CHEMICAL BEHAVIOR OF PHOSPHORUS OVER TIME IN FERTILIZED SOILS

Tiequan Zhang

Department of Natural Resource Sciences, McGill University
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CHEMICAL BEHAVIOR OF PHOSPHORUS IN FERTILIZED SOILS

ABSTRACT

Ph.D.   **Tiequan Zhang**   **Natural Resource Sciences**

Fertilizer P accumulates in soils, with potential for movement to waterways, causing eutrophication. Fertilizer P reactions in monoculture corn (*Zea mays* L.) production over time will determine environmentally sound soil management practices. Soil P changes over time were determined on a Chicot sandy clay loam (Grey Brown Luvisol) and a Ste. Rosalie clay (Humic Gleysol). Fertilizer P was added at 44 and 132 kg P ha^{-1} and to the Chicot soil only, manure containing 60 kg P for the first five years. Mehlich-3 (M3) extraction, soil P fractionation, ^{31}P NMR analysis, P in leaching water, and path analysis were measured. Added P increased M3 P more when manure was also added, and in clay soils. To increase M3 P by 1 kg ha^{-1} required from 3.6 to 8.1 kg ha^{-1} fertilizer P, and when "net" fertilizer additions were used, fertilizer required was from 1.8 to 5.3 kg P ha^{-1}. Moderately labile organic P (Po) decreased at 0 added P. With P at the rate of plant removal, inorganic (Pi) and Po fractions were unchanged. Excess P increased labile P and resistant P through moderately labile Pi. More P remained in labile Pi fractions when manure P was added, or in the soil with the higher clay content. Soil organic P levels increased upon fertilization only in the sandy loam soil. Labile and moderately labile Po could be estimated using monoester phosphate values determined by ^{31}P NMR. Inorganic P values in gravitational water increased above 0.05 mg P L^{-1} when soil labile Pi increased above 108 mg kg^{-1} in the sandy loam soil and 69 mg L^{-1} in the clay soil. Thus soil P movement was related to inorganic P additions. Increased fertilizer P did not increase organic P leaching losses. Fertilizer P in corn production may result in groundwater eutrophication.

RÉSUMÉ

Ph.D.   **Tiequan Zhang**   **Sciences des ressources naturelles**

L'engrais P s'accumule dans le sol au cours des années et il y a danger de migration du P aux eaux souterraines et de surface, causant l'eutrophisation. Les réactions dans le sol du P durant la production du maïs (*Zea mays* L.) ont été étudiées dans un loam sablo-argileux Chicot (Gleysol gris brun) et dans une argile Ste. Rosalie (Gleysol humique). Le P sous forme d'engrais chimique fut appliqué au taux de 44 et 132 kg P ha^{-1} sur deux sites et du fumier liquide contenant 60 kg P fut épandu annuellement pendant les cinq premières années sur le Chicot seulement. Le P extrait par la méthode Mehlich-3 (M3), les différentes formes du P de fractionnement et le P dans l'eau de lessivage ainsi que les formes de P analysées par ^{31}P NMR ont été mesurés. La combinaison du P sous forme d'engrais chimique et du fumier a augmenté le P M3 plus que le P ajouté seul. Dans le sol argileux l'augmentation de P M3 suivant les applications de P sous forme d'engrais chimique fut plus élevée que dans le loam sablo argileux. Accroître le P M3 de 1 kg ha^{-1} requérait de 3.6 à 8.1 kg ha^{-1} an^{-1} d'engrais P, et quand le P exporté par les plantes était déduit du P ajouté (l'addition corrigée), la quantité d'engrais P requise pour augmenter le P M3 d'un kilogramme était de 1.8 à 5.3 kg P. Le P modérément disponible et le P organique (Po) ont diminué quand aucun engrais P n'était ajouté. Avec un ajout de P équivalent au taux de prélèvement par les plantes, le P inorganique (Pi) et le Po furent inchangés. Avec un ajout supérieur au prélèvement, le P disponible et le P résistant ont augmenté en passant par le chemin du P modérément disponible. Une plus grande quantité du P ajouté demeurait sous forme disponible quand du fumier était aussi ajouté, surtout dans le sol argileux. Les fractions de P organique ont augmenté avec la

ii

fertilisation dans le Chicot seulement. Le P disponible et modérément disponible pourrait être

estimé par les valeurs du phosphate monoester déterminées par ^{31}P NMR. Les quantités de

Pi dans l'eau gravitationnelle ont augmentés au dessus de 0.05 mg P L^{-1} quand le Pi disponible

du sol était au-dessus de 108 mg kg^{-1} dans le sol loam sablo argileux et au-dessus 69 mg L^{-1}

dans le sol argileux. Le lessivage du Pi était relié à l'addition de P. Le fertilisant P utilisé dans

la production de maïs peut causer l'eutrophisation de la nappe d'eau.

PREFACE

This dissertation is composed of six Chapters preceded by an Introduction and followed by a section of General Conclusions and Future Research. Chapter 1 is a general literature review which establishes the context of the study, generates hypotheses to be tested, and presents objectives to be achieved. The next five Chapters constitute the body of the thesis. Chapter 2 focuses on the effect of long-term continuous P addition on soil Mehlich-3 P in various soil-fertilizer systems using "net addition" criteria. This Chapter consists of two parts, results on a Chicot soil and a Ste. Rosalie soil. Parts of this Chapter were published in the Canadian Journal of Soil Science (1995, 75:361-367), thus Chapter 2 follows the format of the Canadian Journal of Soil Science. Chapters 3 and 4 present dynamics of soil P fractions and inter-relationships between soil P fractions and soil P input in a Chicot sandy clay loam and a Ste. Rosalie clay soil, respectively. Soil P transformations are compared in two soils with contrasting texture. Chapter 3 was accepted for publication in the Soil Science Society of American Journal (March-April, 1997), and Chapter 4 has been submitted to Plant and Soil (September 18, 1996). Chapter 5 discusses the nature of soil organic P in long-term fertilized soil based on ^{31}P NMR determinations, and is prepared for submission to Soil Biology and Biochemistry. Chapter 6 evaluates effects of long-term P fertilization on P values in gravitational soil water and soil P movement, and has been submitted to the Canadian Journal of Soil Science (August 1, 1996). Connecting paragraphs are inserted between the Chapters. A brief summary is provided in General Conclusions, followed by Future Research which outlines needed additional studies.

In accordance with the regulation of the Faculty of Graduate Studies and Research of

McGill University, the following statement excerpted from the Guidelines for Thesis

Preparation (McGill University 1995) is included:

Candidates have the option of including, as part of the thesis, the text of one or more papers submitted or to be submitted for publication, or the clearly-duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.

*If this option is chosen, **connecting texts that provide logical bridges between the different papers are mandatory**. The thesis must be written in such a way that it is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.*

*The thesis must still conform to all other requirements of the "Guidelines for Thesis Preparation". **The thesis must include:** A Table of Contents, an abstract in English and French, an introduction which clearly states the rationale and objectives of the study, a comprehensive review of the literature, a final conclusion and summary, and a thorough bibliography or reference list.*

Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

*In the case of manuscripts co-authored by the candidate and others, **the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extend**. Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-adhered papers.*

The candidate has been fully responsible for both conducting the original studies and

for preparing the manuscripts. All five papers included in this thesis were co-authored by the

candidate and his supervisor Dr. A.F. MacKenzie. Assistance was given by Dr. A.F.

MacKenzie through general guidance and editorial comments during the preparation of the

manuscripts. In addition, Dr. B.C. Liang was a co-author of the manuscript in Chapter 2. Dr.

B.C. Liang carried out management practices of field plots till 1992 and provided comments

on the manuscript. Dr. F. Sauriol who co-authored in Chapter 5 contributed in the analysis

of ^{31}P NMR, and comments on the manuscript.

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I dedicate this work to my wife, Qingchou, and my son, Wei, for their understanding, continuing supports, and patience in daily life, and my new-born son, Davin-Jin, for his arrival and love.

CONTRIBUTIONS TO KNOWLEDGE

The studies presented in this thesis contained new and unique information on the fate of P in long-term fertilized soil-corn systems. Changes in soil P components were determined as a function of time using techniques of fractionation, ^{31}P NMR and analysis of leaching water. Changes of soil P fractions with time were outlined using path analysis in relation to soil-fertilizer-plant systems. Major contributions to knowledge include the following,

1. Fertilizer P required to increase soil available P (Mehlich-3) varied depending on soil type, fertilizer source and P rate. By using net fertilizer addition criteria, the increase in available P per added kg fertilizer P was much greater than when calculated by conventional methods. Therefore, for comparative purposes net fertilizer additions were superior as they removed disparities due to yield and P uptake differences. Using net fertilizer addition criteria, it was found with the clay soil that less fertilizer P was required to raise soil available P by a unit value compared with the sandy clay loam soil. Manure further reduced the amount of P needed to increase available P.

2. Soil organic P (Po) decreased with time and was the major source of soil available P to corn in non-fertilized clay soil. Both soil inorganic P (Pi) and Po fractions remained constant in the coarser soil when inorganic P was added at low rates, indicating an equilibrium between added P and crop P removal.

3. With fertilizer P addition greater than crop removal, labile Pi (bicarbonate extractable) and moderately labile Pi (NaOH extractable) were the major sinks of residual fertilizer P in both soils. Increased residual fertilizer P due to increased P addition enhanced

conversion of soil P to Ca-bound P or residual P which were relatively stable. Manure addition and increased clay content reduced conversion of soil P from labile Pi to moderately labile Pi and thus soil P fixation. Moderately labile Pi was converted to labile Pi with time and consequently was subject to plant uptake and leaching.

4. The role of moderately labile Pi was as a major link in the movement of added P to labile Pi (plant available P). This link can be bypassed if manure is added with the inorganic P. Moderately labile Pi was also a link between residue-P and labile Pi when zero-P was added.

5. Phosphorous concentrations in gravitational soil solution were soil labile Pi dependent. Threshold values varied with soil. A threshold value of labile Pi of 108 mg kg^{-1} for the coarser soil and 69 mg kg^{-1} for the clay soil resulted in dissolved inorganic P above the critical value of 0.05 mg L^{-1}. Soils with labile Pi above these threshold values can cause contamination of water ways.

6. Organic P was increased or maintained by high rates of added fertilizer P and acted as an intermediate in P cycling in soil-corn systems. However, high rates of fertilizer P did not increase Po in gravitational soil water. Increased soil Po with increased fertilizer rates did not increase Po leaching.

7. Monoester P was the most important component of soil Po, consistent with soil types, but varying with P fractions. Monoester P was present in larger amounts in moderately labile Po than in labile Po and may have been more protected from biological degradation as moderately labile Po.

8. ^{31}P NMR is a simpler technique than chemical analyses for determination of soil Po.

Conversion coefficients of 1.54 and 1.20 can be used to determine total soil labile and

moderately labile Po, respectively, from monoester P in that fraction.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Corn has become a dominant crop in Quebec because of its potential for grain production. Monoculture for corn production on about 300,000 ha is a common management practice in Quebec. Studies of maximum grain corn yield in Quebec have shown that corn yield can be as high as 15.2 Mg ha^{-1} (Liang et al. 1992). Increased crop dry-matter production enhances crop residue returns to soil and thus soil organic C (Liang and Mackenzie, 1992).

One of the important factors controlling high grain yield is phosphorous (P) fertilizer application which supplies crop P requirements. However, crop utilization of inorganic P fertilizers in the year of application is only about 10-15% of P applied (Tisdale et al. 1993). This is largely because (1) there is limited soil volume occupied by the plant root system and relatively short diffusion distance of phosphate anions in soil solution and (2) the conversion of fertilizer P to sparingly soluble inorganic and organic P reduces plant availability. Continued applications of P fertilizer are often required to maintain a given level of crop production (Barrow, 1980). Accordingly, a substantial amount of applied P can accumulate in the soil and subsequently convert to different soil P compounds with various bioavailability. Meanwhile, increased saturation of binding sites of soil particles from increased soil P could accelerate P release through desorption/dissolution, and thus increase transportation of soil P to waterways.

Crop residue returns to soil could alter P transformations in the soil-plant system, and in turn, influence the availability of soil residual P to crops and P mobility in the soil.

Efficient use of fertilizer P in cropping systems is often evaluated from the agricultural

1

point of view on short-term bases through changes in soil test values. There is a gap in studies of long-term fertilization and cropping on P transformations in soil. This information is essential for developing sustainable management practices that increase crop yields and farmer returns, and maintain and improve soil fertility while minimizing environmental contamination.

CHAPTER 1

GENERAL LITERATURE REVIEW

1.1. Present Concerns with Phosphorus

Phosphorus is one of the three major essential nutrients to plant. Primary minerals in soils contribute a limited amount of plant P needs. Often soil P has to be supplemented by fertilizer P. The magnitude of P fertilization has been greatly increased due to increased potential for crop yield, a result of utilization of advanced agricultural techniques, especially improved hybrids.

It has been estimated that there is $19,705 \times 10^6$ Mg (as P) of world phosphate reserves and $87,810 \times 10^6$ Mg (as P) of world phosphate resource (Cathcart, 1980). These values may vary, however, the P resources will be eventually exhausted with world consumption of P fertilizer at a rate of 12×10^6 Mg P year^{-1} (FAO, 1962-1979).

Phosphorus fertilizers added to soil mainly accumulate due to low use efficiency. In general, crops take up only from 10 - 15% of added fertilizer P (Tisdale et al. 1993), the remainder accumulating in the soil.

Eutrophication of water bodies is an environmental problem that is currently of major concern. It has been shown that P is an element governing eutrophication (Uunk, 1991). Agricultural land is a major source of P contributing to water bodies (Sharpley et al. 1994).

Clearly, serious concerns exist with P about exhausting of resources, farmers' returns, and environmental damage. The solutions of these concerns are to develop effective management practices for soil-plant-water systems. Studies of chemistry and behavior of P in soil-plant system are the key for understanding and improving P cycling in agricultural systems.

1.2. Reactions of Fertilizer P in Soil

Soil solution P released from fertilizer particles can react with soil components in different ways; adsorption, precipitation, immobilization by micro-organisms and plant roots. Thus, various forms of inorganic (Pi) and organic P (Po) can be produced in soil.

1.2.1. Soil inorganic P

The major sinks for Pi in soil solution are generally adsorption of soil P to soil surfaces and conversion to secondary P minerals. These reactions of P in soil follow two rather distinct patterns: an initial rapid reaction involving exchange of P for anions (such as OH^-) on the surface of Fe- and Al-oxides (Hingston et al., 1967; Kuo and Lotse, 1972; Rajan and Fox, 1975; Rao and Sridharan, 1984) followed by a much slower reaction.

Slower reactions are considered to involve (1) slow sorption (Ryan et al. 1985; Hooker et al., 1980) and (2) precipitation (Low and Black, 1950; Rajan and Fox, 1975; Lindsay, 1979). A distinction between sorption and precipitation was pointed out by Ryden and Pratt (1980). Sorption requires the structure of sorbent to remain essentially unchanged as the process progresses even through its surface activity decreases. This leads to a higher concentrations maintained in solution at a greater surface-saturation than that at a lower saturation. In the precipitation process, the surface activity remains constant. However, where precipitates are heterogeneous solids, with one component restricted to a thin outer layer because of poor diffusion (Sposito, 1984), it is difficult to distinguish between the two processes of slow sorption and precipitation.

1.2.1.1. Slow sorption

At low P concentrations (10 to 100 μM), where precipitation processes do not take place, continuous loss of P in soil solution has been attributed to diffusive penetration into soil particles, diffusion into surface defects and pores and adsorption in inter-particle pores (Parfitt, 1989). Changes of a mono- to a binuclear surface complex can occur (Kafkafi et al. 1967). Slow P sorption due to the presence of surface pores has been reported for synthetic Fe oxides (Madrid and Arambarri, 1985). In general, the slow sorption processes involve formation of covalent Fe-P or Al-P bonds on Fe and Al oxide surfaces (Willett et al. 1988).

Slow reactions are mainly a function of Fe- and Al-oxide contents (Ryan et al. 1985), calcium carbonate content (Solis and Torrent, 1989), temperature (Barrow, 1980), and time. Kinetics of slow reactions were found to be insensitive to soil moisture content or soil type such that reactions in solution may not be the rate-limiting processes (Parfitt, 1978), and slow reactions perhaps occur at the original sorption site (Ryden et al., 1977).

Sorption rates of P by soil components decrease with time, but reactions can continue for a long period. Peña (1990) found that slow sorption, i.e., between 6 and 126 days after P addition, averaged only about 5% of the rapid, initial 6-days sorption. It is often doubtful whether the reaction reaches equilibrium. These slow reactions may not be useful for indexes of labile P and may affect P bioavailability (Barekzai and Mengel, 1985). Characteristics and consequences of soil P sorption *in situ* need to be evaluated after long-term additions of fertilizer P.

1.2.1.2. Precipitation

Based on the principle of solubility product, a number of early investigations of P chemistry in soil have been conducted using solubility isotherms (Kittrick and Jackson, 1955a and b, 1956). The results indicated that in soils with low pH, variscite and strengite are the probable P minerals, whereas in soils with high pH, calcium P minerals (e.g., apatite) are dominant (Savant and Racz, 1973; Lindsay, 1979). However, it was concluded that variscite and fluorapatite cannot control the P concentration in soil solution, because of the extremely slow dissolution rate of Fe-, Al-, and Ca-phosphates in soil (Murrman and Peech, 1969).

Precipitated P compounds are affected by characteristics of the soil solution and the soil, and therefore P precipitation could be much more complex in farmers' fields than in laboratory studies. Addition of fertilizer P leads to the formation of strongly concentrated P solutions and often a low pH in the vicinity of the fertilizer granule where P concentration could be as high as 1.5 to 12 M and pH can be as low as 1 (Sample et al. 1980), dependent on P source. This acidification effect may cause degradation of clay mineral structures, dissolution of $CaCO_3$, and subsequent precipitation of amorphous Al-phosphates and Ca-phosphates (Cole et al. 1953; Freeman and Rowell, 1981). Particles of Fe and Al oxides may become coated by Fe- and Al-P films when exposed to those solutions (Moreno et al. 1960). Local soil conditions leading to precipitation of Fe-, Al-, and Ca-phosphate usually change with time. However, in the long run, the formation of various Al- and Fe-phosphates may depend mostly on 'average' soil properties.

The initial compounds precipitated are likely metastable and will usually change with time into more stable and less soluble compounds, or re-dissolve in soil solution. However,

stable phosphate products are unlikely to govern P concentration in soil solution (Ryden and Pratt, 1980). Therefore, the various calcium phosphates are more likely to govern the P concentration through sorption-desorption precesses in alkaline soils (Ram and Rai, 1987). In acidic or slightly acidic soils, the surface-active amorphous Al-hydroxides and Fe-oxides tend to dominate the process of P fixation through adsorption, instead of Al^{3+} and Fe^{3+} reactions in soil solution (Ram and Rai, 1987). As a result, it seems there is little immediate significance of precipitation processes in soil P transformation.

1.2.2. Soil organic P

Phosphorus in soil solution can also be taken up by plant roots, bacteria, or fungi, so that soil Po could be formed through immobilization of soluble Pi. Those forms of soil Po can be classified into three groups; (1) inositol phosphates, the major constituent with inositol hexakis- and pentakisphosphates, comprising up to 60% of soil Po (Tate, 1984), and primarily of plant origin, (2) nucleic acids, added at a greater rate than inositol phosphates, but mineralized in most soils much more rapidly and incorporated into microbial biomass, with only small quantities existing in soil (Condron et al., 1985), and (3) phospholipids, dominated by choline phosphoglyceride, followed by ethanolamine phosphoglyceride (Dalal, 1977). Other soil Po compounds can be sugar phosphates (Anderson and Malcolm, 1974) and phosphate proteins contributing to trace amounts of soil Po. Over one-half of the soil Po cannot be accounted for in known compounds (Stevenson, 1986).

Association of Po is with high molecular-weight fractions (Brannon and Sommers, 1985; Baker, 1975; Veinot and Thomas, 1972). Brannon and Sommers (1985) inferred that

Po was covalently bonded to humic compounds with molecular weights exceeding 10,000.

It was also found that as much as 40% of soil Po is associated with the fulvic and humic

fractions (Brannon and Sommers, 1985). Organic P is located mainly in the fulvic acid

fraction (Kaila, 1963; Moyer and Thomas, 1970; Veinot and Thomas, 1972; Dalal, 1977). It

was shown that one mechanism for Po incorporation into model humic materials involved the

linkage of a phosphate ester-amino compound with synthetic humic materials prepared by

oxidative polymerization of polyphenols (Brannon and Sommers, 1985).

Soil Po can account for from 15 to 80% of total soil P (Stevenson, 1986). The

content of Po in soil varies from < 100 μg/g to over 1300 μg g^{-1} (Halstead and McKercher,

1975; Uriyo and Kesseba, 1975). The Po content of the soil decreases with depth in much

the same way as organic C (Pearson and Simonson, 1939) and is generally higher in clay soil

than in coarse-textured soils, but lower than in humus soils (Kaila, 1963). Management

practices of cultivation and fertilization, high soil pH, and poor drainage conditions can

adversely affect the Po content of soils.

1.3.   Analysis of Soil P Forms:

Because of varying reaction processes, soil P has markedly different forms. The

complexity of soil P forms and interactions among these various forms and soil components

has resulted in a need for isolation of soil P compounds through fractionation. The present

fractionation methods have been mainly extraction related procedures.

Using chemical extraction, Chang and Jackson (1957) divided soil P into Al-P, Fe-P,

Ca-P, occluded Fe-P and occluded Al-P. This procedure was modified to include a step for

correction of reabsorption of phosphate (Williams and Walker, 1967) and to render the procedure more suitable for use with calcareous soils (Syers. et al. 1972). However, the exclusion of soil Po limits the use of these procedures.

More recently, Hedley et al. (1982b) sequentially fractionated soil P into 1) resin-extractable inorganic P (Pi), the most biologically available Pi (Amer et al., 1955; Sibbesen, 1977), 2) sodium bicarbonate-extractable Pi and -Po, labile Pi and Po sorbed on the soil surface plus a small amount of microbial P (Bowman and Cole, 1978), 3) sodium hydroxide extractable-Pi and -Po, compounds held more strongly by chemisorption to Fe- and Al-components of soil surfaces (Ryden et al., 1977; McLaughlin et al., 1977), 4) hydrochloric acid extractable-Pi - mainly apatite-type minerals (Williams et al., 1971), and residual P - the more chemically stable Po forms and relatively insoluble Pi forms. These Pi and Po fractions, sometimes called pools, vary in their availability to plants. The procedure has been used successfully to study P transformations in temperate (Hedley et al., 1982b) and tropical soils (Tiessen et al. 1983), although Po in each individual fraction has not been identified.

Analysis of soil Po can been performed indirectly through extraction using either acid or base extractants (Bowman and Cole, 1978). Organic P in soil extractant can be further subdivided using chromatography or electrophoresis techniques (Anderson, 1980) into various components, such as inositol phosphates, phospholipids, nucleic acids, phosphoproteins, and acid-soluble esters. However, only about one-third of soil Po can be accounted for by these compounds (Stevenson, 1986).

An alternative approach developed recently is to use ^{31}P nuclear magnetic resonance (NMR) to obtain both qualitative and quantitative estimation of various forms of Po

(orthophosphate monoesters, phosphates diesters, phosphonate, and teichoic acid), and Pi (inorganic orthophosphate, pyrophosphate, and polyphosphate) in soil alkaline extracts (0.5 M NaOH) (Newman and Tate, 1980; Tate and Newman, 1982; Emsley and Niazi, 1983; Hawkes et al., 1984; Condron et al. 1985, 1990). More recently, a chelating, cation-exchange resin has been used to prepare the soil extracts for ^{31}P-NMR analysis. It has been claimed that the cation-exchange resin method was more suitable for use with NMR analysis (Adams and Byrne, 1989).

^{31}P NMR can reveal stabilities of various forms of soil Po. For example in grassland soils cultivated for over 20 years, orthophosphate diesters decreased more rapidly than orthophosphate monoesters (Hawkes et al., 1984). The major advantages in using ^{31}P-NMR are that (1) it is analytically less complex than the detailed partition chromatography techniques otherwise required for identifying specific Po compounds, and (2) it gives an almost full recovery of extracted Po (Tate and Newman, 1982; Hawkes et al., 1984; Condron et al. 1985).

Clearly, using ^{31}P NMR technique can be useful for understanding soil P transformations through identification of Po compounds.

1.4. Factors Affecting P Transformations

Transformations of P in soil are a function of soil texture, pH, organic matter, $CaCO_3$, Fe- and Al-oxides, temperature and moisture, and reaction time. In a given agricultural soil, however, cropping and fertilization, which alter the status of soil organic matter and P concentrations in the soil solution, will be the most important factors influencing P cycling in

the soil.

1.4.1. Effects of fertilization and cultivation

Long-term cropping of soil without fertilizer addition results in the depletion of soil P (Haas et al. 1961; Hedley et al. 1982b), whereas fertilization could result in accumulation of P in the soil. The extent of P accumulation will depend on both fertilizer rate and years of application.

Results obtained by Barber (1979) in soils of a rotation-fertility experiment over a 25-year period showed accumulation of P occurred when P application rates exceeded 22 kg ha^{-1} yr^{-1}. Net losses of P at lower fertilizer P rates were accounted for by crop removal. After a long-term rotation of oats-wheat, wheat-potatoes-barley-sunflowers in a sod-podzolic soil, Frid and Prokhorova (1987) found that the use of constant rates of mineral fertilizers for a finite number of years with any initial mobile P level resulted in a more or less constant level of mobile phosphate. Unfortunately, total P accumulation in the soil was not measured in this study.

Using a modified Chang and Jackson (1957) procedure of soil P fractionation, Sadler and Stewart (1975) measured changes in forms and availability of soil Pi during the 2.5-yr period following field application of orthophosphate in three soils of an Oxbow Catena. Results indicated that the 31 to 67% of applied P recovered as Pi remained in plant available forms after two months of application. However, available form(s) differed from soil to soil, mainly as Ca-P in calcareous and Orthic Chernozemic soils and Al-P and Fe-P in the Gleysol soil. Subsequently, carbonate sorbed P converted to Al-P in the calcareous profile, resulting

in a further 70% reduction in P availability while no further reduction of P availability occurred with time in the Gleysol soil.

Kumar et al. (1993) conducted a study in three western Australian soils that had been fertilized up to 5 years previously with rock phosphate (RP) and superphosphate. They found that carbonate sorbed P and Al-P from soils fertilized with superphosphate, and Ca-P from soils treated with apatetic RP, decreased with time after fertilization. Residual P accounted for 63 to 67% of added fertilizer P. Soil P loss from the 0-10 cm depth accounted for 20 to 37% of added P.

Unfortunately, a considerable amount of the work on P transformations in the soil has excluded the isolation of Pi pools from Po pools. Since organic matter is lost at a rather rapid rate when soils are first placed under cultivation (Campbell, 1978), much of the initial loss of P could be hypothesized as losses of Po. Modification of soil Po may occur when fertilizer P is added.

Thompson et al. (1954) reported a decrease in the Pi and Po content of surface soils due to cultivation. Data obtained by Haas et al. (1961) for the soils of 15 dryland experiment stations in the U.S. Great Plains showed that total P was reduced by an average of 8% by cropping with wheat over a period of 30 to 48 years. They found losses of P to be approximately 0.3% per year, with the organic fraction accounting for the majority of the loss.

Hedley et al. (1982b) in a study involving Black Chernozemic soils taken from a permanent pasture and an adjacent cultivated field (65 years), fractionated soil P into Pi and Po pools. Neither site had received P fertilizer, and a wheat-wheat-fallow rotation was used on the cultivated soil. Total P content of the cultivated soil decreased by 29% and the major

loss of total P was Po and residual P. Of the total P lost, 22% was from the extractable Po forms, whereas 52% originated from stable P. Thus, considerable mineralization of Po occurred during cultivation to supply crop P needs. Similar results were obtained by Mckenzie et al. (1992a) in a study focusing on effects of different cropping systems (continuous wheat, fallow-wheat, and fallow-wheat-wheat) on soil P fractions in the soil. Moreover, in a Luvisolic soil, in addition to Po, continuous cropping without fertilizer addition also resulted in a decrease of resin-Pi, NaOH-Pi, and HCl-Pi (Mckenzie, 1992b). The addition of P fertilizer at a rate of 6 kg ha^{-1} in the first 49 yr and at a rate of 22 kg ha^{-1} in the last 6 yr increased total P and all Pi fractions, but had no effect on labile Po forms (Mckenzie et al. 1992a). Sharpley and Smith (1983) in studying the changes in total P, Po and Pi as influenced by cultivation and fertilization of eight soils in U.S., found an average decrease of 43% in the soil Po, although fertilization increased the total P by 25%. As a result of fertilization and Po mineralization, Pi was increased by 118%, with plant available Pi increased by 84%. Thus, it is apparent that addition of P fertilizer, and the maintenance of adequate labile Pi may not improve soil Po, nor prevent substantial losses of Po from soil. This may be attributed to inadequate C inputs into the soil to supply energy and substrate for the transport of P into the microbial cell.

1.4.2. Cropping effects

Cropping can modify soil P transformations through addition of crop residues and release of exudates into the soil in the vicinity of the roots, creating an unique volume called the rhizosphere.

1.4.2.1. Crop residue effect

Additions of organic materials to the soil can result in the rapid conversion of substrate C into soil biomass. Depending on the P status of the substrate, soil P may be mineralized or immobilized. Chauhan et al. (1981) showed that when soils with an adequate supply of labile Pi were incubated with cellulose, labile and moderately labile Po increased. However, when the level of labile Pi in the soil was low, additions of cellulose had no influence on the amount of Po in the soil, and upon subsequent cellulose additions, microbial degradation of added cellulose became limited by the P supply. Therefore, dynamics of soil Po relies on the ratio of soil organic C to labile Pi. Whether there is a cumulative effect of crop residue return on soil Po remains to be studied.

1.4.2.2. Phosphorous transformation in the rhizosphere

Plants absorb P from soil solution, and at the same time, release materials into the rhizosphere. Because of the effect of plant roots, chemical, physical, and biological properties of rhizosphere soil are markedly different from the bulk soil. These differences show up mainly as 1) lower pH due to different cation/anion ratio of plant root uptake, 2) low-molecular-weight organic acids secreted by, or exuded from plant roots, 3) a larger amount of organic C as a result of root exudates and materials sloughed off root surfaces, and thus 4) a larger amount of microorganisms in the rhizosphere. As a consequence, within the rhizosphere P could redistribute among the various forms of soil P and P availability to plants could change.

Researchers have examined soil P undergoing transformations in the rhizosphere.

Hedley et al. (1982a; 1983) studied plant induced changes in the rhizosphere of rape (*Brassica napus var.* Emerald) to determine fractions of P depleted due to plant uptake. In the control treatment, they noted that rape roots drew primarily on resin exchangeable Pi, NaHCO$_3$-Pi, and NaOH-Pi associated with no change of soil pH during the first 21 days of cultivation. After 41 days, the pH of the rhizosphere soil fell sharply. In addition to a depletion of resin Pi, NaHCO$_3$-Pi, and NaOH-Pi, there was a substantial depletion of acid-soluble forms of soil Pi and residual soil P. It was suggested that acidification of the rape rhizosphere led to the dissolution of acid-soluble forms of Pi. However, the authors stated that there was no evidence for significant hydrolysis of soil Po. In contrast, they found a slight increase in Po in the rhizosphere soil, possibly due to the buildup of root debris and microbial P. In the treatment fertilized with P, 60% of the added P was recovered as resin Pi, while the remaining P was largely in the NaHCO$_3$-Pi and NaOH-Pi fractions. There was little movement of added P to the HCl-Pi and residual P and only small Po gains in the NaOH-Po. Trends of depletion in the NaHCO$_3$-Pi and NaOH-Pi or alkali-soluble fractions were similar. Plant uptake from the fertilized soil was virtually all from resin and alkali-soluble Pi. There was no change in rhizosphere pH and no significant depletion of acid-soluble P up to day 20 and a 9% decrease after 41 days. Hedley et al. (1983) concluded that P-deficient rape plants draw on acid-soluble soil P reserves, whereas P-sufficient plants only take up soil P that will desorb at the original soil pH.

Gahoonia and Nielsen (1992) conducted a study in which the depletion of inorganic and organic P in the rhizosphere of rape grown under conditions in which the rhizosphere soil pH decreased, remained constant or increased at equal nutritional levels. The root-induced

decrease of soil pH from 6.7 to 5.5 increased the depletion of $KHCO_3$-Pi and residual P by 34% and 43%, respectively. Depletion of $KHCO_3$-Po was not affected by a change in rhizosphere pH. With constant or increased pH, depletion of NaOH-Pi was 17% and NaOH-Po was 22% higher than with decreased pH. Substantial amounts of $KHCO_3$-Po were mineralized and withdrawn from the rhizosphere.

Clearly, there is potential for plants to use many types of phosphate. This information is important for development of P management strategies in soils with high fertilizer P residual values.

1.5. Soil P Mobility and P Loss

Soil P mobility and P loss have not been considered to be significant in P cycling. However, with increased soil P values, as well as increased eutrophication of surface water, this approach has to be re-evaluated.

1.5.1. Soil P mobility

Mobility of phosphate anions in the soil depends on the nature of mineral surfaces and oxide coatings since phosphate anions are strongly adsorbed by mineral constituents such as clays and sesquioxides (Parfitt, 1978). Thus, mobility of phosphate in the soil is related to the soil P forms.

Organic P anions can move to a greater depth than Pi in soils. Martin (1970) and Halstead and Mckercher (1975) found that there was an accumulation of inositol phosphate in some B horizons. Selected Po compounds, such as, glucose 6-phosphate, choline

phosphate and adenosine triphosphate, had a higher mobility than the phosphate anion in B horizons of both grassland and forest soils (Frossard et al., 1989). Several studies demonstrated appreciable downward movement of P following the field application of manure which resulted in elevated P levels at 60 to 120 cm depths. In contrast, application of inorganic fertilizer P resulted in much less downward movement of P than that with manure P (Chater and Mattingly, 1979).

Decomposition of organic residues could contribute to soil P mobility. Studies have indicated that the mobility of P in soil is enhanced by additions of decomposable organic matter. Mechanisms involved are presumably as follows (Stevenson, 1994):

1). formation of chelate complexes with Ca, Fe, and Al, and subsequently release of phosphate to water soluble forms,

2). competition between humate and phosphate ions for adsorbing surfaces, thereby preventing fixation of phosphate,

3). formation of protective coatings over colloidal sesquioxides, with reduction in phosphate adsorption, and

4). formation of phospho-humic complexes through bridging with Fe and/or Al.

Evidence obtained by McDowell et al. (1980) shows that concentrations of PO_4-P and organic C in soil solutions increased as residue loading rates were increased. Thus management practices which increase the loading of crop residue may increase P mobility.

1.5.2. Soil P loss

Soil P losses can occur through soil erosion, surface water runoff and leaching. In most soils, P is retained close to the site of application. The main mechanism of P losses is physical erosion of the topsoil and loss of solution P in surface runoff (Khasawneh et al., 1980). The P loss through leaching has been considered to be small.

Recorded leaching losses of P ranged from 7 g ha^{-1} yr^{-1} in New Hampshire and 15 g ha^{-1} yr^{-1} in Illinois prairie landscapes to 500 g ha^{-1} yr^{-1} in glacial outwash in New Zealand (Smeck, 1985).

Soil P loss through runoff could be much greater than through leaching. Sharpley (1993) reported that total soil P loss in runoff ranged from 213 to 3860 g ha^{-1} yr^{-1} in the Southern Plains region of Oklahoma and Texas. Forms of P in runoff can be both dissolved P and the P associated with solid soil particles. Thus, the amount of P in runoff is a function of desorption-dissolution reactions controlling P release from soil, fertilizer reaction products, vegetative cover, and decaying plant residues and other physical properties, such as particle size (Sharpley, 1993).

In sandy soils, which have both a low capacity to retain water and a low buffering capacity for phosphate, appreciable P applied may be moved from the site of application, and the removal can be as high as 80% of the P applied (Ozanne et al., 1961). In flat fields, phosphate may be lost mainly by leaching from soils in which the phosphate sorption capacity has been saturated by P fertilization.

Because of public concerns regarding eutrophication of natural waters arising from increased phosphate fertilization of agricultural land, further studies of phosphate behavior

in soils are essential (Sharpley and Menzel, 1987; Van der Zee et al., 1989).

1.6. Modeling of Soil P Cycling

Soil P cycling is extremely complicated and involves many processes, which are modified by climatic effects. A typical concept model for soil P cycling is that of Stewart (1980). Simulation models have been developed from different points of view. These models include Half-life models (Larson et al., 1965; Larsen and Probert, 1968), the Middleton model (Middleton 1983), the Gunnarsson model (Gunnarson, 1982), the Jones model (Jones et al. 1984a,b; Sharpley et al. 1984), the Wolf and Janssen model (Wolf et al. 1987; Janssen et al., 1987); the Saroa and Biswas model (Saroa and Biswas, 1989); and the Swartzendruber and Barber model (Swartzendruber and Barber; 1965; Watkinson, 1989).

Among the models presently available, the one proposed by Jones et al. (1984a,b) and Sharpley et al. (1984) must be the most ambitious model in terms of predicting complex of soil P behavior. This model involved the definition of 53 parameters and description of seven P compartments: stable Pi, active Pi, stable Po, fresh Po, labile P, fertilizer P, and crop P including grain, stover, and root P. The model was shown to simulate changes in soil Po, soil test P values with and without fertilizer addition, responses of wheat and corn to soil test P, and fertilizer P required to maintain the P supply at sufficient levels for wheat and corn in the Great Plains of the United States. However, the precision of some of the simulation was shown to decrease considerably with extension of the time period. The process of P cycling was not directly included.

Path analysis has been used to develop models for soil P cycling in the soil-plant

system (Tiessen et al., 1984; and Beck and Sanchez, 1994). Promising results provided information of pathways of P transformation in soil, as well as sinks of added P and sources of plant available P.

1.7. Conclusion, Hypothesis, and Objectives

From this review of the literature it is evident that the P cycle in the soil-plant system is complex. Transformations of P in soil not only involve many Pi and Po compounds, but also are affected by soil properties, cropping, and fertilization rate. Slow sorption plays an important role in long-term soil P transformations. Both soil Pi and Po may be significantly affected by cropping and fertilization. Fixed soil P forms may be reversible. Plant roots have the potential to use all forms of soil P including sparingly soluble Fe- and Al-P and residual P. Experiments have mainly involved individual forms of soil Pi under addition of fertilizer P at normal P rates. Dynamics of soil Po over time have received less attention. Soil Po fractions derived from Hedley's procedure have not been identified, although this procedure has been widely used. Pathways of soil P transformation and the effects of long-term fertilization at increased P rates on these pathways have not been evaluated. As P accumulates, need for fertilizer P should gradually be reduced. The prediction of P changes with fertilization is necessary for rational long-term soil P management.

It is hypothesized that long-term continuous use of fertilizer P at high rates will have a cumulative impact on P cycles in soil-corn systems, and these effects will be modified by input of organic C from crop residue and organic manure. Consequently, the long-term effect will inherently influence pathways of soil P transformation, soil P fertility, P mobility in the

soil profile, as well as loss potential of soil P. Detailed hypotheses are as follows.

1) Due to the significant role of slow sorption of soil P during long-term transform-
   ations and soil P desorption processes, certain fractions of residual fertilizer P will
   be available to subsequent crops.

2) Residual soil Pi will encourage bio-synthesis of soil Po through immobilization
   because of returns of corn residues and/or organic manure with high C:P ratios. This
   effect will be a function of fertilizer rates and soil texture. Since labile-Po may be
   easily mineralized, soil Po pools will be moderately labile.

3) Because of rapid decomposition of diester phosphates, increased soil Po will mainly
   consist of monoester phosphates.

4) Increased loading of soil P with P fertilization will exhaust the phosphate sorption
   capacity of soil particles. As a consequence, P mobility in soil profile and the
   potential of a soil to lose P through leaching will be increased.

As a consequence, the objectives of this thesis were:

1) to examine changes in soil test P as a function of added inorganic P with and without
   organic manure in two long-term fertilized soils under continuous corn,

2) to quantify soil P fraction changes and model long-term soil P transformations using
   path analysis,

3) to determine the nature of soil Po fractions isolated from Hedleys' procedure using
   ^{31}P NMR, and

4) to evaluate soil P loss potential through leaching and establish relationships to soil

P level and texture.

CHAPTER 2

LONG-TERM CHANGES IN MEHLICH-3 EXTRACTABLE P

IN TWO TEMPERATE SOILS UNDER CONTINUOUS CORN (*Zea mays* L.)

2.1. Abstract

Rates of change of soil nutrient levels during crop production can be used to evaluate the long-term economic value and sustainability of fertilizer practices. Objectives were to quantify changes in Mehlich-3 extractable P due to additions of inorganic and manure P in corn (*Zea mays* L.) production. Surface (0 - 20 cm) and subsoil (20 - 40 cm) samples were collected after harvest from 1984 to 1993 on a Chicot sandy clay loam soil (Grey Brown Luvisol) and from 1988 to 1994 on a Ste. Rosalie clay soil (Humic Gleysol). In the Chicot soil, manure P at 60 kg P ha^{-1} plus inorganic fertilizer P at 132 kg ha^{-1} yr^{-1} increased extractable P 1.0 kg for every 4.2 kg added P if only topsoil P was considered, for every 3.2 kg added P if net P addition was considered, and for every 2.1 kg added P with subsoil P included and net P addition considered. Without manure, 132 kg P ha^{-1} yr^{-1} increased Mehlich-3 extractable P by 1.0 kg for every 8.1 kg P added, or 5.3 kg P added if net P addition criteria was used. At the low rate of 44 kg P ha^{-1} with manure P, Mehlich-3 levels increased by 1.0 kg P for every 3.2 kg net added fertilizer P. Extractable P remained constant when inorganic fertilizer P was added without manure, probably because crop removals equaled fertilizer additions. To increase soil test P, manure combined with high P rates was more effective per unit added P than low P rates or added P without manure. In the Ste. Rosalie soil, Mehlich-3 extractable P remained constant over time when zero-P was added. Phosphorus fertilization at rates from 3.6 to 5.2 kg ha^{-1} increased soil Mehlich-3 P by 1 kg ha^{-1} when crop P removal was not counted and from 1.8 to 2.7 kg P ha^{-1} added inorganic P when net P addition was used. High P rates were less effective in increasing soil Mehlich-3 P than low P rates. Addition of inorganic fertilizer P had generally a greater impact on

Mehlich-3 P in Ste. Rosalie than Chicot soil.

2.2. Introduction

Fertilizer P application rates must be related to soil nutrient levels, and these levels are influenced by previous fertilizer use. As a consequence, knowledge of the rate of increase or decrease of residual P from fertilizer applications and crop removal is essential to plan long-term fertilizer programs.

Crop utilization of inorganic fertilizer P in the year of application is generally less than 25% (Sadler and Stewart, 1974; Read et al., 1973). Soils receiving P fertilizer, therefore, often experience an accumulation of residual P (Sharpe et al., 1984), which may become available in later years (Ridley and Tayakepisuthe, 1974).

After 16 years of P fertilization, Halvorson and Black (1985) reported that single applications of 22, 45, 90, and 180 kg P ha^{-1} on a glacial till Williams loam raised the average levels of soil test P (Olsen's method) by 1, 2, 4, and 8 mg P kg^{-1} soil, respectively. In a Honeoye fine sandy loam soil, Peck et al. (1975) found that total applications of concentrated superphosphate over 10 years of 248 kg P ha^{-1} increased available soil P (Morgan's method) from 10 to 186 kg P ha^{-1}. In a five year study on irrigated sandy soil in Nebraska, Rehm et al. (1984) found that 22 kg P ha^{-1} applied annually for corn (*Zea mays* L.) increased soil test P (Bray and Kurtz No. 1) by 1 mg kg^{-1} soil for each 9.6 kg P ha^{-1} applied. Increased soil test P with manure application was also reported (Vivekanandan and Fixen, 1990).

Changes in soil test P levels are dependent on soil type, fertilizer rate and interactions among fertilizers, crops, and management practices. The objective of this study was to

evaluate changes in Mehlich-3 extractable P as influenced by long-term P fertilization of corn in two Quebec soils with contrasting textures.

2.3. Materials and Methods

2.3.1. Experimental design and management practices

Field experiments with corn (*Zea mays* L.) were initiated on the Chicot site in 1984 and on the Ste. Rosalie site in 1988, at the Emile A. Lods Agronomy Research Center, near Montreal, Canada (45°25'45"N, 73°56'00"W). Mean annual air temperature is 6.2°C and mean annual rainfall is 929 mm. Experiments on both sites were continued through 1995. The soils used in this study belong to a Chicot series, a sandy clay loam (Grey Brown Luvisol; fine-loamy, mixed, frigid Typic Hapludalf) and a Ste. Rosalie clay (Humic Gleysol; fine, mixed, frigid, Typic Humaquept) (Table 2.1.).

On the Chicot site, the long-term experiment began as a 2 by 2 by 2 by 2 factorial design with four randomized complete blocks from 1984 to 1986. Initial treatments included two hybrids (code named A and B, see Appendix), two plant populations (90,000 and 65,000 plants ha^{-1}), two rates of fertilization, and irrigated and non-irrigated regimes. Irrigation treatments were replaced by two row spacing treatments and then by additional fertilizer rates from 1987 to 1993. Fertilizer treatments at P rates of 44 (normal rate) and 132 (high rate) kg P ha^{-1} associated with hybrid A and plant population of 90,000 plants ha^{-1} which were retained through out the study were selected for this study. Sufficient N (170 and 400 kg ha^{-1} as N in normal and high P rates plots, respectively), K (170 and 400 kg ha^{-1} as K$_2$O in normal and high P rates plots, respectively), Mg (30 kg ha^{-1} for both P rates plots), and S (30 kg ha^{-1}

27

for both P rates plots) were added to balance crop nutrient requirements. Liquid cattle manure with a P content of 15 kg Mg^{-1} dry matter was applied and incorporated in all plots at a rate of 4000 kg dry matter ha^{-1} yr^{-1}, following harvest from 1984 to 1988. Treatments were applied to the same plots each year. Each plot was 5m by 8m from 1984 to 1990 and 5m by 7.5m from 1991 to 1993.

At the Ste. Rosalie site, initial treatments included seven fertilizer rates, and two hybrids (code A and B) at 90,000 plants ha^{-1} with a completely randomized block design and four replicates. Plot size remained constant at 5m by 6.5m. Treatments associated with fertilizer P rates and hybrid A were involved in this study. These treatments included 0, 44, and 132 kg P ha^{-1}. As with Chicot site, sufficient N, K, Mg, and S were added to each plot.

On both sites, plots were normally seeded in the first ten days of May. Corn was seeded at an approximate depth of 5 cm using a Gaspardo (Model SP510, Gaspardo, Morsano AL Taglimento, Italy) with three adjustable planter drills. Hand-thinning to desired populations was done in mid June. Seeds pretreated with diazinon, lindane, and captan were used to control soil insects and to prevent seed-borne diseases. In order to control quackgrass (*Agropyron repens* L.), glyphosate was applied at a rate of 2.1 kg ha^{-1}, a.i., 4 days prior to secondary tillage operations. Broadleaf weeds and grasses were controlled with a preplant incorporated application of 4.3 kg ha^{-1} a.i. of alachlor and 1.75 kg ha^{-1} a.i. of atrazine.

Corn ears were harvested normally with a combine (Nurserymaster Elite, Wintersteiger America, Salt Lake City, Utah) in the second week of October from two central rows in each plot. Grain was weighed, sub-sampled and analyzed for yield, and P content. Total grain P removals were calculated. After harvest, stover was chopped onto the original plots. Plots

28

were ploughed to a depth of 20 cm in late October each year. Secondary cultivation in spring consisted of two passes of a disk harrow at a depth of 10 cm followed by one pass of a spring tooth harrow.

2.3.2. Soil sampling and P analysis

Soil was sampled shortly after harvest. One soil core sample was taken on a treatment replicate base using a hydraulically operated sampling tube of 7.5 cm diameter at a 20 cm interval up to 40 cm. In order to reduce spatial variation, four additional soil samples were taken at the soil depth of 0 to 20 cm in the same plot. Five surface soil samples were mixed thoroughly and a subsample taken to represent the surface soil. Soil was air-dried and crushed to pass a 2.0 mm sieve after removing visible root and crop residues. Soil P was extracted with the Mehlich-3 solution (Mehlich, 1984). Extracted P was determined with a Technicon Auto-Analyzer (Technicon Industrial System, Tarrytown, NY) using ammonium molybdate and ascorbic acid (Murphy and Riley, 1962).

2.3.3. Statistical analysis

Statistical analyses were performed using the Statistical Analysis System (SAS Institute, 1985). To separate the effect on Mehlich-3 extractable values of inorganic fertilizer from organic manure on the Chicot site, the experimental period was divided into two stages; stage one from 1984 to 1989 in which Mehlich-3 extractable values were influenced by annual applications of both inorganic and organic manure and stage two from 1989 to 1993 in which Mehlich-3 extractable values were affected by annual additions of inorganic fertilizer only.

Cumulative amounts of fertilizer P applied were considered to be the independent variable. The model used was as follows:

$$M\text{-}3\ P = b_0 + b_1 FP + b_2 FP^2$$

where M-3 P was Mehlich-3 extractable P (kg ha^{-1}), FP was the cumulative amount of fertilizer P applied (kg ha^{-1}), b$_0$ was the intercept, and b$_1$ and b$_2$ were coefficients of regression. Stepwise regression, backward elimination, and forward selection (SAS Institute, 1985) were used. Equations were established based on each combination of fertilizer rate and soil depth during the two stages. On the Ste. Rosalie site, Mehlich-3 P was related to years of corn production.

2.4. Results and Discussion

2.4.1. Chicot site

Mehlich-3 extractable P levels in surface soils (0-20 cm) were influenced by fertilizer P rate and year, while Mehlich-3 extractable levels for P in the subsoil (20-40 cm) were influenced by fertilizer P rate (Table 2.2.). An interaction between fertilizer P rate and year was noted with Mehlich-3 extractable P in both surface and subsoil samples.

Mehlich-3 extractable levels for P in the surface soil increased linearly with added P in the 132 kg ha^{-1} rate plots (Fig. 2.1.) and quadratically in the 44 kg ha^{-1} fertilizer rate plots (Fig. 2.2.) from 1984 through 1989 when both inorganic and organic liquid manure P were applied. At the end of six years application, Mehlich-3 extractable P levels increased above initial levels by 262 kg P ha^{-1} for the 132 kg ha^{-1} rate and 109 kg P ha^{-1} for the 44 kg ha^{-1} rate (Table 2.3.). It required 4.2 kg manure plus inorganic fertilizer P to increase Mehlich

extractable P by 1.0 kg at the 132 kg ha^{-1} inorganic fertilizer rate with manure P, and about 5.2 kg fertilizer P at the 44 kg ha^{-1} rate of added inorganic P. Deducting P taken up by the crop resulted in a calculated value of 3.2 kg net fertilizer P to increase extractable P by 1.0 kg at both 44 and 132 kg ha^{-1} fertilizer rates. The identical value of extractable P change per unit added P when crop P is deducted lends some credence to the use of this technique. However, added P tends to decrease in solubility and availability with time. Because fertilizer P is absorbed over a relatively short period of time, deductions for crop P removal could be meaningful.

At the 132 kg ha^{-1} rate of inorganic fertilizer P, extractable P from the 20 to 40 cm depth increased by 130 kg ha^{-1} over the first six years. If this increase is added to the surface increase of 262 kg P ha^{-1}, then it required only 2.8 kg fertilizer P to increase extractable P by 1.0 kg or 2.1 kg fertilizer P if crop uptake were deducted.

Increase of Mehlich-3 extractable P in the 20 to 40 cm depth must have been the result of downward movement of fertilizer P. Bowman and Savory (1992) reported that available inorganic P and total organic P were high in deep layers (2.25-2.55 m) of calcareous soil. Ozanne et. al (1961) found that 17 to 80% of applied P was lost by leaching from loamy sand soils. Organic anions from liquid manure could compete with phosphate anions for adsorption sites on surfaces of soil particles, and thus, favour phosphate movement down the soil profile.

Mehlich-3 extractable level for P in the surface soil increased continuously in the 132 kg ha^{-1} rate plots during the subsequent four years of corn production (1989-1993) in which inorganic fertilizer P only was added (Fig. 2.1.). However, increases in Mehlich-3 extractable P of 65 kg P ha^{-1} were less than in the first six years. Mehlich-3 extractable P increased by

1 kg P ha^{-1} soil for each 8.1 kg P ha^{-1} applied as fertilizer. If P uptake by corn was deducted from added fertilizer, then 5.3 kg net fertilizer P increased extractable P by 1.0 kg. This value can be compared to results of other studies where amounts of inorganic fertilizer P required to change the soil test P levels ranged from 5.6 to 9.6 kg ha^{-1} using Bray and Kurtz No. 1 as P extractants (Rehm et al., 1984).

For P rates of 44 kg P ha^{-1} yr^{-1}, Mehlich-3 extractable P remained constant (Fig. 2.2.) due to a near-equilibrium between P fertilizer addition and crop P removal in grain (Table 2.3.). This lends some credence to the approach whereby crop P removal is deducted from added fertilizer P to give a "net" addition rate.

2.4.2. Ste. Rosalie site

Fertilizer rate and year of corn production and interaction of fertilizer rate with year had significant effects on Mehlich-3 extractable P in surface soil, but not in subsurface soil (Table 2.2.).

Mehlich-3 extractable P in surface soils was unchanged in zero-P plots (Fig. 2.3.). Over seven years, about 81 kg ha^{-1} soil P was removed by crops. Thus, Mehlich-3 extractable P was maintained from crop residues, mineralization of soil organic P, and desorption/dissolution of inorganic P.

In the fertilized plots at P rates above 44 kg ha^{-1}, Mehlich-3 extractable P in surface soils increased linearly with year of fertilization. Compared with zero-P plots, Mehlich-3 extractable P increased by 59 and 259 kg P ha^{-1} in plots receiving 44 and 132 kg P ha^{-1}, respectively (Table 2.4.). Thus, 5.2 and 3.6 kg ha^{-1} of added inorganic P were required to

increase soil Mehlich-3 extractable P by 1.0 kg ha^{-1} for 44 and 132 kg ha^{-1} fertilizer rates, respectively, when crop P removals was not deducted from the added fertilizer. When crop P removal was deducted, 1.8 kg ha^{-1} of net added fertilizer P was required to increase 1.0 kg P ha^{-1} Mehlich-3 extractable P for the P rate of 44 kg P ha^{-1} plots and 2.7 kg P ha^{-1} for the P rate of 132 kg P ha^{-1} plots. Therefore, increased P rates increased the degree of P fixation, presumably due to increased diffusion of phosphate ions into inner-particle space, and subsequently the increased P adsorption (Parfitt, 1989).

The values are smaller than those for the Chicot soil in which 5.3 kg P ha^{-1} of net added fertilizer P was required to increase surface soil Mehlich-3 P by 1.0 kg ha^{-1}. The results imply that P fixation by clay materials is a slow reaction (Parfitt, 1989). The greater surface area of the clay soil means that P sorption was less saturated in terms of surface areas. Slow P sorption due to large surface area has been reported for synthetic Fe oxides (Madrid and Arambarri, 1985).

2.5. Conclusions

Increases of extractable P with added P were greater when manure was present and when higher P rates were applied to the Chicot soil. In both cases the effect could be related to increased saturation of adsorption sites and reduced P fixation per unit added P. In the case of manure additions reduced P fixation due to the presence of competing organic anions could also be hypothesized. Calculated increases per unit of added P were greater when fertilizer P minus crop P uptake (or "net" fertilizer additions) were used and when subsoil increases were included. Whether the latter approaches are justified depends on the relative

availability of subsoil P and rates of P uptake and fixation. Thus the range of added P required to increase extractable P 1.0 kg was 2.0 to 8.0 kg P. The value used depends on P rates, presence of manure and soil types.

In the Ste. Rosalie soil, no decrease was found in zero-P plots over time, implying possible mechanisms for supplying soil Mehlich-3 P from other fractions. Rates of increase of extractable P by 1.0 kg changed with increased "net" inorganic fertilizer P rate from 1.8 to 2.7 kg P ha^{-1}, but decreased with rates of added P if only P additions were used. Due to rapid diffusion of phosphate ions into inter-particles of soil under high concentration, it is hypothesized that soil P fixation increased with increased fertilizer P, and thus "net" fertilizer rate seems more appropriate to calculate soil test changes with fertilization.

Table 2.1. Selected soil properties (0-20 cm) for Chicot soil in the spring of 1984 and for Ste. Rosalie soil in the spring of 1988.

Property	Chicot	Ste. Rosalie
Organic C^z, (g kg^{-1})	15.2	32.0
Organic N^y, (g kg^{-1})	1.74	2.90
Mehlich P^x (kg ha^{-1})	112	84
Mehlich K^x (kg ha^{-1})	155	377
Mehlich Ca^x (kg ha^{-1})	2680	7688
Mehlich Al^x (g kg^{-1})	1.1	1.1
Mehlich Fe^x (g kg^{-1})	3.7	3.5
Oxalate Al^w (g kg^{-1})	1.9	3.7
Oxalate Fe^w (g kg^{-1})	4.3	2.5
pH (0.01 M CaCl$_2$)	5.66	6.03
Clay (g kg^{-1})	280	710
Silt (g kg^{-1})	220	190
Sand (g kg^{-1})	500	100
Bulk density, (Mg m^{-3})	1.34	1.24
Field capacity (%, v/v)	35.9	52.7
Drainage	Well drained	Under-drained

^{z}Walkley-Black procedures (Nelson and Sommers, 1982).
^{y}Semi-micro Kjeldahl method (Bremner, 1965).
^{x}Mehlich-3 method (Mehlich, 1984).
^{w}Acid ammonium oxalate extractable Fe or Al (McKeague et al. 1971).

Table 2.2. Statistical significance of effects of fertilizer rate and year of corn production on Mehlich-3 extractable P.

Depth	Factor	Chicot site	Ste. Rosalie site
0-20 cm	Fertilizer (F)	**	**
	Year (Y)	**	**
	F by Y	*	**
20-40 cm	Fertilizer	**	NS
	Year	NS	NS
	F by Y	*	NS

**, *: Significance at P levels of 0.01 and 0.05, respectively.

NS: Not significant at P level of 0.05.

Table 2.3. Effect of fertilization on P uptake by corn and on Mehlich-3 extractable P in the 0-20 cm depth of a Chicot soil.

Fert. P rate	Initial Mehlich-3 P	Inorganic P applied	Manure P applied	Total applied P	P removed by corn	Final Mehlich-3 P
--- kg P ha⁻¹ ---

$$\text{kg P ha}^{-1}$$

Fert. P rate	Initial Mehlich-3 P	Inorganic P applied	Manure P applied	Total applied P	P removed by corn	Final Mehlich-3 P
1984-1989 (inorganic and manure P applied)						
44	120	264	300	564	229	229
132	104	792	300	1092	264	366
1989-1993 (inorganic P applied)						
44	229	176	0	176	170	229
132	353	528	0	528	184	418
1984-1993						
44	120	440	300	740	399	229
132	104	1320	300	1620	448	418

Table 2.4. Effect of fertilization on P uptake by corn and on Mehlich-3 extractable P in the 0-20 cm depth of a Ste. Rosalie soil period from 1988 to 1994.

Fert. P rate	Initial Mehlich-3 P	Total added P	P removed by corn	Final Mehlich-3 P
		kg ha^{-1}		
0	75	0	81	106
44	86	308	213	139
132	69	924	243	344

Fig. 2.1. Cumulative added fertilizer P at the high inorganic P rate and Mehlich-3 extractable P in a Chicot sandy clay loam soil, with manure P at 60 kg ha^{-1} for the first six years and inorganic P at 132 kg ha^{-1} for each year.

0-20 cm: M-3 P = 215 + 0.123 FP
R² = 0.78

20-40 cm: M-3 P = NS

0-20 cm: M-3 P = 104 + 0.240 FP
R² = 0.96

20-40 cm: M-3 P = 87.0 + 0.119 FP
R² = 0.88

Inorganic P

Manure plus inorganic P

Cumulative added P - FP (kg/ha)
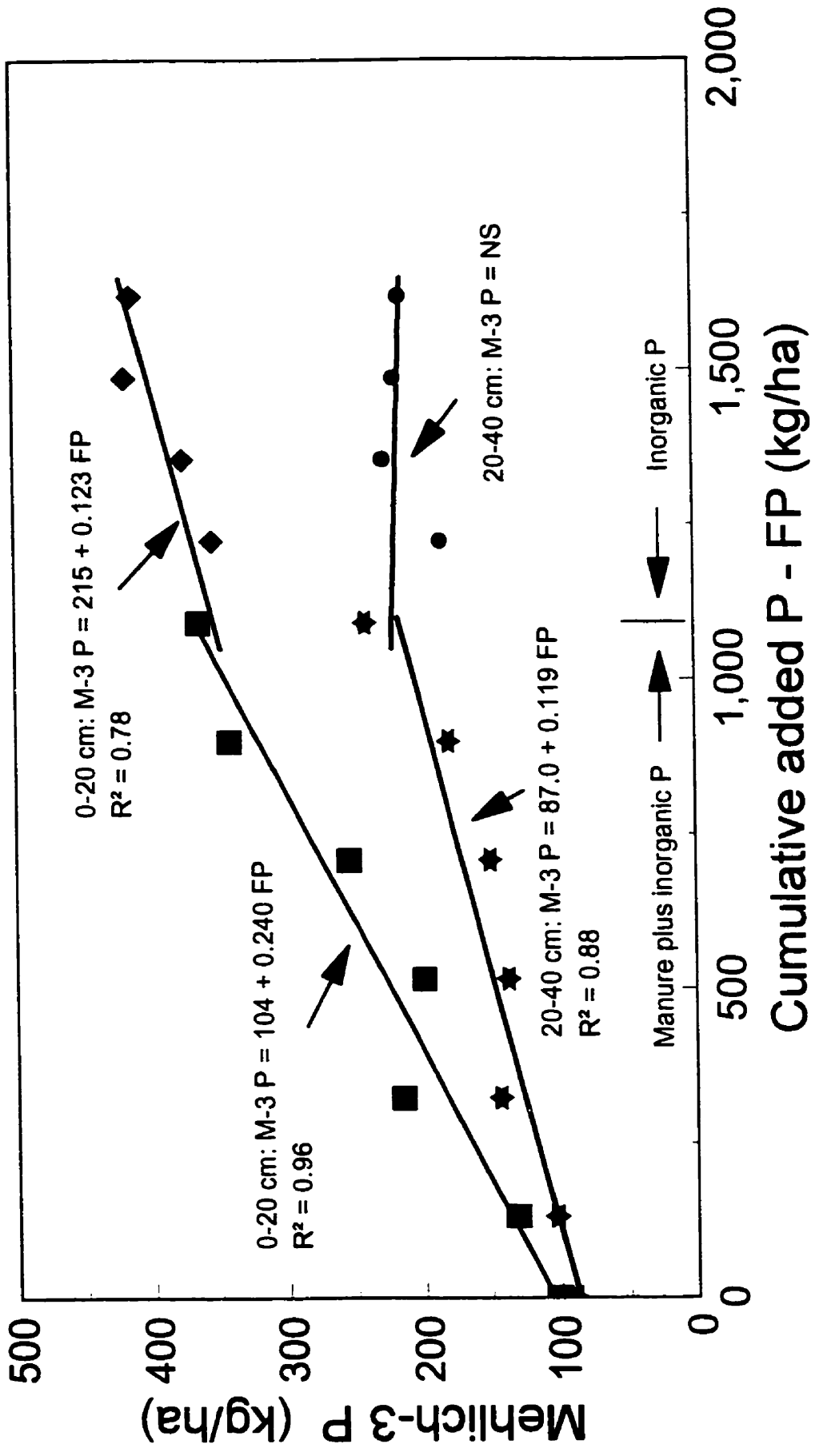
Mehlich-3 P (kg/ha)

Fig. 2.2. Cumulative added fertilizer P at the normal inorganic P rate and Mehlich-3 extractable P in a Chicot sandy clay loam soil, with manure P at 60 kg ha^{-1} for the first six years and inorganic P at 44 kg ha^{-1} for each year.

0-20 cm: M-3 P = NS

0-20 cm: M-3 P = 120 + 0.628 FP - 0.000772 FP²
R² = 0.87

20-40 cm: M-3 P = NS

Manure plus inorganic P   Inorganic P

Mehlich-3 P (kg/ha)

Cumulative added P - FP (kg/ha)

Fig. 2.3. Effect of P fertilization on soil Mehlich-3 extractable P over 7 years of monoculture corn production in a Ste. Rosalie clay soil.

P132: M-3 P = 88.1 + 35.6 year
$R^2 = 0.94$

P44: M-3 P = 83.8 + 8.09 year
$R^2 = 0.83$

P0: M-3 P = NS

Year

Mehlich-3 P (kg/ha)
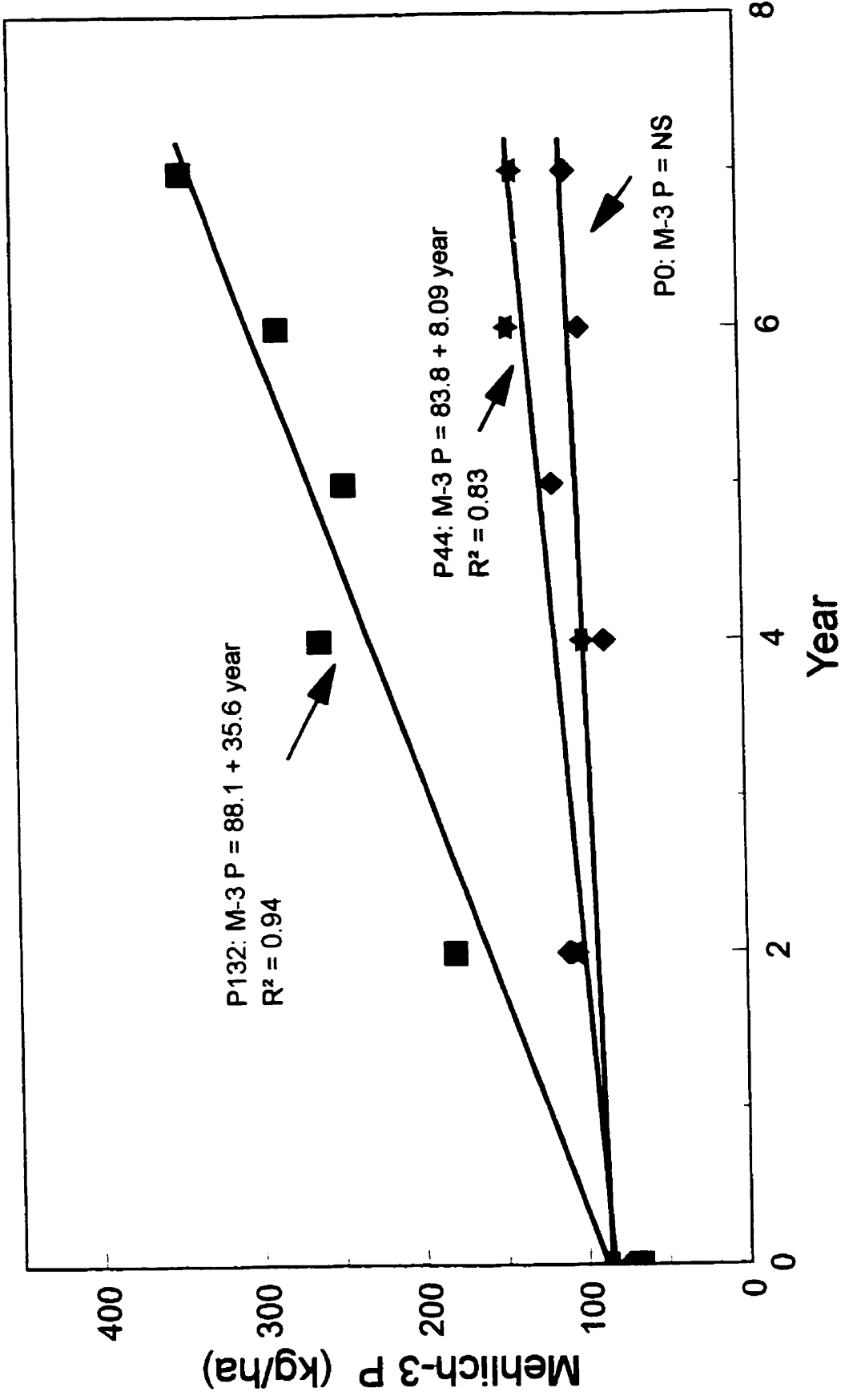
CONNECTING PARAGRAPH

Results from Chapter 2 provide a simple means of using net gains of P from fertilization to estimate the amounts of soil test P that accumulated in different soils under long-term corn. They do not, however, give any clear indications of the soil P reserves which are not extractable with Mehlich-3 solution. Results showed that Mehlich-3 P in one soil did not change, even when corn crops extracted P for 7 years. Therefore there is a need to quantitatively estimate P reserves which may subsequently become available to crops. Chapter 3 discusses changes of P fractions and pathways of transformations in various fertilizer systems on a Chicot sandy clay loam soil. This Chapter is a slight revision of the manuscript which has been accepted for publication in the Soil Science Society of American Journal (March-April issue, 1997).

CHAPTER 3

CHANGES OF SOIL PHOSPHOROUS FRACTIONS UNDER LONG-TERM

CORN (*Zea mays* L.) IN A CHICOT SANDY CLAY LOAM SOIL

3.1. Abstract

Corn (*Zea mays* L.) monoculture is a common management practice due to high production levels with economic and agronomic advantages. Phosphorus (P) reactions in soil affect sustainable and economic corn management and environmental quality. The objectives were to quantify changes of soil P fractions as related to additions of manure and inorganic P over time using a modified Hedley fractionation scheme. A field experiment was conducted on a Chicot sandy clay loam soil (Grey Brown Luvisol; fine-loamy, mixed, frigid Typic Hapludalf) from 1984 to 1993. With an annual rate of 60 kg P ha^{-1} manure P plus 44 kg P ha^{-1} inorganic P, labile inorganic P (Pi; Bicarb-Pi) increased and moderately labile Pi (NaOH-Pi) decreased. A higher annual P rate of 132 kg P ha^{-1} plus manure P increased soil Pi through Bicarb-Pi, NaOH-Pi, and stable Ca-bound Pi (HCl-Pi). Inorganic P at either rate combined with manure P decreased labile Bicarb-Po fractions and increased moderately labile NaOH-Po, with the result that total extractable soil organic P (Po) increased. Without manure, 44 kg P ha^{-1}, approximately equal to P removal by the crop, resulted in no change in soil P fractions except for residual P (Res-P) which decreased. Soil Po and Pi levels increased continuously in soil fertilized with 132 kg P ha^{-1} inorganic P only. With the manure-inorganic system, 86% of the Bicarb-Pi was supplied from added inorganic P, indicating reduced P fixation compared with the inorganic P system. NaOH-Pi and Res-P were soil P sinks, with Res-P being supplied from both the NaOH-Po and HCl-Pi fractions. In contrast, NaOH-Pi in the inorganic P system was the major source for Bicarb-Pi.

3.2. Introduction

Monoculture for corn (*Zea mays* L.) production is a common management practice because of its high potential for grain production. Grain corn yields can reach 18.4 Mg ha^{-1} in eastern Canada (Stevenson et al., 1990). In achieving high production levels, continuous fertilization can result in increased soil levels of phosphorus (P) (Zhang et al., 1995). In Quebec, over 60% of the soils used for monoculture crop production have been deemed to have excessive P levels (Tabi et al., 1990). Direct analysis of different soil P species is difficult, and selective dissolution procedures have been employed to detect distributions of plant available P (Chauhan et al., 1981), soil organic P (Po) (Stewart and Oades, 1972), and inorganic P (Pi) (Chang and Jackson, 1957). In recent years, a sequential extraction procedure (Hedley et al., 1982b) has been developed to fractionate soil P into Pi and Po forms of varying plant availability (Hedley et al., 1982b). This technique has been used in temperate (Hedley et al., 1982b) and tropical (Tiessen et al., 1991) soils to study transformations of soil P fractions. It was found that decreases in soil P over 65 years of cultivation mainly came from organic P forms in Mollisols (Hedley et al., 1982b).

Path analysis is a powerful technique to determine transformations in P fractions (Tiessen et al., 1984; Beck and Sanchez 1994; Xie et al., 1991). This or similar techniques require the development of conceptual models which are used to establish relationships among different entities (Li, 1975). The availability of soil P to plants depends on the replenishment of soil labile P from other P fractions, and this replenishment can be estimated from path analysis (Beck and Sanchez, 1994). Such information is essential for modeling P dynamics in the soil-plant system, and is important in resolving management conflicts between increasing

cost of P fertilizer (Korol and Girard, 1994) and low fertilizer P efficiency (Sadler and Stewart, 1974).

Beck and Sanchez (1994) using path analysis showed that inorganic P extracted with NaOH was a major sink for added P in fertilized soil and organic P was a major source of labile P in unfertilized soil during 18 years of crop production in Peru. Tiessen et al. (1984) effectively explained differences in interactions among the P fractions in soils of Brazil through path analysis. They found that labile P in Mollisols was associated with inorganic bicarbonate and hydroxide extractable P. In Ultisols they found that labile P was largely from organic P. Thus, soil P transformations can vary depending on soil type, climatic conditions, and management practices.

Objectives of the present study were 1) to quantify soil P fraction changes upon addition of inorganic and manure P in 10 years of corn monoculture production, and 2) to model long-term soil P transformations using path analysis.

3.3. Material and Methods

3.3.1. Experimental design and management practices

Soil characteristics, treatments, and management practices are noted in Chapter 2.

3.3.2. Stover sampling and analysis

Ten plants in each plot were taken and weighed for yield determination. Sub-sample was taken after stover was chopped and analyzed for moisture and P contents. Determination of stover P concentration was conducted using H_2SO_4-H_2O_2 wet-digestion procedure

(Thomas et al. 1967) and molybdate-ascorbic acid method (Murphy and Riley, 1962) using a Technicon Auto-Analyzer (Technicon Industrial System, Tarrytown, NY) from 1984 to 1992 and a QuikChem AE Automated Ion Analyzer (Lachat Instruments, Milwaukee, WI) in 1993.

3.3.3. Soil sampling and soil P fractionation

Composite soil samples consisting of five cores were randomly taken to a depth of 20 cm in each treatment replicate shortly before fertilization and planting in the springs of 1984 to 1993 except for 1986 and 1990. Soil was air-dried and crushed to pass a 2 mm sieve after removing visible root and crop residues and further ground to <100 mesh size.

Subsamples of 0.5 g were sequentially extracted (Fig. 3.1.). A portion of the bicarbonate and hydroxide extracts was acidified to precipitate extracted organic matter and the supernatant analyzed for Pi. Another portion of bicarbonate and hydroxide extracts was digested in an autoclave (103.4 kPa, 121°C for 1.0 hr) with acidified ammonium persulfate oxidation and analyzed for total P. The difference between total P and Pi was considered to be organic P (Po) (Tiessen and Moir 1993), although it should be emphasized that P differences were not absolute. Total P in the residue after the sequential extraction was determined after digestion with concentrated sulfuric acid and hydrogen peroxide. Inorganic phosphate in all extracts and digestion solutions was determined colorimetrically with the molybdate-ascorbic acid procedure (Murphy and Riley, 1962). Thus, soil P was separated into bicarbonate P (Bicarb-Pi/Po), hydroxide P (NaOH-Pi/Po), acid Pi (HCl-Pi), and residue P (Res-P). The Res-P fraction, plant non-available P, may consist of either Po or Pi or both.

This portion of soil P is chemically stable. It was assumed that Res-P is mainly Po compounds causing variation of Res-P during cultivation and cropping (Hedley et al., 1982b). In order to verify this conjecture, Res-P was further partitioned into Po (NaOH-2-Po), Pi (NaOH-2-Pi), and final residual P (Fres-P) by adding an extra extraction with 0.1 M NaOH after the 1.0 M HCl extraction.

3.3.4. Data analysis

All statistical analyses were performed using the Statistical Analysis System (SAS Institute, 1989). Since measurements of soil P fractions from various years were obtained on samples from the same plots, year and fertilizer level were tested as repeated measures with four replicates (Winer, 1971; Cole and Grizzle, 1966). Regression analysis was run with soil P fraction level as dependent variable and cumulative added fertilizer P (CFP) as independent variable calculated using the following formula;

$$CFP = \sum_{i=0}^{n} (P_m + P_f); \qquad n = 0,1,2,... \qquad [3.1]$$

where CFP represents the cumulative added fertilizer P in the nth year, n represents the order of year, and P_m and P_f represent added P as manure and inorganic fertilizer P, respectively in the ith year.

Path analysis allows the decomposition of zero-order correlation coefficients into direct and indirect effects (Li, 1975). Direct effects are termed path coefficients and are standardized partial regression coefficients (β), measured in units of standard deviation. Therefore, a path coefficient of 0.59 means that with changes of 1 unit of the independent

variable, the dependent variable will change by 0.59 units. For several variables affecting a resultant variable at the same time (such as X1 and X2 affecting Y) β's are additive. For several variables affecting a resultant variable in chain (such as X1 affecting X2 affecting Y) β's are multiplicative.

Path analyses were employed to evaluate the relationships among different soil P fractions as well as soil inputs of Po and Pi in a conceptual model representing the soil P cycle. Path analyses were carried out following the techniques of Li (1975). In the case where the relationship between two variables was not linear, logarithmic transformation was performed. In order to evaluate soil P cycles in both manure-inorganic and inorganic systems, ten years of data were pooled across both 44 and 132 kg ha^{-1} fertilizer rates and separated into two groups; group one from 1984 to 1989 in which both inorganic and organic manure P were added and group two from 1989 to 1993 in which inorganic P was applied alone.

Calculations of cumulative soil Pi and Po inputs involved in path analysis were carried out on an annual treatment replicate base. Phosphorus added with manure was found to have 63% Pi and 37% Po (Barnett, 1993). Root biomass was estimated at 14% of aboveground dry matter production (Montgomery, 1913) with a P content of 0.2%. Cumulative inputs of Pi and Po were thus determined as the sum of added Pi and Po as fertilizers of inorganic and organic manure and crop residues including stover and root biomass from 1984 to 1989 and as inorganic fertilizer and crop residues from 1990 to 1993 using the following formulas;

$$CPi = \sum_{i=0}^{n} (Pi_f + Pi_m); \quad n = 0,1,2,... \quad [3.2]$$

Where CPi (kg P ha^{-1}) is the cumulative soil Pi input in the nth year, n is the order of year, Pi_f (kg P ha^{-1}) is the inorganic P added as inorganic fertilizer in the ith year, and Pi_m (kg P ha^{-1}) is the inorganic P added with manure in the ith year.

$$CPo = \sum_{i=0}^{n} (Po_m + Po_s + Po_r); \quad n=0,1,2,... \quad [3.3]$$

Where CPo (kg P ha^{-1}) is the cumulative soil Po input in the nth year, n is the order of year, Po_m (kg P ha^{-1}) is the organic P added as manure in the ith year, Po_s (kg P ha^{-1}) is the organic P added as stover in the ith year, and Po_r (kg P ha^{-1}) is the organic P added as root biomass in the ith year.

Changes in P fractions with time were converted to kg ha^{-1} from mg kg^{-1} by using bulk density values.

3.4. Results and Discussion

3.4.1. Changes in soil P fractions

Fertilization level and year of corn production significantly influenced all soil P fractions ($P < 0.01$). The fertilization level by year interactions were also significant ($P < 0.01$) on all soil P fractions.

3.4.1.1. Inorganic P plus manure P - 1984 to 1989

In 44 kg ha^{-1} rate plots, soil Bicarb-Pi increased linearly with time at a rate of 14.2 kg P ha^{-1} year^{-1} (Fig. 3.2), whereas soil NaOH-Pi decreased linearly at a rate of 15.9 kg P ha^{-1} year^{-1} (Fig. 3.3). Increased Bicarb-Pi with cumulative fertilizer P resulted from the addition

of P in the manure. This view was supported by the constant levels for Bicarb-Pi when only inorganic P was applied (Fig. 3.2). Soil NaOH-Pi is held strongly by chemisorption to Fe and Al components of soil surfaces (Ryden et al., 1977) and is considered as moderately labile soil P. The decrease of NaOH-Pi in this study confirmed the findings of Mnkeni and MacKenzie (1985) and Xie et al. (1991), who reported that the addition of organic material to soil tended to decrease P sorption, possibly due to competition between phosphate ions and organic materials for retention sites in the soil.

Soil HCl-Pi appeared stable when inorganic P plus manure P were added at the 44 kg ha^{-1} rate (Fig. 3.4). As a consequence, total extractable Pi (Bicarb-Pi, NaOH-Pi, and HCl-Pi) declined at an annual rate of 6.1 kg P ha^{-1} in 44 kg ha^{-1} rate plots (Fig. 3.5).

In 132 kg ha^{-1} fertilizer rate plots, additions of inorganic plus manure P resulted in linear increases in all soil Pi fractions, but slopes differed with the fraction (Figs. 3.2-3.4). Bicarb-Pi increased at a rate of 36.5 kg ha^{-1} year^{-1}, 2.6 times faster than in the 44 kg ha^{-1} rate plots. NaOH-Pi and HCl-Pi accumulated at annual rates of 27.8 and 21.1 kg ha^{-1}, respectively. Total extractable soil Pi accumulated at an annual rate of 85.4 kg ha^{-1} during the six years (Fig. 3.5). This increase of soil Pi represented 45% of the added inorganic and manure P.

Of the increases in soil Pi fractions, 76% was found in Bicarb-Pi, a fraction considered to be largely available to plants (Olsen et al., 1954). NaOH-Pi is considered to be slowly available to plants by desorption (Tiessen et al., 1984) and HCl-Pi is believed to be unavailable to plants.

Changes in soil Po fractions displayed different patterns between fractions and between

inorganic fertilizer P levels (Figs. 3.6 and 3.7). For the 44 kg ha^{-1} rate plots, Bicarb-Po declined to 33% of its initial level, with most of the decline in the first few years (Fig 3.6).

For the high P rate plots, changes in Bicarb-Po decreased, following a similar pattern to that of 44 kg ha^{-1} rate plots. Soil Bicarb-Po is considered as labile Po sorbed on the soil surface plus a small amount of microbial P (Bowman and Cole, 1978). The decreases in soil Bicarb-Po with added manure probably resulted from accelerated mineralization caused by addition of organic C. Campbell et al. (1986) working in semi-arid conditions with a Black Chernozem (Mollisol) reported increased mineralization of organic N compounds with added manure. However, they found no changes in Po with added manure. The dissimilarity in Po changes may come from the amount of added organic C and climatic effects.

The NaOH-Po fraction increased rapidly at first then slowed in relation to added fertilizer P in both 44 and 132 kg ha^{-1} rates plots (Fig. 3.7). At the end of six years, soil NaOH-Po increased by 135 and 178 kg ha^{-1}, with average increases of 27.0 and 35.5 kg ha^{-1} year^{-1} in the 44 and 132 kg ha^{-1} rate plots, respectively. This increase in soil NaOH-Po for both fertilizer treatments could be the result of biological immobilization of soil Pi. Some of the soil Pi removed by corn plants was probably converted to soil organic P through return of residues. Similarly, some soil Pi may be taken up by microorganisms to form Po in microbial detritus (McLaughlin et al., 1988). Newly formed soil Po compounds seem easily extractable with 0.1 M NaOH solution, and may mostly consist of inositol phosphates due to their relative microbiological resistance (L'Annunziata and Fuller, 1971).

For the 44 kg ha^{-1} rate of fertilizer, net accumulation of total extractable soil Po (Bicarb-Po + NaOH-Po) occurred at an annual rate of 6.4 kg ha^{-1} and at 12.6 kg ha^{-1} for the

high fertilizer rate (Fig. 3.8). This net increase was due to a greater increase in NaOH-Po than decrease in Bicarb-Po. From 20 to 39% of manure and crop residue organic P was recovered in extractable Po compounds, based on the estimated inputs of 32 kg ha^{-1} year^{-1} Po.

Combined additions of inorganic fertilizer P with manure P significantly increased the soil Res-P fraction (Fig. 3.9). Soil Res-P increased linearly with added fertilizer P at annual rates of 26.2 and 40.2 kg ha^{-1} for the 44 and 132 kg ha^{-1} fertilizer rates, respectively. Soil Res-P fraction accounted for 25% of added fertilizer P in the 44 kg ha^{-1} rate plots and 21% of added fertilizer P in the 132 kg ha^{-1} rate plots. Further partition of this fraction of soil P with a second NaOH extraction into NaOH-2-Pi, NaOH-2-Po, and Free-P (data not shown) indicated that 98.7% of the variation in Res-P caused by additions of inorganic plus manure P was accounted for by increases in NaOH-2-Po compounds, whereas 0.8% and 0.5% of the variation in Res-P was accounted for by increases in NaOH-2-Pi and Free-P, respectively.

The sum of Bicarb-Po, NaOH-Po, and NaOH-2-Po included in Res-P can provide an estimation of soil extractable Po. Thus 31 and 27% of added fertilizer P in forms of inorganic P and manure P were accounted for by soil extractable Po in the 44 and 132 kg ha^{-1} rate plots, respectively.

3.4.1.2. Inorganic P - 1989 to 1993

In 44 kg ha^{-1} rate plots, all soil Pi and Po fractions remained largely unchanged. Corn grain P uptake was about 40 kg ha^{-1} year^{-1}, and thus added fertilizer P at 44 kg ha^{-1} year^{-1} approximately balanced these losses. In 132 kg ha^{-1} rate plots, all soil Pi fractions changed significantly with time, but each P fraction followed a different pattern (Figs. 3.2-3.4).

In 132 kg ha^{-1} P rate plots soil Bicarb-Pi increased linearly with cumulative added P, but at a greater rate with inorganic P compared with the manure-inorganic P (Fig. 3.2). Soil NaOH-Pi fraction increase was linearly related to cumulative fertilizer P (Fig. 3.3). An exception was the HCl-Pi fraction which decreased to near its initial level after buildup in the manure plus inorganic P system (Fig. 3.4). This effect was attributed to a decrease in Ca-bound Pi accompanying an increase in soil organic matter and Po (Cole and Heil, 1981). Such an increase in soil organic matter was earlier reported on these plots (Liang and MacKenzie, 1991). Total extractable soil Pi determined as the sum of Pi fractions in high rate plots appeared to increase linearly at a rate of 59.4 kg ha^{-1} year^{-1} (Fig. 3.5), an equivalent of 45% of added fertilizer P.

In 132 kg ha^{-1} plots soil Bicarb-Po increased linearly by 143% from its initial level in 1989 (Fig. 3.6). Soil NaOH-Po also increased, though at a decreasing rate (Fig. 3.7). Thus, inorganic fertilization at the increased P rate enhanced the formation of soil Po compounds at an annual rate of 43.1 kg ha^{-1}, equivalent to 33% of the added fertilizer P. It also seems that Bicarb-Po and NaOH-Po both require time to reach a new equilibrium in this continuous corn system.

In both 44 and 132 kg ha^{-1} rate plots soil Res-P decreased linearly with respect to cumulative fertilizer P (Fig. 3.9). These trends were opposite to that of the manure-inorganic system. Further partition of the Res-P fraction into NaOH-2-Po, NaOH-2-Pi, and Fres-P again showed that 97.7% of the changes in Res-P (data not shown) was accounted for by NaOH-2-Po components. This finding is consistent with the results obtained by Hedley et al. (1982b) who reported that over half of the total soil P loss resulted from residual P fractions

after 65 years of cropping, and confirmed the conjecture of Hedley et al. (1982b) that a major part of residual P losses consisted of Po compounds.

3.4.2. Interrelationships of soil P fractions and effects of soil P input - soil P cycles

Simple correlation coefficients for the manure-inorganic P system showed that both labile fraction Bicarb-Pi and stable fraction Res-P were positively related to all fractions at $P<0.05$ level except Bicarb-Po and NaOH-Pi (Table 3.1). For the inorganic P system, labile Bicarb-Pi was positively correlated with fewer fractions, NaOH-Po and -Pi, and Bicarb-Po, as well as added Pi (Table 3.2). Res-P was positively related to HCl-Pi, but negatively related to added Po. Thus correlation values were not consistent across the two systems. This implies a different fate of added P with or without manure.

3.4.2.1. Manure-inorganic system.

Path analysis showed that 86% of the variation in Bicarb-Pi was due to the addition of inorganic fertilizer P (Fig. 3.10). The moderately labile Pi (NaOH-Pi) was mainly the direct result of inorganic P addition ($\beta = 0.54$) and indirect effect through inorganic P fertilization reaction products HCl-Pi ($\beta = 0.57 \times 0.43$). The path coefficient between NaOH-Pi and Bicarb-Po was significant ($P < 0.05$), and it appears that the decomposition of Bicarb-Po contributed to NaOH-Pi. However, an overall effect of added Po from crop residues and manure was a decrease in NaOH-Pi ($\beta = -0.81 \times 0.61$). This finding suggests a negative effect of added manure on soil NaOH-Pi levels. The significant incoming paths to NaOH-Pi along with non-significant coefficients of outgoing paths to Bicarb-Pi and Res-P suggest that

NaOH-Pi was an interim reservoir of soil P.

Bicarb-Po and NaOH-Po acted as sinks for added Po and sources for NaOH-Pi and Res-P. Res-P was stable and constituted another sink of soil P, predominantly supplied from added Pi through HCl-Pi ($\beta = 0.57 \times 0.21$) and from Bicarb-Pi and added Po through NaOH-Po ($\beta = 0.32 \times 0.93$ and $\beta = 0.60 \times 0.93$). These fractions were probably the result of fertilizer-reaction products with the soil. Tiessen et al. (1983) also demonstrated that Res-P contained a large portion of organically bound P in tropical soils, as noted in our observations.

There was a negative impact of added manure P on Res-P through a combination of negative effect on Bicarb-Po, and a positive effect of Bicarb-Po on Res-P ($\beta = -0.81 \times 0.19$).

3.4.2.2. Inorganic system

Previously, it was shown that Res-P in the inorganic P system declined with continuing fertilization. The decrease in Res-P was assumed to be as a consequence of formation of secondary Al or Fe inorganic phosphates (NaOH-Pi). The conceptual model of soil P was modified for the manure-inorganic system by changing the path direction between Res-P and NaOH-Pi (Fig. 3.11).

Path analysis showed that 96% of the variation in Bicarb-Pi, an available form of P, was explained by NaOH-Pi (Fig. 3.11). Variability in NaOH-Pi was explained mostly through added inorganic P (partial $R^2 = 0.98$), although it could also be replenished from mineralization of Bicarb-Po and Res-P. As a consequence, the effect of inorganic P fertilization on Bicarb-Pi was indirect through formation of NaOH-Pi, probably associated

with the formation of amorphous and crystalline Al and Fe phosphates (Williams et al., 1980). Comparable results were reported by Beck and Sanchez (1994) who found in a Typic Paleudult soil that the effects of P applications on resin-Pi, considered as plant available P along with Bicarb-Pi (Hedley et al., 1982b), were indirect through the formation of both HCl-Pi and NaOH-Pi.

Bicarb-Po and NaOH-Po acted as sinks of both added Po and newly formed Po, and P passed through these forms to NaOH-Pi. The regression coefficient of 0.97 between Bicarb-Pi and NaOH-Po supports the idea that formation of NaOH-Po was enhanced by accumulation of Bicarb-Pi, although mechanisms are not clear. Newly formed NaOH-Po contributed to NaOH-Pi through labile Bicarb-Po. Therefore, the NaOH-Pi fraction acted as the major reservoir of soil P in the inorganic P system. The same result was obtained by Beck and Sanchez (1994) working with a Typic Paleudult in Peru after 18 years of crop production. This suggests that a long time is needed to complete fixation of added fertilizer P.

3.5. Conclusions

Changes in P fractions with long-term corn monoculture were related to both added manure and rate of inorganic P fertilizer. When manure was added, most P fractions reacted to added P similarly across P rates, but changing patterns differed in P fractions. Manure addition tended to promote the formation of less labile Po at the expense of more labile Po. When inorganic P was added alone, most P fractions accumulated with time with addition at the 132 kg ha^{-1} P rates, whereas most P fractions remained stable with addition at the 44 kg ha^{-1} P rates, indicating that additions and removals were in equilibrium.

NaOH-Pi was sensitive to the balance between P addition and P removal, and thus could be used to assess long-term P fertilization. Bicarb-Pi seemed to reflect the balance between P addition and P removal regardless of the form of added P, and could be used to assess P addition effects.

Path analysis was useful in linking changes in soil P fractions and clarifying concepts on P transformations in soil. Differences in pathways due to addition of manure indicated that in the manure-inorganic system soil Po accumulated finally as Res-P through NaOH-Po. Further, Res-P along with NaOH-Pi acted as major sinks of the added P. A significant part of the added P was found as Bicarb-Pi which was assumed to constitute the immediate source of plant available P. In the inorganic system without manure most Bicarb-Pi was indirectly supplied from fertilizer P through moderately labile NaOH-Pi. Consequently, manure addition reduced or delayed the process of Pi fixation as NaOH-Pi while increasing available P as Bicarb-Pi.

Available P seemed to come from Pi fractions, as noted by Tiessen et al. (1984) for Mollisols. Phosphorus forms labeled as organic, although important in Ultisols (Tiessen et al. 1984) and in non-fertilized Paleudults (Beck and Sanchez 1994), were less related to available P in this study, probably due to the addition of inorganic fertilizer P and the importance of Pi forms.

Table 3.1. Pearson correlation coefficients ($P<0.05$) for soil P fractions as influenced by inorganic P fertilization under continuous corn when organic manure was present in a Chicot sandy clay loam soil.

	Bicarb-Pi	NaOH-Pi	HCl-Pi	Bicarb-Po	NaOH-Po	Res-P	Added-Po	Added-Pi
Added Pi	0.93	-	$(0.57)^z$	-	0.93	0.96	0.89	1.00
Added Po	0.88	-	-	-0.81	0.88	0.87	1.00	
Res-P	0.94	-	0.62	(-0.53)	0.90	1.00		
NaOH-Po	0.85	-	-	-0.71	1.00			
Bicarb-Po	(-0.56)	-	-	1.00				
HCl-Pi	0.74	0.64	1.00					
NaOH-Pi	(0.56)	1.00						
Bicarb-Pi	1.00							

^{z} Correlation coefficient in brackets is significant at $P<0.1$ level.

Table 3.2. Pearson correlation coefficients ($P<0.05$) for soil P fractions as influenced by inorganic P fertilization under continuous corn in a Chicot sandy clay loam soil.

	Bicarb-Pi	NaOH-Pi	HCl-Pi	Bicarb-Po	NaOH-Po	Res-P	Added-Po	Added-Pi
Added Pi	0.96	0.99	-	0.95	0.94	-	-	1.00
Added Po	-	-	(-0.68)[z]	(0.65)	-	-0.85	1.00	
Res-P	-	-	0.76	-	-	1.00		
NaOH-Po	0.91	0.95	-	0.87	1.00			
Bicarb-Po	0.94	0.97	-	1.00				
HCl-Pi	-	-	1.00					
NaOH-Pi	0.98	1.00						
Bicarb-Pi	1.00							

[z] Correlation coefficient in brackets is significant at $P<0.1$ level.

Fig. 3.1. Modified procedure for P fractionation.

0.5 g soil

↓

30 ml 0.5 M NaHCO3, pH 8.5, shake 16
hrs, centrifuge, pass through 0.45 micron   ⟶   **Bicarb-Pi & -Po**
filter

↓

30 ml 0.1 M NaOH shake 16 hrs,
centrifuge   ⟶   **NaOH-Pi & -Po**

↓

30 ml 1.0 M HCl shake 16 hrs,
centrifuge   ⟶   **HCl-Pi**

↓

H2SO4 - H2O2 digestion
at 360 degree celcius, 3 hrs   ⟶   **Residual P**

Fig. 3.2. Changes in soil NaHCO$_3$-Pi with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. * and **; statistically significant at levels of $P<0.05$ and 0.01, respectively. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

Left panel:

270
240 Normal rate
     ■ Y = 98.3 + 0.0513X; R² = 0.92*
     ● NS

Bicarb-Pi (mg P kg⁻¹soil) — $Bicarb\text{-}Pi$ (mg P kg^{-1}soil)

$Y = 98.3 + 0.0513X;\quad R^2 = 0.92^*$

NS

IP + OP →|← IP

0   200   400   600

Right panel:

270
240 High rate
     ● Y = 81.8 + 0.0707X;   R² = 0.95**
     ◆ Y = 29.6 + 0.124X;   R² = 0.86*

$Y = 81.8 + 0.0707X;\quad R^2 = 0.95^{**}$

$Y = 29.6 + 0.124X;\quad R^2 = 0.86^*$

IP + OP →|← IP

0   400   800   1,200   1,600

Cumulative P added (kg P ha⁻¹) — Cumulative P added (kg P ha^{-1})
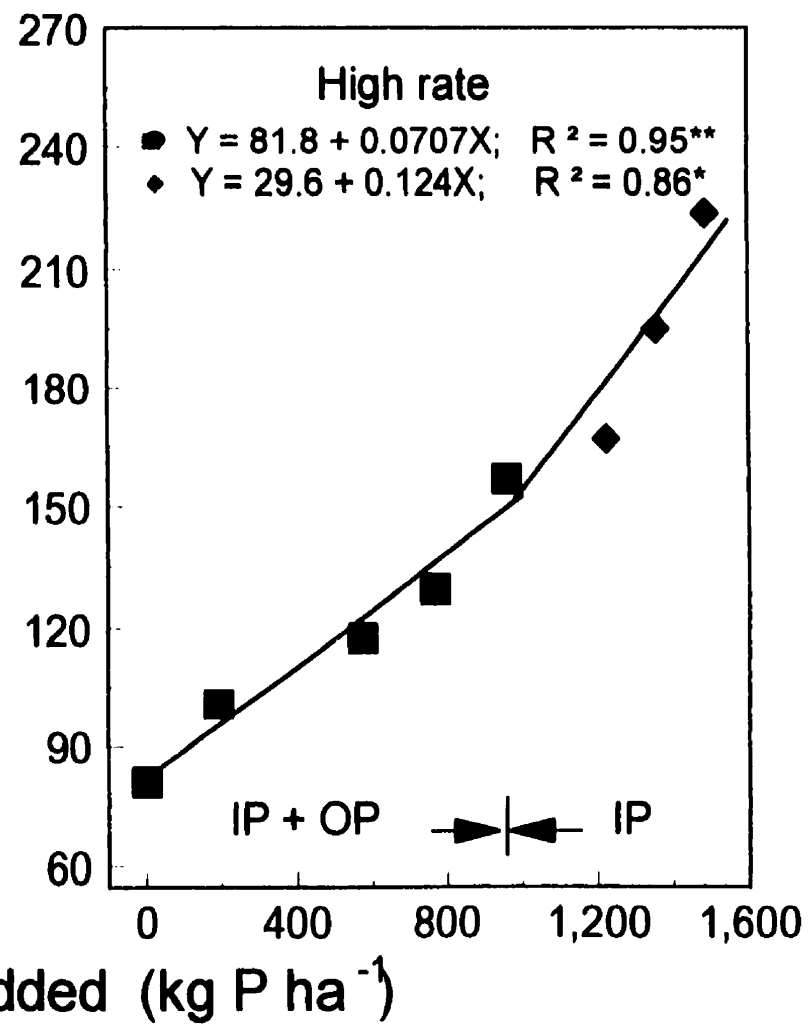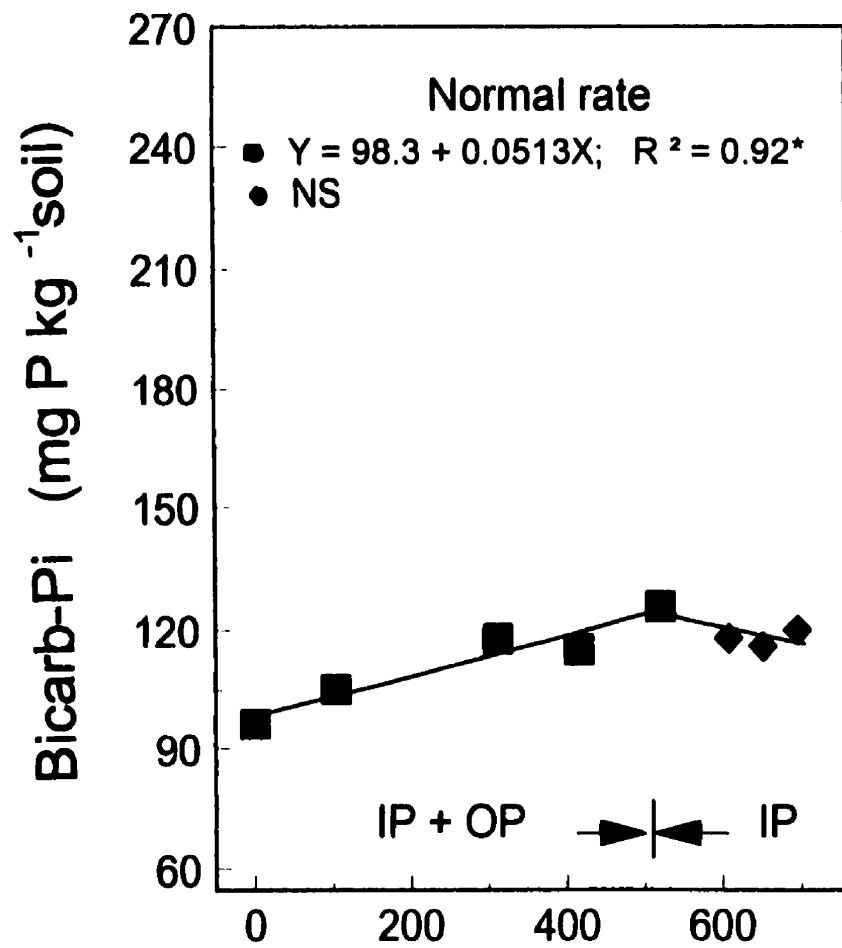
Fig. 3.3. Changes in soil NaOH-Pi with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. * and **; statistically significant at levels of $P<0.05$ and 0.01, respectively. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

NaOH-Pi (mg P kg^{-1} soil)

Normal rate

■ Y = 226 - 0.0572X; R^2 = 0.85*
◆ NS

IP + OP   IP

High rate

■ Y = 197 + 0.0538X;   R^2 = 0.86*
◆ Y = 146 + 0.111X;   R^2 = 0.98**

IP + OP   IP

Cumulative P added (kg P ha^{-1})
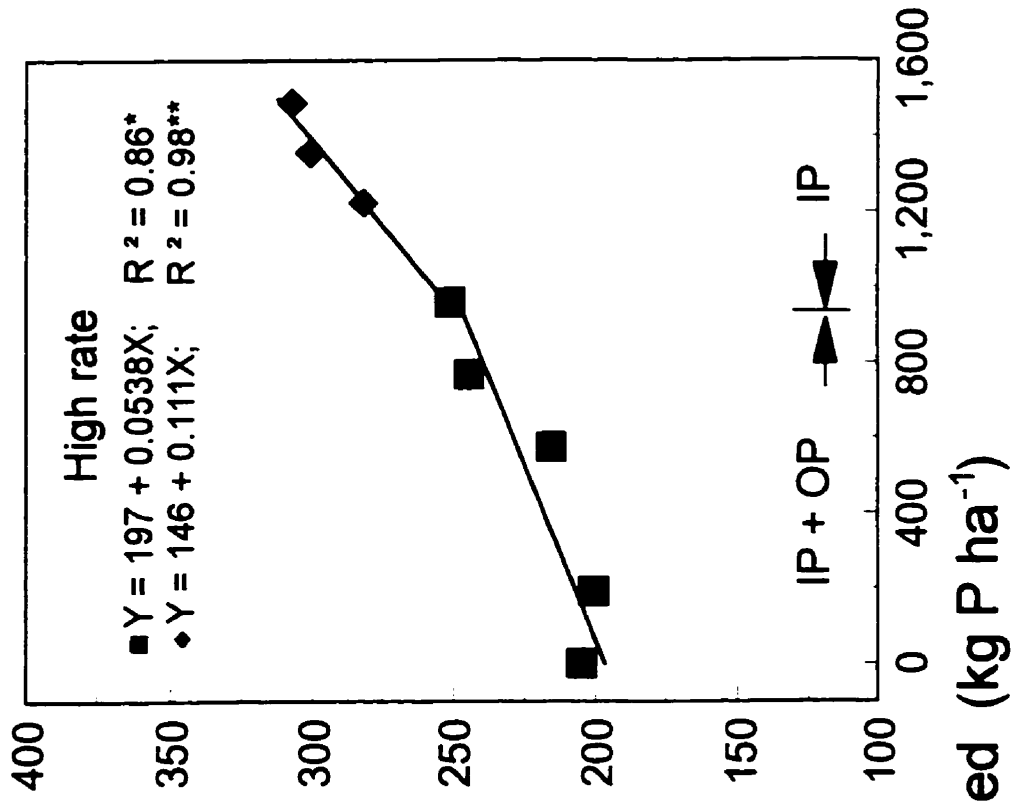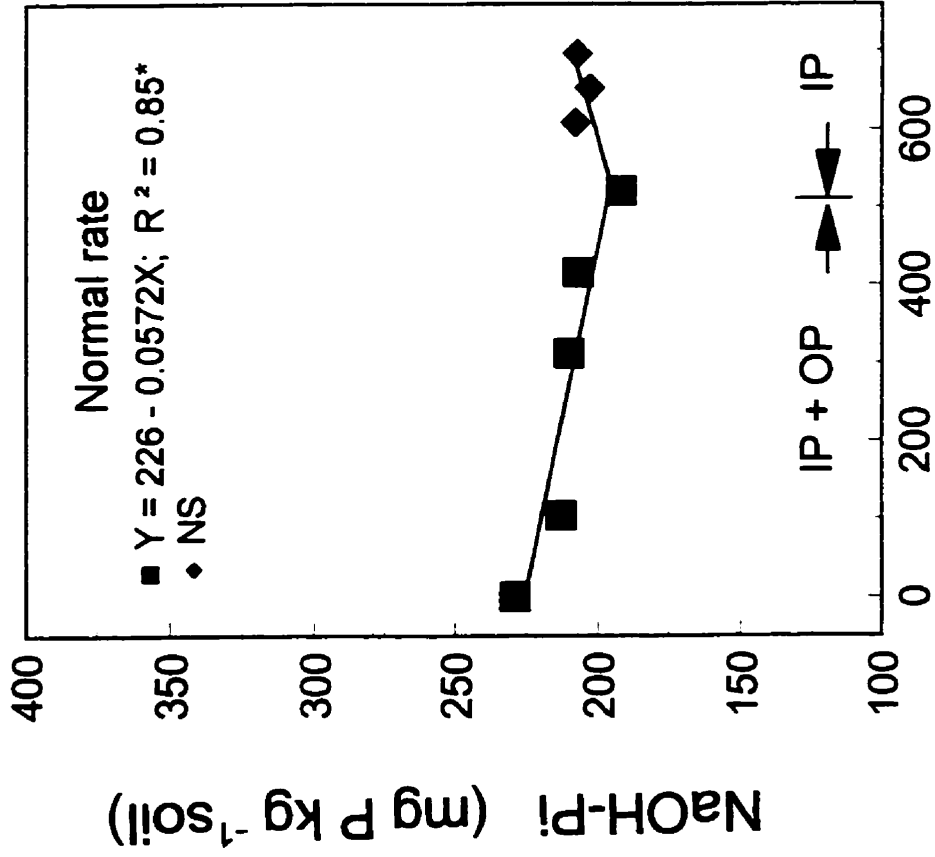
Fig. 3.4. Changes in soil HCl-Pi with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. *; statistically significant at $P<0.1$ level. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

High rate

$Y = 425 + 0.0412X; \quad R^2 = 0.81^{\dagger}$
$Y = 1019 - 185\log X; \quad R^2 = 0.80^{\dagger}$

Normal rate

NS
NS

HCl-Pi (mg P kg^{-1} soil)

Cumulative P added (kg P ha^{-1})

IP

IP + OP
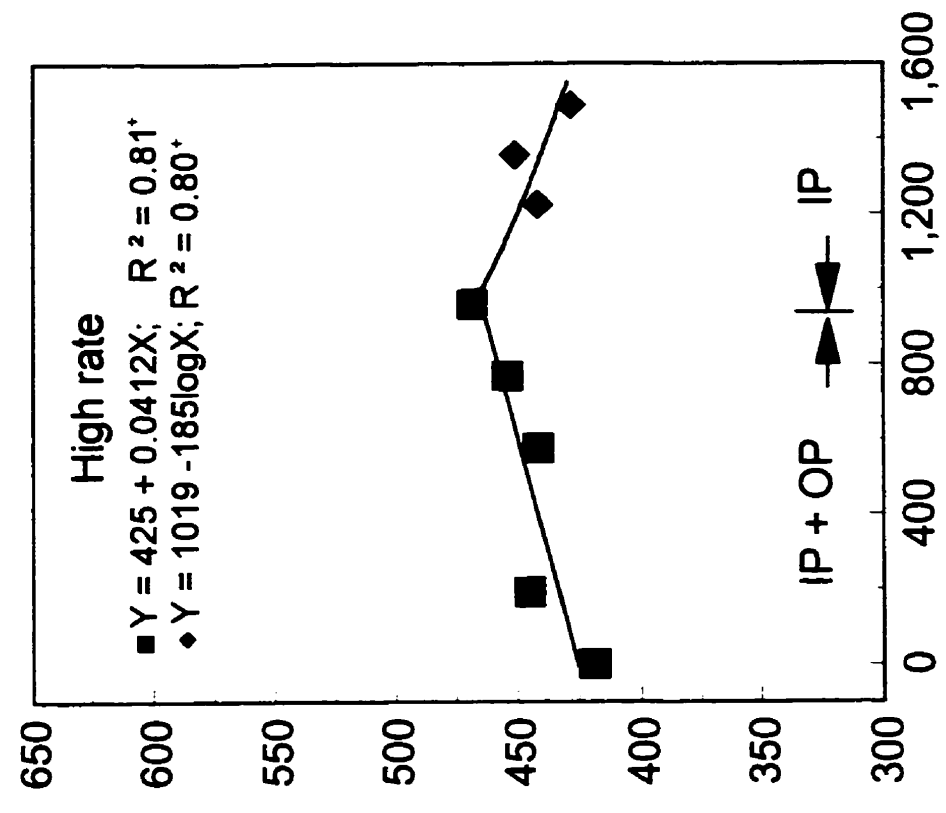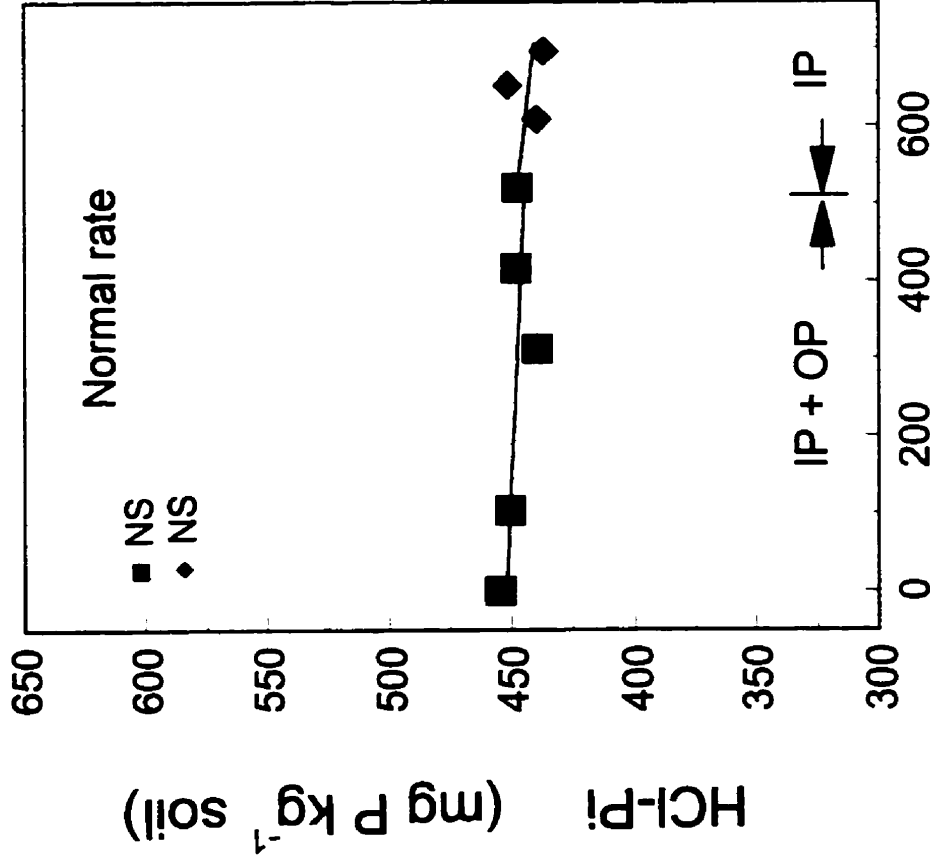
Fig. 3.5. Changes in soil total extractable Pi with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. ˙ and **; statistically significant at levels of $P<0.1$ and 0.01, respectively. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

Normal rate

■ Y = 775.9 - 0.0218X; R² = 0.64 [+]
◆ NS

High rate

■ Y = 703.4 + 0.166X; R² = 0.95 [**]
◆ Y = 706.7 + 0.168X; R² = 0.86 [+]

IP + OP ◄──┼──► IP

Total - Pi (mg P kg⁻¹ soil)

Cumulative P added (kg P ha⁻¹)
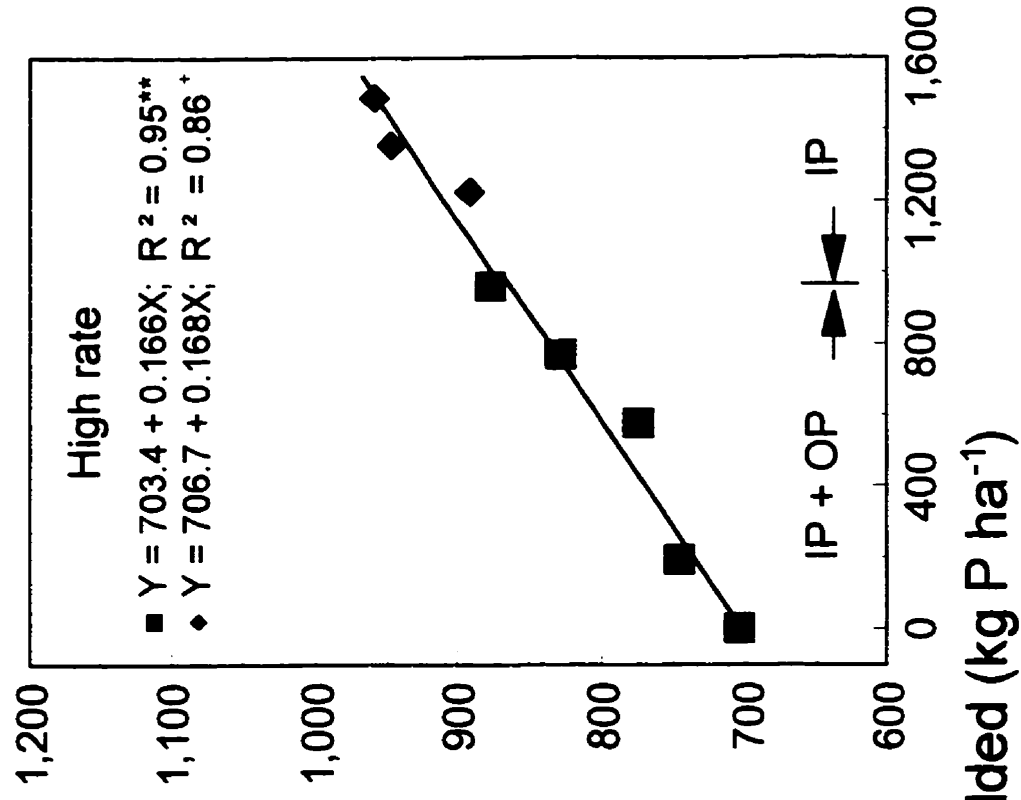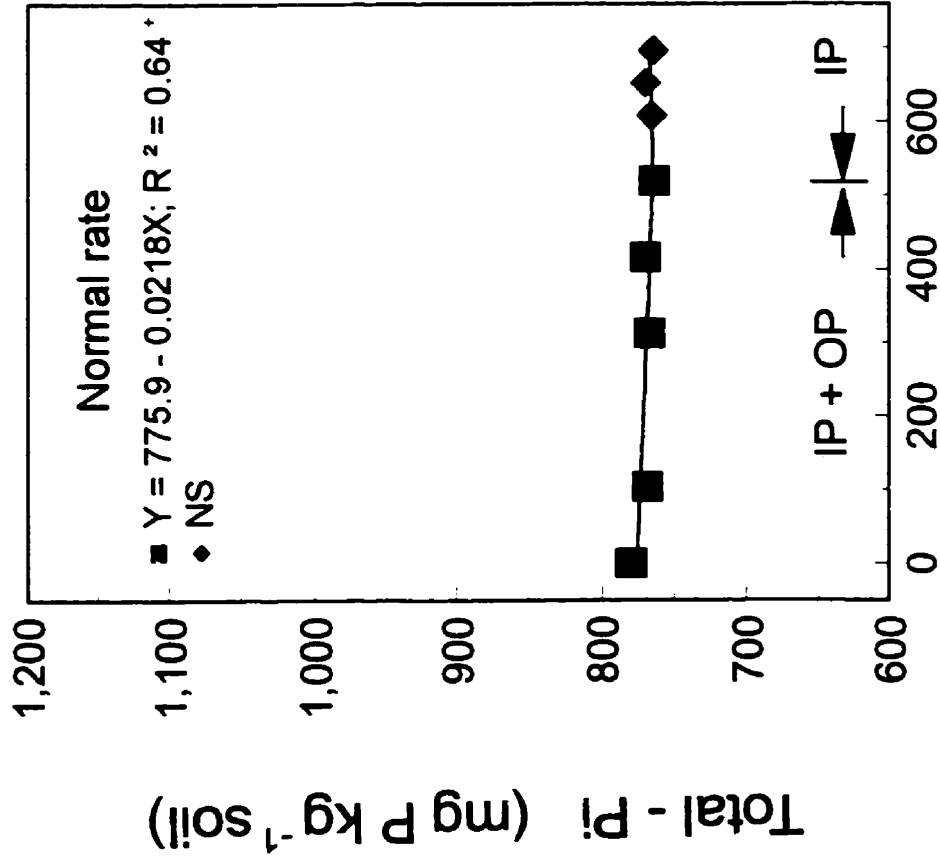
Fig. 3.6. Changes in soil $NaHCO_3$-Po with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. * and **; statistically significant at levels of $P<0.05$ and 0.01, respectively. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

Figure showing Bicarb-Po (mg P kg⁻¹ soil) versus Cumulative P added (kg P ha⁻¹) for Normal rate and High rate.

Normal rate:
■ Y = 59.1 - 14.6 logX; R² = 0.93**
♦ NS

High rate:
■ Y = 55.0 - 7.83 logX; R² = 0.90*
♦ Y = -61.0 + 0.0983X; R² = 0.97**
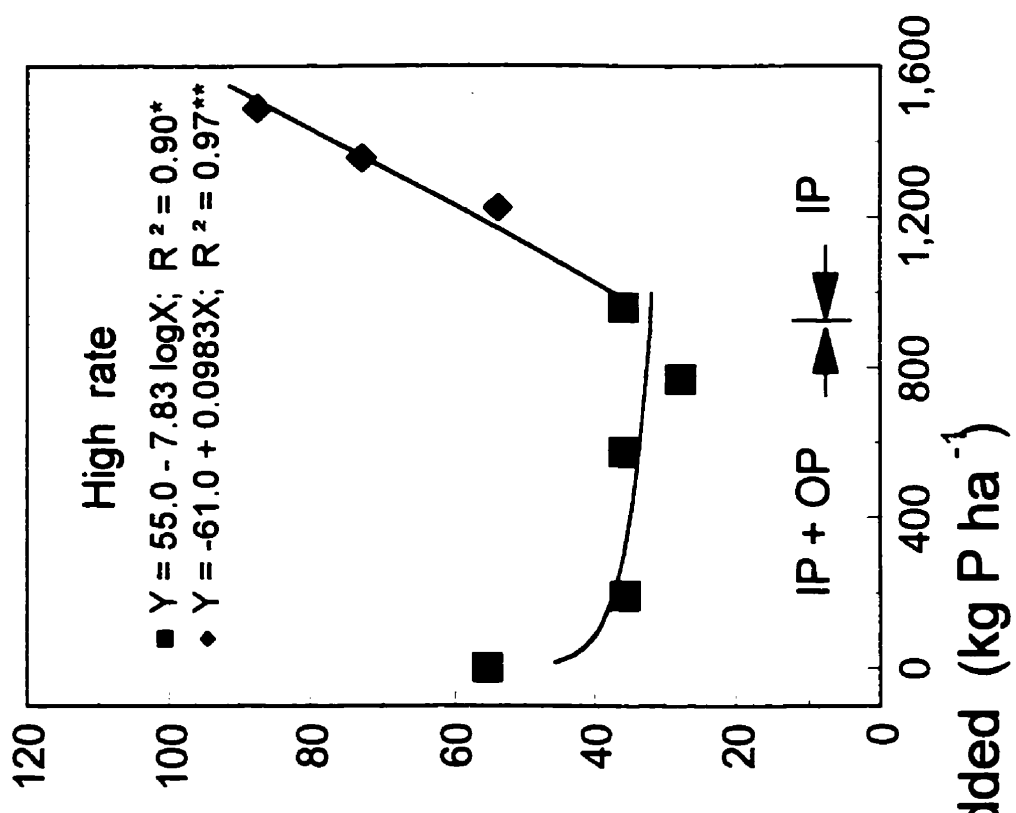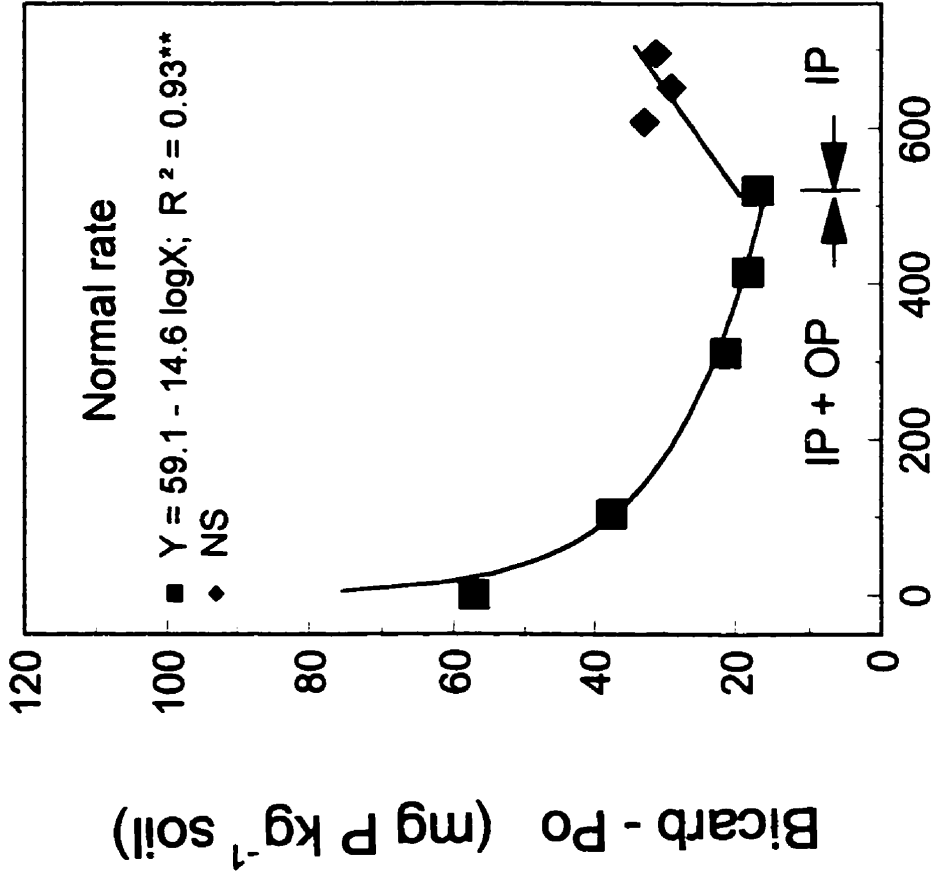
Fig. 3.7. Changes in soil NaOH-Po with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. ‾, *, and **; statistically significant at levels of $P<0.1$, 0.05, and 0.01, respectively. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

Normal rate

$Y = 86.7 + 18.6 \log X; \quad R^2 = 0.89*$

NS

High rate

$Y = 90.5 + 22.2 \log X; \quad R^2 = 0.98**$

$Y = -35.6 + 66.1 \log X; \quad R^2 = 0.81^+$

IP + OP   IP

IP + OP   IP

NaOH - Po (mg P kg^{-1} soil)

Cumulative P added (kg P ha^{-1})
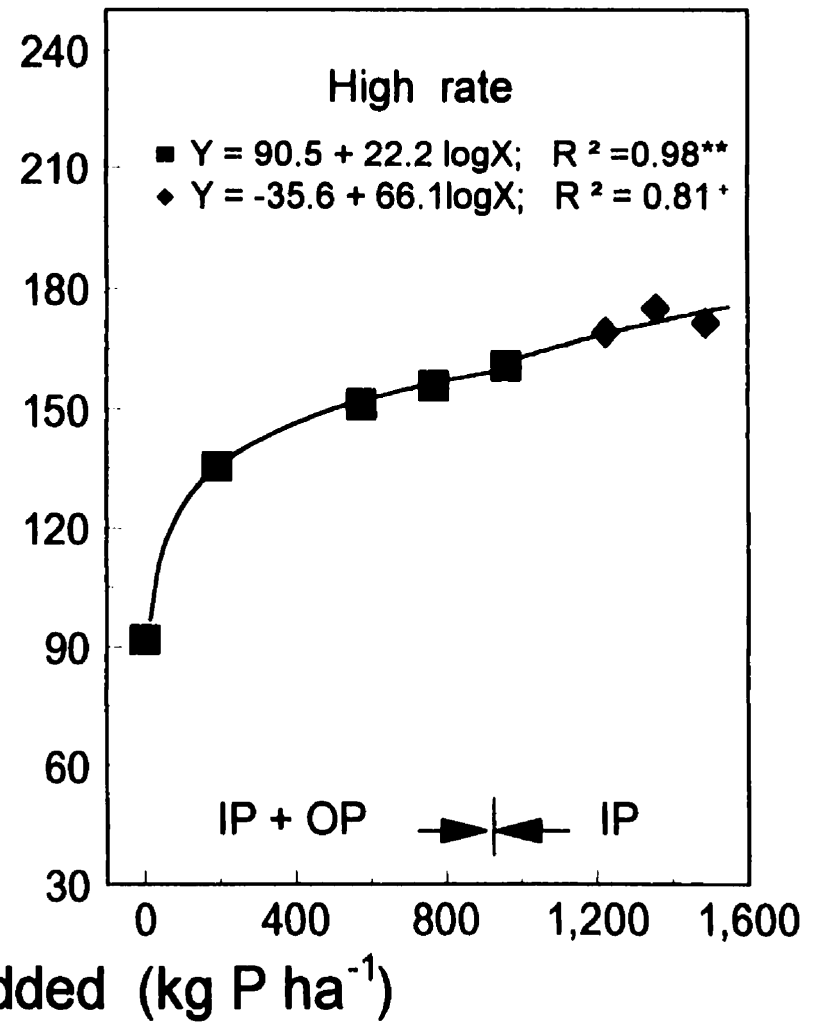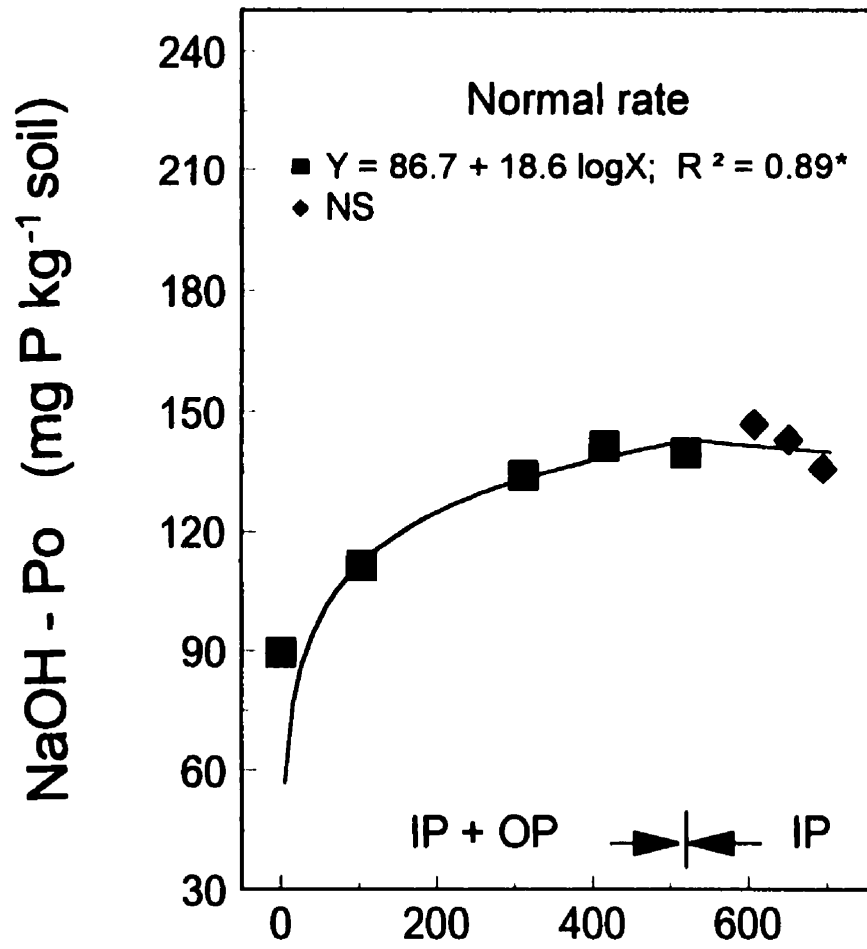
Fig. 3.8. Changes in soil total extractable Po with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. * and **; statistically significant at levels of $P<0.05$ and 0.01, respectively. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

High rate

Y = 154.4 + 0.0452X; R² = 0.88*
Y = 78.2 + 0.122X;   R² = 0.98**

Normal rate

Y = 147.2 + 0.0229X; R² = 0.88*
NS

Cumulative P added (kg P ha⁻¹)

Total - Po (mg P kg⁻¹ soil)

IP

IP + OP

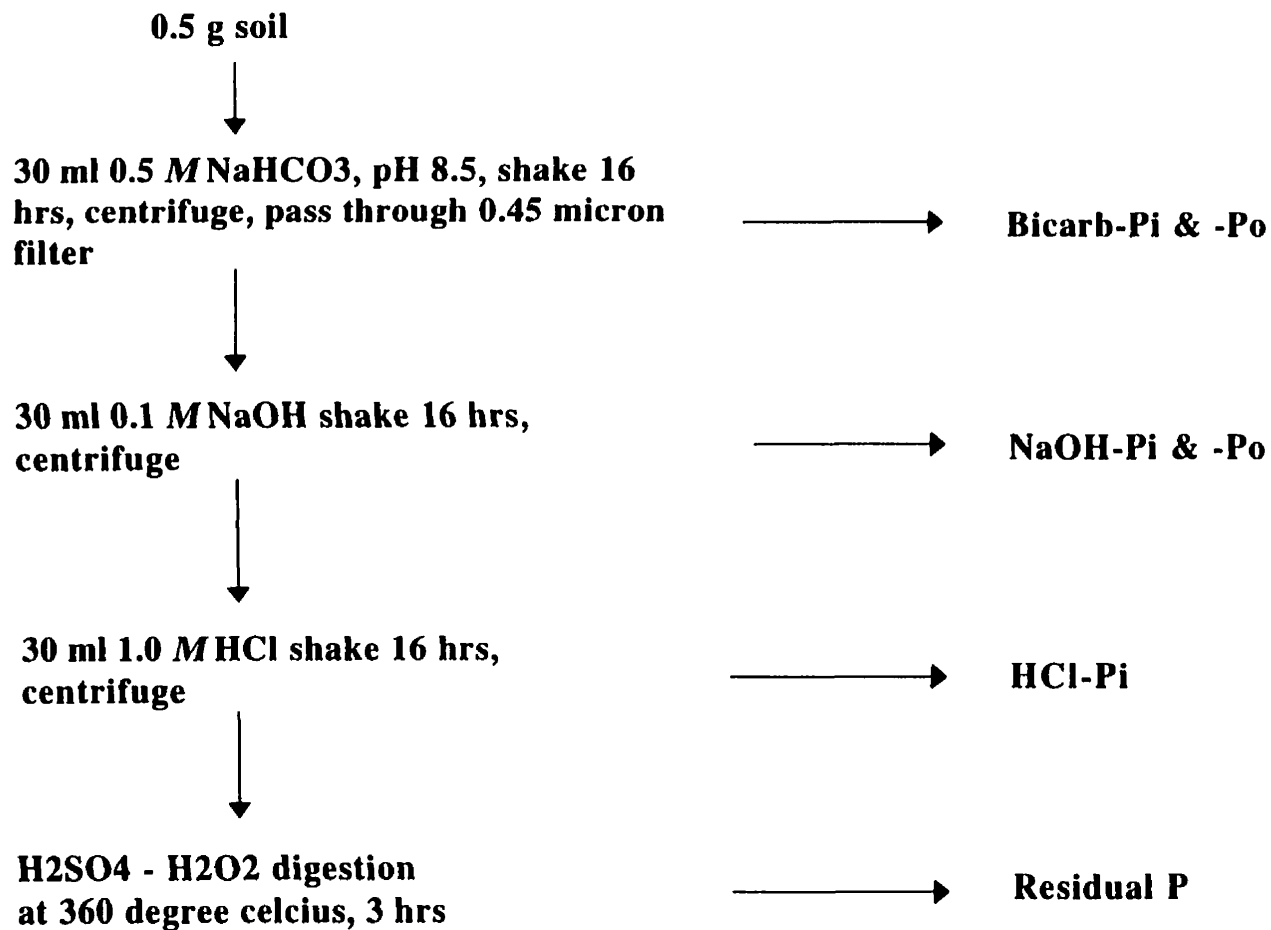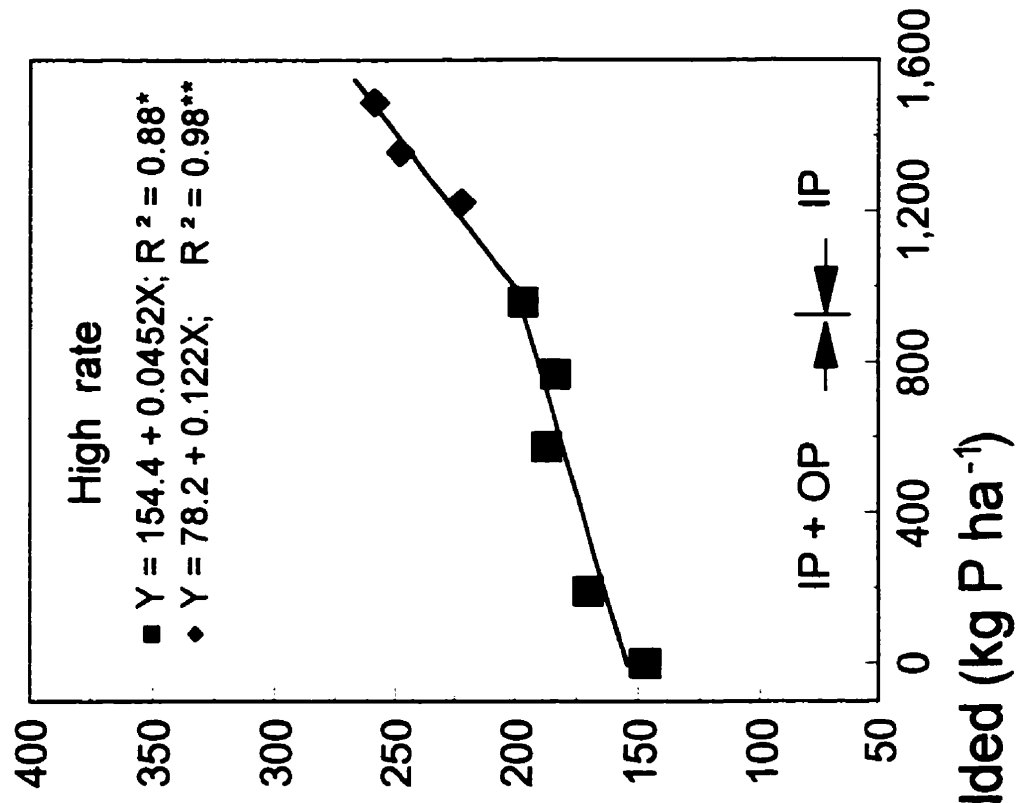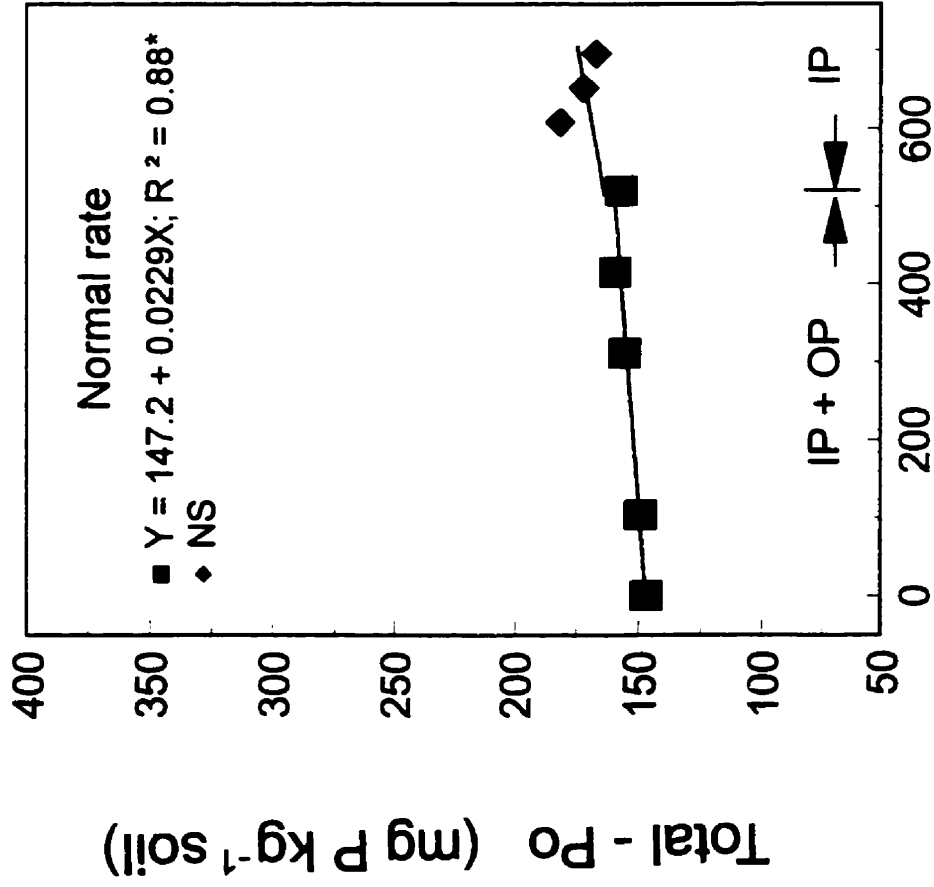Fig. 3.9. Changes in soil Residual-P with cumulative added inorganic (IP) and manure P (OP) under continuous corn in a sandy clay loam soil. * and **; statistically significant at levels of $P<0.05$ and 0.01, respectively. NS; not significant. Normal rate = 44 kg P ha^{-1}; High rate = 132 kg P ha^{-1}.

Normal rate

■ Y = 109 + 0.0941X; R² = 0.95**
◆ Y = 222 - 0.114X;   R² = 0.92*

IP + OP →|← IP

High rate

■ Y = 114 + 0.0782X;   R² = 0.91**
◆ Y = 318 - 0.127X;   R² = 0.96*

IP + OP →|← IP

Res - P (mg P kg⁻¹ soil)
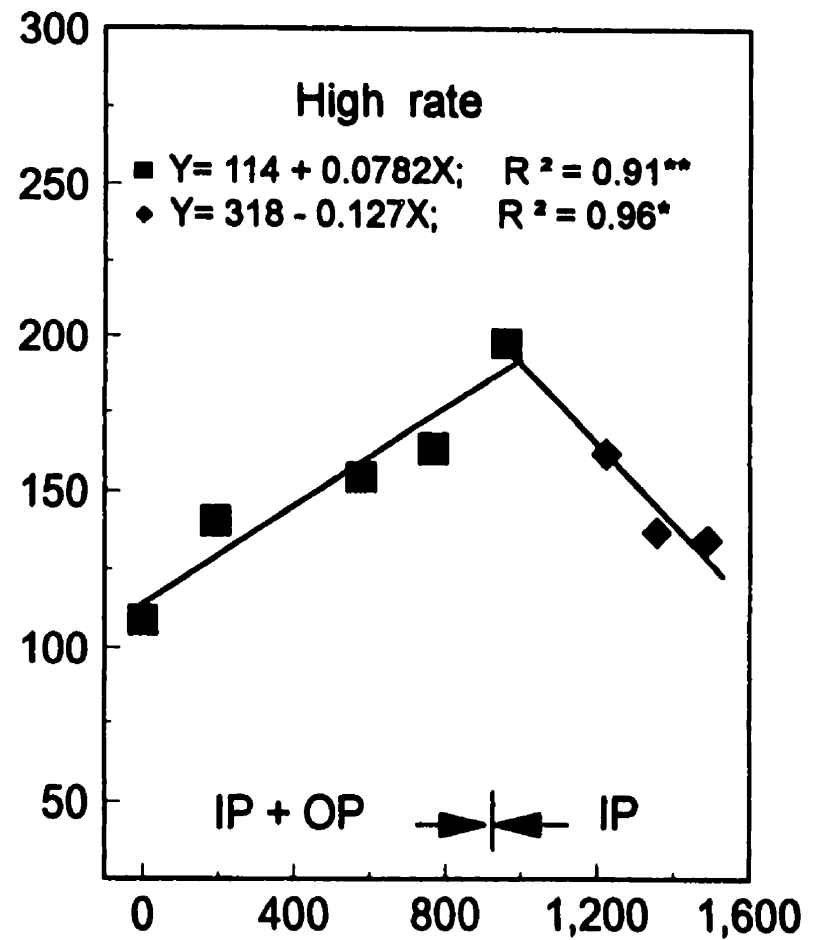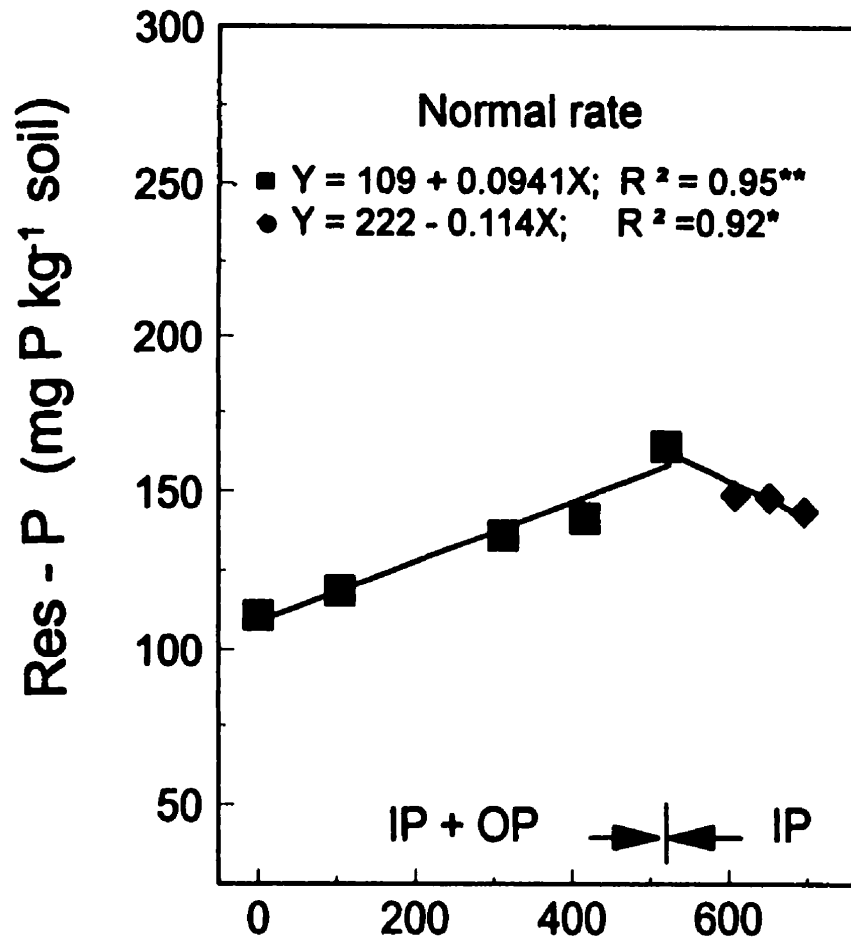
Cumulative P added (kg P ha⁻¹)

Fig. 3.10. Relationships among labile and stable components of soil P in a sandy clay loam soil under monoculture corn with fertilizer applications of inorganic P plus manure P (% indicates the partial correlation between connected components. Paths with broken lines are not in structural equations for path analysis).
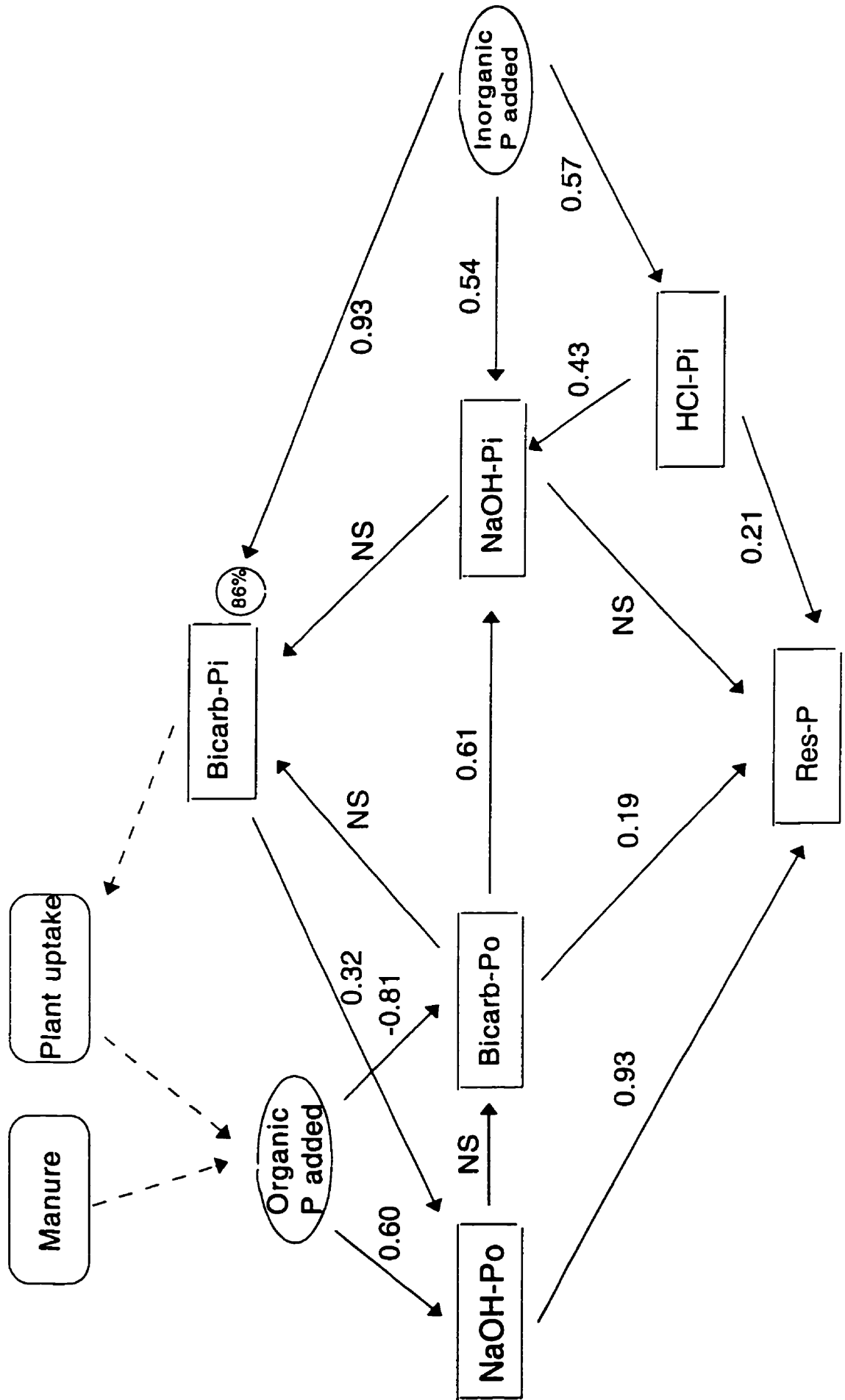
Fig. 3.11. Relationships among labile and stable components of soil P in a sandy clay loam soil under monoculture corn with fertilizer application of inorganic P only (% figures indicates the partial correlation between connected components. Paths with broken lines are not in structural equations for path analysis).
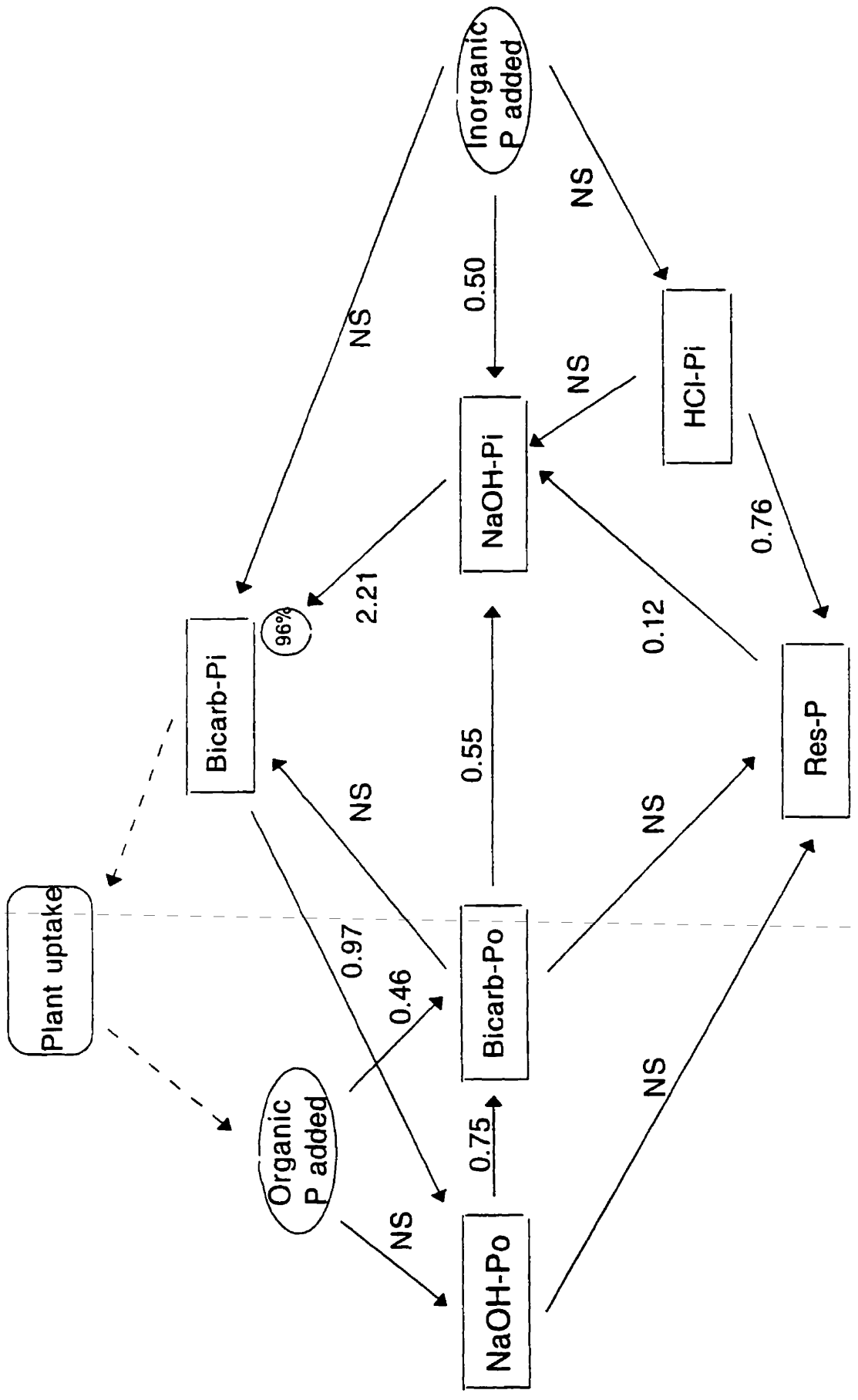
CONNECTING PARAGRAPH

Results from Chapter 3 showed that changes in soil P fractions varied with fertilizer P rates and P sources in a sandy clay loam soil and thus pathways of soil P transformations differed. Soil clay content may affect P sorption and conservation of soil organic C, and thus is of importance in soil inorganic and organic P cycling. The next Chapter provides information on dynamics of P fractions in a clay soil. Thus, comparisons based on soil texture are possible. Studies of dynamics of soil P in a clay soil was felt to be necessary to establish a range of effects of added fertilizer P in soil-crop systems. Chapter 4 discusses changes of P fractions and pathways of transformations in a Ste. Rosalie clay soil.

CHAPTER 4

CHANGES OF PHOSPHOROUS FRACTIONS UNDER LONG-TERM CORN

(*Zea mays* L.) IN A ST. ROSALIE CLAY SOIL

4.1. Abstract

Limited efficiency of fertilizer P may be improved through an understanding of soil P cycling. This study examined sequential changes in soil organic P (Po) and inorganic P (Pi) in a Ste. Rosalie clay (Humic Gleysol; fine, mixed, frigid, Typic Humaquept) under continuous corn with and without P fertilization. Soil P was fractionated into Bicarb-Pi and Po, NaOH-1-Pi and Po, HCl-Pi, NaOH-2-Pi and Po, and Residue-P. In the non-P fertilized plots, soil Po declined by 14% from the initial value after six years of corn production, whereas soil Pi fractions were unchanged. The losses of soil Po were mainly from NaOH-1-Po and represented 65% of the P removed by crops. NaOH-2-Po accounted for 60% of soil Po. Added fertilizer P increased $NaHCO_3$-Pi and NaOH-1-Pi in plots receiving 44 and 132 kg ha^{-1} yr^{-1} and increased Residue-P in plots receiving 132 kg ha^{-1} P. Although NaOH-1-Po decreased slightly in the plots receiving 44 kg ha^{-1} yr^{-1} P fertilizer, total soil extractable Po was maintained in P fertilized plots. From 16 to 22 kg P ha^{-1} Po in crop residue was needed to account for soil Po losses. The importance of Po in soil fertility decreased with increased inorganic fertilizer P rate. Path analysis in the non-P plots indicated that Bicarb-Pi was supplied directly from Bicarb-Po and indirectly from Hres-P (NaOH-2-Pi and Po plus Residue-P) through NaOH-1-Pi. In P fertilized plots, Bicarb-Pi was the major sink of residual fertilizer P. However, NaOH-1-Pi was closely related to Bicarb-Pi and could supply Bicarb-Pi. Results suggested that NaOH-1-Pi as well as Bicarb-Pi are important for assessment of soil fertility and environmental risks.

4.2. Introduction

Added phosphorus (P) accumulates in soil after long-term crop production (Tabi et al., 1990) due to low fertilizer efficiency in the year of application (Read et al., 1973; Sadler and Stewart, 1974). Increased soil P can modify fertilizer management practices and increase movement to surface waters causing eutrophication (Sharply et al., 1994). The status and fate of P in long-term fertilized soils must be determined to achieve sustainable crop production and ensure environmental quality.

Phosphorous fertilizer exceeding crop removal is found mainly as adsorbed P on surfaces of soil particles and associated with amorphous Al and Fe oxides (Wagar et al., 1986; Beck and Sanchez, 1994). Formation of these intermediate P products is reversible and some phosphate returns to the soil solution when solution P is reduced (Beck and Sanchez, 1994). Thus, the concepts of "P fixation" may have been oversimplified.

Organic P can account for 20 to 80% of soil total P (Stevenson, 1986). Additions of fertilizer P could lead to increased soil organic P through net immobilization. Generally, net immobilization of P occurs when the C/P ratios of crop residues are 300 or more; net mineralization of organic P occurs when the ratio is 200 or less (Stevenson, 1986). Large C returns to soil in crop residues could be expected to increase soil organic P.

Soil P can be fractionated into five inorganic P pools, three organic P pools, and one residual P pool (Hedley et al., 1982b). The procedure has been successful in characterizing labile and more stable inorganic P and organic P in incubated soils (Hedley et al. 1982b), and in prairie soils upon long-term cultivation (Tiessen et al. 1983). With data derived from this procedure, concepts of soil P transformations have been developed (Beck and Sanchez, 1994,

Zhang and MacKenzie, 1997) using path analysis. Beck and Sanchez (1994) found that organic P was the primary source of plant-available P on a non-fertilized Typic Paleudult soil in Peru. In a fine loamy Typic Paleudult (Beck and Sanchez, 1994) and a Chicot sandy clay loam soil (Chapter 3), inorganic P extractable with 0.1 M NaOH was the major sink of excessive added fertilizer P, but desorption was rapid enough to maintain high levels of plant available P.

Objectives of this study were to evaluate temporal trends in soil P fractions under continuous corn on a temperate clay soil and to assess soil P dynamics in both fertilized and non-fertilized soils using path analysis.

4.3. Materials and Methods

Soil characteristics, treatments, management practices and sampling and P analysis of stover and grain have been described in Chapters 2 and 3.

Composite soil samples consisting of five cores were taken randomly to a depth of 0.20-m in each plot shortly before fertilization and planting in the spring of 1988, 1989, 1991, and 1993. Preparation of soil samples are noted in Chapter 3.3.2.

Soil P was sequentially fractionated (Fig. 4.1) into Bicarb-Pi & Po, NaOH-1-Pi & Po, HCl-Pi, NaOH-2-Pi & Po, and Residue-P. However, for comparative purposes the sum of NaOH-2-Pi & Po and Residue-P was calculated and named as Hres-P, which is the same as Res-P in Chapter 3. Hres-P was used for path analyses. Stover samples from 1993 were analyzed for organic C.

Statistical analysis and path analysis are noted in Chapter 3.3.3.

4.4. Results and Discussion

4.4.1. Changes in soil P fractions

4.4.1.1. Soil inorganic P

Highly significant effects of P fertilization rate and year of crop production were found on soil Pi fractions except for NaOH-2-Pi on which there was only a year effect and HCl-Pi on which neither P rate nor year effects were found (Table 4.1). As well, interactions of fertilizer rate with year occurred on all soil Pi fractions except for NaOH-2-Pi and HCl-Pi.

Unexpectedly, neither labile Bicarb-Pi nor moderately labile NaOH-1-Pi declined in the non-P plots (Fig. 4.2a and 4.2b), despite a total of 63 kg ha^{-1} P removed by grain corn production over six years. This implies that these soil P forms were replenished from other P forms.

Bicarb-Pi and NaOH-1-Pi increased with time in fertilized plots at rates related to P application (Fig. 4.2a and 4.2b). By the end of six years, soil Bicarb-Pi had increased by 99 and 235 kg P ha^{-1} and soil NaOH-1-Pi by 22 and 107 kg P ha^{-1} for plots receiving P at annual rates of 44 and 132 kg P ha^{-1}, respectively. These increases indicated 36 to 45% of added P was found as Bicarb-Pi and 10 to 16% as NaOH-1-Pi. The results are consistent with findings showing that application of P fertilizer to a Chernozemic soil (Wagar et al. 1986) and a Hapludalf soil (Zhang and MacKenzie, 1997) increased labile and moderately labile Pi fractions.

Soil NaOH-2-Pi increased slightly when fertilizer P was added at the rate of 132 kg P

ha^{-1} over six years (Fig. 4.3a), whereas NaOH-2-Pi in the 44 kg P ha^{-1} rate plots remained unchanged. Thus, increased P rates enhanced P conversion to more stable P forms in soil.

Calcium associated phosphates extractable with 1 M HCl (HCl-Pi) remained constant at all P rates for six years (data not shown). These results indicated either an equilibrium with HCl-Pi or a largely inert P material. This is consistent with results obtained by Soon (1991) in northern Alberta and Sellers (1993) in Saskatchewan, where P fractions dominated by Ca-bound P forms remained unchanged with added P at moderate rates. In contrast, Wagar et al. (1986) found that after five years, a batch application of P fertilizer to a Brown Chernozem increased Ca-bound P forms slightly.

Total extractable soil Pi remained constant in the non-P plots, while it increased linearly with time at rates of 32 and 71 kg P ha^{-1} yr^{-1} in 44 and 132 kg P ha^{-1} plots, respectively (Fig. 4.3b). Increases of total extractable Pi in the fertilized plots represented from 54 to 72% of added fertilizer P, and 69 to 77% of total P differences in comparison with non-P plots. Thus, excessive added fertilizer P was found mainly as Pi in the soil.

4.4.1.2. Soil organic P

Soil levels for Bicarb-Po were influenced by fertilizer rate (Table 4.1). Soil Bicarb-Po in the P fertilized plots was 1.3 to 1.6 times as high as in the non-P plots (Fig. 4.4). Increases of soil Bicarb-Po with fertilization were presumably related to the high Po input from crop residues of previous years. However, no significant time pattern of Bicarb-Po was noted (Table 4.1).

Soil NaOH-1-Po remained unchanged in the high P rate of 132 kg P ha^{-1}, while it

declined logarithmically with year in both the low P rate of 44 kg P ha^{-1} and non-P plots (Fig. 4.5a). From 16 to 25% of the initial soil Po was lost as NaOH-1-Po in 44 kg ha^{-1} and non-P plots over six years of corn production. This finding was similar to that of Hedley et al. (1982b) who reported that after 65 years of cultivation loss of 0.1 M NaOH extractable Po was 68% of total extractable soil Po lost. The NaOH-1-Po loss in non-P plots was assumed to be through mineralization. There were no notable changes in NaOH-2-Po in any of the P fertilized plots (data not shown). This infers that this form of organic P was relatively stable.

It should be pointed out, however, that 409 kg ha^{-1} of NaOH-2-Po across all P rates accounted for 60% of soil Po, implying NaOH-2-Po to be a major Po reservoir. The importance of this portion of soil Po needs to be studied.

Total extractable Po decreased by 41 kg P ha^{-1} in non-P plots, while it remained constant in fertilized plots (Fig. 4.5b). This decrease was equivalent to 14% of the initial soil Po, and 65% of the P removed by the crop. Assuming 48 kg ha^{-i} of Po was added in crop stover and roots (Table 4.2), then a total of 89 kg ha^{-1} Po was mineralized during the six years period. Soil extractable Po was maintained by inputs of 81 to 109 kg ha^{-1} of crop residue Po (Table 4.2) in fertilized plots (Fig. 4.5b). Thus, mineralization of 16 to 22 kg P ha^{-1} yr^{-1} Po was needed to account for Po changes. These values are smaller than those in Oklahoma and Texas soils obtained by Sharpley (1985) who found mineralization contributed 20 to 74 kg ha^{-1} P during the growing season. The lower mineralization rate of Po in this study may be a reflection of cooler climatic conditions and higher C/P ratios of organic inputs (Table 4.2).

Soil residual P increased linearly at a rate of 11 kg P ha^{-1} yr^{-1} when fertilizer P was added annually at the rate of 132 kg ha^{-1} (Fig. 4.6). Clearly, increased fertilizer P above crop

removal enhanced the formation of stable soil P.

4.4.2. Interrelationships between soil P fractions and inorganic and organic P input

In non-P plots path analysis showed that 72% of variation in the level of Bicarb-Pi was explained by variations in Bicarb-Po and NaOH-1-Pi (Fig. 4.7). Soil Hres-P contributed indirectly to Bicarb-Pi through the NaOH-1-Pi fraction ($\beta = 0.65 \times 0.59$). Thus, NaOH-1-Pi was considered only as an intermediary from Hres-P to Bicarb-Pi, because levels of NaOH-1-Pi were unchanged with time (Fig. 4.2b). NaOH-2-Po made up about half of the Hres-P. Therefore, it can be concluded that Po compounds played a significant role in supplying Bicarb-Pi. Results obtained by Tiessen et al. (1984) in a study on 29 Ultisols indicated that 80% of the available P variation was explained by Po fractions. This increase in the role of Po in supplying plant P may reflect the increased importance of Po supply in Ultisols compared to temperate zone soils.

Addition of organic Po as crop residues enhanced mineralization of NaOH-1-Po ($\beta = -0.40$), presumably due to supply of energy with carbohydrates. However, the model only explained 33% of variation of NaOH-1-Po. There was no relationship found between NaOH-1-Po and Bicarb-Pi. The decrease of NaOH-1-Po implies that NaOH-1-Po may contribute indirectly to soil Bicarb-Pi through an unknown variable.

The negative path coefficient between HCl-Pi and Hres-P suggested that the Ca-bound P forms can be replenished through depletion of relatively stable soil P. HCl-Pi is not an important sink in soil P, but once formed is stable.

Path coefficients calculated using both P rates were largely similar to those obtained

separately from each P rate. Therefore, relationships presented in Fig. 4.8 represent pathways of P transformations in fertilized soils.

Labile Bicarb-Pi was supplied either directly from added inorganic P or indirectly from moderately labile NaOH-1-Pi. A total of 93% of the variation of Bicarb-Pi was accounted for by components of inorganic P addition, NaOH-1-Pi, and Bicarb-Po. One unit addition of fertilizer P increased labile Bicarb-Pi by 0.93 (0.60 + (0.75 X 0.45)) units, confirming that Bicarb-Pi was the major sink of added inorganic P (Fig. 4.2). Results from our previous study showed that NaOH-Pi, which was the same as NaOH-1-Pi in the present study, was the major sink for added fertilizer P in a Chicot soil after 10 years of monoculture corn (Zhang and MacKenzie, 1997). Beck and Sanchez (1994) in a Typic Paleudult soil found that the effects of inorganic P fertilization on soil available P, represented by Resin-P and Bicarb-Pi, were indirect through formation of HCl-Pi and NaOH-Pi.

Of Bicarb-Pi, a small portion was used for synthesis of Bicarb-Po compounds (path coefficient = 0.17). However, this newly formed Po balanced the loss of Po in the soil due to cultivation, as there were consistent levels of Bicarb-Po during the six years period.

The Hres-P can be another soil P sink. The buildup of Hres-P resulted from NaOH-1-Po and added inorganic P through NaOH-1-Pi.

4.5. Conclusion

Soil Po declined under continuous corn without P addition. Phosphorus addition increased mainly Bicarb-Pi and secondly NaOH-1-Pi, and maintained soil Po. Only a small portion of added P at the high rates was transformed into the most stable Hres-P. About 60%

of Hres-P was accounted for by Po.

If one assumes that the Bicarb-Pi is the major source of P for the plant, then the pathways to Bicarb-Pi varied depending on whether fertilizer P was added. Without added P Bicarb-Pi was supplied either directly from Bicarb-Po or indirectly from NaOH-1-Po and Hres-P partly through NaOH-1-Pi. Thus, Po reserves were more important than Pi sources. With added P the Bicarb-Pi was supplied from added P and NaOH-1-Pi, which in turn was a source of Pi for Hres-P. Thus the NaOH-1-Pi was a reversible link between Bicarb-Pi and Hres-P, the direction of movement depending on added P. Surprisingly, HCl-Pi did not act as a sink perhaps due to the relatively short period of P addition.

These pathways differ somewhat from those found in a sandy clay loam (Chapter 3), where added P without manure moved to Bicarb-Pi through NaOH-Pi (the same as NaOH-1-Pi in this Chapter). Organic P sources also supplied NaOH-Pi, with the result that NaOH-Pi was the major P source for Bicarb-Pi. With manure, added P moved directly to Bicarb-Pi, bypassing NaOH-Pi. The NaOH-Pi seems to be very sensitive to addition of inorganic P but this inorganic P may bypass NaOH-Pi if manure is added. Manure appears to reduce the activity of NaOH-Pi, probably through sorption of organic materials in competition with inorganic P.

Thus NaOH-Pi plays a key role in the movement of P in soils, and yet it is bypassed in supplying available P with added manure.

Table 4.1. Results of repeated measures analysis of variance of soil P fractions as influenced by fertilization rate and year of continuous corn on a Ste. Rosalie clay soil.

P fraction	Fertilization rate (F)	Year (Y)	F X Y
Inorganic P (Pi)			
Bicarb-Pi	***	***	***
NaOH-1-Pi	***	***	***
HCl-Pi	NS	NS	NS
NaOH-2-Pi	NS	*	NS
$\sum$ Pi fractions	**	***	***
Organic P (Po)			
Bicarb-Po	*	NS	NS
NaOH-1-Po	NS	**	NS
NaOH-2-Po	NS	NS	NS
$\sum$ Po fractions	NS	†	NS
Res-P	*	NS	*

***, **, *, †: Statistical significant at levels of 0.001, 0.01, 0.05, and 0.1, respectively.

NS: Not statistical significant at 0.1 level.

Table 4.2. Total additions of organic C and P over five years of continuous corn in a Ste. Rosalie clay soil.

Fertilizer rates	Organic C†	Organic P†	C/P ratio
------------------------ kg ha^{-1} -------------------------			
0	9360	48	195
44	20800	81	257
132	26100	109	239

† Estimations of total inputs of organic C and P were based on corn stover yields and estimated root biomass production.

Fig. 4.1. Procedure of soil P fractionation.

0.5 g soil

↓

30 ml 0.5 *M* NaHCO3, pH 8.5, shake 16 hrs, centrifuge, pass through 0.45 micron filter ⟶ **Bicarb-Pi & -Po**

↓

30 ml 0.1 *M* NaOH shake 16 hrs, centrifuge ⟶ **NaOH-1-Pi & -Po**

↓

30 ml 1.0 *M* HCl shake 16 hrs, centrifuge ⟶ **HCl-Pi**

↓

30 ml 0.1 *M* NaOH shake 16 hrs, centrifuge ⟶ **NaOH-2-Pi & -Po**

↓

H2SO4 - H2O2 digestion at 360 degree celcius, 3 hrs ⟶ **Residual P**
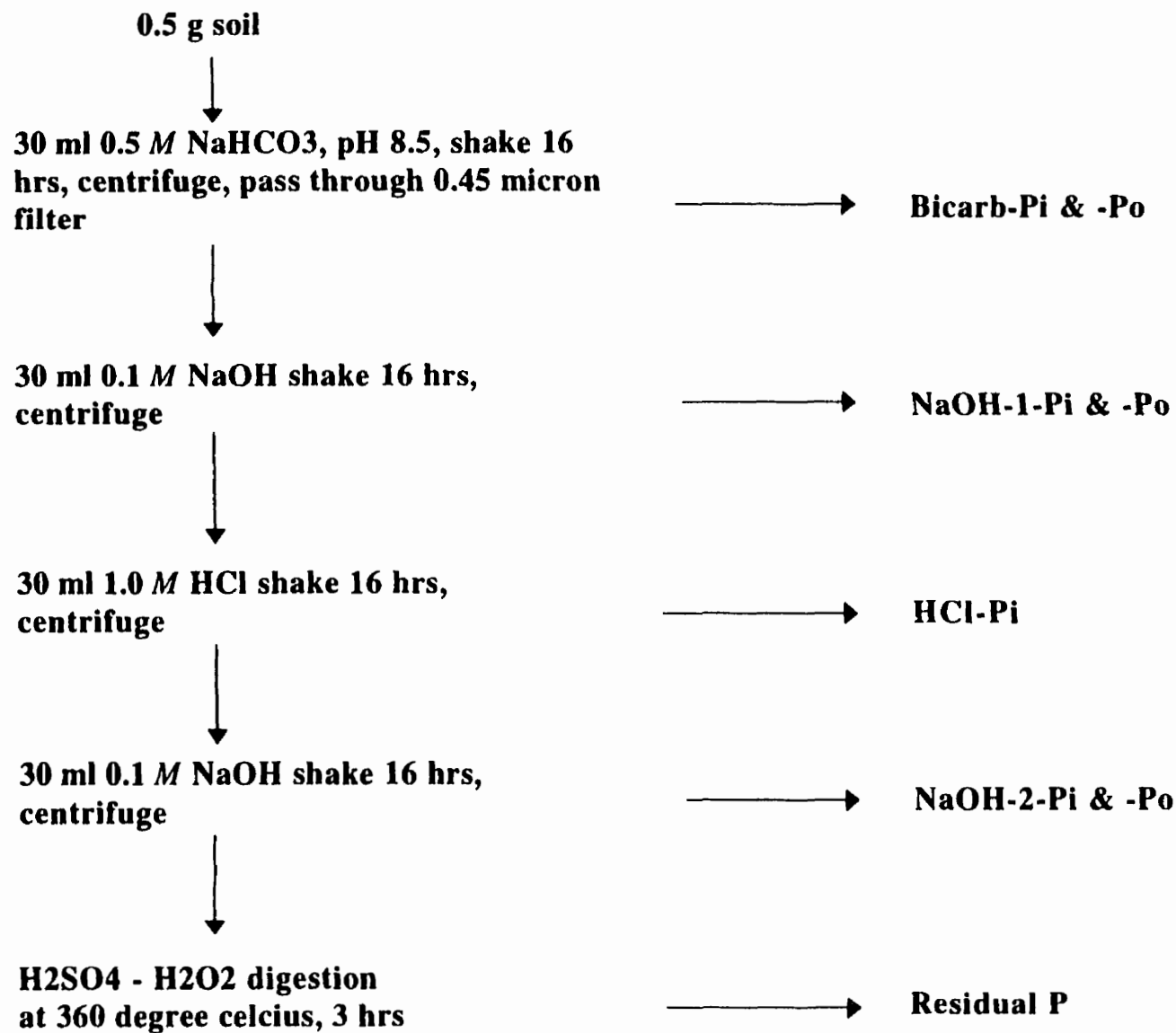
Fig. 4.2. Changes of Bicarb-Pi and NaOH-1-Pi with time under continuous corn in a Ste. Rosalie clay soil. * and **; equation is statistically significant at levels of $P<0.05$ and 0.01, respectively.

Bicarb-Pi

a

◆ 0 P: Y = NS
○ 44 P: Y = 51.2 + 7.96year; $R^2 = 0.91$
● 132 P: Y = 39.3 + 18.9year; $R^2 = 0.99$

NaOH-1-Pi

b

◆ 0 P: Y=NS
○ 44 P: Y = 63.4 + 1.78year; $R^2 = 0.96$
● 132 P: Y = 52.5 + 8.60year; $R^2 = 0.99$

Phosphorus (mg P kg^{-1})

Year
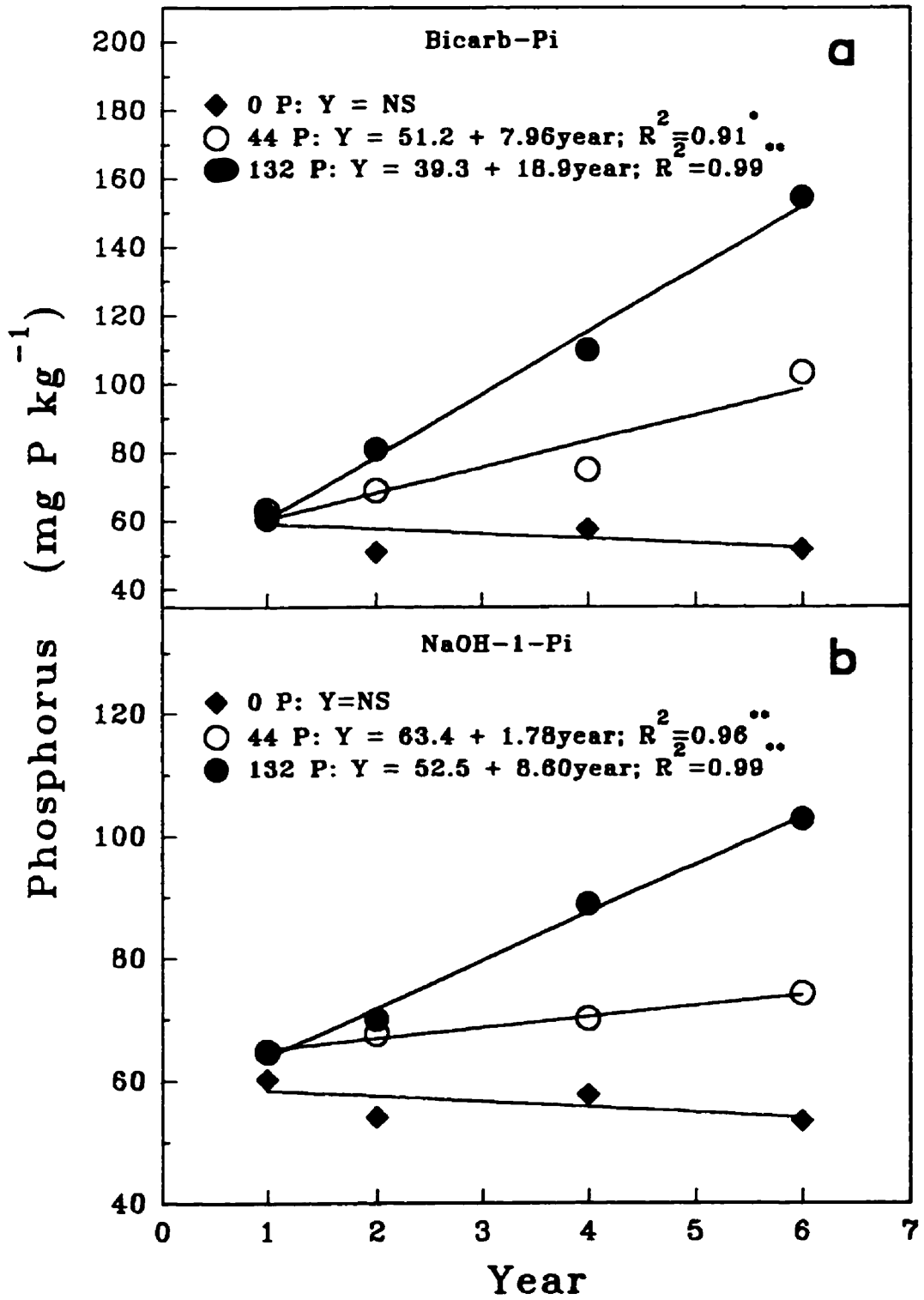
Fig. 4.3. Changes of NaOH-2-Pi and total extractable Pi with time under continuous corn in a Ste. Rosalie clay soil. * and **; equation is statistically significant at levels of $P<0.05$ and 0.01, respectively. NS; equation is not statistically significant at $P<0.1$ level.

a

NaOH-2-Pi

◆ 0 P: Y = NS
○ 44 P: Y = NS
● 132 P: Y = 45.1 + 0.760year; $R^2 = 0.94$*

b

Total extractable Pi

◆ 0 P: Y = NS
○ 44 P: Y = 707 + 12.8year; $R^2 = 0.90$*
● 132 P: Y = 707 + 28.5year; $R^2 = 0.99$**

Phosphorus (mg P kg^{-1})
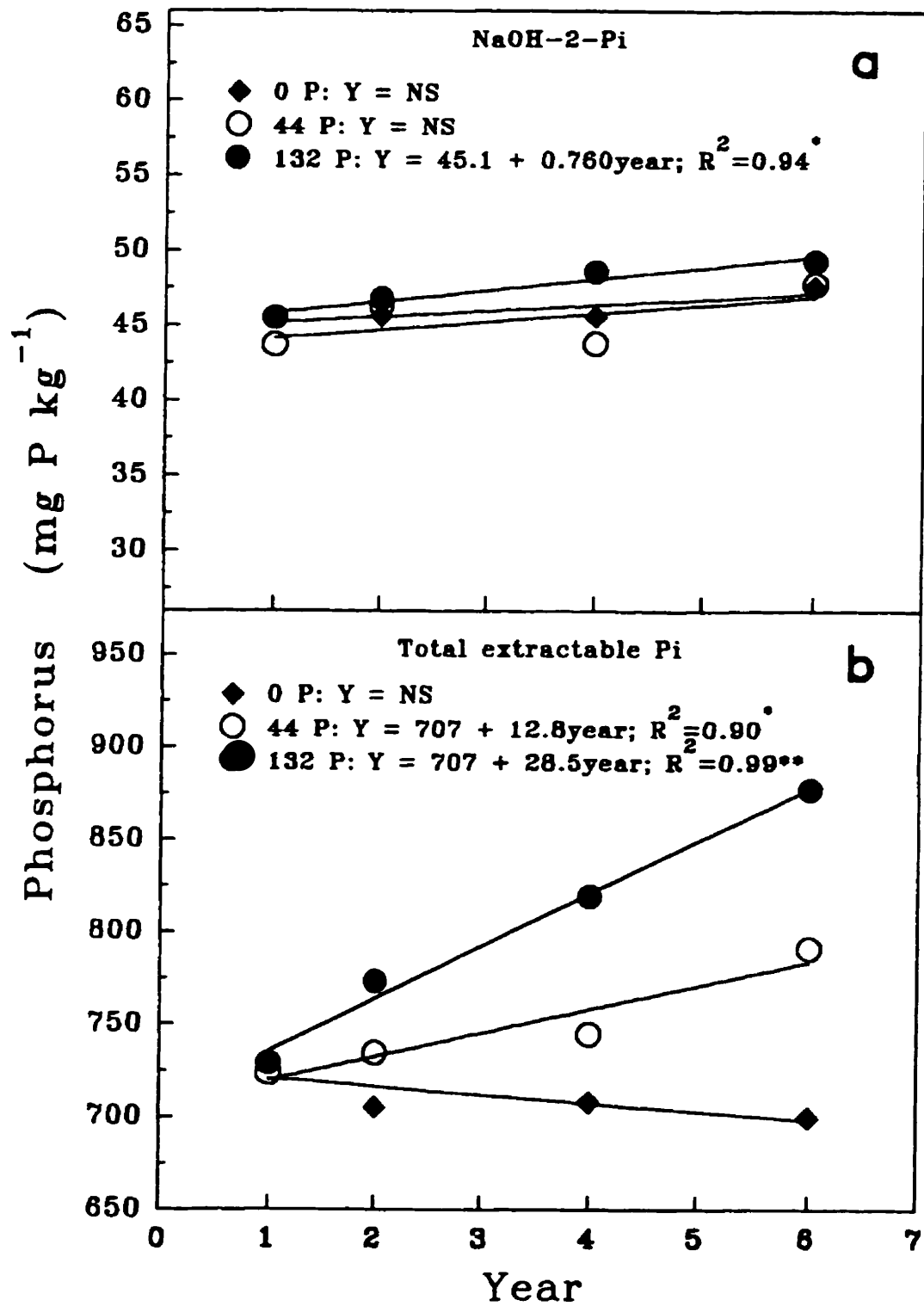
Year

Fig. 4.4. Bicarb-Po as affected by annual fertilizer P rate across six years in a Ste. Rosalie clay soil. Error bar refers to standard error.
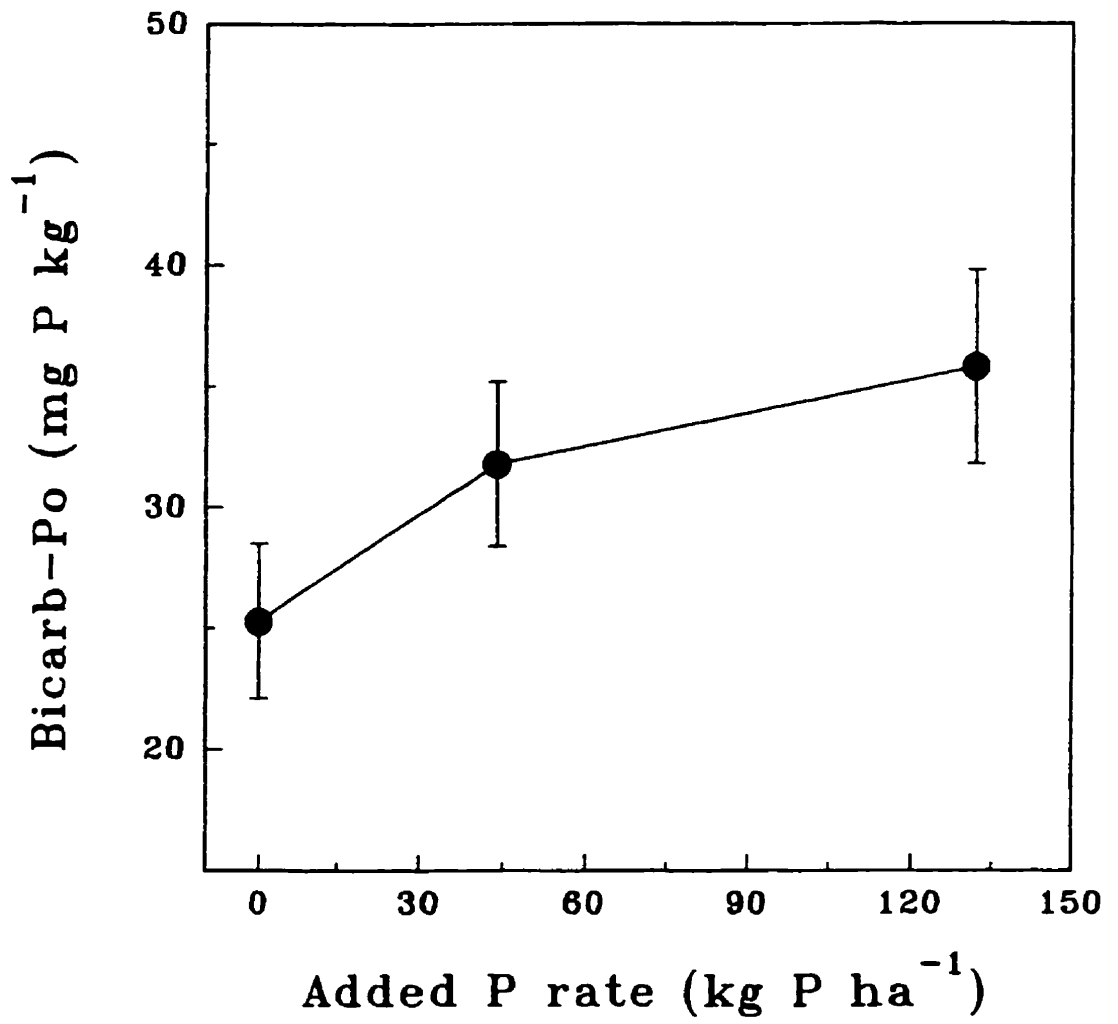
Fig. 4.5. Changes of NaOH-1-Po and total extractable Po with time under continuous corn in a Ste. Rosalie clay soil. * and ⁻; equation is statistically significant at $P<0.05$, and 0.1 levels, respectively. NS; equation is not statistically significant at $P<0.1$ level.

a

NaOH-1-Po

- ◆ 0 P: Y = 98.1 − 13.9 lnyear; R^2=0.92
- ○ 44 P: Y = 93.6 − 8.35 lnyear; R^2=0.92
- ● 132 P: Y = NS

b

Total extractable Po

- ◆ 0 P: Y = 285 − 22.9 lnyear; R^2=0.84 +
- ○ 44 P: Y = NS
- ● 132 P: Y = NS

Phosphorus (mg P kg^{-1})

Year
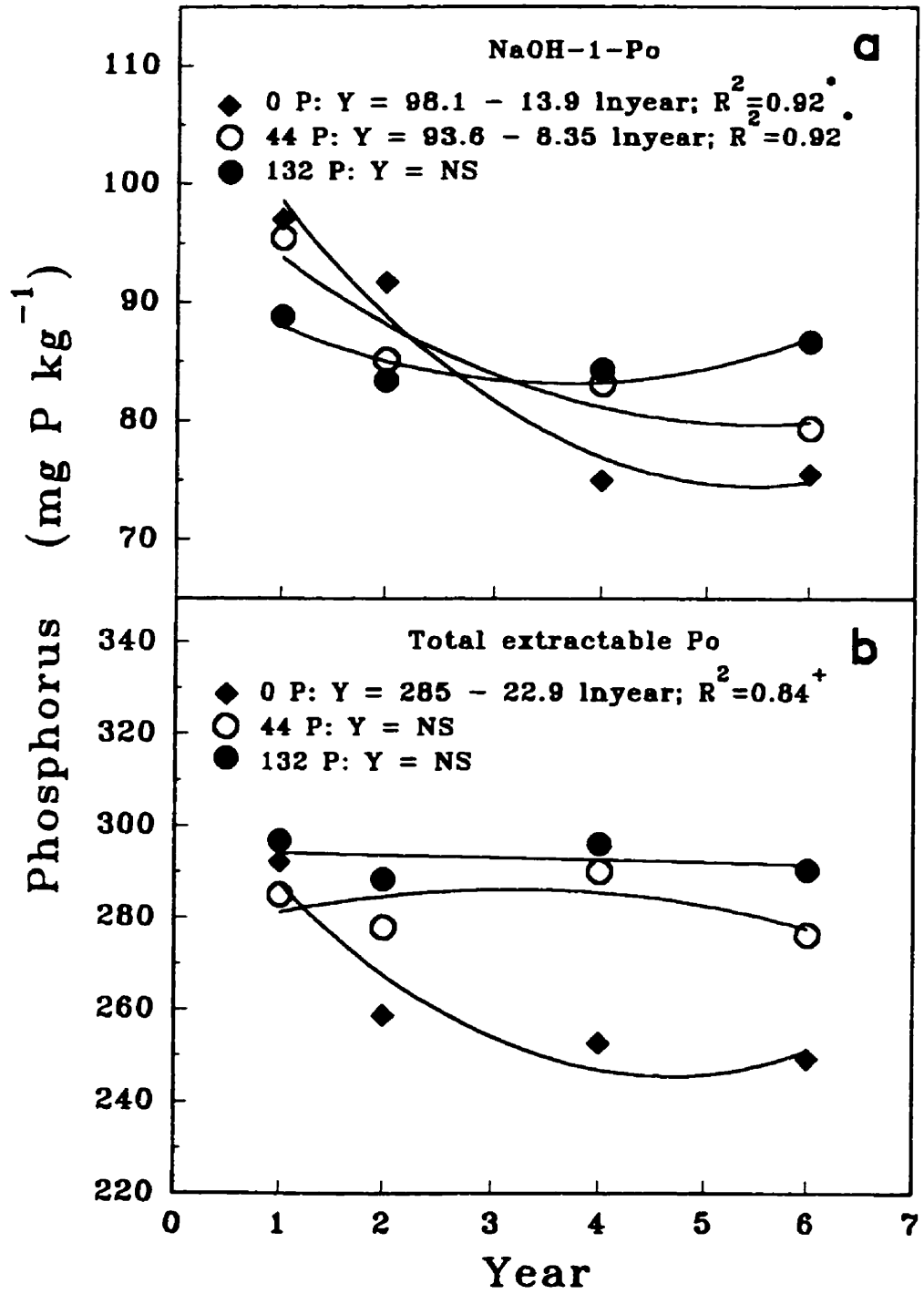
Fig. 4.6. Changes of soil Res-P with time under continuous corn in a Ste. Rosalie clay soil. *; equation is statistically significant at level of $P<0.05$. NS; equation is not statistically significant at $P<0.1$ level.

Figure showing Phosphorus (mg P kg^{-1}) versus Year.

Legend:
- 0 P: Y = NS
- 44 P: Y = NS
- 132 P: Y = 124 + 4.51year; R^2=0.92
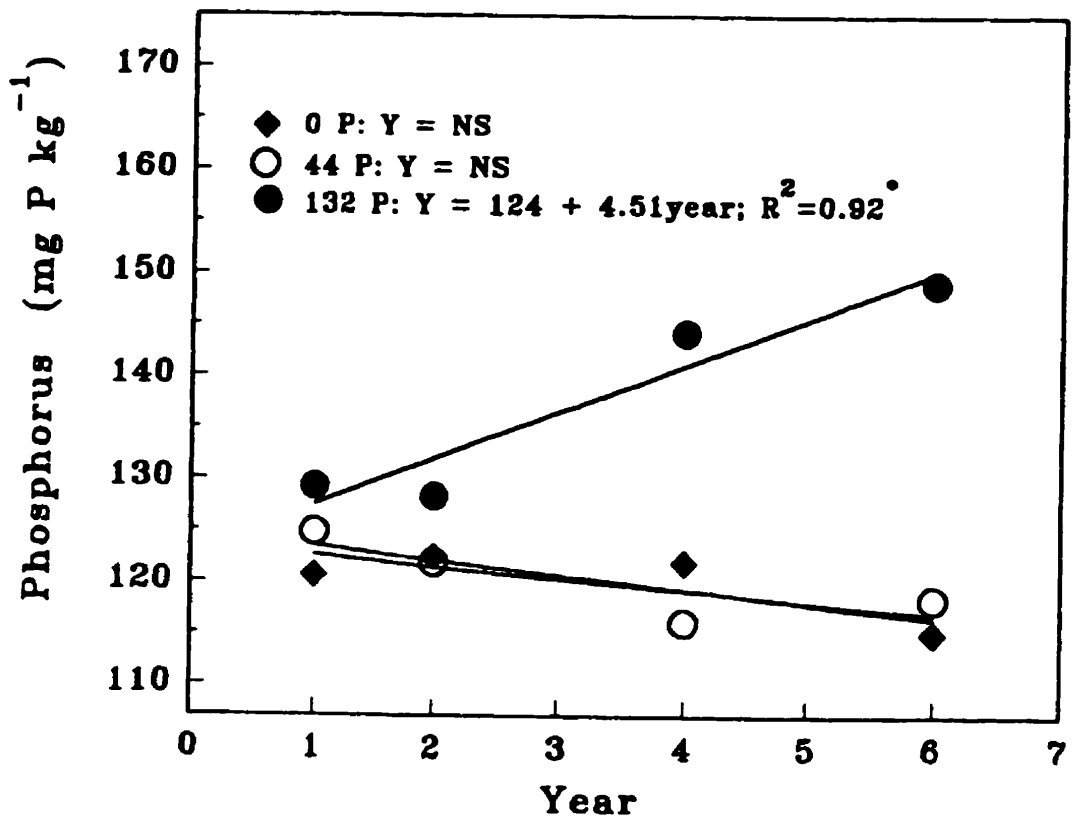
Fig. 4.7. Relationships among components of the soil P cycle in a Ste. Rosalie clay soil under continuous corn without fertilization (% indicates the partial correlation between variables. Variables connected with broken lines are not involved in path analysis)
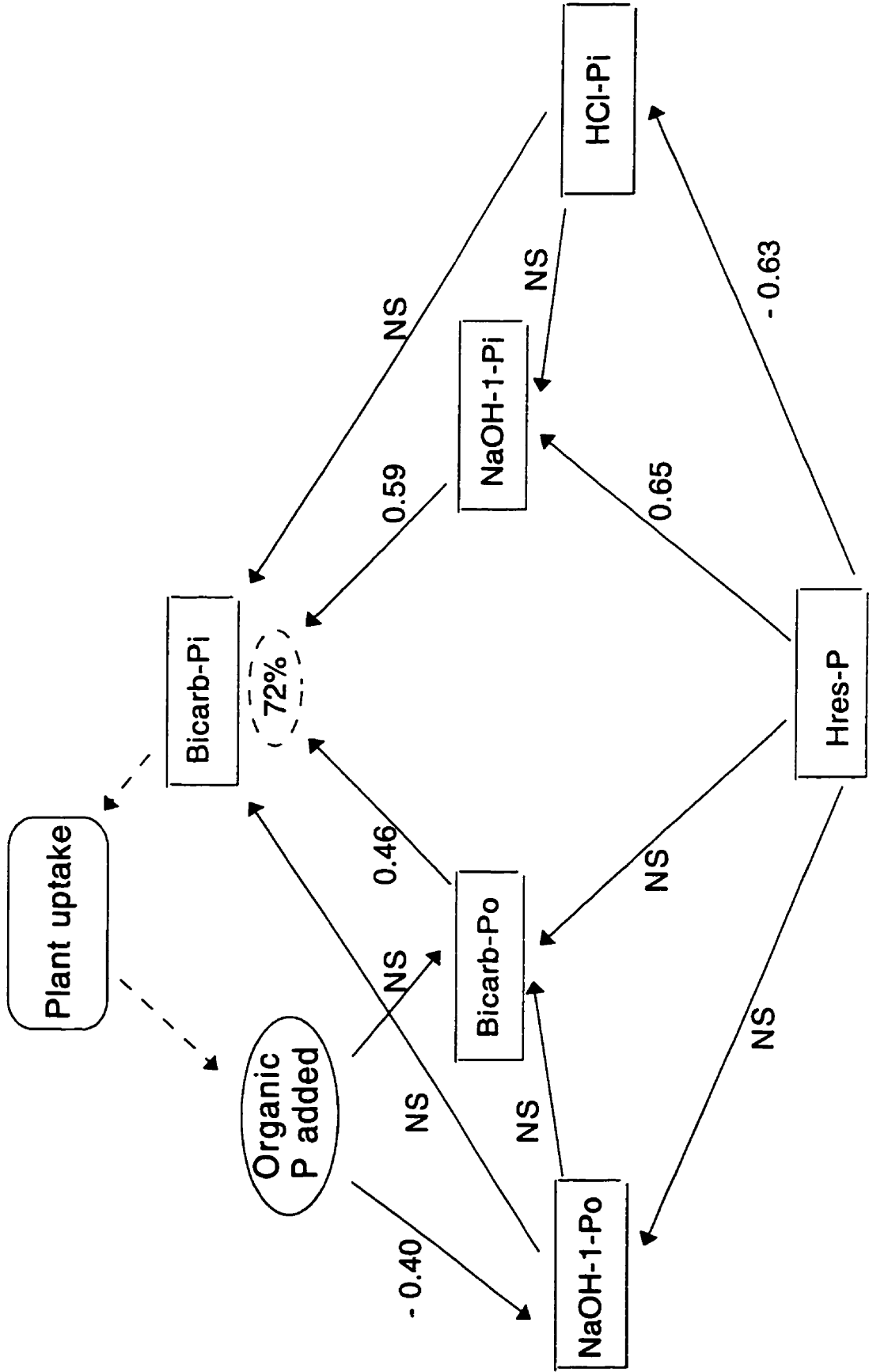
Fig. 4.8. Relationships among components of the soil P cycle in a Ste. Rosalie clay soil under continuous corn with inorganic P fertilization (% indicates the partial correlation between variables. Variables connected with broken lines are not involved in path analysis).
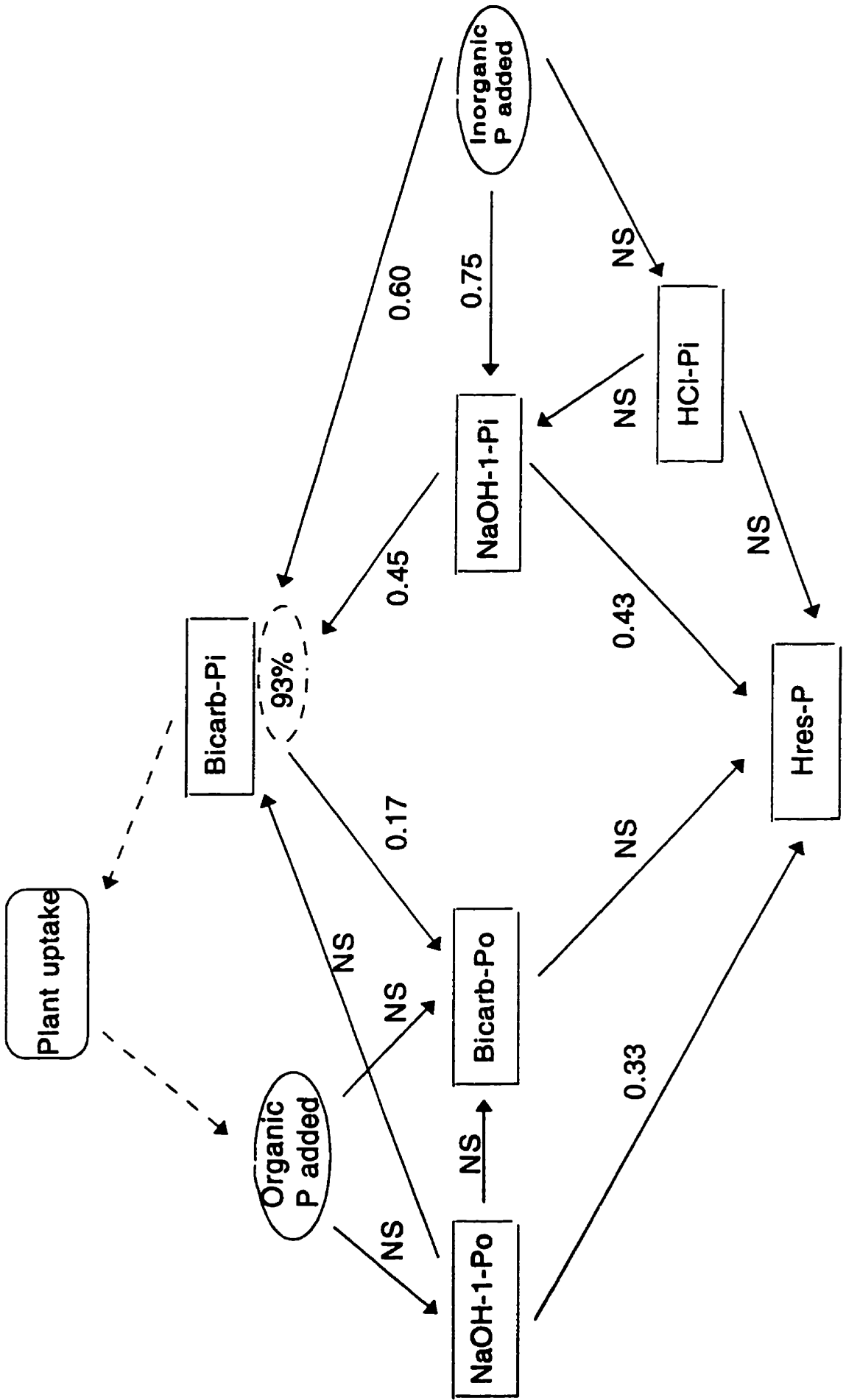
CONNECTING PARAGRAPH

In Chapters 3 and 4, organic P fractions were found to be dynamic and of varying importance in soil P cycling. However, indirect determination of soil organic P based on the difference between two soil analyses may cause large errors, is cumbersome, and does not identify constituents. In the following chapter, direct measurements of constituents of organic P using ^{31}P nuclear magnetic resonance (NMR) were carried out to determine the nature of soil organic P fractions and relationships to cropping and P fertilization.

CHAPTER 5

NATURE OF SOIL ORGANIC PHOSPHORUS AS EFFECTED BY LONG-TERM

FERTILIZATION UNDER CONTINUOUS CORN (*Zea mays* L.):

A ^{31}P NMR STUDY

5.1. Abstract

A large proportion of soil P in temperate agricultural soils is as organic P (Po) which may play a significant role in supplying plant available P and contribute to soil P losses. Thus, the dynamics of soil Po must be better understood with respect to components. Soil samples taken from two long-term corn fertilization experiments on a Chicot sandy clay loam (Grey Brown Luvisol) and a Ste. Rosalie clay (Humic Gleysol) were analyzed for Po components using ^{31}P NMR. Soil Po extracted with 0.5 M NaHCO$_3$ (Bicarb-Po) consisted mainly of monoester phosphates (40-81%) with a small amount of diester phosphates (0-15%) and some unidentified organic P compounds. For soil Po extracted with 0.1 M NaOH (NaOH-Po), monoester phosphates accounted for 70-85%, followed by diester orthophosphates at 0-8%, and some unidentified organic P forms. Monoester P was a constant component of Po within any one soil P fraction. Changes of monoester P with cropping varied with fertilizer P rates, soil types, and soil P fractions. In the Chicot soil, monoester P extracted with NaHCO$_3$ decreased with addition of fertilizer P at the rates of 44 kg ha^{-1} and increased with P rates of 132 kg ha^{-1}. Monoester P extracted with NaOH increased with increased fertilizer P rate. In the Ste. Rosalie soil, monoester P in NaHCO$_3$ extracts decreased when zero-P was applied, but increased with P fertilization. Monoester P in NaOH extracts decreased with zero-P addition and the effect was reduced with fertilizer P additions. There was no P rate effect on monoester P in either NaHCO$_3$ extracts or NaOH extracts. Dynamics of soil Po fractions can be reflected by changes of monoester P. Bicarb-Po and NaOH-Po can be determined using conversion coefficients of 1.54 and 1.20, respectively, from monoester P.

5.2. Introduction

From 30 to 60% of the total phosphorus (P) in temperate agricultural soils occurs in organic forms (Zhang and MacKenzie, 1997; Chapter 4). Mineralization rates determine organic P (Po) availability to plants. Calculated inorganic P (Pi) released through mineralization of soil Po can reach up to 60% of total crop P removal in an unfertilized soil in eastern Canada (Chapter 4) or one-third of the average removal in crops in some English soils (Chater and Mattingly, 1979). However, components of soil organic P are substantially unknown (Dalal, 1977).

Soil organic P accumulated with additions of animal manure and increased inorganic fertilizer P (Oniani et al. 1973; Chapter 3). Phosphorous fertilization at a rate of 35 kg P ha^{-1} of inorganic P for 121 years increased orthophosphate monoester and polyphosphate in a Batcombe soil under continuous hay (Hawkes et al., 1984). Oniani et al. (1973) found that farmyard manure, alone or with superphosphate, had converted to organic P in 100 years in a neutral arable soil at Rothamsted. In contrast, continuous cropping without fertilizer addition resulted in the depletion of soil Po (Hedley et al. 1982b). As a result, dynamics of soil organic P are a function of management practices.

^{31}P NMR provides a direct method for characterizing P forms in soil. Newman and Tate (1980) first employed ^{31}P NMR to distinguish P compounds in five New Zealand soils. Inorganic orthophosphate and orthophosphate monoesters were the major forms of soil P. The results showed great diversity of P forms, and included compounds with NMR signals ascribed to phosphonates, a previously unreported form of soil phosphorus. In a climosequence of soils under natural grassland, the authors (Newman and Tate, 1980; Tate

and Newman, 1982) identified inorganic orthophosphate, orthophosphate monoesters and orthophosphate diester in all but desert soils, where no orthophosphate diesters were found. In some soils phosphonates and polyphosphates were also detected. Similar results were reported in a Brown Chernozem and a Gleysol soil in western Canada (Condron et al, 1990), and highly weathered soils in Western Australia (Adams and Byrne, 1989). Present procedure for characterization of soil organic P using ^{31}P NMR is mainly through extraction of NaOH solutions (Newman and Tate, 1980; Tate and Newman, 1982; Adams 1990; Hawkes et al. 1984; Condron et al. 1990).

The objectives of this study were 1) to examine the chemical nature of soil organic P isolated sequentially by $NaHCO_3$ and NaOH solutions, and 2) to evaluate the effect of P fertilization on P forms under long-term continuous corn in two temperate soils with contrasting textures.

5.3. Material and Methods

5.3.1. Study sites and soil sampling

Soil characteristics, experimental design, and management practices are outlined in Chapter 2.

Surface soils (0-20 cm) were sampled at five randomly selected locations in each plot initially and after 12 years on the Chicot site and 8 years on the Ste. Rosalie site. Soil samples were air-dried and crushed to pass a <2 mm sieve after removal of visible crop residues. Sub-soil samples were further ground to pass <150 μm sieve. Sub-subsamples from four replicates of each site were bulked to form a single representative sample for each treatment.

5.3.2. Soil extraction and sample preparation for analysis of ^{31}P nuclear magnetic resonance (NMR)

Both soil samples from each replicate and a representative sample for each treatment were subjected to extraction and related analysis. Soil samples were extracted with a 1:60 ratio of soil:extractant sequentially with 0.5 M NaHCO$_3$ (pH 8.5) and 0.1 M NaOH. Extraction was carried out by shaking soil with extractant for 16 hours. The suspensions were centrifuged at 16,300 g for 20 minutes at 0°C and vacuum-filtered through 0.45 μm Millipore membrane filters (mixed cellulose ester). Following filtration, the soil samples were washed with distilled deionized water and re-centrifuged to remove residual P extracted by NaHCO$_3$. A total of 480 mL or 720 mL supernatant was prepared for each sample, depending on the P concentration previously determined. The NaHCO$_3$-P fraction (Bicarb-P) was resin treated to remove possible paramagnetic and excess salts. The supernatant was concentrated by lyophilization to 3-5 mL to obtain a suitable P concentration for ^{31}P NMR detection.

5.3.3. Chemical analysis of concentrated soil extracts

Inorganic- and total-P in concentrated extracts was determined on diluted aliquot. Inorganic P was determined after removal of organic matter through acidification and centrifugation. The total P concentration was determined as the inorganic orthophosphate concentration after digestion with acidified ammonium persulphate ((NH$_4$)$_2$S$_2$O$_8$) oxidation. Inorganic orthophosphate present in extracts and digests was routinely assayed by the method of Murphy and Riley (1962). Organic P was calculated by the difference between total P and inorganic P.

5.3.4. Determination of phosphorus by ^{31}P NMR

The concentrated soil extract of 0.5 mL was transferred to NMR tubes of 5 mm diameter. Proton-decoupled ^{31}P-NMR spectra were recorded at 20°C on a VARIAN XL-300 super-conducting NMR spectrometer operating at 121.421 MHZ for ^{31}P. An acquisition time of 1.306 s (spectral width 12,554.9 HZ) and 32 K data point was used with a pulse angle of 30°. A single pulse sequence was conducted (30°C pulse). Chemical shift (δ) in ppm was measured relative to external H_3PO_4 (85%). The assignment of peaks in the ^{31}P NMR spectra was made by addition of known standards to concentrated soil extracts and on the basis of literature references (Newman and Tate, 1980; Tate and Newman, 1982; Adams and Byrne, 1989). Slight variation in chemical shift was expected from sample to sample due to variations in final volume of sample and extraction procedures resulting in differences in pH. Data were acquired using 5-10 HZ line broadening. Data acquisition runs of 3,500-16,000 scans were obtained. The intensity of the signal was determined by integration.

5.4. Results and Discussion

Levels of total Po obtained with ^{31}P NMR were similar to those determined from chemical procedure (Table 5.1). Differences of extracted total Po between the two methods varied from 0.2 to 4.0% with an average of 1.8% for Bicarb-Po and from 1.0 to 5.2% with an average of 2.5% for NaOH extractable Po (NaOH-Po). This is consistent with Adam and Byrne (1989) and Gil-Sotres et al. (1990) who reported little disagreement between the two methods. It was also found that all spectra were virtually identical after the soil extract was

kept in the spectrometer for 28 hrs with the temperature of the sample reaching about 45°C (Hawkes et al. 1984). Thus ^{31}P NMR analysis quantitatively detected Po in soil extracts.

Orthophosphate inorganic P (Pi), monoester phosphates, diester phosphates, polyphosphates, pyrophosphates, phosphonates and small amounts of unknown phosphates were present in soil extracts from both Chicot and Ste. Rosalie sites (Tables 5.2 and 5.3). The Ste. Rosalie soil had lower P contents than the Chicot soil.

In the Chicot soil, Bicarb-Pi orthophosphate increased by 16 mg kg^{-1} soil and NaOH-Pi orthophosphate decreased by 20 mg kg^{-1} in the 44 kg ha^{-1} rate plots over 14 years. As a result, total extractable Pi orthophosphate decreased by 4 mg kg^{-1}. This result can be explained by the similarity in amounts of crop P removal and added P. In contrast, Bicarb-Pi orthophosphate increased by 220 mg kg^{-1} and NaOH-Pi orthophosphate by 107 mg kg^{-1} in the 132 kg ha^{-1} rate plots. In the Ste. Rosalie soil, Bicarb- and NaOH-Pi orthophosphate increased respectively by 45 and 5 mg kg^{-1} in the 44 kg ha^{-1} plots and 139 and 49 mg kg^{-1} in the 132 kg ha^{-1} rate plots over time. Thus, orthophosphate Pi increased with increased fertilizer P rate in both soils. This result confirms that the orthophosphate Pi in these extracts was the major sink of residual added P (Chapters 3 and 4). However, neither Bicarb- nor NaOH-Pi orthophosphate was changed in the zero-P plots in the Ste. Rosalie soil.

The dominant Po form was monoester phosphates found in both Bicarb- and NaOH-extracts (Tables 5.2 and 5.3). More monoester P was found in the NaOH-Po (70-85%) compared with the Bicarb-Po (40-81%) in both soils. Trends of monoester P with time or P rate were not marked. An exception was the NaOH-Po fraction in the Chicot soil in which monoester Po increased with time and P fertilizer rate. In the Ste. Rosalie soil, monoester P

in NaOH-extracts was slightly reduced with time, although added P tended to nullify this reduction. Monoester P tended to be more stable in NaOH-extracts which are assumed to be in association with oxides of iron and aluminum (Ryden et al., 1977) than in Bicarb-extracts which are presumably more labile sorbed P.

Diester Po ranged from 0 to 15% of Po and varied among soils, treatments and P fractions. There was slightly more diester P in the NaOH-extracts than the Bicarb-extracts in both soils. The effect of cropping varied between soils with the Bicarb-extractable diester P increasing with time in the Ste. Rosalie soil and decreasing in the Chicot soil. Diester P in the NaOH-extract varied between soils as values increased from 0 to 6.7 mg kg^{-1} with cropping in the Chicot soil and decreased with time but was unaffected by fertilizer P in the Ste. Rosalie soil. For the most part, diester P was persistent in soils, except for the Bicarb fraction in the Chicot soil.

Polyphosphates and pyrophosphates were largely restricted to NaOH-extracts with small amounts in both soils and amounts tended to increase with cropping. An exception was in the Chicot soil where polyphosphates in Bicarb-extracts were present in the initial samples. These P components are generally considered to be microbial in origin and may indicate microbial activities in cultivated soils.

Phosphonates at 1 mg kg^{-1} were only found in the NaOH extracts of the initial soil samples from Ste. Rosalie site, indicating that their presence was negligible.

Unknown P forms were relatively high in both soils and both fractions. There was some evidence of increased amounts with increased fertilizer use and cropping. The importance and composition of these P compounds remains to be determined.

The use of ^{31}P NMR is particularly useful for the detection of monoester P forms. Monoester P was a relatively constant proportion of each soil Po fraction (Fig. 5.1), regardless of soil, treatment or cropping. Proportions were 65% for the Bicarb-Po and 83% for the NaOH-Po fraction (Fig. 5.2). Thus, one unit increase or decrease of monoester P was the equivalent increase or decrease of 1.54 units of Bicarb-Po and 1.20 units of NaOH-Po. Accumulation of Po was therefore largely related to accumulation of monoester Po. In this regard the use of ^{31}P NMR could be simplified by restriction to the detection of monoester P in comparison studies of soil Po fractions.

Table 5.1. Proportion of organic P in soil P fractions determined by chemical methods and ^{31}P NMR.

Sampling time	Fert. P rate	NaHCO$_3$-P		NaOH-P	
		Chemical	^{31}P NMR	Chemical	^{31}P NMR
	kg P ha^{-1}	----------------------------- % -----------------------------			
Chicot site					
Initial		37.0	36.8	31.0	30.0
After 12 years	44	20.3	22.0	40.9	44.0
	132	23.4	20.0	35.5	38.6
Ste. Rosalie site					
Initial		29.0	29.3	59.0	56.7
After 8 years	0	35.3	31.3	58.0	52.8
	44	23.0	24.8	49.6	50.6
	132	15.1	14.5	40.4	42.4

Table 5.2. Concentrations of P in NaHCO₃- and NaOH-extractable compounds based on amounts of P present in final concentrated extracts and proportional distribution shown by ^{31}P NMR in a Chicot sandy clay loam soil.

| Component | NaHCO$_3$-P | | | NaOH-P | | |
| | Initial | After 12 years | | Initial | After 12 years | |
		44†	132†		44†	132†
	---------------------- mg P kg^{-1} soil ----------------------					
Orthophosphate monoesters	45.9	27.5	59.1	79.0	107	154
Orthophosphate diesters	4.0	0	0	0	2.00	6.70
Polyphosphates	0	0	0	0	2.00	0
Pyrophosphate	0	0	0	0	2.70	2.10
Phosphonates	0	0	0	0	0	0
Unknown	7.00	7.90	21.9	13.5	39.5	38.1
Inorganic orthophosphate	97.7	114	324	207	187	314

† Fertilizer P rates were 44 and 132 kg ha^{-1}, respectively.

Table 5.3. Concentrations of P in $NaHCO_3$- and NaOH-extractable compounds based on amounts of P present in final concentrated extracts and proportional distribution shown by ^{31}P NMR in a Ste. Rosalie clay soil.

Component	NaHCO₃-P				NaOH-P			
		After 8 years				After 8 years		
	Initial	0†	44†	132†	Initial	0†	44†	132†
	------------------------- mg P kg⁻¹ soil ------------------------							
Orthophosphate monoesters	15.2	10.5	23.7	19.9	76.7	56.4	64.2	67.9
Orthophosphate diesters	0	3.90	4.50	3.50	6.80	3.20	6.00	7.10
Polyphosphates	1.7	0	0	0	0	0	0	0
Pyrophosphate	0	0	0	0	0	3.60	5.50	4.00
Phosphonates	0	0	0	0	1.00	0	0	0
Unknown	10.7	11.9	6.80	11.2	6.50	7.80	9.50	12.7
Inorganic orthophosphate	61.0	57.8	106	200	67.8	63.4	72.8	117

† Fertilizer P rates were 0, 44, and 132 kg ha⁻¹, respectively.

Fig. 5.1. ^{31}P NMR spectra of concentrated NaOH extracts of soils taken initially and after 8 years of continuous corn on the Ste. Rosalie site. **a**: initial; **b**: 0 kg P ha^{-1} after 8 years; **c**: 44 kg P ha^{-1} after 8 years; **d**: 132 kg P ha^{-1} after 8 years.

c

d

a

Phosphonates

b

Inorganic orthophosphate

Orthophosphate monoesters

Orthophosphate diesters
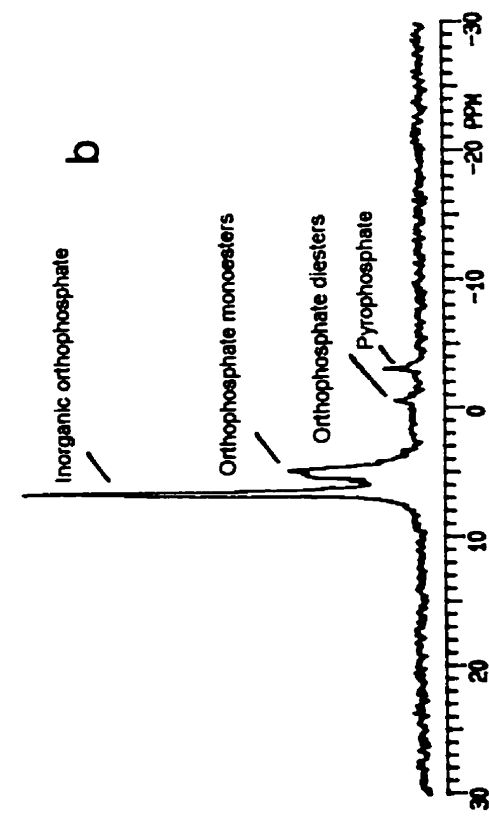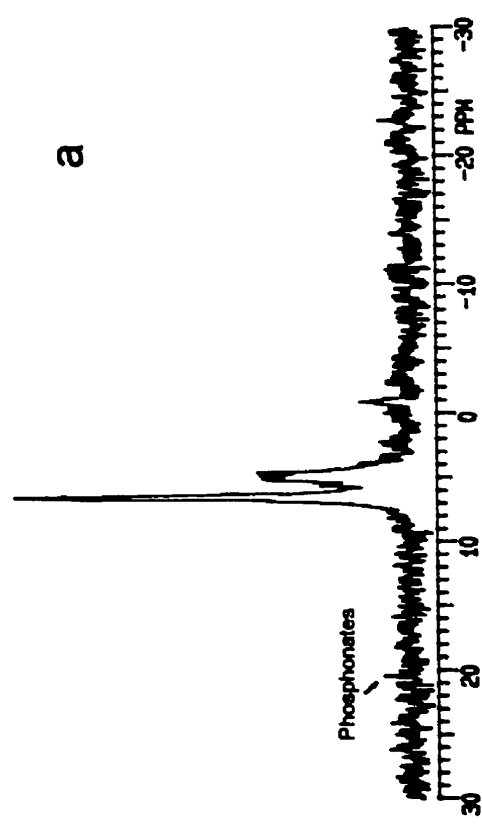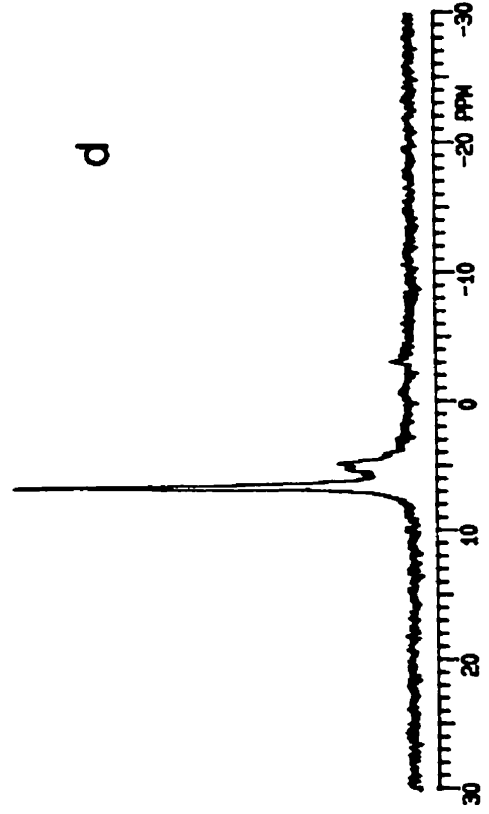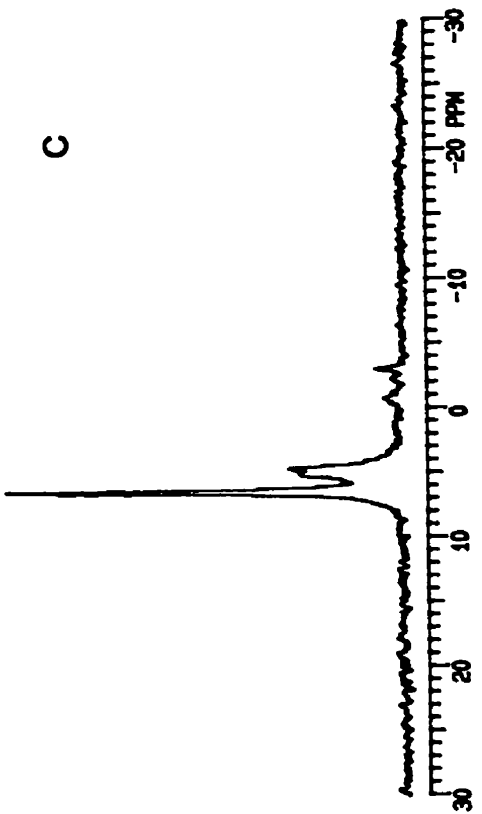
Pyrophosphate

Fig. 5.2. Relationships between monoester phosphates and soil Po fractions in two soils, a Chicot sandy clay loam and Ste. Rosalie clay, under long-term continuous corn. **, and *** indicate that the equation is significant at $P<0.005$ and 0.001 levels, respectively.

Hollowed symbols: Chicot
Filled symbols: Ste. Rosalie

NaOH–Po (HOP):
MOP = −1.75 + 0.834HOP; R^2=0.99[***]

Bicarb–Po (BOP):
MOP = 0.684 + 0.654BOP; R^2=0.89[**]
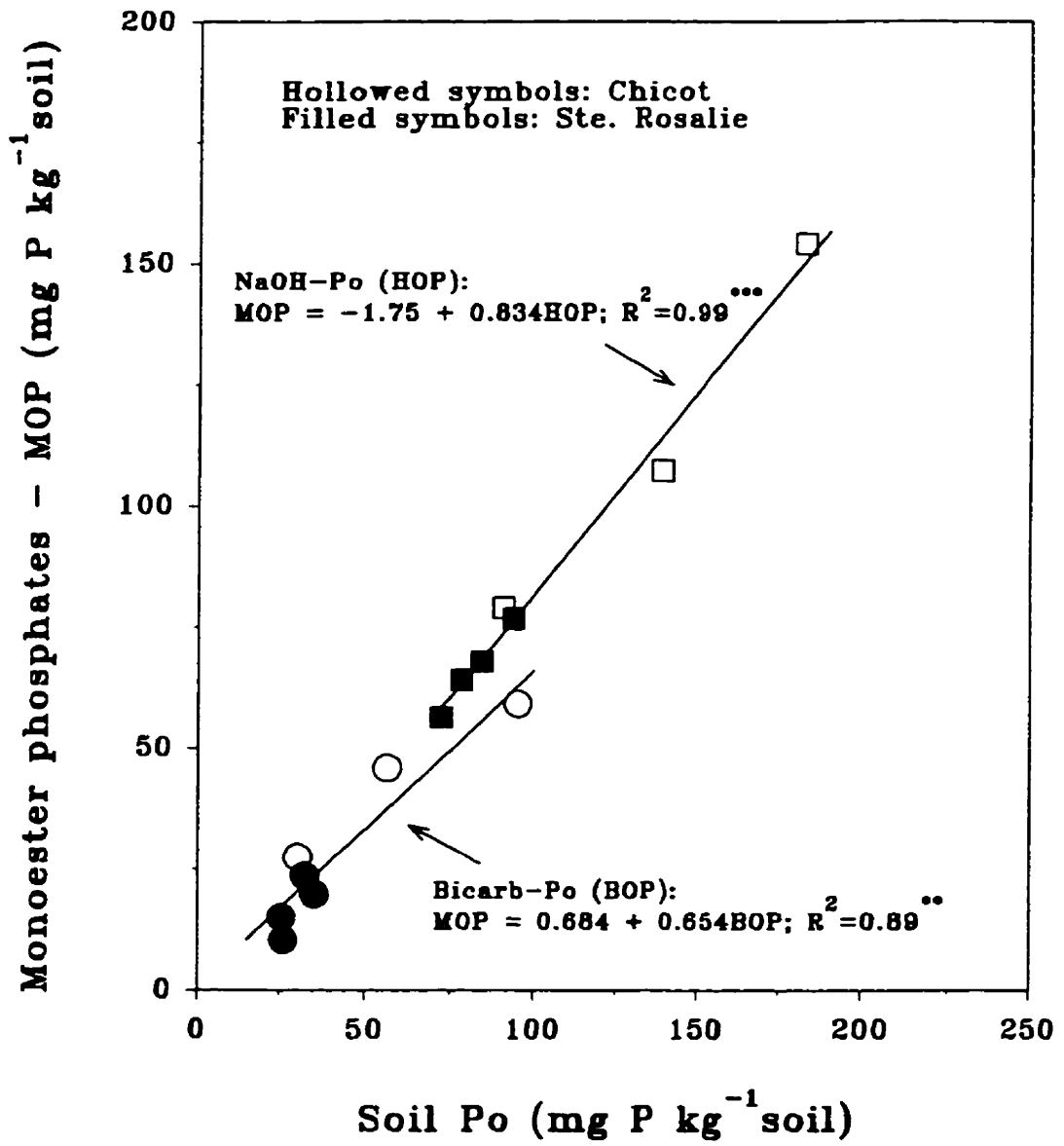
CONNECTING PARAGRAPH

In previous chapters, addition of fertilizer P exceeding crop P removal accumulated as inorganic P and/or organic P in soil. Increases of soil inorganic and organic P were a function of fertilizer P rate and soil properties. Labile and moderately labile inorganic P acted as the sinks of residual fertilizer P. Increased inorganic P will increase saturation of soil P adsorption and consequently the potential for desorption and leaching loss. Organic P has been shown to be leached. Thus, increased inorganic and organic P can be subject to soil P losses. Chapter 6 addresses the study of P fractions in soil gravitational water as a function of soil type and accumulated P.

CHAPTER 6

PHOSPHORUS IN ZERO TENSION SOIL SOLUTION AS INFLUENCED

BY LONG-TERM FERTILIZATION OF CORN (*Zea mays.* L)

6.1. Abstract

Phosphorus from fertilized agricultural land may contribute to ground or surface water P and accelerate eutrophication. With increases in soil P saturation and organic P in long-term P fertilized soils, soil P leaching losses may increase. The effect of long-term P fertilization (6 to 11 years) on inorganic and organic P in soil solutions at zero tension was studied on two soils, a Chicot sandy clay loam (Grey Brown Luvisol) and a Ste. Rosalie clay (Humic Gleysol). Soil solution samples were collected using a cylinder technique and analyzed for total dissolved P (TDP), dissolved inorganic P (DIP), and dissolved organic P (DOP). Levels for DIP ranged from 0.15 to 1.01 mg P L^{-1} and TDP from 0.33 to 1.19 mg P L^{-1} in the Chicot soil. In the Ste. Rosalie soil, values of DIP ranged from 0.06 to 0.23 mg P L^{-1} and TDP from 0.15 to 0.36 mg P L^{-1}. Increasing fertilizer P applications from 44 kg ha^{-1} to 132 kg ha^{-1} increased DIP and TDP in soil solutions in both soils. Soil solution DIP was found to be linearly related to soil inorganic P extractable with 0.5 M $NaHCO_3$. There was no effect of P fertilization rate on DOP values. Thus, increased P leaching with increased P rates was only due to DIP. A threshold value of soil $NaHCO_3$ inorganic P of 108 mg kg^{-1} for the Chicot soil and 69 mg kg^{-1} for the Ste. Rosalie soil caused DIP levels above the critical value of 0.05 mg L^{-1}. Soil P movement below 45 cm during the non-growing season was estimated at 633 to 2732 g ha^{-1} yr^{-1} in the Chicot soil and from 312 to 974 g ha^{-1} yr^{-1} in the Ste. Rosalie soil. Soil P under intensive corn production should be monitored with regards to P accumulation and resulting increases in leaching losses.

6.2. Introduction

Eutrophication restricts the use of surface waters and thus has economic impact. Phosphorus is a key nutrient governing eutrophication of fresh water bodies (Schindler, 1974). Non-point sources of P from agricultural land may contribute a significant portion of P inputs to many freshwater bodies (Sharpley et al., 1994). One pathway for P from agricultural land to ground water is through leaching, which may be a function of soil properties, P fertilization rates, and environmental conditions (Weaver et al., 1988). The few reports on soil P leaching losses have been mainly related to organic soils or organic soil amendments.

Coale et al. (1994) found that concentrations of total dissolved P ranged from 0.05 to 1.4 mg P L^{-1} in a Lauderhill muck soil in southern Florida. Inman et al. (1982) reported PO$_4$-P concentrations of water samples in compost-treated Chester silt loam soil below 0.08 mg L^{-1}. Drainage water from organic soils in New York varied from 0.7 to 5.4 mg P L^{-1}, with 0.6 to 30.7 kg ha^{-1} annual P leaching losses (Duxbury and Peverly; 1978). In mineral soils, organic phosphates can enhance subsurface soil P loss due to their lower affinity for adsorption on soil components (Schoenan and Bettany, 1987). Most P moving in the leachate was in organic forms in two Ohio soils (Reddy et al., 1978).

Soil P loss through leaching is generally considered low in mineral soils due to P fixation (Sadler and Stewart, 1975). However, increased saturation of soil binding sites with phosphate ions may reduce fixation and increase potential P leaching losses. In recent years, the number of soils with soil test P exceeding levels required for optimum crop yields has increased in areas of intensive agricultural and livestock production (Sims, 1992; Tabi et al., 1990). If continuous intensive grain corn production increases soluble soil organic P levels,

this could increase P losses in leaching water.

The objectives were to examine the level of soluble inorganic and organic P in leaching water as a function of long-term P fertilization under continuous corn and to estimate potential P leaching movement in two eastern Canadian soils.

6.3. Materials and Methods

6.3.1. Study Sites, experimental design, and management practices

Description of study sites, soil characteristics, experimental design, and management practices are found in Chapter 2.

6.3.2. Collection of Soil and Soil Solution Samples

Based on the balance of precipitation and potential evapotranspiration, there is a water deficit from May to September and an increase in soil water storage in October in the study area. It is impossible to sample soil water at zero tension during this period. As a result, soil water sampling was carried out in the non-growing season.

Sampling cylinders (6.0 cm i.d. by 90 cm long) with one closed end and three holes (0.3 cm d.) in the wall 10 cm from the closed end were installed in four replicates of the selected treatment plots after harvests of 1993 and 1994. Cylinders were pushed into the soil to 55 cm below the soil surface after removing soil with hydraulically inserted sampling tubes of the same diameter. After the cylinder was installed, close contact of soil with the cylinder was assured by carefully tamping soil around the top of the cylinder. The open end of the cylinder was covered with a glass jar to prevent precipitation entry and evaporation. Thus

water at zero tension could enter but not leave the cylinder.

Samples were collected when available from the time the cylinder was installed until gravitational water was no longer present the next spring. Soil water at zero tension during the non-growing season was mainly dependent on snow melt (Table 6.1). Soil water was collected with a rubber hose connected to a 60 mL syringe. Both rubber hose and syringe were washed with distilled water after each sample and rinsed with the next sample to minimize contamination. At each sampling, approximately 70 mL soil solution was collected from each cylinder and the remaining water inside the cylinder was removed.

Composite soil samples consisting of five cores in each plot were randomly collected from a depth of 0-0.20 m in the spring of 1993 and 1994. Soil was air dried and ground to <100 mesh size after removing visible root and crop residues.

6.3.3. Phosphate Determinations

Aliquots of water samples were vacuum-filtered through 0.45 μm Millipore membrane filters (mixed cellulose ester) within 2.0 hours of collection. The filtered samples were stored at 2°C and analyzed for dissolved inorganic P (DIP) within 24 hours of collection. Samples were frozen when laboratory analyses could not be performed as noted. A portion of the sample was digested by acidified ammonium persulphate (($NH_4)_2S_2O_8$) oxidation in an autoclave (USEPA, 1983) and analyzed for total dissolved P (TDP). TDP and DIP analysis were conducted using a QuikChem AE Automated Ion Analyzer (Lachat Instruments, Milwaukee, WI) and ascorbic acid reduction (USEPA, 1983). Using this method, Si interference was considered to be insignificant as a Si concentration of approximately 14 mg

Si L^{-1} would be required to produce a 0.005 mg P L^{-1} positive error in orthophosphate (Lachat Instruments, Milwaukee, WI). Interference of Fe^{+3} was also insignificant, because concentrations of Fe^{+3} for all samples were lower than 0.5 mg L^{-1}. Glassware was washed with 1:1 HCl and rinsed sequentially with distilled and deionized distilled water. Dissolved organic P (DOP) was calculated from the difference between TDP and DIP.

6.3.4. Soil analysis

Soil samples were extracted with 0.5 M $NaHCO_3$ (pH 8.5) solution by shaking for 16 hours (Hedley et al., 1982b). Suspensions were vacuum-filtered through 0.45 μm Millipore membrane filters. Extracts were acidified to precipitate extracted organic matter and the supernatant was analyzed for inorganic P using the procedure of Murphy and Riley (1962).

6.3.5. Phosphorous leaching estimates

Mean concentrations of DIP, DOP, and TDP were calculated across annual sampling periods by averaging the concentrations for each individual replicate to obtain a value for P leaching. Soil P movement was estimated from mean P concentrations and estimated drainage fluxes from an adjacent site of 236 mm in 1993/94 and 215 mm in 1994/95 over the non-growing season (P. Enright, 1996, personal communication).

Precipitation and air temperature data (Fig. 6.1) were collected from the weather station located within 0.5 km of the experimental sites. Precipitation was similar between the two years but temperatures were colder in 1993/94 compared with 1994/95.

Statistical analysis were conducted using the SAS program (SAS Inst., 1989).

Analysis of variance using repeated measures was performed using PROC GLM to test effects of fertilizer P rate and sampling date on soil solution P fractions, and PROC GLM was used to test effects of P fertilizer rates on soil P movement.

6.4. Results

6.4.1. Soil solution P concentration

The effect of fertilizer P rate on DIP at both sites and both years was significant (Table. 6.2). Sampling date influenced concentrations of DIP in the Chicot soil during 1994/95 and in the Ste. Rosalie site in both years. Concentrations of DOP were not affected by fertilizer P rate except in the Ste. Rosalie site during 1993/94 where values changed significantly with sampling date. An interaction between fertilizer P rate and sampling date was noted only with DIP in the Chicot site during 1994/95.

6.4.1.1. Chicot site

Soil solution DIP increased with increasing fertilizer P rate, but varied with sampling date (Fig. 6.2). DIP levels in plots receiving 132 kg P ha^{-1} yr^{-1} ranged widely over the observation period, but average DIP values across all sampling dates were relatively constant between years at 0.94 and 1.08 mg P L^{-1} in 1994 and 1995, respectively. With fertilizer rates of 44 kg P ha^{-1} yr^{-1} DIP concentrations also ranged widely within any one year but mean values for each year were similar at 0.16 mg P L^{-1} and 0.14 mg P L^{-1}.

DOP concentrations were generally lower than DIP values, with an average of 0.14 mg P L^{-1} in 1994 and 0.22 mg P L^{-1} in 1995 (Fig. 6.3). The value of DOP on April 18 was the

highest at 0.5 mg P L^{-1}.

TDP concentrations, followed a similar pattern to DIP. The TDP concentrations averaged 0.27 and 1.10 mg P L^{-1} in 1994 and 0.39 and 1.27 mg P L^{-1} in 1995 for plots receiving 44 and 132 kg ha^{-1} yr^{-1} fertilizer P, respectively.

6.4.1.2. St. Rosalie site

In the spring of 1994, concentrations of DIP in soil water were similar in the plots receiving 0 and 44 kg P ha^{-1} yr^{-1} P rates, but higher at the 132 kg P ha^{-1} rate (Fig. 6.4). The DIP concentration averaged 0.05 mg P L^{-1} for the 0 and 44 kg P ha^{-1} yr^{-1} P rates, and 0.15 for the 132 kg P ha^{-1} yr^{-1} rate in 1994 and 1995.

Warm weather (Fig. 6.1) resulted in percolating water from snow melt in December of 1994 and January of 1995, as well as from March 10 to March 29 of 1995 (Table 6.1). For the 0 P plots, DIP concentrations dropped sharply immediately after initial percolating water on December 8 of 1994, while the DIP concentrations decreased more gradually in the 44 kg ha^{-1} yr^{-1} P rate plots (Fig. 6.4). In both 0 and 44 kg P ha^{-1} P plots, DIP reached similar concentrations with an average of 0.03 mg P L^{-1} by March 10 and remained at that level until March 29. For the 132 kg P ha^{-1} yr^{-1} plots, DIP concentrations peaked on the 16th of January of 1995.

Levels of DOP increased throughout the sampling period in 1994, while values for DOP generally remained constant in late 1994 and 1995 (Fig. 6.5). Fertilizer rates did not have a consistent effect on DOP concentration. An average concentration of DOP over all P rates was 0.10 and 0.13 mg P L^{-1} in April and May of 1994 and late 1994 - 1995 periods,

respectively.

The TDP concentrations paralleled those of DIP.

6.4.2. Relationships between NaHCO₃ extractable Pi (NaHCO₃-Pi) and DIP

There was a significant linear relationship between DIP in soil solution and soil inorganic P extractable with NaHCO₃ at both sites (Fig. 6.6). Slopes were markedly different between the soils ($P < 0.01$), with values of 0.00724 mg P L⁻¹ per mg soil P kg⁻¹ for the Chicot site and 0.00162 mg P L⁻¹ per mg soil P kg⁻¹ for the Ste. Rosalie site. Thus, the calculated threshold values of NaHCO₃-Pi above which DIP increased above the critical value of 0.05 mg L⁻¹ were 69 and 108 mg kg⁻¹ for Ste. Rosalie and Chicot soils, respectively.

6.4.3. Soil P movement beyond the 45 cm soil layer during non-growing season

At both sites, high fertilizer P rates enhanced estimated soil P leaching as DIP. On the Chicot site, estimated DIP downward movement assuming drainage of 215 to 236 mm varied at the 44 kg ha⁻¹ P yr⁻¹ rate from 310 to 374 g P ha⁻¹, depending on the year. In contrast, estimated DIP movement in 132 kg P ha⁻¹ yr⁻¹ rate plots ranged from 2210 to 2310 g P ha⁻¹. Concentration of DOP and thereby DOP movement was not affected by rate of added P (Table 6.3).

On the Ste. Rosalie site, maximum DIP movements were 346 g P ha⁻¹ in 1993/94 (Table 6.3). In 1994/95, DIP movements increased from 118 to 679 g P ha⁻¹. In general, rates at 0 or 44 kg P ha⁻¹ yr⁻¹ were similar but at 132 kg P ha⁻¹ yr⁻¹ were much higher.

DOP movements were not affected by added fertilizer P rate, averaging 232 g P ha⁻¹

in 1993/94 and 271 g P ha^{-1} in 1994/95.

6.5. Discussion

Generally, DIP and DOP levels varied with time of sampling and soil type, but were comparable with other studies (Izuno et al. 1991; Ron Vaz et al. 1993; Heckrath et al., 1995). Dissolved inorganic P was higher at the 132 than the 44 kg P ha^{-1} yr^{-1} rate in both sites, indicating that fertilizer P at high rates was capable of moving in solution at least 45 cm down the profile. There were no differences in solution P between 0 and 44 kg P ha^{-1} treatments where 0 rates could be compared. This lack of increase could be a result of plant uptake near the 44 kg P ha^{-1} rate over the period of study (Liang et al. 1993) and thus P would not be expected to substantially accumulate in soils at these fertilizer P rates. Drainage water P was also related to P fertilization rates in clay soils of southern Ontario (Culley et al., 1983).

The linear relationships between NaHCO$_3$-Pi and DIP found in the present study implies a sorption-desorption reaction between DIP and NaHCO$_3$-Pi. Previous experiments (Chapters 3 and 4) showed that fertilizer P accumulated predominately as 0.5 M NaHCO$_3$ and 0.1 M NaOH extractable inorganic P. As these forms are considered to be relatively labile, P fixation was felt to be partly reversible. Sharpley (1981) and Sharpley et al. (1992) found that soluble P transport depended on desorption-dissolution reactions controlling P release from soil into drainage water, which is consistent with our data.

Thus the lower level of DIP in the Ste. Rosalie site relative to the Chicot site could be a result of lower level of extractable P in the Ste. Rosalie site (Table 2.1). However lower DIP levels in the Ste. Rosalie site compared with the Chicot site could also be attributed to

movement of water in fissures in the Ste. Rosalie site. As the Ste. Rosalie site is well aggregated, macro pores may result in rapid movement of percolating water and thus reduced DIP concentrations.

Dissolved organic P remained relatively constant indicating little buildup of soluble organic P with added P. Consequently long term fertilization with P would not be expected to increase DOP. The DOP is normally considered to be more mobile (Schoenan and Bettany, 1987) and more implicated in movement to ground water than DIP.

Concentrations of DIP were above the critical level of 0.05 mg P L^{-1}, and TDP above the critical value of 0.1 mg P L^{-1} (USEPA, 1976; Vollenweider and Kerekes, 1980) for eutrophication of waterways. Solution P movement below 45 cm in the soil profile could be reduced due to further P sorption on subsoil materials less saturated with P. Amounts of P estimated to be lost through leaching below 45 cm depth were low at 0.3 to 2.7 kg TDP ha^{-1}, even given the uncertainty of the leaching soil solution volume. These values must be considered as maxima assuming further P sorption reactions will occur below 45 cm. However, given the probable continuing saturation of P sorption sites below 45 cm with time, long term P fertilization should be monitored as to soluble P movement if environmental effects of P fertilization are to be evaluated.

Table 6.1. Dates for collection of soil water sample at zero tension in Chicot and Ste. Rosalie sites.

Site	Sampling date				
	1994			1995	
	April	May	December	January	March
Chicot	11 13 18^z				20 25 29
Ste. Rosalie	11 13 18 22 27	2	8	16	10 15 25 29

^{z}Soil water samples at zero tension were not available in all treatments on this date.

Table 6.2. Statistical significance of effects of fertilizer P rate and sampling date on dissolved P forms in leachate at zero tension in no-growing seasons of 1993/94 and 1994/95.

Site	Source	1993/94		1994/95	
		DIP^z	DOP^y	DIP	DOP
Chicot	Fertilizer (F)	**	NS	*	NS
	Sampling date (D)	NS	NS	**	NS
	F x D	NS	NS	*	NS
Ste. Rosalie	Fertilizer (F)	**	NS	**	NS
	Sampling date (D)	*	**	**	NS
	F x D	NS	NS	NS	NS

^{z}Dissolved inorganic P.

^{y}Dissolved organic P.

* and **: Significant at $P<0.05$ and 0.01 levels, respectively.

NS: Not significant at $P<0.05$ level.

Table 6.3. Calculated values of soil solution P movement beyond 45 cm soil depth in corn plots during the non-growing season.

Site	Annual fertilizer P rate	Soil P movement			
		DIP^z		DOP^y	
		1994	1994/95	1994	1994/95
	kg P ha^{-1}	---------------------------- g ha^{-1} ----------------------------			
Chicot	44	374	310	259	529
	132	2210	2310	395	422
	Significance	**	*	NS	NS
Ste. Rosalie	0	128	118	184	261
	44	95	235	218	267
	132	346	679	294	295
	Significance	*	**	NS	NS
	Polynomial trend comparison	E	Q		

^{z}dissolved inorganic P.

^{y}Dissolved organic P.

* and **: Significant at $P < 0.05$ and 0.01 levels, respectively.

NS; Not significant at $P < 0.05$ level.

E and Q: Exponential and quadratic responses, respectively.

Fig. 6.1. Monthly average temperature (MAT) and cumulative precipitation (CP) in the experimental area during non-growing seasons of 1993/94 and 1994/95.

Fig. 6.2. Dissolved inorganic phosphorus (DIP) in soil solution samples at zero tension in the Chicot sandy clay loam soil in 1994 and 1995. Error bars refer to standard error.
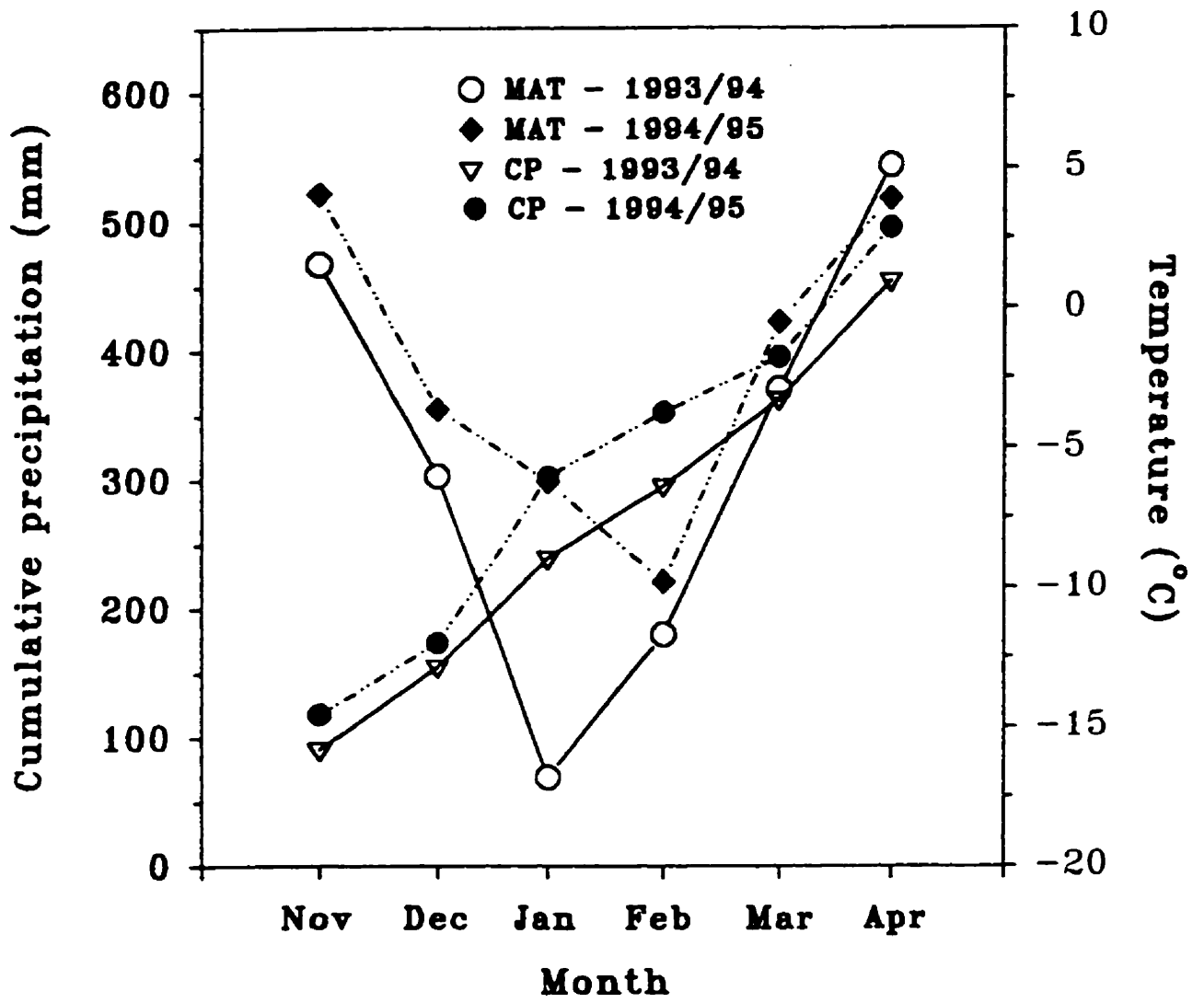
P rate (kg ha^{-1}):
○ 44
● 132

Fig. 6.3. Dissolved organic phosphorus (DOP) in soil solution samples at zero tension in the Chicot sandy clay loam soil in 1994 and 1995. Error bars refer to standard error.

Organic P (mg L^{-1})

P rate (kg ha^{-1}):
○ 44
● 132

Apr 11 Apr 13   Apr 18   Mar 20   Mar 25   Mar 29

1994   1995

Fig. 6.4. Dissolved inorganic phosphorus (DIP) in soil solution samples at zero tension in the St. Rosalie clay soil during 1994 and 1994/95 non-growing season. Error bars refer to standard error.

Inorganic P (mg L^{-1})

P rate (kg ha^{-1}):
○ 0
● 44
▽ 132

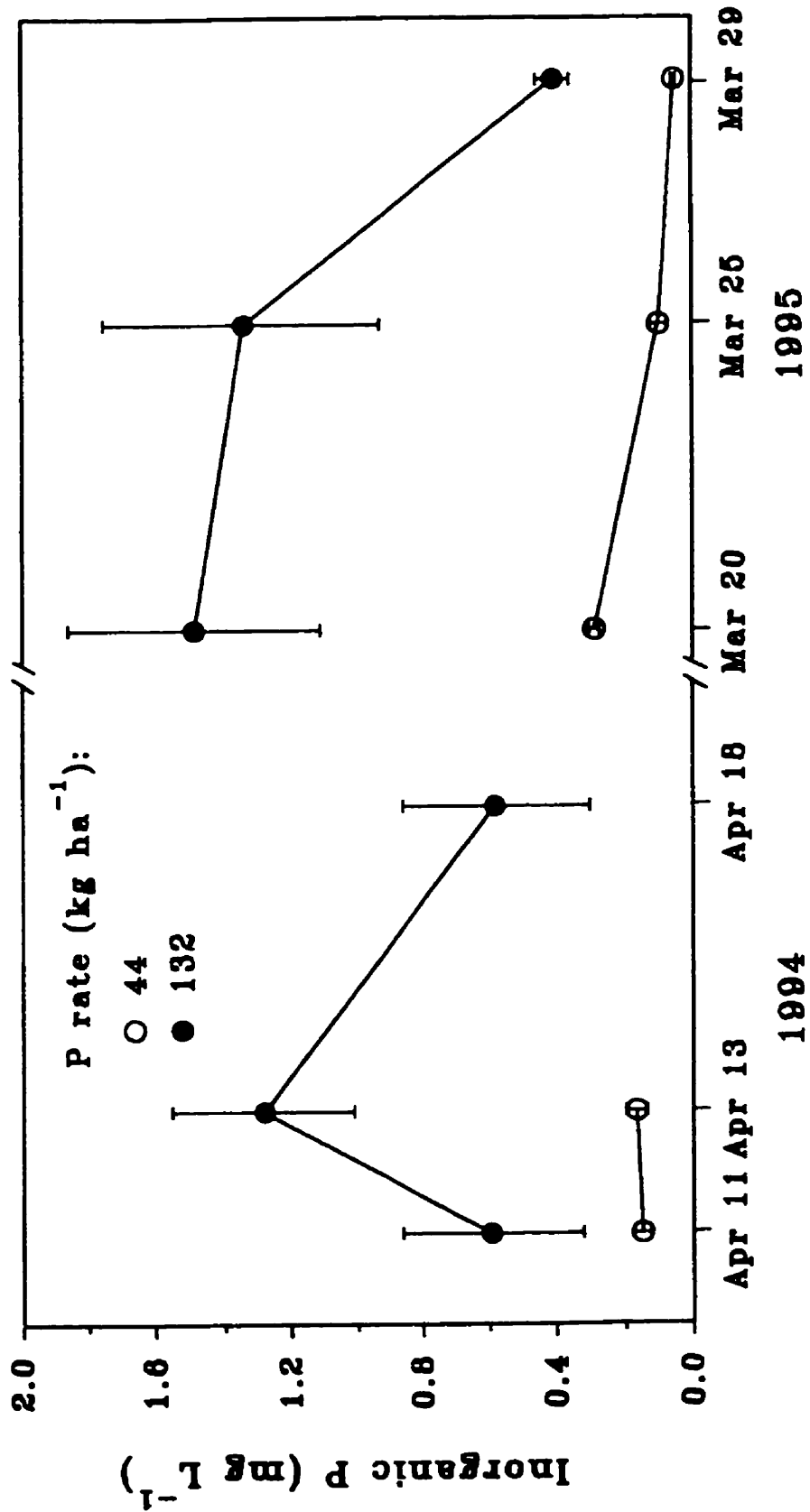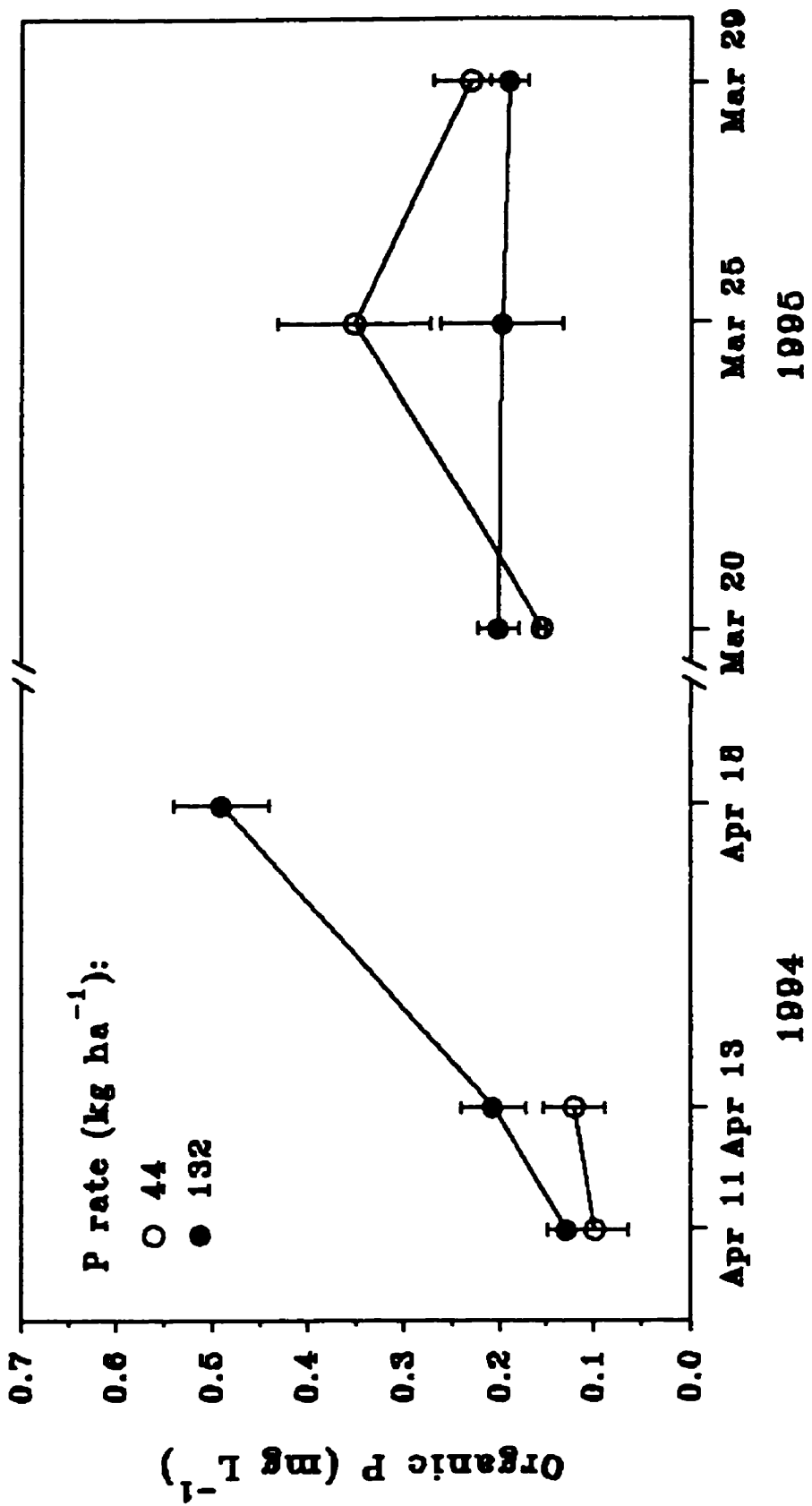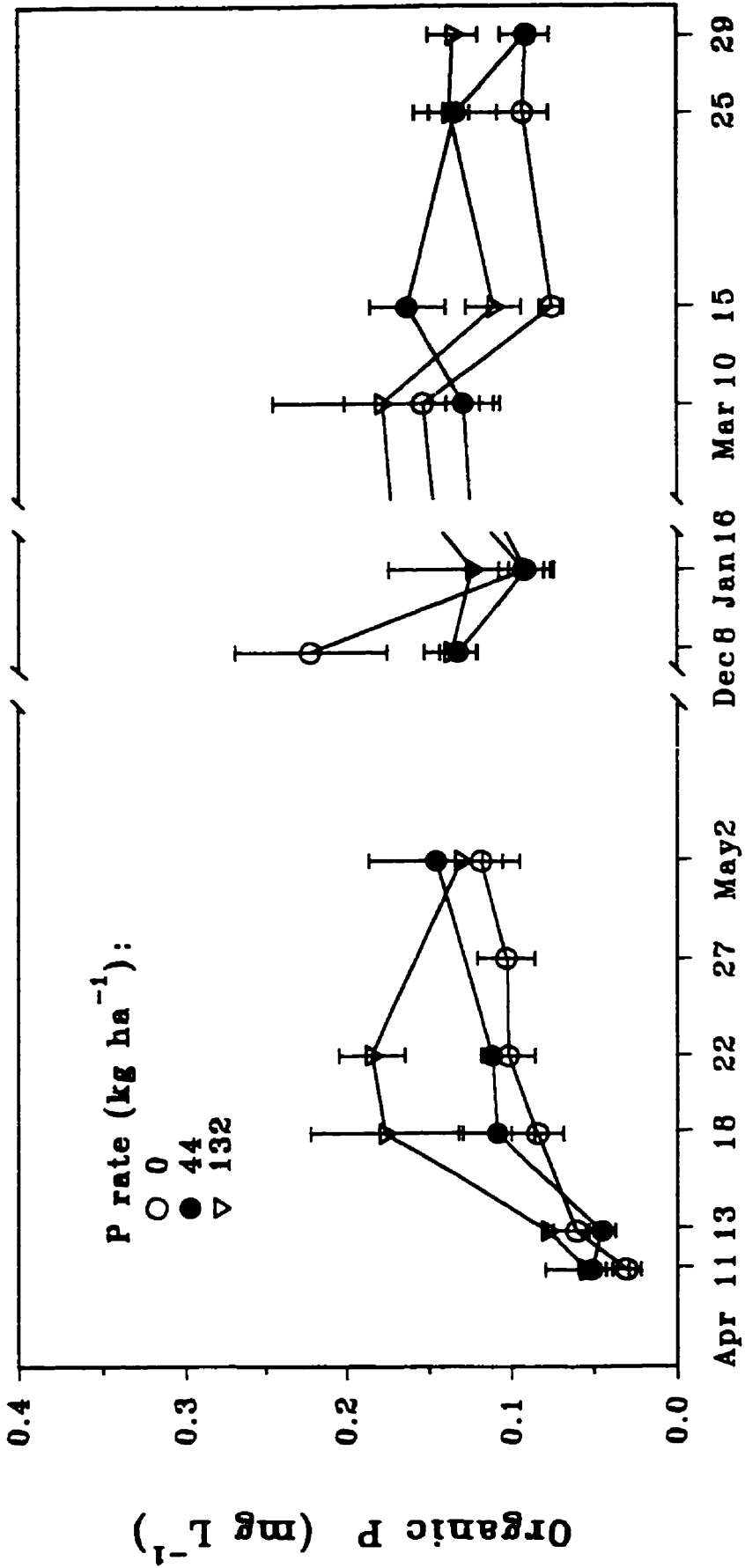Apr 11 13   18   22   27   May 2   Dec 8 Jan 16   Mar 10   15   25   28

1994/95

Fig. 6.5. Dissolved organic phosphorus (DOP) in soil solution samples at zero tension in the St. Rosalie clay soil during 1994 and 1994/95 non-growing season. Error bars refer to standard error.

Organic P (mg L⁻¹) vs. 1994/95 dates. P rate (kg ha⁻¹): ○ 0, ● 44, ▽ 132.

Fig. 6.6. Relationships between soil $NaHCO_3$ extractable inorganic P ($NaHCO_3$ - Pi) and dissolved inorganic P (annual treatment means across all sampling dates) in soil water at zero tension during two years at two sites. Treatments included fertilizer P rates of 44 and 132 kg ha^{-1} yr^{-1} in the Chicot soil and 0, 44, and 132 kg ha^{-1} yr^{-1} in the Ste. Rosalie soil.
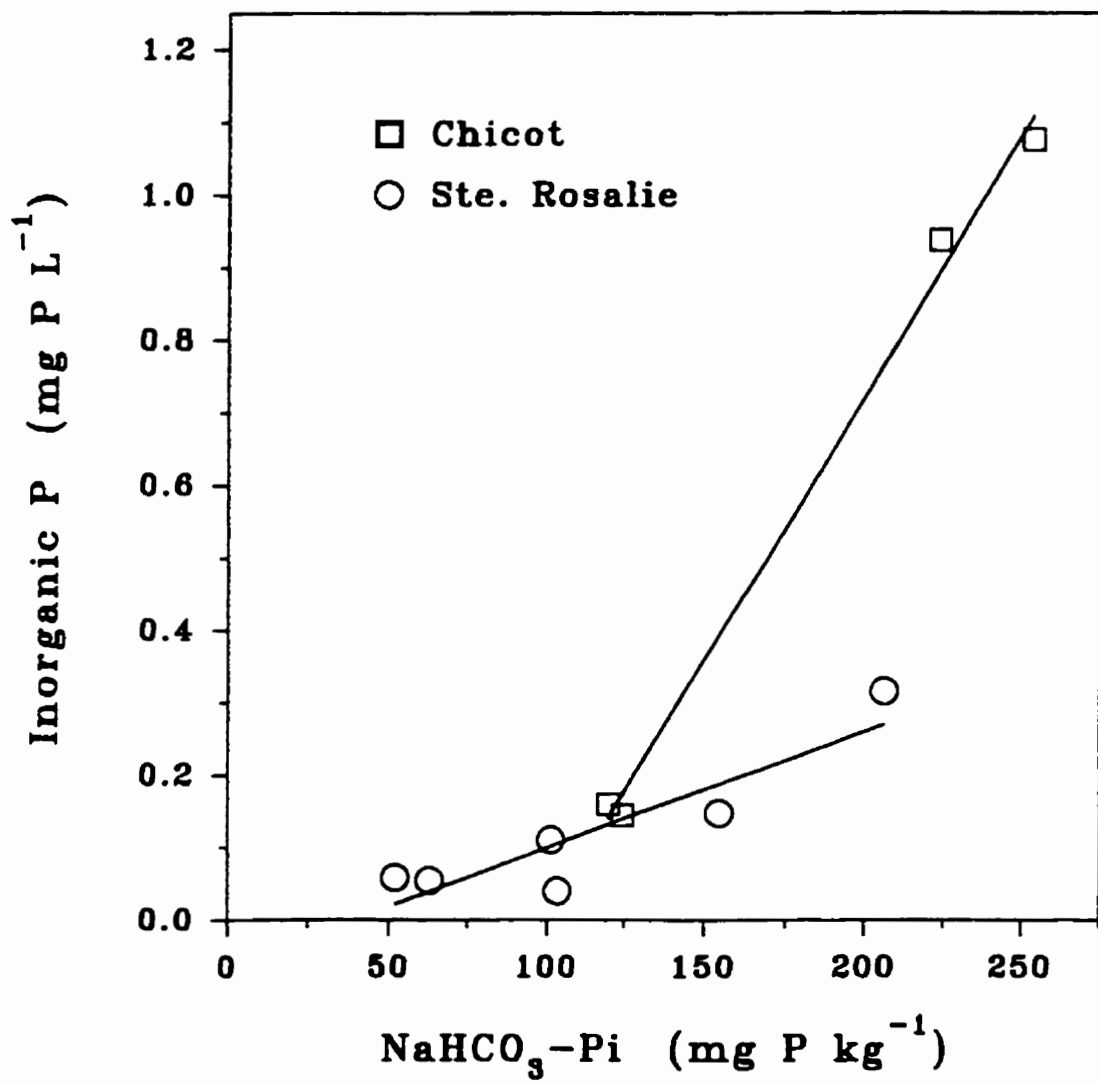
GENERAL CONCLUSIONS AND FUTURE RESEARCH

General Conclusions

Dynamics of soil P varied with soil-plant-fertilizer systems. Soil available P estimated as Mehlich-3 P remained constant under continuous corn without P addition for seven years in the clay soil. In the coarser soil, P addition at the low rates maintained soil available P, indicating equilibrium between P addition and crop P removal.

Residual fertilizer P accumulated in soil when fertilizer P addition exceeded crop P removal. Part of the residual P was available to the subsequent crops. The availability of residual P differed, and in turn, the amount of fertilizer P required to increase soil available P varied with soil type, fertilizer source and P rate.

Using net addition criteria, from 5.3 kg ha^{-1} inorganic P was needed to increase soil available P by 1 kg ha^{-1} in the coarser soil, compared to 1.8 to 2.7 kg ha^{-1} in the clay soil. Thus, fixation of residual fertilizer P was greater in the coarser soil than clay soil due to lower clay content. Clay tends to adsorb and retain P in an available form.

Manure P plus high rates of inorganic P was more efficient at increasing soil available P than low rates or added P without manure. From 2.1 to 3.2 kg ha^{-1} of net added P was required to increase soil available P by 1 kg ha^{-1}. Two mechanisms involved in the reactions of residual fertilizer P in soil can be hypothesized: 1) increased saturation of binding sites on soil components with phosphate ions and organic anions; and 2) competition of organic anions with phosphate ions for binding sites.

In both soils, however, soil Mehlich-3 P pool accounted for only from 19% to 55% of net added fertilizer P. From 45% to 81% of the residual fertilizer P was converted to forms not extractable with Mehlich-3 solution. These forms were best studied using fractionation

techniques.

The immediate effect of excess fertilizer P on soil Pi fractions was to increase labile Pi ($NaHCO_3$ extractable) and moderately labile Pi (NaOH extractable) in soil-inorganic fertilizer P systems. Added inorganic P at high rates increased Residue-P in the clay soil and NaOH-Po in the sandy clay loam soil. In spite of these differences resulting from the added P at the high rates, transformations of soil P were generally similar regardless of the P rates.

Manure addition reduced fixation of residual fertilizer P as moderately labile Pi. Compared with inorganic P alone, addition of inorganic P plus manure P decreased the content of moderately labile Pi. Also, the decrease in labile Po and increase in moderately labile Po with fertilizer P and manure resulted in increased total extractable Po. Soil Po was maintained with increased crop residue return from P addition in the clay soil. Clearly, increased soil organic C input either from organic manure or crop residue return increased (absolutely or relatively) soil Po. This effect can be the result of enhanced production of Po compounds and/or impeded degradation of soil Po.

Soil moderately labile Po was depleted substantially with time in the non-fertilized clay soil. Decreased soil Po accounted for 65% of crop P removal over the years. This was consistent with the results from path analysis which showed 72% of soil labile Pi was either directly or indirectly supplied from soil Po fractions. Thus, soil Po was a major source of crop P and may be considered as a supplemental index of soil P fertility. The regional soil available P index, Mehlich-3 P, which estimates mainly inorganic P, should be modified to include Po.

General pathways of transformations of residual fertilizer P in soil for the low inorganic P rate were remarkably similar to those for high P rate in both soils, but those with manure

P differed significantly from those without manure P in the coarser soil. Moderately labile Pi together with stable P (Residue-P) were the major sinks of residual fertilizer P for the manure-inorganic P system, whereas in the inorganic system without manure, moderately labile Pi was the sink for added P. In the clay soil, inorganic fertilizer P accumulated predominately as labile Pi, followed by moderately labile Pi. Consequently, moderately labile Pi was the common sink of added residual P for all the soil-fertilizer systems, with some differences due to fertilizer P source and soil type. Given moderately labile Pi is adsorbed P associated with Fe- and Al-oxides, P fixation was mainly through sorption and the effect was reduced with increased clay content.

Soil labile Pi, considered as plant available P, came directly from added fertilizer P in the inorganic-manure system and moderately labile Pi in the inorganic systems. Thus, initially fixed P associated with Fe- and Al-oxides was converted to available P, an indication of practical significance in both agronomy and the environment.

Soil Po fractions were intermediate in P cycling in fertilized soil-plant systems. ^{31}P NMR results indicated that monoester phosphates were the predominate components in both labile and moderately labile Po with a greater proportion in moderately labile Po than labile Po. Diester phosphates accounted for a small portion in both Po fractions. Thus, soil Po accumulated mainly as monoester phosphates, regardless of the P fractions. The hypothesis that labile Po is mainly diester phosphates was not supported (Gil-Sotres et al., 1990).

Soil Po was a reflection of monoester phosphates, although changes in both labile and moderately labile Po components varied with soil type and P rate. Variation of monoester phosphates accounted for 89% and 99% of variations of labile and moderately labile Po,

respectively, and the factors to convert monoester P to Po fractions were consistent across both soils. Analysis of monoester phosphates may be used to determine soil labile and moderately labile Po.

Increased inorganic P rates increased levels of dissolved inorganic P (DIP) in zero tension soil solution in both soils. Linear relationships were found between DIP in zero tension soil solution and soil labile Pi. However, high levels of soil Po did not increase dissolved organic P (DOP) contents of soil solution. As a result, increased fertilizer P rates coupled with crop residue return increased soil P leaching only in the case of DIP.

Estimation of soil P movement beyond 45 cm soil depth ranged from 312 to 2372 g kg^{-1} during non-growing season, depending on soil type and P rate. The values of soil P leaching are not significant in agronomic terms, but of environmental importance. The coarser soil had obviously greater P movement than the clay soil probably due to higher levels of labile Pi. However, long-term P additions at high rates increased soil P movement remarkably in both soils and raised DIP above the critical P level of 0.05 g kg^{-1}, and thus have potential for environmental damage. Any use of fertilizer P above crop removal values can cause environmental damage. Levels of labile Pi required to produce leaching water above the critical level varied with soil. Soil labile Pi above 108 mg kg^{-1} soil in coarser soils and 69 mg kg^{-1} soil in clay soils would produce DIP above the critical value of 0.05 g kg^{-1}. Management practices should be developed with agronomic and environmental consequences in mind.

Future Research

Significant findings have been made in this research. However, future studies should

consider the following.

1. There is an interaction between cropping systems, inorganic P and organic manure P as regards soil P transformation pathways. In view of manure's role as a soil amendment and nutrient source, it may be a sensitive source of water contamination. Long-term experiments should evaluate the fate of manure P associated with various soil-cropping systems.

2. Sorption of fixed soil P as NaOH-Pi is reversible. A field experiment should be performed to test the duration and the extent of draw-down of soil P fraction in relation to crop needs.

3. Organic P plays a significant role in supplying plant P uptake, especially in un-fertilized soil. Mineralization rate of soil Po *in situ* should be investigated and the supplying potential of Po determined to make more accurate fertilizer P recommendations.

4. Present methods for soil Po analysis are indirect based on the difference between two soil P analysis and this could cause large errors. Hydrolysable inorganic P may also cause errors. Monoester phosphates are the predominate components and govern the dynamics of soil Po. The ^{31}P NMR method should be developed to accurately analyses and predict cycling of soil Po.

5. Phosphate ions leached out beyond 45 cm soil depth with percolating water may be further adsorbed by deeper soil layers, and thus the impact of soil P leaching losses on water bodies can be reduced. Field experiments should be carried out to clarify and determine dynamics of phosphate ion movement with depth and eventually the

effect on drainage water.

6. Pathways of P in soil-corn systems have been refined. For prediction purposes, a dynamic model covering soil P cycling in soil-plant-water systems should be developed further.

7. Economically and environmentally designed management practices should be developed for soils with high P values in order to reduce potential leaching.

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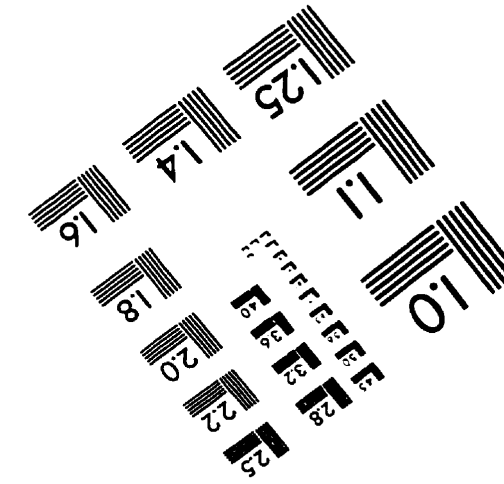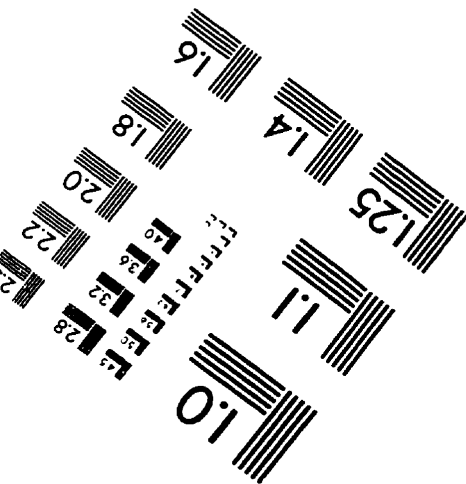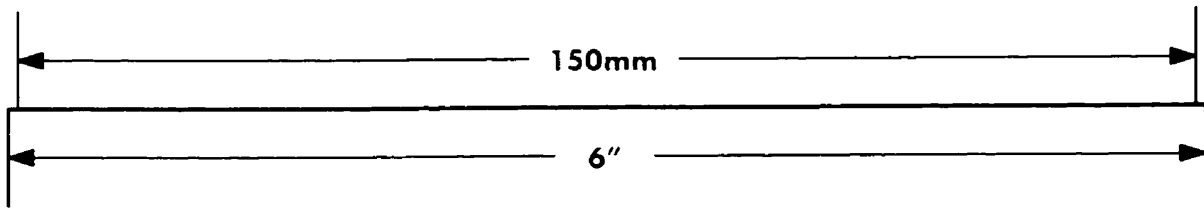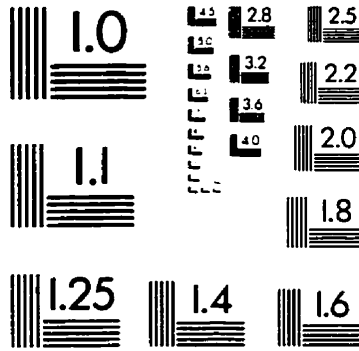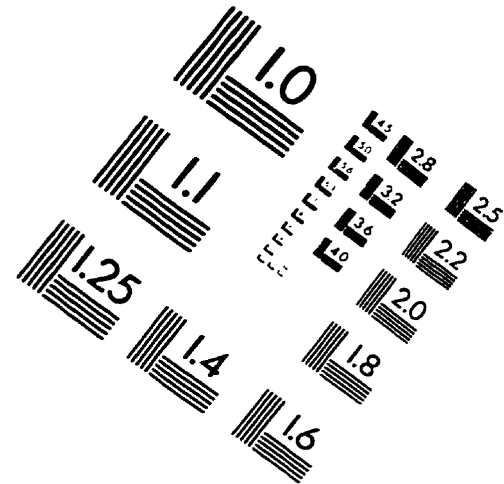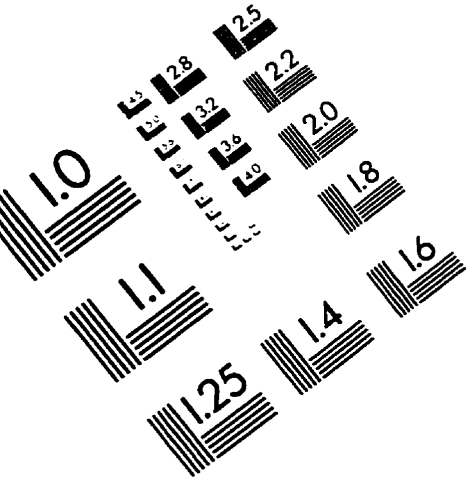
Soil Sci. 75:361-367.

APPENDIX

Hybrids used for long-term experiments on a Chicot and a Ste. Rosalie soil.

Year	Hybrid A		Hybrid B	
	Chicot	Ste. Rosalie	Chicot	Ste. Rosalie
1984	Pioneer 3925		Pioneer 3949	
1985	Pioneer 3925		Coop 2645	
1986	Dekalk-W403		Coop 2645	
1987	Dekalk-W403		Coop 2645	
1988	Dekalk-W403	Dekalk-W403	Coop 2645	Coop 2645
1989	Dekalk-W403	Dekalk-W403	Pioneer 3790	Pioneer 3790
1990	Pioneer 3789	Pioneer 3789	Pioneer 3790	Pioneer 3790
1991	Pioneer 3787	Pioneer 3787	Pioneer 3790	Pioneer 3790
1992	Funks 4120	Funks 4120	Pioneer 3790	Pioneer 3790
1993	Funks 4120	Funks 4120	Pioneer 3790	Pioneer 3790
1994	Funks 4120	Funks 4120	Funks 4120	Funks 4120
1995	Funks 4120	Funks 4120	Funks 4120	Funks 4120

IMAGE EVALUATION
TEST TARGET (QA−3)