ENHANCING PHOSPHORUS AVAILABILITY IN SOME PHOSPHATE FIXING SOILS OF THE TRANSKEI REGION, SOUTH AFRICA USING GOAT MANURE

GICHANGI, E. M.
BApp.Sc. (Hons), Queensland, MSc. (Soil Science), Nairobi

Department of Agronomy, University of Fort Hare,

SOUTH AFRICA

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Promoter:

Professor: P. N. S. Mnkeni
Department of Agronomy, University of Fort Hare,
PB X1314, Alice, 5700, South Africa.

Co-Promoter:

Professor P. C. Brookes
Soil Science Department, Rothamsted Research,
Harpenden, Herts AL5 2JQ UK.

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SUGGESTED SHORT TITLE

Enhancing phosphorus availability in soils using goat manure

DECLARATION

I, **Elias Maina Gichangi** declare that the thesis hereby submitted for the degree *Philosophiae Doctor* at the University of Fort Hare is my own independent work and has not previously been submitted at another university/faculty.

Signature …………………………………….

Date …………………………………….

ABSTRACT

Low availability of soil phosphorus (P) caused by strong sorption of P is a major constraint to agricultural production in most South African soils, particularly those from the high rainfall areas. The aim of this study was therefore to investigate whether combined addition of goat manure with inorganic P fertilizers could enhance P availability in some P fixing soils of the Transkei region, South Africa. The study addressed the following specific objectives (i) to assess P sorption capacities and requirements of selected soils and their relationship with selected soil properties and single point sorption test, (ii) to assess the effects of goat manure and lime addition on P sorption properties of selected P fixing soils (iii) to assess the temporal changes in concentration of inorganic and microbial biomass P fractions following application of inorganic fertilizer P with goat manure in a laboratory incubation experiment, and, (iv) to assess the effects of goat manure application with inorganic phosphate on inorganic and microbial biomass P fractions, P uptake and dry matter yield of maize.

Sorption maxima (S_{max}) of seven soils examined ranged from 192.3 to 909.1 (mg P kg^{-1}) and were highly and positively correlated with sorption affinity constant (r = 0.93, p = 0.01) and organic C (r = 0.71, p = 0.01). The amount of P required for maintaining a soil solution concentration of 0.2 mg P l^{-1} ranged from 2.1 to 123.5 mg P kg^{-1} soil. Soils collected from Qweqwe (a Cambisol), Qunu (an Acrisol), Ncihane (a Luvisol) and Bethania (a Ferralsol) had lower external P requirement values and were classified as lower sorbers, whereas soils from Ntlonyana (a Planosol), Chevy Chase (a Ferralsol) and Flagstaff (a Ferralsol) were classified as moderate sorbers. The results suggested that P availability could be compromised in 43%

of the soils studied and that measures to mitigate the adverse effects of P sorption were needed to ensure that P is not a limiting factor to crop production, where such soils are found.

Goat manure addition at varying rates (5, 10 and 20 tha^{-1} dry weight basis) to two of the moderately P fixing soils from Chevy Chase and Flagstaff, reduced P sorption maxima (S_{max}) compared to the control treatment. Phosphate sorption decreased with increasing amounts of goat manure in both soils but the extent of reduction was greater on Chevy Chase soil than on Flagstaff soil. The relative liming effects of the different rates of goat manure followed the order 20 t GM ha^{-1} > 10 t GM ha^{-1} > 5 t GM ha^{-1}. In a separate experiment, addition of inorganic P at varying rates (0, 90, 180, and 360 kg P ha^{-1}) to Flagstaff soil increased labile P fractions (resin P, biomass P and $NaHCO_3$-P_i) and the increases were greater when goat manure was co-applied. The control treatments contained only 17.2 and 27.5 mg P kg^{-1} of resin extractable P in the un-amended and manure amended treatments, respectively which increased to 118.2 and 122.7 mg P kg^{-1} on day 28 of incubation. Biomass P concentration was increased from 16.8 to 43.9 mg P kg^{-1} in P alone treatments but the fraction was greatly enhanced with manure addition, increasing it from 32.6 to 97.7 mg P kg^{-1}. NaOH-P_i was the largest extractable P_i fraction and ranged from 144.3 to 250.6 mg P kg^{-1} and 107.5 to 213.2 mg P kg^{-1} in the unamended and manure amended treatments, respectively.

Dry matter yield and P uptake by maize grown in the glasshouse were highly and significantly ($p = 0.05$) correlated with the different P fractions in the soil. The correlations followed the order resin P ($r = 0.85$) > NaOH-P_i ($r = 0.85$) > $NaHCO_3$-P_i ($r = 0.84$) >> biomass P ($r = 0.56$) for dry matter yield at 6 weeks after planting. At 12 weeks after planting, goat manure had highly significant effects on resin P and biomass P but had no effect on $NaHCO_3$-P_i and NaOH–P_i. The combination of biomass P, resin P and $NaHCO_3$-P_i explained 75.8% of the variation in dry matter yield of which 63.0% of the variation was explained by biomass P alone. The greatest increase in biomass P occurred when added P was co-applied with 5 or 10 tha^{-1} goat manure. The predictive equation for maize dry matter yield (DM) was: DM (g) = 1.897 biomass P + 0.645 resin P (r = 0.73). Resin P was the fraction that was most depleted due to plant uptake and decreased by 56 to 68% between the 6th week and the 12th week of sampling indicating that it played a greater role in supplying plant available P. The results therefore suggested that the use of goat manure may allow resource poor farmers to use lower levels of commercial phosphate fertilizers because of its effect to reduce soil P sorption. In addition, higher increases in biomass P due to manure addition observed at lower rates of added P indicated that goat manure has potential for enhancing bioavailability and fertilizer use efficiency of small inorganic P applications.

PREFACE

This dissertation is composed of six chapters preceded by an introduction, general hypotheses and presents objectives to be achieved. Chapter 1 is a general literature review which establishes the context of the study. The review focuses on complementarities and synergies between organic and mineral phosphate inputs in relation to P availability in soils. The next six chapters constitute the body of the thesis. Chapter 2 reports results on phosphate sorption properties and relationships of derived sorption values to selected soil parameters in selected soils from the Transkei region of South Africa. An assessment of P requirements for the soils based on the external P requirement values calculated from the Langmuir equations and from a glasshouse pot experiment is also reported in Chapter 2. Chapter 3 reports results on the effects on goat manure addition on P sorption. Results on the dynamics of soil P fractions and their relationships with soil inputs are presented in Chapters 4 and 5 and with plant growth (Chapter 5). A brief summary is provided in the general discussion and conclusions at the end of the dissertation, followed by suggested future research which outlines needed additional studies (Chapter 6).

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DEDICATED

To my late sister and friend Rosemary Wanjiru Gichangi (Mama Ken),

1959 - 2004.

For God so loved the world that He gave His only begotten son that whoever believeth in Him shall never perish but have everlasting life. John 3:16

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Al_{CDB}	dithionite extractable Al
Al_{crys}	crystalline Al
Al_{KCl}	exchangeable Al
Al_{ox}	oxalate extractable Al
b	sorption affinity constant
CEC	cation exchange capacity
C_{eq}	equilibrium concentration
Cv	coefficient of variation
EC	electrical conductivity
EPR	external phosphate requirement
Fe_{CDB}	dithionite extractable Fe
Fe_{crys}	crystalline Fe
Fe_{KCl}	exchangeable Fe
Fe_{ox}	oxalate extractable Fe
FYM	farm yard manure
GM	goat manure
Lsd	Least significant difference
K_p,	fraction of biomass P extracted after fumigation (Brookes *et al.*, 1982).
P_f	P extracted from $CHCl_3$ fumigated samples
P_i	inorganic P
P_{nf}	P extracted from non-fumigated samples
P_o	organic P
P_s	P extracted by exchange resins from non-fumigated soil spiked with P
RDAl	relative decrease in exchangeable Al (%)
RLE	relative liming effectiveness (%)
SI	single point sorption test
S_{max}	sorption maxima

INTRODUCTION

The key roles played by phosphorus (P) compounds in the transformation of solar to chemical energy during photosynthesis and as a provider of chemical energy for biosynthesis in plants make P a singularly important nutrient element. For most smallholder farmers with limited resources, high P deficiency is a factor most limiting to crop productivity and has a profound impact on food security (Warren, 1994; Nziguheba *et al.*, 1998). High P deficiency is most prevalent mainly where strong sorption of P by aluminum and iron oxides and amorphous materials occurs resulting in poor mobility of soil inorganic P (Hinsinger, 2001). Therefore, only a small proportion of soil P is present in the soil solution and available for plant uptake. This leads to the need for large applications of fertilizer P to achieve high yields of arable crops (Warren, 1994; Agbenin and Tiessen, 1995). However, experience gained from temperate regions indicate that long-term use of inorganic and inorganic fertilizers may lead to high accumulation of P in soil with a consequent increase in P loss to surface waters (Kleinman *et al*., 2003; Haygarth and Jarvis 1999; Haygarth and Sharpley 2000).

High levels of P accumulation in soil have been reported under intensive farming systems in parts of Europe and North America, together with consequent increases in P losses to surface waters (Sims *et al*., 2000). The accumulation of P in soil from imported feed is particularly important in areas of intensive livestock production (e.g. pigs, poultry, dairy) where large quantities of manure are applied to land (Sharpley *et al*., 2000; Sharpley and Tunney, 2000; Heathwaite 2003). An additional factor that may contribute to the potential for P loss is nitrogen (N)-based nutrient management systems where manures are applied. Currently recommended rates for manure applications to soil are typically based on the N requirement of the crops to be grown and the plant-available N content of the manure, while the amount of P applied with the manure has not usually been considered when determining recommended application rate (Reddy *et al.*, 1980; Simard *et al.*, 1995). It is therefore crucial to tailor recommendations on manure rates based on P rather than plant N requirements.

In South Africa, crop production levels under the smallholder systems of agriculture are reported to be low, due to poor natural soil fertility coupled with low usage of inorganic and/or organic fertilizers with P being one of the nutritional factors limiting production (Mandiringana *et al.,* 2005). Many of them are also suspected to have high P sorption capacities particularly those from the high rainfall areas which tend to be acidic. Studies on P sorption for soils from the neighbouring provinces of KwaZulu Natal and Mpumalanga reported by Bainbridge *et al.* (1995) and Henry and Smith (2002) indicated that highly weathered soils in those provinces had high sorption capacities ranging from 500 to 1197 mg P kg^{-1}.

The practice of liming acid soils, in order to raise soil pH and precipitate exchangeable Al as insoluble hydroxy-Al has long been recognized as necessary for optimum crop production (Haynes and Mokolobate, 2001). However, in many acid soils large quantities of lime are commonly required to achieve adequate growth of many crops. For both logistic and economic reasons, it is often not practical for resource-poor farmers to apply high rates of lime and fertilizer P to their soils to optimize crop production. There is, therefore, a need to develop more practical and affordable alternatives.

Studies reported in the literature indicate that when manure and fertilizer P are applied together, a synergistic effect occurs whereby available P is increased more than the sum of the increase from either applied singly (Iyamuremye *et al.,* 1996; Nziguheba *et al.,* 1998). Combined application of inorganic P with organic materials is reported to result in larger increases in yields than if either is applied singly (Nziguheba *et al.,* 1998; Ayaga *et al.,* 2006). Besides constituting a source of P as well as other nutrients, organic materials also provide an energy substrate for microbial activity (Palm *et al.*, 1997). Ayaga *et al.* (2006) postulated that addition of manures stimulates the synthesis of soil microbial biomass resulting in increased demand for P, which is immobilized in labile forms, both in the cells of the living soil micro-organisms and their associated pool of metabolites. The turnover of this pool would provide a slow release of inorganic P which the plants can use more efficiently (Ayaga *et al.,* 2006) with a consequent reduction of possibilities of P leaching in soils. There is, however, little or no information available on P dynamics and turnover of the microbial biomass P pool and other P fractions in soils receiving inorganic fertilizer P with animal manures in South African soils and more specifically soils of the Eastern Cape.

STUDY HYPOTHESES AND OBJECTIVES

The specific hypotheses of this study were:

(i) Soils of the Transkei region of South Africa are deficient in P due to their high P sorption capacities and have high P requirements

(ii) Goat manure application decreases P sorption and requirement in these soils

(iii) The concentrations of the more labile P fractions (resin P, microbial P and $NaHCO_3$-P_i) and the moderately labile forms (NaOH-P_i) increases more with co-application of inorganic P and goat manure in soils than when applied singly

(iv) Increased concentrations of the more labile P fractions in soil amended with inorganic P and goat manure improve P uptake and dry matter yield of maize

To test the above hypotheses, the study was undertaken with the following objectives:

(i) to assess the P sorption capacities and requirements of selected soils from the Transkei region of South Africa and their relationship with soil properties

(ii) to assess the effects of goat manure and lime addition on P sorption properties of selected soils of the Transkei region of South Africa

(iii) to assess the temporal changes in concentration of soil inorganic and microbial biomass P fractions following application of inorganic fertilizer P with goat manure in a laboratory incubation experiment;

(iv) to assess the effects of goat manure application with inorganic P on inorganic and microbial biomass P fractions, P uptake and dry matter yield of maize in a glasshouse pot experiment.

CHAPTER 1

1.1 GENERAL LITERATURE REVIEW

Phosphorus (P) is an essential component of all living cells where P compounds are involved in reactions and processes required for the accumulation and release of energy for cellular metabolism, seed formation and root development in plants (Fairhurst *et al.,* 1999). Thus, P deficiency results in reduced plant growth, delayed maturity and a reduction in the quality and quantity of crop yield. The interval from planting to crop canopy closure is prolonged under P deficiency and this may result in increased soil and P losses due to erosion from exposed soil at the onset of the season in tropical regions (Fairhurst *et al.*, 1999).

Compared to other major nutrients, P is by far the least mobile and least available nutrient to plants. It is therefore frequently a major or the prime limiting factor for plant growth (Hinsinger, 2001). Therefore, in most agricultural systems in the tropics the concentration of P in the soil is insufficient for crop growth and must be additionally provided as an external input.

1.1.1 Soil fertility status of South African soils

Crop production levels under the smallholder systems of agriculture in the Eastern Cape Province of South Africa are reported to be low, due to poor natural soil fertility coupled with low usage of inorganic and/or organic fertilizers with P being one of the nutritional factors limiting production (Mandiringana *et al.*, 2005). Many of the soils are also suspected to have high P sorption capacities particularly those from the high rainfall areas which tend to be acidic with low to medium base status. Mandiringana *et al.* (2005) reported that almost 100% of the garden and field soils in three Transkei districts (Elliotdale, Umatata and Mt Fletcher districts) were acidic, indicating that they had the potential to fix added P.

Studies on P sorption for some South African soils and reported by Bainbridge *et al.* (1995) and Henry and Smith (2002) indicated that majority of the soils had high sorption capacities ranging from 500 to 1197 mg P kg^{-1} of soil. Their studies showed that the highest sorbers were weathered red or yellow-brown clays with high oxalate (amorphous) aluminum content especially in soils with a humic-horizon (Figure 1.1) such as Inanda, Kranskop and Magwa forms. Therefore, only a small proportion of added P is present as P ions in the soil solution and available for plant uptake. Limited use of commercial fertilizers, because of their high cost and limited accessibility by smallholder farmers in the communal areas, exacerbates P deficiency in the soils (Mandiringana *et al.*, 2005).

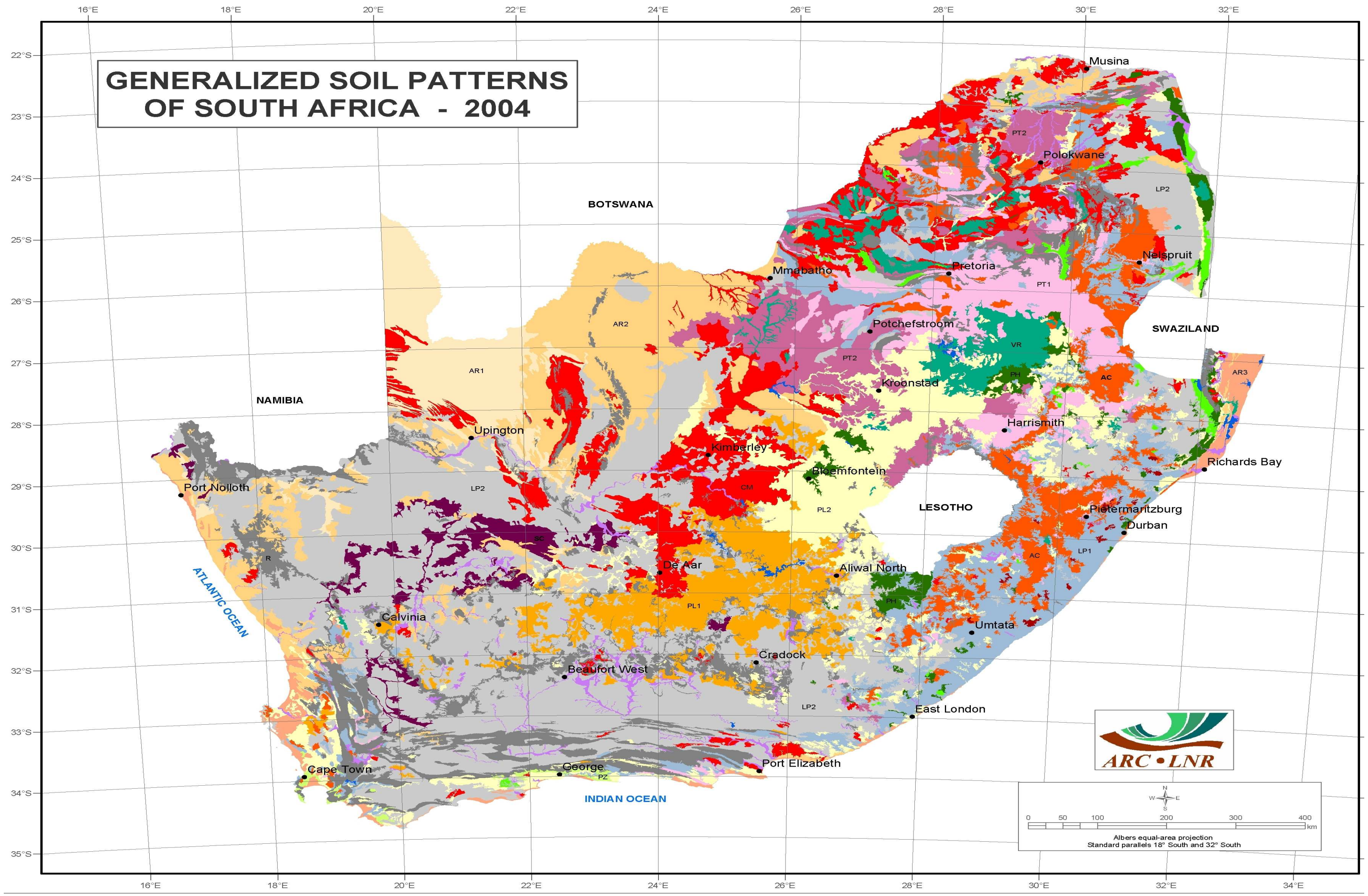

Fig. 1.1 Generalized soil patterns of South Africa (Samadi *et al.,* 2005). The legend is given on page 8

Legend

GENERALIZED SOIL PATTERNS

RED-YELLOW WELL DRAINED, MASSIVE OR WEAKLY STRUCTURED SOILS

🟥	FR	*Red and yellow soils with a low base status and a humic topsoil horizon.*
🟧	AC	*Red and yellow soils with low to medium base status.*
🟥	CM	*Red soils with high base status.*

SOILS WITHIN A PLINTHIC CATENA

🟪	PT1	*Red, yellow and / or greyish soils with low to medium base status.*
🟪	PT2	*Red, yellow and /or greyish soils with high base status.*

SOILS WITH A STRONG TEXTURAL CONTRAST

🟧	PL1	*Soils with a marked clay accumulation, strongly structured and a reddish colour.*
🟨	PL2	*Soils with a marked clay accumulation, strongly structured and a non-reddish colour. They may occur associated with one or more of vertic, melanic and plinthic soils.*

STRONGLY STRUCTURED SOILS, GENERALLY WITH A HIGH CLAY CONTENT

🟩	VR	*Strongly structured cracking soils, mainly dark coloured, dominated by swelling clays (vertic soils). They may occur associated with one or more of melanic and red structured soils.*
🟩	PH	*Soils with dark coloured, well structured topsoil and high base status (melanic soils). They may occur associated with one or more of vertic and red structured soils.*
🟩	NT	*Well drained, dark reddish soils having a pronounced shiny, strong blocky structure (nutty), usually fine (red structured soils). They may occur associated with one or more of vertic and melanic soils.*

SOILS WITH LIMITED PEDOLOGICAL DEVELOPMENT

🟦	LP1	*Soils with minimal development, usually shallow, on hard or weathering rock, with or without intermittent diverse soils. Lime rare or absent in the landscape.*
⬜	LP2	*Soils with minimal development, usually shallow, on hard or weathering rock, with or without intermittent diverse soils. Lime generally present in part or most of the landscape.*
🟪	FL	*Soils with negligible to weak profile development, usually occurring on deep alluvial deposits.*

SANDY SOILS WITH LITTLE OR NO PROFILE DEVELOPMENT

🟨	AR1	*Red, excessively drained sandy soils with high base status, mainly dunes.*
🟨	AR2	*Red and yellow, well drained sandy soils with high base status.*
🟧	AR3	*Greyish, sandy soils.*

STRONGLY SALINE SOILS

🟪	SC	*Strongly saline soils generally occurring in relatively deep deposits in low lying arid areas.*

PODZOLIC SOILS

🟩	PZ	*Soils with a sandy texture, leached and with subsurface accumulation of organic matter and aluminium, with or without iron oxides, either deep or on hard or weathering rock.*

ROCKY AREAS

⬛	R	*Rock with limited soils.*

LARGE WATER BODIES

🟦	W	*Water.*

(Source: Samadi *et al.* (2005)

1.1.2 Soil fertility inputs

Commercial farmers in the Eastern Cape Province of South Africa use both chemical and organic fertilizers to maintain the fertility of their soils and thus their farm soils have relatively high nutrient status (Mandiringana *et al.,* 2005). On the other hand, the small-scale farmers, most of who reside in the communal areas of the province, are risk averse and rarely invest in chemical fertilizers. However, a large proportion of them do use kraal manure to some extent to replenish nutrients in their home gardens and field plots (Mandiringana *et al.*, 2005).

Surveys conducted in four districts of the Transkei (Lusikisiki, Mthatha, Elliotdale, and Mount Fletcher) showed the external sources of nutrients available in the province to include (i) chemical and processed organic fertilizers that can be purchased from dealers (ii) kraal manure that is available in most homesteads in the communal areas, and (iii) other organic wastes such as municipal refuse, logging and wood processing wastes, food processing wastes and sewage sludge found in urban and peri-urban areas of the Province (Mnkeni and Mkile, 2006). In 1998, the Eastern Cape Province had about 1.73 million cattle, 3.28 million sheep and 2.23 million goats in the communal areas (Yoganathan *et al.*, 1998). The animals are communally grazed but most are penned in kraals at night for security allowing the accumulation of large quantities of animal manure (Mnkeni and Mkile, 2006).

The three types of livestock are usually penned separately, except in a few instances where goats and sheep are penned together. This practice affords farmers the opportunity to choose the type of manure they wish to use on their lands. It is estimated that about 1.6 million tons of dry manure are produced in the province each year based on the 1998 livestock census figures (Mnkeni and Mkile, 2006). The surveys also revealed that livestock-keeping households could on average have up to 15 and 19 t of cattle, goat and sheep manure at their disposal every year, respectively. These amounts of manure would be adequate for 2-3 ha of land, which, coincidentally, is the amount of arable land available to most homesteads in the communal areas of Eastern Cape (Mnkeni and Mkile, 2006).

1.2 PHOSPHATE RETENTION IN SOILS

Phosphate retention in soils involves both adsorption and precipitation reactions; but the adsorption is considered to be the most important process controlling P availability in soils over a short period (Lajtha and Harrison, 1995). Specific adsorption (ligand exchange) occurs when P anions replace the hydroxyl groups on the surface of Al and Fe oxides and hydrous oxides (Haynes and Mokolobate, 2001). Precipitation reactions occur when insoluble P compounds form and precipitate. A distinction between adsorption and precipitation was pointed out by Zheng (2001). Adsorption requires the structure of sorbent to remain essentially unchanged as the process progresses even though its surface activity decreases. This leads to a higher concentration maintained in solution at a greater surface-saturation than that at a lower saturation. In the precipitation process, the surface activity remains constant. However, where precipitates are heterogeneous solids, with one component restricted to a thin outer layer because of poor diffusion (Zheng, 2001), it is difficult to distinguish between the two processes of slow adsorption and precipitation. Therefore, for the purpose of this study, P sorption is defined as the loss of orthophosphate from the soil solution which can occur by either adsorption or precipitation.

1.2.1 Adsorption reactions

Adsorption reactions take place on the surfaces of soil colloids (Tan, 1998) and are one of the reactions attributed to the surface chemistry of soil colloids. An important characteristic of the adsorption of P, and other specifically adsorbed anions, is that adsorption increases the negative charge on the surface of the soil (Barrow, 1984). Added P is usually rapidly adsorbed on the surfaces of Al and Fe oxides, which is followed by much slower reactions (Raven and Hossner, 1994). At low pH a strong inverse relationship between soluble P and extractable Al and Fe oxides in acid soils has been reported, (Warren, 1994; Agbenin and Tiessen, 1995) indicating sorption of P on Al and Fe oxides.

Adsorption of P onto Ca-P minerals is considered to dominate in both alkaline and calcareous systems where carbonates are present (Lajtha Harrison, 1995). However, calcareous soils may still have significant levels of Fe and Al oxides, either as discrete components or as coatings on other soil particles, and thus P sorption may be controlled by the presence of metal oxides as in more acidic soils (Lajtha and Harrison, 1995). P sorption studies in calcareous soils derived from limestone have found stronger relationships between P sorption capacity and hydrous oxides of Fe and Al than with soil $CaCO_3$ content (Solis and Torrent, 1989).

1.2.2 Precipitation reactions

As successive increments of soil are contacted by the moving front of the fertilizer solution, dissolving increasing amounts of Fe, Al, Mn, Ca, Mg, and soil derived cations, the solution becomes supersaturated relative to a variety of P compounds (Sample *et a.*, 1980). These compounds slowly precipitate in the soil matrix and the nature of the precipitating compounds are dependent on the kinds and amounts of cations and anions supplied by both the fertilizer and the soil, pH and soil moisture (Sample *et al.*, 1980).

At low soil pH, additions of P to soils can result in precipitation of Al and Fe phosphates, whilst at high pH insoluble calcium phosphates can form (Haynes and Mokolobate, 2001). In many situations, however, specific adsorption reactions are the main regulators of soil solution P concentrations (Barrow, 1984; Warren, 1994). Fertilizer P addition to the soil leads to the formation of strongly concentrated P solution and often a low pH in the vicinity of the fertilizer granule (Sample *et al.*, 1980). This acidification effect could cause degradation of clay mineral structure, dissolution of $CaCO_3$ and subsequent precipitation of amorphous Al-phosphates and Ca-phosphates (Zheng, 2001).

1.2.3 P fixing soils

High P fixing soils are identified as those with clayey topsoils having red colours indicative of high contents of Al and Fe oxides, usually accompanied by a strong granular structure (Sanchez *et al.*, 1997). These can be collectively termed oxidic soils and are mainly classified as Oxisols, clayey Ultisols, rhodic, oxic groups, or sub-groups of clayey Alfisols and Inceptisols in the soil taxonomy (Soil Survey Staff, 1992). In the FAO taxonomy they are classified as Nitisols, clayey Ferralsols and clayey Acrisols (FAO, 2006).

The International Centre for Research in Agroforestry (ICRAF) estimates there are about 530 million hectares of high sorbing soils in Africa, which represents 25% of tropical Africa’s land area of which the bulk are smallholder farms (Sanchez *et al.*, 1997). Soils with the highest P requirements include Andosols, Ultisols and Oxisols which make up 43% of the land area, of the tropics (Sanchez and Salinas, 1981). These soils have the potential to produce high yields if the main chemical constraints to plant growth are alleviated (Sanchez and Salinas, 1981).

1.3 ASSESSING FERTILIZER P REQUIREMENTS IN SOILS

Plant and soil analysis are used extensively to diagnose the P status of farming systems. Adequate P nutrition at the seedling stage is important for plant development. Insufficiency of P at this stage cannot be remedied by side-dressed P because of the lack of mobility of P in soils (Hedley *et al.,* 1995). Therefore, pre-plant soil tests offer a better method of predicting P requirements for establishing crops.

Indices of the abilities of soils to supply P to plants can be determined (a) by extractive tests that measure the concentration of P in solution and the amount of P in a labile form or (b) from the soils phosphate sorption characteristics (Hedley *et al.,* 1995). In both cases P response trials are required to establish the relationship between crop yield and the P supply index. These relationships vary with the crop, climate and soil type. Thus, large numbers of trials are required before soil tests can be used to estimate P fertilizer requirements with any accuracy (Hedley *et al.,* 1995).

1.3.1 Extractive tests

The availability of nutrients to plants depends, among others, on the quantity and the rate at which it is released and replenished in soil solution as it is withdrawn by plants (Raven and Hossner, 1994). In chemical extraction analysis procedures, P availability in soils is normally described by the quantity factor alone (Fairhurst *et al.,* 1999). These procedures extract variable proportions of available and non-available forms of P depending on the extracting agent (Fairhurst *et al.,* 1999). The form of soil P extracted by each test is determined by its solution pH and the reaction of the ions present in the extractant with sorbed or mineral P. For instance, the HCO_3^- and OH^- in the bicarbonate extract promote desorption of P from $CaCO_3$ and Fe and Al hydrous oxide surfaces (Hedley *et al.,* 1995). Bray 1-P and Truog-extractable P are highly correlated to Al-P and Fe-P in acid soils. Hedley *et al.* (1995) showed that pigeon pea and upland rice, respectively, can mobilize Fe-P in their rhizospheres. In such situations, Bray-1-P or Truog-P could be expected to be effective indices of P availability.

Despite their widespread use, chemical extractants are not well understood in terms of their mode of action and selectivity. The pH changes caused by the extractants undoubtedly modify the organic P by changing its solubility or by hydrolyzing it (Rubaek and Sibbesen, 1993). Another major disadvantage of chemical extractants is that they might mobilize some stable and non-labile soil P forms other than those that are truly plant available (Menon *et al.,* 1989).

1.3.2 Sorption isotherms

Adsorption isotherms describe the adsorption of solution ions by solids at constant temperature in quantitative terms. An adsorption isotherm shows the amount of solute adsorbed by an adsorbent as a function of the equilibrium concentration of the adsorbate (Tan, 1998). To generate adsorption data, a known amount of adsorbent is added to a system containing a known amount of adsorbate. The amount of the adsorbate removed from soil solution is assumed to be adsorbed. Equilibrium conditions must prevail and secondary reaction (such as precipitation) must be eliminated or corrected (Harter and Smith, 1981).

Quantitative description of P sorption by soils has more often been done with the Langmuir (1918), the Freundlich (1926) and Temkin (Bache and Williams, 1971) equations. Although these equations were originally derived to describe the adsorption of gases by solids (Villapando and Graetz, 2001), in many cases these models are able to provide adequate mathematical descriptions of P sorption in soils. The most widely used model is the Langmuir equation, which has a distinct advantage over Freundlich and Temkin equations in that it allows estimation of a sorption maximum and a constant that is related to the P binding strength (Sposito, 1982; Villapando and Graetz, 2001).

Langmuir equation

The Langmuir equation was initially derived for the adsorption of gases by solids. Derivation was based on three assumptions: (1) constant energy of adsorption, which is independent of the extent of surface coverage (homogenous surface), (2) adsorption on specific sites with no interaction between adsorbate molecules, (3) maximum adsorption possible is that of a completely monomolecular layer on all reactive adsorbed surfaces (Harter and Smith, 1981). A common form of the Langmuir equation is

$$S = b * C_{eq} * S_{max} / 1 + b * C_{eq}$$

The linear form after rearrangement:

$$C_{eq}/S = 1/b * S_{max} + C_{eq} / S_{max}$$

Where: C_{eq} = equilibrium concentration of adsorbate in question (μg ml $^{-1}$P)

S = the quantity of P sorbed per unit absorbent (μg P g^{-1} soil),

S_{max} = is the adsorption maximum for a monolayer (μg P g^{-1})

b= is the binding energy or sorption affinity constant (ml μg^{-1})

The adsorption maximum (S_{max}) is calculated from the reciprocal of the slope of the adsorption isotherms. This parameter reflects the numbers of adsorption sites available for P adsorption. The sorption affinity constant (b) is derived from the slope and the intercept values of the isotherm. Parameter b reflects the strength with which the phosphate is bonded to the surfaces (Harter and Smith, 1981; Sposito, 1982).

Freundlich equation

The adsorption isotherm in many dilute solutions was formulated by Freundlich (1926) and takes the form;

$$S = k*C_{eq}^{1/n}$$

Where; k and 1/n are constants dependent on soil type. The constant k defines the intensity of sorption whereas n is related to the energy of sorption, which decreases logarithmically in proportion to the fraction of the surface covered; S and C_{eq} are defined similarly as in the Langmuir equation.

The equation can be transformed linearly using $\log_{10}$:

$$\text{Log } S = (1/n) \log C_{eq} + \log k.$$

The implication of this relationship is that adsorption energy decreases exponentially as the extent of covered or reacted surface increases during adsorption (Sposito, 1980). This empirical equation applies to large amounts of adsorbed P but it is not possible to calculate an adsorption maximum. In contrast, the Langmuir equation applies to relative smaller amounts of adsorbed P and consequently at more dilute equilibrium P concentrations (Sposito, 1980). The major advantage of the Langmuir equation over the Freundlich equation is that an adsorption maximum can be related to various soil properties which supply information about the nature of reaction between soil and P fertilizer.

1.3.3 Application and limitations of sorption isotherms relationships

Phosphate sorption relationships have been used successfully to compare the sorption of P by different soils and to determine the P requirements for crops in some highly weathered tropical soils (Warren, 1994; Nziguheba *et al.*, 1998; Duffera and Robarge, 1999). The P requirements estimated from sorption isotherms aim at building up the status of soil P by a single application to a level which thereafter only requires maintenance application to replenish losses owing to plant uptake, removal by erosion or continuing slow reactions between phosphate and soil. It is also assumed that all the P recommended from sorption isotherms is broadcast and incorporated (Henry and Smith, 2003).

1.3.3.1 External P requirement

An approach which uses the external fertilizer P requirement (EPR) concept represents an effort of improving the empirical processes of calibrating soil P tests for fertilizer P recommendations based on the soil P status. The hypothesis of this approach to estimating P requirements is that fewer costly field experiments are required if EPR values can be successfully predicted from the sorption data. The EPR of crops has been defined as the concentration of P in solution known to be non-limiting to plant growth (Henry and Smith, 2004). Hernandez *et al.* (1987) postulated that for a given climate and provided that the soil contains sufficient clay (5% or more) to ensure adequate reserves of labile P, the external P requirement is a crop constant and independent of soil texture and clay mineralogy. Henry and

Smith (2003) showed that the external P requirement decreases with increasing additional P. This shows that P-isotherms are useful for making fertilizer recommendations, as they are sensitive enough to differentiate between low and high P status in the same soil, and respond to build-up of the soil P content by fertilization. The data obtained from P isotherms may therefore, be used to optimize P applications based on plant needs while at the same time minimizing possible P loss to surface waters through leaching.

The amount of P required to be added to maintain an equilibrium concentration of 0.2 mg P l^{-1} ($P_{0.2}$) in soil solution has been shown to be a threshold for many crops, over which no response to P is observed (Beckwith, 1965; Nziguheba *et al.*, 1998). Even though the P concentration required by plants varies, $P_{0.2}$ (mg P kg^{-1}) has been used as a standard for comparing P requirement of different soils (Duffera and Robarge, 1999). In some instances, however, it is necessary to determine fertilizer P requirement at other P concentrations besides 0.2 mg P l^{-1} as the critical value is dependent on plant species and agronomic factors (Fox, 1981). In South Africa, for example, an external P requirement factor of 0.11 mg P l^{-1} has been shown to be suitable for the low to moderately P fixing soils of the tobacco growing areas of Kwa-Zulu-Natal (Henry and Smith, 2006).

1.3.3.2 Limitations of sorption isotherms

Though P sorption relationships have been used successfully to assess the preliminary fertilizer requirements (Warren, 1994; Nziguheba *et al.,* 1998; Duffera and Robarge, 1999), the labour and time involved in constructing P sorption curves make it too expensive for routine soil testing laboratories. Henry and Smith (2003) proposed a single point sorption test procedure for obtaining an index of the P requirement in soils that bypasses the need for constructing multiple point sorption isotherms.

1.4 INFLUENCE OF MANAGEMENT ON P TRANSFORMATIONS IN SOIL

Changes in tillage and fertilizer application practices can alter the dynamics of soil organic matter turnover and the rate of nutrient cycling (O'Halloran, 1993). Transformations of P in the soil are functions of soil texture, pH, organic matter, $CaCO_3$, Fe- and Al-oxides, temperature, moisture and reaction time (Zheng, 2001). However, cropping and fertilization, which alter the status of organic matter and P concentration in the soil solution, are the most important factors that influence P cycling in the soil (Zheng, 2001).

1.4.1 Cultivation

Cultivation of crops depletes soil P through removal of P in the crop, soil erosion (Tiessen *et al.,* 1983) and smaller leaching losses (Sharpley *et al.,* 1995). As most soil P is associated with fine and light soil fractions, accelerated soil erosion may lead to accelerated P loss (Tiessen *et al.,* 1983; Sharpley *et al.,* 1995). Cultivation normally results in the mineralization of soil organic matter and associated organic P (Po) (Frossard *et al.,* 1995). In general, Po mineralization rates are more rapid in tropical soils where Po is an important source of available P (Hedley *et al.,* 1995).

In tropical soils initial net Po mineralization rates may range from 27 to 50 kg P ha^{-1} yr^{-1} for the first year of cultivation after scrub or grass fallow, which is sufficient to provide P for two crops per year (Hedley *et al.,* 1995). In cooler climates where P_o mineralization rates are slower, not enough P may be mineralized during one growing season. A cultivated fallow may be used to provide enough mineral P, N and S for the crop and to conserve moisture (Sharpley, 1985). However, this period of net mineralization is followed by a net immobilization phase as roots and crop residues with high C: P ratios decompose (Hedley *et al.*, 1995).

1.4.2 Fertilization

Variable effects of fertilizer P and manure application of soil P forms are reported in the literature. Long-term cropping of soil without fertilizer addition results in the depletion of soil P (Hedley *et al.*, 1982), whereas fertilization could result in accumulation of P in the soil with the extent of accumulation dependent on both fertilizer rate and years of application (Zheng, 2001).

1.4.3 Organic materials

Among the most promising organically based soil nutrient practices are: animal manure, compost, incorporation of crop residues, natural fallowing, improved fallows, relay or intercropping of legumes, and biomass transfer. Initially, organic resources were merely seen as sources of nutrients, mainly nitrogen (N) (Palm *et al.*, 2001). However, more recently, other contributions of organics extending beyond fertilizer substitution have been emphasized in research, such as the provision of other macro and micro-nutrients, reduction of P sorption capacity, increase in soil organic matter, reduction of soil borne pest and disease spectra in rotations, and improvement of soil moisture status.

Organic and mineral inputs cannot be substituted entirely by one another but both are required for sustainable crop production (Vanlauwe *et al.*, 2002). One key complementarity is that organic resources enhance soil organic matter status and the functions it supports, while mineral inputs can be targeted to key limiting nutrients. Several attempts to quantify the size of added benefits and the mechanisms involved have been made. Vanlauwe *et al.* (2002), for example, reported positive interactions between urea and use of stover and other organic applications. Direct enhancement of phosphate rock solubility was demonstrated by Ikerra *et al.* (1994) with compost and animal manure amended soils in Tanzania.

1.4.3.1 Effects of additions of organic residues on soil pH and Al activity

In acid soils, high levels of exchangeable Al and Fe play a significant role in controlling orthophosphate concentration in the soil solution (Iyamuremye and Dick, 1996; Haynes and Mokolobate, 2001; Erich *et al.,* 2002). Therefore, crop production on these soils can be improved greatly by adjusting the pH to near neutrality (Whalen *et al.,* 2000). Soil acidity is conventionally corrected by application of lime, which raises pH, precipitates Al and can provide Ca (Hue, 1992).

Addition of organic residues to soils has been shown to cause increases in soil pH (Hue, 1992; Noble *et al.,* 1996). The magnitude of the rise in soil pH varies depending on the type of residue, its rate of application and the buffering capacity of the soil. For additions of about 20 t ha^{-1}, increases in soil pH have generally been in the range of 0.2–0.6 pH unit and, with rates of 40–50 t ha^{-1}, increases of 0.8–1.5 pH units have been recorded (Iyamuremye *et al.*, 1996; Noble *et al.,* 1996). Whalen *et al.* (2000) reported higher pH and lower oxalate extractable Al after cattle manure application to the soil and the effect persisted during the 8-week incubation period. An increase in pH confers a greater negative charge on adsorption surfaces and thus tends to reduce P sorption (Iyamuremye *et al.,* 1996). Thus a decrease in P sorption when manure is added to the soil may partially be attributable to the increased soil pH (Iyamuremye *et al.*, 1996).

Mechanisms involved

There are several mechanisms that have been suggested to explain the initial rise in soil pH when organic amendments are applied to soils. These include oxidation of organic-acid anions present in the decomposing residues, ammonification of organic N in the applied residue, specific adsorption of organic molecules produced during residue decomposition and reduction reactions induced by anaerobiosis (Haynes and Mokolobate, 2001). Plant material and animal wastes generally contain an excess of cations over inorganic anions and the balance is maintained by synthesis of organic acid anions, e.g. oxalate, citrate, malate (Haynes and Mokolobate, 2001). Oxidation of these organic acid anions during decomposition of plant material and animal wastes is likely to be a major contributor to an increase in pH (Noble *et al.,* 1996). It has been shown that increases in soil pH following the addition of malate and citrate are highly correlated with CO_2 evolution during the decomposition of these two anions (Noble *et al.*, 1996).

The added organic-acid anions are able to complex protons and these accounts for any immediate rise in soil pH (Yan *et al.,* 1996). That is, if soil pH is less than the dissociation constants (pKa) for the weak organic acids in the added residues, there will be an increase in soil pH due to association of H^+ from the soil with some of the organic anions (Haynes and Mokolobate, 2001). It has been shown that increases in soil pH following the addition of malate and citrate are highly correlated with CO_2 evolution during the decomposition of these two anions (Noble *et al.,* 1996; Yan *et al.,* 1996).

1.4.3.2 Effects of organic residues addition on P sorption and availability

Soil organic matter management through conservation tillage, use of mulches, manures and crop residues plays a key role in efficient utilization of fertilizer P, especially on acid, P deficient soils of the tropics (Hedley *et al.,* 1995). Increased soil organic matter content enhances soil productivity through improvement of soil structure, provision of N, S and P, increased cation exchange capacity, increased soil water holding capacity and alleviation of Al toxicity. All these factors impact negatively on plant growth.

There is considerable evidence in the literature to suggest that the application of organic material to soil may increase P solubility and thus significantly increase the availability of P to plants and decrease P adsorption capacity of soils (Iyamuremye *et al.,* 1996; Nziguheba *et al.*, 1998; Whalen *et al.,* 2000). Erich *et al.* (2002) reported increased plant available P and resin de-sorbable P in soils amended with cattle manure.

The reduced P sorption and increased P availability following application of organic amendments to soils is thought to be due to the cumulative effect of several mechanisms (Iyamuremye and Dick, 1996; Erich *et al.,* 2002). These include release of inorganic P from decaying residues, blockage of P sorption sites by organic molecules released from the residues, a rise in soil pH and complexation of soluble Al and Fe by organic molecules (Iyamuremye and Dick, 1996). Iyamuremye *et al.* (1996) demonstrated that the P sorption capacity of five high P fixing soils in Rwanda was reduced when amended with cattle manure and alfalfa. Sharpley *et al.* (1984) also reported increased resin-P, bicarbonate-P, NaOH-P_i and microbial P in soils following application of tithonia (*Tithonia diversifolia*) with or without triple super phosphate, with a concomitant reduction in P sorption.

Adsorption reactions for organic acids are concentration dependent and adsorption generally increases with decreasing pH (Jones and Brassington, 1998). As a result of specific adsorption reactions, organic acids can compete with P for sorption sites on soil surfaces (Violante and Gianfreda, 1993). Maximum reduction in P adsorption is reported to occur when organic acids are added before P, and their effectiveness in inhibiting P sorption generally increases with decreasing pH (Violante and Gianfreda, 1993). However, whilst some of the newly-added humic material may be adsorbed to oxide surfaces thus reducing P sorption, some of it may react with soluble and exchangeable Al forming new P sorption sites (Haynes and Mokolobate, 2001).

1.4.4 Biological mechanisms of soil P dynamics

Over the years, the effect of organic amendments alone and in combination with mineral fertilizer on P availability and P adsorption/desorption have been investigated but most of the research has mainly focused on the importance of inorganic P (P_i) for plant nutrition. However, organic P (P_o) can account for 20 to 80% of the total P in most mineral soils and contribute significantly to plant nutrition (Sharpley, 1985).

1.4.5 Soil microbial biomass P

Soil microbial biomass consists mainly of bacteria, fungi and other microbiota and has been defined as the living part of the soil organic matter excluding plant roots and soil animals larger than 5×10^3 μm^3 (Goyal *et al.,* 1992). Microbial biomass constitutes the active fraction of soil organic matter, plays a central role in the biochemical processes and is important in determining the quality and health of soil (Belay *et al.,* 2002).

In addition to mediating the turnover of organic P, soil micro-organisms may also constitute a significant reservoir of P (Brookes *et al.*, 1984; Tiessen *et al.*, 1994). Microbial P is reported to range between 6 and 100 kg ha^{-1} (Brookes *et al.*, 1984) with the highest values found in woodland and grassland soils and the lowest in cultivated soils (Brookes *et al.,* 1984). Microbial processes are said to be driven by the availability of decomposable organic carbon, which highlights the importance of sustaining and improving soil organic matter concentrations if large populations of microbes are to be active in the soil. Organic amendments such as manures and plant residues are a major source of organic substrate in the soil (Tiessen *et al.,* 1983).

Various effects of organic manures and mineral fertilizer P on different soil P pools have been reported and they depend mainly on the rates of P applied, P removal by crops, inherent soil properties and climatic conditions. O'Halloran (1993) observed increased labile inorganic P contents in soils receiving manure and triple superphosphate additions compared with just superphosphate additions. In addition to facilitating the turnover of P and being a significant reservoir of P (Brookes *et al.*, 1984; Tiessen *et al.,* 1994), the incorporation of P into microbial cells prevents its strong sorption to soil constituents (Brookes *et al.,* 1984).

Improvement in mobilization of soil P requires a better understanding and management of soil biological processes, particularly how P immobilization and turnover in soils are controlled by environmental (e.g. climate, soil type, topography) and anthropogenic factors e.g. fertilizers, pesticides, crops and tillage (He *et al.*, 2003). However, there is little or no information available on the sizes of microbial biomass and turnover in soils receiving inorganic P fertilizer with manures in South African soils, specifically those from the Eastern Cape. Indeed, very little is known about the long-term effects of manure and fertilizer P on soil P transformations in these soils.

1.4.6 Effects of soil management on P fractions

Several studies have related different P fractions in tropical soils to plant growth (Goyal *et al.*, 1992; Guo and Yost, 1998) or showed the influence of land use and the fate of applied fertilizers (Iyamuremye *et al.*, 1996). There has been success in relating different P fractions to P pools of different plant availability. Iyamuremye *et al.* (1996) found an increase in resin-P_i, $NaHCO_3$-P_i and -P_o, as well as NaOH-P_i after addition of manure or alfalfa (*Medicago sativa L.*) residues to acid low-P soils from Rwanda. In the study of Guo and Yost (1998) in Hawaii, resin-P_i, $NaHCO_3$-P_i, and NaOH-P_i were most depleted by plant uptake on highly weathered soils. NaOH-P_i was important in buffering available P supply while significant depletion of organic fractions could rarely be measured. Bühler *et al.* (2002), summarizing results from various experiments, pointed out that in tropical soils, the amount of different rates of P fluxes are controlled both by physio-chemical factors (mainly sorption–desorption) and by biological reactions (immobilization–mineralization).

1.4.7 Limitations and environmental implications of organic manure use

A major constraint regarding the use of organic inputs is their bulkiness and scarcity. Large quantities are required to provide even a fraction of that required to maintain agricultural production at a desirable level (Nziguheba *et al.,* 1998). For example, 5 Mg of manure containing 0.3% P contains only 15 kg P. The labour required for moving such quantities can be enormous. Production of large quantities of manure may become more difficult as the sizes of farms become smaller in the coming years due to population growth and farm subdivision that will lead to reduction in sizes of herds. Thus low P content, low availability, competing uses and labour will generally preclude exclusive use of manure for P fertilization requirements in smallholder farming. Despite the shortcomings, manures are likely to remain a key resource for soil fertility management in the mixed livestock-arable farming systems which characterize the agricultural sector in most parts of Africa and more so on smallholder systems of South African agriculture. Combining organic and inorganic nutrient sources may provide an efficient use of these scarce resources for maintaining high yields (Nziguheba *et al.,* 1998).

Transport of P by subsurface flow pathways can be an important mechanism of P transfer from land to water, particularly in manured soils (Kuo and Baker, 1982; Eghball *et al*., 1996; Kleinman *et al*., 2003; Butler, and Coale, 2005). Data from a wide range of field and catchment studies have shown that, higher rates of transfer (2-6 kg P ha^{-1} yr^{-1}, up to 17 kg P ha^{-1} yr^{-1}) have been recorded from soil under intensive pastoral or arable farming, especially when animal manure is applied (Gillingham and Thorrold, 2000; McDowell *et al*., 2001; Nash *et al*., 2000). Elsewhere, Mozaffari and Sims (1994) and Kuo and Baker (1982) reached similar conclusions after comparing P profile data from unmanured and manured plots of various mineral and organic soils (Aquic Hapludults, Typic Umbraquults, Typic Fluvaquents, Terric Medisaprists).

1.5 METHODS FOR STUDYING P TRANSFORMATIONS IN SOILS

1.5.1 Ion exchange resins

Resin extraction methods have been favourably employed to estimate plant-available P for soils with large variations in physical and chemical properties. In contrast chemical tests are not always reliable over all soil types (Myers *et al.,* 2005). The ion sink P testing method has an advantage over conventional chemical extractants such as Bray (Bray and Kurtz, 1945), and Mehlich-3 (Mehlich, 1984) because the ion-sink methods function similarly to a plant-root surface adsorbing available P ions from the *in situ* labile P pools in the soil (Myers *et al.,* 2005). The rate of resin P sorption is dependent solely on the rate of P desorption or dissolution from the soil matrix and not on the properties of the resin itself (Cooperband and Logan, 1994).

Ion-exchange materials can be viewed as competitive exchangers with the soil solids that are in dynamic equilibrium with soil solution dissolved species (Cooperband and Logan, 1994). Over time, anion exchange material behaves as either sinks or exchangers of P depending on: (i) the intrinsic anion-exchange capacity of the resin material; (ii) the amount of time in contact with the soil; and (iii) the soil’s P retention capacity (Cooperband and Logan, 1994). Raven and Hossner (1994) reported that the rate of P release was correlated well with plant growth stages. The resin Pi tests have been found to be less sensitive to soil type than the other P tests and they can be used in acid, alkaline and calcareous soils (Menon *et al.*, 1989).

The ability of this method in predicting the amount of fertilizer P needed to achieve maximum crop yield is however often limited, since it estimates only a small portion of labile P and ignores the slow release of sorbed P and soil organic P mineralization (Zheng, 2001). As a growing plant continuously removes phosphate ions from the soil solution, evaluating the capacity of the soil to maintain solution P from all labile pools is therefore important.

1.5.2 Sequential fractionation

Soil P exists in many complex chemical forms, which differ markedly in their behaviour, mobility and bioavailability in the soils. One way of characterising the different P forms present in soils is to consider their role in the soil P cycle and to differentiate these forms in relation with their turnover rate.

Chemical sequential extraction procedures developed by Hedley *et al.* (1982) and Cross and Schlesinger (1995) have been and still are widely used to divide extractable soil P into different inorganic and organic fractions. The underlying assumption in these approaches is that readily available soil P is removed first with mild extractants, while less available or plant-unavailable P can only be extracted with stronger acids and alkali.

The P fractions in order of extraction resulting from the fractionation procedure developed by Hedley *et al.* (1982) and modified by Tiessen and Moir (1993) are interpreted as follows: Resin-P_i represents inorganic P (P_i) either from the soil solution or weakly adsorbed on (oxy)-

hydroxides or carbonates, 0.5 M Sodium bicarbonate (pH 8.5) also extracts weakly adsorbed P_i and easily hydrolysable organic P (P_o)-compounds like ribonucleic acids and glycerophosphate (Hedley *et al.*, 1982). 0.1 M sodium hydroxide extracts P_i associated with amorphous and crystalline Al and Fe (oxy)hydroxides and clay minerals and P_o associated with organic compounds (fulvic and humic acids). 1 M Hydrochloric acid extracts P_i associated with apatite or octacalcium P (Frossard *et al.*, 1995). Hot concentrated HCl extracts P_i and P_o from more stable pools. Organic P extracted by concentrated HCl may also come from particulate organic matter (Tiessen and Moir, 1993). Residual P that remains after extracting the soil with the above extractants represents very recalcitrant P_i and P_o forms. Resin and bicarbonate fractions represent soil P that is both exchangeable and easily mineralizable (Cross and Schlesinger, 1995), which is a minute fraction of the total P pool that is plant available.

1.5.3 Measurement of microbial biomass P in soil

Direct measurement of the P content of the soil biomass is essential for an accurate assessment of the importance of the microbial biomass in P cycling and in crop nutrition (Brookes *et al.* 1982). The usual microbial biomass P determination consist of measuring the difference in inorganic P extracted in 0.5 M $NaHCO_3$ (pH = 8.5) (Brookes *et al.* 1982) or mixed exchange resin membranes (Ayaga, *et al.* 2006) between a control sample and a soil sample fumigated for 24 hours with alcohol free $CHCl_3$. A correction factor (Kp = 0.4) is used to correct for incomplete release of P from microbial cells during fumigation (Brookes *et al.* 1982). Organic P in the microbial cells is easily hydrolysed after cell death and rapture, resulting in the release of mostly inorganic P upon chloroform fumigation of soil microbes (Brookes *et al.* 1982).

Biomass P (Bp) is calculated as:

$$\mathbf{B}\boldsymbol{p}\ \mathbf{(mg\ kg^{-1}\ soil) = (P}\boldsymbol{f}\mathbf{ - P}\boldsymbol{nf}\mathbf{)/(K}\boldsymbol{p}\mathbf{ * 100/R)}$$

Where:

Pf = P extracted from $CHCl_3$ fumigated samples

Pnf = P extracted from non-fumigated samples

Kp = 0.4, the fraction of biomass P extracted after fumigation (Brookes *et al.*, 1982).

R = % Recovery of added P = 100(Ps-Pnf)/50 (Brookes *et al.*, 1982) where:

Ps = P extracted by exchange resins from non-fumigated soil spiked with P

1.6 CONCLUSIONS

From this review of the literature, it is evident that the P cycle in the soil system is complex. The discussion indicates that chemical, physical and biological processes influence the fate of P fertilizer added to soils. Transformation of P in the soil not only involves many inorganic P (Pi) and organic P (Po) compounds but is also affected by soil properties, cropping and fertilization rate. An understanding of these processes, the measurement of the size of the various fractions or pools of P in soils and the rate at which P transfers from one pool to another are all important if we are to help farmers make the most economic use of P fertilizer. Management practices should be developed with agronomic and environmental consequences in mind.

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CHAPTER 2

ASSESSMENT OF PHOSPHATE SORPTION AND REQUIREMENT FOR SOME SOILS OF THE TRANSKEI REGION, SOUTH AFRICA

2.1 ABSTRACT

A good understanding of a soil's P sorption capacity is important for predicting crop response to added P and for identification of appropriate P management strategies. There is, however, little or no information in this regard for soils of the Eastern Cape. This study was therefore conducted to determine the P sorption properties of selected soils from the Transkei region of South Africa and to relate the derived sorption values to selected soil parameters. A further objective of the study was to estimate and verify the external P requirements for the soils estimated from the Langmuir equations. Phosphate sorption characteristics were adequately described by the Langmuir model, with coefficients of determination (r^2) values > 0.95 observed for all the soils investigated. Sorption maxima (S_{max}) ranged from 192.3 to 909.1 (mg P kg^{-1}) and were highly and positively correlated with sorption affinity constant ($r = 0.93$, $p = 0.01$) and organic C ($r = 0.71$, $p = 0.01$). The sorption affinity constant, b, ranged from 0.051 to 0.786 mg P l^{-1} and was low for Bethania, Qweqwe and Qunu suggesting that P was more loosely bound to the soil surfaces and should be more available to plants. The amount of P required for maintaining a soil solution concentration of 0.2 mg P l^{-1} ranged from 2.1 to 123.5 mg P kg^{-1} soil. Soils collected from Qweqwe (a Cambisol), Qunu (an Acrisol), Ncihane (a Luvisol) and Bethania (a Ferralsol) had lower external P requirement values and were classified as lower sorbers, whereas soils from Ntlonyana (a Planosol), Chevy Chase (a Ferralsol) and Flagstaff (a Ferralsol) were classified as moderate sorbers. The results showed that a soil solution P concentration of 0.2 mg P l^{-1} ($P_{0.2}$) was optimal for plant growth in these soils and that the single point test function could be successfully used to predict the external P requirement ($P_{0.2}$) for the soils from Ntlonyana, Ncihane, Qweqwe, Qunu, Bethania and other soils with similar chemical and mineralogical characteristics.

Key words: External P requirement, P-sorption, Single point sorption test

2.2 INTRODUCTION

Phosphorus deficiency in soils is most prevalent where strong sorption of P by aluminum and iron oxides and amorphous materials occurs, resulting in poor mobility of soil inorganic P (Hinsinger, 2001). This is a major contributing factor to reduced effectiveness of added phosphates necessitating the need for larger applications of fertilizer P to achieve good crop yields (Warren, 1994). Many South African soils are suspected to have high P sorption capacities, particularly those from high rainfall areas which tend to be acidic. Phosphate sorption studies on soils from the neighbouring provinces of KwaZulu-Natal and Mpumalanga have shown that highly weathered soils have high sorption capacities ranging from 500 to 1197 mg P kg^{-1} soil (Beinbridge *et al.*, 1995; Henry and Smith, 2002). The highest sorbers are weathered red or yellow-brown clays with high oxalate (amorphous) aluminum content especially those with a humic-horizon such as Inanda, Kranskop and Magwa forms from high rainfall areas. There is presently little or no information on the P sorption behaviour of soils from the Eastern Cape Province, South Africa. Given the role of P sorption in influencing the availability of soil applied fertilizer P, the need for such information cannot be overemphasized.

Phosphate sorption relationships are commonly used in the determination of the external P requirement (EPR) of crops. According to Fox (1981), EPR is the minimum concentration of P in solution that is non-limiting to plant growth. For most crops, the amount of P in equilibrium with 0.2 mg P l^{-1} ($P_{0.2}$) has been shown to be the threshold over which no response to P is observed (Beckwith, 1665; Iyamuremye *et al.*, 1996). Phosphate sorption isotherms are, therefore, used for estimating the P fertilizer requirements of soils by interpolating the amount of P needed to achieve in solution the non-limiting concentration of 0.2 mg P l^{-1}. In some instances, however, it is necessary to determine fertilizer P requirement at other P concentrations than 0.2 mg P l^{-1}, as the critical value is, in some cases, dependent on plant species and agronomic and nutritional factors (Raven and Hossner, 1994).

The labour and time involved in constructing P sorption curves makes the use of sorption isotherm technique too expensive for routine soil testing laboratories. Henry and Smith (2003) proposed a single point sorption test procedure for obtaining an index of the P requirement in soils that bypasses the need for constructing multiple point sorption isotherms. It would, therefore be of interest to determine if the single point sorption procedure could be used as an index for estimating the P requirement of soils in the Eastern Cape.

In view of the above, the objectives of this study were: (i) to quantify and compare the P sorption characteristics of selected soils from the Transkei region of South Africa and to establish their relationship with other soil parameters, and (ii) to estimate and verify the soil external P requirements estimated from the Langmuir equations and to relate those indices with single point sorption test values.

2.3 MATERIALS AND METHODS

2.3.1 Experiment 1. Assessment of phosphate sorption and external P requirement of some soils from the Transkei region using sorption isotherms

2.3.1.1 Soil preparation

Surface soil samples (0-15 cm) were collected from cultivated farmers' fields from four districts (Elliotdale, Umtata, Lusikisiki and Mt. Fletcher) in Transkei, South Africa (Appendix 1). The districts were selected to represent low altitude (0-600 meters above sea level (masl)), medium altitude (700-1100 masl) and high altitude (1500-3000 masl). Detailed sites and soils descriptions of the study area are given in Appendices 2 and 3, respectively.

Most of the soils are dominated by quartz, mica and kaolinite in the clay fraction and contain trace to low amounts of feldspars in the clay fraction (Table 2.1). Some of the soils have chlorite-vermiculite interstratifications in the clay fraction. Quartz is by far the dominant mineral in the silt fraction of all soils examined, followed by feldspars. The dominance of the low-activity clay kaolinite in these soils suggests that the soils could be highly weathered.

Table 2.1 Clay mineralogy of some topsoils from the Transkei region

Site	Quartz	Mica	Kaolinite	Feldspars	Chl-Verm	Hematite
Ncihane	++	++	++	+	+	-
Ntlonyana	+	+	++	+	+	-
Qunu	+++	++	(+)	(+)	-	+
Qweqwe	+	++	+	++	-	-
Bethania	++	++	+	(+)	-	+
Chevy Chase	++	+	++	-	(+)	-
Flagstaff	NA	NA	NA	NA	NA	NA

Chl-Verm = chlorite-vermiculite mixed-layer clays, +++ = very high, ++ = high, + = low, (+) = trace, - = absent. NA = Data not available (Adapted from Mandiringana *et al.*, 2005)

2.3.1.2 Soil characterization

Soil pH was measured both in water and 1.0 M KCl (soil: solution ratio of 1:2.5) using a pH meter with a glass and reference calomel electrode (Model pH 330 SET-1, 82362) after the soil suspensions were shaken for 30 minutes and left standing for 1 hour. Electrical conductivity was measured in water (1: 2.5 soil: water ratio) using a conductivity meter (Model Cond.330i/SET 82362). Organic C and N were determined by dry combustion using a LECO TRUSPEC C/N auto-analyzer (LECO Corporation, 2003). Total P was estimated following wet digestion with H_2O_2/H_2SO_4 (Okalebo *et al.*, 2002)**.** Exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+ were extracted with 1.0 M ammonium acetate at pH 7 (Okalebo *et al.*, 2002) and determined by atomic absorption spectrophotometer. Exchangeable acidity (Al^{3+} + H^+) was determined by extraction with 1.0 M KCl and titration with 0.05 M NaOH (Okalebo *et al.*, 2002). Cation exchange capacity was estimated by the summation of exchangeable cations and exchangeable acidity.

Amorphous Fe and Al (Fe_{ox} and Al_{ox}) were determined in 0.2 M acidified ammonium oxalate adjusted to pH 3.0 with oxalic acid (Warren, 1994). Dithionite citrate bicarbonate-extractable Fe and Al (Fe_{CDB} and Al_{CDB}) were determined by the method of Mehra and Jackson (1960) as cited by Agbenin (2003). Exchangeable Al and Fe (Al_{KCl} and Fe_{KCl}) were extracted with 1.0 M KCl as outlined by Okalebo *et al.* (2002). The extracts were separated by centrifuging at 3000 rev min^{-1} for 10 min and filtered with Whatman No.42 filter paper to get a clear solution. Al and Fe in all the extracts were measured by atomic absorption spectrophotometery. All results are the means of triplicate analyses. Particle size analysis was done by the pipette method as described by Kettler *et al.* (2001).

2.3.1.3 Phosphate sorption isotherms

Three replicate (3.0 g) air-dried milled soil samples (<2 mm) were weighed into 50 ml centrifuge tubes and suspended in 30 ml of 0.01 M $CaCl_2$ of supporting electrolyte containing 0 to 100 mg P l^{-1} as KH_2PO_4 with increments of 10 mg P l^{-1} . Three drops of toluene were added to each container to inhibit microbial activity. The tubes were then stoppered and shaken in an end to end shaker for 24 hours at a room temperature (25 ± 1 ^{0}C) at 100 oscillations per minute (Warren, 1992). Following equilibration, the soil suspensions were centrifuged at 3000 rev min^{-1} for 10 minutes and filtered through Whatman No. 42 filter paper to obtain a clear solution. Phosphorus in the supernatant was then determined by the method of Murphy and Riley (1962). The amount of P sorbed was calculated as the difference between the amount of P added and that remaining in solution (Fox and Kamprath, 1970).

Evaluation of phosphate sorption data

The linear form of the Langmuir one surface equation was used to calculate parameters that are indices of the capacity for, and the intensity of, P sorption by the soil. The Langmuir model was selected because of its simplicity of estimating P sorption maxima and sorption affinity constant.

Sorption of added P, S_i (mg kg^{-1}) was calculated as

$$S_i = [(C_o - C_{eq})V]/ W_s$$

Where; Si is P sorbed, (mg kg^{-1}), C_o is the initial concentration of P added (mg l^{-1}), C_{eq} is the concentration in solution after the 24 hour equilibration (mg l^{-1}), V is the volume of P solution added (l), and W_s is the oven-dry weight of soil (kg).

Sorption data were then fitted into a linearized Langmuir equation

$$C_{eq} * S^{-1} = (S_{max} * b)^{-1} + C_{eq} * S_{max}^{-1}$$

where C_{eq} is the concentration of P remaining in solution after 24 hours equilibration (mg l^{-1}), S is the total amount of P sorbed (mg kg^{-1}), b is a constant related to the binding energy (l mg^{-1}) and S_{max} is the adsorption maximum (mg kg^{-1}).

The sorption maximum (S_{max}) was calculated from the reciprocal of the slope of the adsorption isotherms. This parameter reflects the magnitude of sorption sites available for P adsorption. Soil external P requirements were determined by substituting the desired P concentration into the fitted Langmuir equations (Dodor and Oya, 2000).

2.3.1.4 Single point sorption test

The single point sorption test (SI) was determined as described by Henry and Smith (2006). Simply, 50 ml of solution containing 10 mg P l^{-1} as KH_2PO_4, in 0.002 M $CaCl_2$, and three drops of toluene were added to 2 g of air dried soil (< 2 mm). The suspensions were shaken for 24 hours on an end-over-end shaker, rotating continuously at 100 oscillations per minute. Following equilibration the suspension was centrifuged at 5000 rev min^{-1} for 10 minutes and then filtered through Whatman paper No 42. Phosphorus in the supernatant was then determined by the method of Murphy and Riley (1962). The amount of P sorbed was computed as the difference between the initial P concentration of the additional solution and the final concentration in the supernatant. The single point sorption test was taken as the amount of P sorbed expressed as a percentage of added P (Henry and Smith, 2003).

2.3.2 Experiment 2 Evaluation of external P requirements of two soils in a glasshouse pot experiment

Flagstaff and Qunu soil representing high and low fixing soils, respectively were selected for this study to evaluate the validity of using a soil solution P concentration of 0.2 mg P l^{-1} in these soils for P recommendation. Triple super phosphate containing 20% P was applied in pots containing 7 kg of soil to obtain a range of soil solution P concentrations ($EPRf_{actor}$) of between 0 to 0.35 mg P l^{-1} for both soils.

The treatments were applied by uniformly mixing the added P with the soil in each pot. Nitrogen and K were applied as ammonium nitrate (28 % N) and KCl (53 % K), respectively to all pots at rates equivalent to 200 kg N ha^{-1} and 100 kg K ha^{-1}. In addition, each pot received the equivalent of 5.7 kg Zn ha^{-1}, 2.5 kg Cu ha^{-1}, 4.0 kg Mn ha^{-1}, 0.1 kg Mo ha^{-1}, 1.1 kg B ha^{-1} and 56.1 kg S ha^{-1} after the plants had established. Nutrient carriers were; $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, $MnCl_2.4H_2O$, $Na_2MoO_4.2H_2O$, $Na_2B_4.O_7.10H_2O$ and elemental sulphur, respectively. Treatments were applied assuming that the plough layer (0 -15 cm depth) contained $2 * 10^6$ kg ha^{-1}.

The pots were placed on benches in the glasshouse and arranged in a randomized complete block design in a split plot arrangement with four replications. The soils were the main plots whilst the P rates were the sub plots in a split plot design experiment. Twenty four seeds of oat *(Avena sativa L.)* were then sown in each pot at a depth of 2.5 cm. The plants were thinned after establishment to 16 plants per pot. Tap water was added to the pots to maintain adequate soil moisture for the growing plants as required throughout the growing period.

The shoots were harvested 10 weeks after planting by cutting the shoots 0.5 cm above the soil surface then oven dried at 65°C to a constant weight and dry matter yield determined. The samples were then ground to < 1 mm and analyzed for total P in the whole plant using a H_2SO_4/H_2O_2 wet digestion procedure (Okalebo *et al.,* 2002). Phosphorus in the digest was then determined by the method of Murphy and Riley (1962).

2.3.3 Statistical analysis

Relationships between P sorption parameters and P sorbed to obtain solution P concentration of 0.2 mg l^{-1} ($P_{0.2}$) with selected soil chemical properties were analyzed with simple regression and correlations and tested for significance at $p = 0.05$ using GenStat statistical software (GenStat Release 4.24DE, 2005). Relationships between sorption maxima (mg kg^{-1}), parameter b (l. mg^{-1}) related to the energy of adsorption and external P requirements with soil properties were determined. The contribution of soil properties to sorption parameters were examined using the maximum r^2 improvement stepwise model-building procedure (SAS Institute, 2001). The effects of critical P concentration on dry matter yield and plant P uptake were evaluated using GenStat statistical software (GenStat Release 4.24DE, 2005). Regression analyses were conducted to find models best describing the relationships between critical P concentration (EPR_{factor}) and dry matter yield and plant P uptake.

2.4 RESULTS

2.4.1 Soil characterization

The soils differed in their P status and characteristics expected to affect P retention and release (Table 2.2). All the soils were acidic and their pH_{water} values ranged from 4.6 to 5.6 and 3.9 to 4.9 for pH_{KCl}. Soil pH values in 1 M KCl were lower than those measured in water, indicating that all the experimental soils were negatively charged at their natural pH. The soils were low in organic carbon contents, which ranged from 3.97 to 25.7 g kg^{-1}. The clay in the soils ranged from 12.5 to 33%.

2.4.2 Al and Fe forms

The soils varied greatly in the amounts of exchangeable Al and Fe, oxalate and dithionite extractable Al and Fe oxides (Table 2.3). Exchangeable Al (Al_{KCl}) was highest in the soil from Flagstaff (76.27 mg kg^{-1}) and was not detected in soils from Qweqwe and Bethania, whereas exchangeable Fe was detected in all soils and ranged from 3.20 to 11.00 mg kg^{-1}. Oxalate Al (Al_{ox}) ranged from 0.11 to 3.54 g kg^{-1} of soil. Oxalate Fe (Fe_{ox}) was high in soils collected from Flagstaff, Ncihane and Ntlonyana, ranging from 3.47 to 3.94 g kg^{-1} of soil whereas all the other soils ranged from 0.27 to 0.69 g kg^{-1} of soil (Table 2.3). Dithionite extractable Al (Al_{CDB}) had a similar trend to Al extracted with acidified ammonium oxalate. The difference between Al_{CDB} and Al_{ox} was assumed to be due to the Al^{3+} substituted for Fe^{3+} in the crystalline Fe oxides (Fe_{crys}), which ranged from 0.40 to 2.23 (mg kg^{-1}).

Table 2.2 Selected chemical properties of soils used in the study

Properties	Sampling Sites and Grid References						
	Ntlonyana	Ncihane	Qweqwe	Qunu	Chevy Chase	Bethania	Flagstaff
	$31^{0}46^{1}27^{11}$ S $28^{0}38^{1}16^{11}$ E	$32^{0}00^{1}04^{11}$ S $28^{0}42^{1}33^{11}$ E	$31^{0}41^{1}42^{11}$ S $28^{0}42^{1}09^{11}$ E	$31^{0}46^{1}27^{11}$ S $28^{0}38^{1}16^{11}$ E	$30^{0}50^{1}54^{11}$ S $28^{0}32^{1}12^{11}$ E	$30^{0}39^{1}41^{11}$ S $28^{0}16^{1}45^{11}$ E	ND$^{\delta}$
pH $_{H2O}$	5.0	4.9	5.6	5.5	4.6	5.6	4.7
pH $_{KCl}$	4.3	4.1	4.9	4.9	3.9	4.9	4.0
Total P (g kg^{-1})	0.18	0.18	0.21	0.14	0.17	0.18	0.42
Total N (g kg^{-1})	1.93	0.87	0.81	0.70	0.83	0.16	1.30
Organic C (g kg^{-1})	25.7	11.3	12.3	10.4	15.4	3.97	21.9
Bulk density (kg m^{-3})	1351	1449	1471	1492	1515	1698	1429
Exchangeable acidity (cmol (+) kg^{-1})	0.93	0.83	0.07	0.10	1.27	0.10	1.73
CEC (cmol (+) kg^{-1})	16.53	11.28	15.80	7.39	6.34	4.64	16.19
% sand	21.1	39.0	53.2	40.6	74.7	54.7	21.8
% silt	56.4	45.2	30.3	38.5	12.8	28.0	45.2
% clay	22.5	15.8	16.5	20.9	12.5	17.3	33.0
Soil Form*	Klapmuts	Cartref	Glenrosa	Westleigh	Hutton	Hutton	Inanda
Corresponding FAO Soil units**	Planosol	Luvisol	Cambisol	Acrisol	Ferralsol	Ferralsol	Ferralsol

*South Africa Soil Classification Working Group (1991); **Corresponding FAO (2006) soil units; δ = data not available

Table 2.3 Forms of Al and Fe oxides in soils used in the study

Soil	Exchangeable		Oxalate		Dithionite		Crystalline
	Al	Fe	Al	Fe	Al	Fe	Al
	mg kg^{-1}		g kg^{-1}				
Ntlonyana (Nt)	12.50	11.00	0.41	3.47	2.28	9.24	1.87
Ncihane (Nc)	19.03	9.70	0.42	3.49	1.68	10.12	1.26
Qweqwe (Qw)	0.00	3.63	0.11	0.33	0.51	5.55	0.40
Qunu (Qu)	0.77	3.47	0.12	0.27	1.31	9.91	1.19
Chevy chase (Cc)	48.73	10.40	0.77	0.66	3.00	12.73	2.23
Bethania (Bt)	0.00	3.30	0.18	0.69	1.56	13.20	1.38
Flagstaff (Fs)	76.27	3.20	3.54	3.94	5.70	50.50	2.16

2.4.3 Phosphate sorption

2.4.3.1 Sorption isotherms

Sorption behavior was adequately described by the linearized Langmuir sorption model, with regression coefficient (r^2) values > 0.95 observed for all the soils under study. Sorption isotherms for the seven soils showed that the soils differed considerably in sorption characteristics (Table 2.4). Sorption maxima ranged from 192.3 to 909.1 mg P kg^{-1} and sorption affinity constant ranged from 0.051 to 0.786 (l mg^{-1}) and was smaller for Bethania and Qweqwe. The amount of P required to maintain a soil solution concentration of 0.2 mg P l^{-1} ($P_{0.2}$) ranged from 2.1 to 123.5 mg P kg^{-1} soil (Table 2.4) and as expected the trend was similar to that of the sorption maxima.

2.4.3.2 Single point sorption test

The values for SI, expressed as a percentage, ranged from 9.5 to 86.5% (Table 2.4) and were highly and significantly correlated (r = 0.93) with $P_{0.2}$ (mg P kg^{-1}) values. The SI values were also highly correlated with S_{max} (r = 0.92) and sorption affinity constant b (r = 0.81) (Table 2.4).

2.4.3.3 Relationship between P sorption parameters with soil properties

The correlations of these relationships are given in Table 2.5. Al_{CDB} gave the highest correlations with sorption parameters. Organic C did not show significant correlation with any of the P sorption parameters. However, the general trend showed that organic C was positively correlated to sorption maxima (r = 0.71), the sorption affinity constant b (r = 0.63), and to $P_{0.2}$ (r = 0.70). Soil pH was only significantly and negatively correlated with sorption maxima and the external P requirement parameters (Table 2.5). Exchangeable Al (Al_{KCl}) was positively correlated with sorption maxima (r = 0.93) and the single point soil test (r = 0.93).

A regression of P sorption maxima on Al_{CDB} indicated that 89% of the variance of P sorbed was explained by Al_{CDB} (Table 2.6). Similarly, regressing P sorption maxima with Fe_{CDB} showed that Fe_{CDB} explained 69.8% of the observed variance in sorption maxima, whereas 79.7% of the variation in P sorbed was explained by differences in pH. Similarly, regression of sorption maxima with Al_{KCl} showed that exchangeable Al explained 83.9% of the observed variance. By contrast, only 62.8 and 40.5% of the variance in sorption maxima were accounted for by the changes in Al_{crys} and Fe_{crys} respectively (Table 2.6).

Using stepwise regression procedure ($p = 0.05$), a combination of organic carbon, Al_{KCl}, Al_{CDB} and Al_{ox} explained 93.2% of the variation in S_{max}, of which 87.8% of the variation was explained by Al_{CDB} alone whereas soil organic C and Al_{CDB} jointly accounted for 91.1% of the variation in S_{max}. The functions best fitting the data were the following:

$S_{max} = 85.87 + 150\, Al_{CDB}$ $(r^2 = 0.88)$

$S_{max} = 46.73 + 128\, Al_{CDB} + 78.73\, C$ $(r^2 = 0.91)$

Where; S_{max} = sorption maxima, CDB = citrate dithionate bicarbonate, C = organic carbon,

Table 2.4 Phosphate sorption parameters

Soil series	Linearized Langmuir Equations	S_{max} (mg kg^{-1})	b (l mg^{-1})	(r^2)	SI (%)	EPR ($P_{0.2}$) (mg kg^{-1})
Ntlonyana	Y = 0.0019x + 0.0077	526.3	0.247	0.98	49.4	24.8
Ncihane	Y = 0.0021x + 0.0133	476.2	0.158	0.96	48.1	14.6
Qweqwe	Y = 0.0049x + 0.0961	204.1	0.051	0.96	9.5	2.1
Qunu	Y = 0.0052x + 0.0426	192.3	0.122	0.98	25.5	4.6
Chevy Chase	Y = 0.0018x + 0.0067	555.6	0.269	0.97	79.2	28.4
Bethania	Y = 0.0035x + 0.0368	285.7	0.095	0.96	33.5	5.3
Flagstaff	Y = 0.0011x + 0.0014	909.1	0.786	0.98	86.5	123.5

S_{max} = sorption maxima, b = sorption affinity constant, SI = Single point sorption test,
EPR = external P requirement

Table 2.5 Correlation coefficients describing relationships of P sorption parameters with selected soil variables for soils studied

Parameters	Parameters										
	SI	S_{max}	b	Organic C	Al_{crys}	Fe_{crys}	Al_{CDB}	Fe_{CDB}	Al_{KCl}	Al_{ox}	Fe_{ox}
S_{max}	0.916										
b	0.812	0.931									
Organic C	0.533	0.706	0.626								
Al_{crys}	0.923	0.828	0.737	0.609							
Fe_{crys}	0.670	0.789	0.940	0.349	0.568						
Al_{CDB}	0.848	0.936	0.986	0.597	0.797	0.928					
Fe_{CDB}	0.695	0.831	0.959	0.411	0.582	0.995	0.940				
Al_{KCl}	0.928	0.930	0.916	0.542	0.833	0.828	0.951	0.839			
Al_{ox}	0.725	0.876	0.977	0.526	0.627	0.969	0.970	0.979	0.893		
Fe_{ox}	0.533	0.771	0.638	0.741	0.408	0.449	0.568	0.534	0.515	0.570	
pH_{water}	-0.934	-0.842	-0.662	-0.621	-0.854	-0.439	-0.703	-0.478	-0.851	-0.565	-0.569

S_{max} = sorption maxima, b = sorption affinity constant, KCl = potassium chloride, ox = ammonium oxalate, CDB = citrate dithionate bicarbonate, crys = crystalline

Table 2.6 Relationships of sorption maxima (S_{max}) with selected soil independent variables

Variable (x)	Functions best fitting data	r^2
$pH_{water\ (1:2.5)}$	$Y = 195560^{e-1210lx}$	0.797
Al_{KCl}	$Y = -0.04x^2 +10.99x +257.91$	0.839
Al_{ox}	$Y= 117.75x^2 + 627.34x + 164.93$	0.855
Fe_{ox}	$Y = 44.03x^2 – 67.60x + 316.33$	0.607
Al_{CDB}	$Y = -23.04x^2 + 310.05x – 115.20$	0.894
Fe_{CDB}	$Y = -0.26x^2 + 28.96x + 107.95$	0.698
Al_{crys}	$Y = 95.87^{e0.8836x}$	0.628
Fe_{crys}	$Y = 275.13^{e0.025lx}$	0.405

Y = sorption maxima, KCl = potassium chloride, ox = ammonium oxalate, CDB = citrate dithionate bicarbonate, crys = crystalline

2.4.3.4 Relationship between single point sorption tests (SI) with $P_{0.2}$

Plots of $P_{0.2}$ (mg P kg^{-1}) for the soils showed that the relationship was non-linear (Figure 2.1a and b) and the functions best fitting the data were; $P_{0.2} = 19.157e^{0.026SI}$ ($r^2 = 0.89$) when all the seven soils were included in the model (Figure 2.1a) and $P_{0.2} = 12.868e^{0.040SI}$ ($r^2 = 0.97$) when the soils from Flagstaff and Chevy Chase were excluded from the prediction model (Figure 2.1b).

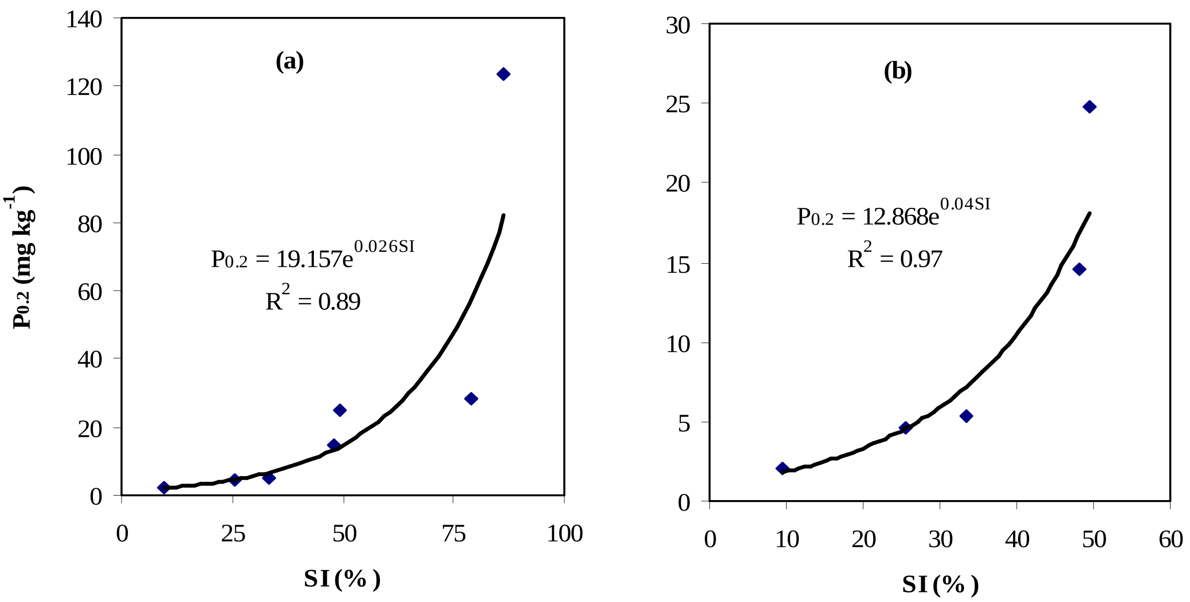

Fig. 2.1 Relationship between $P_{0.2}$ with SI for all seven soils (a) and five soils excluding Chevy Chase and Flagstaff (b)

2.4.4 The effects of external P requirements on dry matter yield and plant P uptake

Dry matter yield was increased significantly (p = 0.05) by addition of fertilizer P when compared with the control. Yields ranged from 1.58 to 3.35 (g plant^{-1}) for Flagstaff soil and from 0.32 to 3.30 (g plant^{-1}) for Qunu soil, respectively (Table 2.7). The yields in the control pots were approximately 47.3% and 9.6% of the maximum yields of the Flagstaff and Qunu soils, respectively. Maximum dry matter yields were achieved at equilibrium P concentrations of 0.20 and 0.25 mg P l^{-1} for Flagstaff and Qunu soils (Table 2.7). Plant P-uptake ranged from 0.09 to 0.89 and 0.01 to 0.82 g plant^{-1} in the Flagstaff and Qunu soils, respectively.

Table 2.7 Effects of soil solution equilibrium P concentrations on dry matter yield and plant P uptake

*EPR factor (mg P l^{-1})	Dry matter (g $plant^{-1}$)	P-uptake (g $plant^{-1}$)
Flagstaff soil		
0.00	1.58 ± 0.15	0.09 ± 0.01
0.05	2.34 ± 0,14	0.41 ± 0.05
0.10	2.76 ± 0.12	0.59 ± 0.06
0.15	2.91 ± 0.20	0.75 ± 0.05
0.20	3.35 ± 0.10	0.87 ± 0.01
0.25	3.16 ± 0.07	0.89 ± 0.05
0.30	3.04 ± 0.06	0.73 ± 0.05
0.35	2.98 ± 0.14	0.79 ± 0.07
Qunu soil		
0	0.32 ± 0.03	0.01 ± 0.01
0.05	1.66 ± 0.22	0.17 ± 0.02
0.10	2.54 ± 0.18	0.37 ± 0.03
0.15	2.90 ± 0.11	0.55 ± 0.03
0.20	3.15 ± 0.21	0.61 ± 0.05
0.25	3.33 ± 0.22	0.75 ± 0.05
0.30	3.23 ± 0.13	0.76 ± 0.02
0.35	3.21 ± 0.17	0.82 ± 0.04
Lsd ($p = 0.05$)	0.22	0.06
s.e.	0.16	0.04
Cv (%)	5.9	7.3

*EPR_{factor} = soil solution P concentrations, s.e. = standard error of treatment means, Cv = Coefficient of variation, Lsd = least significant difference ± = standard deviations

2.5 DISCUSSION

Low soil pH values observed in this study confirm earlier reports on data from the Transkei region that showed that a sizeable number of soils were of low to medium pH (Mandiringana *et al.,* 2005; Bühmann *et al.,* 2006). The soils are low in exchangeable bases which could mainly be attributed to the higher rainfall and warm temperatures that are normally observed in the region leading to intense leaching of bases and accumulation of exchangeable Al in these soils. The low levels of organic carbon are in agreement with observations made by Mandiringana *et al.* (2005) who reported that a large proportion (62-100%) of cultivated field soils in the region had low organic carbon. The organic carbon levels were comparable to the low to very low amounts of organic matter of cultivated soils in other parts of South Africa. These low levels of organic matter have been attributed largely to cultivation practices that tend to accelerate the oxidation of organic matter and hence its depletion (Mandiringana *et al.*, 2005).

The sorption behavior of the soils studied was adequately described by the Langmuir model, with coefficients of determination (r^2) values > 0.95 observed for all the soils under study. The observed differences in sorption maxima among the soils were most likely due to the large variations in the amounts and nature of Al and Fe components present in the soils as shown by positive correlations between the sorption maxima and different forms of Fe and Al extracted. Simple regression analysis showed that the contributions of the various forms to the variance of sorption maxima were in the order $Al_{CDB} > Al_{ox} > Al_{KCl} > Fe_{CDB} > Al_{crys} > Fe_{ox} > Fe_{crys}$. Stepwise regression analysis further showed that, a combination of organic carbon, Al_{KCl}, Al_{CDB} and Al_{ox} explained 93.2% of the variation in S_{max} of which 87.8% of the variation was explained by Al_{CDB} alone. Soil organic C and Al_{CDB} jointly accounted for 91.1% of the variation in S_{max}.

The rather high correlation of Al_{CDB} with P sorption maxima could be attributed to the fact that the citrate dithionite bicarbonate solubilizes both amorphous and crystalline Al and Fe oxides. The stepwise regression coefficients indicated that a unit change in Al_{CDB} (g kg^{-1}) changes P sorbed by 128 mg P kg^{-1} ($r^2 = 0.91$, $p = 0.05$) when organic carbon, and Al_{CDB} were included in the stepwise model. This dependence of P sorption on Al_{CDB} therefore seems to explain the low amounts of P sorbed by soils from Qweqwe, Qunu and from Bethania that had lower amounts of Al_{CDB} and organic C. The function best fitting the data was:

$$S_{max} = 46.73 + 128\ Al_{CDB} + 78.73\ C\ (r^2 = 0.91).$$

The use of this equation could offer a rapid estimation of P sorption in these soils. The results also suggest that citrate dithionite bicarbonate could be the most suitable single extractant for indicating the potential of P sorption in these soils. These findings are in agreement with those of Agbenin (2003), Henry and Smith (2002) and Duffera and Robarge (1999) who also observed that Al_{CDB} had a greater influence on P retention than other Al forms in some tropical soils. Organic C was not significantly correlated with any of the P sorption parameters but it was positively correlated to sorption parameters, and together with Al_{CDB}, explained 91% of the variations in S_{max} in the stepwise regression model referred to earlier. This suggested an active participation of organic matter in P sorption in the experimental soils, possibly through Al-organo complexes as suggested by Haynes and Swift, (1989).

The amounts of P required to obtain a concentration of 0.2 mg P l^{-1} ($P_{0.2}$) in solution were in the range found for other soils in the tropics (Warren, 1994; Iyamuremye *et al.*, 1996; Mehadi and Taylor, 1988; Dodor and Oya, 2000). Duffera and Robarge (1999) for example reported values ranging from 50 to 201 mg P kg^{-1} for surface samples from two Vertisols, an Andosol and an Alfisol collected from farmers' fields, research station farms, and from non-cultivated-non-fertilized areas in Ethiopia. Soils taken from Qweqwe, Qunu, Ncihane and Bethania had lower external P requirement values and thus could be classified as lower sorbers whereas soils from Ntlonyana, Chevy Chase and Flagstaff were moderate sorbers based on the scale of P sorption of Juo and Fox (1977). Therefore 57% of the soils studied were low P fixers while the remaining 43% were moderate P fixers. Since the seven samples used in the study came from only three districts in the former Transkei there is need for a broader study involving soils from other agroecologies in the Province in order to confirm the proportions. Nevertheless, the results suggest that P availability could be compromised in the 43% of soils with moderate P sorption capacity and that measures to mitigate the adverse effects of P sorption may be necessary to ensure that P is not a limiting factor to crop production where such soils are found.

Maximum dry matter yield of oat grown in the glasshouse was achieved at equilibrium P concentrations of 0.20 and 0.25 mg P l^{-1} for Flagstaff and Qunu soils. Apparently, the yields obtained at these concentrations were not significantly different from those obtained at a soil solution P concentration of 0.2 mg P l^{-1} ($P_{0.2}$) reported in the literature to be a threshold for many crops, after which no response to P is observed (Duffera and Robarge, 1999). These results thus showed that a soil solution P concentration of 0.2 mg P l^{-1} ($P_{0.2}$) could be optimal for oats and possibly other crops in these soils. It should, therefore, be given serious consideration as an index for P recommendations for the soils studied. The predictive equations for dry matter yield (DM) were:

$$DM = [13.28EPR_{factor} - 27.78(EPR_{factor})^2 + 1.66] \ (r^2 = 92.33\%) \ \text{(Flagstaff soil)}$$

$$DM = [21.98EPR_{factor} - 41.99(EPR_{factor})^2 - 0.52] \ (r^2 = 95.25\%) \ \text{(Qunu soils)}$$

The single point sorption test (SI) was highly correlated with $P_{0.2}$ (r = 0.93) which, coupled with the high values of the determination coefficient (r^2 = 0.97) observed in this study, suggest that the SI function ($P_{0.2} = 12.87e^{0.04SI}$) could successfully be used to predict the external P requirement ($P_{0.2}$) for the soils from Ntlonyana, Ncihane, Qweqwe, Qunu and Bethania, which are considered to be low P sorbers. Henry and Smith (2003) also found high coefficients of determination (r^2 = 0.98) in the relationship between SI and $P_{0.11}$ for low to moderate fixing soils of the tobacco growing areas of Kwa-Zulu Natal. They also concluded that SI can be used advantageously as a time saving measure to obtain an index of the external P requirement of soils instead of having to produce a full P isotherm.

2.6 CONCLUSIONS

The seven soils studied varied widely in their capacities to sorb P and would therefore react differently to applied P. About 57% of the soils could be classified as low P fixing and the remaining 43% as moderate P fixers. There is thus a need to investigate measures to mitigate against P sorption in the moderately P fixing soils to ensure that P availability is not compromised in these soils. The differences in the P sorption observed between the different soils appeared to be largely related to variations in their citrate dithionite bicarbonate extractable aluminum contents. A soil solution P concentration of 0.2 mg P l^{-1} ($P_{0.2}$) was found to be optimal for plant growth in these soils and could therefore be used as a basis for interpolating external P requirement ($P_{0.2}$) from sorption isotherms. The results further showed that the single point test function could successfully be used to predict the external P requirement ($P_{0.2}$) for the soils from Ntlonyana, Ncihane, Qweqwe, Qunu and from Bethania that are considered to be low P sorbers, thus obviating the need to use multiple point sorption isotherms for the estimation of EPR. Since the sample size used in the present study was small, there is need to carry out a broader sorption study involving more soils from different agroecologies in the province in order to get a more reliable picture of the P sorption status of soils in the Eastern Cape.

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CHAPTER 3

EFFECTS OF GOAT MANURE AND LIME ADDITION ON PHOSPHATE SORPTION OF TWO SOILS FROM THE EASTERRN CAPE PROVINCE, SOUTH AFRICA

3.1 ABSTRACT

The effects of rate of goat manure and lime addition on P sorption by two moderately P fixing soils from Chevy Chase and Flagstaff in the Transkei region of the Eastern Cape Province, South Africa were investigated in a laboratory study. Five treatments consisting of four rates of goat manure (0, 5, 10 and 20 tha^{-1}) and lime were applied to 200 g of soil. The lime treatment was applied to raise soil pH to 6.5. The amended soils were mixed, moistened to 80% field capacity and incubated for 84 days. Treatments were sampled on days 1, 7, 14, 28, 56 and 84 for determination of P sorption and other parameters. Addition of manure reduced P sorption maxima (S_{max}) compared to the control treatment in both soils but the extent of reduction was greater on Chevy Chase soil than in Flagstaff soil. For example, addition of 20 t ha^{-1} of goat manure reduced Smax by 25.4% in Chevy Chase soil but S_{max} was reduced by only 16.4% in Flagstaff soil after 28 days of incubation. These results suggest that the use of goat manure may allow resource poor farmers to use lower levels of commercial P fertilizer because of its ability to reduce soil P sorption. Lime addition to Flagstaff soil initially increased the amount of P sorbed for the first 28 days of incubation but after 56 days of incubation it had the opposite effect of reducing P sorption. By contrast, reduced P sorption was observed soon after lime was added to the Chevy Chase soil. The management implications of these results are that for Flagstaff soil and other similar soils, lime may need to be applied before planting while for soils such as the one from Chevy Chase, lime could be applied at the time of planting for maximum added P availability.

Key words: Exchangeable Al, Goat manure, Lime, P sorption

3.2 INTRODUCTION

Preliminary P sorption studies on seven soils from the Transkei region of the Eastern Cape (Chapter 2) indicated variable P retention capabilities of the soils ranging from 192.3 to 909.1 mg P kg^{-1}. Therefore some of the soils had sufficiently high P retention capacities to significantly decrease the availability of added P to plants. This implies that if no measures are taken to minimize P sorption in the soils, large quantities of P fertilizer will need to be added in order to achieve adequate P concentration in the soil solution for optimal plant growth.

There is considerable literature evidence suggesting that the application of animal manure and other organic materials such as plant residues to soil may decrease its P sorption capacity thereby increasing the availability of P to plants (Easterwood and Sartain, 1990; Haynes and Mokolobate, 2001). The reduced P sorption and increased P availability following application of organic amendments to soils is thought to be the result of the cumulative effects of several mechanisms. These include: blockage of P sorption sites by organic products released from the decomposing residues, a rise in soil pH and complexation of soluble Al and Fe by organic acids and reduction of their concentrations in soils (Hue, 1992). The latter mechanism is essentially a liming effect but no information could be found comparing the relative liming effectiveness of organic materials added to soils to that of agricultural lime.

Goat manure is readily available on most smallholder farms in the Eastern Cape Province of South Africa, being second only to cattle manure in terms of availability (Yoganathan *et al.*, 1998). Ownership of goats is estimated to be 43%. It would be expected that its addition to soil could result in increased P availability through reduced P sorption like other organic materials reported by Hue (1992) and Iyamuremye *et al.* (1996). Understanding the role of goat manure in reducing P sorption in high P fixing soils may provide information that could contribute to its effective use in increasing the efficiency of soil P and added P utilization by crops. This would allow farmers, especially those who operate at subsistence level, to reduce their costs of production by using less P fertilizer.

The objective of this study was therefore; to evaluate the effects of goat manure and lime addition on the P sorption of two high P fixing soils from the Transkei region of the Eastern Cape, South Africa.

3.3 MATERIALS AND METHODS

3.3.1 Soil and goat manure preparation

Surface soil samples (0-15 cm) from cultivated fields in Flagstaff and Chevy Chase in the Transkei region of the Easter Cape, South Africa (herein after referred to as Flagstaff and Chevy Chase) were used in this study. The two soils belong to the Inanda and Hutton forms, respectively (Soil Classification Working Group, 1991), and were selected because of their higher P sorption capacities (Chapter 2). The goat manure used was collected from a goat shed at the University of Fort Hare, Lovedale Research Farm.

3.3.2 Soil and manure characterization

Selected soil properties are presented elsewhere in Chapter 2 (see Table 2.1). Manure pH was measured in water (soil: solution ratio of 1: 5) using a pH meter with a glass and reference calomel electrode (Model pH 330 SET-1, 82362) after the suspensions were shaken for 30 minutes and allowed to stand for 1 hour. Electrical conductivity was measured in water at a 1: 5 soil: water ratio using a conductivity meter (Model Cond.330i/SET 82362). Organic C and N were determined by dry combustion using a LECO TRUSPEC C/N auto-analyzer (LECO Corporation, 2003). Total soil P, K, Ca, Mg and N were estimated following wet digestion with H_2O_2/H_2SO_4 (Okalebo *et al.*, 2002)**.** Total Ca^{2+}, Mg^{2+}, and K^+ were determined by atomic absorption spectrometry and P measured as described by Murphy and Riley (1962). All results are the means of triplicate analyses.

3.3.3 Incubation of amended soils

Five treatments consisting of four rates of goat manure (0, 5, 10 and 20 tha^{-1}) and lime were applied to 200 g of soil. Lime was applied to raise soil pH to 6.5, is reported to be optimal for P availability for most plants (Haynes and Swift 1985). The amounts of lime required were determined by incubating 100 g of moist soils amended with different rates of lime for four weeks and then measuring the pH of the samples. The rate that raised the soil pH to 6.5 was selected. The amounts require were 12 and 3.5 t $CaCO_3$ ha^{-1}, for Flagstaff and Chevy Chase, respectively. The amended soils were then each mixed thoroughly and moistened to 80% field capacity or 19% moisture content (Griffin *et al.*, 2003). Two small holes were made in each container lid to maintain aerobic conditions. The treatments were replicated three times and incubated at 25 ± 1 ^oC in the dark to simulate soil conditions. Sufficient samples (18) were prepared for each treatment and for each soil to allow for sampling at 1, 7, 14, 28, 56, and 84 days of incubation. Soil moisture content was monitored weekly and adjusted to 80% field capacity. At each sampling, the amended soils were air-dried, sieved (<2 mm) and P sorption determined as described earlier in Chapter 2, section 2.3.1.3.

3.3.4 Statistical analysis

Analyses of variance were conducted with GenStat statistical software (GenStat Release 4.24DE, 2005) to determine the statistical significance of treatment effects on P sorption parameters. The analysis of variance was separately performed for each soil since the two soils received different amounts of lime. Where significant differences ($p = 0.05$) occurred, mean separation was done using least significant difference (LSD). Regressions were performed to evaluate the relationships between exchangeable Al and soil pH with P sorption maxima. Non-linear regression analyses were used to find the models best describing the relationships. Unless otherwise stated, mention of statistical significance refers to $p = 0.05$.

3.4 RESULTS

3.4.1 Soil and manure characterization

Selected chemical properties of goat manure are presented in Tables 3.1. The manure used in this study had pH of 8.2, a C: N ratio of 19 and a C: P ratio of 206.

Table 3.1 Selected chemical properties the goat manure (GM) used in the study

Chemical Properties	Quantity
pHwater (1:5)	8.2
EC dS m^{-1}	3.7
C (g/kg)	498
Total N (g kg^{-1})	25.6
Total P (g kg^{-1})	2.4
Total Ca (g kg^{-1})	39.3
Total Mg (g kg^{-1})	18.6
Total K (g kg^{-1})	22.7
C: P	206.6
C: N	19.4

3.4.2 Effects of manure and lime addition on soil solution pH and exchangeable Al

Application of lime significantly increased the pH of both soils relative to the control. The pH of limed soils increased with time, reaching maximum values of 6.58 and 6.42 on day 28 for Chevy Chase and Flagstaff soils, respectively (Figure 3.1). Addition of goat manure (GM) to both soils also significantly increased the soil pH proportionately with increasing amounts of goat manure but the increases were all less than what was achieved with lime (Figure 3.1). The relative liming effects of the different rates of goat manure followed the order 20 t GM ha^{-1} > 10 t GM ha^{-1} > 5 t GM ha^{-1} (Table 3.2). The greatest liming effect on both soils was realized with the application of 20 t ha^{-1} goat manure which on day 28 was 62 and 52% as effective as the lime treatments on Chevy Chase and Flagstaff soils, respectively (Table 3.2).

Generally, the liming effects due to lime and goat manure addition was greater on Chevy Chase than Flagstaff soil (Figure 3.1, Table 3.2). The observed liming effects due to goat manure or lime addition persisted for the entire 84 days of incubation in the two soils (Figure 3.1).

Addition of lime to both soils decreased the amount of exchangeable Al as observed on day 28 (Table 3.2). Day 28 was selected for interpretation of results because the greatest changes in soil pH and P sorption parameters were observed on this day (Figure 3.1, Table 3.3). Consistent with the observed liming effect of goat manure (Figure 3.1), corresponding decreases in exchangeable Al were observed in both soils when goat manure was applied (Figure 3.2). The relative reduction in exchangeable Al (RDAl) at different rates of goat manure followed the order 20 t GM ha^{-1} > 10 t GM ha^{-1} > 5 t GM ha^{-1} for both soils but these reductions were greater in Chevy Chase soil (Table 3.2). The greatest decrease in exchangeable Al was realized with the application of 20 tha^{-1} goat manure on both soils which on day 28 was 89 and 72% as effective as the lime treatment in reducing exchangeable Al on Chevy Chase and Flagstaff soils, respectively (Table 3.2). Addition of goat manure at rates of 10 and 20t ha^{-1} had similar effects on exchangeable Al to lime in Chevy Chase soil (Figure 3.2b, Table 3.2).

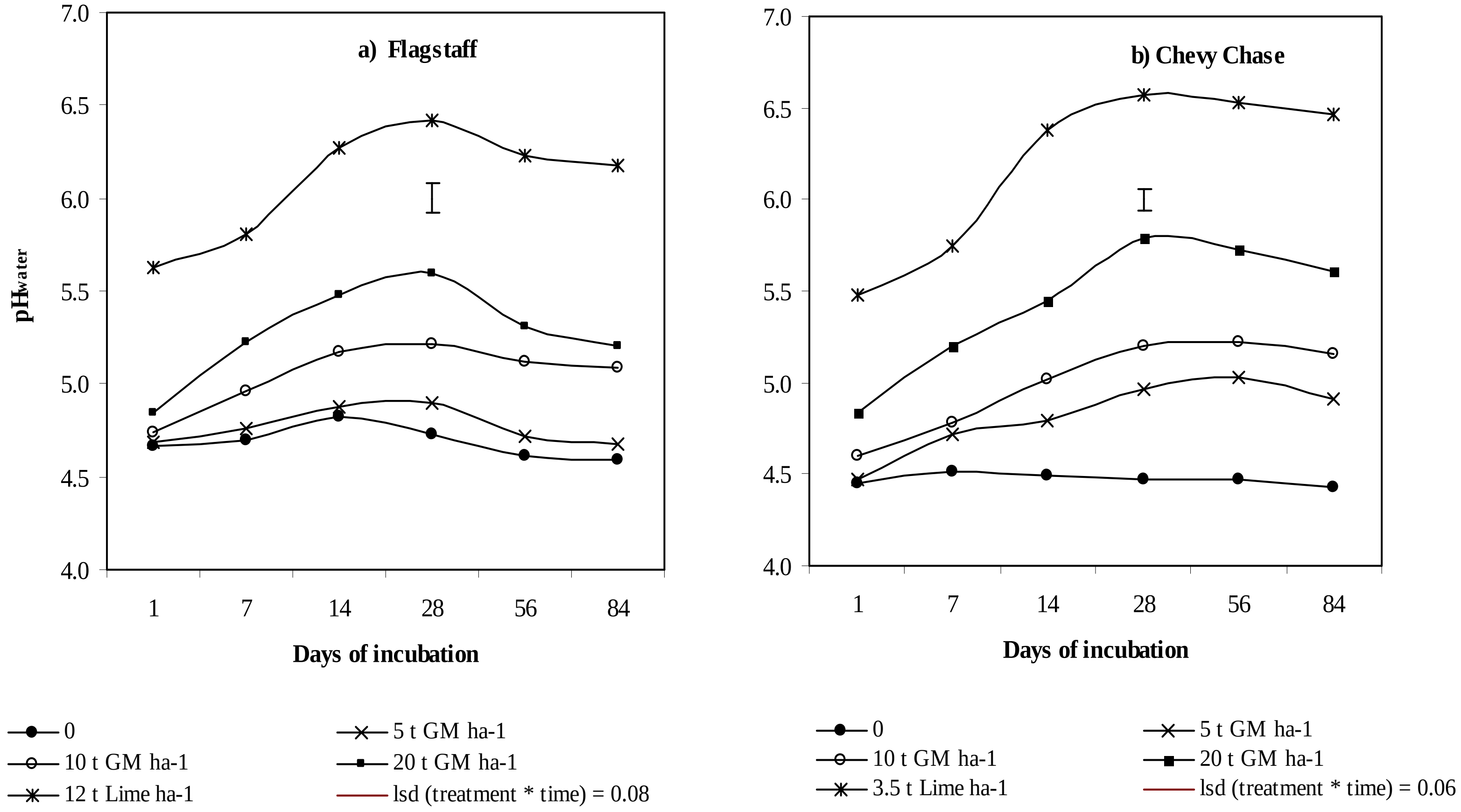

Fig. 3.1 The effects of rate of goat manure (GM) and lime addition on soil solution pH (x-axis not to scale) (bars represent least significant difference p = 0.05)

Table 3.2 Relative liming effectiveness of different goat manure (GM) treatments after 28 days of incubation

Treatments	pH	Relative liming effectiveness (RLE) (%)	Exchangeable Al (mg kg^{-1})	Relative decrease in exchangeable Al (RDAl) (%)
Chevy Chase soil				
Control	4.48	-	40.6	-
5 t GM ha^{-1}	4.97	23	30.0	46
10 t GM ha^{-1}	5.20	34	21.8	82
20 t GM ha^{-1}	5.79	62	20.2	89
3.5 t lime ha^{-1}	6.58	100	17.7	100
LSD$_{0.05}$	0.08	-	5.12	-
s.e.	0.04	-	2.72	-
Flagstaff soil				
Control	4.73	-	77.5	-
5 t GM ha^{-1}	4.90	10	59.2	28
10 t GM ha^{-1}	5.21	29	48.1	45
20 t GM ha^{-1}	5.6	52	30.0	72
12 t lime ha^{-1}	6.42	100	11.3	100
LSD$_{0.05}$	0.09	-	1.8	-
s.e.	0.04	-	0.97	-

For each soil: RLE = (GM Treat. pH – Control pH)/(Lime Treat. pH – Control pH)*100
RDAl = (GM Treat. Ex. Al – Control Ex. Al)/(Lime Treat. Ex. Al – Control Ex. Al)*100. Where Ex. Al = exchangeable Al, GM = goat manure, Treat. = treatment, s.e. = standard error of treatment means

3.4.3 Effects of goat manure and lime addition on soil P sorption maxima

The extent of P sorption varied within each soil depending on the amount and type of amendment applied (Table 3.3). Addition of goat manure consistently reduced P sorption maxima (S_{max}) compared to the control treatment in both soils (Table 3.3). P sorption decreased with increasing amounts of goat manure in both soils but the extent of reduction was greater on Chevy Chase soil than on Flagstaff soil. For example, addition of 20 t ha^{-1} of goat manure reduced S_{max} by 25.4% in Chevy Chase soil but S_{max} was only reduced by 16.4% on Flagstaff soil after 28 days of incubation (Table 3.3).

Lime addition to Flagstaff soil significantly increased the amount of P sorbed in the first 28 days of incubation (Table 3.3). By contrast, reduced amounts of P were sorbed when lime was added to the Chevy Chase soil except on day one of incubation (Table 3.3). The greatest reduction in S_{max} (35.2%) was recorded on day 84 in Chevy Chase soil amended with lime (Table 3.3).

Table 3.3 Effects of rate of goat manure (GM) and lime addition on P sorption maximum (mg P kg^{-1}) during 84 days of incubation

Treatments	Days of incubation						
Flagstaff soil	0	7	14	28	56	84	Pooled mean
Control	892_b	861_b	868_b	871_b	883_a	885_a	877_a
5 t GM ha^{-1}	862_c	844_c	843_c	841_c	859_b	862_b	852_b
10 t GM ha^{-1}	855_{cd}	821_d	816_d	817_d	825_d	829_c	827_c
20 t GM ha^{-1}	847_d	820_d	799_e	728_e	759_e	775_d	788_d
12 t Lime ha^{-1}	911_a	912a	916_a	886_a	836_c	823_c	881_a
$LSD_{0.05}$	13.9	13.8	7.6	6.8	7.5	7.6	16.2
Cv (%)	11.8	14.7	15.3	10.3	12.9	14.5	11.8
Chevy Chase soil							
Control	579.6_b	586.1_a	581.8_a	580.0_a	586.3_a	587.2_a	583.5_a
5 t GM ha^{-1}	577.2_{bc}	570.6_b	567.9_b	563.9_b	576.2_b	575.3_b	571.8_a
10 t GM ha^{-1}	571.9_c	538.6_c	516.3_c	510.4_c	513.2_c	520.3_c	528.4_b
20 t GM ha^{-1}	556.5_d	480.4_d	467.2_d	432.9_d	440.1_d	455.2_d	472.1_c
3.6 t Lime ha^{-1}	593.6_a	455.7_e	426.1_e	396.8_e	389.0_e	380.4_e	440.3_d
$LSD_{0.05}$	7.6	7.5	8.1	10.2	4.7	9.0	21.2
Cv (%)	13.6	16.5	11.2	14.1	9.8	12.9	9.9

Numbers followed by the same letter within columns for each soil are not statistically different (p = 0.05)

3.4.4 Relationship between exchangeable Al and pH with sorption maxima

Exchangeable Al was positively correlated with sorption maxima whereas soil pH was negatively correlated with sorption maxima after 28 days of incubation (Figure 3.2). Regression analysis of sorption maxima with exchangeable Al indicated that 98.4 and 97.5% of the variations in sorption maxima were due to exchangeable Al in Flagstaff and Chevy Chase soils, respectively. Similarly, regressing sorption maxima with soil pH (Figure 3.2) showed that pH changes following addition of amendments accounted for 96.9% and 95.6% of the observed variance for the Flagstaff and Chevy Chase soils, respectively.

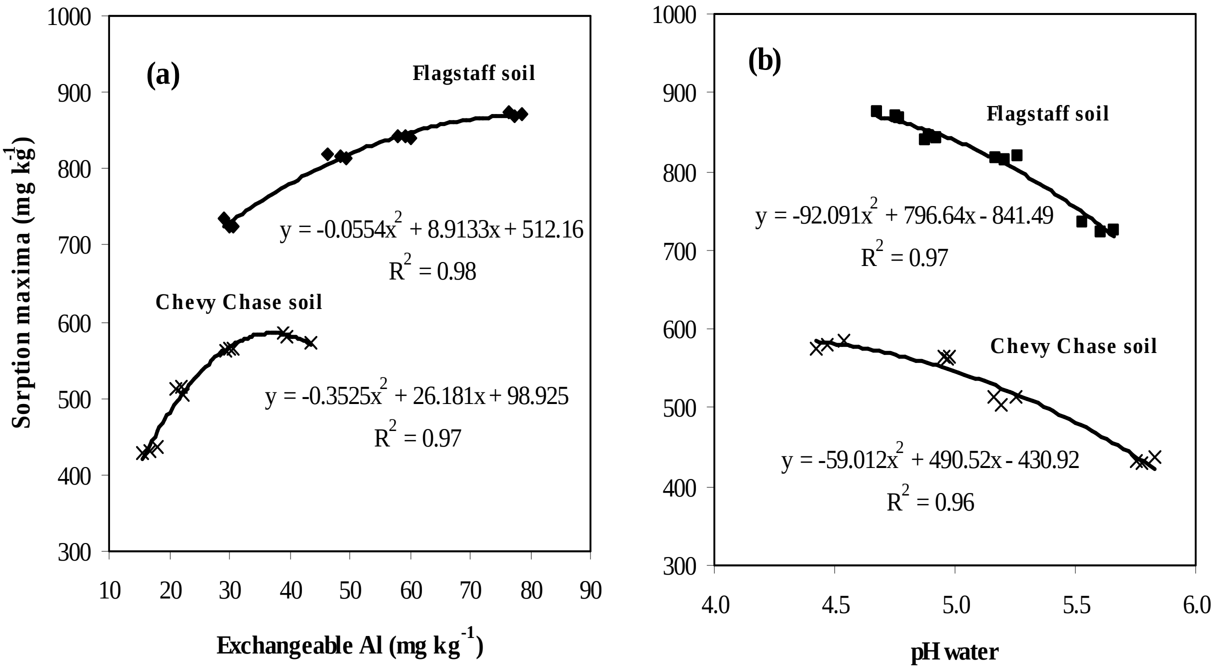

Fig. 3.2 Relationship between exchangeable Al (a) and soil pH (b) with sorption maxima on day 28

3.5 DISCUSSION

The extent of P sorption varied within each soil depending on the amount and type of amendment applied. Addition of goat manure consistently reduced P sorption maxima (S_{max}) compared to the control treatment in both soils but the extent of reduction was greater in Chevy Chase soil than in Flagstaff soil. For example, addition of 20 t ha^{-1} of goat manure reduced Smax by 25.4% in Chevy Chase soil but was only reduced by 16.4% on Flagstaff soil after 28 days of incubation. These results agree with those of Iyamuremye *et al.* (1996) who also observed reduced P sorption in high P fixing Rwandan soils amended with cattle manure and alfalfa residues.

The reduction in P sorption observed with increasing amounts of goat manure could be attributed to the observed increase in soil pH and corresponding decrease in exchangeable Al in the soils following goat manure application. This effect is in agreement with findings of Whalen *et al.* (2000) who also reported higher pH and lower oxalate extractable Al after cattle manure addition to soil. Hue (1992) suggested that such pH changes could be attributed to hydroxyl ions from ligand exchange reactions between organic acids and hydroxyl groups of Al or Fe hydrous oxides and/or the high concentration of basic cations often found in organic materials. The pH increases observed following goat manure application were much higher in Chevy Chase soil than in Flagstaff soil possibly indicating that Flagstaff soil had a higher buffering capacity due to its higher clay content.

Increases in soil pH as was observed in the manure treated soils has been reported to increase the cation exchange capacity of soil colloidal fractions providing extra sorption sites for Al and Fe thus reducing their reactivity in the soil solution (Naidu *et al.,* 1990; Iyamuremye *et al.,* 1996; Ohno and Crannel, 1996). The decrease in exchangeable Al could also have been a result of the precipitation of Al^{3+} ions as aluminum hydroxide by OH^- ions produced during manure decomposition and OH^- ions released from the ligand exchange between organic acids and hydroxyls of Al and Fe oxides, thereby decreasing the number of P sorption sites (Naidu *et al.,* 1990). Added goat manure had a greater relative effect in reducing exchangeable Al than in increasing soil pH suggesting that the observed decreases in P sorption following goat manure application could to a large extent have been due to the inactivation of exchangeable Al. This is further supported by the fact that a greater reduction in P sorption following goat manure application occurred in Chevy Chase soil than on Flagstaff soil, consistent with the greater relative decrease in exchangeable Al following goat manure application to this soil.

The relative effects of goat manure in increasing soil pH, decreasing exchangeable Al and reducing P sorption of the experimental soils increased with rate of manure application. This suggests that repeated seasonal application of the goat manure or the application of higher rates of this level of manure could result in an enhanced expression of the observed effects. Therefore regular application of goat manure or other manures with similar properties to smallholder farms in the Eastern Cape could result in improved soil and fertilizer P use efficiency by crops partly as a consequence of reduced P sorption.

Incorporation of P into the soil microbial biomass is reported to be another mechanism that could significantly increase the availability of P to plants (Harris *et al.*, 1997). The microbial biomass apparently increases P availability by immobilizing soil inorganic P and releasing it later through mineralization during biomass turnover (Iyamuremye *et al.,* 1996). This P is released slowly and taken up by the crop more efficiently and is believed to be one reason for observed synergistic effects on crop growth when organic materials are co-applied with inorganic fertilizer P (Ayaga *et al.*, 2006). It is probable that the application of goat manure to soil would stimulate a large microbial population in soil and thus improve the cycling of soil and fertilizer P. This aspect was the subject of another study (Chapters 4 and 5).

Unlike Chevy Chase soil, lime addition to Flagstaff soil initially increased the amount of P sorbed. Haynes and Swift, (1985) suggested that the initial increase in P sorption following liming could be a result of the formation of new adsorbing surfaces due to the precipitation of exchangeable Al as hydroxy-Al polymers as the pH is raised. The hydroxyl-Al polymers are highly active adsorbing surfaces which can increase P adsorption considerably (Haynes and Swift, 1985). With time, however, crystallization of the amorphous hydroxyl-Al polymers takes place leading to increased negative charges on the lime induced surfaces with a consequential reduction of P retention (Haynes and Swift, 1985; Curtin and Syers, 2001). This could explain the observed reduction in P sorption on day 56 in the Flagstaff soil following the initial P sorption increase of the limed soil. The differing effects of liming on the P sorption of the two soils could be partly because they contained different initial levels of exchangeable Al. Flagstaff soil had a higher concentration of exchangeable Al (76.3 mg Al kg^{-1}) than Chevy Chase soil (48.7 mg kg^{-1}) in the un-amended soils.

The effectiveness of lime in reducing P sorption of Flagstaff soil with a high initial exchangeable Al content was greatly affected by the length of time the lime had reacted with the soil. The reduction in P sorption following lime application was only observed 56 days after the lime was applied while this effect was observed almost immediately on Chevy Chase soil. The management implications of these results are that for Flagstaff soil and other similar soils, P application may need to be delayed following lime addition while for soils of the Chevy Chase type lime could be applied at the time of planting or at the time of P addition to the soil. Since the present study was done under controlled laboratory conditions, the exact timing of lime application will need to be determined under field conditions on a wider range of soils.

3.6 CONCLUSIONS

This study demonstrated that addition of goat manure reduced P sorption in both soils. This implies that combined application of goat manure and inorganic fertilizer P may enable resource poor farmers to use lower levels of commercial P fertilizer and lime in strongly P fixing soils. The highest reduction in P sorption in the manure treatments was recorded on day 28 suggesting the need to synchronize P addition to coincide with the peak periods of maximum reduction in P sorption following amendment addition. The results also showed that the two soils differed with respect to the time when lime effected maximum reduction in P sorption. This effect was observed immediately on Chevy Chase soil but only after about two months following lime application on Flagstaff soil. Therefore, for improved P use efficiency, lime addition to the Flagstaff soil and possibly other soils with similar properties may need to be applied before planting while for soils of the Chevy Chase type, lime could be applied at the time of planting. The exact timing of lime application will need to be determined under field conditions on a wider range of soils.

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CHAPTER 4

CHANGES IN INORGANIC AND MICROBIAL BIOMASS P FRACTIONS FOLLOWING GOAT MANURE AND INORGANIC PHOSPHATE ADDITION TO FLAGSTAFF SOIL

4.1 ABSTRACT

Phosphorus (P) transformations in untreated and manure treated soils at increasing inorganic P application rates were assessed under controlled laboratory conditions using a sequential fractionation procedure. Triple superphosphate was added at rates of 0, 90, 180, 270 and 360 kg P ha^{-1} with or without 20 t ha^{-1} of goat manure (dry weight) and incubated moist for 12 weeks. Resin P, soil microbial biomass P (biomass P), 0.5 M $NaHCO_3$ extractable inorganic P ($NaHCO_3$-P_i) and 0.1 M NaOH extractable inorganic P (NaOH-P_i) concentrations were determined on days 1, 7, 14, 28, 56 and 84. Addition of inorganic P increased all P fractions but the increases were greater when goat manure was co-applied. The control treatments contained 17.2 and 27.5 mg P kg^{-1} of resin extractable P in the un-amended and manure amended treatments, respectively which increased to 118.2 and 122.7 mg P kg^{-1} at the highest rate of P application (360 kg P ha^{-1}) on day 28 of incubation. NaOH-P_i was the largest extractable P_i fraction and ranged from 144.3 to 250.6 mg P kg^{-1} and 107.5 to 213.2 mg P kg^{-1} in the unamended and manure amended treatments, respectively. Inorganic P addition increased the biomass P concentration from 16.8 to 43.9 mg P kg^{-1} in P alone treatments but the fraction was greatly enhanced with manure addition, increasing it from 32.6 to 97.7 mg P kg^{-1}. The largest increase in biomass P due to manure occurred at lower rates of added P indicating the potential of goat manure to enhance the fertilizer use efficiency of small inorganic P applications. This increase in biomass P following goat manure addition implies that it increased the proportion of added P immobilized in microbial cells that would be subsequently released into the soil solution and be available for plant uptake following biomass P turnover.

Key words: P fractionation, goat manure, biomass P, resin-P, $NaHCO_3$-P_i, NaOH-P_i,

4.2 INTRODUCTION

Soil P is the least mobile and least available of the major plant nutrients. Its low availability has been described as `the bottle-neck of world hunger' (Rorty, 1946) and is a major constraint to agricultural production in most South African soils (Henry and Smith, 2006) as well as other highly weathered tropical soils (Warren, 1994). Phosphorus deficiency is mainly caused by strong sorption of P by aluminum (Al) and iron (Fe) oxides and hydroxides and other amorphous materials (Hinsinger, 2001). This necessitates large applications of fertilizer P to overcome P sorption (Bainbridge *et al.* 1995, Henry and Smith, 2002) and to achieve high crop yields (Warren, 1994) unaffordable by resource poor smallholder farmers. Limited nutrient inputs by smallholder farmers, because of their high cost, and limited accessibility, exacerbates soil P deficiency. It is therefore important to investigate affordable P management systems that optimize the integrated use of all nutrient sources (e.g., fertilizers, organic manures, waste materials) suitable for the maintenance of soil fertility and crop productivity.

Incorporation of P into the soil microbial biomass is also reported to be another mechanism that significantly increases the availability of P to plants and which forms a significant pool of plant nutrients (Harris *et al.*, 1997). This pool is said to play a key role in P dynamics in soils by immobilizing inorganic P which is later mineralized (Rubaek and Sibbesen, 1993). The soil microbial biomass (defined as the mass of all soil micro-organisms < about 5000 μm^3) may be considered as a labile reservoir of potentially plant-available nutrients, including P (Brookes, 2004). During the process of biomass turnover, this P may be released slowly and taken up by the crop more efficiently (Parham *et al.*, 2003; Brookes, 2004). For example, Nziguheba *et al.* (1998) reported increased soil microbial biomass P (biomass P) and decreased P sorption following incorporation of *Tithonia diversifolia* (Tithonia) as green manure into an acid soil in western Kenya. This increased P in the soil microbial biomass presumably enhanced turnover and biological cycling of P between labile pools of soil P. These investigators also measured a larger biomass P pool following joint addition of Tithonia with triple superphosphate compared to triple superphosphate alone. Application of inorganic P with organic manures also resulted in larger crop yields than when either were applied singly (Griffin *et al.*, 2003; Ayaga *et al.*, 2006).

Combined application of goat manure and inorganic P in the soil would be expected that its addition to soil as an organic manure would result in increased P availability to plants. Therefore, understanding the role of goat manure in increasing P availability may lead to the development of better soil management systems that could increase the efficiency of soil P cycling and decrease P sorption, so allowing farmers to apply less inorganic P fertilizer. The aims of this study were therefore to evaluate the effects of combined addition of inorganic P and goat manure on the size and distribution of biomass P and inorganic P pools (resin P, $NaHCO_3$-P_i and NaOH-P_i) in a moderately P fixing soil from the Transkei region of South Africa.

4.3 MATERIALS AND METHODS

4.3.1 Incubation of amended soils

The topsoil (0-15 cm) of a soil from Flagstaff, Eastern Cape, South Africa and goat manure which were earlier characterized and reported in Chapters 2 and 3, respectively (see Tables 2.1and 3.1) was used in this experiment. The Flagstaff soil was selected for this study because it had the highest P fixing capacity among the seven soils studied and reported earlier (see Chapter 2, Table 2.4). Two hundred and fifty grams of air-dry soil (< 2 mm) were weighed into plastic containers and five rates of triple super phosphate applied at 0, 90, 180, 270 and 360 kg P ha^{-1} (sieved < 1 mm) was applied as powder with or without goat manure (equivalent to 20 t ha^{-1} on a dry weight basis). The P rates were selected to be multiples of the highest P rate which was determined to maintain a P concentration of 0.2 mg l^{-1} in the soil solution. The amended soils were then mixed thoroughly and moistened to 80% field capacity or 19% moisture content (Griffin *et al.*, 2003). Two small holes were made in each container lid to permit aerobic conditions during incubation. Sufficient replicates were prepared for each treatment to allow sampling at 7, 14, 28, 56, and 84 days. The samples were replicated three times and incubated in the dark at 25 ± 1 ^{o}C. The moisture level of the samples was monitored and corrected weekly. At each sampling, resin P, biomass P and inorganic P fractions ($NaHCO_3$-P_i, and NaOH-P_i) were determined in moist, fresh soil samples as outlined below.

4.3.2 Fractionation of resin P, biomass P, $NaHCO_3$-P_i, and NaOH-P_i

The Hedley *et al.* (1982) fractionation scheme, modified to include biomass P, was used to investigate the sizes and the distribution of soil inorganic P and biomass P fractions (Figure 4.1).

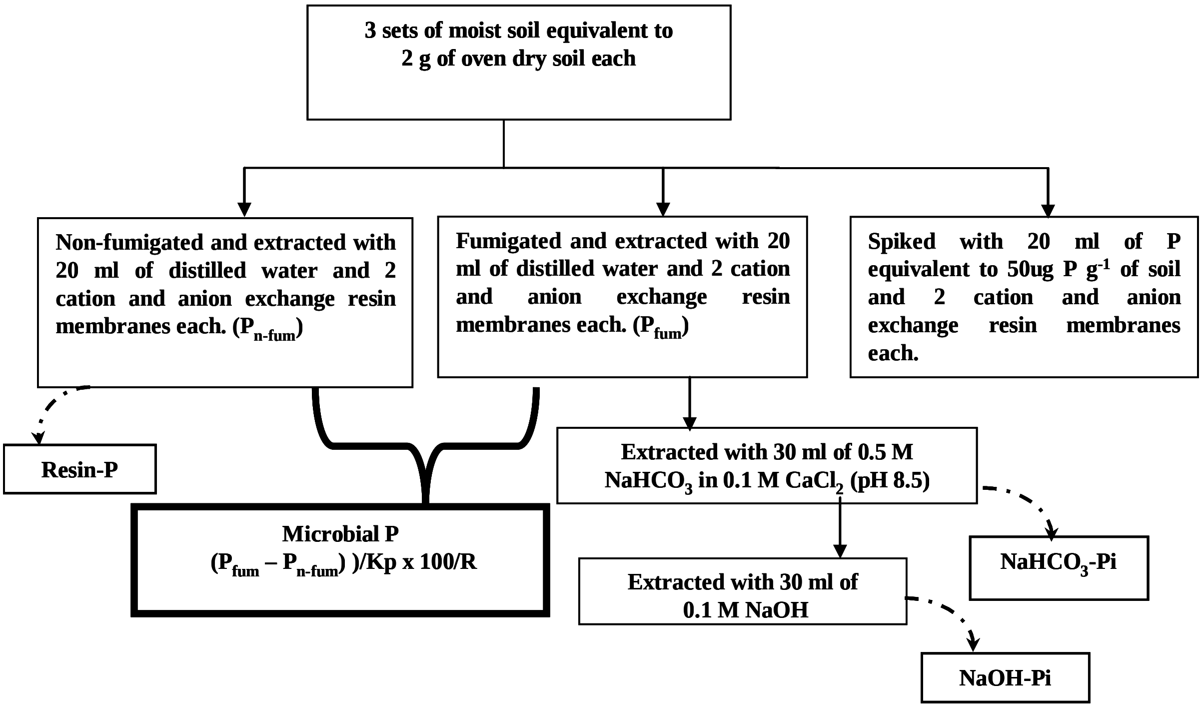

Fig. 4.1 Modified Hedley sequential P fractionation procedure

4.3.2.1 Regeneration of anion and cation resins

Both anion and cation exchange resin membranes were used to determine resin P and biomass P fractions. The use of both cation and anion exchange resin membranes have been reported to extract more P due to removal of cations contributing to the surface charge (Ayaga et al., 2006). Rectangular strips (10 mm x 60 mm) of resins membranes (Anion 103QDP-EO6295A and Cation CR61CIP-MO6095A supplied by Ionic’s inc. Massachusetts) were cut from the packaged sheets and washed 4 times in distilled water then 4 times in 0.5 M HCl. The anion resins were then transferred to a beaker containing 0.5 M $NaHCO_3$ (pH = 8.5), while the cation resin membranes were transferred to a beaker containing 0.5 M NaCl. The contents in the beakers were stirred and the solutions replaced hourly, five times.

4.3.2.2 Extraction procedure

Resin-P and biomass P

The resin strip method of Kouno *et al*. (1995) was used. Portions of moist soil, each containing the equivalent of 2 g oven-dry soil were prepared in three sets. The first set was treated with 1 ml of alcohol free $CHCl_3$ and fumigated for 24 hours at room temperature. The $CHCl_3$ was then allowed to evaporate for 4 hours at room temperature in a fume chamber. Two anion and two cation exchange resin strips, prepared as described above, and distilled water (20 ml) were then added and shaken for 16 hours at room temperature at 175 oscillations per minute (Nziguheba *et al*., 1998). The second set of soils received distilled water, 2 strips of anion and cation exchange and was then shaken, as described above. The third set received P (spiked P) equivalent to 50 ug P g^{-1} soil as KH_2PO_4 (20 ml), resin strips and was then shaken, again as above. After shaking, the resin strips were removed from the soil extracts with tweezers and thoroughly rinsed with distilled water. The P adsorbed by the resins strips was recovered in 20 ml of 0.5 M HCl after shaking for 30 minutes. The inorganic P in the eluents was then determined by the method of Murphy and Riley (1962). The analyses were done in triplicates.

P-Fractions (NaHCO$_3$ - P$_i$ and NaOH - P$_i$)

The soil suspensions remaining after the resin strips were removed from the CHCl$_3$ treated sets were centrifuged at 10,000 rev min^{-1} for 10 minutes and the supernatants discarded. 30 ml 0.5 M NaHCO$_3$ (pH 8.5) was then added to the residue and shaken for 16 hours at 175 oscillations per minute (Nziguheba *et al.*, 1998). The suspensions were then centrifuged at 10,000 rev min^{-1} for 10 minutes and the solutions decanted into plastic containers. To the remaining soil residue of each sample, 30 ml 0.1 M NaOH was added and shaken for 16 hours, centrifuged at 10,000 rev min^{-1} for 10 minutes and the solution decanted into plastic bottles. The P in the supernatant was then determined by the method of Murphy and Riley (1962).

Calculation of biomass P

Biomass P (Bp) was calculated from:

B*p* (mg kg^{-1} soil) = (P*f* – P*nf*)/(K*p* * 100/R)
Where:
P*f* = P extracted from CHCl$_3$ fumigated samples
P*nf* = P extracted from non-fumigated samples
K*p* = 0.4, the fraction of biomass P extracted after fumigation (Brookes *et al.,* 1982).
R = % Recovery of added P = 100(P*s*-P*nf*)/50 (Brookes *et al.,* 1982) where:
P*s* = P extracted by exchange resins from non-fumigated soil spiked with P

4.3.3 Statistical analysis

Statistical analysis was done using GenStat statistical software (GenStat Release 4.24DE, 2005) by running a full model (60 treatments, 59 df), which was further split into a P rate effect (4 df), manure effect (1 df), incubation time effect (5 df), P rate * manure effect (4 df), P rate * incubation time effect (20 df), manure * incubation time effect (5 df), and P rate * manure * incubation time effect (20 df). Differences at $p \leq 0.05$ were considered significant. Net treatment effects were calculated as the differences between the combined inorganic P and manure treatments and the inorganic P alone treatments.

4.4 RESULTS

4.4.1 Soil and manure characterization

Selected soil and manure properties are presented elsewhere in Chapter 2 and Chapter 3, respectively (see Tables 2.1 and 3.1). The soil solution pH was acidic with high concentrations of exchangeable Al, oxalate Al and exchangeable acidity. The concentrations of total organic carbon and nitrogen were low in this soil. The manure used in this study had a pH of 8.2 and had higher concentration of total carbon with a C: N ratio of 19.4 and a C: P ratio of 206.6.

4.4.2 Effects of combined application of inorganic P and goat manure on inorganic P fractions

All P fractions were influenced by P application rate, manure addition and incubation time and interactions were common (Table 4.1). Analysis of variance indicated that all extractable soil P_i fractions changed over time and most differences between the P rates, manure by time interaction were statistically significant (Table 4.1).

The distribution of P pools as determined by sequential extraction following incubation of amended soils up to day 28 is given in Table 4.2. Day 28 was selected for interpretation of results because higher concentrations of biomass P which is considered a significant fraction influencing P availability in soils were observed on this day. Inorganic P (P_i) addition with or without manure significantly ($p = 0.05$) increased the P concentration of all fractions with larger concentrations generally found in manure treatments (Table 4.2). The control treatments where inorganic P was not applied had 17.2 and 27.5 mg P kg^{-1} of resin extractable

P in the non-amended and manure amended treatments, respectively. This P fraction increased to 118.2 and 122.7 mg P kg^{-1} at the highest added P rate (360 kg P ha^{-1}). The resin P was about twice the NaHCO$_3$-P$_i$ concentration. The NaHCO$_3$-P$_i$ fraction ranged from 11.8 to 41.7 mg P kg^{-1} and 13.9 to 41.4 mg P kg^{-1} in the unamended and manure treatments, respectively. The NaOH-P$_i$ was the largest extractable P$_i$ fraction and ranged from 144.3 to 250.6 mg P kg^{-1} and 107.5 to 213.2 mg P kg^{-1} in the same treatments respectively (Table 4.2). The sum of resin-P, NaHCO$_3$-P$_i$ and biomass P (labile P) ranged from 24.1 to 44.8% in the unamended soils and 40.5 to 54.9% in manure amended soils. The labile P$_i$ comprised between 10.9 to 34.0% in the unamended and between 17.1 and 42.5% of the added P in the manure amended soils. Goat manure addition increased the concentrations of biomass P and resin-P but the largest effect was with biomass P. NaOH-P$_i$ fraction decreased with increasing rate of manure addition and there were minimal effects on NaHCO$_3$-P$_i$ fractions (Figure 4.2). Biomass P ranged from 16.8 to 43.9 mg kg^{-1} in the soils treated with inorganic P alone and from 32.6 to 97.7 mg kg^{-1} in the manure plus inorganic P treatments, respectively (Table 4.2). The interactions between inorganic P and manure addition on biomass P were significantly ($p = 0.05$) different (Figure 4.3).

Table 4.1 Summary of analysis of variance (F values) of the effects of inorganic P and goat manure application on different P fractions during 84 days of incubation

Factor	Df	Resin-P	$NaHCO_3$-P_i	NaOH-P_i	Biomass P
Replication	2	2.3 n.s	0.6 n.s	1.4 n.s	2.3 n.s
Manure	1	596.9***	56.9***	1.1 n.s	250.9***
P rate	4	6502.2***	854.8***	591.7***	51.5***
Time	5	1484.2***	92.5***	44.38***	162.1***
Manure * P rate	4	1.7 n.s	1.2 n.s	3.43**	15.4***
Manure * time	5	8.0***	1.2 n.s	27.2***	5.01***
P rate * time	20	103.8***	11.8 ***	11.4***	56.3***
Manure * P rate * time	20	4.7***	0.7 n.s	2.5***	1.5 n.s
Residual (MSE)	118	12.2	5.3	65.3	126.3
Cv (%)		4.3	8.7	4.8	29.6

n.s, not significant, **, *** significant at 0.01 and 0.001 probability level, respectively

Table 4.2 The effects of inorganic P and goat manure (GM) addition on the distribution of P fractions after 28 days of incubation

Treatment	Total P$^{\phi}$ (mg P kg^{-1}) (T)	P fractions (mg P kg^{-1})				Biomass P as a % of total P b/T *100%
		Resin P (a)	Biomass P (b)	NaHCO$_3$-P$_i$ (c)	NaOH-P$_i$ (d)	
Without manure						
0	420	17.2 j	16.8 b	11.8 g	144.3 f	4.0 d
90	465	39.6 h	30.7 b	17.9 f	164.3 e	6.6 cd
180	510	59.2 f	45.9 b	24.9 d	193.5 d	9.0 cd
270	555	93.6 d	49.6 b	34.3 b	227.9 b	8.9 cd
360	600	118.2 b	43.9 b	41.7 a	250.6 a	7.3 cd
With manure						
0	434	27.5 i	32.6 b	13.9 g	107.5 g	7.5 cd
90	479	54.6 g	50.2 b	21.1 e	149.5 f	10.5 bc
180	524	73.5 e	87.7 a	28.3 c	171.0 e	16.7 ab
270	569	103.9 c	97.7 a	35.6 b	196.0 d	17.2 a
360	614	122.7 a	96.9 a	41.4 a	213.2 c	15.8ab
LSD$_{(0.05)}$	-	4.0	34.5	3.1	13.3	6.7
Cv (%)	-	3.3	36.7	6.7	4.3	8.5
s.e.d	-	1.8	16.5	1.5	6.4	3.2

Means followed by the same letters within columns are not statistically different ($p \leq 0.05$). $^{\phi}$ Soil total P + added goat manure and inorganic P (mg kg^{-1}), LSD = Least significant difference, Cv = Coefficient of variation, s.e.d = standard error of the difference of treatment means

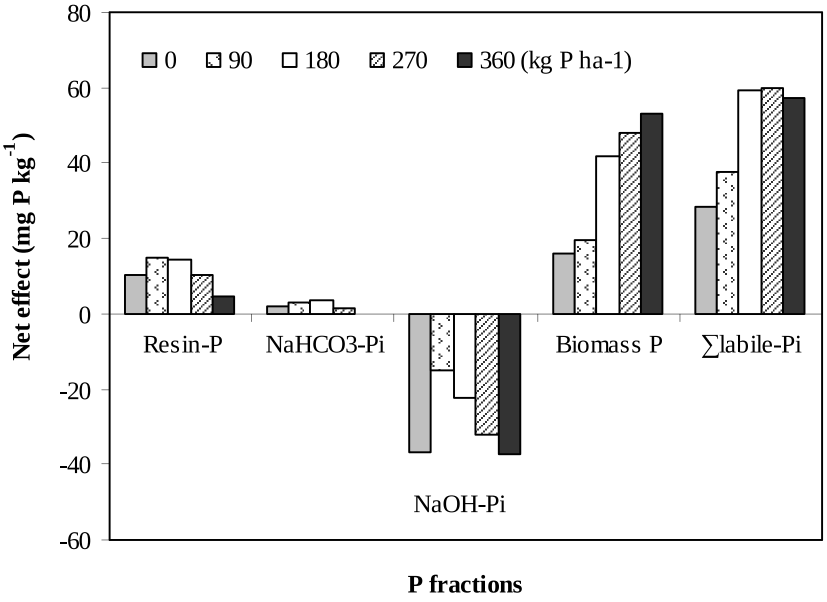

Fig. 4.2 **Net effects of the co-application of goat manure with inorganic P to the various P fractions after 28 days of incubation.**

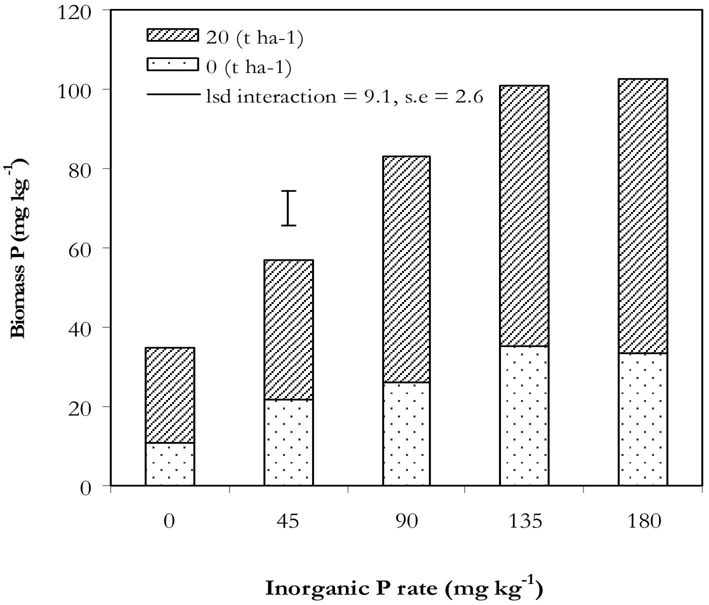

Fig. 4.3 **Effects of combined addition of goat manure and inorganic P on biomass P fraction during 84 days of incubation (bar represents least significant difference at p = 0.05, s.e = standard error of treatment means)**

4.4.3 Effects of incubation time on P fractions

The P concentrations in the different fractions varied considerably between treatments and incubation times (Table 4.1, Figure 4.4). The interactions between inorganic P derived from manure addition and incubation time were significantly ($p = 0.05$) different for resin-P, biomass P and NaOH-P_i fractions (Table 4.1). The resin-P fraction declined shortly after inorganic P addition, with or without goat manure (Figure 4.4). Biomass P significantly ($p = 0.05$) increased following inorganic P addition up to day 28 but declined thereafter (Figure 4.4). The largest increase occurred between 90 and 180 kg added P ha^{-1} P by day 28. Manure amended soils contained more biomass P than soils amended with inorganic P alone (Figure 4.4).

4.4.4 Relationship between added P with different P fractions

All soil P fractions were positively correlated with the rate of addition of added P (Table 4.3). The $NaHCO_3$-P_i was the fraction most strongly correlated ($r = 0.93$) with added P whereas biomass P was the least correlated ($r = 0.55$). Addition of P accounted for 90.4% of the variation in the sum of labile P fractions (Table 4.3) whereas 94.8% of the variance in the sum of the labile P fractions was accounted for by the resin P concentration in the soil. Among the P fractions, biomass P was significantly ($p = 0.05$) correlated with resin P ($r = 0.62$) only.

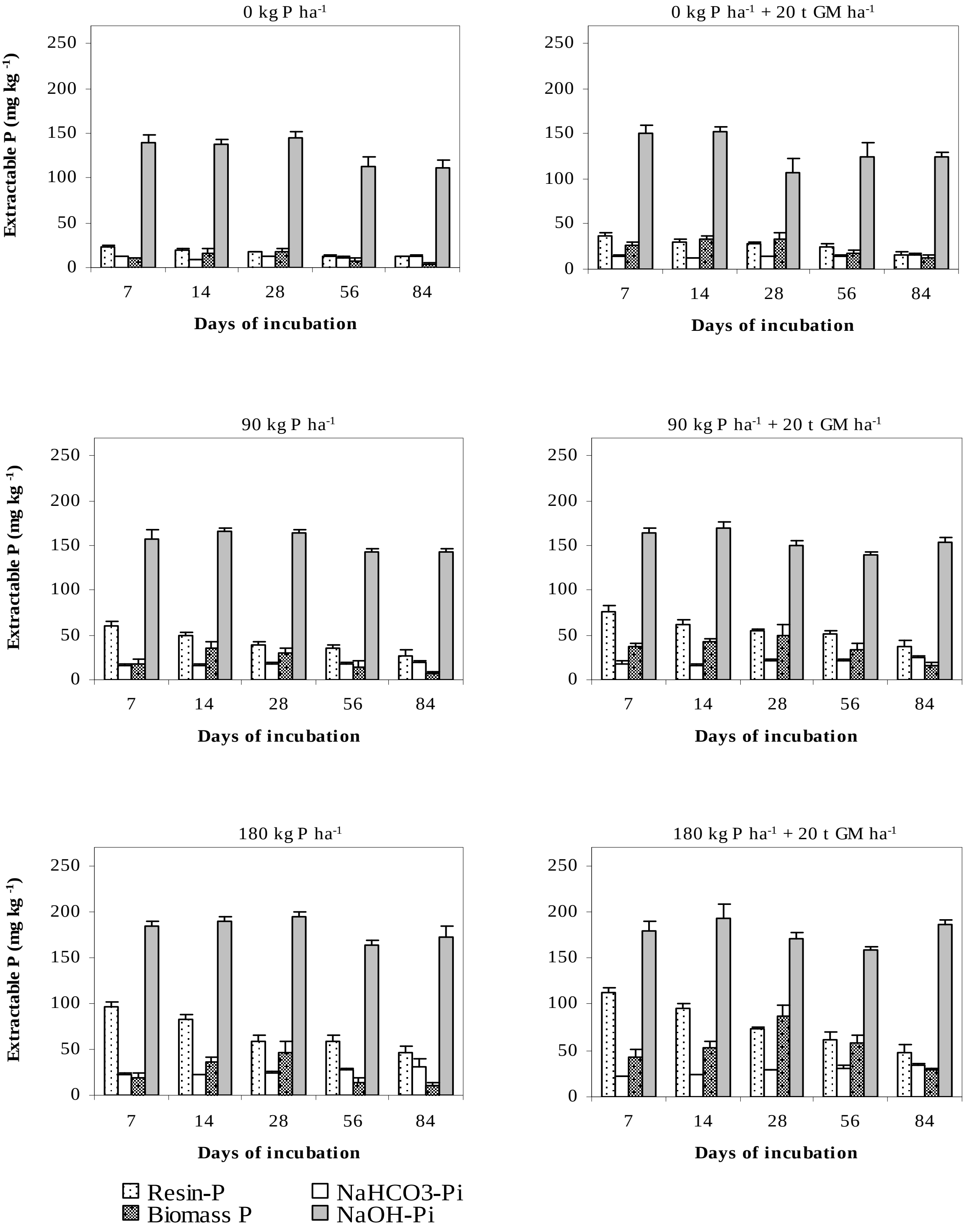

Fig. 4.4 Effects of inorganic P without or with goat manure (GM) on the distribution of P fractions at different incubation periods. (Bars represent standard deviations).

Table 4.3 Correlation coefficients for added P, inorganic-P and biomass P fractions

Properties	Added P	P fractions				
		Resin P	$NaHCO_3$-P_i	NaOH-P_i	Biomass P	Sum of labile P fractions
Added P	1.000					
Resin P	0.904	1.000				
$NaHCO_3$-P_i	0.931	0.716	1.000			
NaOH-P_i	0.893	0.855	0.780	1.000		
Biomass P	0.551	0.624	0.429ns	0.478ns	1.000	
Sum of labile P fractions	0.904	0.948	0.761	0.821	0.819	1.000

ns = not significant at P = 0.05

4.5 DISCUSSION

The P recovered in the different fractions was strongly dependent on the P added to the soil suggesting that an external source of inorganic P was necessary to increase their pool sizes. The proportions of the three inorganic P fractions extracted were in the order NaOH–P_i > Resin-P > $NaHCO_3$–P_i (Figure 4.4). The NaOH-P_i was the largest extractable P_i fraction and thus was the major sink for the applied P. According to Hedley *et al*. (1982) this fraction is less plant-available and usually associated with humic compounds and amorphous and some crystalline Al and Fe oxides in soils.

The resin extractable P concentration is considered to be an indicator of freely exchangeable soil P, either already in solution or in rapid equilibrium with soil solution (Henríquez and Killorn, 2005). It is therefore one of the most plant available soil P fractions. Resin extractable P declined during incubation following P addition to the soil (Figure 4.4), as reported by Agbenin and Tiessen (1995). In contrast, NaOH P_i tended to increase with time (Figure 4.4) seemingly at the expense of resin extractable P, suggesting that the observed decline in resin extractable P with time was a result of P sorption. Daroub *et al*. (2000) reported a similar transfer of added inorganic P from the resin-Pi fraction to the NaOH-P_i fraction.

The results further showed that the NaOH-P_i fraction was relatively smaller in soils where added P was applied with goat manure than when added P was applied alone (Figure 4.4, Table 4.2) indicating that the presence of goat manure helped to minimize the sorption of added P in the soil. This confirms results reported in Chapter 3 of this thesis and other work (e.g. Iyamuremye *et al.*, 1996; Erich *et al.*, 2002) showing that addition of organic materials to soil decreases P sorption. Erich *et al.* (2002) reported increased plant available P and resin P in soils amended with cattle manure in a potato cropping system while O'Halloran (1993) observed increased labile inorganic P in soils receiving manure and triple superphosphate compared with triple superphosphate alone. Similarly, Sharpley *et al.* (1984) and Nziguheba *et al.* (1998) observed decreased P sorption and concomitant increases in resin P, $NaHCO_3$-P and biomass P in soils following application of manure and Tithonia, respectively. The decreased P sorption following application of organic materials is believed to be due to production of organic acids during the decomposition of organic material, which temporarily bind to the oxides and the hydroxides on the surfaces of clay particles (Iyamuremye *et al.*, 1996).

Inorganic P addition increased the biomass P fraction which was further enhanced by manure addition (Table 4.2 and Figure 4.4). Biomass P ranged from 16.8 to 43.9 mg kg^{-1} and 32.6 to 97.7 mg kg^{-1} in the inorganic P alone and manure plus inorganic P treatments, respectively (Table 4.2). There was, however, a significant time x P rate interaction (Table 4.1) so that the size of the biomass P fraction varied with time at all rates of P application (Figure 4.4). Biomass P increased with time at all rates of added P, peaking on day 28 and declining thereafter. The largest increases on day 28 occurred between 90 and 180 kg P ha^{-1} (Figure 4.4). Kouno *et al.* (2002) attributed such increases to uptake of inorganic P from added fertilizer P into the biomass and conversion into other forms of P such as polyphosphates and metaphosphates that serve as cellular storage products. The biomass P fraction was significantly ($p = 0.05$) correlated with added P ($r = 0.56$) suggesting that biomass P has a great potential to protect added P from sorption by soil constituents. The decrease in biomass P after day 28 coincided with an increase in the proportion of the $NaHCO_3$ -P_i fraction (Figure 4.4) suggesting that the observed decrease in biomass P was a result of its mineralization and conversion to inorganic P. The fact that the biomass P peaked at day 28 in the present study suggests that in order to derive maximum benefit from the P protected in biomass P, planting may have to be synchronized such that the peak period for biomass P decline, whereby P may be released, coincides with the period of maximum P demand by the target crop. However, before this can be implemented the peak period for biomass P and its subsequent mineralization will need to be established under actual field conditions.

Although biomass P increased following addition of P added as fertilizer or in goat manure applied singly, a greater total increase occurred when they were applied together. The increase in biomass P in the presence of goat manure seems to have occurred at the expense of the NaOH-Pi fraction (Figure 4.4) showing the protective effect of biomass P on added P. The increased biomass P is assumed to be due to increased synthesis of biomass P in soil following goat manure addition. Previous studies e.g. Iyamuremye *et al.* (1996); Hinsinger, (2001) have shown that soil biomass is increased to a greater extent with combined addition of manure and inorganic P than by inorganic fertilizer alone. More recently, Ayaga *et al*. (2006) reported similar results following manure application to soil in field experiments in Kenya. They postulated that addition of manure stimulated the synthesis of soil microbial biomass resulting in increased demand for P, which becomes immobilized in labile forms in the cells of the living soil micro-organisms and in the associated pool of microbial metabolites. Thus manure further protects the added P from fixation by soil. The turnover of the biomass P pool may therefore provide a slow release of inorganic P that plants can use more efficiently than a single large pulse of P fertilizer, which may otherwise be fixed and removed from the available P pool before plants can use it efficiently (Brookes *et al.*, 1984; Ayaga *et al.*, 2006).

A significant manure x P rate interaction on biomass P was observed (Table 4.1) in that the effect of goat manure on biomass P varied with rate of P application (Figure 4.3). The largest proportional increases in biomass P due to manure addition (Figure 4.3) occurred at the lower rates of P application (90 and 180 kg P ha^{-1}). This implies that application of goat manure together with small inputs of P fertilizers could be a cost effective way of increasing P fertilizer use efficiency in smallholder farms in South Africa, where goat manure and other animal manures are available. Since only one rate of manure application (20 t ha^{-1}) was used in this study a follow up study (Chapter 5) investigated, among other things, if similar improvements in added P availability could be achieved with lower rates of manure application.

4.6 CONCLUSIONS

Addition of inorganic P to soil increased all soil P fractions examined but the increases were greater when goat manure was co-applied. Application of goat manure alone marginally increased soil labile Pi fractions and biomass P, whilst greater increases were obtained with the combined application of P fertilizer with goat manure. The quantities of P recovered in the different fractions were closely related to the amounts of P added to the soil; increasing proportionately with increasing amounts of added P. Manure addition increased soil biomass

P with 17.8 to 24.2% of the added P immobilized by the biomass. This indicates that goat manure provided an energy source for microbial activity that stimulated an increased biomass in the soil, resulting in increased demand for P. The immobilized P would therefore be maintained in labile forms that become potentially plant-available following microbial turnover and mineralization. The largest increase in biomass P following manure addition occurred at smaller rates of added P indicating the potential of goat manure to enhance the efficiency of small rates of P fertilizers. Biomass P peaked on day 28 under laboratory conditions and declined thereafter seemingly due to mineralization and conversion to inorganic P. Further work is now required to determine if this also occurs under glasshouse and/or field cropping conditions. Should this also hold under field conditions, there may be a benefit of synchronizing planting such that the peak period of P demand by the target crop coincides with maximum mineralization of biomass P. The plant availability of the different P fractions as influenced by added goat manure was the subject of a separate study reported in Chapter 5.

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CHAPTER 5

EFFECTS OF GOAT MANURE AND PHOSPHATE ADDITION ON INORGANIC P AND MICROBIAL BIOMASS P FRACTIONS AND THEIR RELATIONSHIP WITH PLANT P UPTAKE AND DRY MATTER YIELD

5.1 ABSTRACT

Results of a previous laboratory incubation study indicated that when goat manure and fertilizer P were applied together, a synergistic effect occurred whereby labile P and biomass P were increased more than when fertilizer P was applied alone. It, however, remained to be established whether the observed effects would translate to improved P availability and plant growth. The objectives of this study were therefore to investigate the effects of the combined applications of different rates of inorganic P and goat manure on (i) the concentration and distribution of soil inorganic and biomass P fractions in the presence of growing plants and, (ii) to relate the P concentrations in these fractions to plant growth and P uptake by maize (*Zea maize*) in a glasshouse pot experiment. Four rates of goat manure (0, 5, 10 and 20 t ha^{-1} dry weight basis) and four rates of inorganic P (0, 90, 180 and 360 kg P ha^{-1}) as triple super phosphate were applied to 7 kg soil portions and maize sown immediately thereafter. Resin-P, soil microbial biomass P (biomass P), 0.5 M $NaHCO_3$ extractable inorganic P ($NaHCO_3$-P_i), and 0.1 M NaOH extractable inorganic P (NaOH-P_i) concentrations were determined at the 6th and 12th week after maize planting and related to dry matter yield and P accumulation in plants. Biomass P was significantly increased by each increment of goat manure up to 20 t ha^{-}

^{1} but manure had no effect on resin P, $NaHCO_3$–P_i, or NaOH–P_i fractions. Addition of inorganic P significantly increased the concentration of all P fractions and followed the order NaOH-P_i >> resin P > biomass P > $NaHCO_3$–P_i. With each increment of added P the largest increases in extractable P were observed in the resin P and NaOH–P_i fractions and only marginal increases in $NaHCO_3$-P_i. At 12 weeks after planting goat manure had highly significant effects on resin P and biomass P but had no effect on $NaHCO_3$-P_i and NaOH–P_i. A significant manure*P rate interaction was observed between all P fractions at 12 weeks after planting. Resin P was decreased by 56 to 68% between the 6th week and the 12th week of sampling and was the most depleted fraction. Dry matter yield and P uptake were highly and significantly ($p = 0.05$) correlated with the different soil P fractions. The correlations followed the order resin P ($r = 0.85$) > NaOH-P_i ($r = 0.85$) > $NaHCO_3$-P_i ($r = 0.84$) >> biomass P ($r = 0.56$) for dry matter yield at 6 weeks after planting. The combination of biomass P, resin P and $NaHCO_3$-P_i explained 75.8% of the variation in dry matter yield of which 63.0% of the variation was explained by biomass P alone. The predictive equation for maize dry matter yield was: DM (g) = 1.897 biomass P + 0.645 resin P ($r = 0.73$). The synergistic benefits to maize growth realized with co-application of lower rates of goat manure with inorganic P indicate the potential of goat manure application in the manipulation of the microbial biomass to improve P cycling and increasing the effectiveness of added P.

Key words: Goat manure, biomass P, resin-P, $NaHCO_3$-P_i, NaOH-P_i, dry matter yield, plant P uptake

5.2 INTRODUCTION

The need to identify efficient plant nutrient management practices to increase and sustain food production is a priority for most African countries mainly due to their rapidly growing populations and limited availability of productive land. Phosphorus is one of the nutrients that cause major limitations in crop production in the tropics and subtropics and which requires management interventions for improved crop yields, especially in the smallholder farming sector.

Phosphorus deficiency is mainly caused by strong sorption of P by aluminium (Al) and iron (Fe) oxides and hydroxides and other amorphous materials (Hinsinger, 2001). This necessitates large applications of fertilizer P to overcome P sorption and to achieve high crop yields (Warren, 1994; Henry and Smith, 2002), unaffordable by resource poor smallholder farmers. Limited nutrient inputs by smallholder farmers, because of their high cost, and limited accessibility exacerbates soil P deficiency. It is therefore important to investigate affordable P management systems that optimize integrated use of all nutrient sources (e.g., fertilizers, organic manures, waste materials) suitable for the maintenance of soil fertility and crop productivity.

Goat manure is readily available on most smallholder farms in the Eastern Cape Province of South Africa, being second only to cattle manure in terms of availability (Yoganathan *et al.*, 1998). It would be expected that addition of goat manure to soil would result in increased P availability through reduced sorption of added P, as found with other similar organic materials (e.g. Hue, 1992; Iyamuremye *et al.*, 1996). Understanding the role of goat manure in enhancing P availability of added P in high P fixing soils may lead to the development of cost effective soil management systems that could increase the efficiency of soil P utilization by crops. This would allow subsistence farmers in the Eastern Cape to apply less inorganic P fertilizer.

The soil microbial biomass is an important reservoir of P in soils (Brookes *et al*., 1984; 2001) and therefore its manipulation may possibly provide a means to improve the availability of both soil P and added P. A preliminary laboratory incubation study (Chapter 4) showed that addition of inorganic P increased labile inorganic P and microbial biomass P fractions and the increases were greater when goat manure was co-applied. Enhanced P availability following combined addition of organic material and fertilizer P was reported previously (e.g. Nziguheba *et al.,* 1998; Griffin *et al.,* 2003; Laboski and Lamb, 2003). This was considered to be because, besides being a source of P and other nutrients, organic materials provide an energy source for microbial activity (Parham *et al*., 2003). Thus, the application of manure or other organic materials stimulates the growth of the soil microbial biomass with a corresponding increase in its demand for P. The biomass then acts as a labile pool of P which is protected from P fixation, and which is potentially plant available (Brookes *et al.* 1984).

The objectives of this study were therefore to investigate the effects of the combined applications of different rates of inorganic P and goat manure on (i) the concentration and distribution of soil inorganic and biomass P fractions in the presence of growing plants and, (ii) to relate the P concentrations in these fractions to plant growth and P uptake by maize in a glasshouse pot experiment.

5.3 MATERIALS AND METHODS

5.3.1 Experimental details

Combinations of four rates of goat manure (0, 5, 10 and 20 t ha^{-1}) and four rates of inorganic P (0, 90, 180 and 360 kg P ha^{-1}) as triple super phosphate were applied by uniformly mixing the added P and manure with 7 kg of air-dry soil in each pot. To ensure other nutrients were non-limiting N and K were applied as ammonium nitrate (28 % N) and KCl (53 % K), respectively to all pots at rates equivalent to 200 kg N ha^{-1} and 100 kg K ha^{-1}. In addition, each pot received the equivalent of 5.7 kg Zn ha^{-1}, 2.5 kg Cu ha^{-1}, 4.0 kg Mn ha^{-1}, 0.1 kg Mo ha^{-1}, 1.1 kg B ha^{-1} and 56.1 kg S ha^{-1} after the plants had established. Nutrient carriers were; $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, $MnCl_2.4H_2O$, $Na_2MoO_4.2H_2O$, $Na_2B_4.O_7.10H_2O$ and K_2SO_4, respectively. Treatments were applied assuming that the plough layer (0 -15 cm depth) of 1 hectare contained 2 x 10^6 kg of soil. The pots were placed on saucers in a randomized complete block design and replicated three times. Two sets were prepared to allow sampling on the 6th and 12th week after planting. They were watered approximately to field capacity and left to incubate overnight to remove the effects of sample handling (sieving, drying and mixing). Maize seeds (DKC 6125) were sown at 4 seeds per pot at a depth of 5 cm and covered with soil. Plants were thinned to 2 plants per pot at 7 days after germination. Water was added to the pots to maintain adequate soil moisture for the growing plants as required.

The shoots were harvested at 6 and 12 weeks after planting to examine changes in P in the different P pools over time, and oven-dried at 65 ^{o}C to a constant weight for dry matter determination. The samples were then ground to pass though a 1 mm sieve and analyzed for total P in the whole plant at week 6 and in the ear leaf blade at week 12. Determination of tissue P concentration was done using a H_2SO_4/H_2O_2 wet digestion procedure (Okalebo *et al.*, 2002). The concentration of P in the digests was determined by the method of Murphy and Riley (1962).

Soil samples were collected at each harvest to determine sequentially the concentrations of various P fractions (resin P, biomass P, $NaHCO_3$-P_i and NaOH-P_i). The method of Kouno *et al*. (1995) was used as described in Chapter 4 for these analyses. Phosphorus uptake was estimated by multiplying the maize P concentration by the respective dry matter yield.

5.3.2 Statistical analysis

Statistical analysis was done using GenStat statistical software (GenStat Release 4.24DE, 2005) by running a full model (16 treatments, 15 df), which was further split to a P rate effect (3 df), manure effect (3 df) and P rate x manure effect (9 df). Differences with $p \leq 0.05$ were considered significant. Simple regressions and correlations were also conducted to obtain relationships between different P fractions, dry matter yield and plant P concentration in the plant. The contributions of P fractions to dry matter yield and total plant P concentrations were examined using the maximum r^2 improvement forward stepwise model-building procedure (SYSTAT, 2000).

5.4 RESULTS

5.4.1 Soil and manure characterization

Selected soil and manure properties are presented in Chapters 2 and 3, respectively (see Tables 2.1 and 3.1). The soil solution pH was acidic with high concentrations of exchangeable Al, oxalate Al and exchangeable acidity. The concentrations of total organic carbon and nitrogen were low in this soil. The manure had a pH of 8.2, a C: N ratio of 19.4 and a C: P ratio of 206.6.

5.4.2 Effects of the co-application of goat manure with fertilizer P on sequentially extracted P fractions.

Goat manure had no effect on resin P, $NaHCO_3$–P_i, or NaOH–P_i but biomass P was significantly increased by each increment of goat manure up to 20 t ha^{-1} at six weeks after planting (Figure 5.1 and Table 5.1). Added inorganic P, however, had a highly significant effect on all P fractions (Table 5.1). As there was no significant manure*P rate interaction (Table 5.1) the effects of added P at different rates on each P fraction were averaged across manure rates (Figure 5.2). The P concentrations in the different fractions followed the order NaOH-P_i >> resin P > biomass P > $NaHCO_3$–P_i. Biomass P did not significantly increase above 90 kg P ha^{-1}. However, the resin P and NaOH-P_i fractions increased almost linearly with each increment of added P. With each increment of added P the largest increases in extractable P occurred in the resin P and NaOH–P_i fractions (Figure 5.2). Only marginal increases in $NaHCO_3$-P_i occurred with each increment of added P.

At 12 weeks after planting, addition of goat manure significantly increased resin P and biomass P but had no effect on $NaHCO_3$-P_i and NaOH–P_i (Table 5.2). In contrast to results obtained at 6 weeks after planting (Table 5.1) a significant manure*P rate interaction was observed for all P fractions at 12 weeks after planting (Table 5.2). The interaction effect was highly significant for resin P and biomass P but only marginally so for $NaHCO_3$-P_i and NaOH–P_i. Increasing rates of manure application significantly increased the concentration of resin-P but this effect was only significant when goat manure was applied at 10 and 20 t ha^{-1} (Figure 5.3a). When no P was added, goat manure increased biomass P slightly when it was applied at rates ≥ 10 t ha^{-1} but large increases in biomass P occurred at all rates of added P with 5 to 10 t ha^{-1} goat manure (Figure 5.3b). Addition of goat manure increased the concentration of $NaHCO_3$-P_i only at the highest rate of added P (Figure 5.3c) and had inconsistent effects on NaOH–P_i (Figure 5.3d).

Table 5.1 Summary of analysis of variance (F values) of the effects of [a]goat manure and inorganic P application on different P fractions and dry matter yield 6 weeks after planting

Factor	Df	Resin P	Biomass P	$NaHCO_3$-P_i	NaOH-P_i	Dry matter yield
Replication	2	0.7n.s	0.7n.s	1.4n.s	0.4n.s	19.0ns
Manure rate	3	2.7n.s	31.9***	2.4ns	0.4ns	2.1ns
P rate	3	288. 8***	28.1***	169.5***	94.8***	188.9***
Manure * P rate	9	0.3n.s	1.1n.s	0.7ns	0.8ns	1.1ns
Residual (MSE)	30	-	-	-	-	-

[a]-dry weight basis, n.s, not significant, *, **, *** significant at 0.05, 0.01 and 0.001 probability level, respectively

Table 5.2 Summary of analysis of variance (F values) of the effects of [a]goat manure and inorganic P application on different P fractions and dry matter yield 12 weeks after planting

Factor	Df	Resin P	Biomass P	$NaHCO_3$-P_i	NaOH-P_i	Dry matter yield
Replication	2	0.6n.s	2.4n.s	1.3n.s	0.5n.s	0.74n.s
Manure rate	3	50.2***	30.1***	2.5n.s	0.2n.s	41.9 ***
P rate	3	1077.2***	117.3***	90.3***	185.1***	219.2***
Manure * P rate	9	3.2**	6.9***	2.4*	3.0*	3.11**
Residual (MSE)	30	-	-	-	-	-

[a]-dry weight basis, n.s, not significant, *, **, *** significant at 0.05, 0.01 and 0.001 probability level, respectively

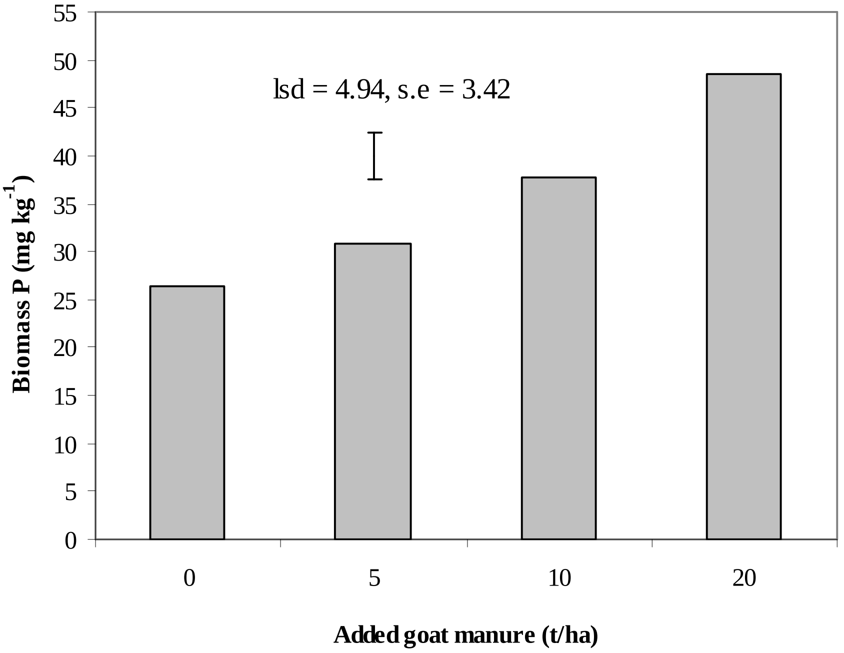

Fig. 5.1 Effects of different rates of goat manure application on soil biomass P at week 6 (Bar represent least significant difference at p = 0.05, s.e = standard error of treatment means).

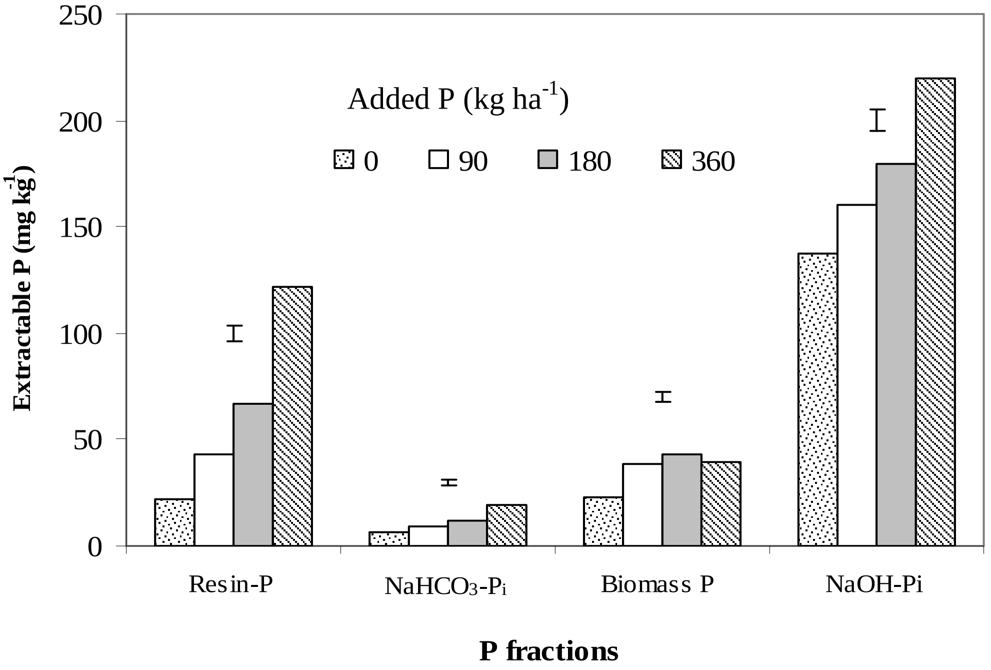

Fig. 5.2 Effects of rate of added inorganic P on soil P fractions at week 6. (Bars represent least significant difference at p = 0.05).

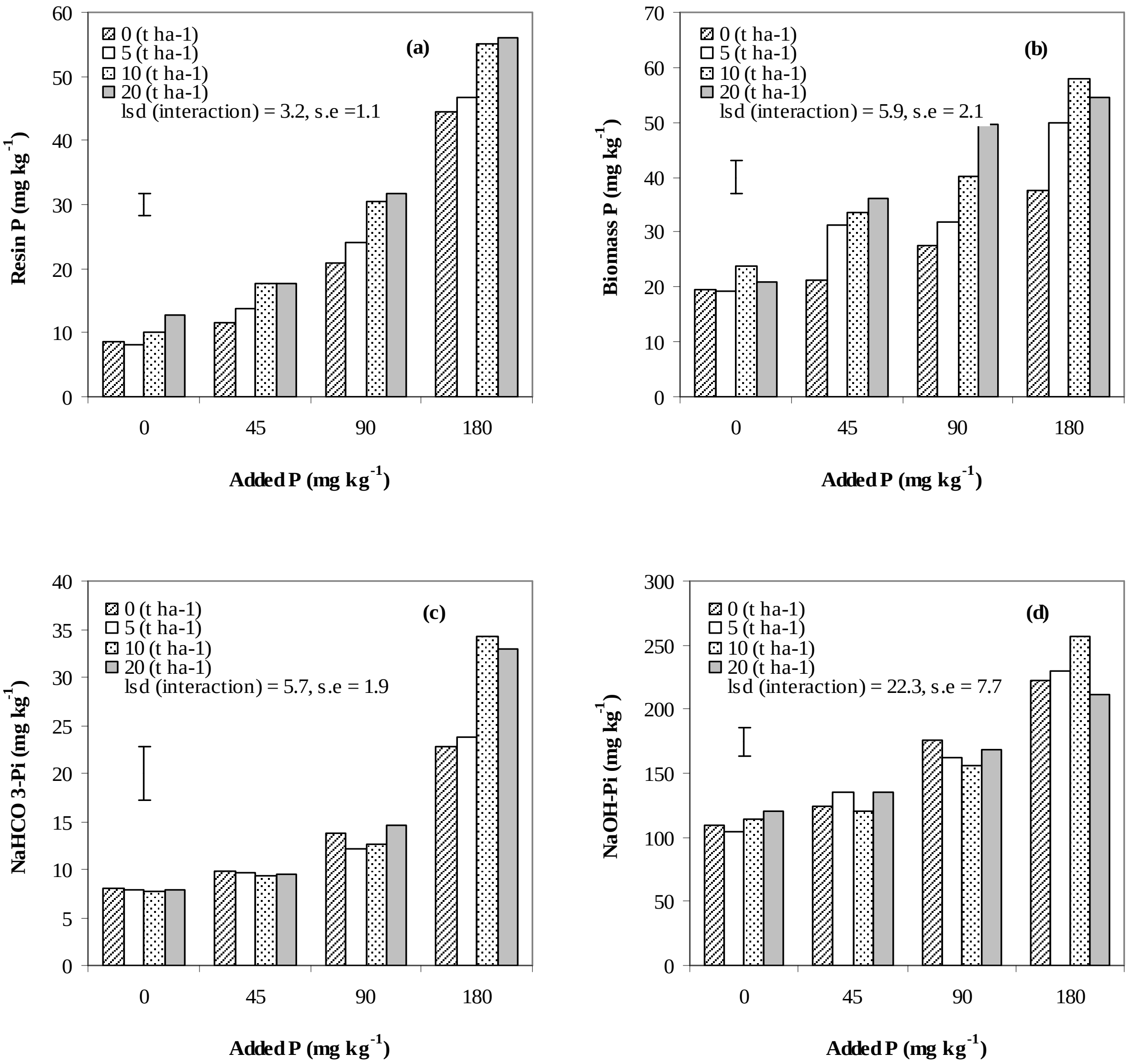

Fig. 5.3 Interaction effects of added goat manure (GM) and inorganic P on resin P (a), Biomass P (b), NaHCO$_3$-P$_i$ (c) and NaOH-P$_i$ (d) 12 weeks after planting. (Bars represent least significant difference at p = 0.05, s.e = standard error of treatment means).

5.4.3 Changes in the P concentration of the various P fractions between sampling periods when inorganic P was co-applied with 5 t ha^{-1} goat manure.

The combined effect of applying 5 t ha^{-1} goat manure with different rates of added P on the concentration and relative distribution of the different P fractions at 6 and 12 weeks after planting is shown in Figure 5.4. At six weeks after planting the concentrations of the P fractions followed the order NaOH–P$_i$ >> resin P > biomass P >> NaHCO$_3$–P$_i$ (Figure 5.4a). After a further 6 weeks of plant growth the distribution of the P fractions changed considerably, notably that of resin P (Figure 5.4b). Resin P was decreased by 56 to 68% between the 6th week and the 12th week of sampling and was thus the most depleted fraction (Table 5.3). By contrast, biomass P was only marginally depleted at P rates < 180 kg P ha^{-1} while at the highest P application rate it was substantially increased (Table 5.3). The NaHCO$_3$–P$_i$ was increased at all rates except at 180 kg P ha^{-1} where it was slightly depleted. The NaOH–P$_i$ was moderately depleted at P rates < 180 kg P ha^{-1} but tended to increase at a rate of 360 kg P ha^{-1}. Consequently at 12 weeks after planting, the order of magnitude of the different fractions changed to NaOH–P$_i$ > biomass P > resin P > NaHCO3–P$_i$ (Figure 5.4b). A similar pattern of P depletion was observed at the other rates of goat manure application (data not shown).

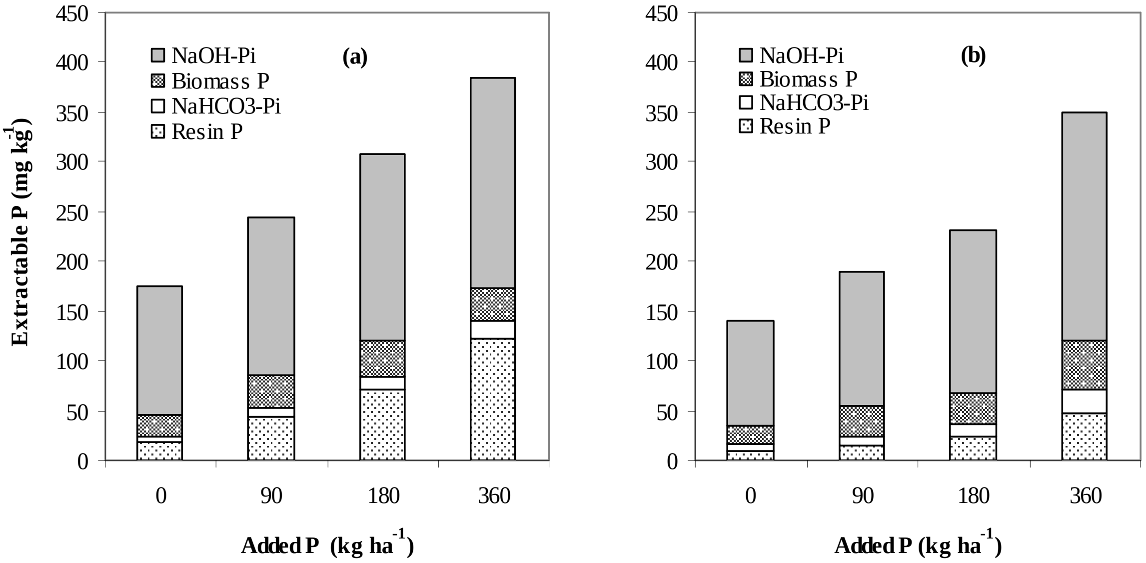

Fig. 5.4 Relative distributions of sequentially extracted P fractions in soil at 6 (a) and 12 (b) weeks after planting as influenced by added P at a manure rate of 5 t ha^{-1}

Table 5.3 Changes in P concentrations of the various P fractions between the 6th and 12th week sampling periods at a manure rate of 5 t ha^{-1}

Added P (kg ha^{-1})	Percent P change				
	Resin P	Biomass P	NaHCO$_3$-P$_i$	Labile P$_i$	Moderately labile P$_i$ (NaOH-P$_i$)
0	-56	-7	37	-19	-20
90	-68	-5	10	-58	-15
180	-66	-14	-2	-68	-13
360	-62	55	30	-32	8

5.4.4 Effects of goat manure and inorganic P addition on dry matter yield and plant P uptake

Maize dry matter yield at 6 weeks after planting was increased significantly ($p = 0.05$) by added fertilizer P but it was not influenced by goat manure addition or its interaction with fertilizer P (Table 5.1, Figure 5.5a). However, at 12 weeks the dry matter yield was increased significantly ($p = 0.05$) by both fertilizer P and goat manure, and was significantly influenced by their interaction (Table 5.2, Figure 5.5b). The largest increases in maize dry matter yield were observed when fertilizer P at different rates was co-applied with 5 t ha^{-1} goat manure. Increasing the manure rate to 10 t ha^{-1} produced a further increase in dry matter yield at the lowest rate of added P (90 kg P ha^{-1}) but not at higher P rates (Figure 5.5b). Co-application of fertilizer P with 20 t ha^{-1} goat manure did not result in further dry matter yield increases. Phosphorus accumulation in the plant tissue followed a pattern similar to that of dry matter yield (Figure 5.6).

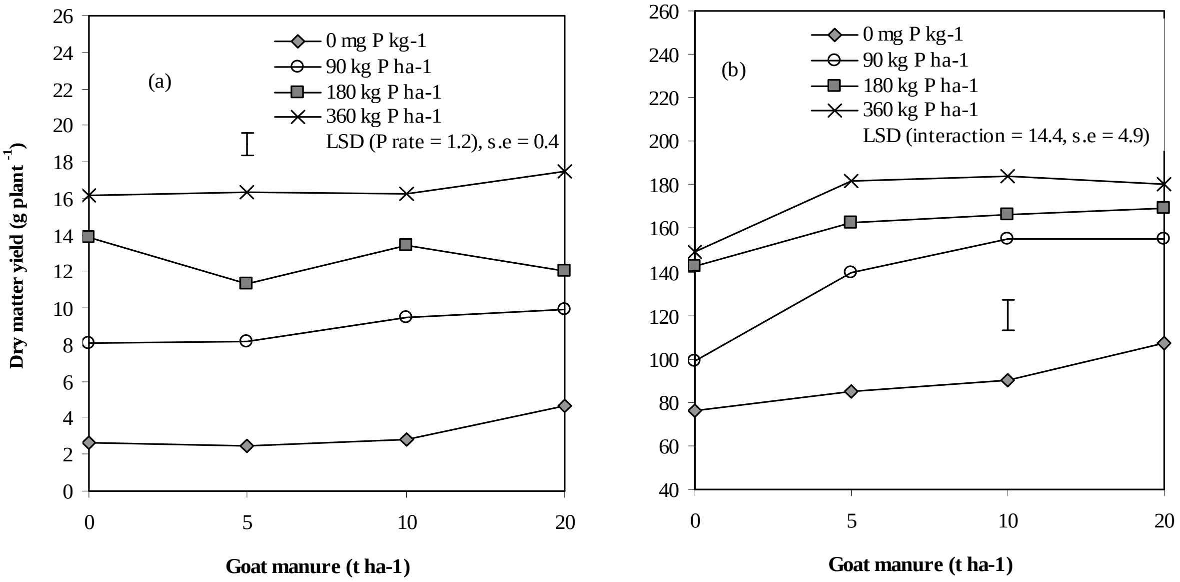

Fig. 5.5 Effects of combined manure and inorganic fertilizer P addition on dry matter yield at 6 weeks (a) and 12 weeks (b) after planting, respectively. (Bars represent least significant difference at p = 0.05, s.e. = standard error of treatment means).

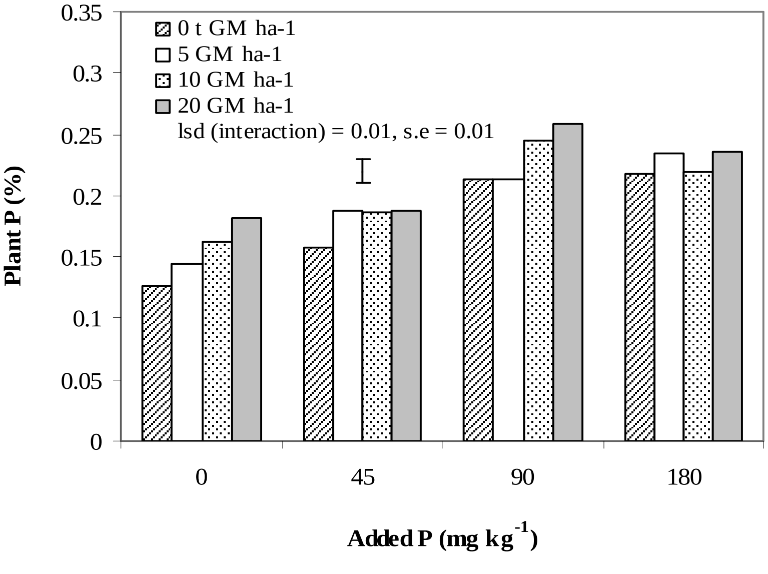

Fig. 5.6 Effects of combined goat manure and inorganic P addition on plant tissue P concentration 12 weeks after planting. (Bar represents least significant difference at p = 0.05, s.e. = standard error of treatment means).

5.4.5. Relationship between added inputs and soil P fractions with dry matter yield

The correlation coefficients between soil P fractions and dry matter yield at the 6 and 12 weeks harvests are given in Tables 5.4 and 5.5, respectively. Dry matter yield and P uptake were highly and significantly ($p = 0.05$) correlated with the different P fractions in the soil. The correlations followed the order: resin P ($r = 0.85$) > NaOH-P_i ($r = 0.85$) > $NaHCO_3$-P_i ($r = 0.84$) >> biomass P ($r = 0.56$) for dry matter yield at 6 weeks after planting. Correlations with plant P uptake followed the same trend (Table 5.4). The order, however, changed at week 12 in that biomass P had the highest correlation coefficient. The correlation coefficients of the P fractions and dry matter yield followed the order: biomass P ($r = 0.84$) > resin P ($r = 0.79$) > NaOH P ($r = 0.73$) > $NaHCO_3$-P_i ($r = 0.64$) (Table 5.5).

Table 5.4 Correlation coefficients for added P, dry matter yield and different P fractions 6 weeks after planting

Properties	P Fractions				Dry matter yield
	Resin P	Biomass P	$NaHCO_3$-P_i	NaOH-P_i	
Resin P	1				
Biomass P	0.406**	1			
$NaHCO_3$-P_i	0.964***	0.422**	1		
NaOH-P_i	0.943***	0.409**	0.970***	1	
Dry matter yield	0.853***	0.557***	0.836***	0.847***	1
Plant P uptake	0.900***	0.571***	0.872***	0.873***	0.984***

*, **, *** significant at 0.05, 0.01 and 0.001 probability levels, respectively

Table 5.5 Correlation coefficients for added P, dry matter yield and different P fractions 12 weeks after planting

Properties	P Fractions				Dry matter yield
	Resin P	Biomass P	$NaHCO_3$-P_i	NaOH-P_i	
Resin P	1				
Biomass P	0.839***	1			
$NaHCO_3$-P_i	0.920***	0.726***	1		
NaOH-P_i	0.933***	0.776***	0.906***	1	
Dry matter yield	0.791***	0.841***	0.639***	0.733***	1

*, **, *** significant at 0.05, 0.01 and 0.001 probability level, respectively

Regression analysis between dry matter yield and different P fractions showed curvilinear relationships (Figure 5.7 and 5.8). The mean dry matter yield increased with increasing P concentrations in all P fractions, with resin P accounting for much of the variation in dry matter accumulation (r^2 = 0.81). The value of the simple regression coefficient of biomass P with dry matter yield generally increased in the second harvest with 80% of the yield variation being accounted for by changes in biomass P as compared to 39% in the first harvest (Figure 5.7). Phosphorus accumulation in the plants followed a pattern similar to that of dry matter yield (data not shown). Since all P fractions were individually highly correlated with dry matter yield and P uptake, forward stepwise multiple regressions were used to determine the P fraction or combination of fractions that had the most influence on plant growth. The combination of biomass P, resin P and $NaHCO_3$-P_i explained 75.8% of the variation in dry matter yield of which 63.0% of the variation was explained by biomass P alone. Biomass P and resin P jointly accounted for 73.3% of the variation in dry matter yield (Table 5.6). The predictive model for percent P concentration in the plant was only significant when biomass P was included in the model and accounted for 63.0% of the variance of P concentration in the plant tissue (Table 5.6).

Table 5.6 Stepwise multiple regression equations between P fractions and dry matter yield (DM) and P concentration in the plant ear leaf blade 12 weeks after planting

Predictive dry matter yield (DM) equations	r^2
DM (g) = 2.535 biomass P	0.63
DM (g)= 1.897 biomass P + 0.645 resin P	0.73
DM (g)= 1.609 biomass P + 1.632 resin P – 1.691 $NaHCO_3$-Pi + 68.527	0.76
Predictive plant P concentration (%P) equation	
% P = 0.002 biomass P + 0.113	0.63

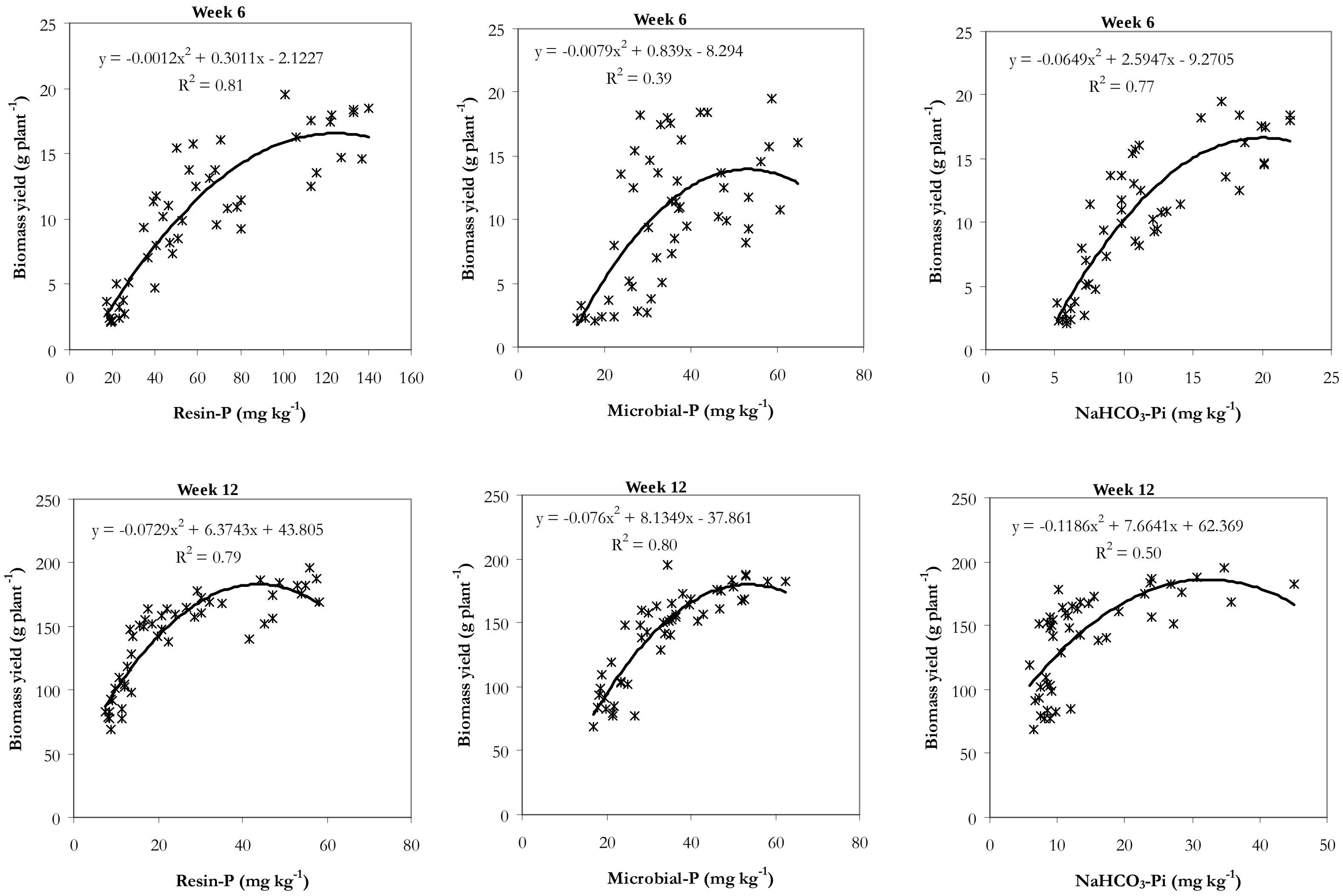

Fig. 5.7 Relationships between dry matter yield and Resin P, biomass P and NaHCO$_3$-P$_i$, at 6 and 12 weeks after planting, respectively

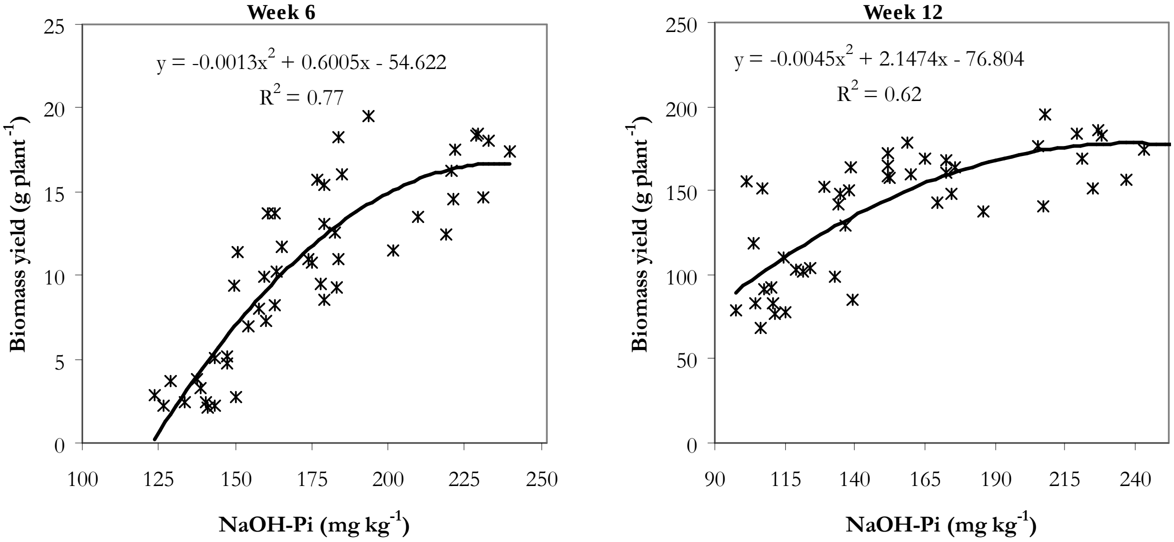

Fig. 5.8 Relationships between dry matter yield and NaOH-P_i at 6 and 12 weeks after planting respectively

5.5 DISCUSSION

The application of inorganic P fertilizer to soil generally increased the P_i fractions extracted by resin, 0.5 M $NaHCO_3$ (pH 8.5) and 0.1 M NaOH. The P concentrations were in the order NaOH–P_i > resin P > $NaHCO_3$–P_i at 12 weeks after planting (Figure 5.3). The P fractions removed by exchange resins and $NaHCO_3$ constitute the labile fraction and it is considered to be biologically and plant available in the short term, because it rapidly desorbs from the surface of soil colloids (Hedley *et al.*, 1982). A larger increase in the sum of these labile P fractions was observed in the fertilizer P plus manure treated soils than in the fertilizer P alone treatments (Figure 5.3). The higher P concentrations in these labile fractions was attributed partly to the addition of P through manure and partly to the effect of organic material added to soil which may have decreased P sorption. The decrease in P sorption was attributed to the possible effect of organic acids produced during the decomposition of organic materials that compete for sorption sites and formation of stable chelates with Fe and Al (Laboski and Lamb, 2003).

At each rate of added P, resin P was the most depleted fraction (56 to 68%) between the 6th and 12th week of planting. As resin P is the most labile P fraction (Bowman *et al*., 1987) it is possible that its depletion was a result of much of it being taken up by plants. It is also likely that some of it was transformed into $NaHCO_3$ extractable P_i as this fraction tended to increase between the 6th and 12th week after planting (Figure 5.4, Table 5.5). The largest proportion of added P was recovered in the NaOH-P_i fraction, accounting for an average of 63.0% and 69.3% of the sum of all P fractions at 6 and 12 weeks after planting, respectively. According to Beck and Sanchez (1994) and Iyamuremye *et al*. (1996) the NaOH-P_i fraction is bound to Al and Fe or their oxides in soils so the generally large concentration of P recovered in this fraction could be attributed to the high concentrations of exchangeable Al in this soil (Table 5.3). The much higher proportion of NaOH-P_i observed at 12 weeks after planting could be attributed to increased sorption of the added P over time while observed increases in this fraction with increasing fertilizer P additions could be attributed to sorption of the P added in excess of plant removal (Hedley *et al*. 1982).

The NaOH extractable P_i was only moderately depleted (13 to 20%) at lower rates of P application ($\leq$ 180 kg P ha^{-1}) and slightly increased at the 360 kg ha^{-1} rate of P application. Saleque *et al.* (2004) also reported some depletion of the NaOH-P_i fraction from a surface soil and suggested that this P fraction could have become mobilized when $NaHCO_3$-P_i became depleted. However, in the present study the resin P, considered the most labile fraction (Bowman *et al*., 1987), was not exhausted (Figure 5.4) and the $NaHCO_3$-P_i fraction generally increased (Table 5.5) so the observed depletion may have been the result of the conversion of some of the P in the NaOH-P_i fraction to recalcitrant P fractions that were not extracted rather than due to mobilization of the labile P pools.

Addition of inorganic P increased the biomass P fraction which was further enhanced by goat manure addition (Figure 5.2 and 5.3b). The greatest increase in biomass P occurred when added P was co-applied with 5 or 10 t ha^{-1} goat manure (Figure 5.3b). These results confirm those reported in the literature (e.g. Nziguheba *et al.,* 1998; Peacock *et al.,* 2001; Ayaga *et al.,* 2006) indicating that addition of manure to soil stimulates growth of microorganisms which, in turn, increases their demand for P. The net effect is an increased soil biomass P and an enhanced capacity of the biomass to compete for P with sorption sites.

Maize dry matter yield after 12 weeks of growth was increased significantly ($p = 0.05$) by both fertilizer P and goat manure and by their interaction (Table 5.4, Figure 5.5b). The largest increases in maize dry matter yield were observed when fertilizer P at a rate of 90 kg P ha^{-1} was co-applied with 10 t ha^{-1} goat manure whereas for rates of added P > 180 kg P ha^{-1} only 5 t ha^{-1} goat manure was needed for maximum yield increases (Figure 5.4b). Co-application of fertilizer P with 20 t ha^{-1} goat manure did not result in further dry matter yield increases. These results indicated that the synergistic effects on crop growth observed when other animal manures are co-applied with inorganic fertilizer (Iyamuremye *et al.*, 1996; Ayaga *et al.*, 2006) can be realized with goat manure. The results further indicated that under the experimental conditions of the present study, lower rates of added P required larger quantities of goat manure and vice versa for maximum benefits to be derived from the synergistic effects.

Correlation and regression analysis showed that maize dry matter yield and plant P uptake were dependent to varying extents on the amount of added P and its effects on the concentrations of labile P (resin P and $NaHCO_3$-P_i) and biomass P in the soil. Both the resin strip and 0.5 M $NaHCO_3$ do not alter the soil properties and their extraction power better mimics the extraction power of plant roots than other reagents commonly used during fractionation (Guo *et al.*, 2000). At six weeks after planting, P derived from these extractants was better correlated with dry matter yield and plant P uptake and explained more of their variations than biomass P. However, when plant growth was terminated after 12 weeks of growth, biomass P emerged as the P fraction most responsible for the observed variations in maize dry matter yield.

Forward stepwise multiple regression revealed that the combination of biomass P, resin P and $NaHCO_3$-P_i explained 75.8% of the variation in dry matter yield of which 63.0% of the variation was explained by biomass P alone whilst biomass P and resin P jointly accounted for 73.3% of the variation. These results suggest that resin P, being the most labile fraction, plays a greater role in supplying plant available P in the early stages of growth. However, when its concentration is severely reduced in later stages of plant growth as demonstrated in this study (Figure 5.4, Table 5.5) other P fractions, notably biomass P, play a greater role in supplying P to plants. It would seem, therefore, that resin P and biomass P in combination would give better prediction of a soil's P supplying potential than when either is used alone. Ayaga *et al.* (2006) did not recognize the significant role of resin P in this regard presumably because they did not evaluate the contributions of the different fractions in earlier stages of crop growth and did not use stepwise regression in the evaluation of their results. The results of the present study, nevertheless, support their findings that biomass P has a great potential in predicting soil P-supply to crops in sub-Saharan Africa and that it is therefore a potentially useful biological index of P availability, especially in P-fixing soils.

Application of goat manure increased biomass P in soils more than any of the other P fractions extracted (Figure 5.2 and 5.3). Therefore, the observed synergistic effects on maize growth as a result of the co-application of goat manure and P fertilizer could have been to a large extent due to enhanced P cycling through the increased biomass P pool. These results concur with others in the literature showing that manure addition increases the availability of

P in soil, resulting in greater plant growth (e.g. Iyamuremye *et al.*, 1996; Nziguheba *et al.*, 1998). Organic P (P_o) not determined in the present study is reported to account for 20 to 80% of the total P in most mineral soils and can be a significant source of plant P when organic materials decompose and the P mineralizes. Thus, the contribution of organic P to P cycling following goat manure addition with inorganic P in these soils needs to be evaluated. Also required are measurements of mineralization rate of soil P_o to determine the supplying potential of P_o to P nutrition to enable more accurate fertilizer P recommendations.

5.6 CONCLUSIONS

The results of this study showed that the distribution of the different P fractions extracted was influenced by plant growth. At the early stage of plant growth (6 weeks after planting) the concentrations of the different fractions followed the order: NaOH-P_i >> resin P > biomass P > $NaHCO_3$–P_i but six weeks later the order changed to: NaOH–P_i > biomass P> resin P > $NaHCO_3$–P_i. Of the different P fractions extracted, resin P was depleted to the greatest extent during the course of plant growth possibly because it is the most labile and plant available fraction but in later stages of plant growth biomass P played a greater role in supplying P to plants. The two P fractions therefore deserve consideration as parameters for predicting P supply to crops. The results further showed that biomass P alone explained 63% of the variations in dry matter yield at 12 weeks and thus has great potential as a biological indicator of P availability for this soil. Consistent with literature reports, the co-application of fertilizer P with goat manure had synergistic effects on maize dry matter yield and P uptake. This effect was apparently due to improved P cycling as goat manure increased the concentration of biomass P at each level of added P to a greater extent than any of the other P fractions. The synergistic benefits to maize growth were realized with the co-application of 90 kg P ha^{-1} with 10 t ha^{-1} of goat manure but the amount of manure could be reduced to 5 t ha^{-1} when higher rates of added P (> 180 kg ha^{-1}) are used. Goat manure, therefore, may be used in the manipulation of the microbial biomass for purposes of improving P cycling and increasing the effectiveness of added P. This work was conducted under glasshouse conditions using relatively small pots. The results therefore now need to be validated under field conditions and using a wider range of soils.

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CHAPTER 6

GENERAL DISCUSSION, CONCLUSIONS AND FUTURE RESEARCH

6.1. General Discussion

Soil P is the least mobile of the major plant nutrients and as earlier stated, its low availability is a major constraint to agricultural production in most South African soils (Henry and Smith, 2006) as well as other highly weathered tropical soils (Warren, 1994). For most smallholder farmers with limited resources, high P deficiency is a factor most limiting productivity and has a profound impact on food security (Warren, 1994). High P deficiency is most prevalent mainly where strong sorption of P by aluminum and iron oxides and amorphous materials occurs resulting in poor mobility of soil inorganic P (Hinsinger, 2001). Therefore, only a small proportion of soil P is present in the soil solution and available for plant uptake. This leads to the need for large applications of fertilizer P to achieve high crop yields (Warren, 1994).

In South Africa, crop production levels under the smallholder systems of agriculture are reported to be low, due to poor natural soil fertility coupled with low usage of inorganic and/or organic fertilizers with P being one of the nutritional factors limiting production (Mandiringana *et al.*, 2005). Earlier reports on data from the Transkei region show that a sizeable number of soils are of low to medium pH (Mandiringana *et al.*, 2005; Bühmann *et al.*, 2006). The soils are low in exchangeable bases which could mainly be attributed to the higher rainfall and warm temperatures that are normally observed in the region leading to intense leaching of bases and accumulation of exchangeable Al in these soils. Many of the soils in the surrounding districts of KwaZulu Natal and Mpumalanga are reported to have high P sorption capacities (Bainbridge *et al.,* 1995; Henry and Smith, 2002).

Identifying appropriate P management strategies requires a good understanding of the fate of applied P and estimating plant available P in different P pools. A review of available literature (Chapter 1) indicated that soil P dynamics are characterized by interaction between physicochemical and biological processes: the immobilization of inorganic P (P_i) by the microorganisms constitutes a withdraw of P_i from the soil solution, while at the same time, P is delivered to the soil solution through mineralization of microbial P and organic P (P_o) (Seeling and Zasoski, 1993; Oberson, 1996). In addition, organic anions released from added organic materials, can affect P sorption and the exchangeability of added P through competition for sorption sites (Iyamuremye *et al.,* 1996). An understanding of these processes and the measurement of the sizes of the various P fractions in soils is important if we are to help farmers make the most economic use of P fertilizer.

Combined application of inorganic P with organic materials is reported to result in larger increases in yields than if either is applied singly (Nziguheba *et al.,* 1998; Ayaga *et al.,* 2006). Besides constituting a source of P as well as other nutrients, organic materials also provide an energy substrate for microbial activity (Palm *et al.,* 2001). Ayaga *et al.* (2006) for example, postulated that addition of manures stimulates the synthesis of soil microbial biomass resulting in increased demand for P, which is immobilized in labile forms, both in the cells of the living soil micro-organisms and their associated pool of metabolites. The turnover of this fraction provides a slow release of inorganic P which the plants can use more efficiently (Ayaga *et al.*, 2006). Little or no information is available on P dynamics and turnover of the microbial biomass P fraction and other P fractions in soils receiving inorganic fertilizer P with animal manures in South African soils and more specifically soils of the Eastern Cape. The main aim of this study was therefore to investigate whether combined addition of goat manure with inorganic P fertilizers would enhance P availability in some strongly P fixing soils of the Transkei region, South Africa.

The study was undertaken to address the following specific objectives (i) to assess P sorption capacities and requirements of selected soils and their relationship with selected soil properties and single point sorption test, (ii) to assess the effects of goat manure and lime addition on P sorption properties of selected high P fixing soils (iii) to assess the temporal changes in concentration of inorganic and microbial biomass P fractions following application of inorganic fertilizer P with goat manure in a laboratory incubation experiment, and, (iv) to assess the effects of goat manure application with inorganic P on inorganic and microbial biomass P fractions, P uptake and dry matter yield of maize.

6.1.1 Phosphate sorption characteristics and external P requirements and their relationships with selected soil properties and single point sorption test

The seven soils studied varied widely in their capacities to sorb P and would therefore react differently to applied P necessitating different approaches to P management in terms of placement and amounts applied. The sorption behavior of the soils studied was adequately described by the Langmuir model, with coefficients of determination (r^2) values > 0.95 observed for all the soils under study. The observed differences in sorption maxima among the soils were most likely due to the large variations in the amounts and nature of Al and Fe components present in the soils as shown by positive correlations between the sorption maxima and different forms of Fe and Al extracted. Stepwise regression analysis showed that, a combination of organic carbon, exchangeable Al (Al_{KCl}), citrate dithionite bicarbonate extractable Al (Al_{CDB}) and ammonium oxalate extractable Al (Al_{ox}) explained 93.2% of the variation in sorption maxima (S_{max}) of which 87.8% of the variation was explained by Al_{CDB} alone. Soil organic C and Al_{CDB} jointly accounted for 91.1% of the variation in S_{max}. The stepwise regression coefficients when organic carbon and Al_{CDB} were included in the stepwise model indicated that a unit change in Al_{CDB} (g kg^{-1}) changes P sorbed by 128 mg P kg^{-1} (r^2 = 0.911, p = 0.05). This dependence of P sorption on citrate dithionite bicarbonate Al therefore seems to explain the low amounts of P sorbed by soils from Qweqwe, Qunu and from Bethania that had low amounts of citrate dithionite bicarbonate Al with corresponding lower levels of organic C. Similar observations have been made in previous reports indicating that citrate dithionite bicarbonate Al contributes more to the retention of P in most soils. Henry and Smith (2002) for example reported from studies conducted on soils from tobacco growing areas of South Africa that citrate dithionite bicarbonate Al had a greater influence on P retention than other Al forms. Similarly, Singh and Gilkes (1990) reported that P sorption capacity in Australian soils was predictable by measurements of citrate dithionite bicarbonate Fe and Al. Citrate dithionite bicarbonate solution could therefore be used as a single extractant to estimate the potential P sorption in these soils.

Maximum dry matter yield of oat was achieved at equilibrium P concentrations of 0.20 and 0.25 mg P l^{-1} for Flagstaff and Qunu soils. Apparently, the yield obtained from these concentrations were not significantly different from those obtained at a soil solution P concentration of 0.2 mg P l^{-1} ($P_{0.2}$) reported in the literature to be a threshold for many crops, over which no response to P is observed (Iyamuremye *et al.,* 1996; Nziguheba *et al.,* 1998; Duffera and Robarge, 1999). These results thus showed that a soil solution P concentration of 0.2 mg P l^{-1} ($P_{0.2}$) could be optimal for oats and possibly other crops in these soils. The single point sorption test (SI) was highly correlated to $P_{0.2}$ ($r = 0.93$) and the high values of the coefficient of determination ($r^2 = 0.97$) observed suggest that the SI function ($P_{0.2} = 12.87e^{0.04SI}$) could successfully be used to predict the external P requirement ($P_{0.2}$) for the soils from Ntlonyana, Ncihane, Qweqwe, Qunu and Bethania, which are considered to be low P sorbers. Henry and Smith (2003) also found high coefficients of determination ($r^2 = 0.98$) in the relationship between SI and $P_{0.11}$ for low to moderate fixing soils of the tobacco growing areas of Kwa-Zulu Natal. They also concluded that SI can be used advantageously as a time saving measure to obtain an index of the external P requirement of soils instead of having to produce a full P isotherm.

6.1.2 Effects of goat manure and lime addition on phosphate sorption

The results of preliminary P sorption evaluation reported in Chapter 2 revealed that the soils used represent a wide range of reactivity towards fertilizer P and that some soils had sufficiently high P retention capabilities to seriously decrease the availability of added P to plants and thus required intervention to minimize the effect. One proposed way of mitigating the effects of P sorption on P availability is to increase soil pH and reduce the activity of exchangeable Al in soil solution through addition of organic materials (Haynes and Swift, 1985). A study conducted to address the question of whether goat manure addition could reduce P sorption in the moderately P fixing soils from Chevy Chase and Flagstaff (Chapter 3) showed that addition of goat manure consistently reduced P sorption maxima in both soils. Phosphate sorption decreased with increasing amounts of goat manure in both soils but the extent of reduction was greater on Chevy Chase soil than on Flagstaff soil. For example, addition of 20 t ha^{-1} of goat manure reduced S_{max} by 25.4% in Chevy Chase soil but was only reduced by 16.4% on Flagstaff soil after 28 days of incubation.

Regression analysis of sorption maxima with exchangeable Al indicated that 98.4 and 97.5% of the variations in sorption maxima were due to exchangeable Al in both soils, respectively. Added goat manure had a greater relative effect in reducing exchangeable Al than in increasing soil pH suggesting that the observed decreases in P sorption following goat manure application could to a large extent have been due to the inactivation of exchangeable Al. This is further supported by the fact that a greater reduction in P sorption following goat manure application occurred in Chevy Chase soil than in Flagstaff soil, consistent with the greater relative decrease in exchangeable Al following goat manure application to this soil. Other studies have reported similar effects after application of fresh or composted animal manure (Eghball, 1999; Whalen *et. al.*, 2000; Erich *et al.*, 2002).

The relative effects of goat manure in decreasing exchangeable Al and reducing P sorption of the experimental soils increased with rate of manure application. This suggests that repeated seasonal application of the goat manure or the application of higher rates of manure could result to an enhanced expression of the observed effects. Therefore regular application of goat manure or other manures with similar properties to smallholder farms in the Eastern Cape could result in improved soil and fertilizer P use efficiency by crops partly as a consequence of reduced P sorption. The results therefore indicate that use of goat manure may allow resource poor farmers to use lower levels of commercial P fertilizer because of the reduced P sorption by the soils.

Although P is considered to be relatively immobile in the soil system, there are mechanisms for P to leave the soil through loss in surface runoff, erosion of sediments and leaching through the soil profile (Zhang *et al.* 2005). Increased saturation of soil binding sites with P ions may reduce sorption and increase potential P leaching losses (Magdoff *et al.*, 1999; Sharpley *et al*., 2000; Zhang *et al.* 2005). Land application of animal manures often results in increased mobilization of P and leaching into ground water (Daniel et al., 1998). In these situations, the environmental fate of P must be assessed.

The effects of liming the two soils on the amount of P sorbed were very variable. Lime addition to Flagstaff soil increased the amount of P sorbed in the first 28 days of incubation but a reduction in P sorption was observed after 56 days of incubation. By contrast, reduction in P sorption following lime application was observed almost immediately on Chevy Chase soil. The initial increase in P retention following lime addition to Flagstaff soil followed by a decrease on day 56 indicated that the effectiveness of lime in reducing P retention is affected by the length of time it reacts with the soil.

The differing effects of liming on the P sorption of the two soils could be partly attributable to the fact that they had different initial levels of exchangeable Al. Flagstaff soil had higher concentration of exchangeable Al (76.27 mg Al kg^{-1}) than Chevy Chase soil (48.73 mg kg^{-1}) in the un-amended soils. Haynes and Swift, (1985) suggested that the initial increase in P sorption following liming could be a result of the formation of new adsorbing surfaces due to the precipitation of exchangeable Al as hydroxy-Al polymers as the pH is raised. The hydroxyl-Al polymers have highly-active adsorbing surfaces which can increase P adsorption considerably (Haynes and Swift, 1985). With the passage of time, however, crystallization of the amorphous hydroxyl-Al polymers takes place leading to increased negative charge on the lime induced surface with a consequential reduction of P retention (Haynes and Swift, 1985; Curtin and Syers, 2001). This could explain the observed reduction in P sorption on day 56 in the Flagstaff soil following the initial P sorption increase of the limed soil. This implies that, for the Flagstaff soil and other similar soils, lime may need to be applied before planting while for soils of the Chevy Chase type, lime could be applied at the time of planting. Synchronizing P addition to coincide with peak periods of maximum benefit of added amendments would be necessary for greater reduction in P sorption by the soils.

6.1.3 Effects of goat manure and phosphate addition on soil inorganic and microbial biomass P fractions and their relationship with P uptake and dry matter yield

Incorporation of P into the soil microbial biomass is reported to be another mechanism that increases the availability of P to plants and which forms a significant pool of plant nutrients (Harris *et al.,* 1997). This fraction is said to play a key role in P dynamics in soils by immobilizing inorganic P which is later mineralized (Rubaek and Sibbesen, 1993). During the process of biomass turnover, this P may be released slowly and taken up by the crop more efficiently (Brookes, 2001; Parham *et al.*, 2003). Two experiments reported in Chapters 4 and 5 investigated this aspect. The results showed that biomass P was significantly increased by each increment of goat manure up to 20 t ha^{-1} but manure had no effect on resin P, $NaHCO_3$–P_i, or NaOH–P_i fractions. Addition of inorganic P significantly increased the concentration of all P fractions and followed the order NaOH-P_i >> resin P > biomass P > $NaHCO_3$–P_i. With each increment of added P the largest increases in extractable P were observed in the resin P and NaOH–P_i fractions and only marginal increases in $NaHCO_3$-P_i.

The results further indicated that resin P most depleted to the greatest extent during the course of plant growth possibly because it is the most labile and plant available fraction but in later stages of plant growth biomass P played a greater role in supplying P to plants. The NaOH-P_i was the dominant P fraction and changed little in response to plant P removal from the soil. The increase of the NaOH–P_i fraction following inorganic P addition to the soil could be explained by the adsorption of P_i through ligand exchange with hydroxyl groups located on the surfaces of Fe and Al hydroxides (Buehler *et al.*, 2002). The resin P, $NaHCO_3$–P_i and NaOH-P_i fractions appeared to be in equilibrium. When resin P and $NaHCO_3$–P_i were high,

$NaOH$-P_i accumulated or remained stable despite plant P removal; when resin P and $NaHCO_3$–P_i were reduced by plant removal, $NaOH$-P_i decreased, and then further declines in resin P and $NaHCO_3$–P_i occurred. The $NaOH$-P_i appeared to act as a buffer for resin P and $NaHCO_3$–P_i in the soil. The increase in resin P fraction due to addition of inorganic fertilizer P is in agreement with the findings of Nziguheba *et al.,* (1998) and Ayaga *et al.*, (2006).

Inorganic P addition increased the biomass P fraction and the fraction was greatly enhanced with manure addition. This was in agreement with other reports (e.g. Iyamuremye *et al.,* 1996; Nziguheba *et al.,* 1998; Ayaga *et al.*, 2006) indicating increased biomass P following manure addition in the soil. The largest improvement in biomass P due to manure occurred at lower rates of added P indicating the potential of goat manure to enhance the efficient use of small inorganic P applications. This increase in biomass P following goat manure addition implies that it increased the proportion of added P immobilized in microbial cells that would be subsequently released into the soil solution and be available for plant uptake following biomass P turnover. Major increases in biomass P were observed on day 28 after incubation which coincidentally was the time when the highest reduction in P sorption following manure addition to the soil was recorded. This indicates high immobilization of P in the microbial biomass and hence a means of protecting it from fixation during this period (Chapter 4).

Dry matter yield and P uptake were highly and significantly ($p = 0.05$) correlated with the different soil P fractions. The correlations followed the order resin P ($r = 0.85$) > $NaOH$-P_i ($r = 0.85$) > $NaHCO_3$-P_i ($r = 0.84$) >> biomass P ($r = 0.56$) for dry matter yield. The statistically significant relationships between resin P with plant growth and P uptake confirms previous reports in the literature (Raven and Hossner, 1994; Myers *et al.,* 2005) that support the use of exchange resins as extractants to assess P availability in soils. The combination of biomass P, resin P and $NaHCO_3$-P_i explained 75.8% of the variation in dry matter yield. Biomass P alone explained 63% of the variations in dry matter yield indicating that changes in biomass P contributed substantially to the synergetic benefits realized from the co-application of goat manure with inorganic fertilizer P. Therefore the manipulation of this fraction through the application of goat manure with P fertilizers can be profitably exploited to enhance added P use efficiency in the Eastern Cape.

The observed positive relationship between dry matter yield and biomass P found in this study, was in agreement with other reports (e.g. Iyamuremye *et al.,* 1996; Belay *et al.,* 2002; Ayaga *et al.*, 2006). This further confirms its potential as a biological indicator of P bioavailability in soils. Increases in crop yield as a result of incorporating manure may be due not only to its biological properties but also due to its nutritional value and improvements in the soil physical properties (Sanchez and Salinas, 1981). Nevertheless, the synergetic benefits to maize growth realized with co-application of low rates of goat manure with inorganic P indicated that the benefits realized were largely due to the effect of the goat manure on microbial biomass P.

6.2 General Conclusions

1. The seven soils studied varied widely in their capacities to sorb P and would therefore react differently to applied P necessitating different approaches to P management in terms of placement and amounts applied.
2. Citrate dithionite bicarbonate extractable Al had greater influence on P retention than other Al forms in the soils examined and therefore could be used to indicate the degree of potential P sorption in these soils and others with similar properties.
3. The single point sorption test (SI) was highly correlated with external P requirement ($P_{0.2}$) suggesting that the SI functions could successfully be used to predict $P_{0.2}$ for the soils from Ntlonyana, Ncihane, Qweqwe, Qunu and Bethania, which are considered to be low P sorbers.
4. Addition of goat manure consistently reduced P sorption maxima in both soils. This implies that use of goat manure may allow resource poor farmers to use lower levels of commercial P fertilizer because of the reduced P sorption and P requirement by the soils.
5. Added goat manure had a greater relative effect in reducing exchangeable Al than in increasing soil pH suggesting that the observed decreases in P sorption following goat manure application could to a large extent have been due to the inactivation of exchangeable Al. Thus, the choice of manure rates should be aimed at reducing the amounts exchangeable Al in acid soils rather than raising the soil pH.

6. Large increases in biomass P due to manure application observed at lower rates of added P indicates the potential of goat manure to enhance the fertilizer use efficiency of small inorganic P applications. The turnover of the biomass P pool may provide a slow release of inorganic P that plants can use more efficiently than a single large pulse of P from organic or inorganic fertilizer, which may otherwise be fixed and removed from the available P pool before plants can use it efficiently.

The evidence presented above indicates that indeed there are important biochemical synergies from integrating goat manure with inorganic P fertilizer. Therefore, combining goat manure and inorganic Ps will be a cost-effective strategy for improving fertilizer use efficiency in P fixing soils of the Eastern Cape where goat manure is readily available.

6.3 Recommendations for future research

Significant findings have been made in this research. However, future studies should consider the following:

1. The trends of P sorption and requirements reported in this study are based on a limited number of soil forms and therefore there is need to carry out a broader sorption study involving more soils from different agroecologies in the province in order to obtain a more reliable picture of the P sorption status of soils in the Eastern Cape.
2. The fact that the biomass P peaked at day 28 in the present study suggests that in order to derive maximum benefit from the P protected in biomass P, planting may have to be synchronized such that the peak period for biomass P decline, whereby P may be released, coincides with the period of maximum P demand by the target crop. However, before this

can be implemented the peak period for biomass P and its subsequent mineralization will need to be established.

3. Organic P (P_o) was not determined in the present study. However, it is reported to account for 20 to 80% of the total P in most mineral soils and a significant source of plant P when organic materials decompose and the P_o mineralizes (Sharpley, 1985; Tarafdar, and Claasen, 1988). The contribution of P_o to P cycling following goat manure addition with inorganic P in these soils needs to be assessed. Also required are measurements of mineralization rate of soil P_o to determine the supplying potential of P_o to P nutrition to enable a more accurate fertilizer P recommendation.
4. Field studies need to be conducted to validate the laboratory and glasshouse studies reported in this thesis. This will have direct applicability to fertilizer P and goat manure uses to farmers.
5. Monitoring studies to determine when manure amended soils become P saturated and pose danger for P losses to surface waters though leaching need consideration. This would be useful in identifying soils with increased risk for P loss and provide information about the risk of leaching P in soils. This will also aid in developing sustainable agricultural systems that optimize the use of agricultural resources for increased yields and at the same time maintaining the quality of the environment.

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APPENDIX 1 MAP OF THE EASTERN CAPE SHOWING THE STUDY LOCATIONS (1- 4)

APPENDIX 2 DESCRIPTION OF STUDY SITES

Site	**Grid Ref**		**Altitude m (ASL)**	**Climate**	**Parent Material**					**Topography**			
	Latitude	**Longitude**			**No. Of kinds**	**Lithology of underlying material**	**Mode of accumulation**	**Degree of weathering**		***TMU**	**Slope**	**Kind**	**Aspect**
								Physical	**Chemical**				
Qunu	$31^{0}46^{1}27^{11}$ S	$28^{0}38^{1}16^{11}$ E	880	Sub-humid	One	Shale	Insitu weathering	Moderate	Advanced	TMU 3 Upper	4%	Straight	SW
Qweqwe	$31^{0}41^{1}42^{11}$ S	$28^{0}42^{1}09^{11}$ E	947	Sub-humid	One	Shale	Insitu weathering	Weak	Weak	TMU 3 Upper	10%	Straight	E
Bethania	$30^{0}39^{1}41^{11}$ S	$28^{0}16^{1}45^{11}$ E	1747	Sub-humid	Two	Sandstone/ Dolerite	Insitu weathering	Advanced	Advanced	TMU 3 Upper	12%	Concave	N
Chevy Chase	$30^{0}50^{1}54^{11}$ S	$28^{0}32^{1}12^{11}$ E	1514	Sub-humid	One	Sandstone	Insitu weathering	Advanced	advanced	TMU 3	6%	Convex	N
Ncihane	$32^{0}00^{1}04^{11}$ S	$28^{0}42^{1}33^{11}$ E	631	Sub-humid	One	Shale	Insitu weathering	Advanced	Advanced	TMU 1	2%	Convex	N
Ntlonyana	$32^{0}00^{1}02^{11}$ S	$28^{0}49^{1}17^{11}$ E	415	Sub-humid	One	Shale	Insitu weathering	Moderate	Moderate	TMU 3	8%	Straight	N
Flagstaff	-	-	-	Sub-humid	One	Dolerite	Insitu weathering	Advanced	Advanced	TMU 4	10%	Straight	N

*TMU = Topographical morphological unit

APPENDIX 3PROFILE DESCRIPTION FOR SOILS USED IN THE STUDY

Site	**Horizon**	**Depth**	**Colour**		**Texture**	**Structure**	**Consistence**		**Coarse fragments/ Roots**	**Diagnostic Horizon**	**Soil Form**
			Dry	**Moist**			**Dry**	**Moist**			
Qunu	A	0 - 50	10 YR 4/2	10 YR 3/2	Sandy clay	Weak, fine subangular blocky	Hard	Friable	Few coarse fragments Few coarse/fine roots	Orthic A	Westleigh (Acrisol)
	AB	50 - 76	5 YR 3/3	5 YR 3/3	Sandy clay	Weak, subangular blocky	Extremely hard	Friable	Few small coarse fragments Few fine roots	Soft plinthic	
	B	76 103	5 YR 3/3	5 YR 3/3	Sandy	Single grain	Hard	Loose	Abundant small coarse fragments	Soft plinthic	
	B	40 - 124	5 YR 4/6	5 YR 4/6	Sandy clay	Fine subangular blocky	Hard	Friable	Few small coarse fragments Few fine roots, no concretions	Red apedal B	
Qweqwe	A	0 - 53	10 YR 5/1	10 YR 3/2	Sandy clay loam	Weak subangular blocky	Very hard	Slightly firm	Few small coarse fragments Many fine roots	Orthic A	Glenrosa (Cambisol)
	B	53 - 84	10 YR 5/3	10 YR 3/2	Sandy clay loam	Weak subangular blocky	Very hard	Firm	Very many large coarse fragments Few fine roots	Lithocutanic B	
Bethania	A	0 - 25	5 YR 4/3	5 YR 3/3	Sandy	Moderate subangular block	Hard	Friable	Few small coarse fragments Many fine roots	Orthic A	Hutton (Ferralsol)
	B	25+	2.5 YR 3/6	2.5 YR 5/8	Loamy sand	Moderate fine subangular block	Hard	Slightly firm	Few small coarse fragments Many fine roots	Red apedal B	
Chevy Chase	A	0 - 50	10 YR 4/3	10 YR 4/3	Sandy	Very weak subangular block (fine)	Soft	Friable	Very few small coarse fragments Many fine roots No concretions	Orthic A	Hutton (Ferralsol)
	B	50+	5 YR 4/5	10 YR 4/3	Sandy	Very weak subangular block (fine)	Soft	Friable	Very few small coarse fragments Many fine roots No concretions	Red apedal B	

(………) Corresponding FAO (2006) soil units

APPENDIX 3 continued ………………

Site	Horizon	Depth	Colour		Texture	Structure	Consistence		Coarse fragments/ Roots	Diagnostic Horizon	Soil Form
			Dry	Moist			Dry	Moist			
Ncihane	A	0 - 48	10 YR 4/1	10 YR 3/1	Sandy clay	Massive	Hard	Friable	Very few fine coarse fragments Few fine roots	Orthic A	Cartref (Luvisol)
	E	48 - 60	10 YR 4/2	10 YR 3/2	Sandy	Single grain	Extremely hard	Slightly firm	Dominant coarse fragments, few roots	E	
	B	60 - 83	5 YR 4/6	5 YR 3/4	Sandy clay	Massive	Extremely hard	Firm	Few coarse fragments No roots	Lithocutanic B	
Ntlonyana	A 1	0 - 48	10 YR 3/1	10 YR 2/1	Sandy clay	Moderate subangular block	Hard	Friable	Few fine coarse fragments, many fine roots, few coarse roots	Orthic A	Klapmuts (Planosol)
	A 2	48 - 65	10 YR 3/2	10 YR 3/2	Sandy clay	Moderate angular block	Very hard	Friable	Few fine coarse fragments, many fine roots,	Orthic A	
	E	65 - 84	10 YR 3/1	10 YR 3/2	Loamy sand	Single grain	Extremely hard	Firm	Many fine coarse fragments, few fine roots	E	
	B	84 - 116	5 YR 3/2	5 YR 4/6	Clay	Moderate medium subangular block	Extremely hard	Friable	Few fine coarse fragments, No roots	Pedocutanic B	
Flagstaff	A	0 - 64	5 YR 3/4	5 YR 3/2	Sandy clay loam	Moderate fine subangular block	Hard	Friable	Few fine coarse fragments, many fine roots, few coarse roots	Humic A	Inanda Hutton (Ferralsol)
	B	+64	5 YR 5/3	5 YR 4/3	Sandy clay loam	Very weak subangular block (fine)	Hard	Friable	Few small coarse fragments Many fine roots	Red apedal B	

(………) Corresponding FAO (2006) soil units