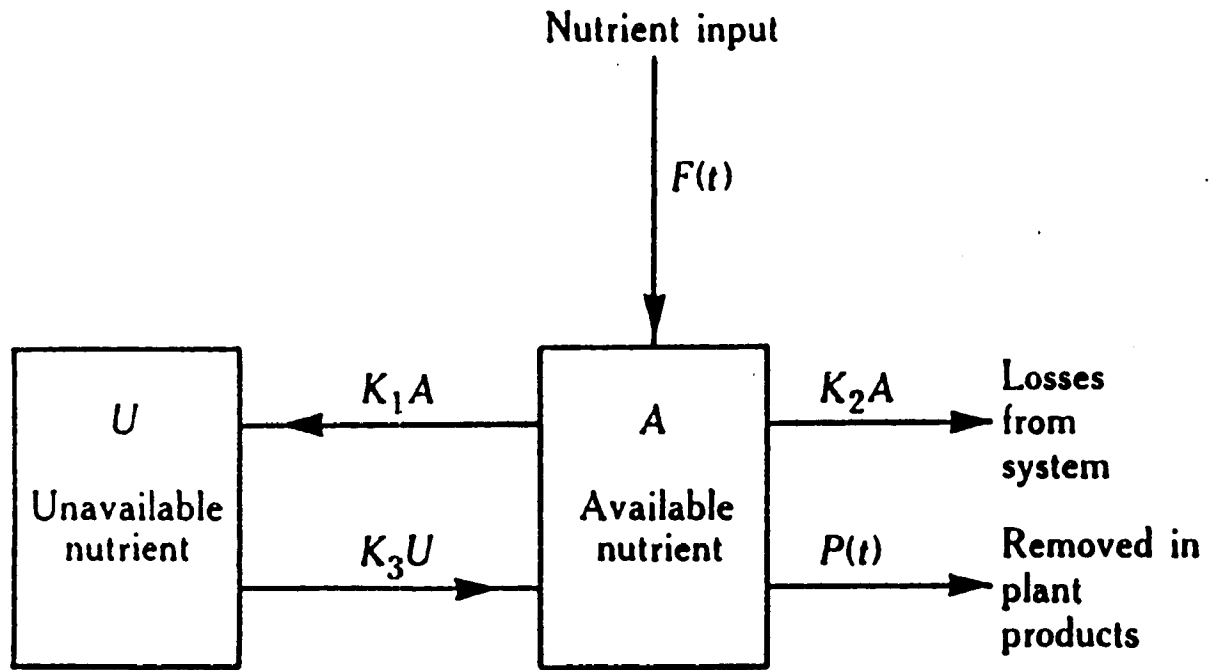


Figure 1. Diagram of nutrient model by Russell (1977).

immobilized. Given the current rates of fertilizer application it is then possible to estimate that residual soil P could range from insignificant to appreciable amounts.

Phosphorus Reactions With The Soil: Available Inorganic Fractions

Phosphate reactions with the soil constituents play an ultimate role in P availability to plants. In this respect, inorganic soil P is maintained in three important fractions pertaining to plant nutrition. The relationship between these fractions can be represented as: Soil solution P <===> Labile soil P <===> Non-labile soil P.

Soil solution P is the fraction from which plant roots directly obtain nutrition, usually in the orthophosphate form (Khasawneh et al., 1979). The P concentration in soil solution of fertile arable soils is about 10^{-5} M. As this is considerably low compared to plant requirements, it is necessary to continuously replenish this pool to avoid P deficiency. The labile P fraction serves this purpose.

Labile soil P consists of P weakly adsorbed on to soil surfaces. This fraction is in equilibrium with solution P and is considered to be potentially available for plant use (Larsen et al., 1965). The concentration of P in this fraction could be 10^2 to 10^3 times greater than in solution (Mengel and Kirby, 1982). As a matter of time and soil P retention characteristics, the labile pool can become more stable and move into the non-labile pool (Barrow and Shaw, 1976).

Non-labile P is strongly held on and within the clay lattices or is occluded by some other precipitation-recrystallization reactions. This fraction reverts slowly into labile P, and is considered to be non-available to plants.

When the soil P equilibrium is disturbed by adding fertilizer, reaction between fertilizer and soil take place in two steps. A rapid step leads to the adsorption of P, and a slow reaction converts P into the more firmly held form (Barrow, 1974; Hayward and Trapnell, 1964). Large and continuous application of P over a period of time will likely reduce the amount and rate of P fixed by the soil, resulting in high available residual P.

The ability of a soil to supply P to plants is governed by the soil buffering capacity (Holford and Mattingly, 1976). This parameter is the ratio between adsorbed P, quantity (Q), and soil solution P, intensity (I), at an equilibrium solution concentration. It is an indication of the ability of the soil to replace a unit change in soil solution P; the relative amount of P needed to replace a unit change in soil solution P; and the soil P requirements to maintain a productive solution concentration. The soil P buffering capacity may be the limiting factor in P uptake (Holford, 1976; Nair and Mengel, 1984). Soils with high buffering capacities usually may only need to maintain low intensities because of their ability to quickly respond to changes in solution P, as long as there is adequate quantity. However, they do require higher levels of quantity to maintain the plant optimum intensities (Holford, 1976; White and Doll, 1971).

Phosphorus buffering capacities are derived from adsorption isotherm plots (Holford, 1976; Parfitt, 1978; Olsen and Khasawneh, 1980).

Plant Use Of Available Residual Soil Phosphorus

Phosphorus applied to the soil is rendered partially unavailable as soil reactions partition it into various pools. The fraction from previous P applications that remains available for plant use has been defined as residual P. This fraction has also been shown to play a recognizable role on crop nutrition and production (Barrow, 1980).

In a review of residual P in Canadian soils, Sadler and Stewart (1974) compiled evidence that this residue can amount to agronomic and economic importance. On some high P fixing soils of North Carolina, Kamprath (1967) showed that residual effects can be noticed even 9 years following a large initial application. Leamer (1963) was able to recover two thirds of a 235 kg P/ha application to New Mexico soils, with 4 years of alfalfa and 1 year of sorghum. When the differences in yields between a single large application and four annual small applications to Kansas soils were compared, Janssen et al. (1985) showed that even though the significant yield from the large application in the first year had disappeared, it was as effective as single applications in the fourth year. In Texas, Matocha et al. (1970) observed that small applications made over a ten year period was as effective as a single large application five years later. Alessi and Power (1980) also observed an increase of 10% in grain yields due to the effect of residual P in North Dakota soils, up to six years following application. In England, Mattingly (1971) even reported that residual effects were superior to fresh effects on potato/sugarbeet plots. When residual P is not as effective as fresh P, it is nonetheless valuable, affecting not only P status but also water holding capacity, organic matter, and

modulus of rupture (Lutz and Haque, 1975). Important as residual P appears, there is a problem in predicting it's availability.

Factors Affecting Plant Use Of Residual Soil Phosphorus

The plant use and availability of residual P is affected by soil environment and other factors. These are mostly factors that affect the solubility of fertilizer P and plant foraging ability. While simple effects have been extensively discussed in the literature, there is no doubt that interactions prevail.

The studies by Mattingly (1968, 1970) and Devine et al. (1968) compared fertilizer sources. They showed that the initial effect of more water soluble superphosphate was superior to rock P while the reverse held true for residual effects. The dissolution of rock P can be slow, especially in non-acid soils, allowing for a longer period of supply with reduced chances of loss. Residual effects of granular fertilizers were superior to the powdered form(Mattingly et al., 1971; Terman et al., 1960). As the period of prior contact with the soil increased, the residual effectiveness decreased (Barrow and Shaw, 1974 and 1975a).

Mattingly and Widdowson (1963) observed that the percentage fresh superphosphate equivalent (the ratio of yield obtained with residual P to that obtained with fertilizer application) increased with the rates previously applied. However, the study by Kamprath (1967) suggests that the rate needed is relative to the soil characteristics. He only saw residual effects following a large application of 612 lb P/A to high P fixing soils. By increasing the fertilizer rates, the length of effectiveness of residual P may also be increased (Leamer, 1963).

The total amount of added P recovered from soils appears to decrease as the soil clay content increases (Campbell, 1965; Bar-Yosef and Akiri, 1978; Barrow and Shaw, 1976). However, Barrow (1973) found a slight trend toward increased residual effectiveness with high buffering capacity.

Increasing temperature contributed to a decrease in residual effectiveness (Barrow and Shaw, 1975b) as a result of enhancing the slow reaction. The relationship with soil moisture is not so simple. When Barrow (1974) incubated soils at moisture contents ranging from air-dried to water logged, before cropping them, he observed that the soil incubated air dry had a better residual effectiveness. This was probably because the limitation on the aqueous phase retarded slow reactions. Increasing the water content of incubation up to the permanent wilting point decreased the residual effectiveness. Further increases up to water logging did not introduce marked decreases in residual value. In conclusion it is important to keep in mind that these factors are interactive and it is not exactly possible to eliminate additive effects. When dealing with different soils, it is helpful that the mechanism involved in the immobilization of residual P is similar (Barrow and Shaw, 1974), as this reduces the complications of interpretations.

Determination of Available Residual Soil Phosphorus

It has been a challenge to Soil Scientists to develop a reliable approach to predict the amount of available residual soil P. The many test methods, modifications, and interpretations attest to its complicated nature. Olsen et al. (1983), Novais and Kamprath (1978),

Bowman et al. (1978), Adepoju et al. (1982), and Aquino and Hanson (1984) have observed significant but variable correlations between chemical soil tests (Bray, Olsen, Merlich) and P uptake and or yield. While these tests were developed to incorporate the many soil fractions that affect soil P, they sometimes react with portions that are not available to the plant. Furthermore, they do not indicate the chemical and microbial transformations that may occur during the season. Isotopic (^{32}P) and resin extraction have also been well correlated with P uptake and yield (Dalal and Hallsworth, 1976 and Bowman et al., 1978). The latter approach has been more reliable because of the absence of a strong chemical. That is not to attempt to refute the importance of quick chemical tests, just to indicate the problem that begins to arise as soil fertility level increases beyond the range used for established interpretations.

Kurtz and Quirk (1965) and Fox and Kamprath (1970) used the displacement of the adsorption isotherm and P requirements by previously fertilized soils to estimate the residual effectiveness. Fitter (1974) used the relationship between P aging and measured $\text{NaHCO}_3\text{-P}$ to predict residual effect of previously applied P. The efficacy of the tests discussed were found to be dependent on soil characteristics and laboratory manipulations, therefore comparisons are on a relative basis. It is thus agreeable that total plant available P is best determined by plants.

In order to more usefully quantify residual P, a relative cropping approach has been utilized. Because of the many factors affecting soil P equilibrium a better approach would be to consider the effectiveness rather than the availability of residual soil P. Barrow and Campbell

(1972) suggest that the residual value should reflect the availability of a previous application relative to its initial availability. Mattingly (1968), Mattingly and Widdowson (1963) and Devine et al. (1968) measured residual P by comparing the effectiveness of previous to fresh P applications for plant growth. The value was referred to as "percentage fresh superphosphate equivalent." This approach assumes that fresh P can duplicate the behavior of residual P. But Mattingly (1971) in another set of experiments found that residual P improved yields over fresh P application. Other concerns of using this approach are that oftentimes it is important to know the fertilization history and the soils must be such that they will respond to fresh P applications. The effect of variations in seasons will influence the measurement of initial and residual effects. Arndt and McIntyre (1963) made adjustments in their calculations to allow for this. They decided that a single season mean yield when multiplied by the ratio of the mean of control plots for all the seasons over the mean of control plots for a single season, would better reflect yields had seasons been similar. More recent investigations have concentrated on determining the P supplying power of soils, as an index for further cultivation practices.

MATERIALS AND METHODS

Ten soils were used in the study, seven of which had been previously cropped and three uncultivated. The descriptions follow in Tables 3 and 4. Soil pH was measured in a 1:1 soil: water suspension and 1:10 soil: 0.01M CaCl₂ suspension using a glass electrode. Textural analysis was made by the hydrometer method (Bouyoucos, 1962). The soil CEC was determined by NH₄OAc saturation and alkaline steam distillation. Total N was analyzed for by the micro Kjeldahl method (Bremner and Mulvaney, 1982). Organic matter was determined by a modified Walkley-Black procedure (Page, 1974).

Greenhouse Experiment

A greenhouse investigation was conducted using the soils described above to monitor plant use patterns of residual soil P in some Michigan soils. In order to accomplish this, surface soil samples (0-15cm) were collected from the field in the autumn. The soils were air-dried and screened to pass through a 4 mm sieve. Havlin and Westfall (1984) observed that P being rather immobile accumulated in the top 7.5cm, and Ozanne et al. (1965) suggest that plant roots proliferate in the top soil, so it was felt that the surface samples should be a good indicator of P supply.

The experimental design was a randomized complete block with four replicates. Three kilograms of soil were placed in pots lined with plastic bags. Each pot was watered to the soil water content at 0.03 MPa (field moisture capacity), and maintained by weighing daily and adding water as needed. Following the initial watering, seeds were planted and thinned to fifteen following emergence. Nitrogen as NH₄NO₃ and potassium

Table 3. Soil classification of some Michigan soils used in a greenhouse study of residual P.

Soil Series	Texture	Family	Previous Treatment
Charity	c	Aeric Haplaquept, fine mixed, mesic	Small grains rotation
Charity (uncultivated)	c	" " "	Grass-shrub fallow
Kalamazoo	sc1	Typic Hapludalf, fine-loamy, mixed, mesic	Small grains
Kalamazoo (manured)	1	" " "	Grass fallow
Spinks	s1	Psammentic Hapludalf, sandy, mixed, mesic	Small grains
Spinks (uncultivated)	s1	" " "	Woody vegetation
Capac	1	Aeric Ochraqualf, fine-loamy, mixed, mesic	Small grains
Montcalm	s1	Eutric Glossoboralf, sandy, mixed, frigid	Potato
Oshtemo	1	Typic Hapludalf, coarse-loamy, mixed, mesic	Small grains
Hillsdale	s1	Typic Hapludalf, coarse-loamy, mixed, mesic	Small grains

Table 4. Chemical and physical descriptions of some Michigan soils used in a greenhouse study of residual P.

Soil	pH		Particle Size			CEC	Total-N	O.M.	Total-P	Moisture ⁺ Capacity
	H ₂ O	CaCl ₂	S	Si	C					
			-----mg/kg-----			cmol(+)/kg soil	-----mg/kg-----			g/kg
Charity	7.8	7.2	80	330	590	26.1	1.7	19	927	290
Charity (uncultivated)	7.6	7.1	90	340	570	35.3	2.7	35	804	300
Kalamazoo	6.6	6.0	510	280	210	9.4	1.0	17	585	180
Kalamazoo (manured)	6.3	5.8	380	410	210	18.3	2.4	24	631	260
Spinks	5.6	4.8	490	360	150	7.9	0.9	13	608	160
Spinks (uncultivated)	6.7	6.4	690	210	100	11.3	1.2	25	401	90
Capac	6.6	4.8	480	370	150	7.1	0.9	16	619	280
Montcalm	6.5	5.7	630	240	130	6.6	0.8	12	631	140
Oshtemo	6.8	6.2	430	380	190	9.7	1.4	17	691	200
Hillsdale	6.6	6.2	790	100	110	3.8	0.6	9	381	70

⁺f.m.c. at 0.03 MPa.

as KCl and K_2SO_4 were supplied at different rates during cropping (Appendix Table 17). Lime applications at 2 g/culture were made before cropping the Spinks soil and at the end of the third cropping for all soils except the Charity soil.

A sequence of 3 sudax (Sorghum sudanese), 1 sorghum (Sorghum bicolor), 2 oats (Avena sativa var Korwood), 3 sudax, and 1 oats was followed. Each cropping period was for 35 days. Plant tops and roots were harvested separately by cutting the plant tops just above the soil, and then passing the soil through a 4 mm sieve to separate the roots. The roots were thoroughly washed with distilled water. All plant matter was dried for 48 hours at 60 °C, weighed and ground to pass through a 0.60 mm sieve using a Wiley mill.

Following the removal of plant roots the soil in each pot was re-mixed and air-dried for approximately 2 days before the subsequent crop. Soil samples were removed when crops 1, 3, 9, and 10 were harvested.

Following is a description of pertinent analyses.

Plant Analyses: Of the dry and ground plant tissue, 250 mg was digested in 5 mL of a $H_2SO_4:H_2O_2$ mix (Parkinson and Allen, 1975). The P concentration was then determined by the ascorbic acid method of Murphy and Riley (1962) and measured on a Bausch and Lomb Spectronic 20 at 880 um.

Bray and Kurtz-P: Two grams of soil samples were shaken at ratios of 1:7, 1:8 and 1:20 (soil:extractant) in Bray and Kurtz-P1 (0.025 N HCl + 0.03 N NH_4F) solution and a ratio of 1:8 in Bray and Kurtz-P2 (0.10 N HCl + 0.03 N NH_4F) solution, for 5 minutes at 220 rpm on an oscillating shaker. The suspensions were then filtered and P determined as above.

Resin Exchangeable P: One gram of soil (<2u) in contact with 2 g of resin (Dowex 2-X4, basic anion) was shaken in 100 mL of water for 24 hrs. The soil and resin were then separated by washing the soil through a 0.3mm sieve with distilled water. The resin was washed in hot 10% NaCl solution (Amer et al.,1954) The volume was diluted to 100 mL with the NaCl solution and P determined as above.

Water Soluble P: Five grams of soil was shaken in 50mL of 0.01 M CaCl_2 solution for 1 hour. The samples were filtered and P determined as above.

Total Soil P: Two hundred milligrams of soil was digested in 3 mL of HClO_4 on an aluminum digest block according to Sommers and Nelson (1972). Following digestion at 203 °C for 90 minutes, samples were cooled, diluted and P was determined as above.

Statistical Analyses

Analyses of data was performed using the Michigan State University MSTAT computer programs. Interpretations were essentially by the methods described by Snedecor and Cochran (1967) and Steele and Torrie (1980).

RESULTS AND DISCUSSION

A greenhouse investigation was conducted to study plant use of residual soil P on a range of soils. Samples were collected from ten sites in South-Central Michigan. Seven of these soils had received annual inorganic P fertilization in the field for an undetermined length of time, but no less than 10 years. One of the soils had once been the site for a dairy operation and the remaining two were unfertilized soils. The soils were characterized in the laboratory by methods that have been used to estimate the intensity, quantity and capacity factors of soil P. These values were then compared for their importance in accounting quantitatively for available soil P as measured by plant uptake.

Crop Yield and Phosphorus Uptake

Dry matter yield and P uptake were used to evaluate the availability of residual soil P. It is recognized that there would be differences in dry matter production between soils, due to inherent differences between soils. However, comparison of P removal, soil tests and physical/chemical characteristics of the soils was envisioned as a means to evaluate the availability of P in a group of heterogeneous soils.

There were significant differences in crop yields throughout cropping (Table 5). The cumulative yield figures suggest that only during the first cropping was there a probable effect of residual P on dry matter accumulation. At this time yields were higher on previously fertilized soils when compared to the uncultivated soils. As cropping progressed, the uncultivated Charity and manured Kalamazoo were as good

Table 5. Summary of cumulative whole plant dry matter yield and phosphorus uptake of 10 consecutive crops grown in the greenhouse on 10 soils with various residual P levels.

Soil	1 Crop ⁺		3 Crops		9 Crops		10 Crops	
	Yield	Uptake	Yield	Uptake	Yield	Uptake	Yield	Uptake
	g/culture	mg/culture	g/culture	mg/culture	g/culture	mg/culture	g/culture	mg/culture
Charity (high P)	27.2	35.5	31.7	65.2	60.7	135.8	66.2	154.0
Charity (uncultivated)	15.5	14.1	31.8	33.3	65.2	93.5	71.5	110.3
Kalamazoo (high P)	36.5	41.9	58.3	87.0	89.5	160.7	94.2	182.4
Kalamazoo (uncultivated)	34.3	31.5	62.9	82.6	92.0	117.3	97.2	124.7
Spinks (high P)	30.9	32.7	55.0	71.1	85.3	130.2	89.4	150.5
Spinks (uncultivated)	10.4	7.5	17.2	14.3	40.6	44.9	44.3	51.7
Capac	30.0	40.7	46.3	84.5	83.7	176.6	88.0	194.3
Montcalm	26.3	35.0	33.8	51.2	58.4	103.1	61.3	117.0
Oshtemo	36.0	53.1	53.9	108.5	90.7	203.4	94.3	224.2
Hillsdale	11.0	8.7	19.2	16.3	40.4	48.5	43.8	57.5
LSD (5%)	4.6	3.8	9.0	15.0	9.5	17.3	9.0	18.5

⁺Each crop was grown for 5 weeks before harvesting tops and roots.

as their fertilized counterparts, while the fertilized Spinks soil remained superior. The former were under grass/shrub fallow, therefore nutrient cycling may have been active enough to maintain adequate nutrient supply. On the other hand, the uncultivated Spinks soil was under wood vegetation. The Capac and Oshtemo soils performed relatively well as the soil tests would suggest. Dry matter yields on the Montcalm and Hillsdale soils were poorer than expected. The current observation would suggest that residual P did not play an important role in influencing the accumulation of dry matter on these soils over the cropping period. To further support this is the weak correlation between soil tests and dry matter yields across the soils ($r=0.23$). Nevertheless, it is possible that the influence of residual P was concealed.

When soils with significantly varying soil P levels do not show significant difference in dry matter yields, a number of factors could be responsible. Among these are: (1) sufficiency of P at the critical levels in soil solution, (2) plant top and root partitioning as a response to nutrient limitations, (3) soil physical characteristics, and (4) plant and or soil nutrient imbalances. Thus it was decided to examine how these factors may have influenced the observations in this study.

The soil buffering capacity is an inherent characteristic of the soil solution P supply. Therefore on various soils, the limiting soil solution P concentration will vary. Weakly buffered soils usually maintain higher solution P concentration while stronger buffered soils maintain lower concentrations (Holford, 1976). Rajan (1973) observed that millet grown on well buffered Hawaiian soils had solution P

requirements ranging from $0.06 - 1.94 \times 10^{-5}$ M. Fox and Kamprath (1970) and Ozanne and Shaw (1967) established that near maximum yields or a lack of response to further P applications could be expected when the soil solution P is maintained at $6.45 - 9.68 \times 10^{-6}$ M. Table 6 shows the soil solution P values observed at intervals over the cropping period. Even though critical levels were not determined for the soils used, when compared to values in the literature only the Hillsdale, uncultivated Kalamazoo and Montcalm soils exhibited critical concentrations at any point during the study. Judging from their production of dry matter, this was not a permanent situation. The low P concentrations in the uncultivated Charity and Spinks, manured Kalamazoo, and Hillsdale soils coincided with deficiency symptoms at the termination of the study. The fertilized Charity and Capac soils also had low P concentrations, but their P capacities and soil buffering capacities would be expected to sustain production on these soils. For this reason, it is presumed that the influence of solution P is not now conclusive.

Some studies that have been conducted with P as with other nutrients have revealed that limitations of soil nutrient content can introduce variations in the ratio of dry matter partitioning between plant tops and roots. Asher and Loneragan (1967) observed that when plant tops respond to P, the total weight of roots may be reduced. Furthermore, Williams (1948) showed that photosynthate translocated down is trapped and used for root growth when P is limiting. Ozanne (1980) suggested that having large root growth may be an evolutionary advantage for survival and growth under limiting conditions. Large root growth may subsequently influence foraging ability and water use. The total shoot and root weights are given in Table 7. It would appear that the lower P

Table 6. Soil solution P levels for 10 soils with various levels of residual P, during a continuous cropping in the greenhouse.

Soil	Period of Sampling ⁺				
	Original Soil	Crop 1	Crop 3	Crop 9	Crop 10
-----[P]M X10 ⁻⁵ -----					
Charity (high P)	1.50	0.20	0.90	0.30	0.23
Charity (uncultivated)	0.20	0.20	0.10	0.50	0.20
Kalamazoo (high P)	3.25	5.56	5.00	3.43	3.10
Kalamazoo (uncultivated)	0.70	0.01	0.01	0.73	0.30
Spinks (high P)	5.00	2.58	0.88	3.35	1.55
Spinks (uncultivated)	1.50	0.96	1.10	2.53	0.97
Capac	6.10	4.35	4.90	1.38	0.20
Montcalm	3.90	1.64	0.01	2.03	2.13
Oshtemo	12.2	7.75	7.23	4.18	3.53
Hillsdale	0.30	0.01	0.01	1.45	0.80

⁺Soil sample following plant harvest.

Table 7. Distribution of total dry matter yield of 10 consecutive greenhouse crops between plant tops and roots.

Soil	Dry Matter Yield		<u>Root Top</u>
	Top	Root	
	-----g/culture-----		
Charity (high P)	52.6	14.6	0.28
Charity (uncultivated)	52.2	19.3	0.37
Kalamazoo (high P)	64.8	29.5	0.45
Kalamazoo (uncultivated)	61.6	35.6	0.58
Spinks (high P)	61.5	27.9	0.45
Spinks (uncultivated)	26.8	17.5	0.65
Capac	62.0	26.0	0.42
Montcalm	43.2	18.2	0.42
Oshtemo	68.5	26.0	0.38
Hillsdale	29.5	14.3	0.48
LSD (5%)	5.3	6.7	

soils have a relatively larger root weight, especially the uncultivated Charity and manured Kalamazoo compared to their fertilized counterparts. There is a possible subtle effect of residual P here. As this observation is still inconclusive, further considerations were made.

Ozanne (1980) suggested that an absence of yield differences could be imparted by the amount of available water in soils. The soils in this study were of different soil moisture capacity and thus maintained through cropping. Care was taken not to introduce any physical imbalances such as compaction, flooding or moisture stress. Table 5 indicates that P uptake was more on the fertilized soils but yields were not always that. Comparison of the soil water holding capacities (Table 4) shows that except for the uncultivated Spinks soil other soils testing lower in P have relatively higher water contents at field moisture capacity. Perhaps this amount of available water influenced the production of comparable dry matter on the lower P soils. It then seems plausible that the soil solution P in the lower P soils may have been low enough to trigger a relatively larger root growth on these soils, which in turn improved water use efficiency. This resulted in the production of similar dry matter yields on the low P soils.

Lastly, visual observations made during cropping suggest that no detectable nutrient imbalances occurred. Cropping was terminated when the uncultivated Charity, manured Kalamazoo, uncultivated Spinks and Hillsdale soils showed P deficiency symptoms. The fertilized soils did not demonstrate P deficiency at this point. Therefore, it is concluded that residual P is beneficial, but such benefits will be observed over a period of time. The length of cropping or production should then be an important factor in estimating the availability of residual soil P.

Phosphorus uptake was higher on the fertilized soils than on the uncultivated soils, except for the Montcalm and Hillsdale soils (Table 5). Since dry matter accumulation on the uncultivated soils was equal to that on some fertilized soils the P concentration was higher on fertilized soils (Table 8). The decrease in uptake vs yield correlation as cropping progressed ($r = 0.92, 0.88, 0.83, 0.81$, respectively) indicates that other soil factors played seemingly increasing roles in dry matter yields as cropping progressed. The direct influence of residual P can be observed in P uptake on the soils. The magnitude of this uptake did not correspond to the order of magnitude of soil test levels, indicating that soil characteristics will influence the rate of removal of P. The Montcalm soil was notably intermediate in performance considering the high soil test level.

Soil Test Values

The Bray P1 extraction method is commonly used in Michigan. However, with the increasing levels of soil P fertility and fertilization, it was of interest to compare the P detected by this method to the plant P use. Christenson and Vitosh (1984) have reported an absence of crop response to further P fertilization. This observation would suggest that only a disproportionately small amount of the soil P was extracted. Thus it was decided to compare a wider soil:solution ratio of 1:20 to a 1:8 ratio. Also increasing the acid strength of the extractant (Bray and Kurtz-P2) but retaining the current ratio was compared. The Olsen method commonly used on calcareous soils, resin extraction and soil solution P were included in this comparison.

Phosphorus soil test values are shown in Table 9. The soils differed significantly in the levels of available soil P as estimated by

Table 8. Phosphorus concentration of plant tops for crops grown in the greenhouse on 10 soils with various levels of residual P.

Soil	Period of Sampling				
	Crop 1	Crop 3	Crop 6	Crop 9	Crop 10
	-----%				
Charity (high P)	0.16	0.23	0.21	0.23	0.39
Charity (uncultivated)	0.12	0.10	0.18	0.24	0.30
Kalamazoo (high P)	0.13	0.21	0.25	0.20	0.63
Kalamazoo (uncultivated)	0.11	0.13	0.15	0.10	0.16
Spinks (high P)	0.11	0.16	0.22	0.20	0.69
Spinks (uncultivated)	0.07	0.11	0.16	0.12	0.25
Capac	0.16	0.27	0.28	0.29	0.54
Montcalm	0.14	0.28	0.24	0.19	0.66
Oshtemo	0.17	0.30	0.31	0.29	0.74
Hillsdale	0.07	0.13	0.16	0.12	0.38
LSD (5%)	0.01	0.01	0.01	0.08	0.15

Table 9. Phosphorus soil test values for 10 soils used in a greenhouse continuous cropping study of residual soil P.

Soil	Soil Test											
	Bray-P1						Bray P-2	NaHCO ₃ -P		AER-P ⁺		
	1:7		1:8		1:20			Initial	Final	Initial	Final	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final		
	-----mg/kg-----											
Charity (high P)	43.4	17.7	49.6	21.7	86.0	47.9	171	114	28.0	11.3	60.8	30.5
Charity (uncultivated)	8.2	6.3	10.2	9.8	23.4	25.6	98.3	84.2	10.4	9.9	24.1	19.1
Kalamazoo (high P)	136	83.5	133	89.1	178	130	172	126	46.9	37.9	102	82.2
Kalamazoo (uncultivated)	51.9	45.9	56.2	46.1	86.0	80.6	88.2	71.9	18.8	16.9	44.8	36.5
Spinks (high P)	132	85.6	129	89.9	170	131	172	128	48.9	23.4	57.5	47.2
Spinks (uncultivated)	45.2	46.7	48.0	45.8	61.7	67.4	75.8	81.6	15.1	14.2	38.7	27.7
Capac	134	56.0	131	60.5	170	99.5	167	121	51.0	24.9	60.8	51.1
Montcalm	239	179	227	220	322	280	307	263	50.3	52.2	97.9	104
Oshtemo	160	96.0	157	99.7	206	136	205	142	51.8	38.2	113	78.7
Hillsdale	75.9	66.4	77.2	68.2	110	106	95.7	92.8	18.0	17.8	32.7	53.5

⁺Anion exchange resin extractable P.

each method. As expected, the uncultivated soils tested lower in inorganic-P than their fertilized counterparts.

Bray P₁ extractions at 1:7 and 1:8 were similar for each soil. Increasing the ratio to 1:20 resulted in more P being extracted. In turn the Bray P₁ (1:20) and Bray and Kurtz-P₂ (1:8) extracted similar amounts of P, except on the high clay and carbonate content Charity soils, where more P was extracted by the latter method. The principle of the Bray test is based on the ability of the F⁻ to reduce Al³⁺ activity by competing with it thus releasing P in Al-P. The H⁺ then solubilizes Ca-P - but not apatite-P (Thomas and Peaslee, 1980). Therefore in cases of clay soils with high base saturation, or calcareous soils, the possibility exists for the H⁺ to be neutralized before it can effectively solubilize Ca-P (Pratt and Garber, 1964; The Council on Soil Testing and Plant Analysis, 1980). This is perhaps the reason for the observed increases in extractable P with wider soil:solution ratio and stronger acid concentration on the Charity soil. The similar P extracted from the acid to neutral soils by the Bray and Kurtz-P₁ (1:20) and Bray and Kurtz-P₂ despite the stronger acid in the latter underscores the predominance of Al-P in these soils. The Bray and Kurtz method effectively detected that the uncultivated Charity soil was a low P soil with the potential for crop response to further P application. Thus this method provides a good degree of confidence as a soil test method on this group of soils.

Olsen-P values were lower than all Bray values. The principle behind this method involves increasing the solubility of Ca-P as a result of precipitation of Ca²⁺ as CaCO₃. Thomas and Peaslee (1980) suggest that while HCO₃⁻ and F⁻ appear to largely remove the same P

compounds, F^- will react more vigorously and remove P unavailable to HCO_3^- ions. The ranking of the soils by magnitude of P extracted is rather similar between the Olsen and Bray methods. However this method was less effective in detecting which soils would respond to P application. This method would not be a suitable soil test on this group of soils.

It has been suggested that resin extraction simulates plant root action and may thus be a better indicator of available soil P. This approach does not include the use of strong chemicals, which reduces the incidence of extracting unavailable P compounds. In this case comparison of magnitude is higher only than the Olsen P and variable with the Bray P1 (1:7, 1:8).

Soil solution P, an intensity factor, was determined by extraction with 0.01M $CaCl_2$ -P (Table 6). As expected the values here are much lower than for the other tests. Capacity factors could be as much as 10^{-2} to 10^{-3} times more than intensity factors (Mengel and Kirby, 1982).

The relationships among and between soil tests are given in Table 10. Linear correlation coefficients are moderate to good, but significant. This suggests that the extractants removed P mainly from the same compounds on each soil, even though in different magnitudes. Furthermore the differences between soil tests before and after cropping were well correlated (Table 11), and P removal by plants from similar compounds may account for this relationship.

The effect of cropping the soils was a general reduction in soil test levels (Figures 2-5). The uncultivated soils and the manured Kalamazoo soil however have slopes approaching zero. On these soils cropping did not account for decreases in inorganic P test levels. In

Table 10. Linear correlation (r) coefficients for the relationship between dry matter yield and P uptake of 10 consecutive crops grown in the greenhouse, and the initial P soil test levels of 10 soils with various residual P levels.

	Uptake 1	Total Uptake	Total Yield	Bray P1			Bray P2	NaHCO ₃ -P	AER-P ⁺	CaCl ₂ -P
				1:7	1:8	1:20				
Bray P1 - 1:7	0.60**	0.42**	0.23 ^{ns}							
- 1:8	0.61**	0.43**	0.23 ^{ns}	1.00**						
- 1:20	0.60**	0.40*	0.20 ^{ns}	0.99**	0.99**					
Bray P2	0.65**	0.47**	0.18 ^{ns}	0.89**	0.86**	0.92**				
NaHCO ₃ -P	0.82**	0.74**	0.50**	0.88**	0.88**	0.85**	0.80**			
AER-P	0.83**	0.68**	0.43**	0.80**	0.81**	0.80**	0.79**	0.83**		
CaCl ₂ -P	0.75**	0.75**	0.48**	0.54**	0.56**	0.52**	0.56**	0.75**	0.74**	

⁺Anion exchange resin P.

**Significant at $\alpha = 0.01$.

*Significant at $\alpha = 0.05$.

^{ns}Not significant at $\alpha = 0.05$.

Table 11. Linear correlation (r) coefficients for the relationship between total dry matter yield and P uptake of 10 consecutive crops grown in the greenhouse, and the differences between initial and final P soil test levels of 10 soils with various residual soil P levels.

	Uptake	Yield	Bray P1			Bray P2	NaHCO ₃ -P	AER-P
			1:7	1:8	1:20			
Bray P1 - 1:7	0.77**	0.49**	1.00					
- 1:8	0.86**	0.63**	0.82**	1.00				
- 1:20	0.87**	0.55**	0.96**	0.88**	1.00			
Bray P2	0.87**	0.57**	0.80**	0.73**	0.89**	1.00		
NaHCO ₃ -P	0.67**	0.49**	0.61**	0.82**	0.70**	0.63**	1.00	
AER-P	0.68**	0.50**	0.29 ^{ns}	0.52**	0.47**	0.61**	0.47**	1.00

**Significant at $\alpha = 0.01$.

^{ns} Not significant at $\alpha = 0.01$.

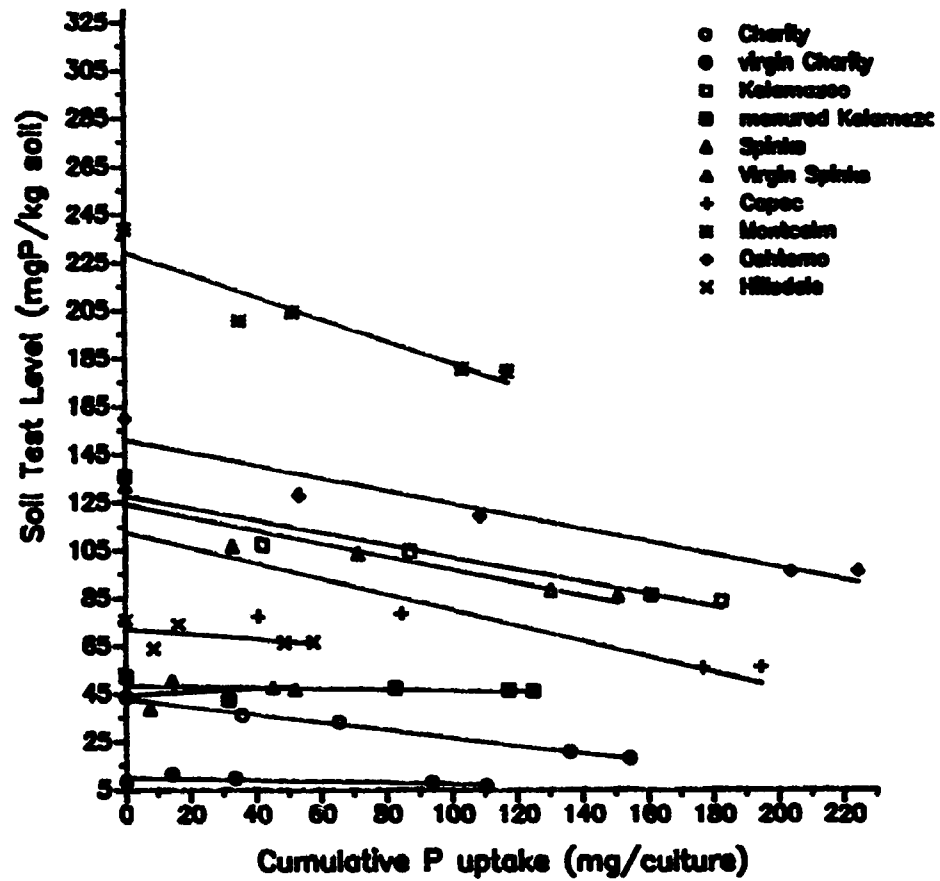


Figure 2. Relationship between Bray and Kurtz P1 (1:7) extractable P and P removal by 10 crops in the greenhouse.

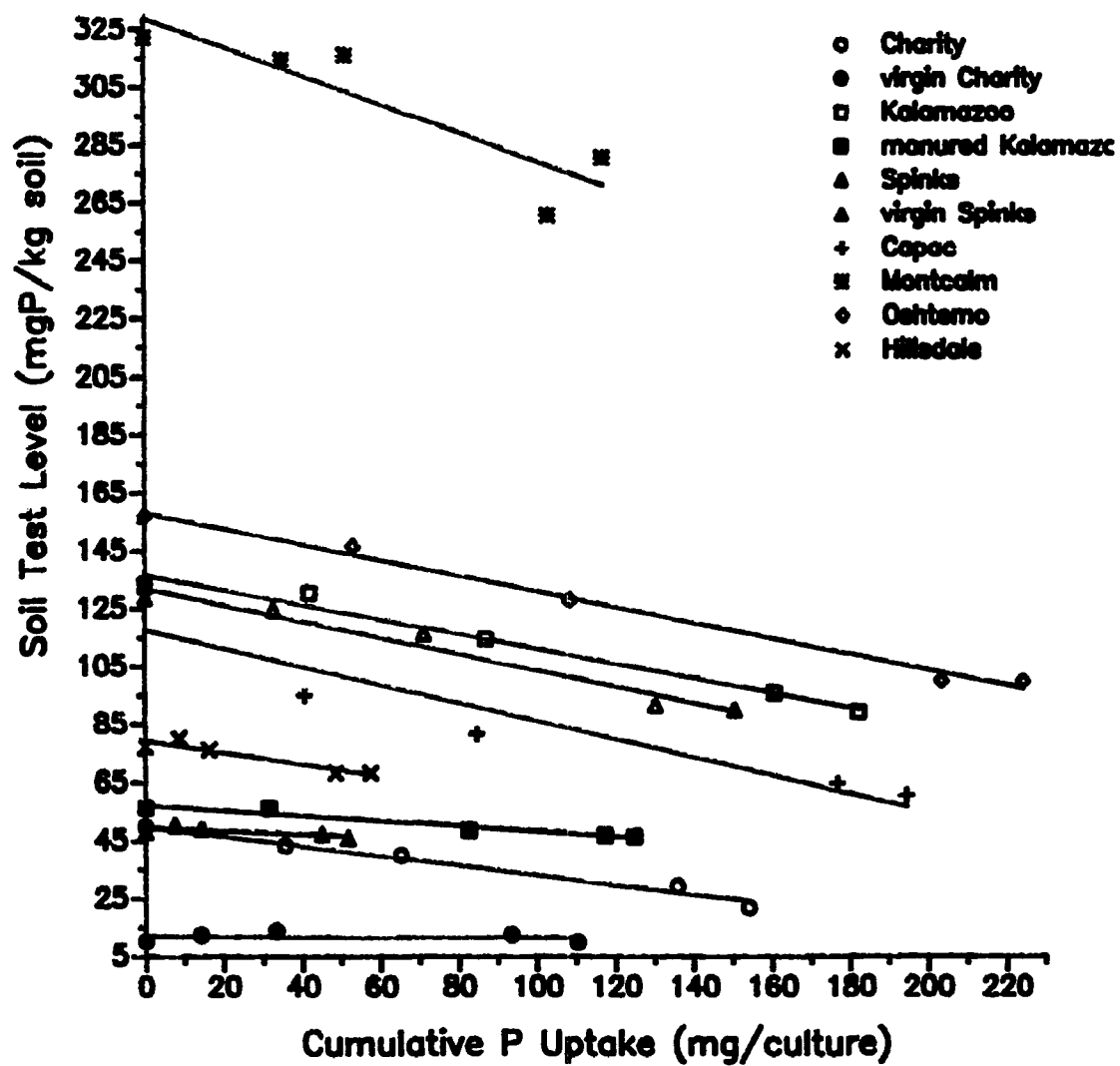


Figure 3. Relationship between Bray and Kurtz P1 (1:8) extractable P and P removal by 10 crops in the greenhouse.

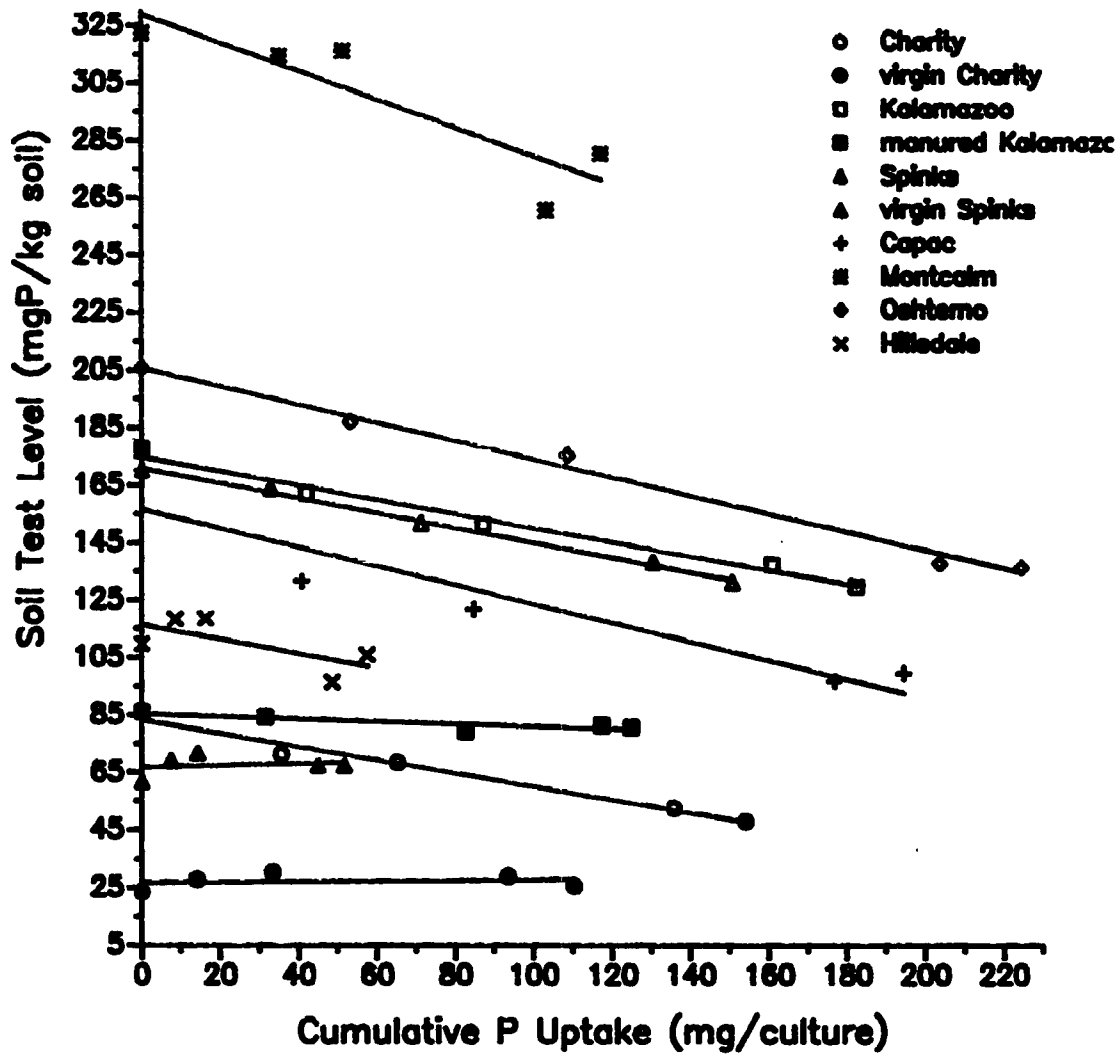


Figure 4. Relationship between Bray and Kurtz P1 (1:20) extractable P and P removal by 10 crops in the greenhouse.

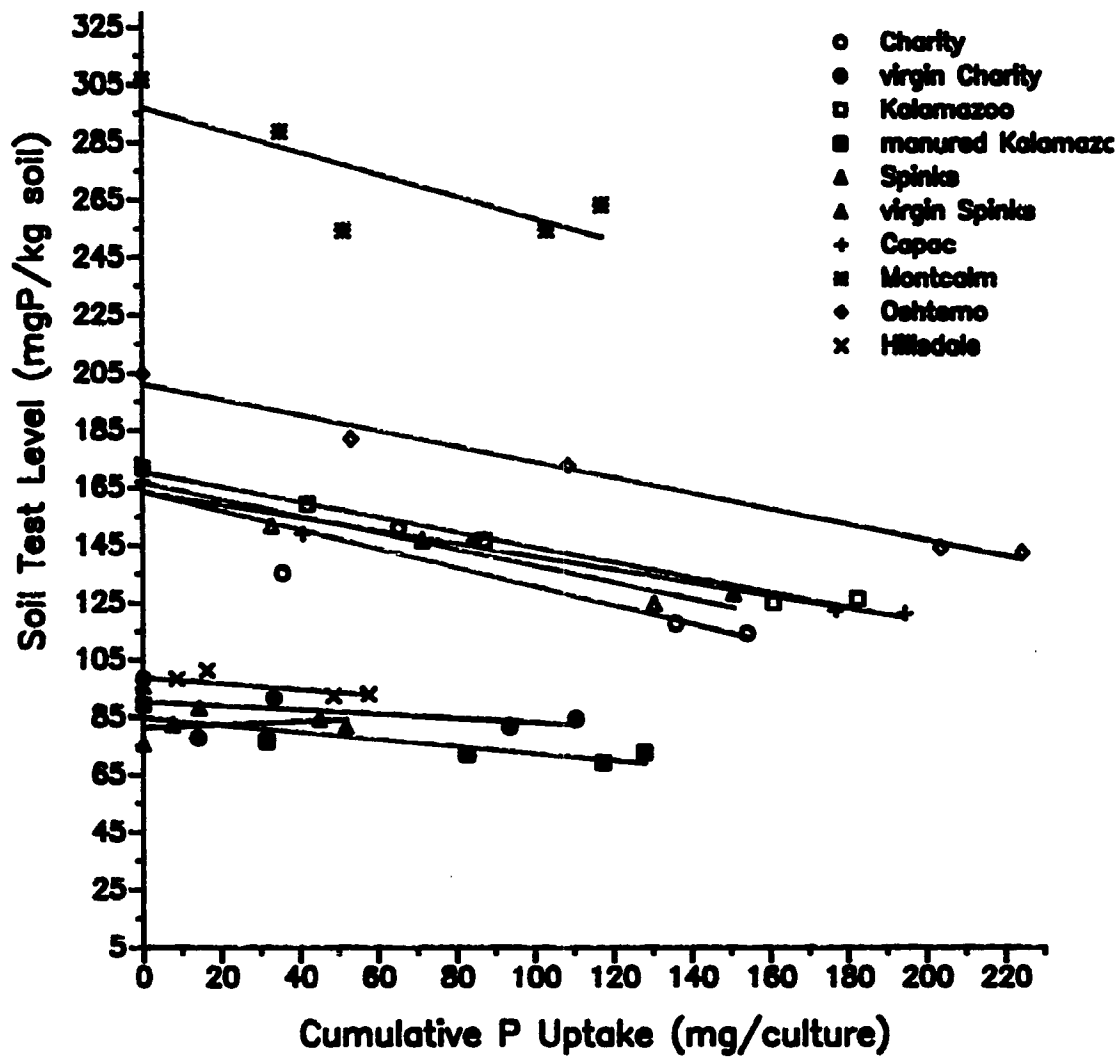


Figure 5. Relationship between Bray and Kurtz P2 (1:8) extractable P and P removal by 10 ten crops in the greenhouse.

fact, test levels during cropping were sometimes higher than at the beginning of cropping (Table 15). There is a strong suggestion that soluble P from organic-P was being released into the inorganic-P fraction of the soil P.

Relationship Between Soil Tests and Plant Response

There was a weak correlation between initial soil tests and plant performance over all soils (Table 10). In many cases dry matter yields rather than nutrient uptake is the measure of returns on investment. However, because of the singular interest in P removal from the soil and the appreciable correlation between yield and uptake, it was decided to use P uptake as the index for plant use of residual soil P.

The linear correlation between soil tests and P uptake over all soils was weak to moderate ($r = 0.40$ to 0.74). In this case the Bray and Kurtz method was least effective ($r = 0.40$) in establishing a linear pattern among this group of soils. A broad range of correlations have been reported in the literature (Dalal and Hallsworth, 1976). Increasing the soil:solution ratio did not seem to improve the correlation, but increasing the acid strength introduced slight improvement. The increased sensitivity to Ca-P on the Charity soils by the latter approach contributed to the improvement in correlation. On the basis of correlation with plant P uptake the Bray and Kurtz method has been shown to be inferior to some other methods on heterogeneous soils (Holford, 1980). Therefore it was of interest to test this hypothesis. The soils were thus grouped into more similar units of comparison. When the soils were arbitrarily separated by clay content ($<20\%$), the correlations were improved for each group, but significantly for the higher clay soils (Table 12). The Bray method has been found to overcompensate for

Table 12. Linear correlation (r) coefficients for the relationship between P uptake of 10 consecutive crops grown in the greenhouse, and the initial P soil tests of 10 soils with various residual P levels, when the soils were stratified.

	% Clay		Bray P1 (1:8) mg/kg		Soil	
	>20	<20	>100	<100	Set 1 ⁺	Set 2 [‡]
Bray P1 - 1:7	0.83**	0.50*	0.57**	0.37 ^{ns}	0.86**	0.23 ^{ns}
- 1:8	0.84**	0.51*	0.56**	0.30 ^{ns}	0.87**	0.24 ^{ns}
- 1:20	0.86**	0.44*	0.60**	0.08 ^{ns}	0.88**	0.24 ^{ns}
Bray P2	0.83**	0.47*	0.59**	0.72**	0.82**	0.40 ^{ns}
NaHCO ₃ -P	0.92**	0.86**	0.27 ^{ns}	0.53	0.59*	0.63*
AER-P	0.91**	0.70**	0.22 ^{ns}	0.58**	0.83**	0.41 ^{ns}
CaCl ₂ -P	0.91**	0.91**	0.69**	0.16 ^{ns}	0.73**	0.67*
n	20	20	20	20	12	28

**Significant at $\alpha = 0.01$.

*Significant at $\alpha = 0.05$.

^{ns} Not significant at $\alpha = 0.05$.

ⁿ Number of soils in stratum

⁺ Set 1 = Kalamazoo, Spinks and Oshtemo soils.

[‡] Set 2 = All other soils.

buffering (Holford, 1980). This results in an under estimation of available P on well buffered soils and an over estimation on weakly buffered soils. It is suspected that this is the reason that correlation with the more buffered soils is improved. Also stratification by soil test level (<Bray P1, 100 mg P/kg >) slightly improved correlations. It appears that by removing the Charity soil with carbonate which interfered with P extraction and the uncultivated soils with organic-P contributions, there was better correlation with P uptake. Extracted P from the Charity soils continued to increase with soil:solution ratio as well as acid strength, indicating that available P is indeed more than detected as suggested by uptake values (Table 15). On the other hand, uptake data suggests that unavailable P may have been extracted on the Montcalm and Hillsdale soils. These two facts may contribute to explaining the poor uptake correlations with the Bray method.

The correlation of P uptake with the Olsen method was moderate ($r=0.74$) and better than for the Bray method. Similar observations of superiority have been reported in the literature (Sims and Ellis, 1983; Holford, 1980). This method is more sensitive to buffering and this is reflected in the better correlation (Table 10) with the $\text{CaCl}_2\text{-P}$, an intensity factor. Separation of soils by clay content improved the correlation in this case as well, but less markedly than for the Bray method. Holford (1980) showed that the Olsen test exhibits a similar sensitivity to buffering as do plants, thus its superiority over a range of soils.

Resin extraction was moderately correlated ($r= 0.68$) with plant P uptake (Table 10). A good degree of confidence has been expressed in this method for its effectiveness in extracting plant available P

(Bowman et al, 1978). In this study, comparatively, it performs well. This method also showed a slight response to stratification by buffering (clay content) (Table 12). The good correlation with intensity further supports the sensitivity to soil buffering. Also, this method proved as effective as the Olsen method on heterogeneous soils.

The $\text{CaCl}_2\text{-P}$ had a moderate but significant correlation with uptake ($r=0.75$). Separation of soils by clay contents increased the correlation, but without difference between groups. Also the length of cropping made no difference (Table 11). Williams and Knight (1963) and Holford (1980) have suggested that the intensity factor may be a more important factor in evaluating P uptake on a set of heterogeneous soils, but Dalal and Hallsworth (1976) expressed some reservations about this generalization. They propose that soil heterogeneity can offset the correlation. Olsen et al. (1983) observed the quantity parameter to be better correlated with plant P uptake than the intensity factor. In this study, the intensity factor gave better correlation values with P uptake on a group of heterogeneous soils.

Accumulation of P was plotted against changes in Bray soil test values (Figures 2-5). As P accumulation increased soil test values decreased. Table 13 shows that the variations in soil test changes were well correlated with plant P uptake. The uncultivated soils did not do as well. They show weaker and more variable correlations. It is suspected that uptake from organic P which was not detected by the test methods here may have contributed to the lower and more variable correlations on these soils. The Montcalm and Hillsdale soils also show variability in correlations between test methods (Table 13). It was suggested that the Bray and Kurtz method sometimes over estimates

Table 13. Linear correlation (r) coefficients for the relationship between P accumulation by 10 consecutive crops grown in the greenhouse and changes in soil test levels during cropping of 10 soils with various residual P levels.

Soil	Bray P1			Bray P2
	1:7	1:8	1:20	
Charity (high P)	-1.00**	-0.99**	-0.99**	-0.90*
Charity (uncultivated)	-0.73 ^{ns}	-0.19 ^{ns}	-0.17 ^{ns}	-0.44 ^{ns}
Kalamazoo (high P)	-0.95*	-0.99**	-0.99**	-0.99**
Kalamazoo (uncultivated)	-0.34 ^{ns}	-0.97**	-0.85 ^{ns}	-0.87 ^{ns}
Spinks (high P)	-0.95*	-0.98**	-1.00**	-0.96**
Spinks (uncultivated)	-0.36 ^{ns}	-0.79 ^{ns}	-0.20 ^{ns}	-0.29 ^{ns}
Capac	-0.86 ^{ns}	-0.93*	-0.94*	-0.98**
Montcalm	-0.92*	-0.54 ^{ns}	-0.89*	-0.80 ^{ns}
Oshtemo	-0.96**	-1.00**	-1.00**	-0.99**
Hillsdale	-0.52 ^{ns}	-0.94*	-0.69 ^{ns}	-0.70 ^{ns}

**Significant at $\alpha = 0.01$.

*Significant at $\alpha = 0.05$.

^{ns} Not significant at $\alpha = 0.05$.

available P on weakly buffered soils. It is likely that unavailable P was detected on these soils contributing to the low correlation.

Similarities in P release mechanism on these soils can be predicted by similarities of the slopes of regression (Table 14). The Charity soils show variable slopes over the test methods. This fluctuation may be the result of carbonate interference with extraction which was discussed above. Also the uncultivated soils varied over test methods but were similar among soils, suggesting a possible similarity in P uptake on these soils. The possible influence of organic P as a source of P for plant use has been suggested. The Kalamazoo, Spinks, Capac and Oshtemo soils each showed similarities in slopes between the test methods. Furthermore the Kalamazoo, Spinks and Oshtemo soils exhibited more similar slopes among soils, which suggests that these soils are more similar in P release mechanism. The validity of this suggestion was tested by comparing the correlation between uptake and soil tests on these three soils against the other soils. Table 12 shows that the Bray and Kurtz-P correlation with uptake was better on these three soils compared to all soils. The correlation decreased for the Olsen method which is better suited to alkaline soils.

In order to further compare plant use of residual P in the soils with soil test results, it was worthwhile to compare the differences between initial and final soil test values and P uptake (Table 15). The change in available P values is variable from soil to soil. This was expected given the different soil buffering capacities and characteristics, and plant performance. Higher testing soils appear to have larger changes in available P values, and this coincides with more P removal from these soils. The uncultivated soils showed little change

Table 14. Slope (b) values for the linear regression relationship between accumulation of P (x) by 10 consecutive crops grown in the greenhouse and changes in P soil test levels (y) during cropping of 10 soils with various levels of residual P.

Soil	Bray P1			Bray P2
	1:7	1:8	1:20	
Charity (high P)	-0.48**	-0.51**	-0.69**	-0.99**
Charity (uncultivated)	-0.09 ^{ns}	-0.03 ^{ns}	-0.03 ^{ns}	-0.21 ^{ns}
Kalamazoo (high P)	-0.78**	-0.75**	-0.75**	-0.78**
Kalamazoo (uncultivated)	-0.06 ^{ns}	-0.27 ^{ns}	-0.16 ^{ns}	-0.39*
Spinks (high P)	-0.81**	-0.84**	-0.78**	-0.87**
Spinks (uncultivated)	0.21 ^{ns}	-0.18 ^{ns}	0.09 ^{ns}	-0.18 ^{ns}
Capac	-0.99*	-0.93**	-0.99**	-0.69**
Montcalm	-1.41**	-0.39 ^{ns}	-1.47**	-1.17 ^{ns}
Oshtemo	-0.81**	-0.81**	-0.96**	-0.81**
Hillsdale	-0.33 ^{ns}	-0.60**	-0.75**	-0.30 ^{ns}

**Significant at $\alpha = 0.01$.

*Significant at $\alpha = 0.05$.

^{ns} Not significant at $\alpha = 0.05$.

in soil test values despite plant P uptake and this strengthens the speculation of organic P contributions to available P in these soils. No explanation can be offered for the increase in test values detected by the Olsen and resin methods on the Montcalm and Hillsdale soils.

The Charity, Kalamazoo, Spinks, Oshtemo and Hillsdale soils supplied more P for plant uptake than the changes in soil test values indicate (Table 15). There was slightly less uptake from the Capac soil than as suggested by the Bray P1 method, but more than by the other methods. The Montcalm soil consistently showed less effectiveness than as suggested by soil test differences.

Delta indice values (initial - final soil test values) were only moderately but significantly correlated with uptake (Table 11). The correlation coefficients ranged from $r = 0.67$ to 0.87 . The good correlation between soil test methods suggest that similar pools of P compounds were detected, and plant P uptake was largely from similar sources.

Table 15. Changes in the P content of 10 soils with various residual P levels, following P removal by 10 consecutive crops grown in the greenhouse.

Soil	Uptake	Bray P1			Bray P2	NaHCO ₃ -P	AER-P
		1:7	1:8	1:20			
		-----mg/culture-----					
Charity (high P)	154	77.1	83.7	114.4	173.4	49.8	90.9
Charity (uncultivated)	110	5.64	1.0	-6.7	42.3	1.4	14.8
Kalamazoo (high P)	182	156.9	132.6	144.0	136.8	27.0	58.4
Kalamazoo (uncultivated)	125	18.1	30.3	16.1	49.8	5.6	25.1
Spinks (high P)	151	138.3	114.9	117.6	131.1	76.5	30.9
Spinks (uncultivated)	52	-4.35	6.7	-17.0	-17.3	2.6	33.3
Capac	194	233.7	210.0	211.8	138.3	78.3	29.0
Montcalm	117	178.8	21.0	125.1	130.8	-5.6	-18.0
Oshtemo	224	191.7	171.3	208.3	187.5	40.5	104.7
Hillsdale	58	28.4	27.1	10.9	8.6	0.6	-62.1

SUMMARY AND CONCLUSION

A greenhouse study and laboratory analyses were conducted to measure plant use of residual soil P on heterogeneous soils with various management histories, and examine the suitability of some current chemical soil test methods in detecting the effectively available residual soil P. Measurements made were plant dry matter yield, P uptake and extracted soil P.

In the greenhouse, dry matter production over 10 consecutive five week crops varied significantly but not linearly with the level of residual P on soils used while P uptake was higher on soils with higher residual values. Plant physiological adjustments such as relative increases in root mass and water use efficiency were proposed as plausible reasons for the similarities in yields between the uncultivated soils and some high P soils. The study was terminated when P deficiency occurred on some lower residual P soils and a moderate P Hillsdale sandy loam soil. Since production would have continued on the other soils, it is conclusive that the influence of residual P on crop yield would be to prolong the ability of soils to support production, but not necessarily to increase seasonal production. Even though residual P improved P uptake by plants, this was not effectively noticed in dry matter yields over the period of this study.

In the laboratory, the effectiveness of the chemical test methods in detecting available residual P was variable. Increasing the extractant volume or acid strength of the Bray method revealed more P in the soils, especially in the Charity clay soil. By comparison, the available residual P values suggested by the methods varied. This confirms the reasoning that only a proportion of the available P is

detected by extraction methods. The usefulness of any method is thus dependent on how well it predicts the likelihood of crop response to further P application to that soil. In this study the Bray and Kurtz method was more effective in detecting the low P soil.

Phosphorus extracted by CaCl_2 , an intensity factor, was better correlated with the plant use of residual P over all soils. In this aspect the NaHCO_3 -P method was similar to the resin method and better than Bray and Kurtz-P method on this set of heterogeneous soils. However, by identifying some soils with similarities in P release the correlation of the Bray and Kurtz-P method was greatly improved and superior to the NaHCO_3 -P. P uptake was not absolutely related to residual P levels in the soils. Deviations were introduced by the Montcalm sandy loam soil which tested high in P but plants didn't remove much of it.

The amount of P removed from most soils was closely accounted for by changes in soil test values. Actual plant P uptake was higher than indicated by soil test changes. Again, the Montcalm sandy loam soil deviated, showing larger changes in soil test than uptake. It is suspected that unavailable P was detected on this soil. The uncultivated Charity and Spinks, and manured Kalamazoo soils gave indications of organic-P mineralization and plant use. Soil tests on these soils were stable through cropping.

In conclusion, this study confirms that intensive cultural practices have raised the residual P levels in Michigan soils. The current levels would be adequate to support long term cropping along with other management practices. The Bray and Kurtz method effectively detects P sufficiency levels, but generally, the current soil test

methods under-estimate the effectively available residual P and this may lead to over-estimations in P recommendations and application. The residual P values of soils can be actively lowered by plant uptake as slow reactions do not appear to be rapid in this case. Such a reduction will reduce the possibilities of P pollution.

CHAPTER 2
SOLUBILITY OF RESIDUAL SOIL PHOSPHORUS
INTRODUCTION

The P compounds that dominate soil solution P vary with soil reactions and regions, among other factors. Any interest to detect such a compound may emanate from the desire to know the source of important contributions to plant P uptake and the soil management implications for crop P use. Out of the movement for such an understanding came two approaches to explain soil P compounds. First, the solubility product principle (Aslyng, 1954) has been beneficial in attempting to explain and predict the chemical behavior of soil P. Secondly, the soil P fractionation method (Chang and Jackson, 1957; Williams et al., 1971) has contributed to detecting quantitative changes in soil P compounds.

It is essential to have a general understanding of the nature of soil P within various regions. Such knowledge will assist in the development and adoption of soil testing practices in new areas, the modification of soil test practices in areas where cultural practices have introduced changes in soil reaction and cultivation practices in general.

In Michigan, intensive cultivation practices have resulted in accumulation of high P levels in some soils. Therefore it was of interest to study the chemical nature of P residue in these soils. The following study was developed to: 1. Predict the P compound most

probably controlling the soil P. 2. Determine the effect of cropping on the soil P solubility. 3. Study the relationship between soil test P and P solubility. 4. Examine the relationship between soil P solubility factors and plant P uptake.

LITERATURE REVIEW

Phosphorus exists in the soil primarily as compounds of calcium, aluminum and iron. The presence in the soil and availability of a specific compound depends upon the region, weathering intensity, soil pH, and cultivation practices. Since plants obtain P directly from the soil solution, it is not certain that the compound present is important except indirectly as far as it's solubility is concerned. Nevertheless, this information can be useful in fertilizer and residual P management practices. It can help to explain the chemical behavior of soil P (Lindsay and Moreno, 1960).

When P is applied to the soil, it undergoes reactions that render it less soluble. Devine et al. (1968) represented the transformation as:
Fertilizer ----> Soil solution ----> Metastable solid ----> stable solid. The mechanism involved in this transformation is initiated by the movement of soil water into the fertilizer particle via capillary or vapor transport (Lehr et al., 1959; Kolaian and Ohlrogge, 1959). The rate of dissolution in the soil then depends on the soil P status and water solubility of the fertilizer (Lawton and Vomocil, 1954; Khasawneh and Hashimoto, 1979). Lehr et al. (1959) showed that granules of ordinary superphosphate, monocalcium phosphate and concentrated superphosphate would dissolve rapidly. In contrast, rock phosphate would dissolve slowly (Khasawneh and Doll, 1978). As water moves into the particles, P would move out resulting in soil solution supersaturated with respect to various P compounds. Phosphate movement would continue until the granule concentration decreases to a level at which there is no osmotic gradient and diffusion ceases (Huffman and Taylor, 1963).

The initial reaction products formed in the reaction of P with soil are metastable. In time they revert into more stable compounds. Reaction products commonly found in neutral to calcareous soils in order of solubility are: dicalcium phosphate dihydrate (DCPD) > dicalcium phosphate (DCP) > octacalcium phosphate (OCP) > B tricalcium phosphate (TCP) > hydroxyapatite (HA) (Lindsay, 1979). Aluminum phosphate (variscite) and iron phosphate (strengite) predominate in acid soils. However, most P compounds contain impurities which considerably influence their solubilities. For instance, carbonate impurities render hydroxyapatite more soluble than in the pure state (Khasawneh and Doll, 1978).

The occurrence of a compound in the soil can be predicted by the solubility product principle (Aslyng, 1954; Withee and Ellis, 1965). A graphical representation of this makes for convenient comparisons. Samples that fall above an isotherm are considered to be supersaturated with respect to it. Conversely samples below an isotherm are undersaturated and the compound in this case is considered to control P in the sample.

Metastable forms of P fertilizer residue have been suggested to be DCPD and DCP (Brown and Lehr, 1959 and Bouldin et al., 1960). These compounds do not remain in the soil for extensive periods following fertilization (Bell and Black, 1970). In many soils with histories of fertilization, P residue has been shown to be in the form of OCP or TCP (Havlin and Westfall, 1984). Apatite is the expected thermodynamic end point of P fertilizers in neutral to calcareous soils. Yet, Fixen and Ludwick (1982) suggest that under arable conditions this end point may not be reached as evidenced by the continued uptake of residual soil P.

Variscite and strengite are possible end products in acid soils. (Chakravarti and Talibudeen, 1962; Lindsay et al., 1959).

Numerous fertilizer compositions can influence the reaction products upon contact with the soil. Ammonium ortho- and polyphosphate fertilizers without calcium or micronutrient cations would dissolve completely leaving no residue in the granule site (Bouldin and Sample, 1959; Khasawneh et al., 1974). The reaction products of many fertilizer compounds have been compiled by Sample et al. (1980).

The ultimate goal of any form of determination of soil P is to ascertain sufficiency for production. Solubility phase products are not quantitative, but they are capable of suggesting soil P supply pattern and adequacy. Cumulative works have shown that if the solid phase is in equilibrium with OCP, then the soil P should be adequate for crop production as it exceeds known optimum ranges (Olsen and Khasawneh, 1980). In their studies, Olsen et al. (1978) and Havlin and Westfall (1984) demonstrate that available residual soil P may be present in an undersaturated state with respect to the metastable compounds. Annual fertilization will modify soil P, therefore as soils are continuously fertilized parent material and weathering intensity become poor indicators of the soil P chemistry.

MATERIALS AND METHODS

A laboratory study was conducted on ten soils from South-Central Michigan to describe the solubility of residual P. A description of the soils and greenhouse study has been given in chapter 1 of this thesis. Soil samples were obtained from each experimental unit in the greenhouse before and during cropping (after crops 1, 3, 9, and 10) for analysis in the laboratory. It is important to point out again that lime application was made to the Spinks soil before the initial cropping, and to all other soils except the Charity at the end of the third cropping.

Soil Analyses

Five grams of soil was shaken in 50mL of 0.01M CaCl_2 for one hour. The suspension pH was then immediately determined using a glass electrode. Samples were centrifuged and filtered. The electrical conductivity was measured on a conductivity bridge with a cell constant of 1. Phosphorus concentration was measured by the ascorbic acid method (Murphy and Riley, 1962) using a Spectronic 20 spectrophotometer at 880 microns. Calcium was measured on an atomic absorption spectrophotometer.

Ionic strengths of the solutions were estimated as a product of the electrical conductivity values and a constant (0.013) (Griffin and Jurinak, 1973). Activity coefficients were calculated by the extended Debye-Huckel equation (Lindsay, 1979). The standard solubility isotherms were established from solubility constants given by Lindsay (1979). Soil phosphate potential ($\text{pH}_2\text{P}_04 + 0.5\text{pCa}$) and lime potential ($\text{pH} - 0.5\text{pCa}$) were calculated by a computer program supplied by Dr. B.G. Ellis¹.

¹ Dr. B.G. Ellis, Professor of Soil Chemistry, Michigan State University.

RESULTS AND DISCUSSION

Chemical Nature Of Phosphorus Residue In Soils

The chemical nature of residual P in some Michigan soils was studied. The soils ranged in soil reaction from pH 4.8 to 7.2 (Table 16), and varied in other soil characteristics (Table 4). The solubility product principle which has been used by many investigators was used to attempt to explain the chemical behavior of soil P.

Figure 6 shows the nature of P residue in these soils as they were when collected from the field. The location of a soil near an isotherm would suggest that P in the soil is in a state of equilibrium with the discrete solid phase or a compound of similar solubility. Changes in the P controlling compound thereafter are gradual and not instantaneous. Where counterpart uncultivated soils are available it becomes obvious that fertilization has increased the solubility of P in these soils. The clustering of soils as observed in this Figure gives the indication that there is an association with the soil reaction. Generally, soils below pH 6.0 are located around the variscite and strengite isotherms, while soils above pH 6.0 fall around the Ca-P compounds. Susuki et al. (1963) observed a similar trend in fractionation studies of some Michigan soils. They showed that the soils with pH 6.0 and above tended to be higher in Ca-P while those below were higher in Al-P.

It is interesting here that some of the soils fall well above the variscite isotherm. This would suggest that more soluble aluminum compounds control the P in these soils. However, given the high soil tests and P activity it is more probable that adsorbed P controls the P in these soils Lindsay et al. (1959) established that more soluble

Table 16. Soil P solubility factors for 10 Michigan soils with various levels of residual P.

Soil	pH (CaCl ₂)	pH ₂ PO ₄	CaCl ₂ -P	pCa	pH ₂ PO ₄ ⁺ 0.5 pCa	pH - 0.5 pCa
			mg/kg			
Charity	7.2	5.3	0.48	2.3	6.5	6.1
Charity (uncultivated)	7.1	6.2	0.06	2.3	7.3	6.0
Kalamazoo	6.0	4.6	1.01	2.3	5.7	4.9
Kalamazoo (manured)	5.8	5.3	0.20	2.3	6.4	4.7
Spinks	4.8	4.4	1.55	2.3	5.5	3.7
Spinks (uncultivated)	6.4	5.0	0.47	2.3	6.1	5.3
Capac	4.8	4.3	1.88	2.3	5.4	3.6
Montcalm	5.7	4.5	1.19	2.3	5.6	4.6
Oshtemo	6.2	4.1	3.78	2.3	5.2	5.0
Hillsdale	6.2	5.7	0.09	2.3	6.8	5.0

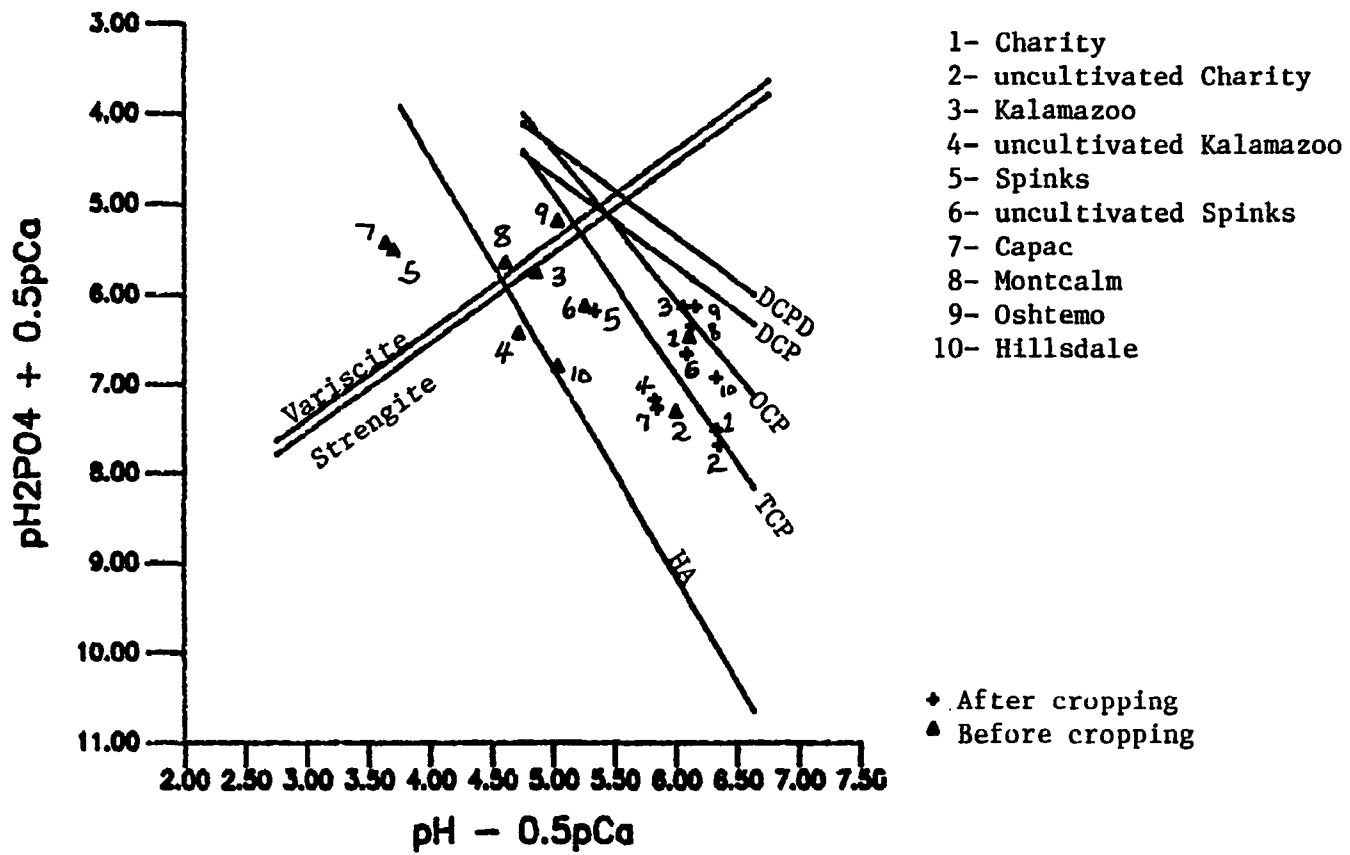


Figure 6. Phosphorus solubility of some Michigan soils before and after a greenhouse cropping study.

aluminum compounds are very unstable, therefore it is not expected that precipitated P would be currently active enough in these soils.

It is often questionable which is more soluble, variscite and strengite. Lindsay (1979) suggests that in less weathered soils where kaolinite-silica is apt to control soil aluminum, variscite would be more soluble. Furthermore, in Michigan soils Juo and Ellis (1968) showed that strengite was less soluble than variscite for plant P uptake; while Susuki et al. (1963) observed that Fe-P did not contribute to P removal by plants. The preceding premise was established in order to suggest that P in the soils which fall below the strengite line is more likely controlled by variscite.

Contrary to previous suggestions that arable soils never have P in equilibrium with hydroxyapatite, two soils are located near this isotherm. The plausible explanations for this observation are that P in the manured Kalamazoo soil is influenced by organic-P cycling, and P in the Hillsdale soil, a sandy loam was rather low and may also have been influenced by organic-P.

The P in the alkaline soils is clearly controlled by OCP/TCP. This would be expected given the soil characteristics. In the final analysis, because of the chemical nature of P in these soils, it should be expected that Al-P and Ca-P are more important sources of P to plants. The extent to which either dominates on a soil could be affected by soil management practices, as observed below.

Effect Of Cropping On Soil Phosphorus Compounds

There was a general decrease in phosphate potential and solubility with the period of cropping (Fig. 6). As result of lime applied, by the end of the study, most of the soils showed P in equilibrium with

OCP/TCP. Despite the changes in lime potential it is important that the phosphorus potentials of the soils was buffered around compounds that are considered to be soluble. Even though the soils were not cropped to P exhaustion, there is no indication that they may have eventually attained equilibrium with HA. The pattern observed on each soil is further discussed below.

While there is a fluctuation in phosphate potential, the Charity soil remains buffered between OCP and TCP (Fig. 7). The P solubility pattern on this soil follows what would have been expected, however the deviation at sample 2 may have been the result of experimental error. This resistance to change increases the likelihood of OCP as the discrete mineral phase. Furthermore it shows a greater P capacity factor than other soils which fluctuate about isotherms (Fixen and Ludwick, 1982). The current observation would suggest that Ca-P was the important source of P in this soil. Also, the nature of P solubility indicates that P would be readily available on this soil. The shift in soil pH between initial and final cropping was from 7.2 to 7.5.

Phosphorus in the uncultivated Charity soil is clustered around TCP (Fig. 8). The variability in phosphate potential is more pronounced here. It is conceivable, but a speculation at best that organic-P mineralization may have been responsible for the pattern observed here. Otherwise no explanation can be offered for the acute increase in solubility at sample 4. Halm et al. (1972) observed that some native grasslands in Saskatchewan released P that exceeded plant requirements. They did not respond to further P fertilization despite a low (3 mg/kg NaHCO₃-P) soil test level. Also, Lindsay and Moreno (1960) suggested that disturbances of P equilibrium by biological processes could be

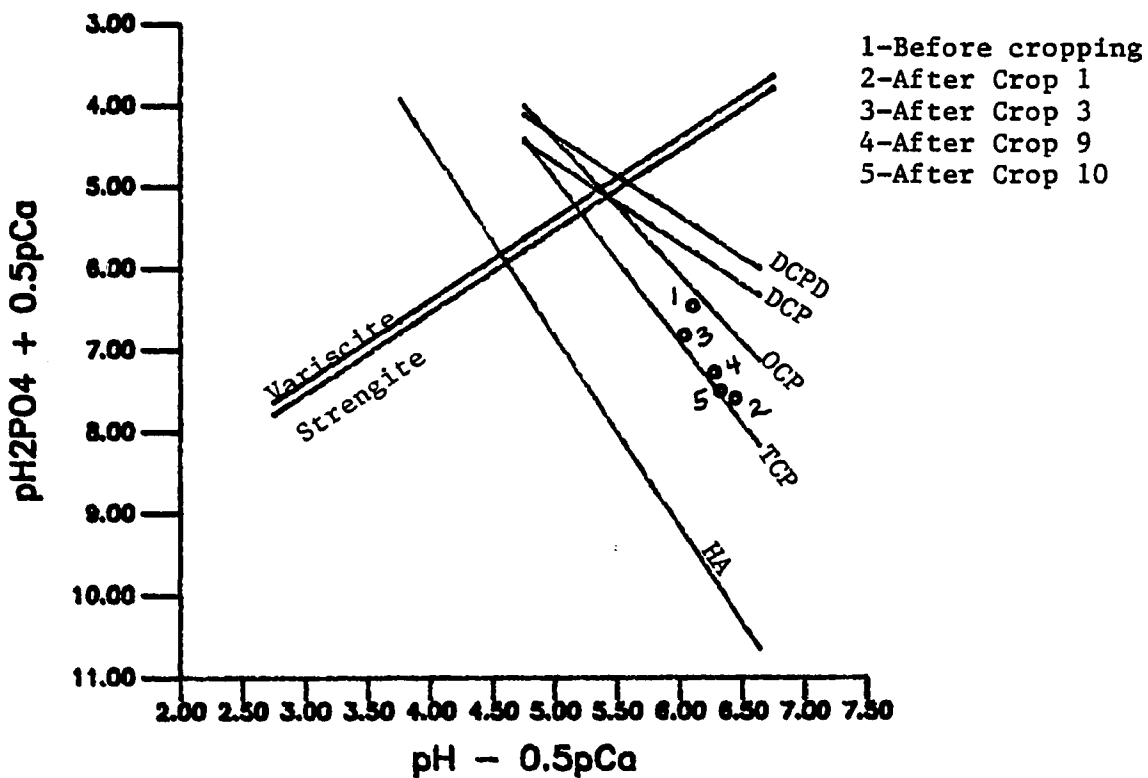


Figure 7. Effect of greenhouse cropping practice on the P solubility of a Charity high P soil.

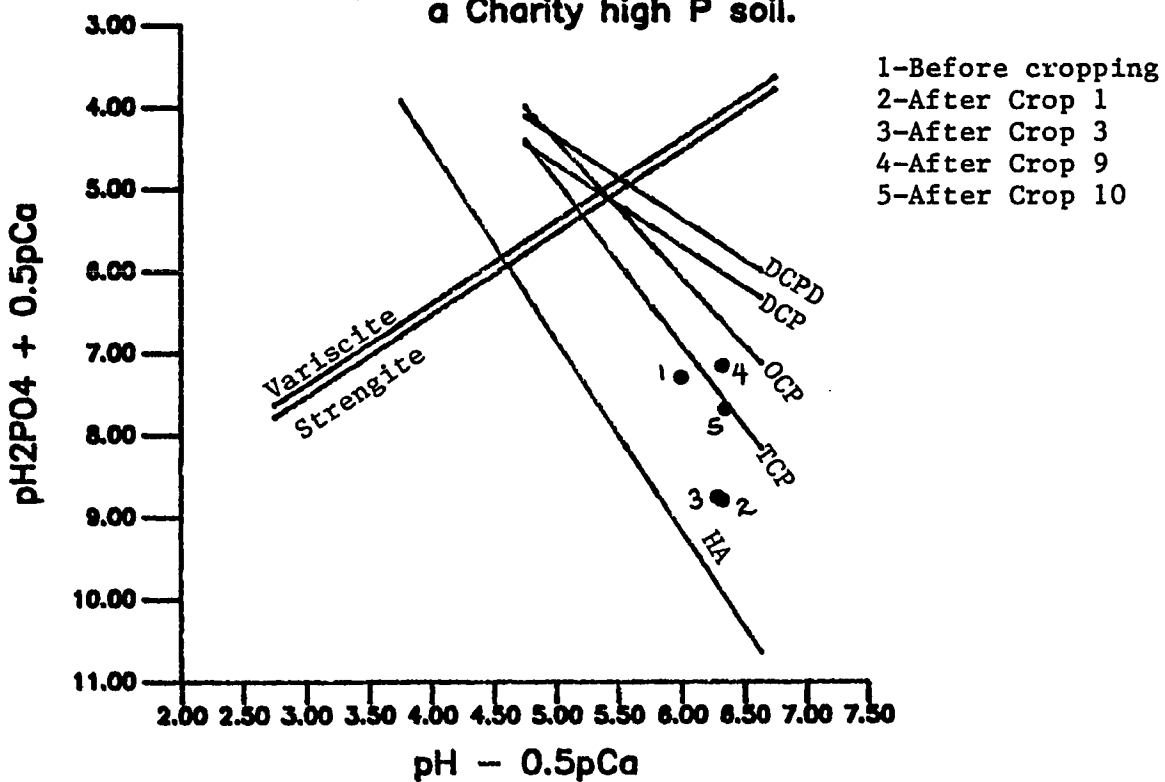


Figure 8. Effect of greenhouse cropping practice on the P solubility of an uncultivated Charity soil.

frequent. In this case, while Ca-P may have been responsible for some uptake, organic-P must have been more important. Soil pH shift was from 7.1 to 7.5. Generally, the P solubility was in agreement with what would have been expected on this low P soil.

The high P level of the Kalamazoo soil suggests that adsorbed P would be more important than precipitated P at the initiation of this study. Nevertheless Figure 9 indicates that Al-P may have been the P compound. It is suspected that the shift above the variscite line at sample 3 was due to the influence of NH_4^+ -N fertilization on the soil. Phosphorus potential remained stable. With the application of lime OCP is precipitated and appears to control soil P. Aluminum P probably was as important as Ca-P for plant use because of the better crop performance registered early in cropping. Soil pH shift was from 6.0 to 7.2. as a result of liming.

It was earlier suggested that organic-P cycling may have been responsible for the location of the manured Kalamazoo soil near the hydroxyapatite isotherm (Fig. 10). Cropping continued to reduce the phosphate potential. However, liming after sample 3 effected TCP precipitation. The P addition from organic sources may account for the shift in phosphate potential, and the solubility was in proportion to the slightly moderate P level in the soil. Organic P would have played a significant role in P uptake here. Soil pH increased from 5.8 to 6.9.

Cropping was not very effective in reducing the PP on the Spinks soil (Fig. 11). Because of the sandy nature and low buffering of this soil, it would appear that in order to maintain the level of solubility, there had to be an appreciable amount of free P in solution. The soil test level supports this thinking. This soil was limed before cropping

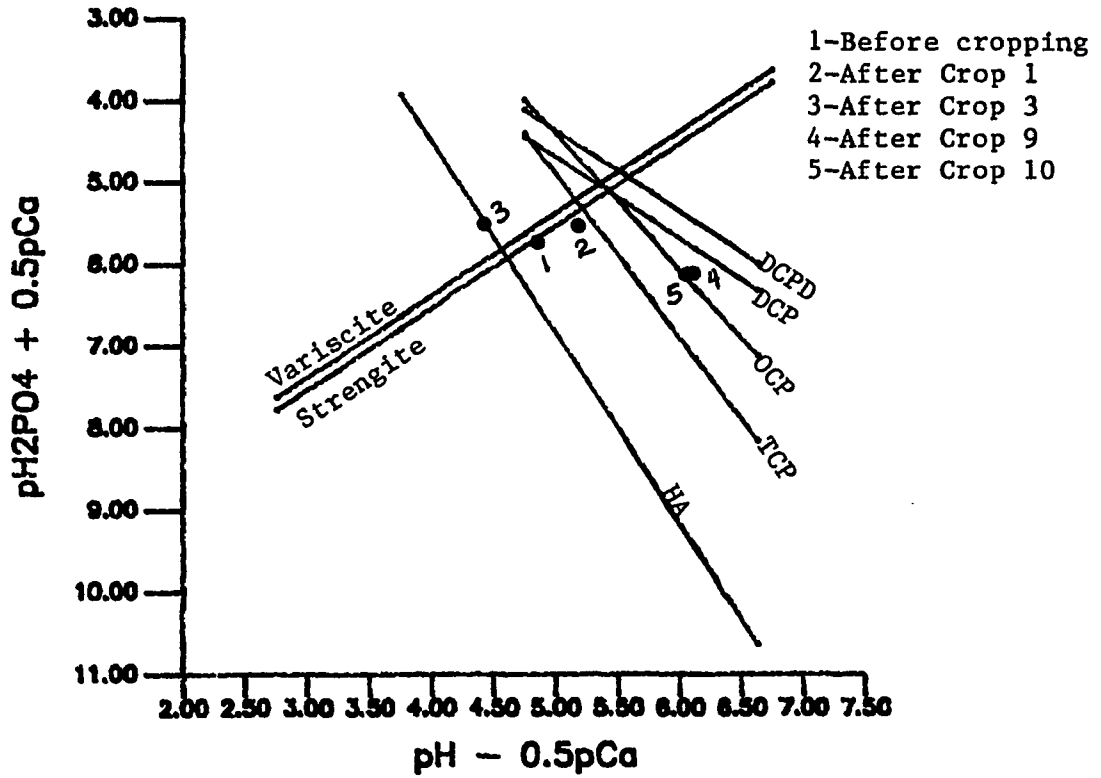


Figure 9. Effect of greenhouse cropping practice on the P solubility of a Kalamazoo high P soil.

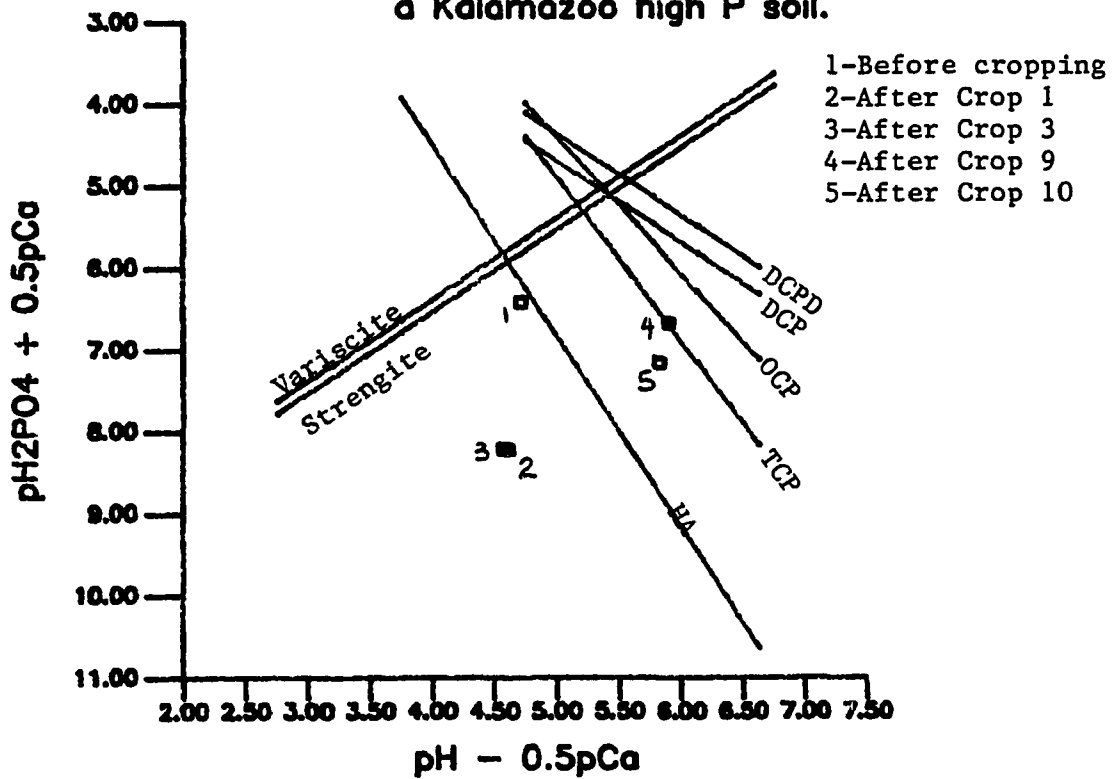


Figure 10. Effect of greenhouse cropping practice on the P solubility of a manured Kalamazoo soil.

and a consequent increase in lime potential is observed. Liming after sample 3 resulted in an increase in solubility, and this would only suggest the solubilizing of variscite. Because of the soil test and soil characteristics it is unlikely that TCP could have controlled P in this soil. It is more probable that Ca-P did not effectively precipitate. Octacalcium phosphate would have been expected a more likely precipitate. Furthermore, the proximity to the variscite isotherm increases the belief that variscite was in control of soil P through the cropping period. Thus Al-P and Ca-P were important for P uptake. Soil pH increased from 4.8 to 6.5 as a result of liming.

Variscite is suspected to have controlled the P activity in the uncultivated Spinks soil at the beginning of the study (Fig. 12). Liming resulted in a gradual increase in the lime potential and cropping gradually decreased the P solubility. However liming after sample 3 increased the P solubility by solubilizing variscite. The rather high phosphate potential is suspected to have been enhanced by organic-P mineralization, which appears to have been beneficial for plant use as suggested by Table 15. Soil pH was increased from 6.4 to 7.3 as a result of liming.

Adsorbed P appears to have been an important fraction in the Capac soil. The solubility state at sample 1 (Figure 13) seems unlikely and may have been due to experimental error. Sample 2 would suggest that variscite may have controlled soil P. The shift at sample 3, again may have been resultant of the effect of ammonium fertilization on soil reaction. Lime application after this period initiated the precipitation of OCP. Al-P and Ca-P contributed to P uptake from this soil. Liming increased the soil pH from 4.8 to 7.0.

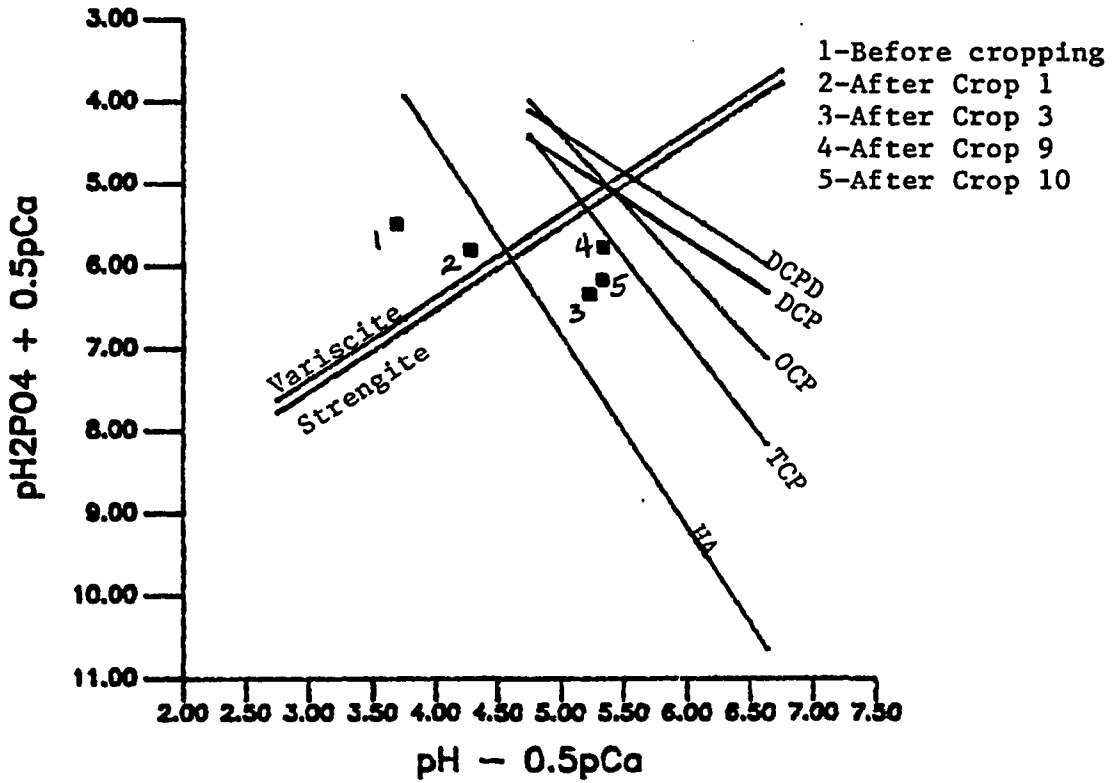


Figure 11. Effect of greenhouse cropping practice on the P solubility of a Spinks high P soil.

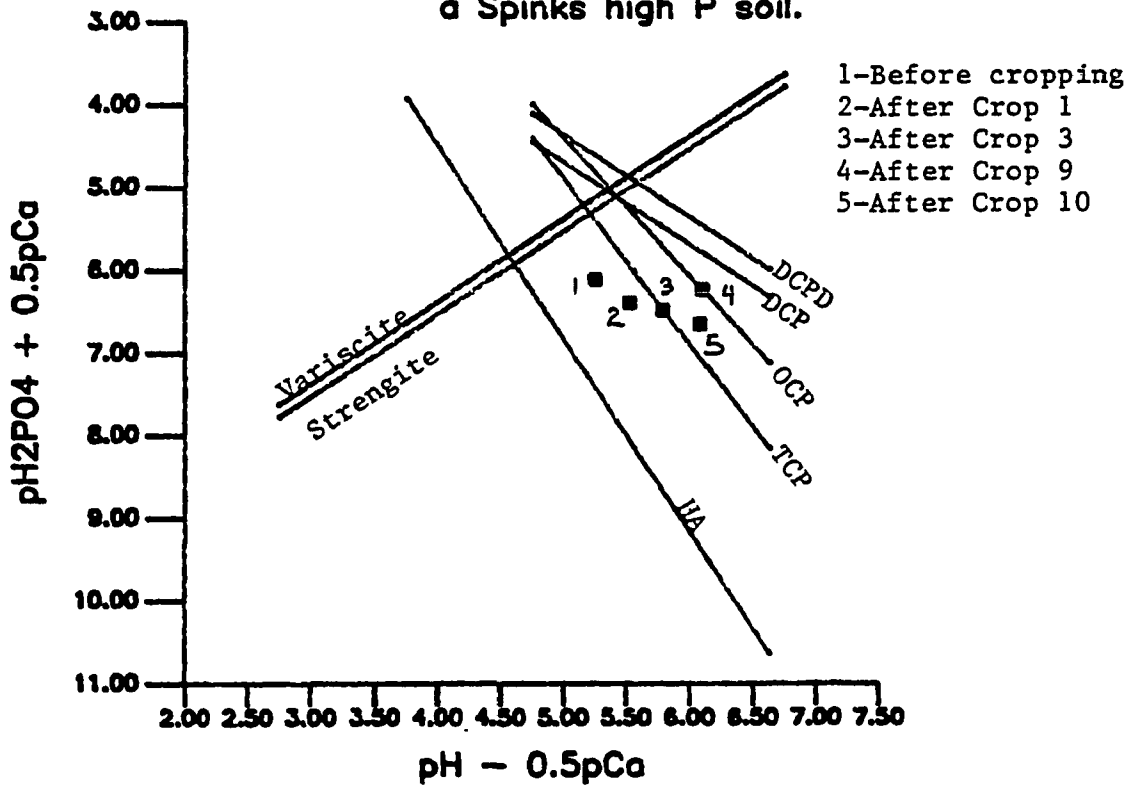


Figure 12. Effect of greenhouse cropping practice on the P solubility of an uncultivated Spinks soil.

Crop performance on the Montcalm soil was disappointing considering the soil test levels. While the soil was buffered around soluble P compounds (Fig. 14) for the most part, the deviation at the third sampling is not understood. This could have been due to experimental error. However, if this soil stayed in this state for any appreciable period during cropping, then this may have contributed to the poor crop growth. Variscite controlled soil P at initiation of cropping. With liming after sample 3, OCP was gradually precipitated. The high P soil test level supports the high state of P solubility in this soil. Aluminum P and Ca-P played important roles in P uptake from this soil. The soil reaction was increased from 5.7 to 7.3 as a result of liming.

Adsorbed P appears to have been an important fraction in the Oshtemo soil. Because of the soil reaction and P potential Al-P might have been present. Initial cropping slightly reduces the solubility, but the effect of ammonium fertilization on the soil reaction resulted in a deviation at sample 3 (Figure 15). The phosphorus potential was stable and at a rather high level of activity. Liming after sample 3 increased the lime potential, and cropping decreased the phosphorus potential. The precipitation of OCP or a more soluble compound reflects the high soil test and ready availability P from this soil. The change in soil reaction as a result of liming was from 6.2 to 7.3. This soil showed good performance in accordance with the current observation. Plant P uptake appears to have been equally supported by both Al-P and Ca-P.

The Hillsdale soil is a weakly buffered soil, and this is reflected in the inability to maintain a good solution P activity (Table 6). Variscite is suspected to have controlled soil P at sample 1 (Figure 16). The rapid drop in solubility is not understood. However the

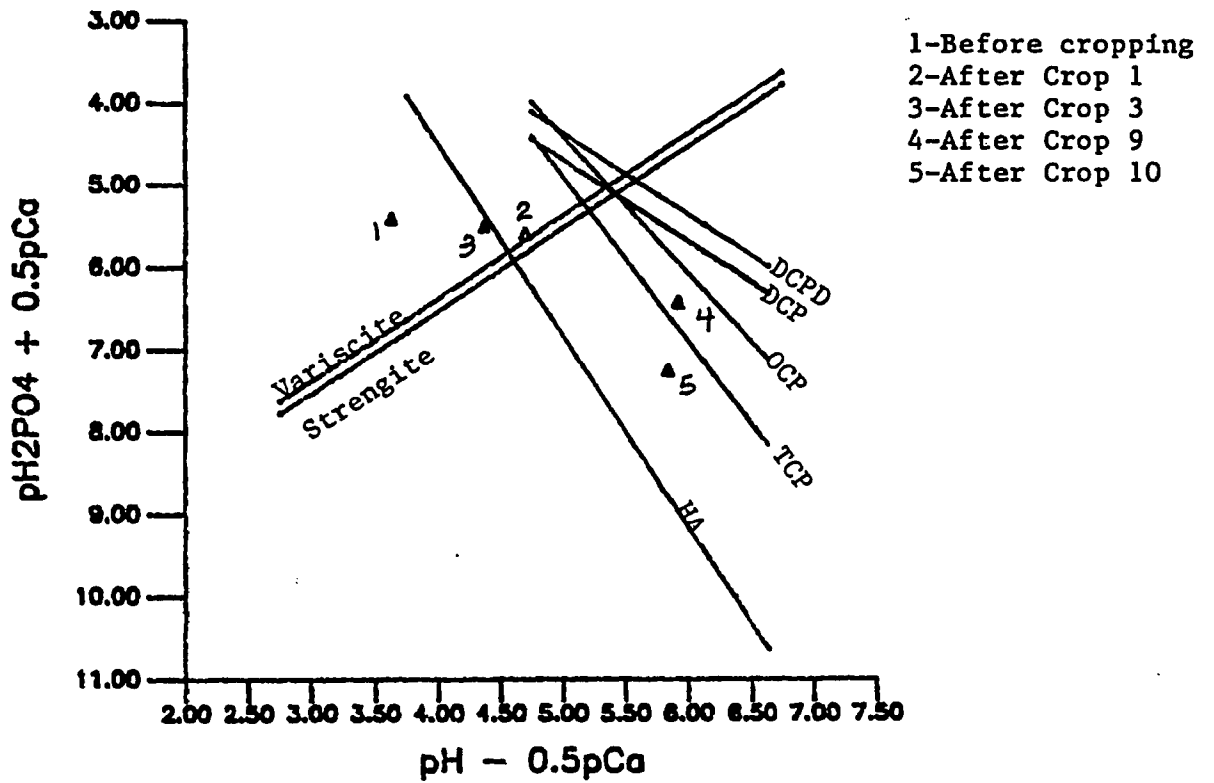


Figure 13. Effect of greenhouse cropping practice on the P solubility of a Capac high P soil.

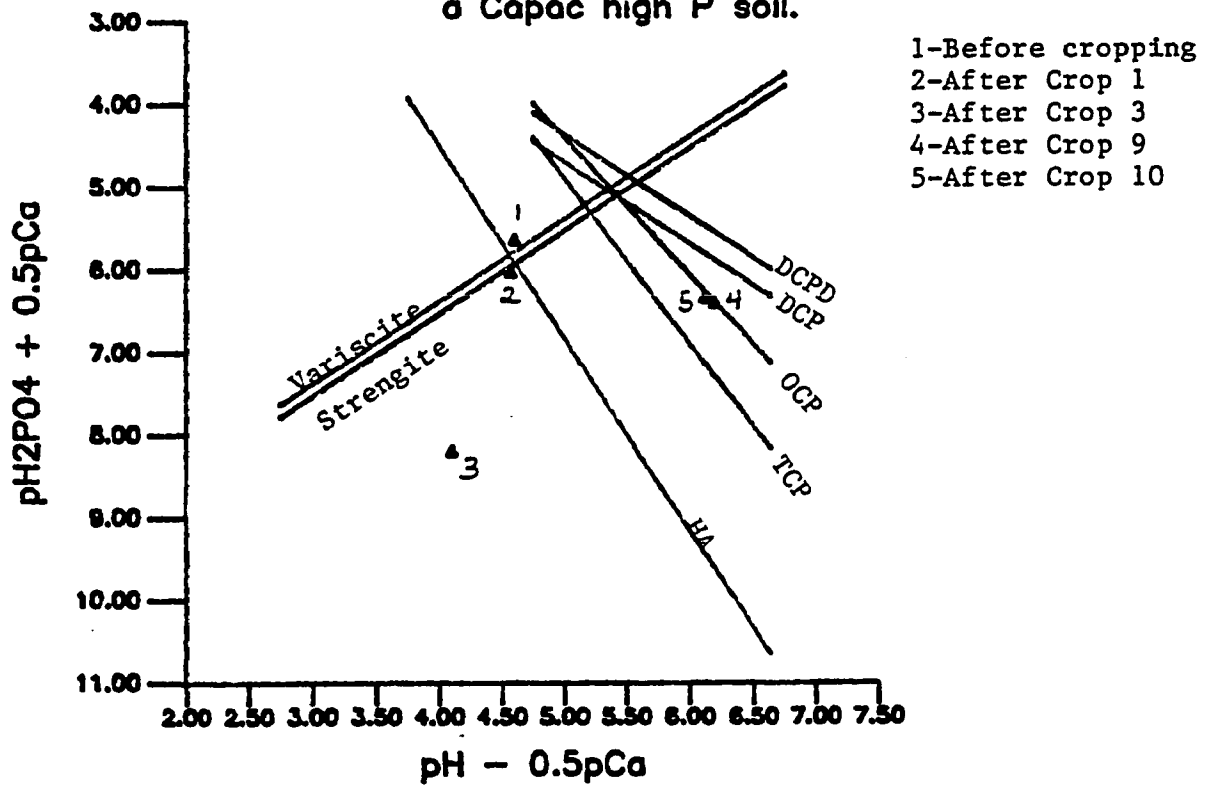


Figure 14. Effect of greenhouse cropping practice on the P solubility of a Montcalm high P soil.

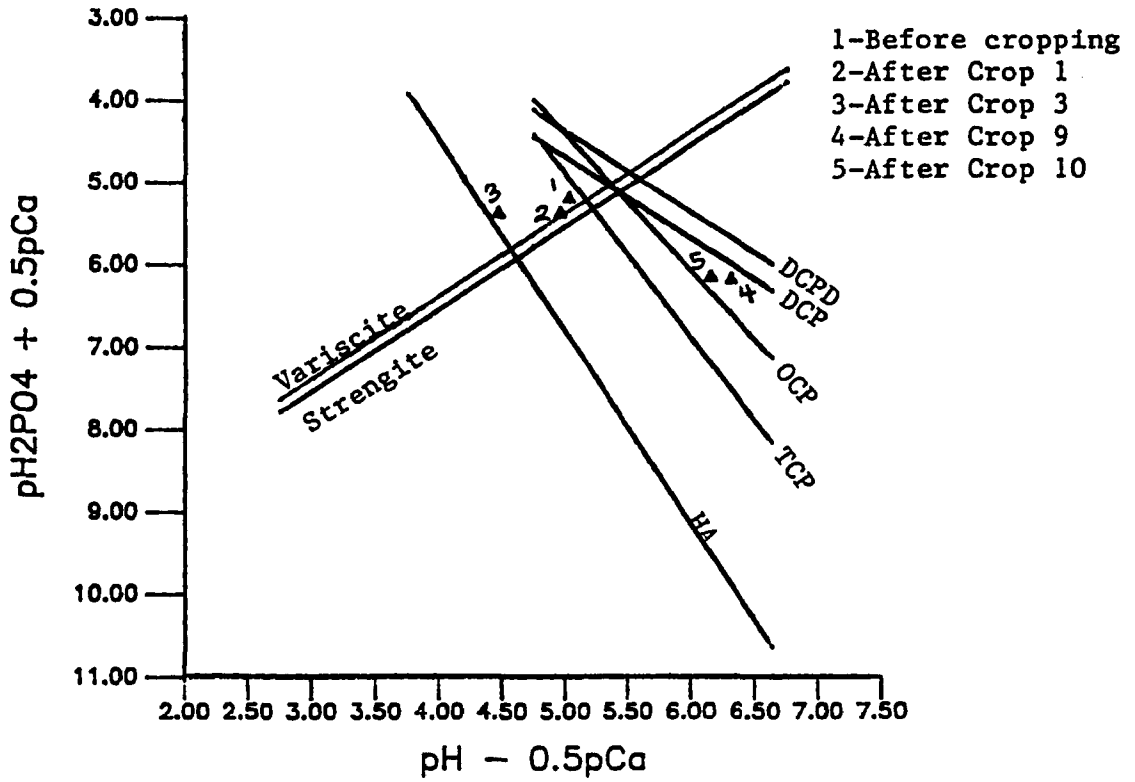


Figure 15. Effect of greenhouse cropping practice on the P solubility of an Oshtemo high P soil.

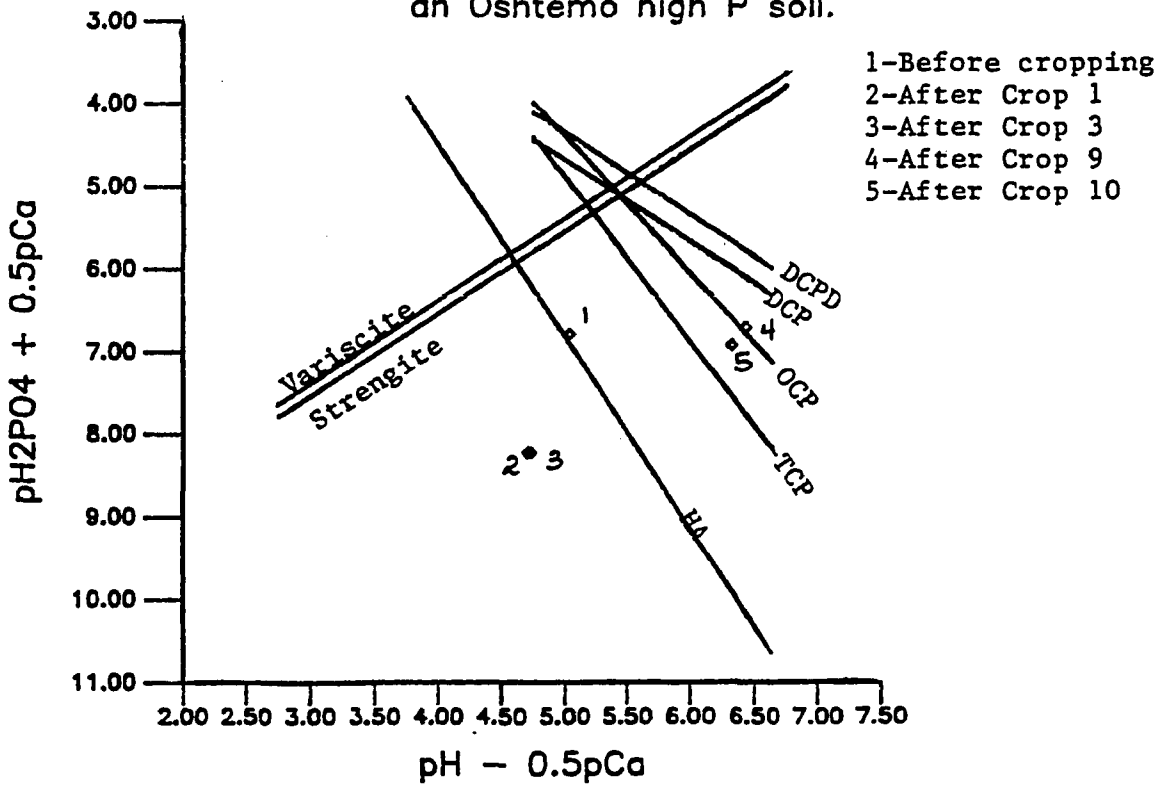


Figure 16. Effect of greenhouse cropping practice on the P solubility of a Hillsdale high P soil.

increase in solubility following lime application after sample 3 would suggest the solubilizing of variscite. Two observations with this soil are questionable - the very low level of P at samples 2 and 3, and the rather high level of solubility following lime application. It may then be possible that there was addition to soil solution P by organic-P cycling. Al-P and Ca-P were used by plants. The initial soil reaction of 6.2 was increased to 7.4 as a result of lime application.

In summary, removal of P and liming resulted in the reduction of P solubility in the soils. As expected, the soil pH was an effective estimate of the P compound that controlled soil P activity. Application of lime while increasing lime potential of soils initiated the solubilizing of variscite and precipitation of OCP/TCP. The nature of the pattern of solubility observed would suggest that plant P uptake was from Al-P and Ca-P, each being more important before and after liming effects, respectively. It would appear that organic-P mineralization contributed a significant portion of the P uptake on the uncultivated soils as suggested in Table 15.

Relationship Between Soil P Compounds And Soil Test Levels

It was of interest to examine the soluble soil P compounds and how they may be related to or have influenced the soil tests. The Bray and Kurtz method is given consideration here because of it's application in Michigan.

Correlation of the soil tests with plant uptake was weak (Table 10). This implies that as far as solubility is concerned, there may have been an inadequate detection or over estimation of the P compound most important to plant uptake across all soils, by the extractant. Soil test results are given in Table 9. Significantly more P was extracted on the

Charity soil as soil:extractant ratio and acid strength were increased. It is then obvious that the acid in the extractant was neutralized by carbonate and there was interference with available P detection. This may contribute to discrepancies in the correlation, moreso as it has been established that Ca-P was important for plant use on this soil. Of further concern would be the uncultivated soils. Even though they showed relatively less available P, and little change in soil tests before and after cropping (Table 9), the soils had moderate phosphorus potentials. It is believed that organic P could have contributed to this potential.

The appreciable stability in P detected on the acid to neutral soils confirms the sensitivity of the Bray extractant to Al-P. It has been suggested that Al-P played a significant role in P supply on these soils.

It is interesting that the levels of P solubility appear to reflect the range of soil test levels. This is a complex index to establish since there is a range of PP for each discrete phase and the soil buffering capacity ultimately affects P activity. Nevertheless, it could be a rough estimation of the level of potential P solubility in soils. Havlin and Westfall (1984) suggested that neutral to calcareous soils testing > 32 mg/kg $\text{NaHCO}_3\text{-P}$ are more likely to be clustered around OCP while soils testing lower would be around TCP. A comparison of the soluble phases with the $\text{NaHCO}_3\text{-P}$ soil tests in this study shows support for their observation (Fig. 6 , Table 9). In the case of the Bray and Kurtz-P (1:8) a test level of 20 mg/kg would more adequately separate the CA-P isotherms. A test level of 130 mg/kg Bray and Kurtz-P for acid to neutral soils would suggest an equilibrium with variscite. The

general trend is of a reduction in solubility with decreasing soil test level.

SUMMARY AND CONCLUSIONS

Laboratory analysis were conducted to examine the chemical nature of available residual soil P. This study would indicate the potential P supply capacity on heterogeneous soils with variable residual P levels, as well as verify the suitability of current chemical soil test method (Bray and Kurtz-P) for use in Michigan.

The results suggest that P fertilization has raised the P potentials in the soils, and the P activity is consequently governed by adsorbed P or a very soluble P compounds. The soil reaction value was a good indicator of the dominant P compound and Al-P and Ca-P would appear to be the more important sources of P for plant use. The acid to neutral reaction of most of these soils and other Michigan soils confirms the appropriateness of the Bray and Kurtz-P method for soil testing. The estimation of available P by this method can be improved by improving it's sensitivity for Ca-P which is of equal importance for plant use, especially with the adjustment of soil reaction to be more alkaline.

Crop production on these soils contribute to a decline in P solubility, however this decline is not of a rapid or an alarming nature even with substantial P removal. On soils where P deficiency was observed the solubility was yet maintained close to the TCP isotherm, a soluble compound. On the higher residual P soils it is certain that P potential can support long term production.

APPENDIX

Table 17. Nitrogen and potassium application schedule for a greenhouse study of residual P in 10 Michigan soils.

Crop	Fertilizer Application			
	Before Planting		2 Weeks	
	Nitrogen ⁺	Potassium [¶]	Nitrogen	Potassium
	-----mg/kg-----			
1	120	50	50	10
2	120	50	-	-
3	50	10	-	-
4	-	-	-	-
5	-	-	-	-
6	50	10	-	-
7	25	10	-	-
8	25	10	-	-
9	-	-	20	10
10	-	-	-	-

⁺Nitrogen as ammonium nitrate.

[¶]Potassium as potassium chloride (crops 1-3) and potassium sulfate (crops 6-9).

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