PHOSPHOROUS DYNAMICS IN SOILS UNDER CONTRASTING LONG-TERM AGRICULTURAL MANAGEMENT PRACTICES IN THE KWAZULU-NATAL MIDLANDS

by

U.MAJAULE

Submitted in fulfilment of the academic requirements for the degree of

Master of Science

in

Soil Science
School of Environmental Sciences
Faculty of Science & Agriculture
University of KwaZulu-Natal
Pietermaritzburg

September 2006
ABSTRACT

Little is known regarding the effects of land use on soil organic matter and P status of South African soils. For that reason, the effects of the main agricultural land uses in the midlands region of KwaZulu-Natal [maize (*Zea mays*), sugarcane (*Saccharum* spp), annual ryegrass pasture (*Lolium multiflorum*), permanent kikuyu pasture (*Pennisetum clandestnum*), gum (*Eucalyptus grandis*) and pine (*Pinus patula*)] on soil organic matter content, microbial biomass C and P and inorganic and organic P pools derived from a modified Hedley P fractionation was investigated on two sites where the long-term history of land management was known.

In comparison with undisturbed native grassland, permanent kikuyu pasture resulted in an increase in organic C, organic P and microbial biomass C and P. Maize and sugarcane production resulted in a decrease in organic C, organic P and microbial C and P. Under annual pasture, gum and pine forests, organic matter and microbial biomass concentrations remained similar to those under native grassland. Under native grassland, extractable organic P accounted for 50% or more of the total P content of soils but under agricultural management with regular applications of fertilizer P, there was an increase in the percentage of total P present as inorganic P.

Agricultural management greatly affected the distribution of P among the various inorganic and organic P fractions. Resin-Pi and NaHCO₃-Pi (the potentially-available forms of Pi) showed similar trends with land use being greatly elevated under kikuyu pasture at both sites and sugarcane and maize at one site. This accumulated Pi was thought to have originated from recent fertilizer applications and possibly recently mineralized organic P. Trends for NaOH-Pi with land use differed greatly from those of the Resin- and NaHCO₃-Pi fractions. Concentrations were notably high under maize and sugarcane production. Of the pools of soil organic P, the NaHCO₃-Po fraction was most greatly affected by land use, being elevated under kikuyu and decreased under maize and sugarcane. This supports the assertion that it is the NaHCO₃-Po fraction that is the most labile soil organic P pool. It was
concluded that land use greatly affects soil organic C and P status, soil microbial biomass C and P contents, soil inorganic P concentrations and the distribution of P among the various P fractions.

A short-term (8 weeks) laboratory incubation experiment was carried out to compare the effects of inorganic (KH$_2$PO$_4$) and organic (cattle manure, poultry manure and maize crop residues) sources of P, applied at a rate equivalent to 30 kg P ha$^{-1}$, on soil inorganic and organic P fractions and the potential availability of soil P. Additional treatments consisted of lime [Ca(OH)$_2$] at 5 ton ha$^{-1}$ and lime plus inorganic P. Applications of lime raised soil pH to a similar extent after 1, 4 and 8 weeks incubation. After 8 weeks, a small increase in soil pH was also noted for the cattle and poultry manure and maize residue treatments. For the inorganic P fractions, substantial treatment effects were observed only for the Resin-P$_i$ fraction. The inorganic P source was more effective than the organic ones at increasing Resin-P$_i$ after 1 and 4 weeks incubation and of the organic sources, cattle and poultry manure were more effective than maize residues. Resin-P$_i$ concentrations generally increased between 1 and 4 weeks incubation but then declined rapidly between 4 and 8 weeks incubation. After 8 weeks incubation, treatment effects on Resin-P$_i$ were small. Concentrations of NaHCO$_3$-P$_i$, dilute HCl-P$_i$ and concentrated HCl-P$_i$ all declined over the incubation period. There was no clear trend with incubation for NaOH-P$_i$ although for the poultry manure and maize treatments, concentrations declined between 4 and 8 weeks incubation. In general, concentrations of NaHCO$_3$-P$_o$ were greater for organic than inorganic P sources after 8 weeks incubation suggesting microbial immobilization of P in these treatments. There were increases in NaHCO$_3$-P$_o$ and concentrated HCl-P$_o$ over the incubation period suggesting progressive immobilization of P from the Pi fractions that declined in concentration during the incubation. Concentrations of NaOH-P$_o$ were not greatly affected by incubation period. The lime treatments, however, had lower NaOH-P$_o$ concentrations than the others suggesting that liming may have stimulated microbial mineralization of P. Residual-P$_o$ concentrations increased over the incubation period. This was attributed to conversion of extractable Pi fractions
into recalcitrant, non-extractable Pi forms and/or immobilization of P into intransigent organic forms.
DECLARATION

I declare that this dissertation represents my own research work and has not been submitted for any degree at any academic institution.

Signed........................................
Ugele Majaule (candidate)

Signed........................................
Prof. R.J. Haynes (supervisor)
ACKNOWLEDGEMENTS

I would like to thank all that have made the completion of this work possible. In particular, I wish to express my sincere gratitude to my supervisor Professor R.J. Haynes for his patience, guidance and invaluable support.

Special thanks to the staff of the discipline of Soil Science for their encouragement during the project. Fellow graduates, Louis Titshall and Mmakgabo Matlou deserve recognition for listening and offering suggestions to some problems. Celestine Gatarayiha is recognized for all his efforts and assistance with statistical analysis.

I owe thanks to my wife, Agy and son, Thabang who supported me through this entire period. Finally, I would like to thank my parents, Phazha and Victor, for encouraging me in all my efforts and instilling in me a desire to succeed. Thanks to my brothers Chebu, Lingy and Milly, and sister Tapi for all the support.

In the loving memory of my late sister Widzani Vanessa Majaule.
TABLE OF CONTENTS

Page

ABSTRACT ............................................................................................................... i
DECLARATION ...................................................................................................... iv
ACKNOWLEDGEMENTS ....................................................................................... v
LIST OF TABLES .................................................................................................... ix
LIST OF FIGURES ................................................................................................ x

CHAPTER 1: GENERAL INTRODUCTION AND STUDY OBJECTIVES .......... 1

CHAPTER 2: PHOSPHORUS AVAILABILITY IN SOILS: A LITERATURE REVIEW ................................................................. 5

2.1 Introduction ................................................................................................... 5
   2.1.1 Soil phosphorus pools ........................................................................... 6
      2.1.1.1 Soil solution P ........................................................................... 7
      2.1.1.2 Active P .................................................................................. 8
      2.1.1.3 Fixed P .................................................................................. 8

2.2 Inorganic P (Pi) ............................................................................................. 10
   2.2.1 Adsorption reactions ........................................................................... 10
   2.2.2 Precipitation reactions ........................................................................ 12
   2.2.3 Factors regulating P adsorption .......................................................... 13
      2.2.3.1 Clay content and mineralogy .................................................... 13
      2.2.3.2 Electrolyte strength and species of cation ................................ 14
      2.2.3.3 Soil pH .................................................................................. 15
      2.2.3.4 Redox potential ..................................................................... 17
      2.2.3.5 Inorganic anions ................................................................... 17
      2.2.3.6 Organic matter content ............................................................ 18
      2.2.3.7 Time ...................................................................................... 19
      2.2.3.8 P saturation ......................................................................... 19

2.3 Organic P ...................................................................................................... 20
2.3.1 Nature of soil organic P ........................................... 20
2.3.2 Soil microbial biomass ........................................... 22
2.3.3 Soil phosphatases .................................................. 24
2.3.4 Mineralization and immobilisation of organic P ............ 25

2.4 Extraction and fractionation of soil P ................................ 28
2.4.1 Chang and Jackson method ....................................... 28
2.4.2 Hedley fractionation method ...................................... 29
   2.4.2.1 Resin – P ...................................................... 29
   2.4.2.2 Bicarbonate – P (NaHCO₃ – P) .............................. 30
   2.4.2.3 Sodium hydroxide – P (NaOH – P) .......................... 30
   2.4.2.4 Hydrochloric acid – P (HCl – P) .............................. 31
   2.4.2.5 Residual – P .................................................. 31
2.4.3 Effects of soil management on P fractions .................... 33
   2.4.3.1 Arable systems and tillage methods ....................... 33
   2.4.3.2 Pasture systems .............................................. 33
   2.4.3.3 Phosphate fertilizers ........................................ 34
   2.4.3.4 Organic amendments ...................................... 35
2.4.4 Soil test extractants for P ....................................... 35

2.5 Conclusions .................................................................. 37

CHAPTER 3: PHOSPHORUS FRACTIONS IN SOILS UNDER
CONTRASTING LONG-TERM AGRICULTURAL
MANAGEMENT PRACTICES .............................................. 39

3.1 Introduction .............................................................. 39
3.2 Materials and methods ............................................... 41
   3.2.1 Sites description and location .................................. 41
   3.2.2 Soil sampling and analyses .................................... 42
3.3 Results ....................................................................... 44
3.4 Discussion .................................................................. 57
   3.4.1 Soil organic matter content .................................... 57
   3.4.2 Soil pH .................................................................. 59
CHAPTER 4: EFFECTS OF ORGANIC AND INORGANIC SOIL AMENDMENTS ON PHOSPHORUS FRACTIONS

4.1 Introduction................................................................................. 69
4.2 Materials and methods.............................................................. 71
4.3 Results...................................................................................... 72
  4.3.1 Characteristics of organic amendments.................................. 72
  4.3.2 Soil pH (KCl)........................................................................ 73
  4.3.3 Labile P.............................................................................. 73
  4.3.4 Moderately labile P............................................................ 74
  4.3.5 Stable P.............................................................................. 75
4.4 Discussion................................................................................ 80
  4.4.1 Effects of soil amendments on soil pH................................. 80
  4.4.2 Effects of soil amendments on labile P................................. 81
  4.4.3 Effects of soil amendments on moderately labile P............... 83
  4.4.4 Effects of soil amendments on stable P............................... 85
4.5 Conclusions............................................................................. 85
LIST OF TABLES

3.1  Some chemical properties of the soils at the two experimental sites.. 47

3.2  Effects of long-term land use on labile P, total extractable organic and inorganic and total P in soils at the two sites.......................... 48

4.1  P concentrations of animal manures and maize residues.............. 72
LIST OF FIGURES

2.1 A representation of the three functional P pools and their relationships ................................................... 9

2.2 Binuclear Fe,OP(O)₂O,Fe bridging surface complex, characteristic of phosphate adsorption on goethite .......................................................... 12

2.3 Effect of background electrolyte on phosphate sorption at various solution P concentrations ................................................................. 15

2.4 Effect of solution pH on the dissociation of unsatisfied hydroxyls at the surface of Fe and Al hydroxides ......................................................... 16

2.5 Specific adsorption reactions of oxalate and metal (Al or Fe) hydrous oxides at mineral edges ................................................................. 19

2.6 Chemical structure of inositol and inositol phosphate (phytic acid).... 21

2.7 Relationships between phosphorus fractions in the P cycle ............ 23

2.8 Relationships between (a) inorganic P immobilization and C/P ratio, and (b) mineralization of organic P and the total organic P content in the soil .................................................................................. 27

2.9 A representation of a modified Hedley sequential fractionation procedure for soil P ................................................................. 32

3.1 Effect of long-term land use on concentrations of total organic C and microbial biomass C and P in soils at site 1 ............................................. 49

3.2 Effect of long-term land use on concentrations of total organic C and microbial biomass C and P in soils at site 2 ............................................. 50
3.3 Effect of long-term land use on concentrations of inorganic P (Pi) extracted from soils at site 1 ......................................................... 51

3.4 Effect of long-term land use on concentrations of organic P (Po) extracted from soils at site 1 ......................................................... 52

3.5 Effect of long-term land use on concentrations of inorganic P (Pi) extracted from soils at site 2 ......................................................... 53

3.6 Effect of long-term land use on concentrations of organic P (Po) extracted from soils at site 2 ......................................................... 54

3.7 Effects of long-term land use at site 1 on the proportions of P present as labile, moderately labile P and stable P ........................................ 55

3.8 Effects of long-term land use at site 2 on the proportions of P present as labile, moderately labile P and stable P ........................................ 56

4.1 Effects of incubation of amendments (1-8 weeks) on soil pH ........ 76

4.2 Effects of incubation of amendments (1-8 weeks) on inorganic P fractions ............................................................... 77

4.3 Effects of incubation of amendments (1-8 weeks) on organic P fractions ............................................................... 79
CHAPTER 1

GENERAL INTRODUCTION AND STUDY OBJECTIVES

The dynamics of soil P are controlled by the interaction of bio-geochemical processes, land-use and cropping practices (Hinsinger, 2001; Oberson et al., 2001; Zheng et al., 2004a). With the increasing emphasis on sustainable agriculture and environmental quality, it is important to quantify the effects of different crop management practices and land use systems on soil P transformations. Declining world P resources and increased pressure on agriculture to feed growing world populations from constantly decreasing agricultural land areas also underscore the need for sustainable P management (Sanyal and De Datta, 1991).

The relative amounts of the different P fractions in soils vary with age of soils, degree of weathering intensity, and land-use. At advanced stages of soil development, the amount of Ca-P held by apatite minerals decreases, whereas organic P, non-occluded Fe- and Al-bound P, Ca-bound P in the form of secondary minerals, and occluded P increases (Matar et al., 1992). However, other factors such as fertilization, liming, irrigation, climate and parent materials also have an immense influence on the relative amounts of the various P forms present. There is a direct relationship between the Ca-P/(Fe + Al)-P ratio and soil pH (Matar et al., 1992). High levels of Fe and Al oxides in tropical and sub-tropical soils dictate that Fe- and Al-P forms are more abundant than secondary Ca-P forms, except in heavily limed soils.

The total content of P in soils varies greatly, with as much as 5.7 billion hectares worldwide being considered P deficient (Hinsinger, 2001). Sandy savannah soils in arid regions have low total P while prairie soils and those derived from volcanic lavas, some coprolitic limestone, and igneous rocks usually have high content of P (Tisdale et al., 1985). Soil solution P concentration is usually in the 5 – 25 ppm range, which is much lower than that of other macronutrients.

Phosphorus deficiency is a major constraint to crop production on many highly weathered and leached acid soils in tropical and temperate regions of the world (Haynes and Swift, 1988; Hedley et al., 1994). Low P availability is attributed to high
Phosphorus uptake by plants is a process limited by the low diffusion rate of P in the soil. Its acquisition by plants is generally proportional to the root surface area in contact with the soil solution (Hinsinger, 2001). Adaptive mechanisms employed by plants on P deficient soils include increased root proliferation, excretion of organic acids and phosphatases, and lowering the rhizosphere pH, all of which enhance P mobility and uptake (Oberson et al., 2001).

Application of P fertilizers can alleviate P deficiency but in the developed nations, soil P surpluses have sometimes resulted in pollution of water resources (Mozaffari and Sims, 1994). The situation is different in most parts of Africa where soil acidity, with associated Al toxicity, as well as P and Ca deficiency, are common growth-limiting factors (Maroko et al., 1999). Deep weathering of these soils due to high rainfall and low evapotranspiration leach out bases (e.g. K, Mg, Ca) and salts from the soil profile, which leaves high concentrations of Al and Fe oxides.

Inadequate return of P to compensate for P losses due to crop and residue removal, leaching or erosion, has caused negative nutrient balances in many tropical soils (Paul and Clark, 1989; Maroko et al., 1999). Increasing productivity solely by high external inputs such as lime, fertilizer, and herbicides, is impractical for most resource-poor farmers because of lack of availability or excessive cost. Fertilizer efficiency is extremely low due to limited soil moisture, or added phosphate is strongly adsorbed by soil surfaces. Organic materials supply soluble P to plants (and other nutrients) and ameliorate Al toxicity by increasing soil solution pH.

In South Africa, acid soils occur extensively in Western and Eastern Cape coastal areas, KwaZulu-Natal, Eastern Mpumalanga and Northern Province (Dekkers, 1971). Large quantities of Al and Fe oxides have been reported for some of representative soil types (Reeve, 1970; Soil Classification Working Group, 1991).
These soils are characterized by severe P limitations for plant growth, high rates of external inputs (e.g. liming, P fertilizers) are required to correct soil acidity and P deficiency, and increase crop productivity in these soils (Bainbridge et al., 1995).

Maize (Zea mays L.), sugarcane, dairy, forests, rangeland are the main agricultural land uses in the midlands region of KwaZulu-Natal (KZN) (Dominy et al., 2001). These practices have been shown to affect soil organic matter content and quality (Dominy et al., 2002; Haynes et al., 2003). Generally, South African agricultural industry is successful, particularly in relation to its neighbouring states. Sugarcane is the single largest crop in the KZN province, and this significant industry sees sugarcane plantations along the coastal belt forming the mainstay of the economy and agriculture. KZN is the country's leading timber producer and contributes about 40 percent of the total plantation output for South Africa.

Dairy farming is another important land use in the region. Common pasture grasses are kikuyu grass (Pennisetum clandestinum), ryegrass (Lolium perenne), browntop (Agrostis tenuis) and white clover (Trifolium repens). Inclusion of clover in pastures is very popular due to its N₂-fixation potential. Generally, pasture grasses are grown annually, perennially, or in mixed cropping rotation systems involving arable crops. In the Midlands region of KwaZulu-Natal, P. clandestinum and L. perenne dominate pastures. Kikuyu has higher dry matter yield (Haynes, 1999), and is grown on permanent basis. Due to its susceptibility to winter frost, ryegrass is sown annually to provide animal forage during the winter months.

P turnover and availability are influenced by crop management (Condron, 2004). Sequential extraction procedures such as that developed by Hedley et al. (1982) offer the option of examining various inorganic (Pi) and organic (Po) pools differing in their origin and bioavailability. Fractionation procedures can yield valuable information about P pathways in soils under various agricultural land uses (Tiessen et al., 1982; Beck and Sanchez, 1996; Maroko et al., 1999). However, the assignment of P fractions to pools of differing plant availability, particularly for low P tropical soils is still inconclusive (Buehler et al., 2002).
This project focuses on aspects of soil P dynamics that are influenced by long-term land use and management practices. Understanding the impacts of cropping systems on soil P pools and fluxes will allow for improved P management. The hypothesis of this research is that the distribution of soil P among various pools is influenced by land use and management practices. A modified Hedley et al. (1982) fractionation procedure will be used to characterize the soil inorganic (Pi) and organic P (Po) in different soil P pools at the same depth (0-5 cm), in different land-use systems. P fertilizers, organic manures and lime will be used to manipulate the transformation of P between the various pools in the soil over a period of 8 weeks.
CHAPTER 2
PHOSPHORUS AVAILABILITY IN SOILS: A LITERATURE REVIEW

2.1 Introduction

Soils vary extensively in their capacities to supply phosphorus (P) to plants because a large proportion of total P is not readily available for uptake. Solution P concentration depends on the solubility of inorganic P minerals and desorption of adsorbed inorganic P, but in highly weathered soils, P bioavailability may depend mainly on organic P (P_o) turnover processes (Beck and Sanchez, 1994). The various P minerals present in soil and the concentration of solution P supported by these minerals are highly dependent on solution pH. The most favourable pH for P availability is near neutral to slightly acid (pH 5.5 – 6.5).

The solution concentration required by most plants varies from 0.01 to 0.3 ppm and depends on the crop species and agricultural intensity (Tisdale et al., 1985). Adequate P plant nutrition depends on the availability of labile P forms in the rhizosphere. Labile P is the readily available portion (fraction) of the total P that exhibits a high dissociation rate and rapidly replenishes decreases in solution P due to plant uptake. The remaining portion of adsorbed P that does not readily desorb is termed non-labile, and is not readily available to plants. Bioavailability of P is regulated by rapid replenishment of labile forms by desorption from the solid phase, by mineralization of soil organic compounds, and on diffusion through the soil solution into the rhizosphere.

Soil P reacts extensively with various soil components, essentially by processes of adsorption and precipitation of phosphate minerals (Sanyal and De Datta, 1991). Interactions of phosphates with Al and Fe hydroxides occur at lower pH and with Ca at higher pH. For variable charged soil surfaces, the decrease in phosphate adsorption with increasing pH is attributed to the decrease in electrostatic potential in the plane of adsorption (Ross, 1989). On the other hand, an increase in P adsorption with increasing Ca^{2+} concentration in the soil solution is attributed to several mechanisms such as: Ca phosphate precipitation, formation of surface complexes
between P that is held on sorption surfaces and Ca in solution, increase in ionic strength of the background solution, increase in electrostatic potential due to Ca ions, and the adsorption of P by freshly precipitated Fe and Al hydrous oxides (Barrow, 1980; Haynes, 1984; Sanyal and De Datta, 1991).

Soil phosphorus (P) is classified into three pools; solution, labile, and non-labile P (McLaren and Cameron, 1990; Guo and Yost, 1998). The inorganic fraction of soil phosphorus occurs in numerous combinations with Fe, Al, Ca, and other elements. Calcium phosphates become insoluble under alkaline conditions, and Fe and Al phosphates are insoluble under acidic soil conditions. Five classes of soluble organic phosphate compounds commonly found in the soil are; inositol phosphates, phospholipids, nucleic acids, nucleotides, and sugar phosphates. The first three are the dominant groups in soils, but inositol hexaphosphate ester (phytic acid) is more stable than the other phospholipids and nucleic acids (Turner et al., 2003).

Distribution of P among inorganic and organic fractions in soils can be influenced by land-use and cultural practices (e.g. crop rotation, fertilization, irrigation, tillage). These factors influence microbial activity, and therefore the availability of organic and inorganic P (McCallister et al., 2002). Conversion from natural to agricultural ecosystems impacts on soil organic matter pools, soil microbial biomass properties and, hence size of soil P fractions. The fractionation of soil P into various organic and inorganic pools with differing levels of plant availability, coupled with understanding of the P adsorption/desorption properties of soils can indeed provide insights into management practices that influence P bioavailability.

2.1.1 Soil phosphorus pools

Phosphorus pools are characterized by the quantities of P they contain and by the time required for the phosphate ions they contain to enter into the soil solution. P pools range from labile P that can be readily desorbed plus P in solution, to non-labile (stable) P held in insoluble metallo-organic complexes (Guo and Yost, 1998). The three (3) pools of P in the soil are: solution, active (labile) and fixed (non-labile) P (Iyamuremye et al., 1996). Soil solution P is often referred to as the intensity factor, whereas the inorganic and organic labile P are collectively called the quantity
factor. The relationship between these pools is defined by the following equilibrium:
soil solution P ↔ Labile P ↔ Non-labile P (Figure 2.1).

The quantity of P in any pool depends on the specific characteristics of the soil, its use and management practices applied. Various reactions and processes are involved in the transformation of P between the 3 pools. Results on the effects of soil amendments on P pools can be inconsistent in part because of variability of sites and extraction methods. Guo and Yost (1998) suggested that grouping soil P fractions into these functional pools can enhance the application of nutrient models in P management.

2.1.1.1 Soil solution P

Maintenance of solution P concentration or intensity for adequate P nutrition in the plant depends on the ability of labile P (quantity) to replace soil solution P taken up by the plant. The ratio of intensity to quantity factors is called the capacity factor, which expresses the relative ability of the soil to buffer changes in soil solution concentration (Ige et al., 2005).

Solution P pool represents phosphate that is readily accessible by plant roots (Guo and Yost, 1998). Plants and microorganisms meet their P requirements by drawing phosphate ions from this pool mainly through production of CO₂ and organic acids (Figure 2.1). P is taken up mostly as inorganic orthophosphate (HPO₄²⁻, H₂PO₄⁻). Phosphorus taken up by plants and microbes is constantly replaced by release from inorganic and organic forms of P associated with the solid phase (Ross, 1989). Inorganic P can be released to solution by desorption and / or dissolution from mineral P associated with Al, Fe, or Ca. In addition, mineralization of organic P and release of P from the microbial biomass contributes to the solution phase. Thus, organic and microbial P dynamics also play important roles in the control and maintenance of inorganic P in soil solution (Condron, 2004).
Amongst soil microorganisms, mycorrhizal fungi play a more important role in plant P acquisition. Paul and Clark (1989) have suggested 3 ways for the prominence of mycorrhizae in solubilization of mineral phosphate in soils:

1. excretion of organic acids and production of CO$_2$;
2. extra surface area and more penetration of soil aggregates, hence more P is drawn; and
3. ability of mycorrhizal hyphae to extract P at lower levels of soil solution concentrations than plant roots.

### 2.1.1.2 Active P

The active P pool (Figure 2.1) is P in the solid phase, which is relatively easily released to the soil solution. As plants take up phosphate from the solution pool, the concentration of orthophosphate ions in this pool are lowered, and to maintain the equilibrium, phosphate from the active pool is released. The active P pool is constituted of inorganic phosphate adsorbed to clay fraction, organic P that is easily mineralized, and some phosphate that is chemically associated with Ca, Al or Fe (McLaren and Cameron, 1990).

### 2.1.1.3 Fixed P

The fixed P pool contains inorganic phosphate compounds that are very insoluble and organic compounds (organic P, P$_o$) that are resistant to mineralization by microorganisms (Guo and Yost, 1998). The inorganic phosphate compounds in this fixed pool are more crystalline in their structure and less soluble compared to the active P pool. However, Buehlera et al. (2002) demonstrated that for P deficient soils, the fixed P pool can be a significant P source.
Figure 2.1 A representation of the three functional P pools and their relationships (Source: Guo and Yost, 1998)
2.2  **Inorganic P (Pᵢ)**

Phosphorus exists in sedimentary, metamorphic and igneous phosphate rock deposits in the form of various phosphate minerals such as fluorapatite ($3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaF}_2$), chloroapatite ($3\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaCl}_2$), and hydroxyapatite ($3\text{Ca}_3(\text{PO}_4)_2\cdot\text{Ca(OH)}_2$). Fluorapatite is usually the most important primary P source and exists as crystals of fine sand and silt size in many rocks and soils (Matar *et al.*, 1992). A variety of soil processes, for example $\text{Ca}^{2+}$ uptake by plants, influence dissolution of P from apatite minerals. P released from these minerals (and organic sources) can be reprecipitated into various secondary phosphates, incorporated into soil organic matter or adsorbed by soil components (Sanyal and De Datta, 1991).

Inorganic phosphorus compounds present in the soil are orthophosphate ($\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$), calcium phosphate, aluminium and iron oxide-phosphates (Cade-Menum *et al.*, 2000). The inorganic P is bound with varying adhesiveness to calcium, iron and aluminium compounds in the soil. The relative significance of each depends primarily on the pH of the soil. Amounts of inorganic, organic and microbial P in soil and the equilibrium concentration of inorganic P in soil solution are determined by a combination of factors. These include soil chemical properties (e.g. clay / hydrous oxide mineralogy, pH, ionic strength) and soil P status as determined by the type, duration and intensity of land use and the associated P inputs (Ross, 1989).

P ‘retention’ or ‘fixation’ can be considered as summation of physical adsorption, chemisorption, precipitation and occlusion (Matar *et al.*, 1992). Adsorption/desorption and precipitation/dissolution equilibria control solution P concentration and therefore, its mobility in soil and bioavailability.

### 2.2.1 Adsorption reactions

Non-specific adsorption or precipitation refers to P retention by coulombic interaction in the outer layer of the adsorbing soil constituent. Under acidic pH conditions – below the point of zero charge (estimated at between pH 7 and 10), polymorphic forms of Al and Fe oxides have a net positive charge and they attract phosphate ions
from solution into exchange sites on their surfaces. In contrast to specific adsorption reactions, phosphate and adsorption surfaces form outer-sphere complexes through water molecules – weak bonding.

Important aspects of the chemical or specific adsorption mechanism are: the surface reaction between phosphate and hydroxyl ions, and the coordination of the adsorbed phosphate ions (Tisdale et al., 1985). During specific phosphate adsorption, the oxygen of the phosphate enters into a six-fold coordination with metal cations hence this process is termed ligand exchange. Adsorption of the phosphate ions is also accompanied by release of hydroxyl groups, which in turn may raise the soil pH. Experimental evidence in support of the ligand exchange process – the displacement of hydroxyl (OH\(^-\)) groups that are in coordination to hydroxylated mineral surfaces includes kinetics of adsorption and desorption; hydroxyl ion release; infrared spectroscopy; and stereochemical inferences (Goldberg and Sposito, 1985).

The interaction of phosphate and the mineral surfaces is considered specific in reference to the stable bonds formed between these soil constituents (Tisdale et al., 1985). Phosphate ions can be irreversibly adsorbed on many soils through binuclear complex formation process in which a bridging ligand forms from the replacement of two surface hydroxyl groups (Figure 2.2). Adsorption of borate, molybdate and arsenate on amorphous Fe and Al hydroxides, especially in weathered soils occurs by binuclear bridging mechanisms (Ross, 1989).

Binuclear, monodentate and bidentate surface complexes of metal hydrous oxides and the phosphate ions is inferred from crystallographic studies and determinations of hydroxyl ion release (Alejandra et al., 2006). The monodentate reversible complex involves replacement of orthophosphate anions by hydroxyl ions, if the process is energetically favoured. Even though infrared spectroscopic studies show bidentate complex of phosphate on dried acidified goethite, under field conditions, where several factors such as water content, organic acids, and pH become significant, the monodentate complex predominates (Goldberg and Sposito, 1985). Binuclear surface complex – an irreversible process, results from formation of a bridging ligand by making a second replacement of a surface hydroxyl when this is geometrically feasible.
Figure 2.2 Binuclear FeOP(O)₃Fe bridging surface complex, characteristic of phosphate adsorption on goethite (Source: Ross, 1989)

2.2.2. Precipitation reactions

Whilst specific adsorption reactions predominate at low-solution P concentrations (Matar et al., 1992), precipitation reactions dominate when the concentration of P and hydroxylated cations (Al, Fe, Ca, Mg) exceeds the solubility product (Ksp) of the newly formed phosphate mineral (Tisdale et al., 1985). Phosphate ions in the soil solution readily precipitate with metal cations to form a range of P minerals. The type of P minerals formed depends on the soil pH because it governs the solution concentrations of metal cations and solubility of phosphate compounds.

In acid soils, the increased solubility of Al and Fe oxides result in high solution concentrations of trivalent Fe and Al (Hinsinger, 2001). Thus, precipitation of Al and Fe phosphates (e.g. strengite, vivianite, variscite) is most favoured between pH values of 4.8 and 5.2. Conversely, in neutral and alkaline soils, dissolution and precipitation reactions associated with calcium (e.g. dicalcium or octacalcium phosphates, apatites) and, and to a lesser extent Mg phosphates, have a large influence on P solubility.
2.2.3 Factors regulating P adsorption

Bioavailability of soil phosphorus depends on several important biological and physicochemical properties which include; ionic strength of the electrolyte solution; soil pH; texture, extent of P saturation, decomposition of organic matter; microbial activity; hydrous oxides of iron (Fe) and aluminium (Al); and the nature and amount of clay (Sanyal and De Datta, 1991; Haynes and Mokolobate, 2001). Charge characteristics of soils are very important because they influence both the cation (CEC) and anion exchange (AEC) properties of soils. Thus, from a soil management perspective, it is very critical to obtain a complete assessment of soil factors that optimise P availability to plants.

2.2.3.1 Clay content and mineralogy

A significant correlation of P sorption parameters with clay content has been reported (Bowden et al., 1980). For example, the Langmuir adsorption maximum is positively correlated to clay content, Fe content, and exchangeable Al (Sanyal and De Datta, 1991). As well as clay content, reactions of P in soils are greatly affected by the mineralogical composition of the clay fraction (Matar et al., 1992).

Phyllosilicate minerals have lower P retention capacity than the amorphous and crystalline oxides (Ross, 1989). P adsorption on these layered silicate clays occurs mainly through Al- and Fe-OH at broken clay lattice edges, where unsatisfied Al$^{3+}$ groups are exposed or, in the case of 1:1 kaolinitic clay, where octahedral Al layers are exposed at the crystal surface. Unsatisfied positive charges may also occur at Si$^{4+}$ groups in tetrahedral clay positions. Phosphate adsorption on 1:1 type minerals such as kaolinite (which has a significant amount of pH-dependent negative charge), is far greater than by 2:1 clays such as montmorillonite. This is mainly due to a higher negative charge density on surfaces of 2:1 clays which repels phosphate anions (Ross, 1989).

Amorphous oxide minerals retain exceedingly high P than do crystalline iron and aluminium hydrous oxides (e.g. hematite and gibbsite) (Ross, 1989). In comparison to crystalline aluminosilicates and calcium carbonate, amorphous oxide minerals can
adsorb up to 1000 times more P (Sanyal and De Datta, 1991). Greater adsorption of phosphate by amorphous Al and Fe hydrous oxides (allophane) than crystalline oxides (gibbsite and goethite) is associated to the former having large number of singly coordinated surface hydroxyl ions (Haynes, 1984).

2.2.3.2 Electrolyte strength and species of cation

There is evidence that the ionic composition, both cationic species and concentration of electrolyte solution influence the adsorption of phosphate through their effects on electrostatic potential on soil colloids (Goldberg and Sposito, 1985). An increase in concentration of electrolyte cations near negatively charged soil colloids make the potential in the plane of adsorption less negative and, hence, increase the adsorption of anions and decrease the potential for their release from sorption sites (Bowden et al., 1980; Barrow, 1987). Since divalent cations have relatively smaller hydrated ionic radius than do monovalent cations, the former are more strongly attracted to lattice surfaces (Ross, 1989). The decrease in electrostatic potential is more marked if the counter cations are polyvalent (Sanyal and De Datta, 1991). Replacement of a divalent ion (e.g. Ca\(^{2+}\)) by a monovalent electrolyte cation (e.g. Na\(^+\)) at colloid surface increases the lattice negative charge of the exchange surface.

As a result, adsorption of phosphorus by soils is influenced by the species of cation in the system. Divalent cations enhance phosphorus sorption relative to monovalent cations. For example, clays saturated with Ca\(^{2+}\) can retain greater amounts of phosphorus than those saturated with sodium or other monovalent cations. Barrow (1987) found that P sorption was consistently greater in CaCl\(_2\) than in NaCl solutions (Figure 2.3). The difference between the two salts was strongly pH-dependent — sorption in the Na solutions declined more rapidly than in Ca medium. This observation has been corroborated by Naidu et al. (1990) who reported increases in P sorption by a limed soil in dilute CaCl\(_2\) supporting medium. Curtin et al. (1992) also found that P sorption in Na\(^+\) saturated acidic clay loam soil was less than that in Ca\(^{2+}\) saturated soil. At pH 6.7, the Ca-soil sorbed 4 times as much P as the Na-soil.
Figure 2.3 Effect of background electrolyte on phosphate sorption at various solution P concentrations (Source: Barrow, 1987)

2.2.3.3 Soil pH

Among the various factors, pH has the largest effect on the adsorption of phosphate, especially by variable charge surfaces. This property governs the reaction mechanisms between soil and phosphate and quantity of phosphorus retention on soil constituents. This is thought to be due to the large effects of pH on P speciation, dissociation of hydroxyl groups, and charge of the variable charge surfaces involved in P fixation (Sanyal and De Datta, 1991). The P species present in the soil affects plant uptake because P is mainly adsorbed as HPO$_4^{2-}$, which prevails in slightly acidic medium (pH < 7). The soil pH level largely controls the solubility of Fe, Al and Ca compounds and, hence, pH directly affects the availability of phosphorus for plant growth.

The potential on the oxides arise from the adsorption of OH$^-$ and H$^+$, and there is no inherent charge on the metal oxides themselves. The surface charge of these MOH$_2^{0.5+}$ and MOH$^{0.5-}$ groups varies significantly with changes in ionic strength, pH, point of zero charge (pH$_o$), and valency of the counter ion (Bowden et al., 1980;
Barrow, 1984). At low soil pH (acidic conditions), the activity of H\(^+\) is higher than that of hydroxyl ions (OH\(^-\)). At this pH level, the surface charge on amphoteric surfaces is positive (Figure 2.4), which coincides with high P sorption and low CEC. At the pH\(_o\), the net charge on the adsorption surfaces is zero (Figure 2.4). Maximum phosphate adsorption by iron and aluminium hydrous oxides in acid soils occurs between pH 2 and 4 (Sanyal and De Datta, 1991). As the pH increases, the surface charge on amphoteric surfaces becomes increasingly negative (Figure 2.4) and results in electrostatic repulsion between these surfaces and phosphate ions (Bowden et al., 1980; Barrow, 1984). The adsorption affinity of sorption sites is decreased at high pH values, with possible net P movement of weakly held P from the soil colloids into solution (Haynes, 1984).

Figure 2.4  Effect of solution pH on the dissociation of unsatisfied hydroxyls at the surface of Fe and Al hydroxides. (Source: Ross, 1989)
2.2.3.4 Redox potential

Soils subjected to fluctuations in water content due to irrigation or rainfall come under the influence of another variable: the redox potential (Lindsay, 1979). This variable is controlled by the concentration of oxygen. During dry periods, the soils become re-oxidized. The decrease in redox potential following flooding by rain or irrigation water can cause transformations of crystalline Al and Fe minerals to the amorphous forms (Matar et al., 1992), which in turn affects P retention properties of soils. The development of plough pans in cultivated soils may also promote reducing conditions. The associated changes in soil pH variously affect P availability depending on the initial pH level and organic matter content of the soil. As the potential of the system decreases, its pH increases. Willet (1989) reported that soils with the greatest increases in extractable P during flooding also had the largest increases in pH.

In reduced systems, Fe and Al phosphates are hydrolyzed by chelatants formed by anaerobic decomposition of organic matter, and P is released to the soil solution becoming available to the plants (Sanyal and De Datta, 1991). Increased P availability due to flooding is also been attributed to the reductive dissolution of Fe$^{3+}$, which releases both sorbed and occluded P into solution. Willet (1989) showed that reduction of the Fe$^{3+}$ to Fe$^{2+}$ oxide was the main P source under flooded conditions. In addition, the positive effect of soil pH on P availability was limited to soils recently fertilized with mineral P. The reductive dissolution of manganese (Mn) oxides can also contribute to P release in flooded soils (Lindsay, 1979).

2.2.3.5 Inorganic anions

The competitive ability of inorganic anions against phosphorus for sorption sites depends on the bond strength of the anion with the sorption surface (Alejandra et al., 2006). Competition between these anions and phosphate determines their ability to release adsorbed P into the soil solution therefore increasing it bioavailability. Specifically, sorbed inorganic anions and acids such as hydroxyl, silicic acid, sulphate, and molybdate can be competitive against phosphate whereas weakly held inorganic anions such as nitrate and chloride do not affect P sorption. In practical
terms, application of compounds containing silicate can block adsorption sites on soil colloids (Haynes, 1984). In deed, specific adsorption of silicate has been reported to desorb previously adsorbed phosphate, which causes increases in solution P (Hue, 1991).

2.2.3.6 Organic matter content

Products of organic matter decomposition may react directly with P sorption sites in the soil resulting in increased solution P concentration and, hence, P plant availability. Sorption of decomposition products of OM may also increase the negative charge of the adsorption surfaces, or lower the point of zero charge (PZC), thus resulting in phosphate repulsion (Bowden et al., 1980).

Evidence that organic matter can modify the sorption of inorganic phosphate (P) by soils and soil components has been drawn from several competition experiments involving P and various organic acids/anions (Hue et al., 1994; Guppy et al., 2005). Although most of these experiments have compared competitive sorption of P to mostly low-molecular weight organic acids/anions (e.g. malate, citrate, acetate), higher molecular weight organic acids (e.g. humic and fluvic acids) are also effective in ion competitive inhibition of P sorption by soil colloids (Guppy et al., 2005). Organic acid anions such as oxalate, citrate, and poly-galacturonate have been shown to be specifically sorbed at soil surfaces in a similar manner to phosphate (Nagarajah et al., 1970). Figure 2.5 shows specific adsorption of oxalate onto metal hydrous oxide surfaces.

In some instances, positive correlation between soil OM content and P sorption has been found in previous studies (Mizota et al., 1982; Sanyal et al., 1993). Therefore, there are contradictory opinions. This has been attributed to Al and Fe organic complexes adsorbing P. The formation of metal bridges results in increased number of sorption sites, decreasing solution P concentration (Owusu-Bennoah and Acquaye, 1989). The metal ligands increase the PZC and, hence, the amount of phosphate anions that can be adsorbed. Complexes involving organic matter may maintain Fe, Al, Mg and Ca ions in solution when their insoluble precipitates (e.g. CaCO₃) could have formed, thereby decreasing potential for P fixation. These facts
account for the contrasting views on effects of organic matter in decreasing P adsorption.

\[
\begin{align*}
&\text{M} \quad \text{OH}_2 \quad \text{OH} \\
&\text{M} \quad \text{OH} \quad \text{OH}_2
\end{align*}
\]

\[\text{CO} \quad \text{C} \quad \text{O} \quad \text{O}^- \quad \text{(Oxalate)}
\]

\[
\begin{align*}
&\text{M} \quad \text{OH}_2 \\
&\text{M} \quad \text{OH}
\end{align*} \quad \text{O} \quad \text{C} \quad \text{O}^{-} \quad \text{OH}^{-} \quad \text{H}_2\text{O}
\]

**Figure 2.5** Specific adsorption reactions of oxalate and metal (Al or Fe) hydrous oxides at mineral edges (Source: Hue, 1992)

### 2.2.3.7 Time

Exchangeability of adsorbed inorganic P with the soil solution decreases with time as the adsorbed P become more strongly bound to mineral surfaces (Condron, 2004). Consequently, its supply to plants is reduced because of decreased solubility and increased adsorption. The reduction in P exchangeability between solution and solid phase is variously referred to as 'fixed' or 'sorbed' P. Hypothetical migration of phosphate into the adsorbing colloids (Matar *et al.*, 1992), is variously regarded as chemisorption, occlusion or absorption. In general, the terms relate to the removal of P from solution and its retention on soil surfaces. This P fixation is the major reason for the continued application to maintain crop productivity in agricultural soils.

### 2.2.3.8 P saturation

When a P deficient soil is fertilized, P is initially rapidly adsorbed on soil colloids, followed by slower adsorption reactions and retention within soil colloids (Hedley *et al.*, 1994). Adsorption of additional P decreases as the quantity of P already adsorbed increases, so that repeated additions increase solution P. That is, as P adsorption surfaces become saturated, applied P is subsequently held less tightly causing an increase in the proportion of P in the labile fractions. P saturation is the
ratio of the amount of sorbed P to the P sorption capacity (Dao and Cavigelli, 2003). A buffer coefficient (BC) for added P is the increase in extractable soil P per unit of applied fertilizer P (Dobemann et al., 2000). Evaluation of fertilizer efficacy requires a detailed knowledge of the adsorption and desorption characteristics of the soils for phosphate.

2.3 Organic P

2.3.1 Nature of soil organic P

The organic forms of P (P₀) are found in humus and other soil organic fractions originating from plant and animal residues. Although the inorganic P content of soils is generally higher than that of organic P, it constitutes a large proportion of the total P (up to 80%) in some soils and provides a source of P for plant uptake (Chen et al., 2001). Mineralization (decomposition) of organic matter, primarily plant residues, releases soluble organic P compounds, and organic anions and as already noted, these compete with P for adsorption sites, thus increasing its bioavailability. In weathered tropical soils, especially in low-input agricultural systems, the organic phosphorus (P₀) is important in replenishing the plant available P (solution) pool (Tiessen et al., 1984).

Organic P content of soils and the ability of soils to recycle this P fraction are largely dependent on the soil organic matter (SOM) content and associated microbial biomass. The P₀ content of soils generally increases with increasing organic C and/or N (Tisdale et al., 1985). P contents of soil organic matter ranges from about 1 to 3% (Matar et al., 1992). Although phosphorus is generally considered immobile in the soil, repeated applications of manure can move organic P compounds to a greater depth than can inorganic P in solution (Letkeman et al., 1996).

Agronomic practices that enhance soil organic matter accumulation also lead to increases in organic phosphorus contents. The benefits of P₀ in replenishing available P₀ can be increased by adopting management practices that maintain or increase the size of the P₀ pool. The build-up in P₀ can be achieved, for example, under zero tillage systems because crop residues are retained on the surface, which
ensures slow mineralization and release of P into the soil solution. In contrast, conventional tillage promotes rapid mineralization due to greater soil aeration and soil temperatures, and therefore cultivated soils usually contain lower organic P than equivalent uncultivated soils.

Although the nature of many of the soil organic (Pₒ) compounds is not yet fully clear (Tisdale et al., 1985), the common ones include: orthophosphate monoesters (e.g. inositol phosphates, mononucleotides, sugar phosphates); orthophosphate diesters (e.g. phospholipids, RNA, DNA); teichoic acids and phosphonates (Cade-Menum et al., 2000). Other P-C, P-N and P-S linkages exist, but phosphate esters (C-O-P) (Figure 2.6) are the predominant form of organic phosphorus in soils.

![Chemical structure of inositol and inositol phosphate (phytic acid)](source: Tisdale et al., 1985)

Figure 2.6 Chemical structure of inositol and inositol phosphate (phytic acid)
(Source: Tisdale et al., 1985)

Phosphate esters, such as inositol phosphates (up to 60% of the total organic phosphorus), nucleic acid phosphorus (5 to 10%) and phospholipid phosphorus (<1%), are bonded to soil organic and inorganic components by mechanisms such as adsorption and are generally less a part of soil humic materials than organic nitrogen or sulphur (Turner et al., 2003). Phytin, the calcium-magnesium salt of inositol hexaphosphoric acid, is the most common form of organic P; constituting 30
- 80% of the total soil organic phosphorus. Condron et al. (1985) determined that over 90% of the organic P fraction was in the inositol phosphate or phytic acid form. Phytic acid is an orthophosphate monoester which is biologically stable in soils (Tisdale et al., 1985). Some organic forms of phosphorus can be assimilated by plants, either directly or after breakdown by enzymes occurring in the root exudates of plants (Horst et al., 2001).

2.3.2 Soil microbial biomass

Soil microbial biomass is composed of fungi and bacteria, and these may increase, decrease, or remain unaffected by management practices (Bardgett et al., 1996). Although the soil microbial biomass comprises only about 2-3% of the total organic carbon in soil, it is reported to play a central role in biochemical processes and serve as a crucial repository for plant nutrients (Chen and He, 2004).

Soil microbes immobilize solution P as microbial P, eventually releasing both readily mineralizable organic P compounds (labile organic P) and more stable organic P forms (Tisdale et al., 1985). The microbial biomass P represents a rapidly cycling P pool because microbial biomass is readily decomposable (Dalal, 1998). Immobilization of P by soil microbes and its slow release through microbial turnover protects P from physico-chemical reactions and, hence, increases its bioavailability because a significant proportion of microbial P is labile (Oberson et al., 2001). Thus, the microbial biomass acts as a transformation agent and as a source and sink for various nutrients (Figure 2.7).

Biological transformation of P is very important as the inorganic transformation in regulating P availability especially in highly weathered soils (Tiessen et al., 1984; Stewart and Tiessen, 1987). Increased emphasis on biological activity in low-input farming systems means that organic and microbial P dynamics are likely to play an important role in overall P availability (Oberson et al., 2001). A direct relationship between organic P and Bray 1 extractable P was reported by Chen et al. (2001).

Soil microbial biomass P and C are very dynamic and fluctuate more over time than total P or organic C (Brookes et al., 1982). The ratio of microbial C and P (C_{mic}, P_{mic})
to total organic C are therefore sensitive indicators of changes in soil organic matter under contrasting management systems (Weigand et al., 1995). Consequently, measurements of soil microbial nutrient pools may reflect effects of different crop management practices on nutrient cycling, even before such effects can be detected by measurements of other nutrient pools (Omay et al., 1997). Chen et al. (2001; 2002) used microbial biomass P as an index of soil P availability, but caution should be exercised in applying soil quality indices, especially when considering soils developed from different parent materials (Chen and He, 2004).

Zero-tillage and legume based crop rotations enhance soil microbial diversity (Doran, 1980). After withdrawing management inputs (fertilizers, liming, grazing), both total microbial biomass and activity in the surface soil horizons are significantly reduced (Bardgett et al., 1996). Although microbial P turnover was not determined in this particular study, the decrease in microbial activity is likely to have resulted in lower microbial P turnover.

![Diagram of phosphorus fractions in the P cycle](Source: Stewart and Sharpley, 1987)
2.3.3 Soil phosphatases

A wide range of microbes produce phosphatase enzymes that mineralise organic P and release inorganic P needed by microorganisms and plants (Hinsinger, 2001). Specific organic P hydrolysis reactions of some phosphatases are presented in the following reactions (Bishop et al., 1994):

- Orthophosphoric acid monoester + H₂O \[ \overset{\text{acid phosphatase}}{\rightarrow} \] alcohol + orthophosphate
- Orthophosphoric acid monoester + H₂O \[ \overset{\text{alkaline phosphatase}}{\rightarrow} \] alcohol + orthophosphate
- Orthophosphoric acid diester + H₂O \[ \overset{\text{phosphodisesterase}}{\rightarrow} \] alcohol + orthophosphate monoester
- *myo*-inositol hexaphosphate + H₂O \[ \overset{\text{phytase}}{\rightarrow} \] *myo*-inositol + orthophosphate pentaphosphate

The phosphatases catalyze the hydrolysis of both esters and anhydrides of H₃PO₄. The enzymes are classified as acid and alkaline phosphatases because their maximum activities occur at low (pH 6.5) and high (pH 11) pH ranges, respectively. In general, soil enzyme activities are used as an indirect measure of microbial activity (Weigand et al., 1995). Acid phosphatase enzymes are released by both microorganisms and higher plants as part of root exudates, whereas alkaline phosphatases are produced mainly by microorganisms (Tabatabai, 1994). To assay for phosphatase activity, a substrate (disodium p-nitrophenyl phosphate) is added to soil, and a buffer is used to maintain the pH at the desired value (pH 11 for alkaline phosphatase). The rate of formation of a hydrolysis product (p-nitrophenol) is proportional to phosphatase activity.

Some crop species (e.g. lupins) have greater efficiency of P acquisition and utilization than cereal crops due to their ability to produce more phosphatases than other crops (Horst et al., 2001). The induction of both extra and intracellular acid phosphatases (ACP) and alkaline phosphatases is a common adaptive strategy by plants to phosphorus deficiency (Hinsinger, 2001). The rapidly dwindling supply of rich phosphate reserves underlies the requirement for crop variety improvement to increase phosphate acquisition and utilization by crops.
2.3.4 Mineralization and immobilisation of organic P

During decomposition, some of the P and other nutrients are assimilated by microbial biomass (immobilization) and some are converted into organic forms ($P_o$). Eventually, both readily mineralizable organic P compounds (labile organic P) and more stable organic P forms are released into the soil (McLaren and Cameron, 1990). Mineralization reactions also release organic anions that compete with P for adsorption sites with Fe, Al and Ca solution species (Hutchison and Hesterberg, 2004). Land-use systems that increase soil organic P enhance soil biological activities, and therefore mineralization of $P_o$ is also greater. Indeed, in general, P mineralization increases as the total soil organic content increases (Figure 2.8).

Nonetheless, the mineralization of soil organic P is also determined by its chemical nature and associated reactivity. For example, the predominance of orthophosphate monoester inositol phosphates in soil may be partly attributed to its association with the structural components of senescent plant material, which limits its susceptibility to mineralization (Stewart and Tiessen, 1987). In contrast, orthophosphate diester forms of organic P (nucleic acid and phospholipid P) are relatively soluble in the soil and are therefore rapidly mineralized. In addition, the susceptibility of soil organic P to mineralization is influenced by physical factors, including particle size aggregate stability and the associated effects of wetting and drying (Adams and Odom, 1985). Mycorrhizae fungi may also increase the solubility and consequent mineralization of soil organic P (Chen et al., 2002).

The mineralization of organic P is determined by its chemical nature and associated reactivity (Condron et al., 1985; Turner et al., 2003). Organic P content in soil extracts is thus characterized by its susceptibility to hydrolysis by phosphatase enzymes. For example, the predominance of orthophosphate monoester inositol phosphates in soil may be partly attributed to its association with the structural components of senescent plant material, which limits its susceptibility to mineralization (Stewart and Tiessen, 1987). In contrast, orthophosphate diester forms of organic P (nucleic acid and phospholipid P) are relatively soluble in the soil and are therefore rapidly mineralized. In addition, the susceptibility of soil organic P
to mineralization is influenced by physical factors, including particle size aggregate stability and soil moisture regimes.

During decomposition of soil organic matter, soil microbes assimilate phosphorus and other nutrients – immobilisation, and this depends on the C:P ratio of the organic material. Net P mineralization has been reported for residues with a C: P ratio below 100, whilst a C: P ratio above 300 results in net immobilization. Results presented in Figure 2.8 show that as the C/Po ratio of residues increased, so did P immobilization. Bishop et al. (1994) suggested that soil microbes are able to utilize labile and less available forms of P, and leads to increases in organic P fractions at the expense of inorganic fractions.

<table>
<thead>
<tr>
<th>C/P Ratio</th>
<th>Mineralization/Immobilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 200</td>
<td>Net mineralization of organic P</td>
</tr>
<tr>
<td>200 – 300</td>
<td>No gain/loss of inorganic P</td>
</tr>
<tr>
<td>&lt; 300</td>
<td>Net immobilization of inorganic P</td>
</tr>
</tbody>
</table>

As well as the C/P ratio, the N/P ratio of decomposing residues regulates the predominance of P mineralization over immobilization. A decrease of either N or P in soil can result in increased mineralization of the other (Tisdale et al., 1985). The ratio of N to P in manures is less than that of crop removal. Thus applications of organic amendments based on plant N requirements result in accumulation of P in soils.

Determination organic P mineralization is difficult because inorganic P (Pi) released from mineralization can be removed from solution (1) P retention on clay and other soil surfaces, and (2) P precipitation as secondary Al\(^{3+}\), Fe\(^{2+}\), or Ca\(^{2+}\)-P minerals (Tisdale et al., 1985). Very few experimental procedures can directly measured changes in soil organic P concentration during mineralization (Bishop et al., 1994). Oehl et al. (2001) applied the principles of isotope exchange kinetics to examine soil organic P mineralization and P cycling through the soil microbial biomass in a soil that was cropped for 20 years.
Figure 2.8 Relationships between (a) inorganic P immobilization and C/P ratio, and (b) mineralization of organic P and the total organic P content in the soil (Source: Tisdale et al., 1985)
2.4 Extraction and fractionation of soil P

Chemical sequential extraction has been widely used to divide soil phosphorus (P) into different inorganic (Pi) and organic (Po) fractions (Oberson et al., 1999; Owusu-Bennoah and Acquaye, 1989). Fractionation procedures (e.g. Chang and Jackson, 1957; Hedley et al., 1982) divide the soil P continuum into fractions based on various chemical extractants. Further, isotopic exchange and sequential P extraction techniques can be combined to investigate the interactions between the labile P pool and the chemical P forms that influence the equilibrium between the solid phase, surface and solution equilibria.

The importance of different P fractions in replenishment of available P, depends on soil properties (Tiessen et al., 1983), weathering intensity and management system (Guo and Yost, 1998). P fractionation methods provide an alternative for characterizing soil P availability and may elucidate some of the problems regarding lack of crop response to P. Measurements of the various soil P fractions are based on extracting solutions which remove inorganic and organic P of increasing chemical stability (Guo and Yost, 1998). Increasingly stronger solutions extract P fractions that are believed to be increasingly less available to plants. The important assumption in the sequential extraction is that readily available soil P is removed first with mild extracting solutions, while less available P pools are extracted with stronger acids and alkali solutions (Hedley et al., 1982).

2.4.1 Chang and Jackson method

The fractionation procedure proposed by Chang and Jackson (1957) extracts mainly strongly retained P and therefore may not be appropriate for studying soil P dynamics that influence uptake by plants (Agbenin and Goladi, 1998). In this method, selective extracting solutions of increasing harshness are used, so that P associated with Al, Fe and Ca is extracted by a combination of ligand exchange and dissolution reactions. The advantage of this method is that extracts used in P fractionation parallel those used for Al and Fe, which allows for relation of P fractions to Fe and Al forms (Cade-Menum et al., 2000), thus characterizing the chemical linkage of P and its degree of availability. However, it does not account for the
organic fraction of soil P (P₀) (Agbenin and Goladi, 1998), despite the significant proportion of this fraction in some soils.

2.4.2 Hedley fractionation method

The method developed by Hedley et al. (1982) and modified by Tiessen and Moir (1993), fractionates the soil P into five inorganic P (Pᵢ), three organic P (P₀) fractions, and one residual P fraction (Figure 2.9). The procedure utilizes extracts of differing strengths and composition, and recognizes readily available P forms as resin Pᵢ, NaHCO₃-Pᵢ, and NaHCO₃-P₀. Other fractions are considered as less labile or stable forms, but in highly weathered soils, these fractions may contribute significantly to plant available P (Beck and Sanchez, 1994).

Currently, variants of the Hedley fractionation, which mostly exclude determination of microbial P, have been used extensively to separate forms of organically bound soil phosphorus from the inorganic fractions (Agbenin and Goladi, 1998; Beauchemin and Simard, 2000). In these approaches, microbial P fraction is assumed to be distributed between the bicarbonate and hydroxide extractions. Further, some methods use concentrated HCl instead of H₂SO₄ (Tiessen and Moir, 1993). Certain authors (Cross and Schlisinger, 1995; Cade-Menum et al., 2000), have raised concerns about the suitability of the Hedley procedure for carbon-rich acid soils because of the difficulty in precipitating organic matter.

2.4.2.1 Resin – P

Extraction using anion exchange resin in bags or on membranes is generally assumed to closely estimate P bio-availability than chemical extractions because they accumulate nutrients from soils through exchange reactions by a similar mechanism to the soil-root interface (Tiessen and Moir, 1993). The resin-extractable pool (resin-P) represents inorganic P (Pᵢ) from the soil solution and that which is weakly adsorbed on sesquioxides, crystalline minerals or carbonates (Tiessen et al., 1984; Richards et al., 1995). Resin – P originates from the most labile P pool, and therefore a good estimator of plant available P, particularly for acid soils (Hedley et al., 1982; Beck and Sanchez, 1994).
P fractions that interact with resin-P fraction are likely to act as sources or sinks of solution P. When the resin P fraction decreases, phosphatase enzyme activity can increase, with a corresponding increase in P mineralization of organic P (Schmidt et al., 1996). Conversely, fertilizer P application rates above crop removal increase resin P content, which suppresses phosphatase activity, and consequently suppresses mineralization of organic P.

2.4.2.2 Bicarbonate – P (NaHCO₃ - P)

Sodium bicarbonate (0.5 M at pH 8.5) extracts weakly adsorbed Pᵢ and easily mineralizable organic P (Pₒ). NaHCO₃ extracting solution (pH 8.5) can affect hydrolysis of surface Al and Fe, therefore releasing Al- and Fe-bound phosphate. The bicarbonate Pₒ fraction consists of compounds like ribonucleic acids and glycerophosphate and may be assimilated by plants (Hedley et al., 1982; Buehler et al., 2002). NaHCO₃ – P is considered as labile Pₒ sorbed on the soil surfaces plus a small amount of microbial P (Schmidt et al., 1996; Zhang and MacKenzie, 1997).

2.4.2.3 Sodium hydroxide – P (NaOH- P)

Sodium hydroxide extractable Pᵢ is assumed to be non-occluded P associated with amorphous and some crystalline Al and Fe hydroxides (Fe- and Al-bound Pᵢ) (Beck and Sanchez, 1994; Buehler et al., 2002). Since the hydroxide Pᵢ is held strongly by chemisorption to Fe and Al components of soil colloids, it is considered as moderately labile soil P (Sharpley, 1991). It is considered to be slowly available to plants by desorption (Zhang and MacKenzie, 1997). In acid soils, this P fraction can act as a sink for P during excess P fertilization, but is also a P source when resin P levels are low (Hedley et al., 1982). In highly weathered P deficient soils, the hydroxide-extractable Pᵢ fraction may be substantially increased by P additions because the high exchangeable Al in these soils (Buehler et al., 2002) results in precipitation of Al phosphates. However, when applied to relatively fertile soils, other P fractions may accumulate P instead of the NaOH-P.

Organic P (Pₒ) associated with chemically and physically protected organic compounds (e.g. fulvic and humic acids) are also extracted by sodium hydroxide.
(0.1M NaOH). These organic materials are reported to be stable and involved in long-term soil P transformations (Guppy et al., 2005). Some workers have identified NaOH extractable P₀ as an important source of P in unfertilized tropical soils (Tiessen et al., 1982; Schmidt et al., 1996). Beck and Sanchez (1994) used path analysis to compare the role of P fractions in replenishing solution P concentration in non-fertilized and fertilized treatments of a long-term continuous cultivation experiment on a Typic Paleudult. The study determined that organic P (particularly NaOH-P₀) was the primary source of plant available P in the non-fertilized system.

2.4.2.4 Hydrochloric acid – P (HCl – P)

A considerable part of soil phosphorus can be dissolved by hydrolysis of soil with hydrochloric acid. HCl – Pᵢ is relatively stable and bound to Ca (Ca-P) and can be associated with apatite minerals (Lehmann et al., 2001). The P₀ removed by this extracting solution may originate from more stable pools from particulate organic matter and as such are considered unavailable to plants (Zhang and MacKenzie, 1997).

2.4.2.5 Residual – P

Residual P constitutes both inorganic and organic P (Condron and Goh, 1989; Agbenin and Goladi, 1998) and is usually extracted with concentrated sulphuric acid. Long term application of P fertilizer, especially in excess of crop needs, often leads to enrichment of this fraction through occlusion of Pᵢ. In addition, residual P can be converted soil organic P via plant, animal, and microbial residues. There is often high correlation between residual P fraction and plant available P (Agbenin and Goladi, 1998; Guo and Yost, 1998). However, such a correlation does not mean that residual P contributes directly to plant uptake (solution P), because the less labile pools can exist in equilibrium with each other, or with moderately labile pools. For example, Agbenin and Goladi (1998) determined that residual-P contributed to resin-P indirectly through bicarbonate-P₀ (NaHCO₃-P₀) and hydroxide P₀ (NaOH-P₀) on a savanna Alfisol under continuous cultivation. The failure by conventional soil test P (STP) methods to extract NaOH-P₀, for example, can result excessive fertilization
rates recommended. Several other studies have shown that this P fraction can serve as a sink and reservoir for soil phosphorus (Beck and Sanchez, 1994).

**Figure 2.9** Modified Hedley sequential fractionation procedure for soil phosphorus (Pi, Po and Pt refer to inorganic, organic and total P, respectively) (Source: O'halloran et al., 1987)
2.4.3 Effects of soil management on P fractions

Crop management practices and land management can greatly affect the partitioning of soil P between the inorganic and organic phases and between the different P\textsubscript{i} and P\textsubscript{o} fractions. Some of the main effects are outlined below.

2.4.3.1 Arable systems and tillage methods

Under arable agriculture, conventional tillage typically results in a decline in soil organic matter content (Selles \textit{et al.}, 1999; Dominy \textit{et al.}, 2001; Dominy and Haynes, 2002). Tillage breaks up soil aggregates and exposes organic matter to microbial attack which was previously physically protected within the aggregate structure. As a result, arable soils under conventional tillage generally have lower organic matter contents than their equivalents uncropped counterparts (Agbenin and Goladi, 1998). Beck and Sanchez (1994) observed a decline in NaHCO\textsubscript{3}-P\textsubscript{o} and NaOH-P\textsubscript{o} in soils under cultivation with a concomitant increase in P\textsubscript{i} the pools. This reflected the mineralization of organic P and its accumulation in P\textsubscript{i} fractions.

Compared to conventional tillage methods, under reduced and zero tillage systems there is an accumulation of organic matter in the surface few cm of soil because the main organic matter inputs are at, or near, the soil surface (Selles \textit{et al.}, 1999). Crop residue management is also an important consideration. Cropping systems where large amounts of crop residues are retained promote accumulation of P in P\textsubscript{o} fractions (Agbenin and Goladi, 1998).

2.4.3.2 Pasture systems

Accumulation of organic P fractions under improved pasture systems when compared to the cultivated sites is common (Condron and Goh, 1989). This is expected because of the large organic matter inputs particularly via turnover of the large, ramified grass root system (Tidsale \textit{et al.}, 1985). Large quantities of plant debris and animal faeces returned to the soil may increase soil organic residues hence, stimulating biological immobilization of soil inorganic P (P\textsubscript{i}) (Condron and Goh, 1989; Agbenin and Goladi, 1998). Some of the inorganic P taken up during the
growth phase of pasture plants is returned to the soil and accumulates in soil organic P forms such as inositol phosphates, nucleic acids and phospholipids (Turner et al., 2003).

In comparison with undisturbed grassland systems, plant productivity is increased under improved pastures due to the use of improved pastures species and the application of lime, fertilizers and irrigation (Condron and Goh, 1989). As a result, there is increased accumulation of soil organic P whilst fertilizer P applications tend to elevate P_i levels. Oberson et al. (1999) observed that in comparison with native savanna, improved pastures maintained higher labile P_o compounds (phosphanates and diester P). The hydroxide –extractable P fraction was found to be most affected by pasture improvement.

2.4.3.3 Phosphate fertilizers

Phosphate fertilizer applications improve soil P status and as a result P_i fractions generally increase (Stewart and Tiessen, 1987; Beck and Sanchez, 1994). In some cases, where soil organic matter is also accumulating, there is also an accumulation of P in P_o fractions.

Stewart and Tiessen (1987) concluded that the inorganic P fertilization results in P_o accumulation only when organic C and N supplies are abundant, whereas inorganic P_i accumulation is a general occurrence. Application of inorganic P fertilizer was found by O'halloran et al. (1987) to result in significant increases in some labile P fractions (resin- and NaHCO_3 – P_i), but to have no effect on NaHCO_3 – and NaOH-P_o in a Brown Chernozemic loam soil. Schmidt et al. (1996) observed accumulation of fertilizer P in the resin- P_i pool at moderate fertilizer rates. Where fertilizer P inputs were in excess of crop uptake, they also observed P accumulation in the NaHCO_3-P_i and NaOH-P_i fractions. The significance of soil texture in P distribution in the soil was confirmed by Tiessen et al. (1983). They observed that in cropped soils with limited P inputs, the decline in P status was mainly characterized by decreases in the inorganic P fraction in a coarse textured soil, whereas in fine textured soil, the decline was exclusively linked to decreases in the organic P fraction.
2.4.3.4 Organic amendments

Increased P availability resulting from organic manure addition is widely reported (Iyamuremye et al., 1996; Zhang and MacKenzie, 1997). Several mechanisms have been implicated in the increase in resin extractable P by organic amendments; (1) mineralization of the residues releases inorganic and labile organic P (Tisdale et al., 1985), (2) during decomposition processes, soil microorganisms release organic molecules which can form complexes with soil solution Al and Fe, thereby reducing its solubility, (3) adsorption of Al on organic residues surfaces, and (4) precipitation of Al with hydroxyl (OH⁻) ions from redox and ligand exchange reactions (Hue, 1992).

Results from several studies have shown that manure addition tends to decrease NaOH-Pi (Agbenin and Goladi, 1998; Zhang and MacKenzie, 1997). This trend can be explained by considering that hydroxide extractable Pi (NaOH-Pi) is associated with Fe and Al components of soil surfaces. As already noted, manure addition would tend to decrease P sorption on these surfaces, mainly because of the competition between phosphate ions and organic materials for adsorption sites (Hue, 1991).

Additions of manure often result in accumulation of soil organic matter and thus an accumulation of organic P (O'halloran, 1993). Qian and Schoenau (2000) found that a single application of liquid swine manure on an Orthic Black Chernozem (pH 7.3) had no effect on the most labile P fractions (resin- and NaHCO₃-Pi), but significantly increased the moderately labile and stable fractions. As they increased incubation time, the concentrated HCl-Po and residual P significantly increased at the expense of NaOH-Po and dilute HCl-Pi. In a related study, Hedley et al. (1982) also reported increases in residual P with incubation time.

2.4.4 Soil test extractants for P

Soil test procedures for P determine the amount of potentially plant available P present in the solution and in labile Pi pools. Plant available P can be inorganic and partly organic, and is usually estimated using bicarbonate solution or dilute acid extracting solutions (Olsen and Sommers, 1982; Paul and Clark, 1989). Commonly
used extraction methods are Mehlich 1 and 3, Bray 1 and Olsen procedures are widely used (Olsen and Sommers, 1982). However, $P_i$ and $P_o$ fractions not measured by these extraction methods contribute to solution P levels and influenced by various soil amendments (Anderson, 1980; Richards et al., 1995).

The Bray 1 extractant (0.03 M NH$_4$F and 0.025 M HCl) is designed to remove the easily acid-soluble P, largely calcium phosphates, and iron and aluminium phosphates. In general, the method is suited for acidic soils (Olsen and Sommers, 1982). The extraction procedure promotes desorption of soil P by increasing soil Fe and Al activity and formation of FeF$_4^-$ and AlF$_4^-$ (Chang and Jackson, 1957). Re-adsorption of soluble P onto colloids is reduced by the action of F$^-$ in the extraction solution (Bray and Kurtz, 1945). Although this extractant performs well in acidic soils, its effectiveness in calcareous soils and soils of high CEC is limited. Under calcareous conditions, CaCO$_3$ neutralises the acid in the extraction solution and CaF$_2$ formed by the reaction between Ca$^{2+}$ and F$^-$ rapidly immobilises P.

The Mehlich III is a modification of the Mehlich II extractant (0.015 M NH$_4$F, 0.2 M CH$_3$COOH, 0.25 M NH$_4$NO$_3$, 0.013 M HCl) and also serves as a multi-element soil extracting solution. The reaction of this extractant in the soil is similar to the Bray I method in that F$^-$ in the extracting solution forms AlF$_4^-$, allowing release of phosphates associated with aluminium into solution. Acetic acid in the Mehlich III reagent reacts with calcium phosphates in the soil to remove P but is less aggressive than equivalent mineral acids. Additionally, it is neutralised less by calcium phosphates than the Bray I extractant.

The Olsen method of soil P determination is effective in both saline and acidic soils. The extractant is 0.5 M NaHCO$_3$, buffered at 8.4 (Olsen et al., 1954). In calcareous soils CO$_3^{2-}$ interacts with Ca$^{2+}$ and precipitates as CaCO$_3$. The change in equilibrium causes a release of P from calcium phosphates, very much similar to P uptake by plant roots under calcareous soils. In acid soils an increase in OH$^-$ concentrations causes Al complex formation and precipitation of iron to Fe$_2$O$_3$. The decrease in solution Al and Fe causes a disequilibrium, which prompts the release of phosphate from oxides minerals.
2.5 Conclusions

P can be strongly adsorbed on sesquioxide surfaces, but P deficiency also occurs in alkaline soils through fixation on calcium carbonate surfaces. In acid soils, P bioavailability is regulated by the chemistry of variable charged sesquioxide surfaces, and to a lesser extent by phyllosilicates. Phosphate ions are strongly adsorbed on these surfaces through specific and/or non-specific mechanisms.

Adsorption of soluble humic materials and organic acids to Al and Fe oxides surfaces decreases the amount of P adsorption sites, and therefore reduces P fixation capacity of acid soils. Efficiency of organic anions on reduction of phosphorus sorption is in part related to their molecular structure, but is also related to the pH of the system. Release of soluble P during organic matter decomposition saturates adsorption sites so that added fertilizer P is taken up by plants.

Long-term fertilizer and manure inputs enhance accumulation of labile P\textsubscript{i} in the surface soil (McKenzie \textit{et al.}, 1992; Beck and Sanchez, 1994; Buehler \textit{et al.}, 2002). Continuous cropping systems without P fertilization decrease soil P fertility. Soil microbial P and organic P (which are very important P sources especially under organic farming systems) are enhanced by agronomic practices that promote soil organic matter accumulation.

Comparative studies of soil P dynamics in forest, pasture and arable sites are limited. Most studies have individually investigated the impacts of cropping practices such as fertilization, crop rotations and tillage, on soil P distribution in pools. There are relatively few studies on the combined effects of cropping sequences and nutrient sources on P forms, especially on a long-term basis. The Hedley P fractionation procedure uses reagents to isolate various pools of inorganic and organic soil P. It extracts readily-available P\textsubscript{i} and labile P\textsubscript{o} fractions and then sequentially extracts the less labile or stable forms. It can be a powerful tool in estimating the interaction of land use systems and management on soil P status. Previous workers (Dominy \textit{et al.}, 2001; Dominy and Haynes, 2002) have identified sites with long-term histories that represent the main agricultural land uses present in the Midlands of KwaZulu-Natal. Thus, application of the Hedley fractionation
technique to soils at the above sites could provide valuable information on the P status of agricultural soils of KwaZulu-Natal.
CHAPTER 3
PHOSPHORUS FRACTIONS IN SOILS UNDER CONTRASTING LONG-TERM AGRICULTURAL MANAGEMENT PRACTICES

3.1 Introduction

Long-term agricultural management practices have a significant impact on soil biological, physical and biochemical properties, usually through the changes in soil organic matter (SOM) and nutrient balances (Lupwayi et al., 2005). Focus on understanding phosphorus (P) fluxes in soils in terms of plant availability is mainly because of its agricultural importance and potential to pollute water resources (O’halloran, 1993). Consequently, effects of contrasting agricultural systems on the distribution and forms of P have been investigated for a large variety of soils under different climatic conditions (Sharpley, 1985; O’halloran et al., 1987; Iyamuremye et al., 1996; Agbenin and Goladi, 1998; Buehler et al., 2002).

Without P fertilization, plant available P is maintained primarily by the microbially mediated mineralization of SOM (Stewart and Tiessen, 1987). However, only small amounts of organic P (Po) are mineralized annually in P deficient soils (Tisdale et al., 1985), so that only a small portion of P bound to organic matter is plant available annually. Lime and P applications are key components for increasing crop productivity on acidic soils (Haynes and Mokolobate, 2001). Long-term application of P fertilizer and manure to agricultural soils increases organic (Po) and inorganic (Pi) P near the soil surface (McKenzie et al., 1992), but the effects can also extend deep into the soil profile (Zheng et al., 2004a). Improvement in soil fertility increases microbial activity and the potential for SOM mineralization and, consequently, may induce transformation of P into microbial, organic, or inorganic forms (Sharpley, 1985).

Maize growers in the midlands region of KwaZulu-Natal are rapidly adopting conservation-tillage systems due to enhanced soil water conservation and loss in soil quality associated with the conventional tillage practices. Well managed arable crops under zero-tillage tend to favour an accumulation of SOM and organic P in the surface layer of soil due to large quantities of crop residues being returned and the
residual effect of fertilizers (Condron and Goh, 1989). Long-term crop rotations which include large N and P fertilization inputs can also have a positive effect on P cycling in cultivated soils through accumulation of P in the soil as well as stimulation of microbial activity (Dalal, 1998; McLaughlin et al., 1988).

A method developed by Hedley et al. (1982) fractionates soil P into five inorganic and three organic fractions. Such a fractionation procedure makes it possible not only to discern the distribution of P between inorganic and organic forms but also to understand the distribution of P within these broad categories into labile, moderately labile and recalcitrant forms. The use of such fractionation procedures has led to an improved understanding of the fate and transformations of added P in agricultural soils (Ball-Coelho et al., 1993; Buehler et al., 2002).

Maize (Zea mays L.), sugarcane, dairy farming, forestry and rangeland are the main agricultural land uses in the midlands region of KwaZulu-Natal (Dominy et al., 2001). The management and cycling of P is likely to differ among these land use forms because the main crops have different P requirements and patterns of uptake and they have different effects on SOM content (Haynes et al., 2003). There are also differences in the amounts of P exported at harvest, and returned to the soil through crop residues. Thus, developing appropriate P management strategies will require a good understanding of the effects of land use forms and management practices on soil P pools. Efficient P cycling and synchronization of P release from organic sources with plant P requirements could reduce fertilizer requirements. In this study, the effects of land use and management practices on soil P fractions were measured using a modified Hedley P extraction procedure (Tiessen and Moir, 1993).
3.2 Materials and methods

3.2.1 Sites description and location

The surface layers (0-5 cm) of soils used in this study were sampled in January 2005 from long-term agricultural fields situated at "Baynesfield Estate" (27°22'S, 30°45'E) and Cedara Agricultural Research Station (29°32'S, 30°17'E), which were designated location 1 and 2, respectively. The climate in the region is sub-humid, warm and consists of summer rainfall and cool, dry winters. The mean annual rainfall for both locations is approximately 880mm. The two locations have the same soil type which is classified as Hutton form (Farmingham series), with a clay content of about 62 % (Soil Classification Working Group, 1991). This well-drained soil is an equivalent of the Rhodic Ferralsol (FAO), or Oxisol (USDA). Its mineralogy is dominated by kaolinite and halloysite, but also has high proportions of crystalline sesquioxides, gibbsite and inter-layered chlorite. Some chemical properties of the soil at each site are presented in Table 3.1.

Undisturbed native sites were identified on unused parts of each farm by Haynes et al. (2003). These sites consisted of shrubs and native grasses, and the burnt grass residue on the soil surface indicated that veld fires had periodically passed through both sites. All of the agricultural fields have a history of fertilization and liming. Typical annual application rates to pasture and arable fields are approximately 100 – 300 kg N ha⁻¹, 50 – 150 kg K ha⁻¹ and 25 – 50 kg P ha⁻¹. Typical application rates for forest soils are approximately 50 – 100 kg N ha⁻¹, 10 – 60 kg K ha⁻¹ and 10 – 25 kg P ha⁻¹ (Haynes et al., 2003). The maize, sugarcane (burnt before harvest), ryegrass and kikuyu pasture sites were irrigated during the dry winter months. At Baynesfield, the permanent kikuyu (Pennisetum clandestinum) and ryegrass (Lolium perenne) pasture were no longer intensively managed or grazed, but at Cedara, pastures were rotationally grazed with dairy cows. Annual ryegrass at both sites was annually cultivated and reseeded whereas kikuyu pasture remained uncultivated for a long time. A summary of the nature of the experimental fields at the two sites is presented below.
Site 1 (Baynesfield ‘Estate’ Farm)
1. >50 years permanent kikuyu (*Pennisetum clandestinum*) pasture
2. >50 years annual ryegrass (*Lolium multiflorum*) pasture
3. >30 years continuous sugarcane (*Saccharum spp.*) burnt before harvest
4. >30 years continuous maize (*Zea mays*) (conventional tillage, CT)
5. >20 years gum (*Eucalyptus grandis*) forest
6. >20 years pine (*Pinus patula*) forest
7. Undisturbed native grassland

Site 2 (Cedara Agricultural Research Station)
1. >50 years permanent kikuyu (*P. clandestinum*) pasture
2. >50 years annual ryegrass (*L. multiflorum*) pasture
3. >25 years continuous maize (*Zea mays*) (conventional tillage, CT)
4. >25 years continuous maize (zero tillage, ZT)
5. >20 years gum (*E. grandis*) forest
6. >20 years pine (*P. patula*) forest
7. Undisturbed native grassland

3.2.2 Soil sampling and analyses

Three separate, randomly chosen plots (approximately 120m x 30m) were selected within each field or forest area. Within each plot, 20 soil samples were taken randomly to a depth of 5 cm. Samples from each plot were bulked to give three replications per land use. The bulked field moist samples were sieved (<0.5 mm), air-dried and then stored for subsequent laboratory analysis. For microbial analyses, samples were re-moistened to field capacity and incubated for 2 weeks prior to analysis.

Soil pH was measured with a glass electrode in 0.1M KCl, using a 1:2.5 (w/v) soil:solution ratio (Rowell, 1994). Total organic C was determined by the Walkley and Black oxidation method (Olsen and Sommers, 1982). Extractable P and exchangeable cations in soil samples were analysed by routine soil testing methods at the KwaZulu-Natal Department of Agriculture Cedara laboratory. Exchangeable Ca and Mg were extracted with 1M KCl (1:10 soil:solution ratio for 10 minutes).
Exchangeable K and extractable P were extracted with AMBIC reagent [0.025M NH₄HCO₃; 0.01M NH₄F; 0.01M EDTA (ethylenediaminetetra-acetic acid) at pH 8.0] using a 1:10 soil: solution ratio for 10 minutes. In the extracts, Ca, Mg and K were analysed by the atomic absorption spectrophotometry and P by the molybdenum blue method.

Microbial biomass P (P_{mic}) and C (C_{mic}) were estimated on pre-incubated samples (2 weeks), based on the difference between extractable P and organic C contents of chloroform-fumigated and unfumigated soil samples. Soils were extracted with the Bray 1 P extractant (0.03M NH₄F, 0.025M HCl) (Olsen and Sommers, 1982) and 0.5M K₂SO₄ (C_{mic}) (Vance et al., 1987) respectively. K factors of 0.34 and 0.38 were used to calculate the microbial P and C pools, respectively.

A modified version of the Hedley et al. (1982) procedure was used to fractionate soil P and is schematically presented in Figure 2.9. After shaking the soil solutions with the various extracting reagents for 16 h and centrifugation at 10,000 rpm for 10 minutes, the aliquots were filtered through 0.45mm filter discs. Aliquots of the NaHCO₃ and NaOH extracts were acidified with 0.1 – 0.3 ml 0.9 M H₂SO₄ to precipitate the extracted organic matter and the inorganic phosphate in all the extracts was determined colometrically with the molybdate-blue method. Aliquots of the 0.5M NaHCO₃ (pH 8.5), 0.1M NaOH, 0.5 M HCl, and concentrated HCl extracts were digested in the autoclave (103.4 kPa, 121 °C) by acidified ammonium persulfate oxidation and analysed for total P (Tiessen and Moir, 1993). Organic P in the extracts was calculated from the difference between total P and Pi. All laboratory analyses were carried out in duplicate. Concentrated H₂SO₄ and H₂O₂ were used to digest the residue containing insoluble Pi and the most stable Pₜ forms (Residual-P). P in the resulting digested solution was analysed as outlined above.

Statistical analyses of data were carried out using the Genstat 8 package. The data were analysed as a completely randomised design with three replications (Nsabimana, 2002) although the land use types were not truly replicated within a formal experimental design.
3.3 Results

Some chemical properties of the soils are presented in Table 3.1. Land use forms and cropping practices had significant effects on soil organic matter status and soil pH. Pine forest soil had the highest pH in Baynesfield, and the lowest in Cedara. In general, the majority of soils collected from Cedara had a higher pH than those from Baynesfield. Soil pH in arable fields (maize and sugarcane) at site 1 was lower than that in the native grassland or other land uses. However, at site 2, pH values under maize, kikuyu and native grassland tended to be higher than those under the other land uses.

In both sites, arable crop production (sugarcane and maize) decreased organic C content by 30-50% relative to the control plots (Figure 3.1a and 3.2a). Cultivation (maize, CT and sugarcane) decreased organic C more than the zero-tillage (maize, ZT) (Figure 3.1a). Permanent pasture plots and forest soils (at site 1 only) showed significant accumulation of organic C above the undisturbed native grassland soils. At site 2, there was a loss of organic C under gum forest but not under pine. At both sites, extractable P was lowest under native grassland and of the other land uses, lowest under gum forest (Table 3.1). At site 1, sugarcane had very high extractable P levels. There were no obvious trends for exchangeable Ca and Mg with land use. At site 1, sugarcane and to a lesser extent kikuyu had high exchangeable K levels while at site 2, kikuyu had extremely high exchangeable K values (Table 3.1).

Microbial biomass C and P contents generally showed a similar trend with land use to organic C, and at both sites, permanent kikuyu pasture had the highest microbial biomass (Figures 3.1 and 3.2). At both sites, Pmic was considerably higher under native vegetation (24 – 27.2 mg P kg⁻¹) than maize cultivation (8.8 – 15.5 mg P kg⁻¹). Annual pasture in Cedara significantly reduced microbial biomass relative to the native soil, and maintained Pmic and Cmic levels similar to those under maize (ZT) (Figure 3.5a and b). Maize (CT) resulted in the lowest microbial biomass contents at both sites. Values for the microbial quotient (Cmic:Corg) followed a similar pattern with land use as microbial biomass C, and ranged from 0.52 to 1% (Figures 3.1b and 3.2b).
At Baynesfield, large differences in Resin-Pi, NaHCO$_3$-Pi and NaOH-Pi were observed due to differences in land use (Figure 3.3). For Resin-Pi and NaHCO$_3$-Pi kikuyu pasture and sugarcane clearly had the greatest values and values for maize were also elevated above those of the other land uses. For NaOH-Pi, trends with land use differed greatly from those of Resin-Pi and NaHCO$_3$-Pi. That is, greatest values were observed for maize although values for kikuyu pasture and sugarcane were still elevated above those for the other land uses. Kikuyu pasture had the greatest values for dilute HCl-Pi and concentrated HCl-Pi. Differences due to land use were less pronounced for concentrated HCl-Pi than for the other Pi fractions.

In comparison with the other land uses at Baynesfield, labile organic P (NaHCO$_3$-Po) was very high under kikuyu pasture (Figure 3.4a). There were also significant differences in NaOH-Po due to land use with sugarcane having the greatest values and maize the lowest. For concentrated HCl-Po, variations due to land use were not great with highest values being recorded for annual ryegrass and lowest values for maize.

At Cedara, Resin-Pi and NaHCO$_3$-Pi were clearly greatest under kikuyu pasture and not greatly affected by the other land uses (Figure 3.5a and b). For NaOH-Pi, values were greatest under kikuyu and clearly greater for other land uses than that under native grassland. A similar trend was observed for concentrated HCl-Pi. For the dilute HCl-Pi fraction, kikuyu pasture and pine forest soils had values that were elevated well above those of other land uses.

For NaHCO$_3$-Po, at Cedara, values followed the order: kikuyu pasture > native grassland > ryegrass pasture = maize (ZT) > maize (CT) = gum forest = pine forest (Figure 3.6a). For NaOH-Po, levels under maize (CT) and maize (ZT) were notably low and highest values were observed under native grassland. By contrast, for concentrated HCl-Po, values were highest under kikuyu pasture and maize (ZT) and lowest under ryegrass pasture, gum and pine forest.

A summary of the data from the P fractionation is presented in Table 3.2. Labile P [defined as easily extractable Pi (Resin-Pi plus NaHCO$_3$-Pi) plus readily mineralizable Po (NaHCO$_3$-Po)] was greatest under kikuyu pasture at both
Baynesfield and Cedara. At Baynesfield, lowest values were under native grassland but at Cedara lowest values were recorded under gum forest. Total extractable inorganic P was greatest under kikuyu and maize at Baynesfield and greatest under kikuyu at Cedara. At Cedara, values were also notably high under maize (CT) and (ZT). At both sites, highest values for total extractable organic P were recorded under kikuyu pasture. Organic P was also relatively high under native grassland at both sites and in the soil of these undisturbed sites, organic P accounted for 50% or more of the total soil P content. Residual P was greatest under kikuyu at Baynesfield and ryegrass at Cedara. In comparison with native grassland, residual P was similar or often greater under agricultural land uses at both sites.

The distribution of P between labile, moderately labile and stable P forms for the different land uses at the two sites is summarised in Figures 3.7 and 3.8. It is evident that at both sites there was a shift towards a greater percentage of P being present in the labile fraction (and concomitant decrease in the percentage contribution of the stable fraction) under kikuyu pasture. At site 1, this also occurred to a lesser extent under maize and sugarcane. At site 1 there was a notable increase in the percentage of P present in stable forms under gum and pine forest. However, at site 2, this trend was not evident.
<table>
<thead>
<tr>
<th>Land use</th>
<th>pH (KCl)</th>
<th>AMBIC extractable P (ppm)</th>
<th>Exchangeable nutrients (ppm)</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1 (Baynesfield)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Native grassland</td>
<td>5.0</td>
<td>5</td>
<td>1120</td>
<td>424</td>
<td>398</td>
<td></td>
</tr>
<tr>
<td>Kikuyu</td>
<td>4.9</td>
<td>68</td>
<td>1523</td>
<td>342</td>
<td>552</td>
<td></td>
</tr>
<tr>
<td>Ryegrass</td>
<td>4.7</td>
<td>8</td>
<td>1287</td>
<td>515</td>
<td>387</td>
<td></td>
</tr>
<tr>
<td>Sugarcane</td>
<td>4.9</td>
<td>161</td>
<td>1281</td>
<td>267</td>
<td>853</td>
<td></td>
</tr>
<tr>
<td>Maize (CT)</td>
<td>4.4</td>
<td>95</td>
<td>1103</td>
<td>240</td>
<td>423</td>
<td></td>
</tr>
<tr>
<td>Gum forest</td>
<td>4.3</td>
<td>7</td>
<td>674</td>
<td>259</td>
<td>185</td>
<td></td>
</tr>
<tr>
<td>Pine forest</td>
<td>6.4</td>
<td>15</td>
<td>2457</td>
<td>464</td>
<td>263</td>
<td></td>
</tr>
<tr>
<td>LSD (0.05)</td>
<td>1.3</td>
<td>12</td>
<td>476</td>
<td>57</td>
<td>178</td>
<td></td>
</tr>
<tr>
<td>Site 2 (Cedara)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Native grassland</td>
<td>5.2</td>
<td>6</td>
<td>1358</td>
<td>386</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Kikuyu</td>
<td>5.2</td>
<td>92</td>
<td>1762</td>
<td>538</td>
<td>1331</td>
<td></td>
</tr>
<tr>
<td>Ryegrass</td>
<td>4.3</td>
<td>25</td>
<td>941</td>
<td>195</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>Maize (CT)</td>
<td>5.3</td>
<td>19</td>
<td>931</td>
<td>249</td>
<td>275</td>
<td></td>
</tr>
<tr>
<td>Maize (ZT)</td>
<td>5.5</td>
<td>24</td>
<td>1699</td>
<td>433</td>
<td>413</td>
<td></td>
</tr>
<tr>
<td>Gum forest</td>
<td>5.0</td>
<td>15</td>
<td>2573</td>
<td>494</td>
<td>303</td>
<td></td>
</tr>
<tr>
<td>Pine forest</td>
<td>4.0</td>
<td>53</td>
<td>2783</td>
<td>391</td>
<td>411</td>
<td></td>
</tr>
<tr>
<td>LSD (0.05)</td>
<td>1.4</td>
<td>9</td>
<td>530</td>
<td>128</td>
<td>259</td>
<td></td>
</tr>
<tr>
<td>Land-use</td>
<td>Labile P</td>
<td>Total extractable organic P</td>
<td>Total extractable inorganic P</td>
<td>Residual P</td>
<td>Total P</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>----------</td>
<td>----------------------------</td>
<td>-------------------------------</td>
<td>------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td><strong>Site 1 (Baynesfield)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Native grassland</td>
<td>87</td>
<td>666 (51) (^4)</td>
<td>217 (17)</td>
<td>426</td>
<td>1309</td>
<td></td>
</tr>
<tr>
<td>Kikuyu</td>
<td>897</td>
<td>1366 (45)</td>
<td>1006 (33)</td>
<td>643</td>
<td>3015</td>
<td></td>
</tr>
<tr>
<td>Ryegrass</td>
<td>114</td>
<td>760 (52)</td>
<td>303 (21)</td>
<td>386</td>
<td>1449</td>
<td></td>
</tr>
<tr>
<td>Sugarcane</td>
<td>451</td>
<td>586 (28)</td>
<td>968 (47)</td>
<td>513</td>
<td>2067</td>
<td></td>
</tr>
<tr>
<td>Maize (CT)</td>
<td>254</td>
<td>247 (13)</td>
<td>1190 (63)</td>
<td>430</td>
<td>1867</td>
<td></td>
</tr>
<tr>
<td>Gum forest</td>
<td>113</td>
<td>452 (36)</td>
<td>269 (21)</td>
<td>533</td>
<td>1254</td>
<td></td>
</tr>
<tr>
<td>Pine forest</td>
<td>105</td>
<td>516 (37)</td>
<td>347 (25)</td>
<td>550</td>
<td>1413</td>
<td></td>
</tr>
<tr>
<td><strong>Site 2 (Cedara)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Native grassland</td>
<td>113</td>
<td>1115 (63)</td>
<td>240 (13)</td>
<td>411</td>
<td>1766</td>
<td></td>
</tr>
<tr>
<td>Kikuyu</td>
<td>464</td>
<td>1119 (27)</td>
<td>2505 (61)</td>
<td>456</td>
<td>4080</td>
<td></td>
</tr>
<tr>
<td>Ryegrass</td>
<td>140</td>
<td>783 (33)</td>
<td>972 (41)</td>
<td>644</td>
<td>2399</td>
<td></td>
</tr>
<tr>
<td>Maize (CT)</td>
<td>119</td>
<td>516 (26)</td>
<td>1097 (55)</td>
<td>389</td>
<td>2002</td>
<td></td>
</tr>
<tr>
<td>Maize (ZT)</td>
<td>157</td>
<td>520 (25)</td>
<td>1089 (52)</td>
<td>467</td>
<td>2076</td>
<td></td>
</tr>
<tr>
<td>Gum forest</td>
<td>73</td>
<td>665 (38)</td>
<td>636 (36)</td>
<td>442</td>
<td>1743</td>
<td></td>
</tr>
<tr>
<td>Pine forest</td>
<td>112</td>
<td>845 (37)</td>
<td>1025 (44)</td>
<td>411</td>
<td>2281</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)Labile P = resin P + NaHCO\(_3\)-Pi + NaHCO\(_3\)-Po (Schmidt et al., 1996)
\(^2\)Total organic P = NaHCO\(_3\)-Po + NaOH-Po + conc. HCl -Po
\(^3\)Total inorganic P= resin P + NaHCO\(_3\)-Pi + NaOH-Pi + dilute HCl -Pi + conc. HCl -Pi
\(^4\)Values in parenthesis are percent contribution of each fraction to total P
Site 1 (Baynesfield)

Total Organic C (LSD = 6)

Soil microbial C (LSD = 152)

Soil Microbial P (Lsd = 3)

Figure 3.1 Effect of long-term land use on concentrations of total organic C and microbial biomass C and P in soils at site 1. Values for microbial quotient (microbial biomass C/ organic C) are shown in parenthesis above microbial biomass C histograms.
Site 2 (Cedara)

Total Organic C (LSD = 9)

Soil Microbial C (LSD = 183)

Soil Microbial P (LSD = 3)

Figure 3.2 Effect of long-term land use on concentrations of total organic C and microbial biomass C and P in soils at site 2. Values for microbial quotient (microbial biomass C/organic C) are shown in parenthesis above microbial biomass C histograms.
Site 1 (Baynesfield)

**Resin Pi (LSD = 3)**

- Kiowu
- Rye
- Sugar cane
- Maize (CT)
- Gum
- Pine
- Native

**NaHCO3-Pi (LSD = 44)**

- Kiowu
- Rye
- Sugar cane
- Maize (CT)
- Gum
- Pine
- Native

**NaOH- Pi (LSD = 53)**

- Kiowu
- Rye
- Sugar cane
- Maize (CT)
- Gum
- Pine
- Native

**Dilute HCl-Pi (LSD = 14)**

- Kiowu
- Rye
- Sugar cane
- Maize (CT)
- Gum
- Pine
- Native

**Concentrated HCl-Pi (LSD = 27)**

- Kiowu
- Rye
- Sugar cane
- Maize (CT)
- Gum
- Pine
- Native

**Figure 3.3** Effect of long-term land use on concentrations of inorganic P (Pi) extracted from soils at site 1 using a modified Hedley sequential fractionation procedure.
Figure 3.4 Effect of long-term land use on concentrations of organic P (Po) extracted from soils at site 1 using a modified Hedley sequential fractionation procedure.
Figure 3.5 Effect of long-term land use on concentrations of inorganic P (Pi) extracted from soils at site 2 using a modified Hedley sequential fractionation procedure.
Figure 3.6 Effect of long-term land use on concentrations of organic P (Po) extracted from soils at site 2 using a modified Hedley sequential fractionation procedure.
Figure 3.7 Effects of long-term land use at site 1 on the proportions of P present as labile \([\text{Resin-Pi} + \text{NaHCO}_3-(\text{Pi+Po})]\), moderately labile P \([\text{NaOH-(Pi+Po)} + \text{dilute HCl-Pi} + \text{concentrated HCl- (Pi+Po)}]\) and stable P (residual P).
Figure 3.8 Effects of long-term land use at site 2 on the proportions of P present as labile [Resin-Pi + NaHCO₃-(Pi+Po)], moderately labile P [NaOH-(Pi+Po) + dilute HCl-Pi + concentrated HCl- (Pi+Po)] and stable P (residual P).
3.4 Discussion

3.4.1 Soil organic matter content

Soil organic matter content (SOM) depends on the balance between the rates of input and losses of carbon from the soil. Differences in the organic C content in the various land uses can be related principally to the quantity and quality of plant material produced, and its removal or incorporation into the soil (Dalal, 1998).

Maize and sugarcane monoculture resulted in least soil organic C content at both sites (Figures 3.1a and 3.2a). Mechanized clearing of native grasslands for agricultural purposes can lead to compaction, reduction of infiltration and increase in surface run-off and erosion of surface soil. This results in a reduction in measured soil organic C content (Lal, 1997). In addition, tillage and intensive cropping following conversion from natural vegetation typically cause a decrease in organic C content through their effects on plant biomass returned to the soil and rate of oxidation and mineralization of SOM (Dominy et al., 2001). Cultivation increases SOM breakdown because it aerates and disrupts soil aggregates which exposes previously protected SOM to microbial degradation (Haynes and Beare, 1996).

Lower biomass input in arable soils is due to wider plant spacing, removal of the harvested crop, residue removal, and/or volatilisation of residue C during pre-harvest burning of sugarcane residues (Wood, 1985; van Antwerpen and Meyer, 1996). Robertson and Thorburn (2001) reported that when the trash is burnt, more than 80% of the organic matter and nutrient in the trash are lost. Despite more frequent cultivation of the maize (CT) field, it still maintained similar SOM (Table 3.1) to that under the sugarcane field probably because the sugarcane was pre-harvest burnt.

Moisture and nutrient deficiency can limit microbial activity, especially during the dry season (Degens, 1998). In contrast, irrigation and the addition of lime and
fertilizers (often N and P), undertaken to improve crop yields can increase soil microbial biomass (Neale et al., 1997). Nonetheless, lime-induced increases in organic matter loss have been reported previously (Balduck et al., 1994). Chana and Heenana (1999) found that most of the loss in organic C due to liming was in the light fraction (LF) because, although it was bound to macroaggregates, it was not physically protected from microbial attack. Higher soil pH in maize fields, particularly at site 2 (Table 3.1), possibly enhanced microbial activity and therefore increased the rate of SOM decomposition.

Maize (ZT) had significantly (P<0.05) higher organic C content than that of maize (CT) (Figure 3.2a). This reflects the results of 30 years of direct drilling and stubble retention. Other studies also showed greater accumulation organic C and P in surface soils (0-5cm) under zero-tillage than in conventional tillage (Paustian et al., 1997; Selles, et al., 1999). Under zero-tillage crop and weed residues are left at the surface to decompose. As a result there is a build up of soil organic matter close to the soil surface. In contrast, cultivation mixes crop residues into the surface layers and results in a more uniform distribution of organic C and nutrients in the plow layer (Powlson and Jenkinson, 1981; Haynes and Knight, 1989).

Long-term deposition of tree litter at the soil surface prior to harvesting and replanting of new forests increased organic C contents in forest soils. Relatively little SOM is lost because of infrequent and incomplete harvesting done on forest land. The organic matter on the 0-5 cm surface horizon and in the lower layers is maintained by relatively slow oxidation resulting from cool, shaded microclimatic conditions and from the lack of soil disturbance that occurs in arable soils. These factors may explain why pine and gum forest soils had a higher organic C content than native grassland soil in site 1 (Figure 3.1a). This was true for pine soils at site 2. Some forest litter also contains more lignin than grasses (Parton et al., 1997), hence its decomposition and oxidation occur at slower rates.
As expected, organic C content (Figures 3.1a and 3.2a) under permanent kikuyu pasture was much higher than in other land uses. Irrigation, liming and fertilization applications increase plant dry matter production under improved pastures (Haynes and Beare, 1996). Higher organic matter inputs in intensively managed pasture systems come from senescing plant materials (e.g. plant roots and tops), exudation of organic compounds from plant roots, and turnover of large microbial biomass found in the rhizosphere (Gregorich et al., 1994; Paustian et al., 1997). Thus, pasture crops provide higher and steady plant residue inputs than do arable crops. When grazed, more than 90 % of the P in the forages is recycled to the soil as animal excrement (Haynes and Knight, 1989; Sparling, 1992). Under permanent pastures annual tillage is not performed so organic matter decomposition is not favoured.

Organic C concentration in the annual ryegrass field at Baynesfield was higher than that at the native grassland, but the opposite was true for the annual pasture at Cedara. The effect of annual pasture on soil organic matter status will be the consequence of a balance between high organic matter inputs (particularly by the turnover of grass roots) and the destructive effect of annual tillage. Evidently, at Baynesfield, the greater organic matter inputs had a dominant effect while at Cedara the tillage effect dominated. Nevertheless, at both sites organic C content was greater under annual ryegrass than maize (CT) which reflects the greater organic matter inputs under pasture than maize.

3.4.2 Soil pH

Soil acidity can be a limitation to crop production in the study soils because they are naturally acidic. That is, at site 1, pH values under annual ryegrass, sugarcane, maize (CT) and particularly gum forest were below those of the native grassland. Similarly, at site 2, values under ryegrass, gum and pine forest were below those under native grassland. Soil acidification in agricultural soils is due to application nitrogen fertilizers and export of basic cations (Ca$^{2+}$, Mg$^{2+}$, K$^+$) from the soil through crop harvests (Yan et al., 1996).
Nitrification of NH$_4^+$ originating from N fertilizers and organic residues releases H$^+$ ions into the soil solution (Tisdale et al., 1985). As nitrate (NO$_3^-$) is leached down the profile Ca$^{2+}$, Mg$^{2+}$ and K$^+$ usually serve as the counter-ions. This leaves high concentrations of H$^+$ in the surface layer, hence the pH drops. Acidification in soils managed under zero tillage is often more pronounced than that under conventional tillage (Haynes and Knight, 1989) due to higher infiltration rates, which accelerate leaching of nitrate and basic counter-ions. However, the data (Table 3.1) shows that the maize (CT) and ZT had similar pH. This may be due to surface application of lime to both systems of tillage.

The low pH (3.77) of pine forest soil at Cedara is probably attributable to accumulation of cations in the tree biomass (Essex and Williams, 1993), leaching of basic cations and its relatively higher organic matter content (Figure 3.5 a). Organic matter decomposition can contribute to soil acidity due to CO$_2$ evolution and formation of carbonic acid, production of organic acids and chelates. Forest soils, as a rule have favorable soil structure for water infiltration, and this can promote leaching of basic cations to a greater extent than in agricultural soils (Allan and Chapman, 2001).

### 3.4.3 Soil microbial biomass C and P

Microbial biomass is linked to the availability of C and nutrients from decomposing organic matter (Selles et al., 1999). Consequently, Cmic and Pmic generally followed the same trend as organic C content (Figures 3.1 and 3.2). The accumulation of organic C in pasture and native grassland soils had a positive effect on soil microbial biomass. Fertilization, liming and irrigation of pasture fields have positive indirect effects on microbial biomass by enhancing plant growth and root exudates would increase microbial growth and activity (Merckx et al., 1985; Oberson et al., 1999). When the residues are incorporated either through cultivation or soil faunal activity (e.g. earthworms), plant litter P enters into the soil microbial biomass. Dalal et al. (1991) measured an increase in soil microbial biomass C and N due to N fertilization.
Arable fields had the least microbial biomass contents due to lower organic C contents, annual tillage (soil disturbance), and the falling effect during winter months (Alvarez et al., 1998). Regular pesticide, insecticide and herbicide applications could also potentially decrease microbial biomass size and activity (Dalal, 1998). The relatively low pH in arable soils at site 1 could have also contributed to lower microbial biomass size, as the microbial biomass is often related to pH and low biomass values are common in acidic soils (Vance et al., 1987). In an Alfisol, microbial biomass decreased due to 8 years of application of 80 kg N ha\(^{-1}\) to wheat, presumably due to lowering of soil pH (Ladd et al., 1994).

Maize (CT) fields generally had the least microbial biomass content at both sites (Figures 3.1 and 3.2). Zero-tillage increased the surface concentration of total organic C, microbial C and P and bio-available nutrients (P, Ca, K, Mg). Deposition of plant residues at the soil surface under ZT favours high soil microbial activity in the surface layers (Selles et al., 1999). Similarly, Doran (1980) showed that populations of bacteria, actinomycetes, and fungi increased 2-to 6 fold as a result of retaining crop residues on the soil surface. Networks of hyphae are more easily established in soil that is minimally disturbed than in soil under conventional tillage, and the microflora of soil under ZT is mainly dominated by fungi (Roper and Gupta, 1995). These factors make soil under long-term ZT systems a more favourable environment for microbial activity.

The microbial quotient can be a useful indicator of the influence of management practices on organic C because it responds more rapidly to changes in soil C than total organic C (Sparling, 1992). At both sites, permanent kikuyu pasture had the highest microbial quotient, which indicates greater labile C input under permanent dairy pasture. Our results show that the microbial quotient was generally low, ranging from 0.52 to 1% (Figures 3.1b and 3.2b), but within the range of reported values of 0.27 – 7% (Omay et al., 1997).

The high microbial biomass under kikuyu pasture, and to a lesser extent native grassland and exotic forests, is important for the productivity and long-term
sustainability of these land uses. This is because microbial biomass is a source of labile organic matter, a source and sink of major plant nutrients and an agent for break down of organic residues as well as the formation of humus (Dalal, 1998). Immobilisation of Pi by microbes and its gradual release via microbial turnover protects P from fixation into the less accessible P pools (Magid et al., 1996). Furthermore, a significant portion of microbial P (some obtained from sparingly-soluble Pi forms) is considered readily available for plant assimilation (Oberson et al., 2001).

3.4.4 Labile P (Resin-Pi, NaHCO$_3$-Pi, NaHCO$_3$-Po)

Low resin-P contents (Figures 3.3a and 3.5a) under native grassland in the studied soils support findings of many other studies that phosphorus (P) is an important limiting factor (next only to nitrogen) to the productivity of acidic soils. With no external inputs, the native vegetation relies on mineralization of Po and turnover of microbial biomass P to satisfy its P demands. Plants growing in P limited soils develop adaptive mechanisms to meet their P requirements. They are able to acquire poorly-soluble P by excreting chelating agents (Ae et al., 1990), increasing root surface area, or colonisation with mycorrhizal fungi (Loes and Ogaard, 2001).

The increases in extractable P and labile Pi fractions (resin and NaHCO$_3$-Pi) in soil under arable and pasture cropping systems are attributable to long-term P additions (Zhang and McKenzie, 1997). Repeated fertilizer P additions increase labile P, with more occurring as Pi than Po (McKenzie et al., 1992; Griffin et al., 2003). Zheng et al. (2004b) also reported an increase in the inorganic P (Pi) (resin-P, NaHCO$_3$-Pi, and NaOH-Pi) fractions on a Humic Gleysol under various cropping systems in soils amended with mineral fertilizer and liquid dairy manure.

Higher fertilization rates of pasture swards, and plant P uptake efficiency by forage plants significantly increased NaHCO$_3$-Pi concentration in kikuyu pasture relative to maize cultivated soil. Forage crops exude organic acids and enzymes
more than cereals such as barley, which enhances P uptake (Condron, 2004). Since NaHCO₃-Pi represents inorganic P weakly absorbed on surfaces (Lehmann et al., 2001), it is possible that forage plants dissolved more Pi from the solid phase into solution. In the long term, more soil microbial biomass under kikuyu soils may also mineralize more Po compared to maize cultivated soils (Table 3.1). It is also probable that fertilizer P rates to kikuyu pastures were greater than those to arable crops and over a 20-50 year period this resulted in greater accumulation of Pi and Po.

The labile NaHCO₃-Po fraction was particularly high under kikuyu dairy pasture (Figures 3.4a and 3.6a). The high concentrations of labile Po represent a high potential for mineralization and subsequent release of plant-available Pi (Tiessen et al., 1982). The high values under kikuyu pasture are presumably a reflection of the high rate of P cycling under a highly productive permanent grazed pasture. Not only is the pasture highly productive (above-ground production is about 10-16 Mg ha⁻¹ yr⁻¹) but most of the above-ground herbage P is recycled through the grazing cows and returned to the soil in the form of dung.

3.4.5 Moderately labile P (NaOH-Pi, NaOH-Po, dilute HCl-Pi, conc. HCl-Pi, conc. HCl-Po)

The moderately available pool was a significant characteristic of this soil, reaching 77 % of total extractable P in kikuyu pasture at site 2 (Figure 3.8). Accumulation of NaOH-Pi in arable (maize and sugarcane) and pasture soils indicates that annual P applications have resulted in accumulation of P in this fraction (Schmidt et al., 1996). It has been postulated that the chemical nature of the reaction products of water-soluble P fertilizers in soil is influenced by the predominant cations present (Tisdale et al., 1985). Thus, in the studied soils, added Ca phosphate fertilizers are mainly converted to adsorbed and mineral forms of P associated with Fe and Al, whereas in calcareous soils, major reaction products are mainly calcium bound forms of P (Sample et al., 1980). Indeed, the
concentration of NaOH extractable Pi is often positively correlated with the Fe and Al oxide contents (Delgado and Torrent, 2000).

Soil NaOH-Pi is considered to be held strongly by chemisorption to amorphous Fe and Al minerals (Tiessen et al., 1984) and is considered as moderately labile soil P (Lehmann et al., 2001). Consequently, large NaOH-Pi contents in the studied soils can be related to their high concentrations of ammonium-oxalate-extractable Al and Fe (Dekkers, 1971; Soil Classification Working Group, 1991).

Figure 3.5c show that the conventionally tilled maize plot had a higher concentration of NaOH-Pi as the zero-tilled plot. Under ZT systems, fertilizer is surface-applied and accumulates near the soil surface whilst under CT fertilizer is mixed intimately with the soil during tillage operations. Lack of fertilizer incorporation minimises contact between fertilizer granules and the soil surfaces, and therefore lowers P fixation of the applied P to oxides and mineral surfaces. Thus soils under maize (ZT) had higher concentrations of Resin-, and NaHCO$_3$-Pi and lower concentrations of NaOH-Pi than those under maize (CT). Additions and retention of lime on the surface layer of a zero-tilled soil may also tend to reduce P fixation hence lower the size of NaOH-Pi fraction. That is, the higher pH under ZT would have tended to inhibit P adsorption and favour P desorption.

The large quantities of NaOH-Pi and HCl-Pi in surface layers of unfertilized forest soils can be partly related to activities of macroorganisms. The burrowing effects of earthworms may deposit unweathered mineral particles near or on the soil surface. Mobilization of these unweathered primary mineral particles from deeper layers of the soil can contribute small amounts of concentrated HCl-P in the upper soil layers because P in this fraction is considered to form part of the structure of primary minerals (Guo and Yost, 1998). P that is released by earthworm activities may also be fixed to Fe and Al hydroxides, and consequently increase NaOH-Pi and HCl-Pi. These processes may well have also been operative in the commercial exotic forests used in the present study.
Nonetheless, accumulation of NaOH-Pi in forest soils, particularly in site 2, likely to have been primarily as a result of fertilizer P additions.

The sparingly soluble Ca-bound P fraction (dilute HCl-P) was typically low in most of soils but its concentration was elevated under kikuyu and pine forest at both sites (Figures 3.3d and 3.5d). The reason for this is unclear since, with the exception of pine forest at site 1, these sites did not have particularly high pH values (which would favour accumulation of Ca-bound P). Perhaps some of this fraction represents residual fertilizer Pi.

Enhanced mineralization of organic Po under cultivation invariably leads to a decline in Po fractions, and in this study the decline was greater under maize (CT) than maize (ZT) (Figure 3.6). For example, the proportion of total extractable Po constituted 25 and 39% of total P in the maize (CT) and maize (ZT), respectively. The decrease in Po pools despite P fertilization of maize and annual pasture systems are consistent with studies from temperate grassland soils reviewed by Stewart and Sharpley (1987) which showed that soils under cultivation decreased Po due to mineralization. Such a finding is not surprising since a decrease in the organic C content under arable agriculture, as noted previously, would be expected to result in an associated decrease in Po. Interestingly, this decline in Po occurred concomitantly with increases in NaHCO\textsubscript{3}-Pi and NaOH-Pi. Organic P released from decomposing plant residues can be rapidly mineralized in cultivated soils thus increasing NaHCO\textsubscript{3}-Pi (Zheng et al., 2004b). It is observed that liming increased soil pH in Cedara maize fields (Table 3.1), and in turn, this could have enhanced microbial activity and microbial demands for carbon substrate and nutrients (including P), thereby accentuating mineralization of organic matter and Po (McKenzie et al., 1992). It is, therefore, possible that mineralization of Po resulted in the increases in resin-Pi, NaHCO\textsubscript{3}-Pi and NaOH-Pi, particularly in kikuyu, maize and annual ryegrass fields (Figures 3.3 and 3.5). Nonetheless, a substantial proportion of these increases in moderately labile Pi fractions are likely to have originated directly from dissolution of fertilizer P and its subsequent reactions with soil components.
The proportion of organic P in the labile and moderately labile P pools in the soil surface increased significantly under kikuyu. This was expected because the annual addition of crop residue to soils in pasture is greater than under arable systems and there was a substantial accumulation of organic matter under kikuyu. Eventually, the net rate of Po accumulation due to long-term fertilization of pasture slows down as a result of increasing mineralization so that in the long-term, the rate of Po formation is balanced by the rate of Po mineralization (Anderson, 1980). According to Sharpley and Smith (1985), the accumulation in moderately labile Po indicates a general improvement in soil P fertility under cultivation.

3.4.6 Stable P pool (residual P)

Fertilizer P applications increase the soluble or labile P pools in the short term, but this P can be transformed into moderately labile and non-labile P pools over a period of time (Sample et al., 1980). In addition, crop utilization of inorganic phosphorus fertilizers in the first year is generally less than 25% (Wagar et al., 1986), which leaves fertilizer residues to accumulate as various forms. Accumulation of residual P (occluded P) above the control occurred in many of the soils (Table 3.2). Increases in residual P are due to slow reactions, which continually remove P from the soil solution (Henry and Smith, 2004). Thus, a build up of residual P may represent a loss of the effectiveness of P fertilizer applications because as this fraction increases, it diminishes the availability of the residues of past P fertilizer applications to plants (Barrow, 1980). Nonetheless, in limed acidic soils, the residual Pi can contribute significantly to crop growth through the formation of unstable labile inorganic Ca phosphates (Lookman et al., 1996). It is important to note here that residual P also includes very stable, complexed organic P (Beck and Sanchez, 1994). Thus, part of the residual fraction that has accumulated is in organic that are not readily mineralizable.
3.4.7 Relative contribution of Po and Pi

Whilst agricultural land use had both positive and negative effects on the total extractable organic P content of soils (depending upon its effect on soil organic matter content) it caused clear increases in total extractable Pi at both sites. This reflects the fact that inorganic P is applied to agricultural soils regularly and that this P tends to accumulate preferentially in the Pi fractions (McKenzie et al., 1992; Selles et al., 1995; Griffin et al., 2003). Under native grassland, organic P made up 51% of total P at Baynesfield and 63% at Cedara (Table 3.2) showing the importance of this form of P in natural systems (Beck and Sanchez, 1994; Dalal, 1998). Slow mineralization of this Po provides Pi for plant growth. Interestingly, total extractable Pi made up only 17 and 13% respectively of total soil P under native grasslands at Baynesfield and Cedara. By contrast, it made up over 50% of total P in some agricultural land uses which again underlines the increased significance of Pi pools under agricultural management.

A similar trend was observed between organic C and NaOH-Po for land uses at both sites (Figures 3.1, 3.2, 3.4, and 3.6). The NaOH-Po is primarily derived from humic compounds generated from plant-residue decomposition (O'halloran et al., 1987; Selles et al., 1999). Thus, the amount of organic matter and its rate of humification can be expected to influence the content of NaOH-Po fraction. Organic C declined more under maize (CT) than maize (ZT) and that tendency was also evident in total extractable Po (Table 3.2). For example, total organic P constituted 25 and 38%, respectively of total P in the maize (CT) and maize (ZT) treatments.

3.5 Conclusions

Conversion from natural vegetation to long-term agricultural production led to changes in soil properties. The results provide evidence that when native grasslands are brought under long-term maize and sugarcane production, with no return of residues, there is an appreciable breakdown of soil organic matter
(SOM). In contrast, long term pasture and forestry result in maintenance or accumulation of SOM.

High concentrations of total P have accumulated in the surface horizon (0-5cm) of agricultural soils due to intensive P fertilization, in part because P is generally immobile in soil. In the fertilized systems, total P was higher and P accumulated preferentially in the inorganic fractions. P composition of the native vegetation was dominated by organic P (Po) forms, with a major portion of Po in the moderately available pool. As expected, organic P content of soils showed a broadly similar trend to that for organic C, decreasing under maize/sugarcane, increasing under kikuyu pasture and being maintained or decreased under exotic forests. Application of a modified Hedley fractionation procedure showed that agricultural land management greatly affected the distribution among the various pools. Resin-Pi and NaHCO₃-Pi (the potentially available Pi pools) showed similar trends with land use being notably elevated under kikuyu pasture at both sites and under sugarcane and maize at one site. This presumably reflects regular P applications at these sites in the recent past. Concentrations of NaOH-Pi showed different trends to Resin-Pi and NaHCO₃-Pi since this fraction represents strongly-adsorbed Pi that may have originated from Pi applied or mineralized some time ago that has become strongly bound to metal oxide surfaces. A large portion of the P that had accumulated in organic form under kikuyu pasture was present in the NaHCO₃-Po fraction. This fraction also contributed greatly to the loss of soil organic P that occurred under arable cropping, confirming that it is a labile form of organic P.

The focus of this project was on the 0-5 cm surface layer of the soil. Further investigation is required to the effects of these practices at deeper soil depths, because effects of cropping systems and nutrient sources on P forms have been reported to extend deeper into the soil profile (Zheng et al., 2004a). Short-term (0-5 years) observations can also provide further information on the rate of accumulation and the nature of P applied to soil.
CHAPTER 4
EFFECTS OF ORGANIC AND INORGANIC SOIL AMENDMENTS ON PHOSPHORUS FRACTIONS

4.1 Introduction

Soil acidity is a serious constraint to crop production in the sub-Saharan African soils (Chepkwony et al., 2001). In addition, highly-weathered acid soils are generally rich in Al and Fe hydrous oxides and therefore have a high P fixing capacity (Moller et al., 2000). Thus, applications of lime and fertilizer P (often at high rates) to such soils are frequently necessary for crop production (Haynes and Swift, 1988). When P is added to acidic soils, it is often adsorbed by soil colloids, accumulating in inorganic forms (Pi) with different degrees of plant availability (Sanchez and Uehara, 1980). The high cost and other socioeconomic constraints to the use of inorganic P fertilizers have generated considerable interest in the utilization of organic amendments. Hue (1990) reported that inorganic P fertilizers were more efficiently utilized by crops when applied with organic amendments such as green manure or animal wastes.

Large amounts of animal manure are produced as wastes from housed animal operations in South Africa. For example, poultry production is concentrated in confined feeding operations. There is also an increasing trend for beef production to be carried out in intensive feedlot operations. Large quantities of manures from poultry enterprises and feedlots are therefore available to be applied to local arable and pasture fields. If the plant requirement for N is used as the primary consideration for manure application, P tends to be oversupplied and it accumulates in soils (Tisdale et al., 1985).

The behaviour of P in amended soils is an important component for making nutrient management plans that maximize economic benefits and minimize environmental risks. Often, the tendency is to manage soil organic amendments based on the total P content. This approach would be justified if P in organic...
residues behaved similarly to that in inorganic fertilizers. However, it is known that P in organic residues is present in a number of forms (Sharpley, 1985).

Incubation experiments with organic and inorganic P inputs have shown that it is possible to study the transformation and distribution of added and native soil P into different pools after various incubation times (Hedley et al., 1982; Adams and Odom, 1985; Sharpley and Moyer, 2000). P transformation in incubated soils depends on factors such as P forms and application rates, incubation time and temperature, and soil properties (McLaughlin and Champion, 1987; Adeli et al., 2005).

P fractionation procedures that divide inorganic and organic P into fractions of various origins and availabilities (e.g. Hedley et al., 1982) are powerful tools in appraising the fate of P added to soils. In the previous chapter, the technique was used on agricultural sites where the long-term history of land management was known. However, such fractionations can also be used in short-term incubation studies to investigate the fate of P added to soils from various sources. For example, Kashem et al. (2003) treated soils with organic amendments and fertilizer P (NH₄H₂PO₄) at 0 - 614 mg P kg⁻¹ and found that cattle manure resulted in net immobilization of P, whereas biosolids led to net mineralization. They showed that P sorption in the inorganic P fertilizer-amended treatments increased NaHCO₃-extractable P at the expense of solution P. Chauhan et al. (1981) found that inorganic P fertilization combined with labile C sources stimulated P accumulation in incubated soils. Sharpley and Sisak (1997) found that poultry litter leachate P was less available than KH₂PO₄ when incubated with 193 soils for 7 days. An incubation study on clay soils from South Africa showed that 30 - 60% and 80 - 90% of added P (KH₂PO₄) was transformed into less labile pools after 1 and 60 days, respectively (Ochwoh et al., 2005).

P transformations in local soils amended with common organic amendments such as livestock manures and crop residues has received limited study. A
measure of the forms of P in soil treated with different soil amendments, and how these forms change with time, could improve our understanding of the management of land applications of these amendments to agricultural soils. The objective of this study was to follow the transformations and distribution of added P in organic and inorganic sources after different incubation periods, by use of a sequential P extraction procedure.

4.2 Materials and methods

The soil used in this experiment was a Hutton form (Farmingham series) [Rhodic Ferralsol (FAO)] and the sample was obtained from a site at Cedara Agricultural Research Station. According to the Soil Classification Working Group (1991), this soil is sandy clay, with a clay content of about 62 %. It had the following properties: organic C = 72 g/kg, pHKCl = 3.8, exchangeable Ca, Mg, and K of 2783, 391 and 411 ppm and AMBIC P = 53 ppm.

The organic P sources used in the study were maize residues (stem portions), poultry and dairy cattle manures. They were selected to represent common alternatives to inorganic P fertilizers, while varying widely in their physical and chemical characteristics. Maize residues were obtained from past trials in the Department of Agrometeorology (UKZN). Dairy cattle and poultry (layers) manure were obtained from the Department of Animal Science, also of the University of KwaZulu-Natal. Maize residues were oven-dried at 80 °C for 48 hours, whereas cattle and chicken manure were air-dried. Samples were ground (<0.5mm), digested in nitric and perchloric acids (HNO₃ and HClO₄), and the total P content was determined by the molybdenum blue method (Olsen and Sommers, 1982). Soluble inorganic P was extracted by the AMBIC method as applied to soil samples.

The incubation experiment consisted of 7 treatments: (i) control, (ii) dairy cattle manure (Cattle), (iii) poultry manure (Poultry), (iv) maize residues (Maize), (v) Ca(OH)₂ (Lime), (vi) KH₂PO₄ (PF), and (vii) Ca(OH)₂ plus KH₂PO₄ (Lime x PF).
To 100 g air-dried soil samples in 1L plastic containers (fitted with lids), the equivalent of 30 kg P ha\(^{-1}\) was added as KH\(_2\)PO\(_4\) (12 mg P per 100 g soil) or organic sources, thoroughly mixed, and soils were watered to 70 % field capacity. Lime was added to soil as Ca(OH)\(_2\) at 5 ton ha\(^{-1}\) (200mg Ca(OH)\(_2\) per 100g soil) to the appropriate treatments. The soils were incubated for 8 weeks at room temperature (25\(^{\circ}\)C). Each treatment combination was replicated 9 times in a completely randomized block design. At the end of each incubation period (1, 4 and 8 weeks), 3 replicates were removed and the soils air-dried, ground (<0.5mm) and stored for sequential P extraction (Tiessen and Moir, 1993). Soil analyses were carried out in duplicate. Details of the analytical methods used have been outlined previously (see section 3.2.2).

The data was analysed using analysis of variance (ANOVA) for a completely randomised block design in Genstat 8 software. Differences between means were compared by using the l.s.d. tests at 5% level of significance.

4.3 Results

4.3.1 Characteristics of organic amendments

Total P concentrations in the organic P sources ranged from a low of 1,450 mg P kg\(^{-1}\) for maize residues, to as high as 14,500 mg P kg\(^{-1}\) for poultry manure (Table 4.1). Extractable inorganic P as a percentage of total P was greatest for poultry manure (30%), followed by dairy manure (17%), and then maize residues (9%).

<table>
<thead>
<tr>
<th>Material</th>
<th>AMBIC extractable P</th>
<th>Total P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poultry manure</td>
<td>4350 (30)(^1)</td>
<td>14500</td>
</tr>
<tr>
<td>Cattle manure</td>
<td>892 (17)</td>
<td>5250</td>
</tr>
<tr>
<td>Maize residues</td>
<td>131 (9)</td>
<td>1450</td>
</tr>
</tbody>
</table>

\(^1\)Values in parenthesis are percent contribution of each fraction to total extractable P (Total P)
4.3.2 Soil pH (KCl)

The measured pH for the control and the organic residue-amended soils was lower than the original pH value (Figure 4.1). As expected, addition of Ca(OH)\textsubscript{2} caused a rapid and significant (P≤0.05) increase in pH for the duration of the study (Figure 4.1). Incubation of soil for 1 week after the addition of Ca(OH)\textsubscript{2} increased soil pH from 3.6 (control) to 4.17 and 4.2.

The addition of KH\textsubscript{2}PO\textsubscript{4} alone (PF) did not show the effect soil pH. Addition of organic residues at the rate applied in this study resulted in no significant effects on soil pH after 1 and 4 weeks of incubation but significantly (P≤0.05) increased it relative to the control after week 8 (Figure 4.1). There was a significant (P≤0.05) decrease in pH for all soils with increasing incubation time, particularly after 8 weeks of incubation (Figure 4.1). Averaged across the 8 weeks incubation (actual values in parentheses), soil pH increased in the order: PF (3.5) < Control (3.5) < Dairy (3.6) = Maize (3.6) = Poultry (3.6) < Lime x PF (4.1) = Lime (4.1).

4.3.3 Labile P (Resin-P\textsubscript{i}, NaHCO\textsubscript{3}-P\textsubscript{i}, NaHCO\textsubscript{3}-P\textsubscript{o})

Differences between P fractions in soil treated with various soil amendments and sampled after 1, 4, and 8 weeks are presented in Figures 4.2 and 4.3 and Appendix 4.1. There was a significant (P≤0.05) treatment effect on resin-extractable P at all sampling dates. In comparison with the 1 week sampling, Resin Pi concentrations in the control decreased by 11 and 62% after 4 and 8 weeks, respectively. However, for the amended soils Resin Pi concentrations were higher after 4 than 1 week incubation. Concentrations at 8 weeks were markedly lower than those after 1 or 4 week incubation. In comparison with the control, incubating the soils for 1 week increased Resin Pi in the order: Maize < Poultry = Cattle < Lime x PF = PF, whereas Lime decreased it marginally (Figure 4.2a; Appendix 4.1). After 1 week, the calculated percent P recovery in the Resin Pi fraction was 33 and 42% for poultry and dairy cattle manures, respectively.
The calculated percentage P recovery was 50% for the Lime x PF treatment and 58% for PF.

Treatment effects on the NaHCO₃-Pi fraction were only significant after 8 weeks. A dramatic decrease in NaHCO₃-Pi occurred in all soils including control between 1 and 4 weeks incubation. After 1 week, the amount of NaHCO₃-Pi varied from 75 to 95 mg P kg⁻¹, but it ranged between only 13 and 20 mg P kg⁻¹ after 8 weeks incubation.

For control, Cattle, Maize, PF and Lime x PF, concentrations of NaHCO₃-Po (Figure 4.3a) increased progressively between 1 and 4 and 4 and 8 weeks incubation. However, for Poultry and Lime treatments, concentrations were similar after 1, 4, and 8 weeks incubation. Significant treatment effects on NaHCO₃-Po concentrations were only noted at the 1 week sampling time. At this time, concentrations followed the order: Poultry = Lime > Lime x PF > Cattle > Control = Maize.

Total labile P was significantly (P≤0.05) increased by all treatments, except Maize, after 1 week incubation (Appendix 4.1). After 4 weeks, PF and Lime x PF treatments had greater labile P concentrations than the others but after 8 weeks there were no significant treatments differences. Total percent contribution of labile P to total extractable P decreased with increasing incubation time. Labile P constituted 5 - 6% and 3% of total P after 1 and 8 weeks, respectively.

4.3.4 Moderately labile P (NaOH-Pi, NaOH-Po, dilute HCl-Pi, conc. HCl-Pi, conc. HCl-Po)

Significant treatment effects were noted for NaOH-Pi at all three sampling times (Figure 4.2c; Appendix 4.1). At 1 week, values for Poultry were greater than those for the other treatments. At 4 weeks, Maize and Lime x PF had values greater than control. At 8 weeks, the PF and Lime x PF treatments had greater
values than maize. Values for NaOH-Pi were generally lower after 8 than 4 weeks incubation.

Analysis of variance showed that treatment effects for NaOH-Po were significant ($P \leq 0.05$) at all sampling dates (Figure 4.3b; Appendix 4.2). The actual contributions of NaOH-Po to total extractable $P$ were large relative to other labile $P$ fractions. NaOH-Po tended to be lower for the lime and Lime x PF treatments than the others at each sampling time (Figure 4.3b). On average, NaOH-Po accounted for 6 and 8% of the total $P$ in Lime- and animal manure-amended soils, respectively.

Large concentrations of dilute HCl-extractable $P$ (Ca-P) were found after 1 week, but these decreased sharply in all treatments with increasing incubation time, particularly between 4 and 8 weeks (Figure 4.2d). There were no significant treatment effects on dilute HCl-Pi (Appendix 4.2). Dilute HCl-Pi constituted the least percentage of total $P$ ($< 1\%$) in samples incubated for 8 weeks, with or without soil amendments.

Effects of soil amendments on concentrated HCl-extractable $P$ were insignificant ($P \leq 0.05$). HCl-extractable $P$ constituted a significant proportion of total extractable $P$, with more present as Pi than Po (Appendix 4.1). Both forms were greatly reduced by incubation relative to the original soil, which indicates fixation of $P$ into these fractions.

4.3.5 Stable $P$ pool (residual $P$)

The residual fraction was significantly increased by incubation relative to the original soil. It constituted the largest $P$ fraction (more than 60% of total $P$) after incubation and increased steadily with increasing incubation time (Appendix 4.2).
Figure 4.1 Soil pH following incubation (1-8 weeks) with no P addition (control) or with cattle manure (Cattle), or poultry manure (Poultry), or maize residues (Maize), or lime (Lime), or KH$_2$PO$_4$ (PF), or lime plus KH$_2$PO$_4$ (Lime x PF) applied at 12 mg P kg$^{-1}$ soil.
Figure 4.2 (a) Resin –Pi, (b) NaHCO$_3$-Pi, (c) NaOH-Pi, (d) dilute HCl-Pi, and (e) conc. HCl-Pi in soils following incubation (1-8 weeks) with no P addition (control) or with Cattle manure (Cattle), or poultry manure (Poultry), or maize residues (Maize), or lime (Lime), or lime plus KH$_2$PO$_4$ (Lime x PF), or KH$_2$PO$_4$ (PF) applied at 12 mg P kg$^{-1}$ soil. (continued)
Figure 4.2 Continued.
Figure 4.3 (a) NaHCO$_3$-Po, (b) NaOH-Po, and (c) conc. HCl-Po in soils following incubation (1-8 weeks) with no P addition (control), or with cattle manure, or poultry manure, or lime, or lime plus KH$_2$PO$_4$, or maize residues, or KH$_2$PO$_4$ applied at 12 mg P kg soil.
4.4 Discussion

4.4.1 Effects of soil amendments on soil pH

As expected, application of Ca(OH)₂ rapidly and significantly (P≤0.05) increased soil pH above that in the original soil (un-incubated), control and other treatments. The soil pH increase with lime incorporation involves liberation of OH⁻ ions, hydrolysis of H⁺ and eventually, precipitation and replacement of Al³⁺ and Fe²⁺ ions from adsorption sites by exchangeable cations such as Ca²⁺ (Adams and Odom, 1985).

Addition of organic residues also resulted in small increases in pH above that of the control after 8 weeks incubation (Figure 4.1). The addition of the residues was based on their P content rather than liming potential. Nonetheless, several reports indicate increases in soil pH following application of animal manures and crop residues to soils (Iyamuremye et al., 1996; Nwoke et al., 2004). Several workers (Bessho and Bell, 1992; Noble et al., 1996) have reported soil pH increases and concomitant decreases in exchangeable Al and Al saturation following plant residue incorporation. The decrease in exchangeable Al has been attributed not only to its precipitation due to elevated pH but also to adsorption of Al onto decomposing organic residues (Hoyt and Turner, 1975).

The tendency for pH to decline over the incubation period (Figure 4.1) is probably related to the formation of NO₃⁻-N during the nitrification process (Hoyt and Turner, 1975; Adeli et al., 2005). During nitrification, two H⁺ ions are released per unit of NH₄⁺ converted to NO₃⁻. In addition, during organic matter decomposition, CO₂ and H⁺ are produced, which also account for the decrease in soil pH at the end of the incubation (Cabrera et al., 1993).
4.4.2 Effects of soil amendments on labile P

Anion exchange resins extract P from soil solution rather than dissolving soil surfaces or P-containing minerals (Tiessen and Moir, 1993). Resin extractable Pi in this study accounted for less than 2% of total P, indicating that the resins extracted a very small fraction of the total soil P pool. Higher Resin Pi concentrations have been reported for soils with less total extractable P (O'halloran et al., 1987; Smith et al., 2005). Most of the inorganic P in this soil is associated with Al and Fe oxides and apparently held strongly so it is not readily extractable with resin via the removal of P from the soil solution.

For amended soils, Resin-Pi increased significantly between 1 and 4 weeks, but then decreased significantly with further incubation time. Indeed, after 8 wk, labile Pi fractions and total labile P in all soils were reduced to levels below those observed at week 1. This trend has been confirmed by other workers who found that in acidic soils, P application initially increases extractable Pi but it later decreases (Kashem et al., 2003; Ochwoh et al., 2005). The reduction in available Pi over time is not surprising. As time of P contact with the soil increases, P becomes strongly sorbed to Fe and Al oxide surfaces through the formation of stable multidentate ligands (Sanyai and De Datta, 1991). Buehler et al. (2002) found that labelled P transformed from the Resin-Pi to NaHCO₃-Pi fraction with increasing time. The decreases in Resin-Pi and NaHCO₃-Pi can therefore be attributed to fixation of Pi into the residual pool and also microbial uptake of Pi and its conversion to labile Po forms. Indeed, both the residual P and the NaHCO₃-Po pools increased in magnitude during the incubation.

The magnitude of the increases in labile P in amended soils after 1 and 4 weeks incubation (Appendix 4.2) reflects the effectiveness of P sources in furnishing readily soluble P (Sharpley et al., 1984). Application of cattle and poultry manures significantly (P≤0.05) increased Resin Pi after 1 and 4 weeks, whereas maize residues had no significant effect on Resin Pi at any stage (Appendix 4.1). In addition, the differences between organic amendments on Resin Pi were
greatest after 1 week incubation. These results are probably due to the differing properties of the residues. Table 4.1 shows that 17 and 30% of total P was in extractable inorganic form in cattle and poultry manures, respectively. In contrast, 9% of total P in maize residues was inorganic. The addition of more Pi in the animal manures would have favoured larger increases in Resin Pi.

Gagnon and Simard (1999) found that materials with high P and low C:P ratios released larger amounts of P. Poultry manure generally has low C:P (25) and C:N (11) ratios (Adeli et al., 2005). Nwoke et al. (2004) determined that maize residues had C:P and C:N ratios of 396 and 25, respectively. This was in contrast to a C:P and C:N ratios of 93 and 22, respectively, for farmyard manure. The critical C:P ratio above which there is P immobilization by soil microorganisms is about 300, whereas P mineralization takes place if the ratio is 200 or less (Tisdale et al., 1985). Thus, slower decomposition of maize residues due to relatively higher C:N ratio and immobilization of P due to the high C:P ratio may explain the insignificant effects of maize residues on Resin Pi at all sampling times. By contrast, it is likely that dairy cattle manure and poultry manure stimulated net P mineralization due to their relatively lower C:P ratios.

As already noted, the increases in NaHCO₃-Po with increasing incubation time (Appendix 4.1), were probably due to microbial uptake of P mobilized from labile Pi fractions can perhaps also from the less accessible fractions, such as the dilute HCl-extractable Pi (Ca-P), which decreased more than all the fractions after 8 wk of incubation (Figure 4.2d). Most reports indicate that NaHCO₃-Po fraction contains P of microbial origin and is labile (Hedley et al., 1982; Tiessen et al., 1993; Schmidt et al., 1996). This immobilization of Pi into labile Po fractions can be very important for increasing P availability, particularly in high P fixing soils (Hedley et al., 1982). Chauhan et al. (1981) effectively demonstrated a positive relationship between solution Pi concentration and microbial P uptake. They also found that inorganic P fertilization combined with labile carbon sources such as cellulose, stimulated Po build-up under laboratory conditions.
The PF and Lime x PF treatments caused greater increases in Resin Pi than did the organic amendments (Appendix 4.1). In addition, application of Cattle, Poultry and Maize generally resulted in greater accumulation of P as total Po than the Lime, PF, and Lime x PF treatments (Appendix 4.1). These observations support the findings of Tran and N'dayegamiye (1995) that mineral P fertilizer additions significantly increase labile P, but with more as Pi than Po.

The benefits of liming on P availability are clearly illustrated by the substantial increases in Resin-Pi above the control in the Lime treatment after 4 weeks incubation (Figure 4.2a). This effect was, however short-lived and not evident after 8 wk. The effect is most likely due to an increased pH decreasing adsorption and promoting desorption of orthophosphate. Increased soil pH causes the charge on the adsorbing surfaces of Fe and Al oxides to become more negative thus favouring desorption of the negatively charged orthophosphate anion (McLaren and Cameron, 1990). There is also the possibility of liming inducing increases in soil microbial activity with a resultant increase in mineralization of Po (Neale et al., 1997). Although there were no discernable decreases in NaHCO$_3$-Po induced by liming, there were notable decreases in NaOH-Po with limed treatments having the lowest values for this fraction at each sampling time (Figure 4.3b).

### 4.4.3 Effects of soil amendments on moderately labile P

The NaOH-Pi fraction was not greatly affected by treatments although it was surprisingly low in the Poultry and Maize treatments after 8 weeks incubation. The reason for this notable decline in these two treatments is not clear. Nonetheless, there was a tendency for NaOH-Pi to decrease between 4 and 8 weeks incubation in most of the treatments (Figure 4.2c). These results could suggest dissolution/ desorption of P bound to sesquioxides and its enrichment into the residual pool. The NaOH-Po fraction was not greatly affected by treatment except that the Lime, and to a lesser extent Lime x PF treatments
tended to have lower concentrations than the others. As already noted, this could
well be attributable to lime-induced mineralization of Po.

The high contents of dilute (0.1M) HCl-extractable Pi (Ca-P) in all soils after 1
week increase the probability of Ca phosphates in the soil because this extracting
solution mainly removes Ca-bound P (Ochwoh et al., 2005). Significant amounts
of Ca (2783 ppm; Table 3.1) in this soil increase probability of Ca-phosphates
precipitation. However, Ca-phosphates in acidic soils are not stable (Lindsay,
1979; Pierzynski et al., 1990), which may account for the dissolution of P in this
fraction due to incubation (Figure 4.2d). The initial concentrations of dilute HCl-Pi
could also be at least partially an error of the fractionation technique. In the
sequential fractionation procedure, dilute HCl extraction follows NaOH extraction
(Tiessen and Moir, 1993). Due to high pH conditions that occur NaOH extraction,
PO$_4^{3-}$ released from Al and Fe minerals can resorb to, or precipitate as calcium
minerals, resulting in an underestimation of NaOH-extractable P and
overestimation of Ca-P (Benzing and Richardson, 2005). Thus, some of the P
initially associated with Al and Fe minerals may have been misidentified as Ca-P.
To prevent this problem, use of selective chelating agents (e.g. 0.02 M Ca-NTA
with dithionate for extraction of Al- and Fe-P followed by 0.05M EDTA to extract
Ca-P) has been suggested (De Groot and Golterman, 1990: cited in Bezing and
Richardson, 2005).

Concentrated HCl-P represents more recalcitrant Pi and Po forms (Guo and
Yost, 1998). An increase in these fractions during incubation would therefore,
represent a further loss of P availability. In fact, whilst concentrations of conc.
HCl-Po increased over the incubation period, concentrations of conc. HCl-Pi
tended to decrease particularly between 1 and 4 weeks incubation. Thus, there
was no progressive accumulation of Pi in this pool; in fact, it acted as a source of
P for other pools.
4.4.4 Effects of soil amendments on stable P (residual P)

The residual-P fraction was the largest fraction in all incubated soils and increased over the incubation period (Appendix 4.1). Previous reports have indicated that residual-P constitutes both inorganic and organic P (Condron and Goh, 1989; Agbenin and Goladi, 1998). The increase in the residual-P with increasing incubation time in both the control and treated soils can be related to precipitation of insoluble P compounds, reactions of adsorbed P whereby it becomes bound to soil components and immobilization of P into organic forms that are not readily extractable with resin, NaHCO₃, NaOH, or HCl.

4.5 Conclusions

In view of the large differences in easily-soluble Pi content between the various P sources, treatment effects on soil P fractions were in general, surprisingly small. The main effect was mainly on the potentially-available Resin-Pi fraction which, as expected, tended to be greater for the inorganic P source than for the organic ones. The declines in Pi fractions during incubation (Resin-Pi between 4 and 8 weeks, NaHCO₃-Pi between 1 and 4 weeks and dilute HCl-Pi between 1 and 4 and 4 and 8 weeks) was accompanied by progressive increases in the sizes of the NaHCO₃-Po and concentrated HCl-Po fractions. This suggests progressive microbial immobilization of Pi during incubation. An exception was the limed treatments which tended to have low NaOH-Po concentrations suggesting lime-induced net mineralization of Po. The progressive increase in residual P during incubation may also reflect progressive conversion of extractable, adsorbed Pi in recalcitrant, non-extractable, inorganic forms over time.

Overall, the results of this study in terms of the availability of P from various sources were rather inconclusive. Further, studies should grow plants so that the availability can be gauged more decisively via plant uptake.
CHAPTER 5

GENERAL CONCLUSIONS

Conversion of native grassland ecosystems to long-term maize and sugarcane monoculture resulted in significant decline in soil organic matter (SOM). Soil cultivation enhances organic matter loss because it increases soil microbial activity through aeration and exposure of physically protected soil organic C. In contrast, permanent pasture and forestry systems led to accumulation of SOM. Thus, pasture and, to a lesser extent, forestry could form an integral part of management strategies for improving organic matter contents in soil. In particular, the use of pastures in rotation with crops would be an appropriate way of maintaining organic matter under cropping. Nonetheless, as shown here, annual pastures maintain rather than counterbalance the effect of grass in increasing organic matter inputs. Thus, pastures of 3 or 4 years duration in rotation with annual arable crops might be a more appropriate option.

Soil microbial properties were affected by both land use and management practice. In agreement with other reports, permanent kikuyu pasture, forestry and native grassland ecosystem had a favourable influence on soil microbial biomass C and P. The relatively higher microbial biomass in these fields compared to maize fields could be ascribed mainly to high organic matter levels (i.e. more organic substrate for microbial growth). Soil disturbance with an attendant loss of organic matter and possibly also the persistent use of agrochemicals contributed to lower microbial biomass under conventionally-tilled arable systems. The larger substrate and nutrient inputs in the surface layer of soil under zero tillage due to surface retention of crop and weed residues will have contributed to higher microbial biomass relative to conventionally-tilled soil.

Decades of mineral P fertilization of the agricultural soils increased total extractable P in the surface horizon (0-5 cm). A change in the distribution and amounts of P within inorganic (Pi) and organic P (Po) pools also occurred due
conversion to agricultural uses. The quantity of Po followed a similar pattern to the organic C contents, confirming findings from previous work that the transformation of Po and organic C are linked. Fifty percent, or more, of the P in undisturbed soils was in organic form. Such results reflect the fact that within native ecosystems, the labile P pool is maintained primarily by the microbially-mediated mineralization of organic P. In agricultural systems, the release of organically bound P would be strongly influenced by factors such as residue management and tillage methods because they influence organic matter accumulation and decomposition. Total extractable Po increased under permanent kikuyu pasture and some forestry. Thus, cycling of P through the organic fractions may well have a substantial influence on P availability in these systems. By contrast, under arable systems much of the readily-mineralizable organic P has already been lost so P supply is presumably more dependent on adsorption/desorption of Pi and fertilizer Pi inputs. Indeed, comparison of soils under long-term maize monoculture to undisturbed soils shows an overall increase in total extractable Pi (Pi) compared to a decrease in the total extractable organic P (Po). This shows that successive applications of P fertilizer to these tilled soils accumulate mainly in inorganic forms while at the same time the Po fraction is being diminished. The results for arable soils also indicate a larger total extractable Po pool under maize (ZT) compared to maize (CT), indicating that soil P dynamics differ according to cropping practices. Accumulation of organic matter in the surface layer of soil under ZT results in an accumulation of Po in the soil. Much of this Po presumably arises from immobilization of fertilizer P during organic matter accumulation.

It is often reported that the NaOH-Po is the main sink and source of P in deeply weathered soils. The largest P fractions in both the fertilized soils and native grasslands are the NaOH-P, concentrated HCl-P and residual P. It appears that these fractions are the main sinks of added P in this soil. Al and Fe hydrous oxides, common in tropical and subtropical soils, bind the applied and native P, rendering it unavailable for plant uptake even though total levels may be high. Inorganic P fertilization of arable-cropped soils increased Pi fractions associated
with Al and Fe oxide surfaces (i.e. NaHCO₃-Pi and NaOH-Pi). Not surprisingly the dilute HCl-Pi, which represents P associated with Ca minerals, constituted a small proportion of total P in most soils, with exception of the kikuyu pasture and pine forest sites.

The incubation experiment showed that applications of P from various organic and inorganic sources can have significant effects on P fractions in the short-term. In particular, the addition of organic and inorganic P sources increased soil levels of total P as would be expected. Incubation resulted in a change in dominance of organic P in original to inorganic P in incubated soils. Application of KH₂PO₄ at the rate of 30 kg P ha⁻¹ and Ca(OH)₂ at 5 ton ha⁻¹ rapidly increased labile P than animal manures and crop residues. These results are due to high solubility of KH₂PO₄ and the fact that residues have to first decompose before P is released. However, in the long-term, P sorption may decrease the availability of P derived from commercial fertilizers more than that of organic residue-derived P. This is because residue P is released more slowly so that a growing crop can potentially use it more effectively and also organic anions derived from the residues can become adsorbed to oxide surfaces thus blocking P adsorption sites. Thus, short-term incubation studies, such as that performed here, need to be followed up by long-term field investigations.

It will be important to extend this research and investigate the effects of the various land uses and management practices on P forms at deeper soil layers. Further, the impacts of soil amendments on P fractions can be evaluated under field conditions, in the presence of crops. Although increases in soil P fractions were noted in the incubation experiment, it was not certain whether the increases occurred due to transformation of native P between pools or whether they resulted from applied P. Isotopic labelling of added P has been applied to great effect in tracing the pathways of P in soils and this could be a fruitful area where this research could be extended in the future. The use of isotopic tracers in association with sequential fractionation procedures would enable the pathways
of movement of applied P (from inorganic or organic sources) to be followed in
detail both within and between Pi and Po fractions.
APPENDICES

Appendix 4.1 Concentration of soil P fractions (mg P/kg soil) in soil with various amendments after 1, 4, 8 weeks of incubation

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Resin Pi</th>
<th>NaHCO₃⁻Pi</th>
<th>NaHCO₃⁻Po</th>
<th>NaOH⁻Pi</th>
<th>NaOH⁻Po</th>
<th>0.1M Conc. HCl-Pi</th>
<th>Conc. HCl⁻Pi</th>
<th>Conc. HCl⁻Po</th>
<th>Residual P</th>
<th>Labile P</th>
<th>Total P Po</th>
<th>Total P Pi</th>
<th>Total P (sum)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Week 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>12c</td>
<td>83ab</td>
<td>13c</td>
<td>86b</td>
<td>196ab</td>
<td>138</td>
<td>197b</td>
<td>17ab</td>
<td>1538</td>
<td>108d</td>
<td>227ab</td>
<td>470b</td>
<td>2280</td>
</tr>
<tr>
<td>Cattle</td>
<td>17a</td>
<td>95a</td>
<td>16c</td>
<td>83b</td>
<td>218a</td>
<td>129</td>
<td>220ab</td>
<td>22a</td>
<td>1490</td>
<td>127bc</td>
<td>256a</td>
<td>543ab</td>
<td>2289</td>
</tr>
<tr>
<td>Poultry</td>
<td>16ab</td>
<td>87ab</td>
<td>43a</td>
<td>102a</td>
<td>159bc</td>
<td>139</td>
<td>243ab</td>
<td>27a</td>
<td>1473</td>
<td>145a</td>
<td>228ab</td>
<td>586a</td>
<td>2287</td>
</tr>
<tr>
<td>Maize</td>
<td>12bc</td>
<td>89ab</td>
<td>11c</td>
<td>90ab</td>
<td>154bc</td>
<td>136</td>
<td>237ab</td>
<td>13bc</td>
<td>1545</td>
<td>112cd</td>
<td>179b</td>
<td>563ab</td>
<td>2287</td>
</tr>
<tr>
<td>Lime</td>
<td>11c</td>
<td>75b</td>
<td>42a</td>
<td>79b</td>
<td>145c</td>
<td>128</td>
<td>256a</td>
<td>5c</td>
<td>1531</td>
<td>129abc</td>
<td>192b</td>
<td>559ab</td>
<td>2282</td>
</tr>
<tr>
<td>PF</td>
<td>19b</td>
<td>83ab</td>
<td>27b</td>
<td>88ab</td>
<td>238a</td>
<td>131</td>
<td>237ab</td>
<td>7c</td>
<td>1457</td>
<td>129abc</td>
<td>272a</td>
<td>557ab</td>
<td>2286</td>
</tr>
<tr>
<td>Lime x PF</td>
<td>18a</td>
<td>83ab</td>
<td>35ab</td>
<td>87b</td>
<td>154bc</td>
<td>123</td>
<td>250ab</td>
<td>10bc</td>
<td>1527</td>
<td>136ab</td>
<td>199b</td>
<td>561ab</td>
<td>2287</td>
</tr>
<tr>
<td>LSD (P≤0.05)</td>
<td>4</td>
<td>15</td>
<td>8</td>
<td>14</td>
<td>45</td>
<td>NS</td>
<td>55</td>
<td>8</td>
<td>6</td>
<td>6</td>
<td>30</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>CV (%)</td>
<td>14</td>
<td>10</td>
<td>17</td>
<td>9</td>
<td>14</td>
<td>6</td>
<td>13</td>
<td>30</td>
<td>8</td>
<td>8</td>
<td>15</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td><strong>Week 4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>11c</td>
<td>15a</td>
<td>35</td>
<td>94c</td>
<td>156abc</td>
<td>97</td>
<td>170bc</td>
<td>25c</td>
<td>1681</td>
<td>61c</td>
<td>216</td>
<td>387c</td>
<td>2283</td>
</tr>
<tr>
<td>Cattle</td>
<td>19b</td>
<td>17ab</td>
<td>35</td>
<td>95bc</td>
<td>177ab</td>
<td>104</td>
<td>160c</td>
<td>45a</td>
<td>1638</td>
<td>71bc</td>
<td>257</td>
<td>396abc</td>
<td>2290</td>
</tr>
<tr>
<td>Poultry</td>
<td>18bc</td>
<td>13ab</td>
<td>37</td>
<td>94c</td>
<td>203a</td>
<td>97</td>
<td>165bc</td>
<td>38ab</td>
<td>1627</td>
<td>68bc</td>
<td>278</td>
<td>386bc</td>
<td>2291</td>
</tr>
<tr>
<td>Maize</td>
<td>16bc</td>
<td>14ab</td>
<td>37</td>
<td>112ab</td>
<td>181a</td>
<td>94</td>
<td>173bc</td>
<td>38ab</td>
<td>1623</td>
<td>67bc</td>
<td>256</td>
<td>410abc</td>
<td>2289</td>
</tr>
<tr>
<td>Lime</td>
<td>12bc</td>
<td>11b</td>
<td>39</td>
<td>107bc</td>
<td>124bc</td>
<td>95</td>
<td>175bc</td>
<td>38ab</td>
<td>1657</td>
<td>74ab</td>
<td>201</td>
<td>400abc</td>
<td>2280</td>
</tr>
<tr>
<td>PF</td>
<td>28a</td>
<td>18a</td>
<td>39</td>
<td>103bc</td>
<td>147abc</td>
<td>97</td>
<td>182ab</td>
<td>33b</td>
<td>1643</td>
<td>85a</td>
<td>219</td>
<td>425abc</td>
<td>2288</td>
</tr>
<tr>
<td>Lime x PF</td>
<td>28a</td>
<td>18a</td>
<td>33</td>
<td>128a</td>
<td>120c</td>
<td>99</td>
<td>198a</td>
<td>45a</td>
<td>1621</td>
<td>78ab</td>
<td>198</td>
<td>472a</td>
<td>2290</td>
</tr>
<tr>
<td>LSD (P≤0.05)</td>
<td>7</td>
<td>6</td>
<td>NS</td>
<td>18</td>
<td>56</td>
<td>NS</td>
<td>19</td>
<td>8</td>
<td>NS</td>
<td>11</td>
<td>NS</td>
<td>82</td>
<td>NS</td>
</tr>
<tr>
<td>CV (%)</td>
<td>17</td>
<td>17</td>
<td>16</td>
<td>10</td>
<td>20</td>
<td>8</td>
<td>13</td>
<td>47</td>
<td>5</td>
<td>8</td>
<td>17</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td><strong>Week 8</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>5b</td>
<td>19a</td>
<td>47</td>
<td>82abc</td>
<td>183abcd</td>
<td>2</td>
<td>164</td>
<td>54</td>
<td>1727</td>
<td>71</td>
<td>284</td>
<td>271</td>
<td>2282</td>
</tr>
<tr>
<td>Cattle</td>
<td>8a</td>
<td>15bc</td>
<td>51</td>
<td>95ab</td>
<td>178bcd</td>
<td>2</td>
<td>158</td>
<td>48</td>
<td>1735</td>
<td>74</td>
<td>277</td>
<td>278</td>
<td>2290</td>
</tr>
<tr>
<td>Poultry</td>
<td>5b</td>
<td>18ab</td>
<td>47</td>
<td>70bc</td>
<td>207a</td>
<td>2</td>
<td>189</td>
<td>21</td>
<td>1731</td>
<td>70</td>
<td>275</td>
<td>283</td>
<td>2289</td>
</tr>
<tr>
<td>Maize</td>
<td>7ab</td>
<td>13c</td>
<td>52</td>
<td>59c</td>
<td>202ab</td>
<td>2</td>
<td>150</td>
<td>53</td>
<td>1749</td>
<td>72</td>
<td>307</td>
<td>230</td>
<td>2286</td>
</tr>
<tr>
<td>Lime</td>
<td>6ab</td>
<td>17ab</td>
<td>44</td>
<td>93ab</td>
<td>159d</td>
<td>3</td>
<td>197</td>
<td>38</td>
<td>1726</td>
<td>67</td>
<td>241</td>
<td>316</td>
<td>2283</td>
</tr>
<tr>
<td>PF</td>
<td>6ab</td>
<td>19a</td>
<td>47</td>
<td>96a</td>
<td>196ac</td>
<td>3</td>
<td>169</td>
<td>21</td>
<td>1731</td>
<td>71</td>
<td>263</td>
<td>293</td>
<td>2287</td>
</tr>
<tr>
<td>Lime x PF</td>
<td>5b</td>
<td>20a</td>
<td>47</td>
<td>102a</td>
<td>170cd</td>
<td>4</td>
<td>178</td>
<td>44</td>
<td>1720</td>
<td>71</td>
<td>260</td>
<td>309</td>
<td>2289</td>
</tr>
<tr>
<td>LSD (P≤0.05)</td>
<td>3</td>
<td>3</td>
<td>NS</td>
<td>26</td>
<td>28</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>CV (%)</td>
<td>24</td>
<td>11</td>
<td>17</td>
<td>18</td>
<td>9</td>
<td>13</td>
<td>18</td>
<td>29</td>
<td>17</td>
<td>13</td>
<td>12</td>
<td>14</td>
<td>8</td>
</tr>
</tbody>
</table>

1. Labile P = resin P + NaHCO₃⁻Pi + NaHCO₃⁻Po
2. Total organic P = NaHCO₃⁻Po + NaOH⁻Po + conc. HCl⁻Po
3. Total inorganic P = resin P + NaHCO₃⁻Pi + NaOH⁻Pi + dilute HCl⁻Pi + conc. HCl⁻Pi

Means followed by the same letter in a column at the same incubation time are not significantly different at P≤0.05 level, NS: no significant difference (P≥0.05)
Appendix 4.2 Calculated P recovery (%) in P fractions for soil treated with various amendments and incubated for different times

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Resin P</th>
<th>NaHCO$_3$-Pi</th>
<th>NaHCO$_3$-Po</th>
<th>NaOH-P$_i$</th>
<th>NaOH-P$_o$</th>
<th>Dilute HCl-Pi</th>
<th>Conc. HCl-Pi</th>
<th>Conc. HCl-Po</th>
<th>Residual –P</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Week 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle</td>
<td>42</td>
<td>12</td>
<td>25</td>
<td>-25</td>
<td>167</td>
<td>-75</td>
<td>192</td>
<td>42</td>
<td>-400</td>
</tr>
<tr>
<td>Poultry</td>
<td>33</td>
<td>4</td>
<td>250</td>
<td>133</td>
<td>-325</td>
<td>8</td>
<td>383</td>
<td>83</td>
<td>-542</td>
</tr>
<tr>
<td>Maize</td>
<td>0</td>
<td>6</td>
<td>-17</td>
<td>33</td>
<td>-367</td>
<td>-17</td>
<td>333</td>
<td>-33</td>
<td>58</td>
</tr>
<tr>
<td>Lime</td>
<td>-8</td>
<td>-8</td>
<td>242</td>
<td>-58</td>
<td>-442</td>
<td>-83</td>
<td>567</td>
<td>-100</td>
<td>-58</td>
</tr>
<tr>
<td>PF</td>
<td>58</td>
<td>0</td>
<td>117</td>
<td>17</td>
<td>333</td>
<td>-58</td>
<td>333</td>
<td>-83</td>
<td>-675</td>
</tr>
<tr>
<td>Lime x PF</td>
<td>50</td>
<td>0</td>
<td>183</td>
<td>8</td>
<td>-367</td>
<td>-125</td>
<td>442</td>
<td>-58</td>
<td>-92</td>
</tr>
<tr>
<td><strong>Week 4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle</td>
<td>67</td>
<td>2</td>
<td>0</td>
<td>8</td>
<td>175</td>
<td>58</td>
<td>-83</td>
<td>167</td>
<td>-358</td>
</tr>
<tr>
<td>Poultry</td>
<td>58</td>
<td>-2</td>
<td>17</td>
<td>0</td>
<td>392</td>
<td>0</td>
<td>-42</td>
<td>108</td>
<td>-450</td>
</tr>
<tr>
<td>Maize</td>
<td>42</td>
<td>-1</td>
<td>17</td>
<td>150</td>
<td>208</td>
<td>-25</td>
<td>25</td>
<td>108</td>
<td>-483</td>
</tr>
<tr>
<td>Lime</td>
<td>108</td>
<td>-4</td>
<td>33</td>
<td>108</td>
<td>-287</td>
<td>-17</td>
<td>42</td>
<td>108</td>
<td>-117</td>
</tr>
<tr>
<td>PF</td>
<td>142</td>
<td>3</td>
<td>33</td>
<td>75</td>
<td>-75</td>
<td>0</td>
<td>100</td>
<td>67</td>
<td>-317</td>
</tr>
<tr>
<td>Lime x PF</td>
<td>142</td>
<td>3</td>
<td>-17</td>
<td>292</td>
<td>-300</td>
<td>17</td>
<td>233</td>
<td>167</td>
<td>-500</td>
</tr>
<tr>
<td><strong>Week 8</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle</td>
<td>25</td>
<td>-4</td>
<td>33</td>
<td>108</td>
<td>-42</td>
<td>0</td>
<td>-50</td>
<td>-50</td>
<td>67</td>
</tr>
<tr>
<td>Poultry</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>-100</td>
<td>200</td>
<td>0</td>
<td>208</td>
<td>-275</td>
<td>33</td>
</tr>
<tr>
<td>Maize</td>
<td>17</td>
<td>-6</td>
<td>42</td>
<td>-192</td>
<td>158</td>
<td>0</td>
<td>-117</td>
<td>-8</td>
<td>183</td>
</tr>
<tr>
<td>Lime</td>
<td>8</td>
<td>-2</td>
<td>-25</td>
<td>92</td>
<td>-200</td>
<td>8</td>
<td>275</td>
<td>-133</td>
<td>-8</td>
</tr>
<tr>
<td>PF</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>117</td>
<td>108</td>
<td>8</td>
<td>42</td>
<td>-275</td>
<td>33</td>
</tr>
<tr>
<td>Lime x PF</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>167</td>
<td>-108</td>
<td>17</td>
<td>117</td>
<td>-83</td>
<td>-58</td>
</tr>
</tbody>
</table>
REFERENCES


Haynes, R.J. and Knight, T.L. 1989. Comparison of soil properties, enzyme activities, levels of biomass N and aggregate stability in soil profile under


