The Role of Phosphorus Cycling and Soil Physical Properties in Governing the Bioavailability of Phosphorus in a Tropical Ultisol

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ABSTRACT

The role of organic P (Po) and the fate of residual fertilizer P was studied in an aggregated Typic Palehumult. In a field experiment four crops were grown during a 2-yr P build-up phase (P inputs to each crop exceeded P removal) followed by another four crops during a 2-yr residual phase where no additional P was added. The net P input for each of the four P treatments was 0 (0P), 155 (LP), 310 (MP) and 930 (HP) kg P ha^{-1} by the end of the build-up phase. In the HP treatment, yield and P uptake declined by 15% and 36% during the residual phase. Mehlich-1 extractable P was a poor index of available P as the value required for optimal yields shifted over time from 2 mg P kg^{-1} to over 5.5 mg P kg^{-1}. A sequential P fractionation procedure measured labile, moderately labile, and recalcitrant inorganic (Pi) and Po over time. Labile Pi pools were a poor index of P availability and behaved similarly to Mehlich-1 in relation to yield. In control (0P) treatments, however, a 50% yield decline was positively correlated with labile Pi and Po. About 8.5, 55 and 37% of the fertilizer P was recovered in the labile, moderately labile and recalcitrant Pi pools, respectively, 104 days after application. Little subsequent change in residual fertilizer P distribution among pools indicate the decline in P availability did not result from P conversion to less labile forms. Autoradiographs of adsorbed ^{32}P showed that P was initially adsorbed to a 0.188 mm layer around soil aggregates (reactive mass). The reactive mass of different aggregate size fractions was linearly related to P adsorption ($r^2 = 0.96$), P dissolution ($r^2 = 0.99$) and linear buffer coefficients derived from P adsorption isotherms ($r^2 = 0.98$). These results suggest the decline in P availability was due to P diffusion into aggregates where it became unavailable due to slow diffusion out. Many soil P test methods destroy aggregates during extraction, measuring total labile P, some of which may be occluded within aggregates and plant unavailable. These results document the influence of soil aggregation on P availability and may also have important ramifications for understanding pollutant retention in soil.

CHAPTER 1

INTRODUCTION

Phosphorus deficiency limits crop productivity in many highly weathered acid soils. These soils dominate the upland tropics where agricultural productivity must increase to support a rapidly growing population (Sanchez, 1976; Cochrane, 1969). Improving P fertilizer use efficiency in upland systems is imperative since farmers generally have little capital. Farming systems on these soil are typically low input with little or no fertilizer use. In many cases legumes are included in the crop rotation. Legumes, which in symbiosis with *Rhizobium* can reduce and assimilate atmospheric N_2, add N to the system through crop residues, roots, and root exudates. Biological nitrogen fixation, however is highly dependent on P availability (Mappaona and Kitou, 1995 - N fixing trees; Cassman et al., 1993 - soybean; Wan Othman et al., 1991 - cowpea; Robson et al., 1981 - subterranean clover; Graham and Rosas, 1979 - common bean). Therefore, P management affects not only P fertility but the potential input of N into these systems.

Soil P is supplied to plants from the native inorganic (Pi) and organic (Po) soil P reserves and fertilizer. Understanding the contributions from each of these sources to the availability of P in upland cropping systems is crucial for developing P management strategies which optimize P-use efficiency and profit.

Availability of P in Highly Weathered Soils

Parent materials are the only source of P in soils other than minimal inputs from precipitation (Smeck, 1973). Phosphorus is generally present as apatite in unweathered parent material (Stevenson, 1986). As soils weather bases and silica are leached from soils and Al and Fe oxy-hydroxides are formed allowing the formation of relatively stable Al and Fe phosphates (Hsu, 1977). Phosphorus is also leached from the soil resulting in a decline in total P over time (Smeck, 1973).

In the tropics 33% of the soils are classified as either Oxisols or Ultisols (Sanchez, 1976) which by definition have a base saturation of less than 35%. As much as 15% of tropical soils have a high P adsorption or fixation capacity (Hanson, 1992) due, in part, to the high content of Fe and Al oxides. Olsen and Watanabe (1957), for example, found in laboratory studies that weathered soils adsorbed two-fold more P than less weathered soils. Furthermore, the adsorbed P was held with five times more bonding energy by the weathered soils compared to less weathered soils indicating that the Fe and Al phosphates formed are very stable and contribute little to the plant available P pool.

Due to the decline in total P and the formation of Fe and Al oxides, the weathering process leads to P deficient soils. Ninety percent of the soils in the Amazon basin, for example, are P deficient (Cochrane and Sanchez, 1982). In cropping systems on these soils much of the P available to plants is derived from mineralized organic P.

Organic P

The only P present when a soil first begins to develop is in the inorganic form. Solubilization of primary Pi in primary minerals supports plant growth, which in turn contributes plant residues and root exudates that provide substrates for the accumulation of organic matter and Po (Walker and Syers, 1976). Therefore as soil undergoes weathering and the subsequent decline in Pi, the relative abundance of Po generally increases. In tropical soils, 60-80% of the P may be in organic form compared to 20-50% in temperate soils (Sanchez, 1976). However, there are many examples where the proportions of Po in tropical soils overlap with the range found in temperate soils (ie. Mueller-Harvey et al., 1985 - W. Africa; Neptune et al., 1975 - Brazil). Regardless of the relative proportion of Po in these soils, the reduced total P content and often high P adsorption capacity found in many highly weathered tropical soils accentuates the importance of Po as a source of P for plant growth in these soils (Duxbury et al., 1989).

Despite its importance, relatively little is known about the chemistry of Po in soil. In soils where Po has been chemically characterized approximately 40% of Po resides in unidentified organic compounds (Anderson 1980). Organic P forms which have been identified include inositol phosphates, nucleic acids, phospholipids, and trace amounts of phosphoproteins and metabolic phosphates (Stevenson, 1986). The most abundant form of Po is inositol phosphate which are esters of hexahydrohexahydroxy benzene and represent 80 to 90% of the identified Po (Stevenson, 1986).

The average soil C:N:P ratio is 140:10:1.3 (Stevenson, 1986). Sanchez (1976) suggested that a wide C:P ratio is a symptom of P deficiency. This hypothesis, however, is not widely accepted. In fact, both C:N and C:P ratios are remarkably similar in tropical soils and temperate soils although they tend to be more variable in tropical soils (Duxbury et al., 1989; Sanchez et al., 1982). The variability of C:P ratios is much greater than C:N ratios. To explain this variability, McGill and Cole (1981) suggested that the behavior of Po which is in ester form (C-O-P) will likely differ from N which is covalently bonded directly to C (C-N). Thus mineralization rates of Po and organic N may differ because of the different carbon substrates involved.

The availability of Po to plants is difficult to quantify because only a small portion of Po may be biologically active (Stewart and Tiessen, 1987) and the released $H_2PO_4^-$ may be quickly fixed into inorganic forms. The greatest effects of Po on crop fertility have been noted in the tropics (Anderson, 1980). Friend and Birch (1960) observed in some East African soils that wheat yields were better correlated with total Po content than inorganic soil P tests. In Ghana and Nigeria, Smith and Acquaye (1963) and

Omotoso (1971) reported that cocoa yields and Po levels were positively correlated. More recently, Sattel and Morris (1992) found that plant P uptake was correlated with moderately labile Po in some Sri Lankan Alfisols. Also, in a long-term field study on a Brazilian Ultisol with low P fixation capacity, Beck and Sanchez (1994) found that changes in the size of the Po pool explained 44% of the variation of Pi adsorbed to anion exchange resins in unfertilized treatments.

While these studies demonstrate the importance of Po to crop P uptake little is known about the magnitude of its contribution to P fertility and crop P uptake (Anderson, 1980).

Availability of Fertilizer P

The availability of Pi is the dominant factor controlling soil P fertility in fertilized cropping systems (Beck and Sanchez, 1995). Highly weathered soils have the capacity to adsorb large quantities of P. For example, Rajan and Fox (1972) reported that a Hawaiian Inceptisol and Oxisol adsorbed 8400 and 1240 mg P kg^{-1} six days after P was added to the soil. The effectiveness of adsorbed fertilizer P in relation to plant uptake declines with time (Barrow, 1980). Understanding the cause of declining P availability in fertilized soils is imperative for developing long-term P management strategies.

Initial rapid adsorption reactions of P to soil

When P fertilizer is applied to soil there is an initial fast adsorption reaction followed by a long-term slow reaction before reaching equilibrium. The fast reactions normally take place within a few hours to 7 days (Munns and Fox, 1976; Chen et al., 1973). The mechanism responsible for the fast reaction, based on evidence from kinetic analysis, OH^- release, infrared spectroscopy, and stereochemical calculations, is widely believed to involve ligand exchange in which $H_2PO_4^-$ or HPO_4^{-2} replace OH^- on colloidal surfaces (Goldberg and Sposito, 1985).

Slow reactions and proposed mechanisms

Subsequent slow reactions are believed to be much more important in controlling soil P availability and residual P effectiveness than the fast reactions (Munns and Fox, 1976; Agbenin and Tiessen, 1995). The mechanisms of the slow reactions are not well understood, although, many believe it to be a diffusion controlled process. Barrow (1983) suggested that solid-state diffusion (diffusion of P into mineral crystal defects) controls the slow reaction of P with soil. Based on P adsorption studies in synthetic goethite (no crystal defects) and natural goethite, Parfitt (1989) suggested either solid-state diffusion or diffusion of P into micropores between aggregated minerals. Cabrera et al. (1983) and latter Madrid and De Arambarri (1985) observed P adsorption to be much slower in lepidocrocite than goethite. In contrast to goethite, lepidocrocite consists of many small crystals which form larger aggregates with micropores between them which may have slowed adsorption rates. Further evidence of slow P diffusion in micropores is provided by Willet et al. (1988) using electron probe micro-analysis and Nye and Stauton (1994) who estimated P diffusion into soil micro-aggregates less than 212 µm.

Equilibrium in adsorption studies is not normally reached due to the short time frame of the experiments, which make it difficult to determine how long the slow reactions continue. The time required for P to reach equilibrium depends in part, on mineralogy (Parffit, 1989: Willet et al., 1988) and pH (Cabrera et al., 1981; Chen et al., 1973). In cases where equilibrium has been attained, Willet et al. (1988) found that ferrihydrite equilibrated with solution P after 260 days and with well crystallized goethite after only 3 days. Torrent et al. (1994) assumed that hematite had equilibrated with P within 75 day. Understanding the rate at which P reacts with soil minerals, however, will not necessarily explain the slow decline in plant available P under field conditions because the decline in available P may continue for many years. For example, McCollum (1991) found extractable P values declined during a 26 year period on a North Carolina Ultisol, which could not be explained by crop P removal from the soil. Likewise, Lins et al. (1985) and Smyth and Cravo (1990) reported a continuous decline in soil extractable P during a four to five year period in Brazilian Oxisols and Entisols.

The decline in available P is due, in part, to mixing, through tillage operations, and diffusion of fertilizer P in the soil profile (Williams and Simpson, 1965). Granular fertilizer is normally used so that the distribution of applied P within the soil is initially heterogeneous. While mixing may cause a decline in available P, P availability declines even when the initial P distribution is homogeneous, such as when P is applied as a powder (Parfitt et al., 1989; Terman et al., 1960) or as a solution (Barrow et al., 1977). Terman et al. (1960) found that the decline in P availability was more rapid when superphosphate was applied as a powder than as granules. Therefore, other mechanisms, in addition to mineralogy and mixing of P in soil, must also contribute to the decline in available P.

Conversion of P to less soluble (less labile) forms over time has frequently been proposed as a mechanism leading to the decline in available P. A fractionation procedure was developed by Chang and Jackson (1957) to study the distribution of P among Ca-, Al-, and Fe- associated phosphates during the soil weathering process (ie. Westin and de Britio, 1969; Williams and Walker, 1969). and the movement of residual fertilizer P among P fractions (Shelton and Coleman, 1968; Yost et al., 1981). These researchers found that residual fertilizer P associated with Al phosphates was converted to less available Fe phosphates over time. There are problems, however, interpreting results from the procedure of Chang and Jackson. Specifically, Pi may reprecipitate during the ammonium fluoride extraction and the separation of Al- and Fe- associated P is unreliable (reviewed by Olsen and Khasawneh, 1980).

Hedley et al. (1982) devised an alternative scheme aimed at quantifying labile Pi, Ca-associated Pi, Fe- and Al-associated Pi as well as labile and stable forms of Po. While this method has been used to determine the fate of residual fertilizer P in less weathered soils (Wager et al., 1986; Aulakh and Pasricha, 1991) it has not been used on highly weathered soils with high P adsorption capacities.

The role of soil aggregates in controlling P availability

Phosphorus diffusion into and out of natural soil aggregates may control the availability of fertilizer P. Although, diffusion controls the rate of P adsorption by minerals (discussed earlier), the role P diffusion into soil aggregates plays in controlling P availability has received little attention. Horn and Taubner (1989) found that the flux of K out of large aggregates was slower than out of small or crushed aggregates. This difference was attributed to longer diffusive path lengths in large aggregates. Since the diffusion of P is much slower than that for K (Barber, 1984), slow diffusion in and subsequently out of aggregates could be responsible for the decline in plant P availability observed in field studies. The small intra-aggregate diffusion coefficient reported by Nye and Stauton (1994), further supports this hypothesis.

Although, the direct effect of aggregate size on P adsorption and subsequent availability has not been studied, several investigators have observed effects of soil aggregation on the adsorption reaction. Munns and Fox (1976) and Fox and Kamprath (1970) noticed in adsorption studies that the adsorption rate was slower for soils in which the aggregates broke up slowly while being agitated on a shaker. Similarly, Barrow (1975) observed that shaking the soil, which destroys aggregates, increased the rate of the adsorption reaction compared to soils that were not agitated.

Highly weathered tropical soils frequently contain large portions of water stable aggregates due to high levels of Fe and Al oxides (Uehara and Gillman, 1981) or organic matter (Perez-Escolar and Lugo-Lopez, 1969). For example, Grohmann (1960) reported that 48 and 36% of aggregates were greater than 2 mm in diameter in a cultivated Brazilian Oxisol and Ultisol. Because of the highly aggregated nature of these soils and the slow P diffusion rates in aggregates (Nye and Stauton, 1994), the role of aggregates in controlling P availability needs to be carefully examined.

Research Objectives

The objectives of this thesis research were to first examine the role of Po in controlling P fertility and second to determine the cause of declining fertilizer P availability on a highly aggregated, high P fixing Typic Palehumult. Available P was estimated by extractable P values (Mehlich-1) and crop uptake and yield during a four year field experiment with three P input treatments and a control without P addition.

Changes in the size of the Po fraction and its distribution pools of varying lability (from the procedure of Hedley et al., 1982) were examined in relation to total soil C and N and P availability in the unfertilized control treatment.

Two approaches were used to understand the decline observed in residual P availability. First, data from the P fractionation procedure of Hedley et al. (1982) was used to monitor the fate of fertilizer P in different Pi pools to test whether the P was moving into less labile P pools as suggested by Yost et al. (1981) and Shelton and Coleman (1968). Second, the fate of applied P in aggregates was examined to test whether slow P diffusion into and subsequently out of aggregates limited plant P availability.

CHAPTER 2

ASSESSMENT OF RESIDUAL FERTILIZER PHOSPHORUS

Abstract

Knowledge of residual benefits from previously applied phosphorus (P) is crucial to maximize economic return to current P inputs. This study measured the residual benefits of P fertilizer on three crops of soybean in a maize-soybean rotation grown on an Ultisol. Residual P was the cumulative net P input from four consecutive soybean crops during a two year P build-up phase. The P inputs during the build-up phase were (kg P ha^{-1} per crop): control (0P)=no P inputs; low P (LP)=50, 35, 35, 35; moderate P (MP)=100, 70, 70, 70; and high P (HP)=300, 210, 210, 210. During the residual phase yield and P uptake in all P regimes declined with each successive crop. The relative decline was greatest in the LP regime where yield declined by 61% and P uptake by 71% between crops 4 and 8. Even with P inputs of 930 kg P ha^{-1} (HP), yield and P uptake declined by 15% and 36%, respectively over the same period. The decline in P uptake with time was not related to Mehlich-1 extractable P. Initially, optimum yields were achieved with Mehlich-1 values of 2 mg P kg^{-1}, however, HP Mehlich-1 values by crop 8 remained greater than 5 mg P kg^{-1} yet yield and P uptake declined significantly. The rapid decline in residual P benefits in this soil is in contrast to many reports of long lasting residual P benefits in highly weathered soils. Our

results suggest that frequent applications of small amounts of P may be more economical in the long-term than applying large amounts of P to this soil.

Introduction

Phosphorus deficiencies are common in highly weathered, fine-textured, sesquioxide-rich Oxisols and Ultisols that dominate upland areas in the tropics. Agricultural productivity of these soils must increase to support a rapidly growing population. However, phosphate rock is a finite, nonrenewable resource. Present world reserves indicate that there is a limited amount of phosphate rock which can be mined profitably under current economic conditions (Van Kauwenbergh, 1992). Therefore, management strategies that maximize P-use efficiency and are cost effective must be developed.

A major constraint to managing these soils is P fixation, the transformation of ortho-phosphate into less soluble forms through reactions with the soil. Current theory proposes two processes for P fixation. The first is a rapid reaction, usually reaching a steady state within a week, where P is adsorbed to the soil surfaces. The second is a slow reaction resulting in a continued, long-term decline of P in soil solution (Munns and Fox, 1976). Although the mechanism for the slow reaction is not well understood, its influence on residual P effectiveness is important in developing efficient long-term management strategies (Munns and Fox, 1976).

On a Hawaiian Oxisol, Fox et al. (1971) found maximum yields were maintained up to nine years after a single massive application of P (up to 1320 kg P ha^{-1}), suggesting large, long-term residual benefits. Their study and others on both Ultisols and Oxisols, are the basis of P management strategies that use large quantities of P to quench the fixation capacity of the soil (Sanchez and Uehara, 1980; Kamprath, 1967). Barrow (1980), however, pointed out that although yields can be sustained for several years after large P applications, it does not preclude slow reactions decreasing plant available P over time and thus reduce the residual benefit.

When measured nine years after application, McCollum (1991) found 66% of applied P had entered phosphate pools with P desorption rates that were too slow to meet plant uptake requirements on an Ultisol. In long-term studies on Brazilian Oxisols where P was added to each crop, Yost et al. (1979) and Smyth and Cravo (1990) found that relative yield and P uptake between different P input regimes remained constant over time, indicating that available P lost to adsorption was roughly equal to P added.

A key issue for improving P efficiency in highly weathered soils is whether applying large amounts of P is an efficient strategy for optimizing P uptake and crop yields. The present experiment was designed to measure the residual benefits and effectiveness of four P regimes applied to an Ultisol with high P fixation capacity described by Cassman et al. (1993). Residual P benefit was assessed in terms of crop yield and P uptake, soil test indicators of plant-available P, and the efficiency of residual P to support crop growth.

Materials and Methods

The experimental site was 320 m above sea level on the island of Maui, Hawaii. Mean annual rainfall was 1800 mm. The soil was classified as a Humoxic Tropohumult, but has since been tentatively classified (pending approval by National Resources Conservation Service) as a Haiku clay (clayey, oxidic, isohyperthermic Typic Palehumult). Initial soil characteristics are given in Table 2-1. The soil fixed large amounts of P, requiring 630 mg P kg^{-1} to raise the soil solution P level to 0.2 mg P L^{-1} using the method of Fox and Kamprath (1970).

Table 2-1. Initial soil characteristics of the Haiku clay (clayey, oxidic, isohyperthermic Typic Palehumult).

	Soil depth (cm)	
Parameter	0-25	25-50
Bulk density (g cm^{-3})	1.25	1.28
pH (1:1 soil/water)	4.8	4.6
Mehlich-1 extractable P (mg P kg^{-1})	0.9	0.6
Total carbon (g kg^{-1})	32.9	28.8
Total nitrogen (g kg^{-1})	2.5	1.8

The experiment was initiated in the fall of 1988 with a control (no P added) and three P input regimes (Table 2) applied to nodulating (NOD) and non-nodulating (NONNOD) soybean (*Glycine max* (L. Merr. cv. Clark) isolines. Treatments were arranged in a completely randomized split plot design with four replicates. Main plots were P-input regimes and subplots were NOD and NONNOD isolines. After four crops with repeated P additions (P build-up phase) the cumulative net P input (P added as fertilizer - P removed in harvested crop biomass) for each regime was -30, 99, 235, and 843 kg P ha^{-1} for the NOD isoline control (0P), low P (LP), moderate P (MP), and high P (HP) regimes, respectively (Cassman et al., 1993) (Table 2). Details of crop management and P balance in the P build-up phase are reported by Cassman et al. (1993).

Table 2-2. Phosphorus fertilizer input and cumulative net P input to eight crops: control (0P), low P (LP), moderate P (MP), and high P (HP). Cumulative net P input is the sum of the fertilizer P inputs minus P removed by the crop.

			P input/Cumulative net P input			
Crop	Season	Crop	0P	LP	MP	HP
			---------- kg P ha^{1} -----------			
1	Fall 88	Soybean	0/-6	0/40	100/86	300/283
2	Summ 89	Soybean	0/-17	0/57	70/132	210/465
3	Fall 89	Soybean	0/-23	0/81	70/187	210/658
4	Summ 90	Soybean	0/-30	0/99	70/235	210/843
5	Fall 90	Maize	0/-35	0/92	0/227	0/831
6	Summ 91	Soybean	0/-40	0/85	0/215	0/815
7	Fall 91	Maize	0/-46	0/79	0/206	0/801
8	Summ 92	Soybean	0/-50	0/73	0/198	0/785

Evaluation of the residual phase started at crop 4, the last crop in the build-up phase to receive P, and continued to crop 8 (Table 2-2). Maize was grown during the fall (crops 5 and 7) and NOD and NONNOD soybean were grown in the summer (crops 6 and 8). For the purposes of this paper, the assessment of residual P on plant parameters will include only NOD soybean summer crops (crops 4, 6, and 8) due to species and seasonal effects on yield and P uptake. The NONNOD were used to estimate biological nitrogen fixation by the N-difference method. The target seeding rate for soybean was 400,000 plants ha^{-1} planted with 60 cm between rows, but in crop 6 plant density had to be thinned to a uniform 250,000 plants ha^{-1} due to bird damage of some plots at emergence.

Lime ($Ca(OH)_2$) to maintain the soil pH at 5.5, 200 kg K, 50 kg Mg, 10 kg Zn, 0.05 kg B and 0.5 kg Mo ha^{-1} were applied and incorporated before planting the eighth crop. These rates are similar to those applied before crops 1 and 3 during the build-up phase (Cassman et al., 1993). Weeds and pests were controlled as needed and irrigation was applied through surface drip irrigation. Solar radiation, temperature, and rainfall were recorded at 30 minute intervals using a CR-21 micrologger (Campbell Scientific, Inc., Logan, Utah).

Soybean was harvested at maturity from 2 m of the inner three rows of each 3 m X 5 m plot for yield determination. Following harvest all above ground biomass was removed from plots. Dried tissue samples (70°C) were analyzed for N using a C-H-N analyzer (LECO CHN-600) and P following Kjeldahl digestion (Throneberry, 1974) and colorimetric analysis (Murphy and Riley, 1962).

Ten soil cores were taken from each plot from 0-25 and 25-50 cm. Soils were air-dried, passed through a 2-mm sieve, and analyzed for P using the Mehlich-1 extractant (0.05 M HCl + 0.0125 M H_2SO_4, 1:10 soil/solution, 5-minute shaking) (NOTE:

this is the same as the double-acid method used by Cassman et al. (1993)). Adsorption isotherms using a wet/dry cycle followed by the Mehlich-1 extraction were performed on surface soils in all P regimes from crops 1, 4, and 8 to determine the relationship between added and extractable P (Cassman et al. 1993).

Statistical analysis was performed using a split-plot design with P regimes as main plots and crops as repeated measure subplots (Little and Hills, 1975). Relative dry matter yield of P regimes was compared to Mehlich-1 values for crops 1, 4 and 8. Relative yield was calculated using the mean HP yield of crops 1 and 3 (Fall crops) as a base for crop 1 and the mean yield of crops 2 and 4 (Summer crops) for crops 4 and 8. Estimates of yield potential by the CROPGRO simulation model (Jones et al., 1989) using weather data collected at the experiment indicated differences only between Fall and Summer seasons and not between crops planted in the same season.

Results and Discussion

Yield and P uptake

Growth conditions were similar for all summer crops during the residual phase (Table 2-3). Mean daily total solar radiation averaged 22.2 MJ m^{-2}. Based on the CROPGRO simulation model (Jones et al., 1989) using soil and weather data taken during the experiment, maximum potential dry matter yields were the same for summer crops 2, 4, and 8. Maximum potential yield for crop 6 was 13% less than the other summer crops.

Maximum dry matter yields, in excess of 6000 kg ha^{-1}, were attained in both summer crops (crops 2 and 4) during the P build-up phase (Cassman et al., 1993). Dry matter yields of soybean during the residual phase are plotted against the cumulative net P input (Fig. 2-1). Crop 4 dry matter yields in the LP and MP regimes were 84 and 94% of the maximum yield in the HP regime, respectively. Despite large cumulative net P inputs in the MP regime (Table 2-2), dry matter yields of crops 6 and 8 were 70% and 58% of crop 4 yields. Seed yield, dry matter yield, P uptake, and plant P concentration declined with each successive cropping season in all P regimes with the exception of crop 6 yields in the HP regime (Table 2-4). Low planting density and weather conditions most

Table 2-3. Planting and harvest dates, solar radiation, and total rainfall for each summer soybean crop during the residual phase of the experiment.

	4	6	8
Parameter	1990	1991	1992
Planting date	30 May	13 June	18 May
Harvest date	8 Sept	19 Sept	17 Aug
Mean daily total solar radiation (MJ/m^2)	21.8+/-4.0†	21.7+/-4.6	23.1+/-5.0
Total rainfall (mm)	433	474	535

† +/- standard deviation

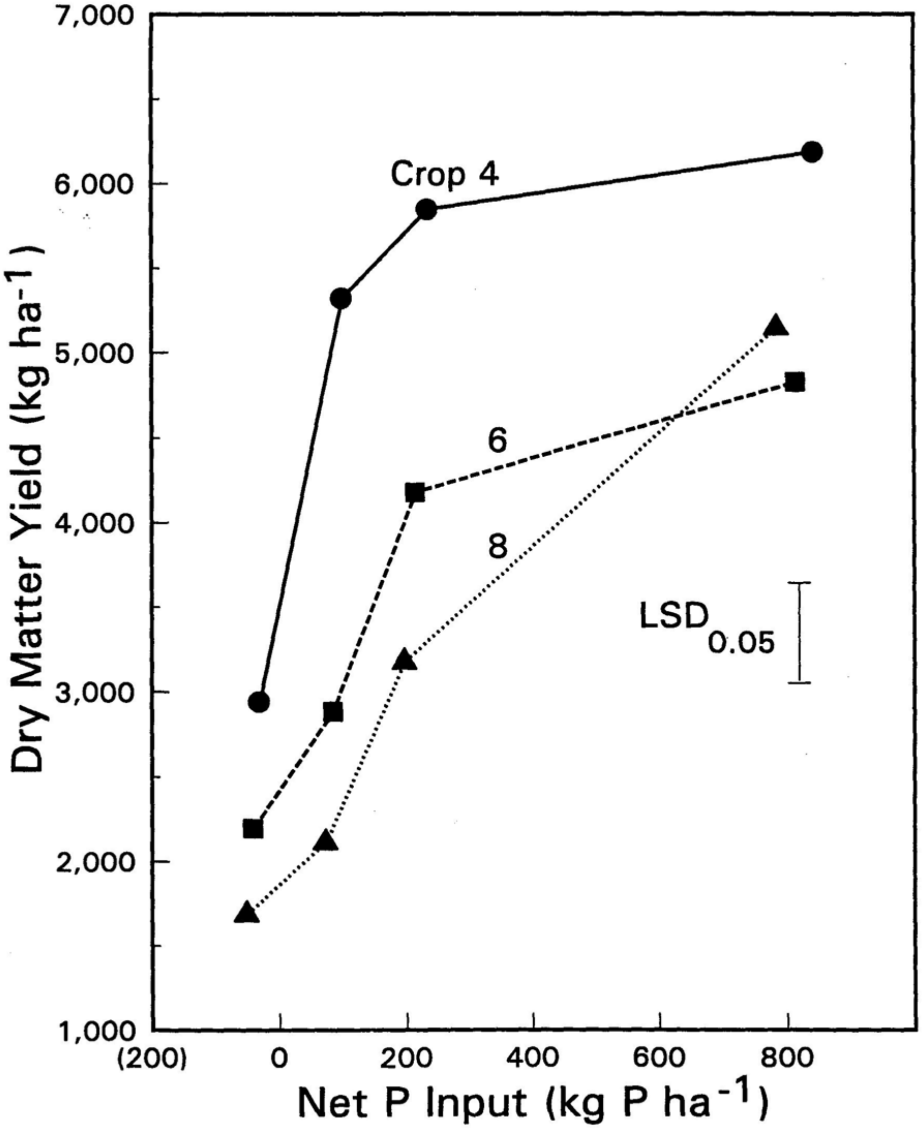

Fig. 2-1. Dry matter yield for crops 4, 6, and 8, as a function of net P input (P added as fertilizer - P removed by crop). The error bar represents the LSD (P=0.05) between different crop yields for the same P input regime.

Table 2-4. Soybean grain and dry matter yield (DMY), whole plant P concentration, P and N uptake, and N$_2$ fixation for crops 4, 6 and 8.

P regime	Crop	df	Grain Yield	DMY	Plant P	Total P	Total N	N$_2$ Fixed
			--kg ha^{-1}---		g kg^{-1}	-------kg ha^{-1}------		
0P	4		1847	2942	2.4	7	130	90
	6		1444	2196	2.5	5	104	75
	8		1047	1686	2.5	4	74	30
LP	4		3389	5326	3.1	17	233	186
	6		1894	2885	2.6	8	133	101
	8		1320	2114	2.5	5	93	43
MP	4		3638	5850	3.7	22	253	205
	6		2677	4182	2.8	12	188	152
	8		1979	3178	2.6	8	137	82
HP	4		3714	6187	4.1	25	260	214
	6		2912	4833	3.5	17	210	176
	8		3174	5153	3.2	16	222	172
			Analysis of Variance Mean Squares					
			X10^{4}	X10^{4}	X10^{-4}	X10^{-1}	X10	X10
P regime		3	678 ***	1966 ***	2301 ***	3761 ***	3324 ***	2948 ***
Error A		9	13	31	40	39	77	83
Crop		2	619 ***	1652 ***	1535 ***	3288 ***	2907 ***	3079 ***
P regime X Crop		6	60 **	130 **	279 ***	242 ***	274 **	275 ***
Error B		23	10	20	22	19	43	41

† OP, LP, MP, and HP had received a net of -30, 99, 235 and 843 kg P ha^{-1} by the beginning of the residual phase (crop 4). There was no further P application made after crop 4.

‡ N$_2$ fixed was estimated using the difference method (total N in nodulating isoline - total N in non-nodulating isoline).
, * indicate significance at .001 and .0001 level.

likely contributed to lower crop 6 yields in the HP regime. Yield declines were significant and were correlated with declining total P uptake and plant P concentration (Table 2-4). The regression between dry matter yield (Y) on plant P concentration (X) for the three P input regimes for all residual-phase crops was:

$$Y = -28861 + 18447X - 2425X^2 \quad (r^2 = 0.96).$$

Based on the above relationship between yield and plant P concentration, crop 6 yields in the HP regime should have been 5997 kg ha^{-1}.

The influence of time on residual P availability was relatively greater in the LP regime where dry matter yield and P uptake declined by 61 and 71%, respectively from crop 4 to crop 8. Despite a cumulative net input of 843 P ha^{-1} in the HP regime at crop 4 there was a 15% reduction in dry matter yield and a 36% reduction in P uptake by crop 8 (Fig. 2-1) and Table 2-4). A large residual benefit from previously applied P was still evident by crop 8, however; dry matter yield in the HP regime was more than 300 kg ha $^{-1}$ greater than in the LP regime.

These results are in contrast to other studies on high P fixing soils. For instance, applications of 1320 kg P ha^{-1} to an Oxisol (Fox et al., 1971) and 680 kg P ha^{-1} to an Ultisol (Kamprath, 1967) maintained yields for nine years. The Ultisol (Kamprath, 1967) had a lower P buffer capacity than this Haiku clay and required only 275 mg P kg^{-1} soil to raise soil solution P to 0.2 mg P L^{-1} (Fox and Kamprath, 1970), which may explain the higher residual P benefits. The Oxisol (Fox et al., 1971), however, had a higher buffering capacity than the soil used in this study (over 1000 mg P kg^{-1} soil to raise the solution P to 0.2 mg P L^{-1}). Longer lasting residual benefits may be due to the larger single P application compared to the incremental P additions made over the two year period in this study. Differences in soil physical properties may also play a role in the extent of residual benefits (Chapter 4).

Biological N fixation was dependent on P uptake (Table 2-4). Di-nitrogen fixation declined in each successive crop due to declining available P. Cassman et al. (1993) established a significant linear relationship indicating 8 kg N derived from N_2 fixation per kg P uptake in the soybean crop at physiological maturity. This relationship agrees well with data from the residual phase.

Extractable P

Mehlich-1 extractable P in each P input regime declined rapidly during the first year of the residual phase, approaching more stable values by crop 8 (Fig. 2-2) similar to results of Lins et al. (1985) and Smyth and Cravo (1990). Between crops 4 and 8, extractable P declined by 15, 40, 44, and 50%, respectively, for P0, LP, MP, and HP. By cycle 8 there were still differences in extractable P between P regimes.

Phosphorus adsorption isotherm equations are presented

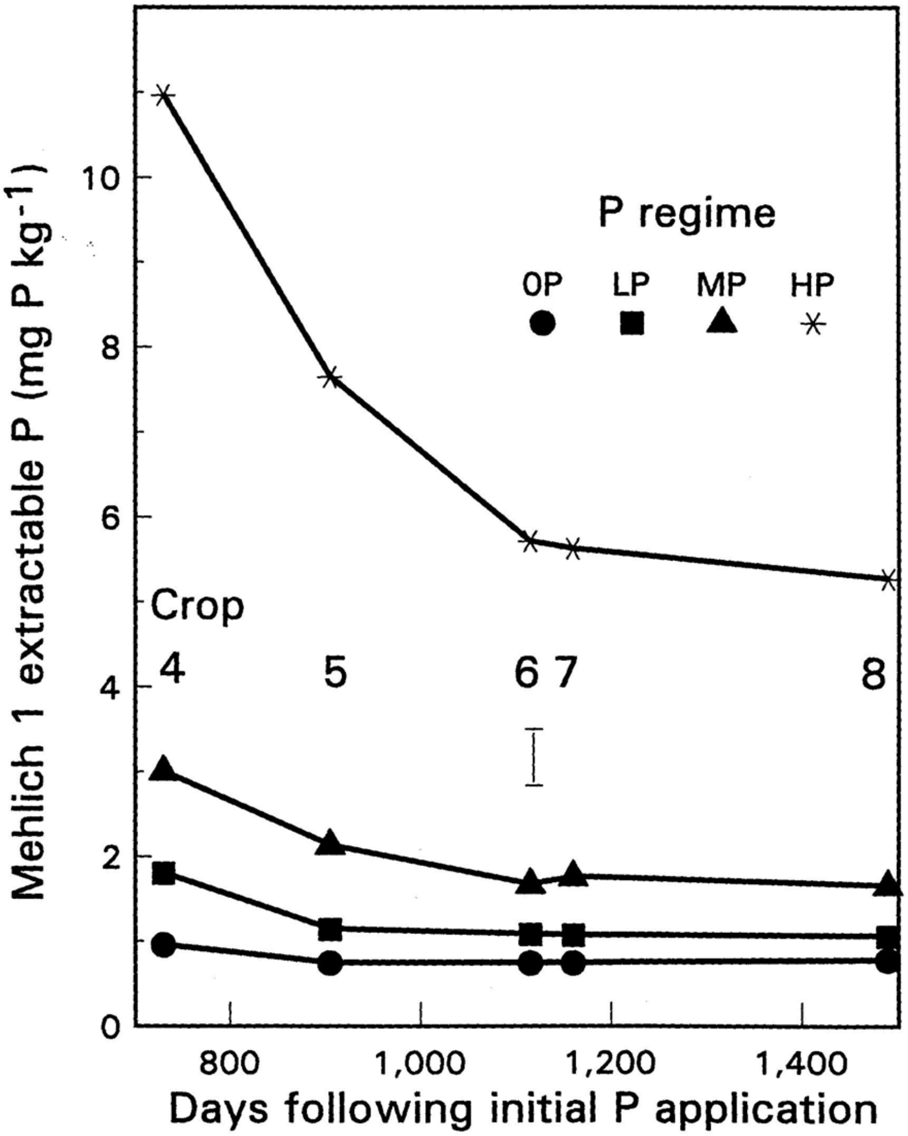

Fig. 2-2. Mehlich-1 extractable P (0-25 cm) during the residual phase of the experiment (crops 4 to 8). The error bar represents the LSD (P=0.05) between P regimes.

in Table 2-5. The coefficients are derived by fitting data to the equation:

$$P_{ext} = a + (b_1)P_{apl} + (b_2)P_{apl}^2 \qquad (1)$$

where P_{ext}, P_{apl} and a are extractable P (mg P L^{-1}), applied P (mg P kg^{-1} soil) and the intercept, respectively, and b_1 and b_2 are linear and quadratic coefficients. The linear buffer coefficient (b_1) increases between crops 1 and 4 indicating a lower P input requirement to obtain a given level of extractable P. During the residual phase, however, b_1 declines, indicating declining P availability and increased buffer capacity.

Table 2-5. Linear and quadratic buffer coefficients† developed from P adsorption isotherms of soil sampled during crops 1, 4, and 8 for each of the P regimes.

P Regime‡	Crop	Initial P (a)	Buffer Coefficients§ b_1	b_2
		mg kg^{-1} soil		
0P	1	0.91	0.038	0.000085
	8	0.87	0.037	0.000067
LP	1	1.05	0.039	0.000076
	4	1.67	0.043	0.000059
	8	1.17	0.038	0.000068
MP	1	1.50	0.042	0.000073
	4	2.56	0.046	0.000057
	8	1.77	0.042	0.000061
HP	1	2.87	0.052	0.000052
	4	7.91	0.062	0.000042
	8	5.10	0.057	0.000048

† Coefficients derived by fitting data to $P_{ext} = a + (b_1)P_{apl} + (b_2)P_{apl}^2$ where P_{ext} = extractable P (Mehlich-1); a = intercept or extractable P with no additional P added; P_{apl} = applied P (mg P kg^{-1} soil).

‡ P regimes were 0P to which P was never added and LP, MP, and HP to which a cumulative of 155, 310 and 930 kg P ha^{-1} added during the build-up phase (crops 1 to 4). The residual phase (crops 5 to 8) never received any P fertilizer.

§ r^2 on all above regression equations was greater than 0.999.

In the 0 to 25 cm layer, decreases in soil P test values result from crop removal of P, conversion of P to less soluble forms, and downward movement of P in the soil profile. Downward movement of P was negligible as extractable P values did not increase measurably in the 25 to 50 cm soil layer after eight crops (data not shown). Moreover, little P movement would be expected in a soil with such high P fixation capacity. Presumably, crop removal of P accounted for most of the decline in extractable P for the P0 regime in which extractable P declined from 0.90 mg P kg^{-1} in crop 4 to 0.79 mg P kg^{-1} by crop 8.

To separate the effects of P removed by the crop from those of P reactions with the soil, extractable P was plotted against the cumulative net P input (Fig. 2-3). If crop removal was the only factor influencing extractable P, then a single line would explain the relationship between extractable P and the cumulative net P input. This data demonstrate that the relationship shifts over time. Although, the regression of extractable P on cumulative net P input was linear and highly significant for each crop, with time there was a significant linear decrease in the slope of each regression (change in extractable P per unit net-P input) (Fig. 2-3 insert). For example, the marginal increase in Mehlich-1 P levels to cumulative net P input for cycle 8 was

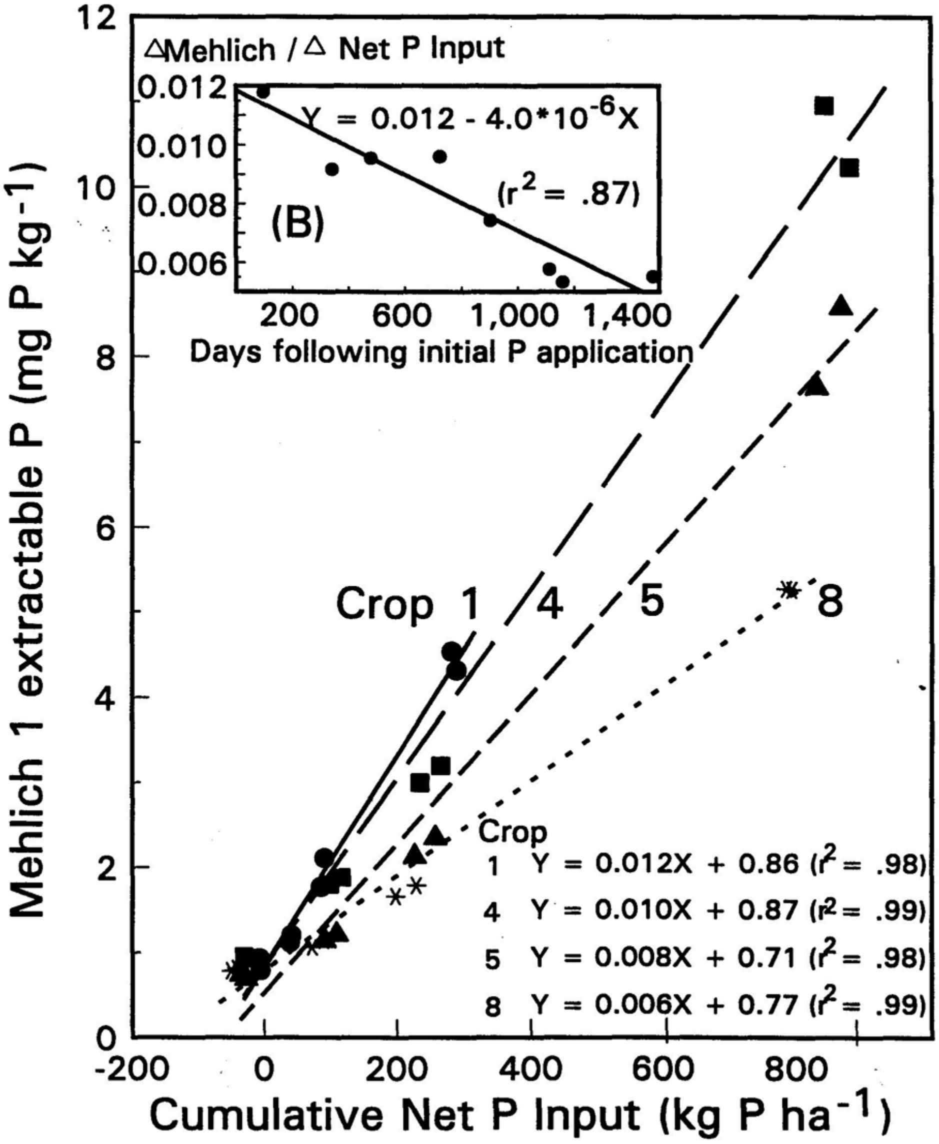

Fig. 2-3. Regression of Mehlich-1 extractable P from crops 1, 4, 5, and 8 on net P input to the soil (P added as fertilizer - P removed by crop). Insert: The regression of slope coefficients in Fig. 3 on days after initial P application for all eight crops in both the P build-up and residual phases.

half the value at cycle 1. This shift over time is consistent with the findings by Yost et al. (1981) and McCollum (1991) who claimed the main mechanism of declining extractable P in this type of soil is due to a slow conversion to less soluble forms.

Critical values of extractable P

The critical value of Mehlich-1 extractable P required to maintain optimum soybean yields shifted over time (Fig. 2-4). Initially (crop 1), 95% of the maximum yield was achieved with a Mehlich extractable P value of approximately 2.0 mg P kg^{-1} (MP regime). By crop 4, the value required for 95% maximum yield had more than doubled and by crop 8, even with an extractable P value of 5.5 only 83% of maximum yield was achieved. Mehlich-1 was also very insensitive in the critical range. For example, in crop 1 a small change in extractable P from 0.95 to 1.8 mg P kg^{-1} soil increased relative yields from 0.54 to almost 1.0.

Yost et al. (1981) and Smyth and Cravo (1990) reported that Mehlich-1 was an effective extractant for predicting crop response to both recently applied and residual fertilizer P in Brazilian Oxisols. In contrast, these results indicate that the Mehlich-1 was not an accurate measure of plant available P for either P build-up or residual phases. Other common soil tests such as Olsen P (Olsen et al., 1954) were no better at predicting crop response to P (data not shown). I suggest that soil physical properties such as soil

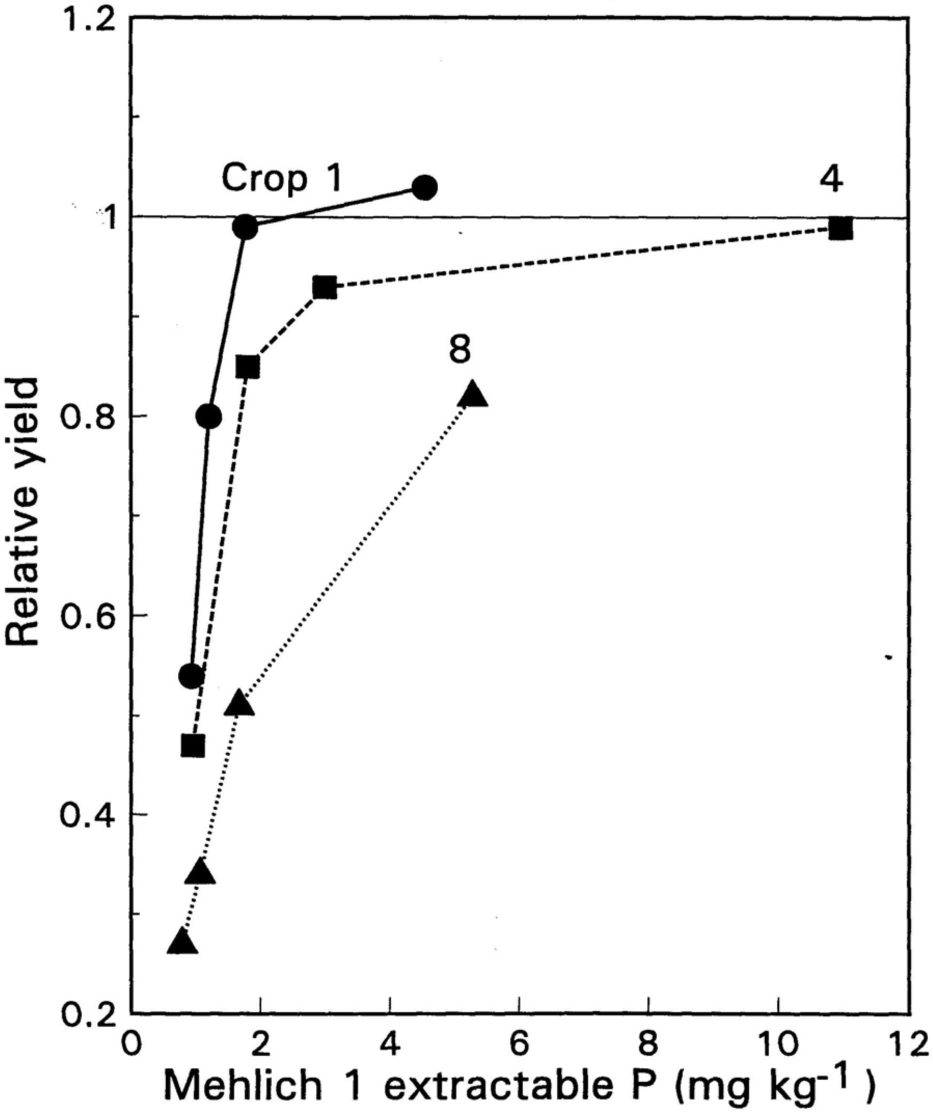

Fig. 2-4. Relative soybean yield of crops 1, 4, and 8 as a function of Mehlich-1 extractable P. Relative yields are based on the mean yield of Fall (for crop 1) and Summer crops (for crop 4 and 8) during the P build-up phase.

aggregation, which is destroyed in these tests, may play a role in the bio-availability of applied P (Chapter 4).

Effectiveness of residual P

Although there is a positive crop yield and P uptake response to previously applied P (Fig. 2-1, Table 2-4), assessing the effectiveness of previously applied P is important to develop improved long-term P management strategies. Two methods were used to evaluate residual P value. First, Fox and Kamprath (1970) defined residual P efficiency as:

$$\text{Residual P efficiency} = (P_o - P_x) / \text{Net P input} \quad (2)$$

where P_o is the P input required to raise the initial soil P solution equilibrium to a specific target value and P_x is the P input required to raise the soil solution equilibrium to the same value after X years. These P adsorption isotherms differed from those of Fox and Kamprath (1970) in that I used Mehlich-1 instead of soil solution P and my incubation protocol included a wet/dry cycle prior to extraction (Cassman et al., 1993). Six mg P kg^{-1} soil was selected as the target extractable P value because by crop 8 this approximated the extractable P value required for maximum yields (Fig. 2-4).

Residual P efficiency at crop 8 is presented for the different P regimes in Table 6. Increasing P inputs decreased soil P fixation capacity as expected (Sanchez and Uehara, 1980); the P input required to raise extractable P to 6 mg P kg^{-1} soil in crop 8 declined with every increase of P input. Residual P efficiency increased with increasing P input levels. Others (Fox and Kamprath, 1970; Yost et al., 1981) have found that efficiency decreased with increasing inputs, which is not consistent with results from measures of P buffering capacity which declines with increasing P input and should make P more available.

Table 2-6. Residual P efficiency, according to Fox and Kamprath (1970), at crop 8 for each P regime calculated from P adsorption isotherms using Mehlich-1 extractant after a wet/dry soil incubation.

P regime	Total P applied	Cumulative net P input†	P required to extract 6 mg P kg^{-1} (P_x)	Residual P efficiency‡	Not recovered P§
	--------kg P ha^{-1}--------			%	kg ha^{-1}
LP	155	73	334	5	69
MP	310	198	278	30	138
HP	930	785	47	37	494

† Cumulative net P input = Total P applied - P removed by crop (see Table 2).

‡ Residual efficiency = $\frac{P_o - P_x}{\text{Net P input}}$ X 100

where

P_o = P required initially (crop 1) to raise Mehlich-1 to 6 mg P kg^{-1} soil (P_o = 338 kg P ha^{-1}) and;

P_x = P required after X years to raise Mehlich-1 to 6 mg P kg^{-1} soil. This value is based on data from adsorption isotherms (Table 5). Soil bulk density was 1.25 g cm^{-3} to a depth of 25 cm.

§ Not recovered P = Net P input - (P_o - P_x)

The amount of unrecovered P (extractable P lost to insoluble P pools) can be estimated using the same assumptions (Table 2-6). Approximately 50% of the total P added in each P input regime was lost to insoluble forms. Given the loss of 494 kg P ha^{-1} to insoluble P pools and declining yields and P availability in the HP regime, a more efficient management strategy for this soil would be to apply small amounts of P to each crop, similar to the LP or MP regimes. By applying P in small increments (Cassman et al., 1993) the cumulative amount of P applied in HP regime could support optimum yields for 13 and 26 crops, respectively.

A second approach to evaluate residual P efficiency is to compare the current effect of P fertilizer or residual P input with the original effect after adjusting for seasonal differences (Arndt and McIntyre, 1963). Barrow (1980) defined this measurement as the relative effectiveness of residual P. For my purposes, since only the summer crops were evaluated and seasonal differences between crops was small (crops were irrigated and mean daily solar radiation were similar for all summer crops), no adjustments to yield or P uptake were made. Although Barrow (1980) only calculated relative effectiveness of residual P for yield and P uptake, the same concept was extended to extractable P and the linear buffer coefficient (b_1 from equation 1) derived from P adsorption isotherms (Table 2-5).

Dry matter yield, P uptake, extractable P, and the linear buffer coefficient during the residual phase were compared with the initial values in the 0P regime (Table 2-7). Initial values of dry matter yield (2009 kg ha^{-1}) and P uptake (6 kg ha^{-1}) were from 0P regime in the first summer crop (crop 2) (Cassman et al., 1993). Initial values for extractable P (0.9 mg P kg^{-1}) and the linear buffer coefficient (b_1) (0.038) were from the 0P regime crop 1. Values greater than one indicate lasting effectiveness of residual P.

Table 2-7. Relative effectiveness† of residual P on dry matter yield (DMY), P uptake, buffer coefficients (b_1), and Mehlich-1 extractable P. Values are relative to initial values‡ for the control (0P).

P Regime	Crop	DMY	P Uptake	Buffer Coef.(b_1)	Mehlich
0P	4	0.76	0.64	-	0.97
	6	0.56	0.49	-	0.76
	8	0.43	0.39	1.00	0.77
LP	4	1.37	1.55	1.05	1.77
	6	0.74	0.68	-	1.10
	8	0.54	0.49	1.00	1.04
MP	4	1.50	2.00	1.21	2.77
	6	1.07	1.08	-	1.70
	8	0.82	0.76	1.11	1.67
HP	4	1.59	2.27	1.63	9.28
	6	1.24	1.52	-	5.72
	8	1.32	1.49	1.50	5.24

† Relative effectiveness of residual P calculated as the ratio of current value of yield or soil test value to the value of 0P at crop 2 or 1, respectively.

‡ Initial values for dry matter yield (3896 kg ha^{-1}) and P uptake (6 kg ha^{-1}) are from 0P regime in the first summer crop (Cassman et al. 1993) and crop 1 0P for the buffer coefficient (0.038) and Mehlich-1 (0.91 mg P kg^{-1}).

In crop 4, residual effectiveness values of all P regimes with a P input were greater than one, as would be expected since this was the last cycle of the build up phase. By cycle 8, dry matter yield and P uptake in the LP and MP regimes, where net P input was 73 and 198 kg ha^{-1}, were less than one indicating no residual effectiveness. The two soil indices of P availability (extractable P and b_1), however, were greater than one throughout the residual phase. This dichotomy indicates that measures of soil P availability over time did not accurately reflect plant available P in this field soil.

Summary and Conclusions

Phosphate management recommendations for high P fixing soils are often made assuming that applied P represents a long-term investment which can be amortized over several cropping cycles. The validity of this assumption requires that applied P remain available over time. Although some studies have demonstrated a long-lasting residual benefit from large P additions, the cost-effectiveness of this P input strategy must be considered relative to the other strategies where small amounts of P are applied to each crop cycle.

These results demonstrate that despite residual benefits, detectable in terms of soil test values and crop response, for up to two years following the P application there is a rapid loss in the effectiveness of applied P. For soils similar to the strongly aggregated Ultisol in this study, applying P in large amounts to quench the fixation capacity of the soil may not be the most cost effective strategy. Instead, it is possible to sustain soybean yields at 84 and 95% of maximum with annual applications of as little as 35 and 70 kg P ha^{-1}, respectively. This strategy also results in small cumulative benefits from year to year that improve both agronomic and P uptake efficiency (Cassman et al., 1993).

Although there was a rapid decline in yield and P uptake after P additions ceased, there was not a concomitant decline in extractable P. As a consequence, the Mehlich-1 extraction method did not produce values indicative of the plant available P and the critical extractable P value for maximum yield shifted upward. Two possible hypothesis may explain this and will be addressed in following papers. First, P uptake may be better correlated with some other more labile soil P pools than Mehlich-1 extractable P. Second, due to the slow diffusion rates and rapid fixation of P in these soils, soil aggregation, which is destroyed in current P extraction methods, may play an important role in governing the short- and long-term contribution of applied P to the plant-available P pools. These two hypotheses will be tested in later chapters (Chapter 3 and 4).

CHAPTER 3

INORGANIC AND ORGANIC PHOSPHORUS DYNAMICS DURING A BUILD-UP AND DECLINE OF AVAILABLE PHOSPHORUS

Abstract

Development of efficient, cost effective P management strategies for highly weathered tropical soils is limited by our understanding of the fate of added fertilizer P and the availability of organic P. A sequential P fractionation procedure (extraction with Fe oxide impregnated filter paper (FeO), 0.5 M $NaHCO_3$, 0.1 M NaOH, 1.0 M HCl, concentrated HCl, and H_2SO_4 digestion) was used to measure progressively less labile inorganic (Pi) and organic (Po) P fractions. The soil, a Typic Palehumult with a high P fixation capacity, was sampled during a four year field experiment with three fertilizer P input treatments and a control. Approximately 8.5, 55, and 37% of the added fertilizer P was recovered from labile (FeO and $NaHCO_3$ Pi), moderately labile (NaOH Pi) and recalcitrant (Conc. HCl Pi and H_2SO_4 P) pools, respectively, 104 days after P fertilizer application. Subsequently, fertilizer P distribution among pools changed little after 104 days. The decline in plant available P after P additions ceased was, therefore, not due to conversion of P to less labile Pi forms. Total Po was 18% of total P and remained constant over time, however, $NaHCO_3$ Po declined at the same rate as soil organic C and total N. All the labile Pi pools were highly correlated with Mehlich-1 and Olsen extractable P

but not with soybean (*Glycine max*) yield. In the unfertilized control, $NaHCO_3$ Po was correlated with labile Pi and soybean yield and P uptake indicating that in unfertilized systems mineralized Po is an important source of plant P.

Introduction

Phosphorus deficiency is a major constraint to crop production on highly weathered acid soils. Efficient, cost effective P management strategies must be developed for these soils, particularly because they dominate the upland tropics where farmers are generally poor. In order to develop efficient P management strategies we must understand the availability of P from inorganic (Pi) and organic (Po) pools and the long-term fate and availability of applied P fertilizer.

As soils weather, bases and silica are lost and Al and Fe oxy-hydroxides are generated, allowing the formation of secondary Al or Fe phosphates (Hsu, 1977). These phosphates generally have low solubility, therefore, the relative significance of Po as a nutrient source generally increases as soils weather (Duxbury et al., 1989; McGill and Cole, 1981). Despite the putative importance of Po in highly weathered soils, few studies have demonstrated a direct relationship between Po mineralization and plant P uptake. Some early studies from Africa report good correlation between wheat (Friend and Birch, 1960) or cocoa (Smith and Acquaye, 1963; Omotoso, 1971) yields and total Po. More recently, several researchers have found that most of the variability in labile Pi can be explained by changes in labile Po in Ultisols (Tiessen et al., 1984; Beck and Sanchez, 1994). These studies suggest that in unfertilized cropping systems Po mineralization is a major source of P assimilated by plants, however, much is still to be learned of the magnitude of its contribution.

In fertilized systems P fertilizer inputs generally exceed crop P uptake causing P to accumulate in soil over time. This is especially true for highly weathered soils, which, due to high amounts of Al and Fe oxides, have high P adsorption capacities. The availability of this residual P is not well understood. For example, in some cases maximum yields were sustained for up to nine years following large initial P applications (Fox et al., 1971; Kamprath, 1967) while I reported (Chapter 2) declining plant P availability one year following a large P application of similar magnitude.

Many soil tests do not account for less available P and Po pools which are in equilibrium with labile Pi pools (Kamprath and Watson, 1980). This may explain why Mehlich-1 extractable P, a commonly used extractant for highly weathered soils, was a poor predictor of residual P availability (Chapter 2). Wager et al. (1986) proposed using the sequential P fractionation procedure of Hedley et al. (1982) to more completely assess the fate and availability of residual fertilizer P. This method uses increasingly stronger extractants to recover progressively less labile P. Highly available Pi is extracted using anion exchange resins while Pi and Po extracted by $NaHCO_3$ represent labile P pools (Bowman and Cole, 1978). Sodium hydroxide extractable Pi and Po represent moderately labile P pools (Tiessen et al., 1984;

Sattel and Morris, 1992), and 1.0 M HCl solubilizes mostly Ca-bound Pi (Williams et al., 1980). Finally, H_2SO_4 P is highly recalcitrant Pi and Po recovered with a concentrated H_2SO_4 digest.

While the Hedley et al. (1982) fractionation procedure has been used to study the fate of residual fertilizer P in soils with low P adsorption capacities (Aulakh and Pasricha, 1991; Wagger et al., 1986) little work has been done on soils with high P adsorption capacities. My objective was to use this procedure to (i) study the fate of residual P over time on a soil with a high P adsorption capacity, (ii) assess the contribution of Po mineralization to plant P uptake and yield, and (iii) test whether labile P fractions were better indices of yield than the Mehlich-1 soil test.

Materials and Methods

The experimental site is 320 m above sea level on the island of Maui, Hawaii (20°54'N, 156°18'W). The soil is classified as a Haiku clay (clayey, oxidic, isohyperthermic Typic Palehumult) weathered from basic igneous rock and volcanic ash. Prior to the experiment, the site was an unfertilized pasture since the early 1940's. Initial characteristics of the surface soil (0-25 cm) were: clay content 60%, pH 4.8 (1:1 soil/water), bulk density 1.25 g cm^{-3}, 32.9 g kg^{-1} organic carbon, and 2.5 g kg^{-1} total N. The soil has a high P-fixation capacity, requiring addition of 630 mg P kg^{-1} to raise the soil solution to 0.2 mg P kg^{-1} (Cassman et al., 1981).

Table 3-1. Phosphorus applications to eight cropping cycles: control (0P), low P (LP), moderate P (MP), and high P (HP).

			P input			
Crop	Season	Crop	0P	LP	MP	HP
			----------kg P ha^{-1}----------			
1	Fall 88	Soybean	0	50	100	300
2	Summer 89	Soybean	0	35	70	210
3	Fall 89	Soybean	0	35	70	210
4	Summer 90	Soybean	0	35	70	210
5	Fall 90	Maize	0	0	0	0
6	Summer 91	Soybean	0	0	0	0
7	Fall 91	Maize	0	0	0	0
8	Summer 92	Soybean	0	0	0	0

The field experiment was initiated in the fall of 1988. Four P treatments were arranged in a completely randomized block design with four replicates. Two crops were grown each year, one in the summer and other in the fall (Table 3-1). The experiment consisted of a build-up phase (crops 1 to 4) when fertilizer P (treble super phosphate) was added to each crop approximately two months before planting and a residual phase (crops 5 to 8) in which no additional P was applied (Table 3-1). During the build-up phase, P inputs in each of the three input treatments (LP, MP, and HP) exceeded that removed by the crop resulting in a build up of soil P. The effectiveness of this residue P was measured during the residual phase. Lime ($Ca(OH)_2$) was applied before crops 1, 3 and 8 to maintain the soil pH at 5.5 and other nutrients were provided as needed to ensure that only P was limiting. Further experimental and management details as well as dry matter yield (DMY) and total plant P uptake for each crop are reported elsewhere (Cassman et al., 1993; Chapter 2).

Soil samples from 0 to 25 and 25 to 50 cm depths were taken at the R5 growth stage of soybean and after tillage but immediately before planting maize. Soil samples were air dried and passed through a 2 mm screen. Mehlich-1 extractable P (0.05 M HCl + 0.0125 M H_2SO_4, 1:10 soil/solution, 5 minute shaking) was measured for soil samples from each plot and Olsen P (Olsen et al,, 1954) on a composite of replicate soil samples from each P treatment. Only soil analysis data from the 0-25 cm depth will be presented since there was no measurable downward movement of P below 25 cm. Total soil C and N were measured using a LECO CHN analyzer after removing gross organic matter and grinding the soil to pass a 0.15 mm screen.

Changes in Pi and Po (0 to 25 cm) over four yr were measured with a modification of the sequential P fractionation scheme of Hedley et al. (1982) (Fig. 3-1). Iron oxide-impregnated filter paper strips (FeO) were used for the first extraction (Menon et al., 1990) instead of anion exchange resins. Sharpley (1991) found that the P extracted by FeO, closely approximated P extracted by anion exchange resins, which extracts primarily physically bound P rather than P compounds of amorphous Al, Fe or Ca. A concentrated HCl extraction was also included to better understand the nature of the more recalcitrant P pool (Tiessen and Moir, 1993). A separate total P analysis, using H_2SO_4 and H_2O_2

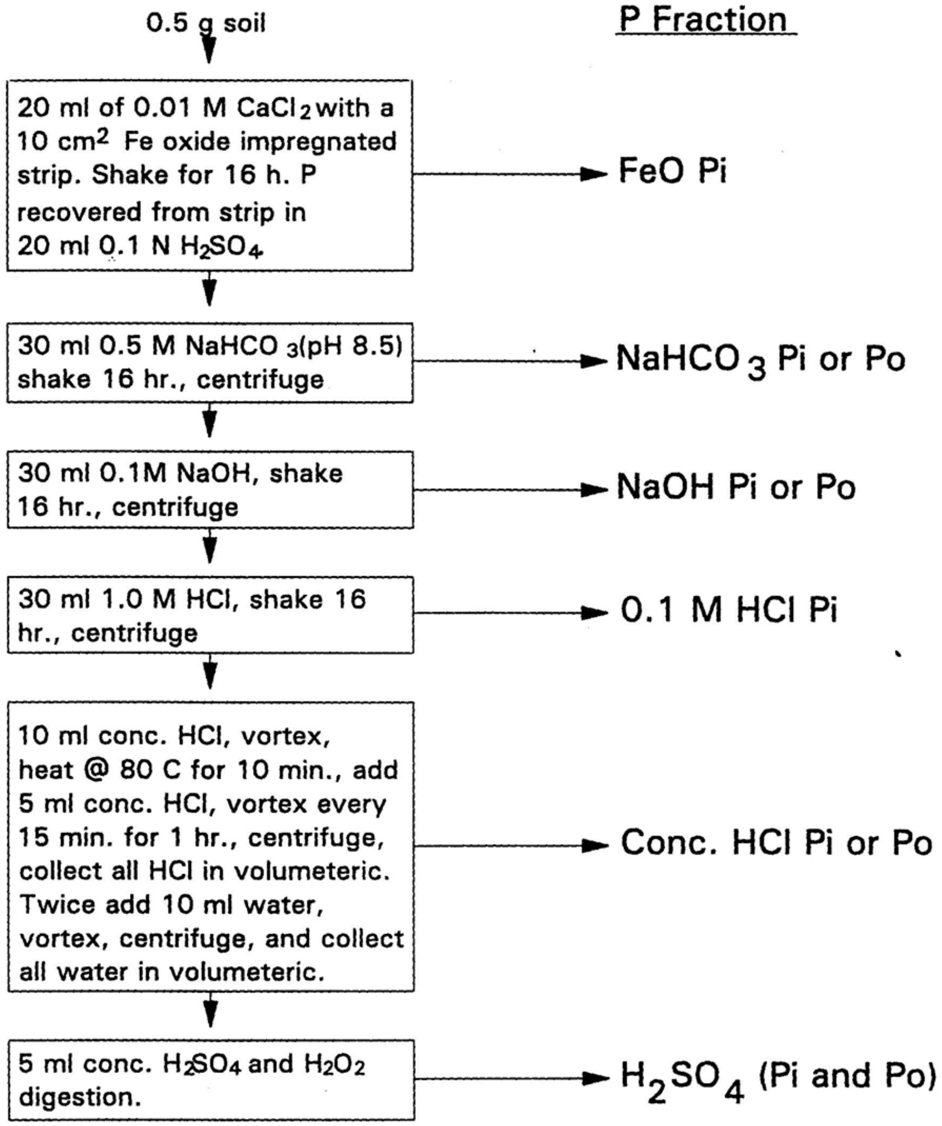

Fig. 3-1. Modified sequential P fractionation procedure (Hedley et al., 1982) and fraction designations.

digestion, was done to verify that the total P in this extraction was equal to the sum of all measured P pools. The fractionation scheme was performed in duplicate on a composite soil sample from each P treatment. To estimate variance, all four replicates of each P treatment were analyzed for soil samples taken at crop 4.

Relationships among measured values of labile Pi and Po, Mehlich-1 P, Olsen P, and P uptake and DMY were determined in the unfertilized control (0P) using PROC CORR (SAS Institute, 1985). Correlations including P uptake or DMY, used only data from the summer soybean crops (crops 2, 4, 6 and 8) so that differences were not confounded by differences due to season or crop species. Correlations between soil variables included samples from all eight crops.

Results and Discussion

Total soil P

Total soil P (sum of all individual P pools) was initially 1780 mg P kg^{-1} soil in the control (OP) treatment (Fig. 3-2). Of the total P in the control, 69% was inorganic, 18% organic, and 12% H_2SO_4 P (highly recalcitrant Pi and Po). Despite the large amount of P in this soil, P availability severely limited soybean DMY and P uptake (Cassman et al., 1993; Chapter 2).

With additions of P fertilizer, total soil P increased during the build-up phase due to P inputs exceeding P removal and declined during the residual phase due to crop P uptake

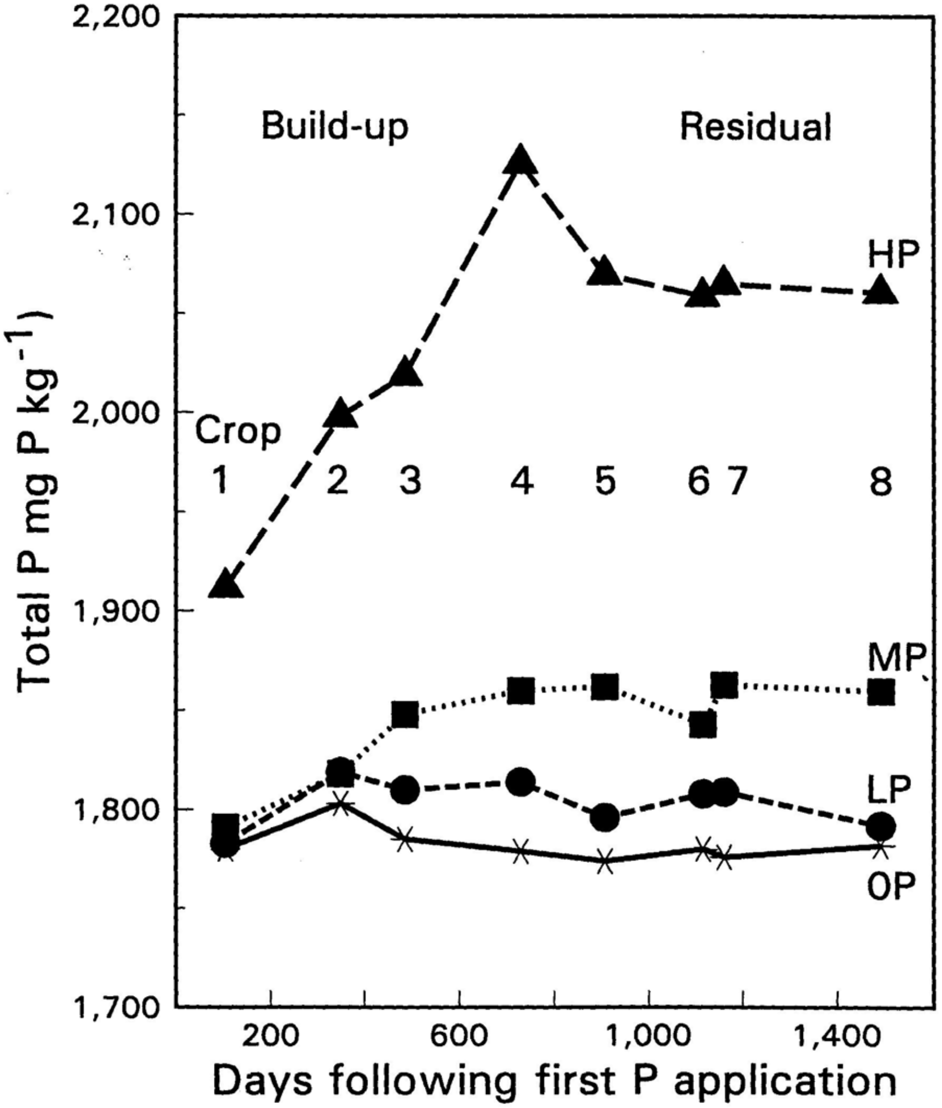

Fig. 3-2. Total soil P (sum of all P fractions) during a P build-up and residual phase for four P treatments: no P added (0P), low P (LP), moderate P (MP), and high P (HP).

and removal (Fig. 3-2). Recovery of fertilizer P from soil was calculated as the sum of all Pi pools in either LP, MP or HP, minus sum of all Pi pools in OP. On average, -37% (LP), -13% (MP) and +12% (HP) of the calculated cumulative net fertilizer P input (P added as fertilizer - P removed by crop) was recovered.

Inorganic and H_2SO_4 P

Labile Pi pools, FeO and $NaHCO_3$ Pi, were initially only 0.1 and 0.4% of total Pi in the OP treatment as estimated from the data in Fig. 3-3. Sodium hydroxide Pi, moderately labile P, was 18% of total Pi. No P was recovered in the 1 M HCl pool indicating little or no recoverable Ca-bound phosphate, as expected in highly weathered soils (Smeck, 1973; Walker and Syers, 1976). The recalcitrant Conc. HCl Pi pool was the largest pool and accounted for 82% of total Pi.

Additions of P fertilizer to each crop during the P build-up phase (crops 1 to 4) resulted in significant increases in all Pi pools (Fig. 3-3). In contrast, Pi in each pool declined during the residual phase (crops 5 to 8), when no fertilizer P was added. Because extractable P did not increase with time in the 25-50 cm layer (data not shown), the decline in Pi in the 0-25 cm soil layer was due to crop P removal or redistribution among P pools. Although the size of the H_2SO_4 P pool fluctuated over time there was an increasing trend in the 0P, MP, and HP treatments, however, differences between P treatments were not significant (Fig.3-5).

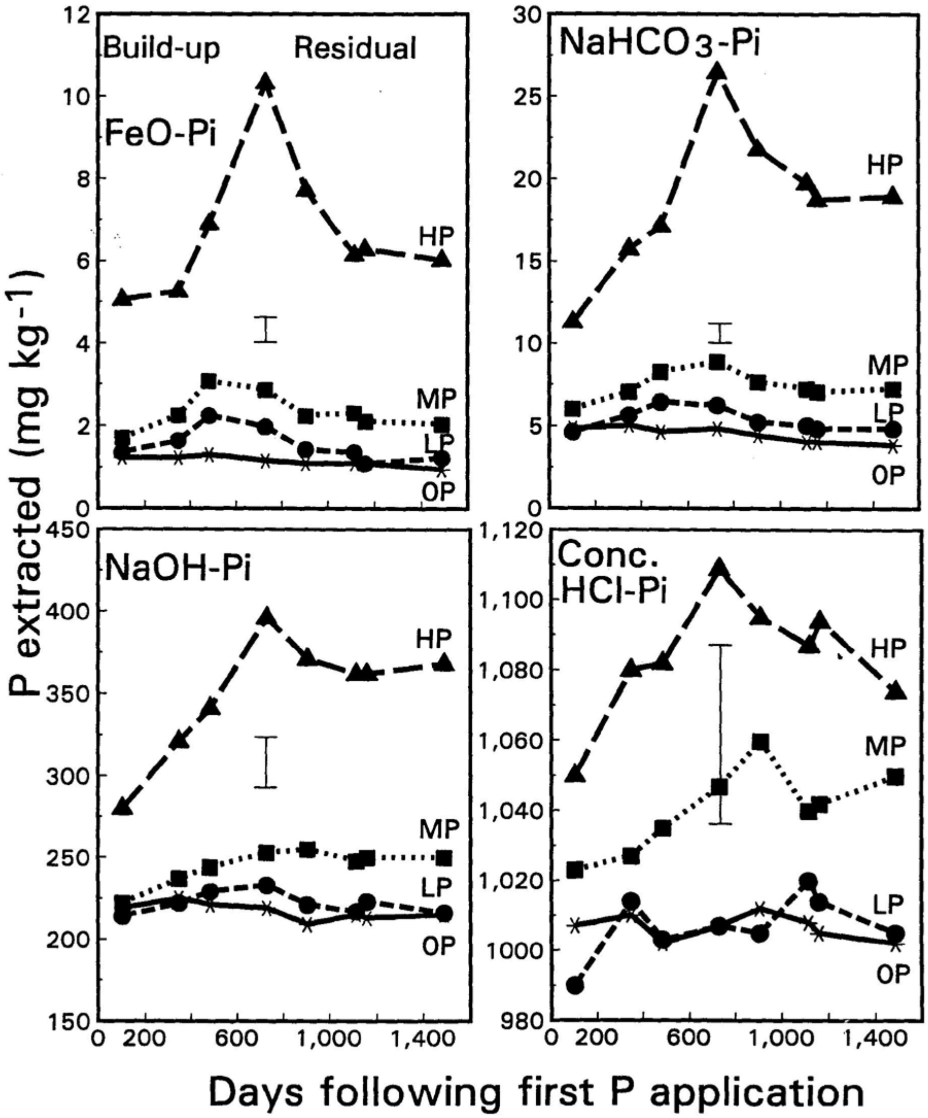

Fig. 3-3. Inorganic P pools (Pi) during a P build-up and residual phase for four P treatments: no P added (0P), low P (LP), moderate P (MP), and high P (HP). Error bars represent LSD (P<0.05) for comparison of crop 4 means.

Fertilizer P recovered in each Pi pool in the HP treatment was calculated as the difference between P in the HP and 0P treatments. The percent of fertilizer P recovered over time from each Pi pool in the HP treatment is shown in Fig. 3-4. To simplify the presentation, FeO and $NaHCO_3$ Pi were combined to form the labile Pi pool and the Conc. HCl Pi and H_2SO_4 P to form the recalcitrant pool. The primary sink for applied P in this soil was the moderately labile NaOH Pi pool, from which 52-58% of the fertilizer P was recovered. This is consistent with results from a Brazilian Ultisol (Beck and Sanchez, 1994). The proportion of fertilizer P recovered from labile and recalcitrant pools was 7.5-10% and 33-41%, respectively. Considerably more P is recovered in labile pools in soils with low P fixation capacities. For example, most fertilizer P was recovered in the labile pool (48%), followed by the moderately labile (43%) and recalcitrant (9%) Pi pools from two Canadian Chernozemic soils five to eight years after P application (Wager et al., 1986). Similarly, 31% of fertilizer P remained in the labile fraction eight years after application in an Indian Entisol (Aulakh and Pasricha, 1991). The proportion of applied P recovered in each pool changed very little between crop 1 and 8 (Fig. 3-4). Because the soil was sampled 104 days after P application in crop 1, these results demonstrate that fertilizer P equilibrated rapidly among the various P pools. Thus, the observed decline in plant available P (Chapter 2) cannot be explained by the conversion of P to less soluble

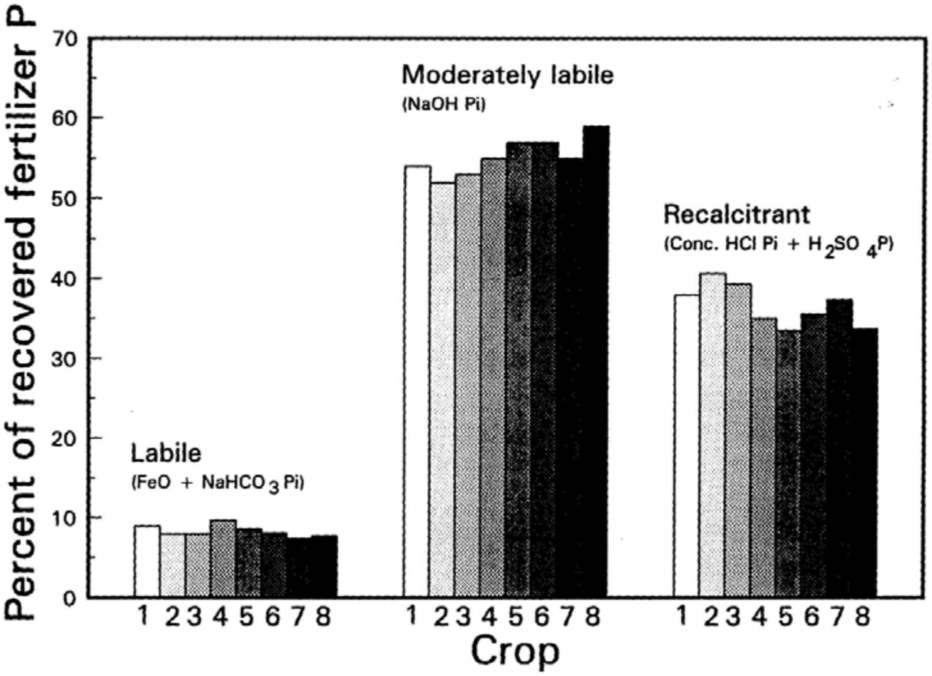

Fig. 3-4. Percent of added fertilizer P recovered in labile, moderately labile, and recalcitrant pools from the high P treatment for all eight crops.

forms. Others have found that P changes from Al-associated P to less soluble Fe-associated P over time (Yost et al., 1981; Shelton and Coleman, 1968). The fractionation procedure they used (modified Chang and Jackson, 1957), however, has some problems separating Al- and Fe- associated Pi reliably (reviewed by Olsen and Khasawneh, 1980).

Organic P, carbon and nitrogen dynamics

Total organic Po (Po_t) (the sum of $NaHCO_3$, NaOH, and Conc. HCl Po pools) was 334 mg P kg^{-1} soil and accounted for 18% of the total P in the 0P treatment (Fig. 3-5). Sodium bicarbonate, NaOH, and Conc. HCl Po accounted for 10, 80, and 10% of Po_t, respectively. Organic P values were not significantly affected by P treatment. Since P input did not affect soybean root mass (Cassman et al., 1993) and all aboveground biomass was removed after each crop, treatment differences in organic P input in this study were small.

There was no net change in the NaOH and Conc. HCl Po pools during the course of the experiment (Fig. 3-5) although accurate measurement of Conc. HCl Po was difficult due to the relatively high amount of Pi in the Conc. HCl pool. Despite the lack of detectable trends in the size of these Po pools with time, cycling of P between them is possible.

The most labile Po pool ($NaHCO_3$) declined from a mean of 35 to 30.5 mg P kg^{-1} soil between crops 1 and 8. This decline represents a net loss of approximately 14 kg Po ha^{-1} during the four-yr experiment and is assumed to result from

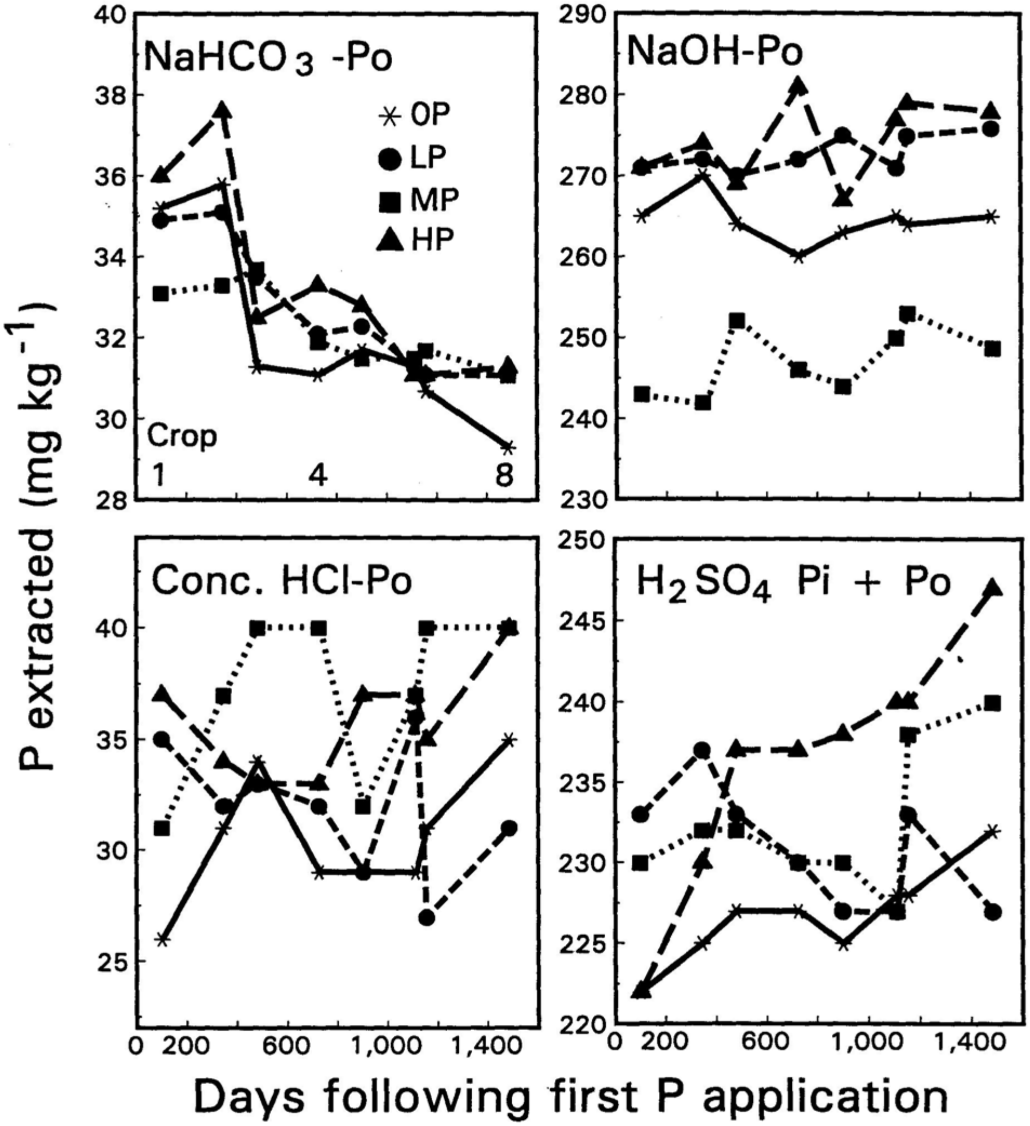

Fig. 3-5. Organic and H_2SO_4 P pools for four P treatments during the four-year experiment: no P added (0P), low P (LP), moderate P (MP), and high P (HP). Crop 4 means were not significantly different between P treatments.

mineralization (Beck and Sanchez, 1994). Duxbury et al. (1989) proposed that mineralization of esters (P generally forms esters with C) is regulated by the demand for the nutrient. This data, however, suggest that P mineralization was independent of P availability since the decline in $NaHCO_3$ Po was not affected by the quantity of P inputs (Fig. 3-5).

Organic C declined from 31.6 to 28.0 g C kg^{-1} soil and N declined from 2.26 to 2.01 g N kg^{-1} soil during the four year cropping period (Fig. 3-6). Both C and N declined at approximately the same rate, maintaining a C:N ratio between 13.5 and 14. Since Po_t remained constant, the C:Po_t ratio declined from 95 to 84 between crops 1 and 8. The variability in C:Po_t ratios relative to C:N ratios observed in this study may result from the formation of P-esters (C-O-P), while N is covalently bonded to C. Therefore, Po mineralization may be uncoupled from C and N mineralization (McGill and Cole, 1981) increasing variability among C:Po_t ratios compared to C:N ratios (Stevenson, 1986). The $NaHCO_3$ Po pool, however, declined at a rate almost identical to that of C and N (Fig. 3-6) and a relatively constant C:$NaHCO_3$ Po ratio of 885 was maintained over the course of this experiment. Similarly, Tiessen et al. (1992) found that NaOH Po declined at about the same rate as C in a Brazilian soil. Thus, certain Po fractions may be coupled to C and N mineralization.

Relationship of P pools to yield and P uptake

Mehlich-1 extractable P is commonly used to estimate

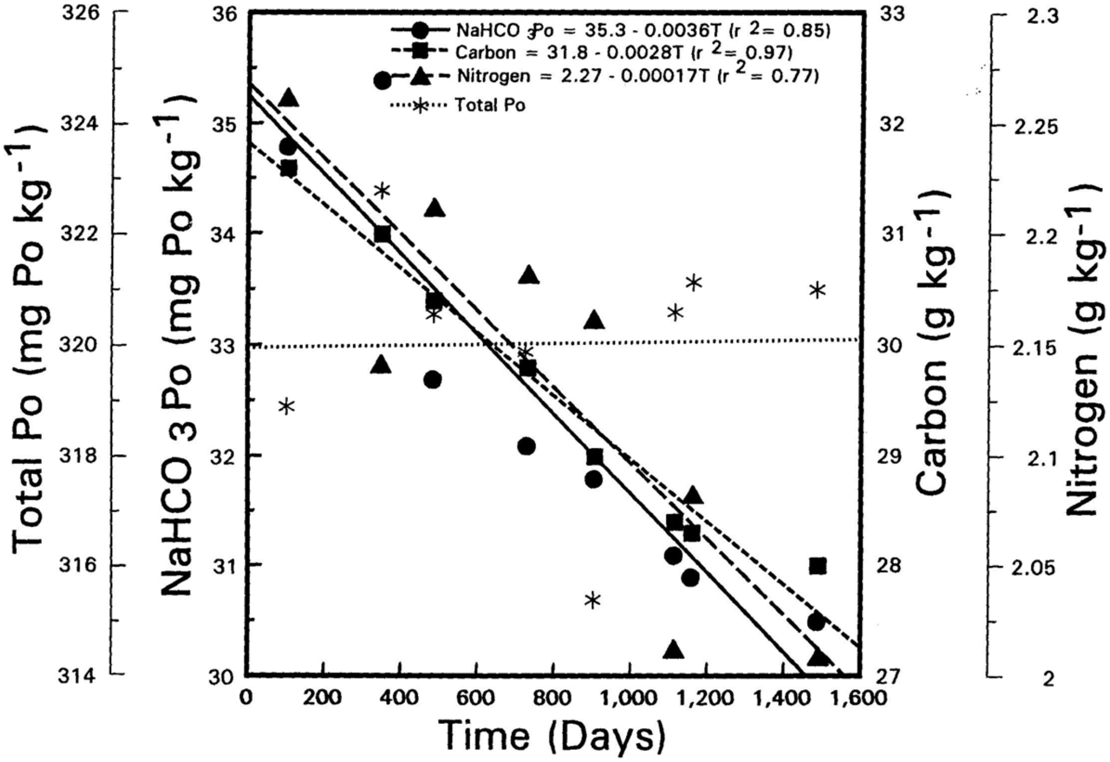

Fig. 3-6. Changes in total soil carbon, nitrogen, Po and $NaHCO_3$ Po during eight consecutive crops over four years.

plant available P in highly weathered soils. However, I found (Chapter 2) that Mehlich-1 P was a poor indicator of plant-available P. Mehlich-1 values required to achieve 95% of maximum yield shifted from less than 2 to more than 5.5 mg P kg^{-1} soil during the four-yr experiment. The sequential P fractionation procedure allowed evaluation of other labile Pi pools which may be better correlated with yield than Mehlich-1. All the measured Pi pools were highly correlated with each other and with Mehlich-1 ($r > 0.91$) (data not shown). The relationship between the P extracted by these methods and relative yield for crops 1, 4, and 8 were almost identical (Fig. 3-7). With each extraction method the value to reach 95% of maximum yields increased with time. Also, the P extracted by each method was relatively insensitive to yield in the range where crop yield was most responsive to added P

Table 3-2. Pearson correlation coefficients† among soil extraction methods and between methods and soybean dry matter yield (DMY) and P uptake for the unfertilized treatment (0P). Correlations with (DMY) and P uptake include only the summer crops (crops 2, 4, 6 and 8) (n=4) while correlations of soil extractable P values include all eight crops (n=8).

	DMY	P uptake	Mehlich	Strip Pi	Bicarb Pi
Bicarb Po	0.95	0.99	0.87	0.82	0.81
Bicarb Pi	0.95	-	0.76	-	
Strip Pi	0.95	-	0.76		
Mehlich	0.95	0.95			
P uptake	0.99				

† Only correlations where $P < 0.05$ are shown.

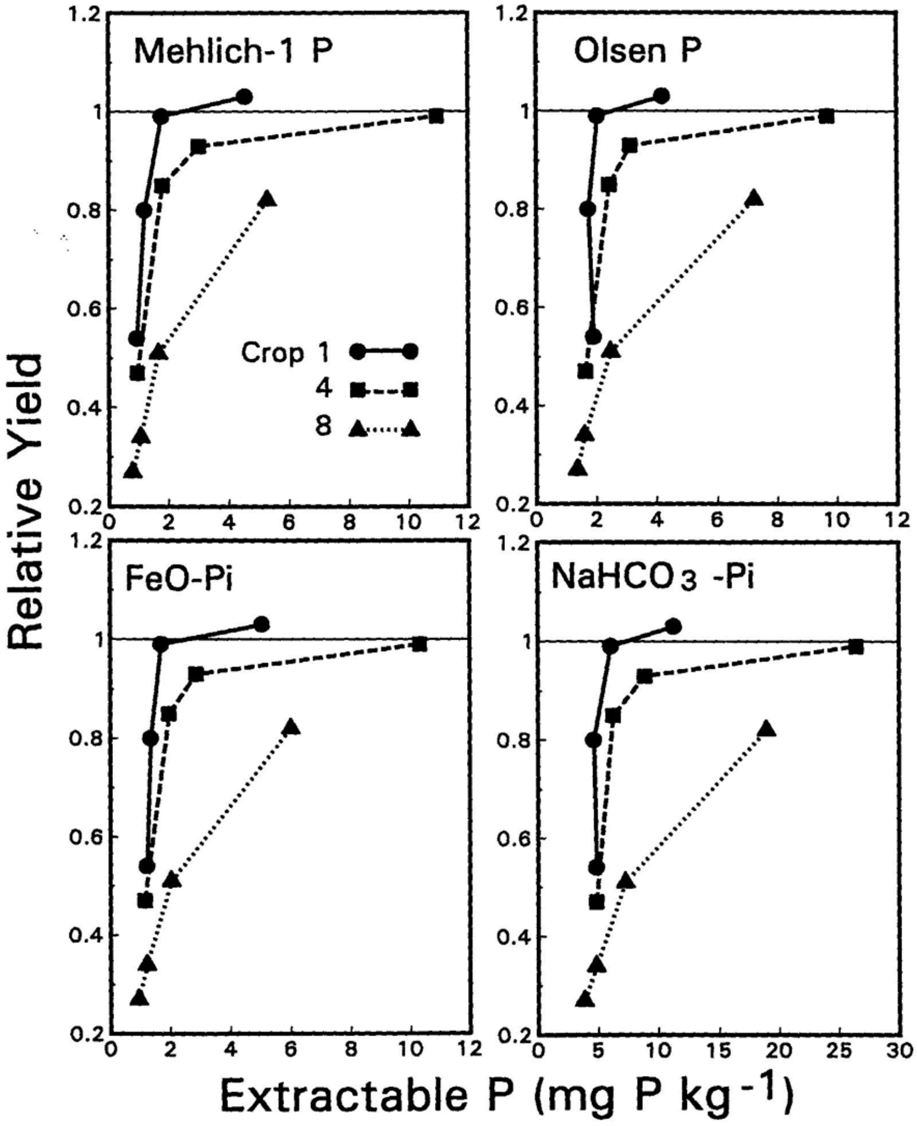

Fig. 3-7. Relative yield of soybean for crops 1, 4 and 8 as a function of Mehlich-1 P, Olsen P, Strip, and $NaHCO_3$ Pi. Relative yields are based on the mean yield of fall (for crop 1) and summer crops (for crop 4 and 8) during the P build-up phase (Cassman et al., 1993; Linquist et al., In Review a).

as shown by the initial steep slope of the curves in crops 1 and 4.

Organic P is a major determinant of P fertility in unfertilized systems (Beck and Sanchez, 1994). Correlations between $NaHCO_3$ Po, FeO and $NaHCO_3$ Pi pools, Mehlich-1, P uptake and DMY values from the unfertilized control (0P) are presented in Table 3-2. Soybean DMY and P uptake in the 0P treatment declined from 3895 to 1686 kg ha^{-1} and from 11.1 to 4.3 kg P ha^{-1} between crops 2 and 8 (Chapter 2). Sodium bicarbonate Po was positively correlated with FeO and $NaHCO_3$ Pi pools, Mehlich-1, confirming results of others (Beck and Sanchez, 1994: Tiessen et al., 1984). These data also demonstrate that $NaHCO_3$ Po was correlated with plant P uptake and DMY when there were no P fertilizer inputs. In contrast moderately labile NaOH Po was correlated with plant P uptake in some Alfisols (Sattel and Morris, 1992) and total Po with crop yields in some African soils (Friend and Birch, 1960; Smith and Acquaye, 1963; Omotoso, 1971).

In this experiment, no other Po pool was correlated with any Pi pool, DMY or P uptake. Also, in the P input treatments (LP, MP, and HP) none of the Po pools were correlated with yield because P inputs only affected Pi pools and Pi is the primary determinant of plant available P in fertilized cropping systems (Beck and Sanchez, 1994).

Summary and Conclusions

Using a modified P fractionation procedure (Hedley et al., 1982) the fate of applied P on an Ultisol with a high P adsorption capacity was determined. Most fertilizer P (52-58%) was recovered in the moderately labile NaOH Pi pool followed by the recalcitrant (33-41%) and labile (7.5-10%) Pi pools. Fertilizer P approached equilibrium with the various P pools within 104 days of application. The continual decline in plant available P observed during the two years following P application (Chapter 2) was not, therefore, the result of P movement into less labile forms. While labile Pi pools were correlated with Mehlich-1 and Olsen P, all were poor indicators of available P in this soil.

Neither $NaHCO_3$ Po mineralization rate nor size of any Po pool was affected by P fertilization. While NaOH and Conc. HCl Po remained constant during the four yr experiment, $NaHCO_3$ Po declined at a rate similar to the decline in C and N, implying that $NaHCO_3$ Po mineralization may be coupled to C and N mineralization. Only in the unfertilized control, was $NaHCO_3$ Po correlated with DMY and P uptake as well as with FeO and $NaHCO_3$ Pi, indicating that Po mineralization is a critical source of crop P in low-input systems.

The failure of labile Pi values, be it from common soil test methods or one of the measured P pools, to predict crop performance and P uptake and our inability to determine the cause of declining P availability when this soil is fertilized suggests other phenomena contribute to the control of P availability. The role that aggregates and slow P diffusion play in governing P availability may help explain these phenomena (Chapter 4). A soil test which incorporates the chemical phenomena, as I have discussed here, with soil aggregate size distribution will likely improve the precision of soil tests as well as the short- and long-term availability of applied P.

CHAPTER 4

AGGREGATE SIZE EFFECTS ON PHOSPHORUS ADSORPTION AND INDICES OF PLANT AVAILABILITY

Abstract

Despite extensive research on P-adsorption chemistry, the ability to predict plant available P remains imprecise. Although many tropical soils have an unusually high degree of aggregation little attention has been given to the affects of aggregation on P-adsorption and subsequent availability. Autoradiography of adsorbed ^{32}P and P adsorption by aggregate fractions less than 0.375 mm suggested that added P was initially adsorbed to a 0.188 mm layer around aggregates. This layer is defined as the reactive mass. When P was added to a mixture of aggregate size fractions, P adsorption increased from 50 to 245 mg P kg^{-1} as mean aggregate diameter decreased from 3.4 to 0.375 mm. These differences were not related to aggregate mineralogy or particle size distribution but rather to reactive mass (r^2=0.96). Similarly, the reactive mass of aggregate size fractions was linearly related to P dissolution from aggregates (r^2=0.99) and the linear buffer coefficient derived from P-adsorption isotherms (r^2=0.98). Buffer coefficients were 73% greater when aggregates were destroyed than when the natural soil distribution of aggregates was maintained. Movement of initially adsorbed P appears to diffuse very slowly into the interior. Once inside large aggregates, however, P may not be

immediately available for plant uptake due to slow diffusion out of aggregates. Analysis of aggregates from a field experiment support these conclusions from laboratory experiments. Therefore, aggregate size distribution should be considered in short- and long-term management decisions and in testing soil for available P.

Introduction

In an aggregated soil, solute movement is primarily through inter-aggregate pores. Water within aggregates is assumed to be immobile and transport of solutes into aggregates occurs primarily by diffusion (Fong and Mulkey, 1990). Diffusion of P within aggregates is very slow. For example, Nye and Stauton (1994) estimated the intra-aggregate P diffusion coefficient of a sandy soil to be $1.5 \times 10^{-12} cm^2 s^{-1}$. This is in contrast to an average soil diffusion coefficient of 1×10^{-8}-$10^{-11} cm^2 s^{-1}$ (Barber, 1984).

Gunary et al. (1964) found that added P was initially adsorbed on the outside of synthetic aggregates. Subsequent equilibration of P within large aggregates could theoretically take many years due to slow diffusion rates. For instance, the average linear diffusive movement (L) over time (t) can be estimated by: $L = ((2Dt)^{1/2})$ where D is the diffusion coefficient (Barber, 1984). Using Nye and Stauton's (1994) estimate of D, the diffusive movement of P in one year would be at most 0.1 mm. Similarly, P diffusion from within aggregates to the aggregate surface in contact with the bulk soil solution may be too slow to meet plant requirements. Horn and Taubner (1989), for example, found that K flux out of aggregates was inversely related to aggregate size.

Although some soils with a high P adsorption capacity can support maximum yields with small applications of P (Cassman et al., 1993), large P applications may have little long-term residual benefit (Chapter 2). In contrast, other P-fixing soils require large initial applications to reach maximum yield but maintain high yields over time without additional P inputs (Fox et al., 1971). Highly weathered tropical soils frequently contain a large proportion of water stable aggregates due to high levels of iron and aluminum oxides (Uehara and Gillman, 1981). While some have implied that soil aggregation slows the adsorption reaction and subsequent equilibrium in laboratory studies (Munns and Fox, 1976; Fox and Kamprath, 1970), the effects of aggregates has not been quantified. The prevalence of large aggregates in many soils with high P adsorption capacity indicates the need for better understanding of how aggregate size and size distribution influence P-adsorption and subsequent availability.

I reported that several commonly used extraction methods were poor indicators of available P on a highly aggregated Ultisol (Chapter 2 and 3). Most soil P test methods require sieving, grinding and shaking soil samples which destroy aggregates and expose P adsorption sites not normally exposed under field conditions. The objective of this research was to examine the affects of aggregate size and size distribution on P adsorption and availability in a highly aggregated Ultisol. My goal was to explain both the short- and long-term affects of applied P that was not predicted by existing soil test methods (Chapter 2 and 3).

Materials and Methods

Soil collection and aggregate characterization

The soil used in this study was sampled from a long-term P management experiment (Cassman et al., 1993; Chapter 2). It is classified as a Haiku clay (clayey, oxidic, isohyperthermic typic Palehumult). Soil was sampled from the top 25 cm of four replicate plots of the control treatment which had never received P (0P) and the high P treatment (+P) which had received cumulative inputs of 930 kg P ha^{-1} (Cassman et al., 1993) two years before sampling. Four crops over two years were grown between the last P application in 1990 and the 1992 soil sample used in this study.

After collection, soil was passed through a 4 mm sieve and air dried. Nine aggregate size fractions were obtained using the wet sieving method described by Elliot (1986). The fractions were 2.8 to 4.0, 2.0 to 2.8, 1.0 to 2.0, 0.5 to 1.0, 0.25 to 0.5, 0.15 to 0.25, 0.09 to 0.15, 0.053 to 0.09, and < 0.053 mm. The corresponding mean aggregate diameter (MAD) of each fraction is 3.4, 2.4, 1.5, 0.75, 0.375, 0.2, 0.12, 0.098, and < 0.027 mm.

Each aggregate fraction from the 0P treatment was analyzed for carbon content, after passing through a 0.15 mm sieve, using a Leco CHN analyzer, sand and clay content by the hydrometer method (Gee and Bauder, 1986) and clay mineralogy by X-ray diffraction followed by quantitative mineralogical analysis of the X-ray diffraction pattern using the SIROQUANT computer program (Sietronics, Pty. Ltd., 1983).

Inorganic and organic P extracted by 0.5 M $NaHCO_3$ and 0.1 M NaOH and the amount of unextracted residual P for each aggregate fraction from the 0P and +P plots was measured using the sequential P fractionation procedure of Hedley et al. (1982).

General laboratory protocol

To preserve aggregate structure, laboratory studies were conducted by placing 1 g of aggregates in 10 cm diameter plastic petri dishes, except where otherwise noted. This amount of soil made a single layer of aggregates in the bottom of the petri dish, uniformly exposing the outer surfaces of both large and small aggregates to the bulk solution. To prevent aggregate disruption when solution was added, the petri dishes containing air dry aggregates were placed in a closed chamber with a humidifier for 2 hours which raised the moisture content of aggregates to approximately 0.13 g H_2O g^{-1}. In comparison, moisture content, at saturation, was about 0.22 g H_2O g^{-1} for this soil. During incubation, petri dishes were placed on an orbital shaker at 50 rpm which agitated the solution while maintaining aggregate integrity for at least 100 d. More vigorous shaking destroyed aggregates.

All incubations were conducted at room temperature (24 - 27°C). Phosphate analysis was performed by the method of Murphy and Riley (1962).

^{32}P Autoradiographs

The distribution of adsorbed P within aggregates over time was observed using autoradiography (Gunary et al., 1964). One gram of aggregates with a MAD of 3.4 mm were slowly brought to saturation with 0.01 M $CaCl_2$ and placed in petri dishes containing 30 ml of 0.01 M $CaCl_2$ with 6.2 µg P ml^{-1} labeled with 50 µCi ^{32}P. After 3, 14, and 28 days of agitation, aggregates were removed, placed on filter paper to remove the free solution, and air dried. Aggregates from each time point were put in separate molds containing melted paraffin wax. After the wax solidified, 0.5 mm thin sections of the aggregates were prepared with a microtome. Thin sections were placed between two layers of cellophane and placed on X-ray film in film canisters for six min.

P sorption by different aggregate size fractions

The fate of added P applied to a mixture of aggregate size fractions was determined by combining 1 g of each of the seven aggregate fractions with MAD of 3.4, 2.4, 1.5, 0.75, 0.375, 0.2, and 0.12 mm in a petri dish. Two P treatments were imposed by adding 30 ml of 0.01 M $CaCl_2$ containing no P (control) or 186 mg P kg^{-1} soil as $Ca(H_2PO_4)_2 \cdot H_2O$ (+P) to separate petri dishes. Aggregates were kept in solution and agitated for either 1, 7, 30, or 100 d. All treatments were replicated twice. Solutions were decanted and the aggregates were air dried. The aggregates were then separated into the original size fractions by dry sieving, and each fraction was ground to pass a 0.15 mm (100 mesh) sieve. Total P in each size fraction was measured after digesting 0.5 g of the ground aggregate in H_2SO_4 and H_2O_2 for 5 hrs. Phosphorus adsorbed by each aggregate fraction was calculated as the difference between the control and the +P treatment. Phosphorus adsorption after 1 and 7 d was essentially the same so results were combined for presentation.

Dissolution of P from aggregates

Dissolution of P from various aggregate sizes was measured by placing 10 g of five previously moistened aggregate fractions with MAD of 2.4, 1.5, 0.75, 0.375, and 0.2 mm in a 10 cc syringe filled with 0.01 M $CaCl_2$ and packed at both ends with glass wool. Fresh Mehlich-1 extractant (0.05 M HCl and 0.0125 M H_2SO_4) was pumped continuously through the syringes at a rate of 1 ml min^{-1}, providing about one macropore volume of extractant every 5 min. The solution was collected periodically over 56 h and an aliquot filtered through a 0.45 µm membrane filter before P analysis. Aggregates smaller than those with a MAD of 0.2 mm could not be used in this system because preferential channelling of the extractant was a problem.

Aggregate size effects on P adsorption isotherms

To determine how aggregate size affects the soils buffering capacity, P adsorption isotherms were performed separately on six aggregate size-fractions with MAD of 3.4, 2.4, 1.5, 0.75, 0.375, and 0.2 mm. In addition, isotherms were performed on a ground sample of the 2.4 mm MAD fraction passed through a 0.15 mm sieve ("2.4 grd" in Fig. 4-5) and a soil sample which had not been separated by aggregate fraction ("natural" in Fig. 4-5). Samples were slowly shaken in P solution continuously for six days as described previously to avoid aggregate disruption during the adsorption period. Also, using a soil sample which had not been separated by aggregate fraction, an isotherm was performed using the standard method of Fox and Kamprath (1970) to determine the effect of vigorously shaking the sample 30 min twice daily, which destroys aggregates, on the estimated soil buffer capacity. Soil:solution ratios for all isotherms was 1:30. Phosphate was added to the samples at 0, 42, 84, 168, and 336 mg P kg^{-1} soil.

Results and discussion

Aggregate characterization

Aggregates with diameters greater than 1 mm accounted for 51% of the total soil mass (Table 4-1). All aggregate size fractions had similar organic P extracted by $NaHCO_3$ and NaOH, particle size distribution, and clay mineralogy. The exception was the two smallest fractions (<0.053 mm and 0.053-0.09 mm), which together represented only 2% of soil mass (Tables 4-1 and 4-2). Organic P extracted by $NaHCO_3$ and NaOH averaged 26 and 257 mg P kg^{-1} soil, respectively. Mean carbon content was 26.6 g kg^{-1} and clay and sand averaged 610 and 40 g kg^{-1} soil, respectively. Of the minerals present, goethite, gibbsite, and kaolin were the minerals with significant P sorption capacity. Goethite, which averaged 210 g kg^{-1} clay, has the highest adsorption capacity (Jones, 1981; Parfitt, 1989).

Table 4-1. Properties of different aggregate size fractions from Haiku clay series (clayey, oxidic, isohyperthermic typic Palehumult).

Aggregate diameter	Organic P†		Carbon	Clay	Sand	Proportion of aggregate fraction in soil‡
	$NaHCO_3$	NaOH				
mm	--- mg P kg^{-1} ---		------g kg^{-1}------			%
2.8-4.0	24.0	259	27.5	620	49	12
2.0-2.8	26.8	262	27.0	610	50	15
1.0-2.0	26.7	261	26.8	620	60	24
0.5-1.0	28.5	263	27.1	610	51	21
0.25-.05	26.0	266	27.1	620	40	16
0.15-0.25	27.4	268	27.1	610	37	7
0.09-0.15	26.9	262	26.8	620	51	3
0.053-.09	24.6	252	26.4	590	90	1
< 0.053	21.0	218	23.3	--	--	1

† Determined with a modification of the Hedley et al. (1982) procedure.

‡ Aggregates were initially passed through a 4 mm sieve after sampling from the field.

Table 4-2. Clay mineralogy of different aggregate size fractions from a Haiku clay soil†.

Aggregate diameter	Goethite	Anatase	Hematite	Quartz	Kaolin	Illite	Gibbsite	Other‡
mm				g kg^{-1} clay				
2.8-4.0	217	114	64	163	76	328	29	14
2.0-2.8	247	69	67	162	89	310	38	17
1.0-2.0	206	101	58	139	84	361	35	16
0.5-1.0	208	102	59	129	85	364	32	20
0.25-0.5	206	84	58	154	84	361	32	20
0.15-0.25	216	110	54	153	78	337	30	22
0.09-0.15	222	85	56	133	80	345	49	30
0.05-0.09	158	79	55	128	79	436	30	37

† Oxalate extractable soil material (Fe, Al, Si, Mn) is 102 g kg^{-1}soil (Jackman et al. In Press).

‡ interstratified illite and smectite.

Distribution of applied P in aggregates

Autoradiographs of cross sections from aggregates incubated in ^{32}P solution show that P was initially adsorbed and remained on the periphery of soil aggregates for 28 d (Fig. 4-1). Willet et al. (1988) and Gunary et al. (1964) also found that P was initially adsorbed to the surface of ferrihydrite particles and synthetic aggregates coated with amorphous iron.

If P is initially adsorbed only to outer surfaces of aggregates it follows that smaller aggregates, which have greater surface area per unit mass, should adsorb more P than larger aggregates when P is added to a mixture of aggregate size fractions. Evidence that smaller aggregate fractions adsorbed more P than larger ones is provided in Fig. 4-2a. Total P at day 1 and 7 increased from 1860 to 2025 mg P kg^{-1} soil MAD decreased from 3.4 to 0.375 mm. Initial P adsorption by each aggregate size fraction (total P in +P - total P in control) increased from 55 to 245 mg P kg^{-1} soil as MAD decreased from 3.4 mm and 0.375 mm.

There was no further increase in P adsorption as MAD decreased below 0.375 mm (Fig. 4-2a). This is consistent with data from Fig. 4-5 and suggests that added P is initially adsorbed throughout aggregates of this size and smaller. The mean radius for 0.375 mm aggregates is 0.188 mm. Thus, under these experimental conditions, P appears to be initially adsorbed to a depth of 0.188 mm. Rough outer surfaces and small cracks or micropores are the likely reason for rapid

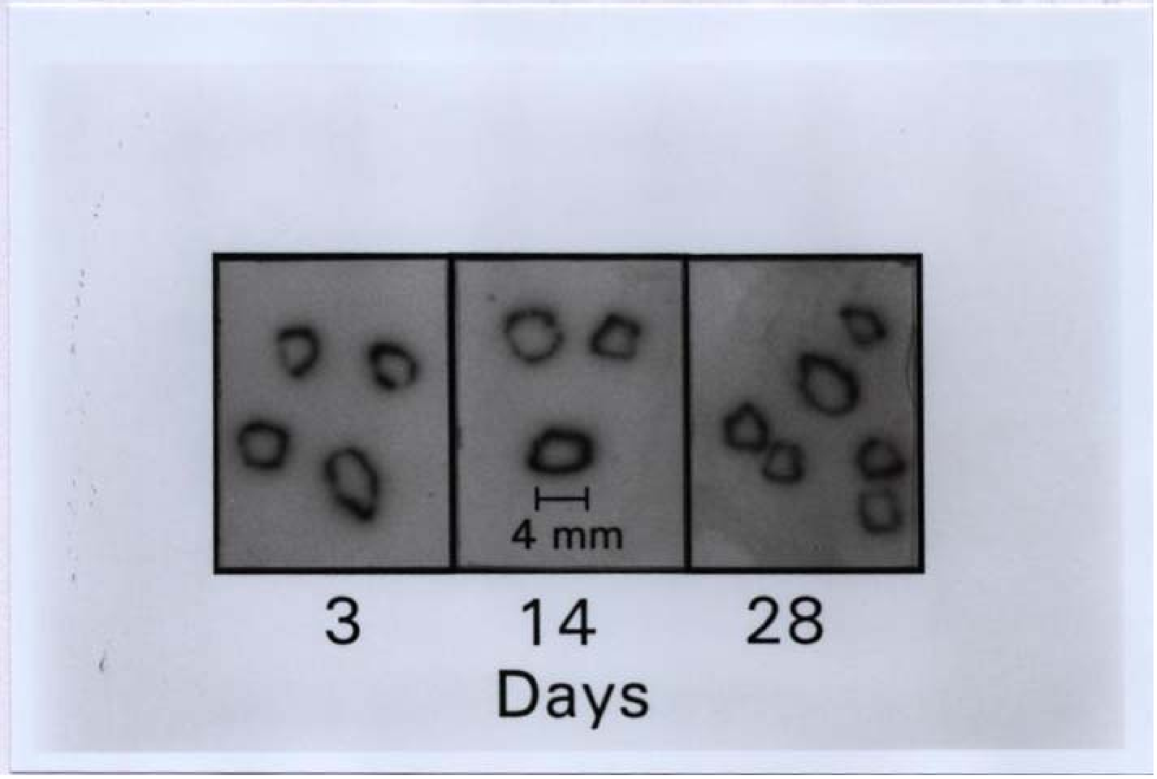

Fig. 4-1. Autoradiographs of cross-sections of aggregates exposed to ^{32}P labeled solution for 3, 14, and 28 days.

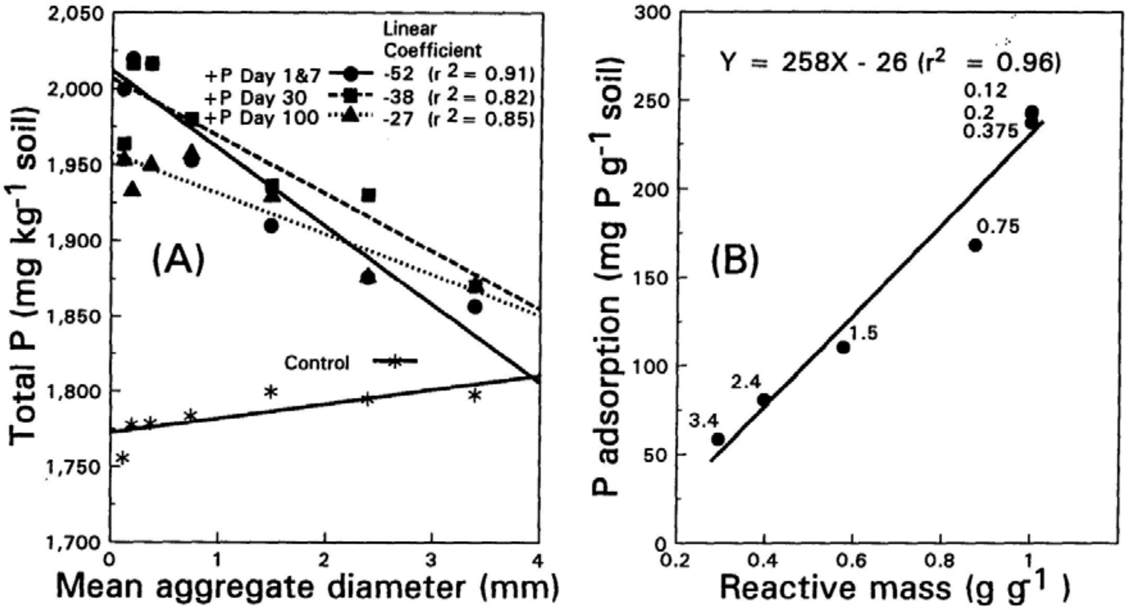

Fig. 4-2. A) Total P in each aggregate fraction after exposure to a common P solution containing 186 mg P kg^{-1} soil (+P) or no P (control) for 1, 7, 30, and 100 days. Data for day 1 and 7 were essentially identical and were combined for presentation. **B**) Phosphate adsorption (total P in +P - total P in control) for each aggregate fraction (the mean aggregate diameter (mm) is beside each point) in relation to reactive mass at day 1 and 7. $LSD_{0.05}$ is 54 mg P kg^{-1} and is for comparison of total P in each aggregate fraction at different times.

adsorption of P to this depth. I define the mass of this outer 0.188 mm layer as the "**reactive mass**". For aggregates less than or equal to 0.375 mm in diameter there is 1.0 g reactive mass g^{-1} aggregate. Assuming aggregates approximate spheres of uniform density, the MAD can be used to estimate the reactive mass of each aggregate fraction (Table 4-3).

Table 4-3. Reactive mass of various aggregate fractions (g reactive mass g^{-1} total aggregate mass). Values are the mass of aggregate to a depth of 0.188 mm.

Aggregate diameter	Mean diameter	Reactive mass
--------------- mm	----------------	$g\ g^{-1}$
2.8-4.0	3.4	0.296
2.0-2.8	2.4	0.399
1.0-2.0	1.5	0.578
0.5-1.0	0.75	0.875
< 0.25-0.5	< 0.375	1.0

Regression of P adsorption at days 1 and 7 against reactive mass was linear and highly significant ($r^2 = 0.96$) (Fig. 4-2b). Thus, when P is added to a soil it is concentrated on the outside of aggregates and, therefore, higher solution P values are maintained in the inter-aggregate bulk solution where plant roots take up nutrients. This may explain why, on this highly aggregated soil, 50 to 100 kg P ha^{-1} produced optimal yields (Cassman et al., 1993) despite recommended applications of over 500 kg P ha^{-1} based on standard soil test methods (Cassman et al., 1981).

I hypothesize that equilibration following P addition will occur through redistribution of P by diffusion from smaller, P-rich aggregates to larger aggregates of lower P content. At equilibrium, therefore, the P content of each aggregate fraction in Fig. 4-2a should be similar because the mineralogy and clay content of each fraction was comparable (Tables 4-1 and 4-2). A significant decrease in the slope of the relationship between total P and MAD as incubation time increased from 1 and 7 d to 100 supports this redistribution hypothesis (Fig. 4-2a).

Dissolution of P from aggregates

After P is adsorbed to soil, P availability to plants is determined by the rate of desorption or dissolution into the soil solution. I tested whether aggregate size affected the rate of P dissolution in a continuous flow system using Mehlich-1 extractant (Fig. 4-3a). The rate of P extraction was essentially linear with time to 56 h, and inversely proportional to aggregate size. The rate of P extraction (linear coefficient, Fig. 4-3a) from the 0.15-0.25 mm fraction was double that of the 2.0-2.8 mm fraction.

Unlike the adsorption studies, where P adsorption did not increase in aggregate fractions with MAD less than or equal to 0.375 mm (Fig. 4-2 and 4-5), dissolution of P from aggregates was greater from aggregates with a MAD of 0.2 mm than 0.375 mm (Fig 4-3). This indicates that the depth of the reactive mass layer which governs P dissolution and

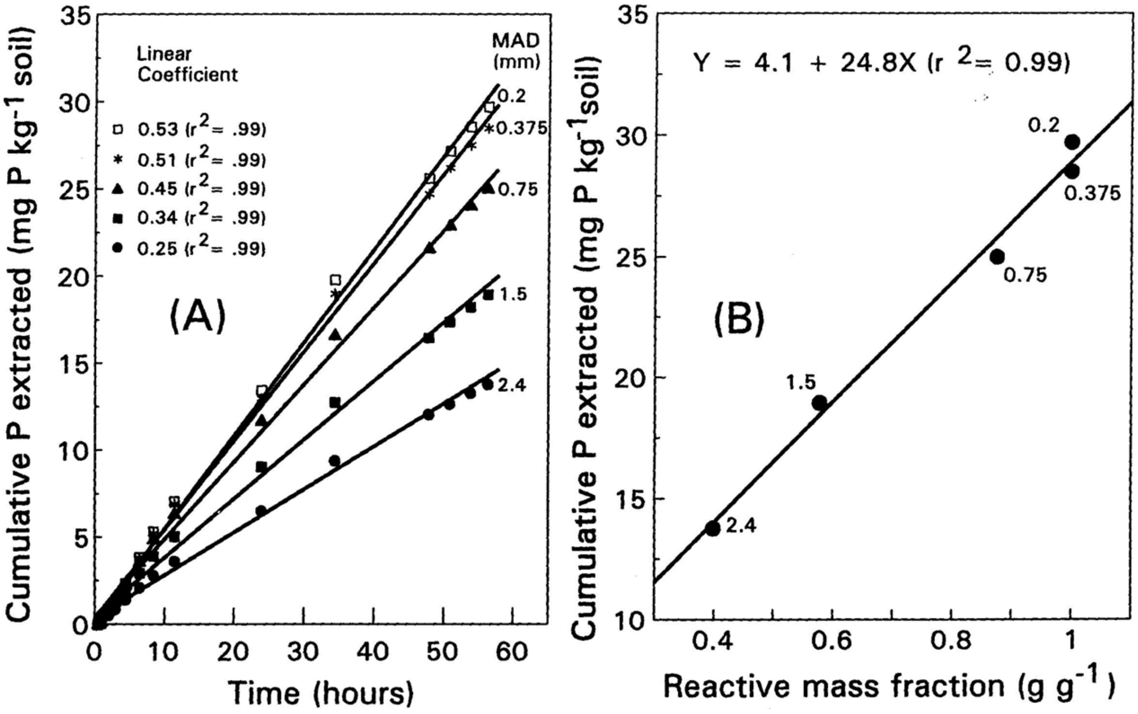

Fig. 4-3. **A**) Cumulative P recovered after continuous extraction from different aggregate size fractions and (**B**) cumulative P recovered after 56 hours of continuous extraction as a function of reactive mass. The mean aggregate diameter (MAD) for each aggregate fraction is beside each point.

desorption from aggregates may be smaller than for adsorption, perhaps due to a hysteresis effect. Aggregate size below which dissolution would not increase could not be determined using my methodology. Therefore, the reactive mass derived from adsorption studies was used (Table 4-3). The relationship between cumulative P extracted after 56 hours and estimated reactive soil mass was linear and highly significant (Fig. 4-3b). Likewise, linear coefficients of the regressions in Fig. 3a relating cumulative P extracted versus time were linearly related to reactive mass ($r^2 = 0.99$).

Horn and Taubner (1989) found that K flux from large aggregates was slower than from small aggregates due to longer diffusion path lengths. Diffusion rates are much slower for P than they are for K (Barber, 1984). These results suggest that diffusion from the interior of aggregates would contribute little P to the inter-aggregate bulk solution because the cumulative short-term dissolution of P from aggregates was closely related to the reactive mass, which only includes a surface layer of 0.188 mm (Fig. 4-3b). Thus, once inside larger aggregates of this soil P may not be immediately plant available.

Crop P uptake declined by 34% two years after a cumulative 930 kg P ha^{-1} had been applied to this soil (Chapter 2). The decline in P availability was not the result of conversion of P to less labile P forms (Chapter 3). Nye and Stauton (1994), based on P diffusion in micro-aggregates

(< 0.212 µm in diameter), suggested that slow diffusion of P into aggregates is a likely mechanism of the slow continual reactions of P with soil observed in many lab experiments. These results support their hypothesis. Diffusion of P into the interior of aggregates is a likely cause of the decrease in plant available P measured in this soil.

P content of aggregates from field soil after fertilization

To verify whether these phenomena occur in the field the P content of different aggregate size fractions taken from the long-term P management experiment was measured (Cassman et al., 1993; Chapter 2). Soil was sampled from two treatments: control plots without applied P (0P) and plots which received a total of 930 kg P ha^{-1} (+P) to four consecutive crops with the last application two years prior to sampling. Total inorganic P (the sum of the $NaHCO_3$, and NaOH extractable Pi, and residual P fractions (Hedley et al., 1982)) increased in the +P treatment as MAD decreased from 3.4 to 0.75 mm (Fig. 4-4). These results are similar to data in Fig. 4-2, where smaller aggregates with greater reactive mass adsorbed more P than larger aggregates.

The Pi content of both +P and 0P aggregates decreased as MAD decreased below 0.75 mm (Fig. 4-4). In field soils, where P is removed by plant uptake, small aggregates should become relatively more depleted than large aggregates over time because the rate of dissolution from small aggregates is

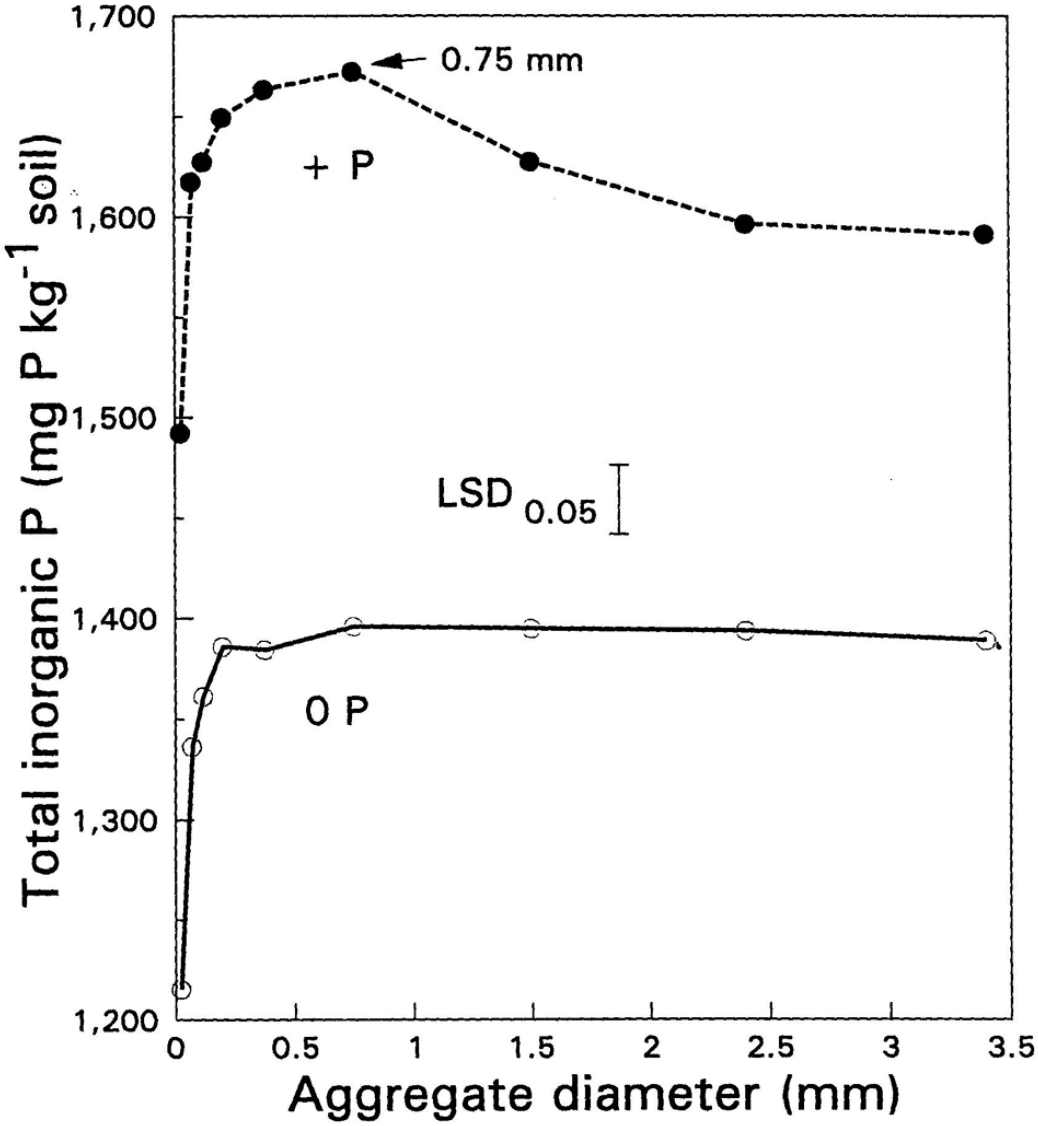

Fig. 4-4. Total inorganic P in aggregates following a four year field experiment. Cumulative P applied to field plots: 0 kg P ha^{-1} (0P) and 930 kg P ha^{-1} (+P). Soil was sampled two years after last P application. LSD is for comparison of P in different aggregate size fractions.

greater than from large aggregates (Fig. 4-3), while the equilibration of P status between large and small aggregates appears to be a much slower process. The low Pi content of the two smallest aggregate fractions is likely due to a combination of plant uptake and low clay and goethite contents (Table 4-1 and 4-2).

Data from Fig. 4-4 also indicate the process of P diffusion and subsequent equilibrium after initial P adsorption is very slow. Soil from these plots was sampled two years following the last P application and yet aggregates from the +P treatment still had different P contents from the applied P.

Aggregate size effects on buffering capacity

Phosphate adsorption isotherms are commonly used to measure the P-buffer capacity of soil. Buffering capacity (slope of the regression curve - Barber, 1984) was inversely related to aggregate size when MAD ranged from 3.4 to 0.75 mm (Fig. 4-5). Soil samples where the MAD was less than or equal to 0.375 mm, due either to sieving, grinding ("2.4 grd") or vigorous shaking ("Fox and Kamprath"), had the highest buffering capacity and were similar.

Adsorption isotherm data were fit to a quadratic equation of the following form:

$$\text{P adsorbed} = b_1(\text{solution P}) + b_1(\text{solution P})^2.$$

Coefficients of determination (r^2) for these regressions were

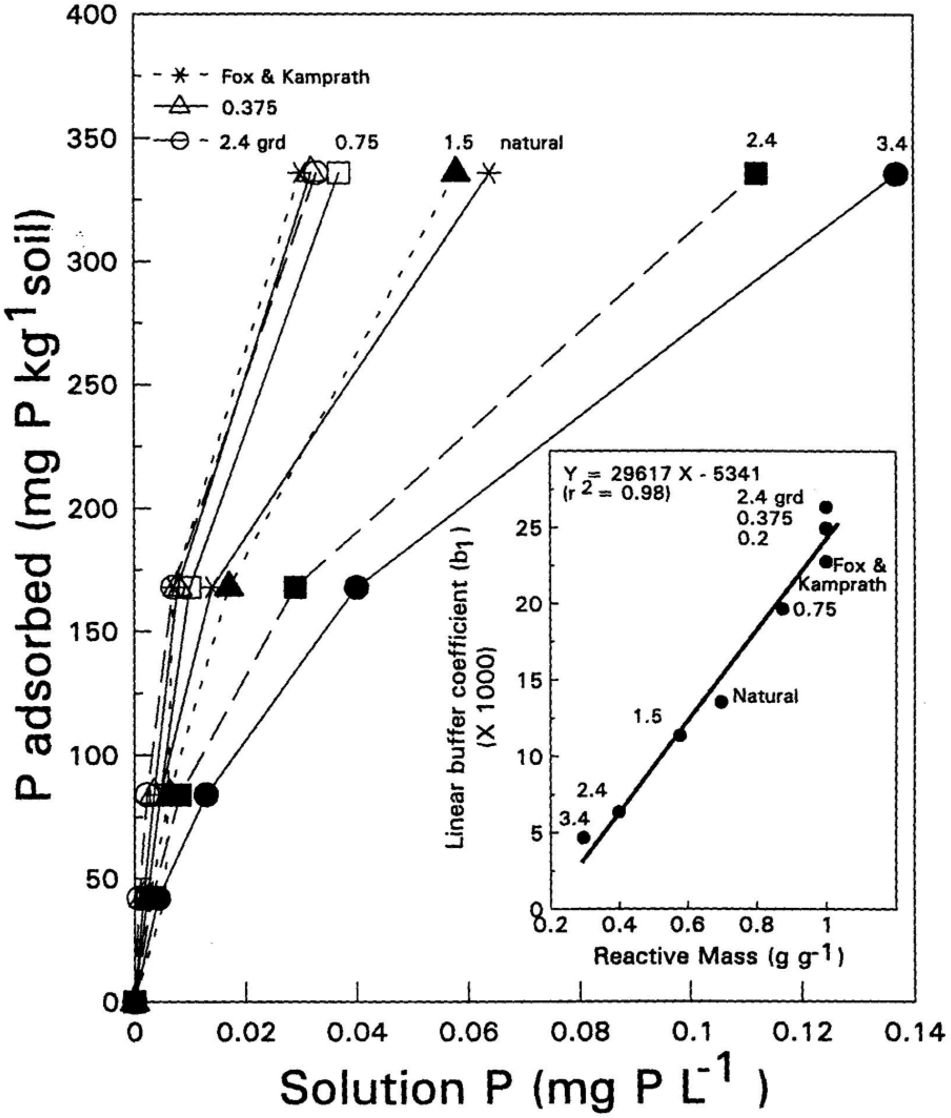

Fig. 4-5. A) Phosphorus adsorption isotherms of five aggregate size fractions (the mean aggregate diameter (MAD) of each fraction is beside each point), an aggregate fraction with a MAD of 2.4 mm ground to pass a 0.15 mm sieve (2.4 grd), unsieved soil with aggregates intact (natural) and unsieved soil done using the method of Fox and Kamprath (1970). **B**) Regression of linear buffer coefficients (b_1) against reactive mass.

greater than 0.99. The linear buffer coefficient (b_1), which explained over 90% of the variation in the amount of P adsorbed, was regressed against reactive mass. The reactive mass for the "natural" soil was calculated using the aggregatesize distribution of this soil (Table 4-1). The reactive mass using the Fox and Kamprath (1970) method was assumed to be 1.0 g g^{-1} because shaking destroyed all the aggregates. The fit was linear and highly significant (Fig. 4-5, insert) indicating that aggregate size had a large influence on soil P buffering capacity. Clay content is highly correlated with soil buffering capacity due to high specific surface area (Cox, 1994). However, fertilizer recommendations based on clay content as proposed by Lins et al. (1990) will not necessarily be precise across a range of soil types, particularly if aggregate size distribution vary widely, since reactive clay surfaces may be occluded within aggregates.

My results suggest that standard soil tests which destroy aggregates either by grinding, sieving, or vigorous shaking over estimate P fertilizer recommendations of actual soil P availability under field conditions because diffusion-limited P adsorption sites are exposed during laboratory analyses. For example, the P requirement to attain solution P values of 0.03 mg P L^{-1} using the Fox and Kamprath (1970 method was 100 mg P kg^{-1} greater than the P requirement estimated with undisturbed (natural) soil (Fig. 4-5). Similarly, the recommended P application rate, based on the Fox and Kamprath P-adsorption isotherm method, was more than 500 kg P ha^{-1} in earlier experiments on this soil (Cassman et al., 1981). However, Cassman et al. (1993) found that applications of as little as 50 and 100 kg P ha^{-1} to this soil produced yields that were 80 and 100% of maximum yield.

Standard extraction methods did not predict the availability of previously applied P over time (Chapter 2 and 3). Critical extraction values to attain optimal yields increased over time. In most standard extraction methods soils are passed through a 2 mm sieve and shaken in extractant, destroying soil aggregation. Therefore, extraction methods may not be precise because total labile P is measured, however, labile P within aggregates may not be plant available. Soil extraction and P-adsorption isotherm methods in which the integrity of soil aggregates is maintained will reflect the true reactive mass of field soil and therefore I speculate that estimates of P fertilizer requirements will be more precise than present methods.

Summary and Conclusions

Soil aggregation greatly affects P adsorption, estimates of soil P buffering capacity, P dissolution, and therefore plant P availability in this soil. Following P addition to this soil, P adsorption was initially restricted to the outer 0.188 mm of aggregate (reactive mass). Since applied P initially reacts with only a fraction of the soil mass, it is concentrated and thus higher solution P values are maintained. Therefore, the initial P requirement of highly aggregated soils should be lower than less aggregated soils. In support of this hypothesis, Cassman et al. (1993) found that in this aggregated soil, despite a high P fixation capacity, relatively low P inputs were required for optimal yields. Over time, however, applied P slowly diffuses into the aggregates where it becomes unavailable due to slow diffusion rates out of aggregates. This may explain the rapid decline in residual P availability on this soil (Chapter 2). Standard soil tests were inadequate in estimating plant available P over time on this soil (Chapter 2 and 3). Most soil tests destroy aggregation and measure total labile P, however, some P inside aggregates may be chemically labile but unavailable for plant uptake. Soil test methods and short- and long- term fertilizer recommendations may be improved if soil aggregation is considered in the interpretation of results or if aggregate integrity is maintained during soil tests. However, more work needs to be done to determine the significance of aggregation on a wider range of soils.

CHAPTER 5

GENERAL SUMMARY AND CONCLUSIONS

Crop yield, P uptake, and extractable P values indicated that residual P availability declined rapidly once P applications ceased. The decline in residual P availability was most evident in the low and moderate P input treatments, although even when there was a net P input of 930 kg P ha^{-1}, soybean P uptake and yield declined by 34 and 15%, respectively, within two years of the last application. Furthermore, Mehlich-1 and Olsen P, common measures of available P, were poor predictors of crop response to P. Over time, extractable P values to achieve desired yield increased by more than two fold.

A sequential P fractionation procedure was employed to study the effect of P dynamics among labile, moderately labile, and recalcitrant Pi and Po pools and relate changes in these pools to P availability. Yields of the unfertilized control treatment declined by over 50% during the course of the experiment, and both yield and P uptake were positively correlated with the size of the labile ($NaHCO_3$) Po pool. This result is consistent with Beck and Sanchez (1994) who concluded that P from Po mineralization is an important source of plant available P in unfertilized systems. None of the Po pools were correlated with P uptake, yield, or extractable P values in the fertilized treatments. While changes in Pi pools where fertilizer P was added were large, there was no effect on Po pools.

In the high P treatment the fraction of fertilizer P recovered in the labile, moderately labile, and recalcitrant Pi pools was 8, 53, and 39%, respectively, 104 d after P application. There was little change in P distribution among Pi pools over time, indicating the decline in available P was not due to fertilizer P becoming less labile. Also, the labile Pi pools measured using this sequential fractionation procedure behaved almost identically to Mehlich-1 extractable P and Olsen P with respect to yield and P uptake and were thus poor methods for estimating available P.

Slow diffusion of P in aggregates may explain why residual P availability declined with time and why current soil test methods were poor indices of plant available P. The results indicate that smaller aggregates adsorbed proportionally more P than larger aggregates and that the rate of P dissolution from this soil was also controlled by aggregate size. Analysis of these results indicate that applied P was initially adsorbed on the outside 0.188 mm layer of aggregates (reactive mass). Following initial adsorption, presumably P diffusion into aggregates was extremely slow due to small intra-aggregate diffusion coefficients (Nye and Stauton, 1994). Conversely, once P diffused into aggregates, it is not immediately available for plant uptake because of slow diffusion out of the aggregate.

Total P content of different aggregate size fractions from the field experiment verified that these phenomena occur in the field. Therefore, slow diffusion in and then out of aggregates appears to explain the decline in plant available P observed in this highly aggregated soil.

The extractable P methods used in this study were poor indicators of plant available P. Protocols for these tests and many others require grinding and shaking soil which destroy aggregates. When aggregates are destroyed exchange sites are exposed that would not normally not be exposed in the field. Thus, these soil test methods measure total labile P but much of this P would likely be occluded within aggregates and unavailable for plant uptake under field conditions.

These results have important implications for P management decisions and developing improved soil test methods. First, highly weathered aggregated soils may be P deficient despite high total P contents, because much of the P is occluded within aggregates where diffusion limits its availability to plants. For example, the total P content of this soil was 1800 mg P kg^{-1}, yet without P fertilizer it was extremely P deficient and under repeated cultivation P uptake and yields continued to decline.

Second, large crop responses may be obtained with small repeated applications of P despite high P fixation capacity. Since applied P is initially adsorbed to a fraction of the soil mass on the periphery of aggregates (reactive mass) it is more concentrated and maintains higher soil solution P concentration. On this soil, for instance, applications of 35 to 100 kg P ha^{-1} to each crop produced yields which were 80 to 95% of maximum (Cassman et al., 1993) although recommended rates based on current soil test methods were in excess of 500 kg P ha^{-1} (Cassman et al., 1981).

Third, the decline in residual P effectiveness will be greater in highly aggregated soils. Over time P fertilizer will diffuse into the interior of aggregates. Long diffusion path lengths out of aggregates then limit the availability of interior aggregate P. Some reports indicate that following large single P applications maximum yields can be maintained for up to nine years (Fox et al., 1971; Kamprath, 1967). This strategy may not be economical on highly aggregated soils due to P diffusion into aggregates. Indeed, it would have been much more economical on this soil to apply small but repeated applications as was done in the low and moderate treatments during the build-up phase (Cassman et al., 1993).

Finally, soil test methods and decision support models need to be developed which account for the effect of soil structure on available P. Modifying the Fox and Kamprath (1970) P adsorption isotherm method to maintain aggregate structure resulted in an estimate of soil buffering capacity which was much more reflective of the true buffer capacity than results from standard protocols where aggregates were destroyed. Similarly, other methods could be developed in which common extractants such as Mehlich-1 or $NaHCO_3$ are used but aggregate structure is maintained.

While the effects aggregation on short- and long-term P availability were the focus of these studies, this research clearly has important implications for understanding the retention and release of pollutants in aggregated soil, particularly those which are strongly adsorbed to soil surfaces. Although the data presented in this thesis were obtained from studies of only one soil, the results are consistent with theory. However, further validation of the effects of soil aggregation on P availability is needed on a wider range of soil types.

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