USE OF MINJINGU PHOSPHATE ROCK COMBINED WITH DIFFERENT ORGANIC INPUTS IN IMPROVING PHOSPHORUS AVAILABILITY AND MAIZE YIELDS ON A CHROMIC ACRISOL IN MOROGORO, TANZANIA

BY

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ABSTRACT

Phosphorous deficiency in highly weathered soils is one of the causes of low crop yields in Tanzania. Use of Minjingu phosphate rock (MPR) in combination with organic inputs is considered to be a possible option for increasing P availability and crop yields. However, detailed characterization of organic inputs, the effects of organic inputs when used alone or combined with MPR on soil characteristics and, consequently, maize yields, are limited. The objectives of this study were to characterize farmyard manure (FMY), tithonia, lantana and gliricidia and to evaluate the influence of MPR combined with these organic inputs on soil properties, P availability and maize yields from a Chromic Acrisol. The study consisted of incubation, pot and field experiments. Characterization of organic materials showed that manure and tithonia had more P than the critical value for net P mineralization. Tithonia contained the highest amounts of light molecular weight organic acids (LMWOA), oxalic acid being the most dominant. An incubation experiment showed that all organic materials depressed MPR dissolution, and the depressing effect increased with increase in pH, Ca and P content of the materials. Incubation and pot experiments showed that organic materials at 2.27 g kg^{-1} (5 t ha^{-1}) increased soil pH, exchangeable Ca and decreased exchangeable Al. All organic materials increased labile P pools and reduced P adsorption maximum and P affinity in the incubation and field experiments. This resulted in increase in available P and consequently, in maize dry matter yields (DMY). Under field conditions tithonia increased soil pH, exchangeable Ca and oxalic acid concentration, and decreased exchangeable Al. Tithonia decreased P sorption and increased total labile P, consequently increasing maize yields. The decrease in P adsorption increased with tithonia rates, with the rate of 7.5 t ha^{-1} resulting in the largest agronomic optimum. MPR was superior to TSP (80 kg P ha^{-1}) in increasing pH, Ca, oxalic acid and in reducing exchangeable Al. Both sole MPR and sole TSP reduced P adsorption but the influence of MPR was greater than that of TSP. Tithonia at 7.5 t ha^{-1} had similar P adsorption maximum to sole MPR at 80 kg P ha^{-1}. Combining MPR at 40 kg P ha^{-1} with tithonia at 7.5 t ha^{-1} had adsorption maximum similar to that of sole tithonia at 7.5 t ha^{-1} or MPR at 80 kg P ha^{-1}. Both MPR and TSP increased Ca and P uptake and maize yields in pot and field experiments. MPR was superior to TSP in supplying Ca, oxalic acid and in increasing pH in all seasons. Combining MPR with tithonia had a higher RAE in two out of the three seasons than that under sole tithonia or MPR. Organic materials alone or combined with MPR improved soil pH, Ca and decreased exchangeable Al, consequently increasing P availability and maize yields. Combining MPR with organic materials resulted in increase in P availability by reducing P adsorption rather than by enhancing MPR dissolution. Co-application of MPR with tithonia on Chromic Acrisol is recommended. Evaluation of the influence of tithonia on some chemical, physical and biological soil properties under various climatic conditions and for longer periods of time is essential so as to be able to better exploit this resource.

DECLARATION

I, Susan Tinkishaba Ikerra, do hereby declare to the Senate of Sokoine University of Agriculture that this thesis is my own original work and that it has not been submitted for a degree award in any other University.

Signature--Date 27.10.2004------------------

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DEDICATION

This thesis is dedicated to my parents: My father the late Omwami Concordio John Mahela and my mother Mrs. Ernestina Kabwongelela Mahela.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	Percentage
<	Less than
>	Greater than
°C	Degree Celcius
ADP	Adenosine diphospahte
AEZ	Agroecological zone
ATP	Adenosine triphospahte
AAS	Atomic absorption spectrometer
ARI	Agricultural Research Institute
Al	Aluminium
Al^{3+}	Aluminium ion
C	Carbon
Ca	Calcium
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
COO^-	Carboxylic ion
CEC	Cation exchange capacity
CL	Clay loam
Cm	Centimetre
Cmol(+)kg	Centimole per kilogram
Cu	Copper
Cr^{3+}	Chromium ion

CRD	Completely randomised design
CV	Coefficient of variation
DMRT	Duncan's Multiple Range Test
DMY	Dry matter yield
DMB	Dry matter basis
DNA	Deoxyribonucleic acid
e.g.	Example
et al.	and others
FYM	Farmyard manure
Fe	Iron
Fe^{3+}	Ferric ion
FeO	Iron oxide
FC	Field capacity
g	Gram
g kg^{-1}	Gram per kilogram
g pot^{-1}	Gram per pot
GM	Green manure
H^+	Hydrogen ion (proton) concentration
H_2O	Water
$H_2PO_4^-$	Orthophosphate
H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate ion

ICRAF	International Centre for Research in Agroforestry
ISRIC	International Soil Reference and Information Centre
K	Potassium
K_2O	Potasium oxide
KCl	Potassium chloride
kg	Kilogram
kg P ha^{-1}	Kilogram of phosphorus per hectare
log K_{Al}	Aluminium (complexation) stability constant
M	Molarity
masl	Metres above sea level
Mg	Magnesium
mg	Milligram
mg P kg^{-1}	Milligram of phosphorus per kilogram
ml	Millilitre
Mn	Manganese
mm	Millimetre
millimol kg^{-1}	Millimole per kilogram
M L^{-1}	Moles per litre
MPR	Minjingu phoshate rock
N	Nitrogen
Na	Sodium
NaOH	Sodium hydroxide
NO_3^-	Nitrate ion
NH_4^+	Ammonium ion

ns	Not significant
nd	Not detected
nm	Nanometer
OC	Organic carbon
OH^-	Hydroxyl ion
P	Phosphorus
pH	Negative logarithm of hydrogen ion concentration
Po	Organic phosphorus
Pi	Inorganic phosphorus
PO_4^-	Phosphate ion
P_2O_5	Phosphorus pentoxide
PSI	Phosphorus sorption index
PR	Phosphate rock
PRs	Phosphate rocks
RAE	Relative agronomic effectiveness
RCBD	Randomized complete block design
rpm	Revolutions per minute
RF	Rockefeller Foundation
RNA	Ribonucleic acid
S	Sulphur
SA	Sulphate of ammonia
SSA	Sub-Saharan Africa
SSP	Single super phosphate
SPR	Standard phosphorus requirement

SUA	Sokoine University of Agriculture
TSBF	Tropical Soil Biology and Fertility
TSP	Triple super phosphate
Wt	Weight
Zn	Zinc

CHAPTER ONE

1.0 INTRODUCTION

In Tanzania, continual cropping without concurrent use of manure and or /inorganic fertilizers has reduced soil fertility, leading to low crop yields. Smaling *et al.* (1993) reported negative balances of -27, -4 and -18 kg ha^{-1}, for N, P and K respectively, and this was attributed to nutrients uptake by crops, and other losses like erosion and run-off. Consequently, current maize yields ranging between 0.5 to 1.5 t ha^{-1} have been recorded, compared to 5 t ha^{-1} attainable with adequate nutrient supply (Ikerra and Kalumuna, 1991; Ndaki, 2001). Whereas nutrient replenishment through application of mineral or organic amendments is possible, small-scale farmers are constrained by several socio-economic factors. The use of inorganic fertilizers by resource-poor farmers is limited by the high prices, frequent unavailability, and low benefit cost ratios (Palm *et al.*, 1997, 2001) of the amendments.

Organic inputs, which are seen as possible alternatives, are often low in both N and P. As reported by Palm *et al.* (2001), application of 5 t dry matter ha^{-1} of the most commonly available organic materials can presumably meet the N requirement of the 2 t ha^{-1} maize yield level, but cannot meet the P requirements. Consequently, low nutrient contents of organic resources necessitates application of large quantities, inevitably demanding high labour inputs for preparation, transportation and application.

In addition to the nutrient depletion problem, another major problem is the conversion of plant nutrients, in particular P found or added to soils, into forms not available to plants. A large proportion of agricultural soils in Tanzania include Ferralsols, Acrisols and Luvisols, which cover about 52% of the Tanzanian total land area (Hathout, 1983; de Pauw, 1984). These soils have medium to high P-fixation capacities (Assenga and Mrema, 1991; Mwakisimba, 1999). Thus, phosphorous deficiency arising from P fixation is one of the causes of decline in crop production in these soils (Ikerra and Kalumuna, 1991; Mnkeni *et al.*, 1994; Ikerra *et al.*, 1994). Although retention characteristics of the P fixing soils of Tanzania have been described (Assenga and Mrema, 1991; Ikerra and Kalumuna, 1991; Assenga, 1993; Mwakisimba, 1999), the strategies that help to reduce P fixation have been poorly investigated and highly segmented.

Application of large quantities of P fertilizers to boost stocks and quench P sorption sites is one of the management strategies proposed to reduce P fixation (Buresh *et al.*, 1997; Sanchez and Jama, 2002), but the large investment required is prohibitive, especially in small-scale farming systems. Research in western Kenya has shown that application of green manures from agro-forestry tree prunings can reduce soil P sorption and increase P availability (Nziguheba *et al.*, 2000). However, changes in the soil properties that induce the P release were not determined. The effect of organic amendments on P adsorption depends on a number of factors like their quality and quantity, soil types and the agro-ecological conditions (Singh and Jones, 1976; Iyamuremye *et al.*, 1996a; Nziguheba *et al.*, 2000).

In Tanzania, little is known about the characteristics of the most common organic materials, the effects on P sorption and P availability or changes in soil properties culminating from their use (Babili, 1999). Further, characterization of organic acids in terms of types and concentrations generated by various organic materials, and their effect on P sorption in the soil, is lacking in Eastern Africa (Nziguheba, 2001).

As pointed out by Palm *et al.* (1997), water-soluble P fertilizers are expensive to resource poor farmers. However, several phosphate rock deposits like Minjingu and Panda phosphate rocks are available in Tanzania (Van Kauwenbergh, 1991; Van Straaten, 1997, 2000), which could be used as a source of P for plants, at lower costs than water-soluble P fertilizers especially in areas near the deposits. However, most of these phosphate rocks are of igneous origin, with low reactivity and therefore unsuitable for direct application (Buresh *et al.*, 1997; Smithson *et al.*, 2001). On the other hand, the soft Minjingu phosphate rock (MPR) has medium to high reactivity and may be suitable for direct application (Smithson *et al.*, 2001; Szilas, 2002).

The effectiveness of phosphate rocks has been shown to increase when applied in combination with organic materials such as farmyard manure or compost (Ikerra *et al.*, 1994; Mahimairaja *et al.*, 1995). Invariably, the composition of different organic materials, hence their effects on the release of P from phosphate rocks (PRs), vary depending on location due to different growth conditions and method of preparation. Thus, these organic materials need to be evaluated on a location-by location basis and unfortunately little has been done in Tanzania on this issue.

Information on application rates, combinations, and the effect on nutrient availability, especially when organic materials are combined with inorganic fertilizers, is scanty (Ikerra *et al.*, 1994; Mowo, 2000).

Although organic inputs alone may not solve the soil nutrient deficiency problems and sustain high crop yields, they remain a viable option for soil fertility improvement because they improve the physical and chemical properties of soils (Ikerra *et al.*, 1999, 2001). Proper mixing of organic materials with MPR may increase soil labile organic and inorganic P through their depressing influence on P fixation (Singh and Jones, 1976; Nziguheba *et al.*, 2000) and their effect on MPR dissolution (Ikerra *et al.*, 1994). Improvement of P availability from MPR could help to alleviate soil P problems in some soils at a much lower cost than using the more expensive soluble P sources such as TSP. The major drawback of MPR is the low solubility in soils of high pH, high Ca and low P buffering capacity (Semoka *et al.*, 1992; Mnkeni *et al.*, 1994; Mowo, 2000; Szilas, 2002). Integrated use of organic materials and MPR could improve availability of P from MPR.

Limited studies in Tanzania revealed that the agronomic effectiveness of MPR increased during the first year of application when combined with high quality farmyard manure (FYM) but not with low quality compost (Ikerra *et al.*, 1994). Farmyard manure, however, is not abundantly available, implying that other available organic materials (e.g. green manures from agro-forestry tree prunings, non-leguminous local shrubs, or leguminous cover crop manures) could be evaluated since they are more available in smallholder farms than FYM.

Information pertaining to the effects of these green manures when combined with MPR on P release and availability to plants in Tanzania is scanty, site specific, and is lacking for Morogoro. The effect of these materials when co-applied with MPR on P availability to plants depends on their composition, decomposition rates, capacity to acidify the immediate environment, their ability to reduce P fixation, and soil type (Zaharah and Bah, 1997; Savini, 2000; Babili 1999; Waigwa *et al.*, 2003).

In the light of the knowledge gaps highlighted above, the general objective of this study, therefore, was to evaluate the effects of combining MPR with different types of green manure (GM) and farmyard manure (FMY) on the release of P from MPR and response of maize to the released P and the organic materials.

The specific objectives were:

(i) To characterize *Gliricidia sepium*, *Lantana camara*, *Tithonia diversifolia* and farmyard manure in order to establish their nutrient contents, types and quantities of light molecular weight organic acids (LMWOA) contained in the organic materials, and their potential for use with MPR as sources of P for plants.

(ii) To determine the contribution of the above named organic materials on soil chemical properties that affect P availability.

(iii) To assess the effect of the organic amendments in reducing P sorption and their influence on different P pools.

(iv) To evaluate the effects of combining MPR with different types and proportions of the organic materials on available P, P fractions and maize grain yields.

(v) To determine the optimal quantities and quality of the organic materials which, when combined with MPR, will give the highest P release, P availability to plants and finally increase the agronomic effectiveness of MPR.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Role of phosphorus in plant nutrition

Phosphorus is one of the essential macronutrients in plant nutrition and occurs in most plants in concentrations between 0.1 and 0.4%, as simple and complex organic compounds. Its major physiological and metabolic roles in the plant include energy storage and transfer in the form of adenosine di- and tri-phosphate (ADP and ATP) as a constituent of coenzymes, nucleotides, nucleic acids (RNA and DNA), phosphoproteins, phospholipids and sugar phosphates (Tisdale *et al.,* 1993).

The form in which P is available to plants is dependent on soil pH (Bohn *et al.*, 1979). Plants absorb P in the form of the primary or secondary orthophosphates ($H_2PO_4^-$ and HPO_4^{2-}) depending on soil pH. At pH <7.2, the primary orthophosphates ($H_2PO_4^-$) are the most dominant in many agricultural soils while the secondary orthophosphate (HPO_4^{2-}) are dominant in soils with pH above 7.2. Phosphate availability to most plants tends to decrease both at high and low soil pH values, consequent to its transformation into forms with low solubilities. Phosphorus availability to most crops is optimal at the pH range of 6.0 to 6.5.

At high pH (>7.5) P in the soil solution is converted into insoluble calcium phosphate compounds while at low pH (<5.5) phosphorus reacts with Al^{3+} and Fe^{3+} to form insoluble Al and Fe-phosphate compounds (Bohn *et al.*, 1979). Total P concentration in soil solutions is rarely greater than 0.03 mg L^{-1} (Sanchez, 1976). For optimum growth, most crops require solution P concentrations higher than 0.03 mg PL^{-1}. Therefore, P is often considered as one of the most limiting nutrients for plant growth in soils (Lopez-Pineiro and Garcia-Navarro, 2001) particularly in highly weathered soils like Feralsols, Luvisols and Acrisols where P availability is further constrained by fixation.

2.2 Soil phosphorus

Total P content in soils ranges from 200 to 5000 mg P kg^{-1} soil, with an average of 600 mg P kg^{-1} soil, while the total P in surface soil ranges from 500 to 1000 mg P kg^{-1} soil (Lindsay, 1979; Tisdale *et al.*, 1993). Phosphorus exists in soils both as organic and inorganic compounds, and each form constitutes about 50% of the total P. Physicochemical and biological reactions in soils act in concert to regulate the solubility of phosphate compounds in soils (Buresh *et al.*, 1997).

Depending on the variation in reactivity and availability for plant uptake, P has been partitioned into different pools (fractions) (Hedley *et al.*, 1982; Tissen and Moir, 1993), namely soil solution P, labile P and non-labile P. Labile P is defined as the P reserve that can replenish soil solution ortho-phosphates ($H_2PO_4^-$ and HPO_4^{2-}) in response to P uptake by plant roots (Beck and Sanchez, 1994). Labile inorganic P (Pi) is therefore the P loosely sorbed and in rapid equilibrium with the soil solution inorganic P. Strongly sorbed inorganic P is only slowly released and made available to plants and is referred to as non-labile P. Soil solution P is readily available for plant uptake. The soil solution P is in equilibrium with the labile and non-labile P pools in soils (Buresh *et al.*, 1997; Van der Eijk, 1997) and consequently this equilibrium controls the ability of soil to supply P to plants. The overall ability of a particular soil to supply P to plants depends on (i) the concentration of inorganic P in soil solution, (ii) the ability of the soil to maintain the solution P concentration, and (iii) the quantity of solid-phase inorganic and organic P that replenishes P in solution.

2.2.1 Inorganic phosphorus

Soil inorganic P is the main source for plant available P in fertilized systems of highly weathered soils like Acrisols (Beck and Sanchez, 1994; Guo *et al.*, 2000). Generally, inorganic P concentrations in the soil solution are controlled by soil microorganisms' activities (Steeling and Zasoski, 1993) and soil physico chemical processes (Buehler *et al.*, 2002). Soluble inorganic P originates from dissolution of primary P minerals, mainly apatite ($Ca_2Ca_3(PO_4)_3(OH.F.CO_3)$. Once in the soil solution, the inorganic phosphorus species, namely $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}, can be (i) taken up by plants; (ii) taken up by soil biota and converted to organic P; (iii) sorbed by soil minerals like hydrous oxides of Fe and Al (P sorption); and (iv) precipitated on surfaces of $CaCO_3$ and on surfaces of layer silicate clay mineral particles (Bohn *et al.*, 1979; Beck and Sanchez, 1994; Buresh *et al.*, 1997).

Inorganic P also occurs in numerous combinations with aluminium as variscite ($AlPO_4.2H_2O$), with iron as strengite ($FePO_4.2HO_2$), with Ca as calcium phosphate ($CaHPO_4.2H_2O$) among other elements (Bohn *et al.*, 1979). Addition of fertilizers and manures results in increase in solution P concentration (Iyamuremye and Dick 1996; Buresh *et al.*, 1997; Nziguheba *et al.*, 2000; Oberson *et al.*, 2001) but a proportion of soil solution P may be rendered unavailable to plants due to P fixation by amorphous and crystalline Al and Fe (oxy) hydroxides and clay minerals, stable organic compounds like fulvic and humic acids, metal and organic P complexes and microbial immobilization. Therefore, management practices which reduce P fixation and increase P desorption are highly desired for P fixing soils.

2.2.2 Organic phosphorus

Organic P (Po) is present in soils in the form of phytin and phytin derivatives, nucleic acids and phospholipids. The levels of organic P in soils vary, ranging from 30-85% of the total P of which only a small fraction of it is labile in the short term (Tiessen *et al.*, 1984; Buresh *et al.*, 1997; Buehler *et al.*, 2002). Most of the soil Po occurs in stabilized soil organic matter fractions like fulvic and humic acids that are not rapidly mineralizable. Microorganisms play a key role in organic P transformations (Magid *et al.*, 1996; Frossard *et al.*, 2000), through excretion of phosphatase enzymes that degrade organic matter (Sinsabaugh *et al.*, 1993), mineralization of P from organic sources (Gressel *et al.*, 1996; Mengel, 1997) and solubilization of sparingly soluble inorganic P compounds (Illmer *et al.*, 1995). Use of available P by plants and soil biota is the driving force for the conversion of inorganic P to organic compounds and subsequent mineralization of organic P (Tiessen *et al.*, 1984, Buresh *et al.*, 1997).

In unfertilised highly weathered soils there is low organic matter content and most of the P is sorbed by hydrous oxides of Fe and Al. Mineralization of organic P pools in these soils has been identified as the main source of plant available P. For instance Tiessen *et al.* (1984) reported that 80% of the variability in labile P in an Acrisol was accounted for by variation in bicarbonate organic P. Similar results have been reported by others (Schimidt *et al.*, 1996; Guo *et al.*, 2000; Oberson *et al.*, 2001; Buehler *et al.*, 2002). Guo *et al.* (2000), working with Vertisols, Gleysols, Acrisols and Ferralsols under intensive plant growth without fertilization, observed that organic P pools were not significant contributors to labile P and that inorganic P pools were the main buffering pools. Changes in organic P in soil can occur due to inorganic P fertilization (Buresh *et al.*, 1997) or application of organic amendments (Iyamuremye *et al.*, 1996b; Zhang and MacKenzie, 1997; Nziguheba, 2001).

The amounts of P in the inorganic or organic fractions and the fluxes of P between these pools are controlled by several factors such as: physico-chemical reactions (adsorption-desorption), biological reactions (immobilization–mineralization), which are influenced by land use systems and climatic conditions (Zhang and MacKenzie, 1997; Maroko *et al.*, 1999; Buehler *et al.*, 2002). Organic P fractions in highly weathered soils contribute significantly to the P nutrition of plants (Sattell and Morris, 1992) because these soils have low levels of inorganic P due to P sorption. Increase in organic P fractions in these soils is desirable because P in organic forms may be better protected from fixation than P present in inorganic forms (Linquist *et al.*, 1997; Mengel, 1997).

Sources of organic phosphorus in soils include plant residues, green manures, microbial biomass and farmyard manure (Oberson *et al.*, 1993; Palm *et al.*, 1997; Phiri *et al.*, 2001). The effect of manures on organic and inorganic P depends on soil type, quality and quantity of the applied organic materials.

Iyamuremye *et al.*(1996b) observed that addition of manure and alfalfa (*Medicago sativa*) to acid, low P soils resulted in decrease in P adsorption and increase in inorganic and organic P fractions, but the effects varied with soil type and quality and quantity of the organic materials applied. Similarly, Nziguheba *et al.* (1998) reported that addition of tithonia, a high quality green manure, to an Acrisol in western Kenya increased both inorganic and organic P. Maize stover, a low quality organic material, had no significant effect on P pools.

2.2.3 Determination of different P fractions in soils

Several soil P tests have been developed for the determination of available P (Buresh *et al.*, 1997; Pierzynski, 2000). While these conventional methods have been in use as indices of plant P availability, they have limitations because both organic and less available P pools are not detected (Yli-Halla, 1991; Sharpley, 2000). Consequently, this has led to underestimation of the contribution of various inputs to available P. Information about all soil P fractions is useful in predicting the bio-availability of P in soil and in monitoring the fate of P after fertilization with different inorganic or organic fertilizers, or other amendments (Nziguheba *et al.*, 2000).

Conventional P tests were developed for use with water-soluble P fertilizers and have proved ineffective in soils fertilized with sparingly water soluble P fertilizers such as PRs as they do not reflect the residual contribution of RP to inorganic P (Mutuo *et al.*, 1999). To overcome this limitation a method developed by Chang and Jackson (1958) and modified by Hedley *et al.* (1982) and Tiessen and Moir (1993) for sequential determination of different soil P fractions was proposed. The main principle underlying the sequential fractionation procedures is that readily available soil P is removed first with mild extractants while the less available P is extracted with strong acids or alkalis.

In the sequential fractionation procedure the different fractions are interpreted as follows: Resin-Pi that represents inorganic P (Pi) either from the soil solution or weakly adsorbed on hydroxides or carbonates (Mattingly, 1975). Sodium bicarbonate 0.5 M at pH 8.5. P (Bic-Pi) also extracts weakly adsorbed Pi (Hedley *et al.*, 1982) and easily hydrolysable organic P compounds like ribonucleic acids and glycerolphosphate (Bowman and Cole, 1978). Both resin Pi and Bic-Pi and Po fractions are considered as biologically available P or labile P (Fixen and Grove, 1990).

Sodium hydroxide (0.5 M, at pH 8.5) extractable Pi and Po is less available to plants and is thought to be associated with amorphous and crystalline Al and Fe hydroxides and clay minerals (Parfitt, 1978) via chemisorption (Williams *et al.*, 1980). It also extracts Po associated with stable organic compounds (fulvic and humic acids) (Bowman and Cole, 1978). Dilute hydrochloric acid (1M HCl) extracts Pi associated with apatite or octacalcium P (Frossard *et al.*, 1995). Hydrochloric acid Pi represents P from calcium phosphates which comprise a significant portion of P in young soils or soils amended with phosphate rocks (Tiessen and Moir, 1993). Although this P pool does not supply plant P in the short-term it can be an important reserve for inorganic P in the long time, resulting in high residual P fertilizer responses. The P extracted by the hot concentrated HCl is not readily available to plants but this P is gradually converted to soil solution P through microbial mineralization. Hence, these P pools are important P sources in the long run. The P which is not extracted by the various extractants explained above contributes to the residual P pools in soils and represents the more recalcitrant P forms.

The magnitude and composition of the different P fractions in soils are influenced by the composition and reactivity of inorganic and organic amendments applied to soil and the land use system (Linquist *et al.*, 1997a; Oberson *et al.*, 2001; Buehler *et al.*, 2002). For instance Buresh *et al.* (1997) in western Kenya reported that application of 250 kg P ha^{-1} as TSP increased the $NaHCO_3$ and NaOH-Pi by 113 mg P kg^{-1} soil at 2 weeks since application to an acid soil with 29%, clay but had no effect on NaOH-Po. The $NaHCO_3$ and NaOH-Pi remained relatively unchanged (106 mg P kg^{-1}) 10 months after application. The recovery of the added P at 10 months was 11 and 59% for the $NaHCO_3$ Pi and NaOH-Pi, respectively. Nziguheba *et al.* (2000) working with an Acrisol observed that seasonal additions of 150 kg P ha^{-1} increased all soil P fractions, but $NaHCO_3$-P was the most affected by changes in management.

When inorganic soluble P fertilizers are applied to soils they undergo dissolution and subsequently become transformed to different P fractions; but the principal sink for applied P is the moderately labile NaOH-Pi pool (Oberson *et al.*, 2001). Working with a Hawaiian Ultisol that contained 60% clay, Linquist *et al.* (1997a) observed that 52-58% of the P applied to the soil as TSP was transformed to the moderately labile NaOH-Pi pool; while 7-10% and 33-41% of the P was in the labile P pool and recalcitrant pools (HCl and H_2SO_4-Pi), respectively, after one year since application.

Buehler *et al.* (2002), working with a Colombian Ferralsol in a 10 year experiment with contrasting land use management systems, reported that resin-Pi, $NaHCO_3$-Pi, and NaOH-Pi represented most of the exchangeable Pi. Organic and recalcitrant inorganic fractions contained almost no exchangeable P. In contrast, for soils with low or no P fertilization, more than 14% of the labelled P was recovered in the NaOH-Po fraction, and HCl-Po showing that organic P dynamics are important when soil Pi reserves are low.

Application of organic soil amendments has been shown to increase labile and moderately labile P fractions in soils but this depends on the quality of the materials and soil type (Iyamuremye *et al.*, 1996b; Nziguheba *et al.*, 2001). Iyamuremye *et al.* (1996b), observed that manure and alfalfa residues increased resin Pi, $NaHCO_3$-Pi and Po and NaOH-Pi in soils of different mineralogies, but wheat straw residues had relatively little effect on P fractions, and this was attributed to wheat's low P content. While the effect of water-soluble P fertilizers on P fractions has received attention (Beck and Sanchez, 1996; Linquist *et al.*, 1997a; Nziguheba *et al*, 2000; Oberson *et al.*, 2001; Daroub *et al.*, 2001; Buehler *et al.*, 2002), little work has been done on other sparingly P sources like phosphate rocks (Mutuo *et al.*, 1999).

2.3 Phosphorus fixation in soils

The amount of plant available P present in the soil solution is controlled by the sorption - desorption processes. Thus, a thorough understanding of these processes is important when attempting to solve P deficiency problems in tropical soils.

2.3.1 Phosphorus fixation defined

Phosphorus fixation is the transformation of the easily–soluble phosphates into insoluble P forms such that their absorption by plants is hindered or completely blocked (Bohn *et al.*, 1979; Van der Eijk, 1997). In soil chemistry, P fixation is interpreted as a process by which P present in solution form is almost irreversibly adsorbed by, or precipitated on, solid soil constituents (Sanchez and Uehara, 1980). Part of the precipitated and adsorbed P, dissolves and desorbs, respectively, when the soil solution P is depleted, by solution that is free of P, or differs in ionic composition. This solution P is readily available to plants and is designated by terms such as extractable P, exchangeable P, reversible P, labile P, or available P. The soil P that dissolves or desorbes at a very slow rate is not readily available to plants and is normally referred to as strongly sorbed P, non-extractable P, non exchangeable P, irreversible P, non-labile P, unavailable P, occluded P, or fixed P (Van der Eijk, 1997).

2.3.2 Phosphorus fixation mechanisms

Various mechanisms have been put forward to explain P fixation by soils, and different soil constituents have been shown to retain P through different mechanisms. Major soil constituents involved in P fixation are hydrous oxides of Fe and Al, silicate clays, organic and inorganic anions, trivalent cations ($Al^{3+}$and Fe^{3+}) and calcium Ca^{2+} and calcium carbonate concretions ($CaCO_3$). Since all soils contain these materials in different proportions depending on soil pH and parent material, P fixation is probably the sum of the contribution of the different mechanisms of P adsorption by the various soil constituents. Phosphorus fixation involves both adsorption and precipitation reactions although adsorption seem more important over the short period (Mehadi and Taylor, 1988). Soil P concentration controls the type of reaction involved in P fixation. Lin *et al.* (1983), found that adsorption prevails at low P concentrations and precipitation at higher concentration. The mechanisms of P fixation can be grouped into (i) precipitation-crystallization reactions; (ii) dissolution and (iii) exchange reactions.

2.3.2.1 Precipitation-crystallization reactions

Precipitation-crystallization reactions occur at low and high soil pH (Sanchez and Uehara, 1980). In soils with low pH, the solubility of both Al and Fe compounds is high and they exist as Al^{3+} and Fe^{3+} in the solution. They react with P to form Al and Fe phosphates (Gerke and Hermann, 1992). The hydrolysis and precipitation reactions involved could be represented by the following reactions:

$$Al^{3+} + 2H_2O \Leftrightarrow Al(OH)_2^{+} + 2H^{+} \text{ (hydrolysis)------------------------(i)}$$

$$Al(OH)_2^{+} + H_2PO_4^{-} \Leftrightarrow Al(OH)_2H_2PO_4 \text{ (precipitation)--------------(ii)}$$

Overall reaction:

$$Al^{3+} + 2H_2O + H_2PO_4^{-} \Leftrightarrow Al(OH)_2H_2PO_4 + 2H^{+}\text{---------------------(iii)}$$

In accordance with the law of mass action, the precipitation of P as Al phosphate (or Fe phosphate) induces further hydrolysis of Al^{3+} (or Fe^{3+}) into soil solution until the ionic activity product of $Al^{3+}(H_2PO_4)^{2-}$ attains the solubility product constant of Al-phosphate (Hsu and Rennie, 1965). The final product, $Al_6(OH)_{12}(H_2PO_4)_6$, is unstable and with time it transforms to more stable forms through further crystallization, for example through the formation of variscite ($AlPO_4.2H_2O$) (Sanyal and De Datta, 1991). Similar reactions take place between Fe and phosphate, eventually causing a decrease of labile P.

Increase in soil pH reduces the activities of $Al^{3+}$and Fe^{3+} in solution and results in a decrease in P retention via reactions with these ions (Sanchez and Uehara, 1980). However, Gerke and Hermann (1992) observed higher P adsorption on humic-Fe surfaces at the pH range of 5.2 and 6.2, which was attributed to increased accessibility of the adsorption sites on the humic compunds. At higher pH there is deprotonation of humate carboxlic groups, which may promote the adsorption of Fe hydroxides.

In calcareous soils with high P concentration, Ca^{2+} activity in the liquid phase is responsible for the formation of insoluble Ca-P compounds (Tunesi *et al.*, 1999). Under such conditions P is precipitated as dicalcium phosphate ($CaHPO_4.2H_2O$), or as compounds of similar properties, by $CaCO_3$. The formation of $CaHPO_4.2H_2O$ can be represented by the following reactions:

$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}$-----------(dissociation/ionisation)-------------------(iv)

$H_3PO_4 \Leftrightarrow HPO_4^{2-} + 2H^+$ (dissociation-ionization)-------------------------------(v)

$Ca^{2+} + HPO_4^{2-} + 2H_2O \Leftrightarrow CaHPO_4.2H_2O$ (precipitation)---------------------(vi)

Overall reaction is:

$CaCO_3 + H_3PO_4 + 2H_2O \Leftrightarrow CaHPO_4.2H_2O + CO_3^{2-} + 2H^+$

In neutral and alkaline soils, P has been reported to be precipitated by divalent cations in the soil solution, the precipitation being controlled by the activities of phosphate ion species and cations in the soil solution, and the solubility of the basic P compounds so formed (Parfitt, 1978).

2.3.2.2 Exchange reactions

When water-soluble P fertilizers are added to acidic soils, much of the P is rendered insoluble within a few hours (Mozaffari and Sims, 1994). This happens through P retention reactions that take place through specific ligand exchange reactions between P and protonated groups on oxy-hydroxides of Fe and Al, which form very stable and insoluble precipitates (Sanyal and De Datta, 1991; Mengel, 1997). The process is normally enhanced by presence of di- or trivalent cations, low pH and high ionic strength of the soil solution. This mechanism is referred to as specific ligand exchange or chemisorption (Mengel, 1997) or metal-bridge bonding or chemo precipitation (Gerke and Hermann, 1992), and is considered the most important mechanism responsible for P fixation in tropical soils because hydrous oxides of Fe and Al are dominant in these soils.

Similarly, anion exchange reactions can take place between phosphate and silicate clays, aquo and hydroxyl groups from silicate clays, and amorphous alumino-silicates, all leading to reversible P retention (Bohn *et al.*, 1979). The reaction takes place on both the edge and planar surfaces of clay minerals and hydrous oxide crystals of Al and Fe. At low equilibrium P concentrations, non-specific anion retention can take place due to anion exchange between P and anions like chloride, nitrate, bicarbonates, silicates, sulphates, selenites, arsenates, or organic matter functional groups (Rajan and Watkinson, 1976). Anion exchange reactions that take place between phosphate and organic anions have long received special attention because of the role they play in reducing P sorption and consequently improving P availability (Fox *et al.*, 1990; Hue, 1991; Violante and Gianfreda, 1993, Staunton and Leprince, 1996).

2.3.2.3 Dissolution and substitution reactions

Retention of P can also take place through dissolution and substitution reactions. At high equilibrium P concentrations, P ions can penetrate into inner layers of the layer silicate clays and allophanes and disrupt the structural bonds that link the metal ions and hydroxyl group in the minerals (Bohn *et al.*, 1979). This results in the creation of new sites for P retention/sorption. After structural silicate disruption, there is formation of aluminophosphate compounds in accordance with the following reactions:

$2Al_2Si_2O_5(OH)_2 \Leftrightarrow 2Al(OH)_2^+ + 2Si_2O_5^{2-}$ (dissolution/disruption)------------(vii)

$2Al(OH)_2^+ + 2H_2PO^-_4 \Leftrightarrow 2Al(OH)_2\text{-}H_2PO_4$ (precipitation)------------------------(viii)

Overall reaction:

$2Al_2Si_2O_5(OH_2) + 2H_2PO_4^- \rightarrow 2Al(OH)_2\ H_2PO_4 + 2S_2O_5^{2-}$

Since this occurs at high equilibrium P concentration, this type of reaction is less important because the P concentration in the soil solution is usually very low except after application of P fertilizers, when high P concentrations then occur around the fertilizer bands or granules.

Chemo-sorption or precipitation first leads to rapid conversion of labile P into soil P forms with properties and behaviour similar to those of native soil P, which are relatively unavailable to plants. Following the rapid reactions, slower reactions such as liquid state diffusion into micropores, solid-state diffusion or discrete precipitation may occur (Yaobing and Thomson, 2000). The P retention/sorption rate and extent depends on: soil chemical characteristics such as soil P status, soil pH, soil organic matter content, extractable Al and Fe, types of clay mineral, amount and reactivity of iron and aluminium oxy-hydroxides (Sanchez and Uehara, 1980). Every soil has its own capacity to react and retain the applied fertilizer depending on its P buffering capacity. Higher rates of P application are needed to influence P in soil solution for soils that have higher buffer capacities (Sanchez and Uehara, 1980). The ability of soil to convert labile P to non-labile P is termed P retention or fixation capacity. Determination of the P retention capacity of a soil is an important step in developing fertilizer requirements (Fox and Kamprath, 1970) for the soil in question.

2.3.3 Determination of P adsorption capacity

Adsorption isotherms have been used to describe the adsorption of P, hence P fixation capacity, by soils (Fox and Kamprath, 1970) and these isotherms have further been used to determine P fertilizer needs for some crops (Fox and Kamprath, 1970). The P adsorption isotherms were originally developed for monolayer gas-solid systems (Langmuir, 1918) hence interpretation of the results when applied to solution-solid phase systems have sometimes been questioned. The equations commonly used to describe and interpret P adsorption by soils and soil constituents include the Langmuir, Freundlich, Brunaur–Emnett Teller equations and mechanistic models (Bohn *et al*., 1979).

2.3.3.1 The Langmuir equation

The Langmuir equation is based on first order kinetic equilibrium reactions (Langmuir, 1918). The derivation of the Langmuir equation is underlined by three assumptions namely: (i) constant energy of adsorption, which is independent of extent of surface coverage, (ii) adsorption on specific sites, which have no interaction and (iii) maximum adsorption possible is of monolayer (Langmuir, 1918).

The common form of the Langmuir equation is:

$x/m = kCb/1+kC$ ---(ix)

where x/m = amount of P adsorbed per unit weight of soil (mg P kg^{-1} soil)

C = equlilibrium P concentration (mg L^{-1})

k = a constant related to binding energy (L mg^{-1})

b = maximum amount of P that can be adsorbed by the soil (P-max) (mg P kg^{-1})

The linear form of the Langmuir adsorption equation has the form:

$C/x/m = 1/kb + C/b$ --(x)

From the linear plot of this equation the maximum adsorption capacity or P-max (b) and bonding affinity or intensity (k) of a given soil can be determined from the inverse of the gradient and gradient/intercept, respectively. The P-max is related to the soil's ability to transform added P in soil solution into forms that are less plant available, through adsorption and precipitation processes. It influences the concentration gradient of P from the mineral surface to the soil solution and thereby the effective diffusion rate of P (Fox and Kamprath, 1970).

Adsorption has sometimes failed to conform to the Langmuir equation. Most studies using the linear form of the Langmuir equation have found the plots to be curvilinear rather than linear, and the affinity values to be variable rather than constant (Taylor and Ellis, 1978; Mehadi and Taylor, 1988). The curvelinear line has been resolved into two (Syers *et al.*, 1973; Taylor and Ellis, 1978; Sposito, 1982) or more slopes (Rajan and Watkinson, 1976), indicating at least two different population sites for P sorption. Gunary (1970) suggested that the Langumuir equation could be improved by adding a square root term to the equation. The reasons advanced by Griffin and Jurinak (1973) for this deviation is that the assumptions underlying the Langmuir model were for gas-solid systems, which do not completely conform to solid-solution systems. For instance, it was shown that (i) adsorption takes place at various sites on the surface; and (ii) it occurs in layers and on separate mineral species nucleated on the surface during the process of adsorption (Griffin and Jurinak, 1973).

It has been argued and suggested that P adsorption data conform to the linear model of the Langmuir equation at low P equilibrium concentration (Syers *et al.*, 1973). At low P concentrations P sorption is through specific adsorption while at high equilibrium P concentration (>15 mg P L^{-1}) (Syers *et al.*, 1973), P sorption involves precipitation reactions in addition to specific adsorption, and hence overestimates the actual P adsorption capacities of the soils. As pointed out by Olsen and Watanabe

(1957), the major advantage of the Langmuir equation is that it is possible to calculate the P adsorption maximum and the relative binding energy term for P sorption.

2.3.3.2 The Freundlich equation

The Freundlich P adsorption equation has the form:

$X/m=aC^{1/n}$

where X/m=adsorbed P per unit weight of soil (mg P kg^{-1}),

C=equilibrium P concentration (mg P L^{-1}),

and (a) and (n) are empirical constants (L mg^{-1}) related to adsorption capacity and affinity factors, respectively.

The linear form is:

$\log X/m=1/n \log C + \log a$ --(xi)

A plot of log X/m vs log C gives a straight line for P adsorption data that conforms to this equation (Bohn *et al.*, 1979). Although the Freundlich equation is often considered to be purely empirical in nature, it has the advantage based on assumptions that ionic affinity decreases exponentially with increasing surface coverage (Warren, 1992; Gikonyo, 1997).

Phosphorus adsorption can also be estimated from the Standard P Requirement (SPR) that is the amount of P adsorbed at a solution P concentration of 0.2 mg L^{-1}. This concentration is often considered as the critical level at which 95% of the maximum yields of most crops can be obtained (Juo and Fox, 1977). Standard phosphate requirement gives a good picture of the combined effect of the soil's affinity (k) and capacity (P-max) for P adsorption. It is positively correlated to P max

(Adetunji, 1994; Gikonyo *et al.*, 2003) and based on the SPR, Fox and Kamprath (1970) rated SPR as follows: SPR<100 (low P fixing); 100 to 400 (moderately P fixing); >400 (high P fixing).

Although the sorption isotherms described above are useful for the characterization of different soils on their sorption capacities, they are laborious and time consuming for routine use. To overcome this limitation some researchers use the Phosphorus Sorption Index (PSI) to estimate the soil sorption capacities (Simard *et al.*, 1994; Mozaffari and Sims, 1994). This approach is rapid and involves determination of P adsorbed at a single solution concentration of 50 mg L^{-1}. The PSI is calculated as:

$$\text{PSI } (\text{L kg}^{-1}) = X/\text{Log } C \text{ --- (xii)}$$

where: X=P sorbed at 50 (mg kg^{-1}),

C=equilibrium P (mg L^{-1}) concentration (mg L^{-1}) at 50 mg P kg^{-1} addition.

The PSI values are well correlated (R^2=0.97) with sorption capacities determined from complete sorption isotherms (Simard *et al.*, 1994; Gikonyo *et al.*, 2003).

2.4 Management options for P fixing soils

Management options for high P-fixing soils have been reviewed by Sanchez and Uehara (1980), Sanyal and De Datta (1991) and Warren (1992). They generally involve manipulation of soil characteristics, associated with P fixation. Some of the proposed strategies to reduce P fixation are discussed below:

2.4.1 Application of organic materials

The effects of organic materials on P-adsorption and plant availability can be broadly divided into two categories (i) effects related to P adsorption and (ii) effects on other soil parameters, which are closely related to P availability.

2.4.1.1 Effect of organic matter on P adsorption and transformation

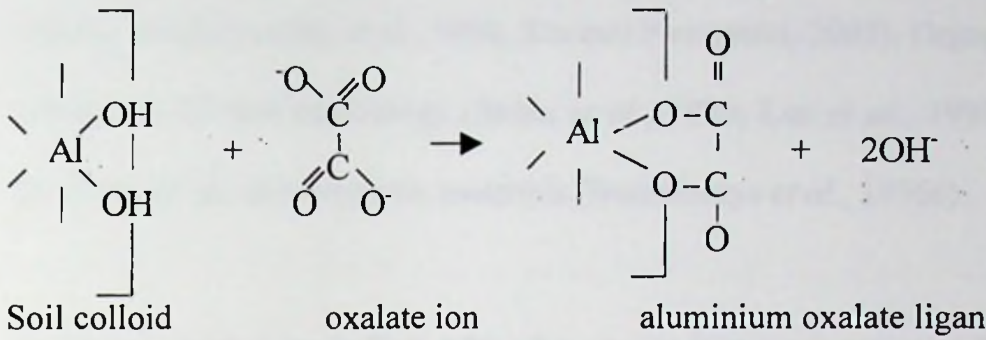
Application of organic materials to soils has been reported to reduce P sorption capacities and to increase P availability. The mechanisms cited include: (i) complexation of polyvalent cations (Fe, Al and Ca) by organic anions, which lowers their activity and prevent the formation of insoluble P salts (Fox and Comerford 1990, Fox *et al*., 1990; Hue, 1992) (ii) competition for adsorption sites, whereby the organic anions replaces phosphates sorbed at metal-hydroxide surfaces through ligand-exchange reactions, consequently increasing P availability (Easterwood and Startain, 1990; Hue 1992; Violante and Giafreda, 1993). The formed metal-organic ligands may block P fixation sites, making the dissolved P more available (Reddy *et al*., 1980; Easterwood and Sartain, 1990) (iii) dissolving of metal-oxide surfaces that sorb P (Bohn *et al*., 1979), (iv) saturation of adsorption sites by P added to the soil from organic matter decomposition (Iyamuremye *et al*., 1996a; Nziguheba *et al*., 2001).

The effect of organic materials on P adsorption by soils depends on the chemical composition and quantity of the organic materials added (Singh and Jones, 1976; Iyamuremye *et al*., 1996a), the type of organic anions produced (Hue, 1991; Bolan *et al*., 1994; Iyamuremye and Dick, 1996; Staunton and Leprince, 1996; Jones, 1998) and the soil type (Iyamuremye *et al.*, 1996a). Nziguheba *et al.* (1998) reported that addition of high quality organic material like *Tithonia diversifolia* (P=2.7 g kg^{-1}, equivalent to 0.27%) to a P fixing Acrisol (SPR=300 mg P kg^{-1}) reduced P adsorption and bonding energies while maize stover (low quality, P=0.7 g kg^{-1}, equivalent to 0.07%) had no such effect. Similarly, Iyamuremye *et al.* (1996a) reported that addition of high quality alfalfa (P=2.43 g kg^{-1}, equivalent to 0.24%) and composted steer manure (P=2.94 g kg^{-1}, equivalent to 0.29%) resulted in reduction in P sorption while low quality wheat straw (P=0.91 g kg^{-1}, equivalent to 0.09%) had no effect. Increase in application rates produced higher effects that varied from one soil type to the other, depending on the soil's mineralogy. Similar results had earlier been reported by Singh and Jones (1976) who concluded that P adsorption would decrease if the organic material added to the soil has equal to or more than, 3.0 g P kg^{-1} (equivalent to 0.03%) while for those materials containing less than or equal to, 2.2 g P kg^{-1} (equivalent to 0.22%), P sorption would increase. Another organic material quality parameter, which has been widely speculated to influence P availability but has not been researched in Tanzania, is the types and concentrations of organic acids produced by different organic materials.

Different organic materials produce different types of organic anions and these exert different influences on P sorption/desorption reactions (Fox *et al.*, 1990; Violante and Gianfreda, 1993; Ohno and Crannel, 1996). Ohno and Crannel (1996) reported that green manures which produced lighter molecular weight organic acids, had a greater depressing effect on P sorption than had the high molecular weight organic acids produced animal manures.

The ability of organic anions to induce P desorption is related to their ability to form stable complexes with Al^{3+}, depicted as the Al stability constant (log K_{Al}). Fox *et al.* (1990) reported that among 16 organic acids studied, release of Al and inorganic P increased exponentially with increasing log K_{Al} values. However, a threshold log K_{Al} value of approximately 4.1 was required before substantial amounts of inorganic P were released. The most effective organic anions were the short-chained aliphatic, di- and tricaboxylic acids while the monovalent types have little effects on P desorption (Hue, 1991; Bolan *et al.*, 1994; Staunton and Leprince, 1996; Jones, 1998).

Organic acids can be divided into three groups according to their Al and Fe complexation capacities, namely: (i) citric [$(CH_2C(OH)CH_2(COOH_3))$], tartaric [$C_2H_2(OH)_2(COOH)_2$] and oxalic [$(COOH)_2$] (ii) malic [$CH_2CH(OH)(COOH_2)$] and malonic [$CH_2(CO_2H)_2$] (iii) acetic (CH_3COOH), succinic [$(CH_2CO_2H)_2$] and formic ($HCOOH$); these groups reflect strong, moderate and weak capacities, respectively. The complexing ability of an acid for Al^{3+} is related to the proximity of OH and COOH groups to the main C chain of the acid. The most effective complexing acids have either two pairs of OH/COOH attached to two adjacent carbons (for example citric and tartaric) or two COOH directly connected as in oxalic acid. Acids in the moderately complexing group have either a pair of OH/COOH attached to a common carbon as in the case of malonic acid. The weak complexers, for example lactic acid, do not have these structural configurations. The relative positions for OH/COOH offer a favourable configuration for the formation of a stable 5- or 6- bond ring structure with Al (Jones, 1998). An example of such a reaction for oxalate (Log K_{Al} = 6.53) is as follows:



………(xiii)

From equation (xiii) the OH^- released leads to an elevation of pH, which increases the electro-negativity of the soil colloid surfaces, hence contributing to P desorption through electrostatic repulsion. Since the stability constants of aluminium and iron oxalates are greater than those of aluminium and iron phosphates, respectively, the former compounds are more stable than the latter (Xia and Pierzynski, 2003), leading to P release.

Light molecular weight organic acids occur in low concentrations in soil solution at less than micromolar to millimolar quantities (Fox and Comerford 1990; Jones, 1998). However, oxalic acid, which has been reported to increase P release from Bh and Bs horizons of Spodosols, can be present at the milllimolar level (Fox and Comerford, 1990; Fox *et al*, 1990). Major sources of these organic acids are root exudates, dead plant materials, leaf litter and farmyard manures decomposition products. Animal manures, particularly poultry manure, contain larger amounts of organic acids (Bolan *et al.*, 1994; Ohno and Crannel, 1996) than green manure litter. Application of these manures can induce P desorption from Al and Fe containing compounds, hence release of P. Organic acids are unstable in soil solution and their concentrations can change rapidly depending on temperature, light, pH and microbial activity (Krzyszowska *et al.*, 1996; Xia and Pierzynski, 2003). Organic acids are also influenced by soil mineralogy (Bolan *et al.*, 1994; Lan *et al.*, 1995) and types and amounts of the added organic materials (Iyamuremye *et al.*, 1996c).

Recent research done in East Africa has shown that green manures from agroforestry trees and local shrubs reduce P adsorption. This was attributed to the replacement of phosphate by the manures' organic anions on adsorption sites of soil constituents. However, the types and concentrations of the suspected organic anions produced, and their effect on other soil parameters, were not established (Nziguheba, 2001). Such information is needed to allow proper selection of green manures for alleviating soil P sorption problems through green manure application.

2.4.1.2 Effect of organic materials on other soil parameters related to P availability

(a) Effect on soil pH

Organic manures can modify soil properties which otherwise limit P availability. Many P deficient soils are acidic. Conflicting accounts of the effect of organic residues on soil pH exist. Soil pH has been observed both to increase (Wong *et al.*, 1998; Tang *et al.*, 1999; Whalen *et al.*, 2000) and decrease (Bolan *et al.*, 1991; Tyson and Cabrera, 1993) upon addition of different types of organic materials. Decomposition of organic materials is depicted by the following enzymatic reaction:

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$R\text{-}CH(NH_2)\text{-}R + 1/2 O_2 \rightarrow R\text{-}CO\text{-}R + NH_3$--------------------------------------(xiv)

R is an organic group/ligand ammonia gas

The hydrolysis of NH_3 produces OH^- that can increase pH according to the reaction:

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$--(xv)

On the other hand nitrification, which takes place under aerobic soil conditions, produces protons and nitrate, which further lower the pH according to the reactions:

$NH_4^+ + 3/2\, O_2 \rightarrow NO_2^- + H_2O + 2H^+$ --(xvi)

$NO_2^- + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$---(xvii)

Therefore, from reactions (xiv) to (xvii) the possible mechanisms advanced to account for increase in soil pH include: (i) adsorption of H^+ ions onto the surfaces of the introduced organic materials (Hoyt and Turner, 1975), (ii) development of reducing conditions due to increased microbial activity during rapid decomposition of the organic matter (Hue, 1992), (iii) addition of basic cations (Noble *et al.*, 1996; Tang *et al.*, 1999; Whalen *et al.*, 2000) and (iv) displacement of OH^- from sesquoxides surfaces by organic anions ligands (Parfitt *et al.*, 1978). High pH then increased the negative charges on phosphate and contributed to decrease in P adsorption through P repulsion (Xia and Pierzynski, 2003).

In contrast, decrease in soil pH has been attributed to (i) release of H^+ associated with organic anions (ii) nitrification process following organic matter decomposition and (iii) decreased cation exchange capacity (Bolan *et al.*, 1991). Low pH causes surface hydroxyl groups to accept protons to form $-OH_2$ groups. Since these groups are easier to displace than hydroxyl, lowering pH increases P sorption by facilitating ligand exchange reactions.

Consequently, the final result of organic materials on soil pH is determined by composition of organic materials, the degree of decomposition and soil pH buffering capacity. The composition of organic materials affected their rate of decomposition (Tian *et al.*, 1992; Palm *et al.,* 1999) and this affected the input of basic cations and organic anions released, and the alkalinity produced, when the organic materials were added to soil (Pocknee and Summer, 1997; Wong *et al.*, 1998; Noble *et al.*, 1996; Tang and Yu, 1999; Tang *et al.*, 1999).

Noble *et al.* (1996) showed that application of tree leaves increased soil pH and this was related to the content of ash alkalinity in the litter, which in turn was closely related to the basic cation contents. Pocknee and Summer (1997) observed that the soil pH change was well correlated with the amount of basic cations present in the plant materials. Wong *et al.* (1998) observed similar effects when he applied plant residue compost, urban waste compost, farmyard manure or peat to various soil types. The increase in pH induced by these organic materials was directly proportional to the basic cation content of the organic materials. Tang *et al.* (1999) found that lupine leaves, which had the highest Ca and Mg concentrations than the other organic materials investigated, produced the highest increase in soil pH.

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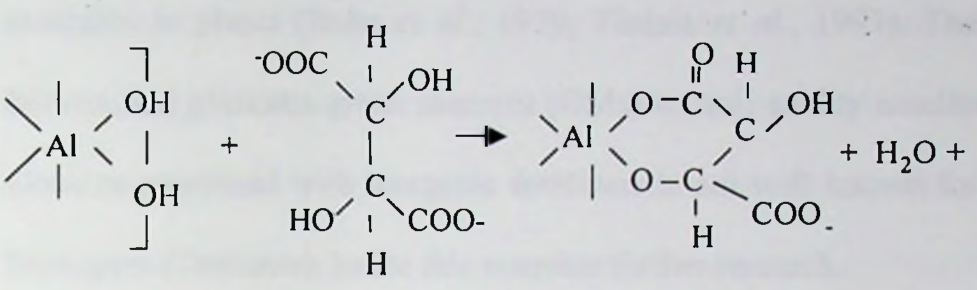
Different organic materials produce various types and concentrations of organic molecules upon decomposition (Jones, 1998). Microbial decomposition of basic-cation containing organic anions like Ca oxalate (CaC_2O_4) or Ca gluconate result in a pH increase analogous to that caused by agricultural lime (Messini and Favilli, 1990; and Pocknee and Summer, 1997), as follows:

$$\underset{\text{Calcium oxalate}}{CaC_2O_4 + \tfrac{1}{2}O_2} \rightarrow \underset{\text{calcium carbonate}}{Ca\,CO_3} + \underset{\text{carbon dioxide gas}}{CO_2\uparrow} \text{-------------} \text{(xviii)}$$

Whalen *et al.* (2000), using strongly and moderately strongly acid soils reported that application of cattle manure at 40 g manure kg^{-1} soil significantly increased soil pH from 4.8 to 6.0 and 5.5 to 6.0 for Gray Luvisol from Beaverlodge and Orthic Gray Luvisol from Vermillion, (Alberta), respectively. The higher pH in manure-treated soil was attributed to the buffering effect of bicarbonates and decarboxylation of organic anions ($R\text{-}CO\text{-}COO^-$) from cattle manure, which consumed protons (H^+) as follows:

$$R\text{-}CO\text{-}COO^- + H^+ \rightarrow R\text{-}CHO + CO_2\uparrow \text{--} \text{(xix)}$$

Organic anions can increase soil pH through ligand exchange between hydroxyl groups of soil Al or Fe hydroxides, whereby the displaced OH^- contributes to the increase in soil pH. For example Hue (1992) observed increase in pH following chicken manure application, which was attributed to ligand exchange reactions with the consequent release of OH^-, as illustrated below:



…….(xx)

(gibbsite)   (tartrate)

The ultimate effect of organic materials on the soil pH depends on the amounts and type of organic materials applied. Hue and Amien (1989), working with Acrisols of pH 4.0 and 50% exchangeable Al, reported significant increase in soil pH and decreases in exchangeable Al after application of cowpea and *Leucaena lecocephala* green manure; but guinea grass had no such effect. The increase in pH increased with application rates of the green manures.

The liming effect of organic materials can sometimes surpass that of lime. Hue (1992) and Mnkeni and MacKenzie (1985) obtained higher pH values in soil solutions treated with organic residues than in those amended with calcium carbonate. This shows that a good selection of organic materials can sometimes act as a substitute for conventional liming mateials in tropical soils. The increase in pH causes an increase in CEC, which results in formation of negative charges on colloidal surfaces, consequently enhancing P desorption (Moshi *et al.*, 1974; Mackay and Syers, 1986). The increase in soil pH will enhance P availability as long as this increase is not greater than 6.8 because at soil pH>6.8-7.0, phosphate can react with Ca^{2+}or Mg^{2+} to form Ca or Mg phosphate which are insoluble, hence not readily available to plants (Bohn *et al.*, 1979; Tisdale *et al.*, 1993). The role of tithonia, lantana and gliricidia green manures (GMs) on soil acidity amelioration when used alone or combined with inorganic fertilizers is not well known for the acid soils of Morogoro (Tanzania); hence this warrants further research.

(b) Effects on surface charge

Highly weathered soils dominated by the kaolinitic type of clays and hydrous oxides of Fe and Al have low cation exchange capacities accompanied by high variable charge (Sanchez and Uehara, 1980; Asenga, 1993). Addition of organic matter to such soil could significantly affect the overall charge properties of the soils and their abilities to retain ions against leaching (Vanlauwe *et al.*, 1996; 2000). Moshi *et al.* (1974) found that negative charges were highest in the surface horizon of forest soils, and within a profile, the negative charge decreased with depth, becoming almost constant below 30 cm for cultivated soils and 60 cm for forest soils. Positive charge on the soil constituents decreased with increasing organic matter, which corresponded to a decrease in orthophosphate sorption. Phan Thi Cong (2000) reported that application of tithonia at 2.5 g kg^{-1} soil substantially increased the negative surface charge density and CEC of a Ferralic Cambisol. The increase in negative charge resulted in decrease in P sorption through repulsion of orthophosphate ions by the negatively charged surfaces (Xia and Pierzynski, 2003).

(c) Effect on exchangeable Al

The high exchangeable Al content that exists in acidic soils can cause crop failure because Al toxicity hinders proper root development when Al concentration exceeds the critical values (Sanchez, 1976; Tisdale *et al*., 1993). Decomposition of organic materials produces organic anions and cations that can increase soil pH and consequently reduce the activity of exchangeable Al and Fe. Addition of crop residues like alfalfa meal has been reported to reduce the activity of soil Al through complexation of the exchangeable Al and soil solution Al^{3+} (Hoyt and Tumer, 1975) by organic anions. Hue *et al*. (1986) and Jones (1998) reported that Al complexation capacities of organic acids were positively correlated with the relative position of OH/COOH groups on their main C chain, positions that favoured the formation of stable 5- or 6-bond ring structures with Al. Phan Thi Cong (2000) reported that application of tithonia at 2.5 g kg^{-1} to a Ferralic Cambisol decreased exchangeable Al from 2.16 to 1.5 cmol(+) kg^{-1} after 49 days of incubation. At 40 g tithonia kg^{-1}, Al concentration was reduced to zero. The concentration of exchangeable Al was significantly and negatively correlated with pH $_{(KCl)}$. However, inorganic fertilizers applied at the same rate of P had no effect on exchangeable Al, and the effect of tithonia was possibly due to the presence of strong metal-binding capacity of organic components in tithonia.

(d) The effect of soil organic matter

Application of organic manures is the main strategy of restoring soil organic matter (Woomer *et al*., 1994; Smaling *et al*., 1997; Vanlauwe *et al*., 2000). The carbon from organic materials supplies energy to soil microorganisms, which control the fluxes between organic P and inorganic P in the P cycle (Phiri *et al*., 2001). Application of organic matter to soils (improves soil structure and moisture holding capacities of the soils), enhances microbial activities of the soils and consequently P turn-over (Goyal *et al.*, 1999). Further, organic matter application increases soil aggregation (Linquist *et al.*, 1997b; Phan Thi Cong, 2000), reduces soil bulk density, consequently enhancing P diffusion rates and hence P availability. For example, small sized soil aggregates have larger specific surface areas than larger sized soil aggregates and this gives the soil a higher capacity to retain (fix) P (Linquist *et al.*, 1997b) because P sorption is a surface phenomenum. An increase in soil aggregation and decrease in specific surface area caused by application of organic matter may increases P availability (Phan Thi Cong, 2000).

Organic materials also supply substantial amounts of the macro and micronutrients that influence nutrient balance in the soil, resulting in enhanced P absorption and uptake (Kretzschmar *et al.*, 1991; Hue *et al.*, 1994, Gachengo *et al.*, 1999). Organic matter acts as a P source through the process of decomposition and mineralization (Nziguheba, 2001).

In view of these advantages, the strategy of using organic materials in alleviating the P deficiency and availability problems in highly weathered soils stands a better chance of ready adoption compared to inorganic fertilizers (Nziguheba *et al.*, 2002). However, organic materials cannot be used as substitutes for inorganic P fertilizers because most of the commonly used organic materials have low P contents, much lower than the critical concentration of 2.4 g P kg^{-1} suggested by Palm *et al.* (2001) for net P mineralization. For example, application of 5 t ha^{-1} on dry weight basis of the a high quality organic material (P=0.24%) could only contribute 10 kg P ha^{-1}, much far below the 18 kg P ha^{-1} required for the production of 2 tonnes of maize grain (Palm *et al.*, 1997). The low P content in most organic amendments necessitates use of large quantities, requiring high labour demand for preparation, transportation, and application to achieve optimum crop production. Given the poor economic status of most farmers in Tanzania, the sole use of organic materials at the required rates is not possible. Integrated use of organic materials with modest rates of inorganic P fertilizers seems to be a feasible alternative for improving P availability and increasing crop yields. Combined application of organic materials with water-soluble P fertilizers is limited by the high fertilizer costs. But, the use of sparingly soluble P sources like MPR might be a more economical option. However, proper combinations of different organic manures (GM and FYM) with phosphate rocks and their effects on P availability and crop yields have not been researched much in Tanzania.

2.4.2 Alternative strategies

Management of P fixing soils can also be through other methods, which include high fertilizer rates, localized fertilizer placement, use of sparingly soluble P fertilizer types and liming of the soil.

Application of high rates of P fertilizers (high input strategy), which aims at saturating the sorption sites (Garden *et al.*, 1997; Simpson *et al.*, 1997; Sanchez and Jama, 2002; Mokwunye and Bationo, 2002), has also been proposed in managing high P fixing soils. However, the major drawback with this strategy is the high capital investment for purchasing fertilizers and equipment to apply the large amounts of fertilizers.

Localized or band application of small quantities of P fertilizers (low input strategy), to saturate the P adsorption capacity of the soil within the band, is another strategy of enhancing P availability in soils with high P fixation/adsorption capacities (Nziguheba *et al.*, 2000; Bationo *et al.*, 1990; Sinaj *et al.*, 2001; Bationo and Mokwunye 2002). Nziguheba *et al.* (2001) reported that annual application of inorganic P fertilizers at rates greater than 50 kg P ha^{-1} reduced the P fixing capacity of an Acrisol in Kenya, although lower rates had no significant effects. Due to the low annual investment capital involved this low input strategy it might be more attractive to small-scale farmers.

Application of high rates of sparingly soluble P containing materials like PRs has been proposed for high P fixing soils to increase available P over a longer period (Buresh *et al.*, 1997, Bationo *et al.*, 1990; Mokwunye and Bationo, 2002). The assumption underlying this approach is that the P released is immediately fixed but, unlike in the case of water-soluble P fertilizers, there is a high residual effect at levels that can support crop requirements of P over several years (Buresh *et al.*, 1997; Sanchez and Jama, 2002). Certain rock phosphates like MPR contain high levels of carbonates and this can have liming effects on soils, consequently decreasing soil P fixation. However, the proposed high rates of PRs, MPR inclusive, have been reported to hinder the dissolution of phosphate rocks (Mowo, 2000).

Application of lime results in an increase in soil pH, and decrease in the reactivity of the fixation sites on the soil colloids, and neutralization of Al and Fe in P fixing soils (Sanyal and De Data, 1991; Iyamuremye *et al.*, 1996a). However the use of lime is constrained by the high capital investment, and is not likely to be adopted by small-scale farmers.

2.5 Phosphate rock dissolution

Phosphate rocks ($Ca_3 (PO_4)_2)_3.CaFx.(CaCO_3)x.(Ca(OH)_2)_2)$ are insoluble in water but sparingly soluble in citric acid. The solubilities of the PRs depend on the chemical composition of the rocks, soil chemical properties, environmental factors, plant rhizosphere effects and soil management factors.

2.5.1 Effect of soil properties/characteristics

The main soil chemical characteristics which influence PR dissolution are reviewed below:

2.5.1.1 Soil pH and exchangeable acidity

Dissolution of PR in soil, using fluoro-apatite as an example, can be expressed by the equation:

$$Ca_{10} (PO_4)_6F_2 + 12\ H_2O \Leftrightarrow 10Ca^{2+} + 6H_2PO_4^- + 2\ F^- + 12OH^- \text{------------------}(xxi)$$

Dissolution of PR consumes protons and releases Ca^{2+}, F^-, $H_2PO_4^-$ and hydroxyl ions. The removal of these products from the reaction site through diffusion, surface exchange, sorption and absorption by plants (Bolan and Hedley 1990; He *et al.*, 1996; Szilas, 2002) enhances PR dissolution. Soil acidity is the main driving force for PR dissolution (Khasawneh and Doll, 1978; Chien *et al.*, 1980; Kanabo and Gilkes, 1987a; Rajan *et al.*, 1996) because soil acidity supplies protons for the forward reaction to take place. Neutralization of the released OH^- ions by protons in an acidic soil sustains the continuation of the PR dissolution process (Khasawneh and Doll, 1978; Hammond *et al.*, 1986a; Rajan *et al.*, 1996). Thus, with increasing proton supply, greater dissolution of PR takes place provided there are also sinks for the released Ca^{2+} and HPO_4^{2-} ions to preclude formation of Ca phosphate (Bolan and Hedley, 1990; Ellis *et al.*, 1995).

For a volcanic soil with pH ranging from 3.9 to 6.5, Bolan and Hedley (1990) reported that the dissolution of various phosphate rocks was almost linearly related to the pH of the soil. Robinson and Syers (1990) reported that dissolution of Gafsa PR after 44 days of incubation was 60% at pH 4.5, but decreased to 30% at pH 6.1. Wright *et al.* (1992) assessed the dissolution of PRs in 32 soils with pH ranging from 3.38 to 6.61 and found that after 30 days of incubation the extent of dissolution was related to pH and ranged from 2.8 to 71.5%.

The dissolution of PRs is usually fast at the beginning of the incubation period and decrease or sometimes stabilize, thereafter (Anderson and Sale, 1993; Ikerra, *et al.*, 1994; He, *et al.*, 1996) and this was more so in high P fixing soils. This was attributed to the gradual saturation of the P adsorption sites (that is reduction of the magnitude of the P-sinks). Anderson and Sale (1993) reported that dissolution of North Carolina phosphate was fast during the first 28 days, but decreased from 73 to 56% after 194 days. Similarly, He *et al.* (1996) reported rapid dissolution of North Carolina PR within 30 days of incubation followed by a slow and steady dissolution stage that persisted for more than 100 days.

The increase in PR dissolution with time is caused by supply of protons (Robinson and Syers, 1990; Robinson *et al.*, 1992b; Wright *et al.*, 1992; Anderson and Sale, 1993). The mechanisms proposed to explain proton production include: (i) the release of H^+ associated with organic anions during organic matter decomposition (Porter *et al.*, 1980), (ii) nitrification under aerobic conditions (Bolan *et al.*, 1991) (iii) increased cation exchange capacity and corresponding decrease in exchangeable acidity and (iv) deprotonation of OH^- groups on soil colloids (Bohn *et al.*, 1979).

The cations unbalanced against anions uptake pattern in nitrogen fixing legumes results in accumulation of organic anions in plant tissue and this stimulates proton production so as to achieve electro-neutrality (Riley and Barber 1971; Wen-Chen Liu *et al.*, 1989; Hoffland, 1992). Liming of an acid soil either by $CaCO_3$ or application of organic materials high in basic cations will result in reduction of PR dissolution due to the fact that liming increases the soil pH and exchangeable Ca. Soil pH can also influences PR dissolution through its influence on the adsorption capacity of soils. Decrease in pH results in an increase in P adsorption capacity of soils with pH dependent charges. Soils with high P adsorption capacity enhance PR dissolution because they have sinks for P and Ca (Kirk and Nye, 1986; Kanabo and Gilkes, 1987b; Szilas, 2002).

2.5.1.2 Calcium in soil solution and exchangeable calcium

Based on the law of mass action, the dissolution of PR as shown in reaction (xxi) proceeds as long as Ca^{2+} concentration in the soil solution is maintained at lower level than in the film surrounding the dissolving PR particle and the ionic products of the dissolution reaction do not exceed the solubility product of calcium phosphate (Mackay *et al.*, 1986; Robinson and Syers, 1991; Robinson *et al.*, 1992b; Rajan *et al.*, 1996). Wilson and Ellis (1984), working with six PRs of different reactivities, observed a linear relationship between the log of Ca^{2+} activity and log of the $H_2PO_4^-$ and HPO_4^{2-} in soil solution. Soil affinity for Ca^{2+} (Ca buffer capacity) promotes the dissolution of PRs because it provides a sink for the Ca^{2+} released from the dissolution of PR. Affinity for Ca^{2+} is high when soil Ca, as a proportion of soil's cation exchange capacity, is low (Robinson and Syers, 1990; Robinson and Syers 1991; Robinson *et al.*, 1992b), which is normally the case when the base saturation and pH values are low. Therefore, PR dissolution would be high when the cation exchange sites available for adsorption for the Ca^{2+} released from the dissolving PR is high (Robinson *et al.*, 1992b). The Ca buffer capacity can be determined from the slope of the curve relating exchangeable Ca^{2+} to Ca^{2+}activity in soil solution (Rajan *et al.*, 1996).

Soils that are rich in Ca^{2+}or free $CaCO_3$ have been found to be poor sinks for the orthophosphates released during PR dissolution (Khasawneh and Doll, 1978). Mackay *et al.* (1986) found that the dissolution of Sechuru PR, as measured by 0.5 M NaOH, increased as exchangeable Ca decreased. Robinson and Syers (1991) reported that when the Ca unoccupied sites were increased by adding a Ca exchange resin (CaER) the dissolution of Gafsa PR increased from 34.1 to 66.8 mmol kg^{-1} after 40 days of incubation.

A sink for Ca^{2+} may be caused by plant uptake, or by chelation by organic anions produced during organic matter decomposition or those produced in root exudates (Chien, 1979). Chelates may also be formed with the Fe^{3+} and Al^{3+} commonly found in PRs (Szilas, 2002), and this may prevent the precipitation of P as Fe and Al phosphates. Kpomblekou and Tabatabai (1994) suggested that chelation by organic acids of metals associated with PRs was responsible for increasing dissolution of PR. Microorganisms, particularily bacteria, have been reported to enhance PR dissolution in soils through production of organic acids which can chelate Ca (Nahas *et al.*, 1996), but use of microorganisms in enhancement of PR dissolution is still limited. Therefore, co-application of PRs with organic materials that are high in Ca content is likely to hinder the PR dissolution due to the common ion effect and lack of a Ca sink.

2.5.1.3 Phosphate in soil solution and phosphate buffering capacity

Soil P, as expressed by the activities of $H_2PO_4^-$ and HPO_4^{2-} in soil solution, plays a role in PR dissolution similar to that played by Ca^{2+} ions in soil (Khasawneh and Doll, 1978). Low activity of $H_2PO_4^-$ or HPO_4^{2-} in soil solution favors PR dissolution as it creates a sink for P (Sale and Mokwunye, 1993; Mnkeni *et al.*, 1994). Sale and Mokwunye (1993) pointed out that Ca^{2+} has a much stronger retarding effect on PR dissolution than phosphate. Soils that are high in both Ca^{2+}, $H_2PO_4^-$ or HPO_4^{2-} ions are not likely to favour PR dissolution (Ambeger, 1978). The dissolution of PR increases with increase in P buffer capacity. The P buffer capacity has been estimated as the slope of the linear part of the curve relating sorbed P and equilibrium P concentration (k value). Soils with high P adsorption capacities have more adsorption sites for P. The P released by the dissolving PR is adsorbed on to such sites, consequently reducing the quantities of the reaction products and thereby enhancing PR dissolution.

2.5.1.4 Soil phosphorus adsorption capacity

Increase in soil P retention capacity creates free sorption sites and consequently increase phosphate rock dissolution (Robinson and Syers, 1990; Wright *et al.*, 1992; Szilas, 2002). Wright *et al.* (1992) reported that it was not the absolute P adsorption capacity *per se* that played the role, but rather it was the number of sites available to adsorb the P released from PR (P buffering capacity or P affinity) which was normally correlated with P sorption capacity. Increase in PR dissolution did not necessarily induce an increase in P availability or in relative agronomic effectiveness (RAE) of the phosphate rocks, especially in high P fixing soils (Kanabo and Gilkes, 1987a; Hammond *et al.*, 1986a; Butegwa *et al*, 1996; Simpson *et al.*, 1997; Szilas, 2002).

Kanabo and Gilkes (1987b) found that increasing the goethite content of a lateritic podzolic soil by 9% using a Fe gel resulted in a 107% increase in PR dissolution of the North Carolina PR, but gave 54% decrease in bicarbonate extractable P compared with the control. Butegwa *et al.* (1996) using Sukulu phosphate rock from Uganda, reported a decrease in RAE of the compacted and partially acidulated Sukulu PR as the soil phosphorus fixation capacity was increased by use of Fe gel from 37 to 62% and 4 to 14% for Hiwassee and Marvyn soils, respectively. Szilas (2002), working with soils from 8 agro-ecological zones (AEZ) of Tanzania, reported that the amount of available P from PR dissolution was not correlated with amount of PR dissolved.

It was found that 72% of the variance in available P ($NaHCO_3$-Pi) could be explained by the amount of P dissolved, initial P level and P adsorption capacity (P-max). The dissolution of MPR (at 300 mg P kg^{-1} soil) ranged from less than 10% during 120 days of incubation in soils with nearly neutral pH and low adsorption capacities to 50% in slightly acidic soil with high P fixation.

Decrease in RAE of PR due to increase in the soil adsorption capacity may be attributed to fixation of the released P from PR as well as the slow dissolution of PR, which may not supply enough soluble P for rapid plant development. Thus, for efficient use of PR, the factors controlling both the PR dissolution and the P availability in the soil solution need to be considered. Addition of green and farmyard manures which have a direct influence on pH, Ca buffer capacity and P sorption capacity may thus have significant influence on PR dissolution and P availability. The effect depends on their quantities, nutrient contents (particularly basic cations) types and concentrations of organic acids, and agro-ecological conditions. Such information is still missing for the Tanzania setting.

2.5.1.5 Soil organic matter

The positive influence of organic matter on PR dissolution has long been observed (Bangar *et al.*, 1985). It seems to arise from the high cation exchange capacity of organic matter and organic acids produced as a result of microbial and chemical transformations of organic debris. The cation exchange capacity (CEC) of mineral soils, depending on their clay content, may range from a few to 50 or 60 cmol(+) kg^{-1} soil, whereas that of organic matter may exceed 200 cmol(+) kg^{-1} soil (Tisdale *et al.*, 1993). Organic matter can therefore, enhance PR dissolution through its influence on surface charge as revealed by CEC and the Ca buffer capacity of soils (Rajan *et al.*, 1996). Various organic acids produced in soils as a result of microbial and chemical transformations of organic debris affect PR dissolution through production of protons and chelation of Ca (Rajan *et al.*, 1996; Bolan *et al.*, 1994; Kpomblekou and Tabatabai 1994; Sagoe, *et al.*, 1998). Therefore, co-application of manures with PRs can be a useful way of enhancing PR dissolution.

Kpomblekou and Tabatabai (1994) found that organic acids dissolved more P than was accounted for by their proton supply, and suggested chelation of the metals associated with P in PRs. Chien (1979) studied the effect of urea on North Carolina P dissolution in two soils of contrasting organic matter contents and reported evidence of the Ca chelating effect of the hydrolysed organic matter. Incorporation of Missouri PR into compost has been reported to improve the release of P, suggesting the occurrence of reactions similar to those in organic soils (Bangar *et al.*, 1985).

The types of organic acids and their concentrations are likely to influence the amount of P released from PRs. Sagoe *et al.* (1998) reported that 13 to 38% of the amount of P dissolved from six PRs from China, USA, Jordan, Sri Lanka, Togo and Tanzania was due to acid protonation while the rest depended on the Ca binding power of the organic acids. These workers dealt with pure organic acids and this might not hold true when dealing with natural organic materials which, besides producing organic acids, also produce basic cations and anions as well as P. These other products might shift the dissolution equation to the left due to common ion effect and their influence on pH. Although it is commonly suggested that composting or co-application of MPR with organic materials will enhance MPR dissolution through the action of organic acids, there has been no data on the relationship between organic acid concentrations arising frm decomposition of organic materials and P release from MPR.

2.5.1.6 Soil moisture

The dissolution of PR is controlled by soil moisture through its influence on movement and removal of PR reaction products from the dissolution sites (He *et al.*, 1996). Soil moisture influences the flux of reactants and reaction products across the soil and solution phases through diffusion process. Increase in soil moisture results in increase in PR dissolution because it creates gradients in reaction products. Weil *et al.* (1994) reported that the dissolution of North Carolina PR in volcanic soils (Typic vitrandepts) increased with increase in soil moisture up to 80% field capacity in a medium P retentive soil (P retention 78%) and up to field capacity in a soil of higher P retention (P retention 91%).

Under field conditions the influence of rainfall on the agronomic effectiveness of PRs has also been reported (Hammond *et al.*, 1986a,b; Babare *et al.*, 1998; Bolland *et al.*, 1992; Szilas, 2002). For instance, Hammond *et al.* (1986a) reported a linear correlation between increase in groundnut and cereal yields compared to control with mean annual rainfall which ranged from 500 to 1300 mm. Szilas (2002) reported that the RAE of MPR in eight different agro-ecological zones of Tanzania was highly affected by moisture stress, and the fertilizer efficiency of MPR increased with increasing rainfall. In general, crop response to PRs is more erratic under low-rainfall conditions (Hammond *et al.*, 1986a).

2.6 Rhizosphere effects

Plants can influence the rate of PR dissolution through secretion of acids or alkali into the rhizosphere, by uptake of Ca and P, and by production of chelating organic acids which complex Ca (Rajan *et al.*, 1996; Mengel, 1997). Under insufficient phosphate supply conditions, symbiotic N fixing legumes have a higher acidifying effect due to production of protons by their roots (Gahoonia and Nielsen, 1992a,b), subsequently enhancing PR dissolution. Similarly, when plants take up NH_4^+ they secrete protons whereas uptake of NO_3^- results in secretion of OH^- and or HCO_3^- ions. The former is manifested in increased P uptake (Moorby *et al.*, 1988; Gahoonia and Neilsen, 1992b) thus sustaining the P-sink in the soil. Gahoonia and Neilsen (1992a) measured the HCl-soluble P, a measure of calcium apatite P remaining in the rhizosphere of rye grass and found more apatite P remaining in the soil supplied with NO_3-N than that supplied with NH_4-N. The observations by Haynes (1992) suggest a greater dissolution of Jordan PR (a medium reactive PR) by lupin (*Lupinus angustifolius*), which decreased rhizosphere soil pH than by barley (*Hordeum vulgare* L.) that increased the rhizosphere pH.

Plant roots secrete organic acids, which lower soil pH and complex the Ca released from the PR, thus creating conducive conditions for PR dissolution (Ae *et al.*, 1991; Hoffland, 1992; Gerke and Meyer, 1995) but the effect varied with crop variety

(Hoffland, 1992). Since Ca is a by-product of PR dissolution, any plant that has high Ca requirement will create a Ca sink and enhance PR dissolution. Some plants have been reported to have high Ca uptakes, for example buchwheat and rape, and are more effective in utilizing P from RPs (Bekele and Hofner, 1993). Besides Ca uptake by plants, Ca released by the PR can be complexed by the organic acids produced by different plants and decomposition of organic matter, consequently in the rhizosphere increasing PR dissolution.

Inoculation of plant roots with mycorrhizae may improve the accessibility of soil phosphate to plants by increasing the contact surface between the soil matrix and the mycorrhizal plant roots, resulting in enhanced P uptake and utilization by plants (Mosse, 1977; Asea *et al.*, 1988). The success of this technology depends on identification of specific fungi for specific plant hosts and this is still a problem requiring more investigation.

2.7 Enhancement of the solubility of PR

There is only a limited number of climatic and soil conditions that enhance solubilization of PR, hence the fast release of P. Treatment or application of PRs with different materials, which enhance dissolution, has been practiced. The treatments include: (i) partial acidulation and compaction (ii) combining PR with elemental S, and (iii) composting PR with manures.

2.7.1 Partial acidulation

Partial acidulation is the treatment of PRs with either sulphuric (H_2SO_4) or phosphoric acid (H_3PO_4) at acid concentrations lower than those required to fully convert PR to water soluble triple super phosphate (TSP) or single super phosphate (SSP). An example of a general reaction when H_2SO_4 is used for partial acidulation of RPs is as follows:

$$Ca_{10}(PO4)_6F_2 + 7yH_2SO_4 + 3YH_2O \rightarrow 3yCa(H_2PO_4)_2.H_2O + 7yCaSO4 + 2y\ HF + (1-y)Ca_{10}(PO_4)_6F_2 \text{------(xxii)}$$

In this equation y represents the degree of acidulation, y is equal to 0.5 and 1 for 50% and 100% acidulation, respectively. The agronomic effectiveness of PRs has been reported to increase with partial acidulation (Bationo *et al.*, 1990; Menon and Chien, 1990; Rajan and Marwaha, 1993; Kimbi *et al.*, 1996). However, this process is expensive and beyond the reach of the poor farmers in Sub Saharan Africa (SSA) (Mapiki and Singh, 1990; Hellums *et al.*, 1992).

2.7.2 Treatment with sulphur compounds

Combining PRs with elemental sulphur has been proposed as one of the methods to enhance PRs dissolution (Rajan *et al.*, 1996). The principle behind the process is that sulphur-oxidizing bacteria (e.g. *Thiobacillus thiooxidans* and *Thiobacillus thioparus)* oxidize the sulphur into sulphuric acid. This reaction results in proton production, thereby enhancing dissolution of PRs. Application of either unreactive or reactive PRs in the form of PR-S^0 granules increases their dissolution in soil and availability of P to plants. However, this release of P is dependent on the PR: S ratio, rock type and presence of the S- oxidizing bacteria in the soil (Kalumuna *et al.*, 1998). Although this technology looks relatively less expensive than partial acidulation the capital required for the granulation of the product might be prohibitive to resource poor farmers.

2.7.3 Composting with organic manures

Both positive and negative results have been reported from composting RP with organic materials. Positive results have been attributed to complexation of Ca^{2+}, Al^{3+} and Fe^{3+} by organic anions and release of H^+ by organic acids during organic matter decomposition, resulting in greater dissolution of PR (Mahimairaja *et al.*, 1995; Rajan *et al.*, 1996) by sustaining the Ca, Fe and Al sinks and provision of protons, respectively.

Increase in P availability and crop yields due to composting PRs with agricultural wastes has been reported by Mishra *et al.* (1982), Bangar *et al.* (1985) and Mishra and Bangar (1986) and with farmyard manure by Welte (1978), Chackraborty (1982), Panda (1990) and Ikerra *et al.* (1994). Contradicting results have been reported by Rastogi *et al.* (1976) and Mowo (2000), when composting PR with farmyard manure and by Mahimairaja *et al.* (1995), using poultry manure.

To date, it is not certain whether co-application of green manures with MPR would increase MPR dissolution. Reports from other workers who used other types of rock phosphates and soils (Zaharah and Bah, 1997; Savini, 2000; Tossah, 2000 and Waigwa *et al.*, 2003) indicated negative effects on PR dissolution. These workers attributed lack of PR dissolution enhancement to the high basic cations, high pH and high proton buffering capacity of the added materials.

Bangar *et al.* (1985) reported that composting unreactive Missouri PR with farm wastes (chopped grasses and tree leaves) increased the citric acid solubility of the PR. Their results from a small-plot field experiment indicated that the product applied on an equivalent total P basis gave grain and straw yields of cluster bean (*Cymopsis tetragonoloba* L) equal to those on application of SSP. Similar results have been obtained by Mishra *et al.* (1984) on pigeon peas (*Cajanus cajan* L.). Work carried out elsewhere indicates that organic materials could enhance crop utilization of P from PRs (El-Banna *et al.*, 1978; Chakraborty, 1982; Dhar and Singh, 1982). Chakraborty (1982) in India reported increased extractable P in all plots which received Purulia PR (India) in conjunction with farmyard manure (FYM), while Dhar and Singh (1982), working with wheat, observed higher yields in plants receiving Purulia PR with compost. Ikerra *et al.* (1994) reported increase in soil extractable P, maize dry matter yields and P uptake on soil treated with MPR plus manure but not with compost. The calcium content of organic manures (Zaharah and Bah 1997; Savini, 2000) and high pH (Mowo, 2000) have been reported as causes for lack of enhancement of PR dissolution by some organic materials. Some farmyard manures (Japenga and Harmsen, 1990; Wong *et al.*, 1998; Wickama and Mowo, 1999; Mowo, 2000) and most GMs (Bessho and Bell, 1992; Noble *et al.*, 1996; Pocknee and Summer, 1997; Tang *et al.*, 1999) have some liming effects when applied to soils. This would most likely result in reducing P adsorption capacity of the soil, consequently reducing MPR dissolution. Therefore, the effect of mixing various organic materials with PRs on PR dissolution will vary from one organic material to the other depending on their chemical characteristics.

The interaction between composted farmyard manure and PR has received considerable research attention, but little is known about the influence of GMs applied together with PRs on PRs solubilization hence P availability under different agro-ecological conditions using different test crops in Tanzania.

2.8 Use of phosphate rocks as a source of P for crop plants in Tanzania

In Tanzania, phosphate rocks occur in various places. Such locations include Panda hills in Mbozi district (igneous PR), Sangu Ilola in Mpanda district (igneous), Ngualla in Chunya district (igneous), and Minjingu in Arumeru district (sedimentary/biogenic) (Van Kauwenbergh, 1991; Van Straaten, 1997, 2000). The deposits at Panda hill amount, to 370 million tons with a P_2O_5 content varying from 14 to 30% (Mchihiyo, 1991). The total estimated reserves of MPR for both soft and hard rock, is about 10 million tons whereas 3.3 million tons are of soft ore and 4.8 million tones hard ore (Van Straaten, 1997). The grade of the soft ore is between 20.4% to 25% P_2O_5 while that of hard ore is 24% P_2O_5. The MPR has a moderate to high neutral ammonium citrate solubility varying from 3.0% to 5.6% of P_2O_5 (Smithson *et al.*, 2001; Szilas, 2002). Due to its relative higher reactivity, commercial mining of soft Minjingu PR started in early 1960s and up to 1999 about 2.4 Mt of soft ore had been mined for agricultural production and research purposes (Szilas, 2002).

A comprehensive database on all the documented research results on MPR in Tanzania has been provided by Szilas (2002). Although many studies have confirmed that MPR is as good as water soluble P fertilizers when used under specific soil conditions, its effect, in most cases is inferior to TSP in the first year of application (Szilas, 2002). Szilas (2002) observed that from ten field experiments scattered in eight different AEZ in Tanzania, MPR proved to be a suitable substitute for TSP in acidic soils. The RAE was around 71% in the first year of application but increased in the second and third years of application to 90-100%. The lower effect of MPR in the first year was attributed to smaller amount of P released from MPR compared to TSP, immediately after application. This effect was higher in areas with moisture stress and high P fixation capacities. There is, therefore, a need to enhance its effectiveness in the first year of application particularly when dealing with annual crops.

Several studies have been conducted on amending the MPR with different materials in order to enhance the rate of P release and increase its agronomic effectiveness in the first year of application. These include use of partially acidulated MPR (Kimbi *et al.,* 1996), use of geological materials such as zeolites (Mnkeni *et al.*, 1994); use of pyrite (Kalumuna *et al.*, 1998) and use of farmyard manure and compost (Ikerra *et al.*, 1994; Mowo, 2000).

Since farmyard manure is not available to all farmers, research using GMs from agroforestry systems and local shrubs in combination with MPR is needed. The interactive effect of different GMs with MPR on MPR dissolution, different P pools, soil P adsorption capacity and other soil parameters that are closely related to P availability like soil pH, Al, Ca and organic acids is unknown in Tanzania. The influence of organic materials on MPR dissolution has been poorly researched

(Ikerra *et al.*, 1994; Kitua, 1997; Nabahungu, 2003) and in certain cases the increased P availability due to organic materials addition has been taken to mean enhanced P release from MPR when the two amendments are co-applied (Mowo, 2000). The increase in soil pH, exchangeable Ca, decrease in exchangeable Al and P adsorption characteristics caused by some organic materials do not favour the claim of enhancement of P release from MPR. The positive effects that are so far documented on enhancement of MPR dissolution could possibly be due to supply of other macro nutrients contained in organic materials that modify soil chemical and physical characteristics.

Integrated use of MPR and GM is possibly a viable option of maintaining soil organic matter and providing other macro elements that are essential for maintaining agricultural productivity. Such a strategy will possibly result in increase in maize yields. No research has been directed towards this goal at present. These knowledge gaps, therefore, form the core of this thesis.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Experimental trial site description

3.1.1 Location

The field study was conducted at the Magadu area of the Sokoine University of Agriculture (SUA) farm along the Mzinga–Morogoro road. The field trial site is located at 6°51′S and 37°38′E on a 3% slope, at an altitude of 530 masl.in agroecological zone (AEZ) E2. Incubation and pot studies were conducted in the soils laboratory and glasshouse of the Department of Soil Science at SUA, Morogoro, and at the soils laboratory of the Faculty of Agriculture and Applied Sciences of the Katholieke University of Leuven (Belgium).

3.1.2 Climate

The area has a sub-humid tropical type of climate and a bimodal rainfall distribution. The short and lighter rains are from October to January, with a peak in December, while the long rains start in February and end in May, with a peak in April. The average total annual precipitation is 892 mm per year. The wettest month is April when rainfall exceeds evapotranspiration. Total annual potential evapotranspiration is 1429 mm. The mean monthly air temperature is about 24.4°C. Mean maximum monthly air temperature ranges from 27.5° C during the coldest months to 32° C during the hottest months, while the mean monthly minimum air temperature ranges from 15.1 ° C during the coldest months to 21.5 °C during the hottest months. Figure 1 shows the mean monthly rainfall and

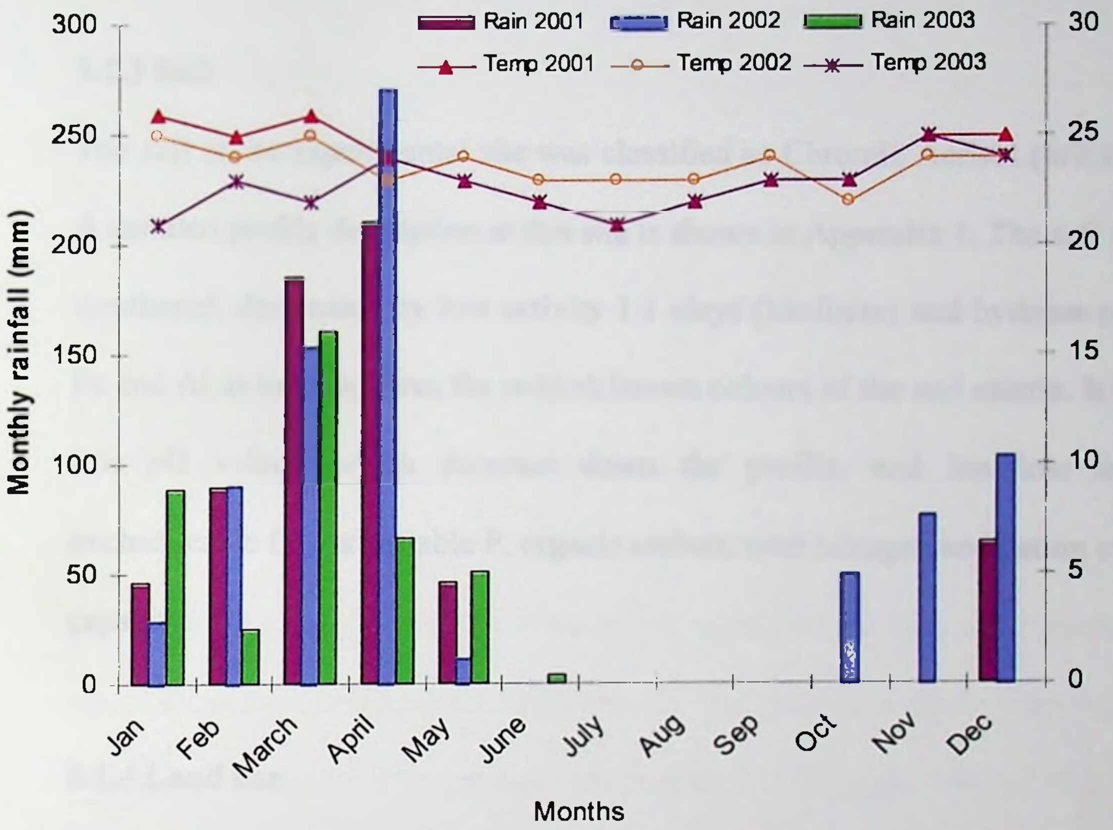


Figure 1. Monthly rainfall and temperatures during the experimental period in 2001 to 2003.

temperatures experienced during the research period from 2001 to 2003, when the field experiment was conducted.

3.1.3 Soil

The soil at the experimental site was classified as Chromic Acrisol (WRB, 1998). A detailed profile description at this site is shown in Appendix 1. The soil is highly weathered, dominated by low activity 1:1 clays (kaolinite) and hydrous oxides of Fe and Al as inferred from the reddish brown colours of the soil matrix. It has very low pH values, which decrease down the profile, and has low levels of exchangeable Ca, extractable P, organic carbon, total nitrogen and cation exchange capacity.

3.1.4 Land use

Small-scale farmers in the adjacent areas grow maize, cowpeas and sorghum. Maize grain yields are very low, ranging from 0.5 to 1.0 t ha^{-1} due to the low levels of plant nutrients, especially phosphorus, as manifested by the P deficiency symptoms. Use of inorganic and organic fertilizers is minimal.

3.2 Preparation of the trial site and soil sampling

The half hectare trial site, was cleared of all vegetation and raked. Twenty soil sub-samples were collected diagonally, from the 0-20 cm soil layer in the plot. Twenty sub samples were composited, mixed properly and air-dried for one week. Soil samples for chemical analysis and for incubation studies were ground and passed through a 2 mm sieve. Soils used for pot studies were sieved through a 6 mm sieve.

3.3 Soil analysis

Soil samples in dulicates were analysed for pH in a 1:2.5 soil:water suspension (McLean, 1965). Exchangeable acidity and Al were extracted by 1M KCl and determined titrimetrically using the method of McLean (1965). Organic C was determined by sulphuric acid-dichromate digestion and colorimetric determination of Cr^{3+} (Anderson and Ingram, 1993). Total nitrogen was determined by the Kjeldahl method (Bremner and Malvaney, 1982). Nitrate nitrogen was extracted using 2M KCl and determined by cadmium reduction (Dorich and Nelson, 1984), while ammonium was determined in the 2*M* KCl extract by the salicylate-hypochlorite colorimetric method (Anderson and Ingram, 1993). The sum of nitrate and ammonium gave the total inorganic nitrogen. Total soil P was determined by the method of Okalebo *et al.* (1993). Extractable P was determined using Bray-1 method (Bray and Kurtz, 1945).

In conjunction with the conventional Bray 1 method, the resin P method (Sibbesen, 1978) was used for determination of extractable P. In resin P extraction, 2.5g soils were shaken with deionized water containing one anion exchange resin bag (Dowex 1-x8 in HCO_3^- form). Phosphorus is desorbed from soil into water and transferred from the solution to the resin sink. The bag was removed from the soil suspension, washed, and shaken with 20 ml of 0.5 M HCl to recover the P from the resin. Phosphorus in the extract was measured colorimetrically at 880 nm by the ascorbic acid-ammonium molybdate method (Murphy and Riley, 1962). This method was used because resins extract the most labile P fractions which are highly correlated with plant available phosphorus (Nziguheba *et al.*, 1998). While most conventional chemical P extractants tend to alter soil chemical properties with the result that their efficiency varies from soil to soil, the resin P extraction does not alter soil properties (Sibbesen, 1978).

Exchangeable bases and CEC were determined using 1M NH_4OAc (pH 7) (Chapman, 1965). Free Fe and Al oxides concentrations were determined using dithionite-citrate-bicarbonate (Mehra and Jackson, 1960). Zinc and Fe were extracted by the DTPA method (Lindsay and Norvel, 1978) and determined using AAS. Particle size analysis was determined by the hydrometer method (Ghee and Bauder, 1986). All laboratory determinations were carried out in duplicates and means are reported.

3.4 Organic materials and MPR analysis

3.4.1 Criteria used in the selection of organic materials

(i) Farm Yard Manure

Farmyard manure (FYM) (referred to as manure in the text) is the most common organic material in the study area. It was selected due to its potential importance in improving soil fertility in the farming system. Although most farmers would like to use it, the stocking rate is too low to produce manure quantities enough for optimal crop production.

(ii) *Lantana camara* (L.)

This is an exotic shrub of the family *Verbanaceae*. The shrub is a common component of the natural bushes growing in the study area and is a serious exotic weed in high rainfall areas in Tanzania. Its propagation is through seeds. It has high nutrient content, especially of P and Mg and was selected due to its high nutrient content (Nziguheba *et al*, 2001) and its availability.

(iii) *Tithonia diversifolia (Hemsley A.* Gray)

This is a shrub of the family *Asteraceae,* commonly called Mexican sunflower. It is found along roadsides, riverbanks and hedges on farm boundaries in the humid and subhumid tropic of Africa, generally at elevations between 500 to 2000 m asl (Jama *et al*., 2000). It is easily propagated from cuttings or seeds and grows fast even under unfavourable conditions like low rainfall and poor soil fertility. It can produce one kg of dry biomass per linear metre annually (Sanchez and Jama, 2002). Tithonia is a good scavenger for nutrients and can accumulate high levels of nutrients, particularly N, P and K (Jama *et al*., 2000; Sanchez and Jama, 2002). Although it is abundantly found near farmers' fields in Tanzania, farmers do not use it despite its potential for soil fertility improvement, probably due to their ignorance of this potential.

(iv) *Gliricidia sepium*

This is a multipurpose tree species of the subfamily *Papilionoideae* in the family *Leguminoseae*. It has potential for soil improvement through biological nitrogen fixation. It is abundant in the study area. It was chosen because of its high nutrient content, particularly N and Ca.

3.4.2 Characterization of the organic materials and MPR

3.4.2.1 Organic materials

Fresh succulent green leaves (with rachis) of lantana, gliricidia and tithonia as GM were collected from the SUA botanical garden, washed thoroughly and chopped into small pieces. Partially decomposed FYM was collected from the unshaded SUA FYM storage area. The GM and FYM were oven dried at 70°C for 24 hours and ground to pass a 0.5 mm sieve. Sub samples were analysed for pH in water at manure: solution ratio of 1:5, and this extraction ratio was used so that enough free water would be available for pH determination, total N (Bremner and Mulvaney, 1982) and P, K, soluble and total C (Anderson and Ingram, 1993). Lignin was determined by the acid detergent fibre method (Van Soest, 1963) and total soluble polyphenols were extracted using 50% aqueous methanol with a tissue sample: extractant ratio of 0.1:50 g L^{-1}. The phenols were then analysed calorimetrically using the Folin-Ciocalteu reagent (Anderson and Ingram, 1993).

Extraction and measurement of light molecular weight organic acids (LMWOA) produced by different organic materials was done according to the method of Bolan *et al.* (1994). This method involved extraction of organic materials with distilled water at a 1:100 organic material:water extraction ratio. The extracts were then, centrifuged at 6000 rpm for 30 minutes and filtered through 0.45 millipore filters. LMWOA were mesuared on a Shimadzu LC 6A high perfomance liquid chromatography (HPLC) equipped with a modified C18 column containing silicon. Peaks for the LMWOA were detected at a wavelength of 210 nm and organic acids in the extracts were identified by comparison with retention time obtained for pure standard organic acids. Peak heights were measured by using Shimadzu SPD-10AVP detector, and these peak heights were used to quantify the released organic acids.

3.4.2.2 Minjingu phosphate rock

A sample of Minjingu PR, obtained from the Minjingu mine in Arusha, was sieved through a 0.15 mm sieve. It was analysed for pH, Bray-1 P, total P, CaO, $CaCO_3$ equivalent and neutral ammonium citrate solubility (NAC). The pH was measured in 1: 2.5 MPR-H_2O mixtures (McLean, 1965). Neutral ammonium citrate solubility was analysed as described by McClellan and Gremillion (1980). Calcium carbonate was determined by the acidification-titration procedure (Loeppert and Suarez, 1996), and its equivalence computed according to Tisdale *et al.* (1993). Cacium oxide content was determined by the wet digestion method using HF-H_2SO4-$HClO_4$ (Hossner, 1996).

For the current study, experiments were conducted using the above-mentioned characterized organic and inorganic amendments. The experiments included incubation studies which aimed at investigating the processes underlying P availability from organic materials and MPR without a crop, the glass-house experiments which further evaluated similar processes and maize dry matter yields during application and residual effects phase under controlled environment, and a field experiment that examined the influence of one organic material combined with inorganic fertilizers on similar processes and maize yields during application and residual effect phases, for three seasons. The details of these experiments are given below.

3.5 Incubation experiments

3.5.1 Effect of light molecular weight organic acids on MPR dissolution

This experiment was carried out to determine the effect of analytical grade oxalic acid concentration, on solution pH and P release from MPR. Different concentrations namely 0, 0.007, 0.014, 0.028, 0.06 and 0.1 M $L^{-1}$of analytical grade oxalic acid were mixed with 1 g of MPR and incubated at 28 °C for three days. Oxalic acid was used because it was identified as the most dominant organic acid produced by the organic materials under study (section 3.4.2.1). After incubation, the samples were centrifuged at 6000 rpm for 30 minutes. The solutions were used for the determination of P and pH using the method of Murphy and Riley (1962) and pH meter, respectively.

3.5.2 Effect of incubation periods on the concentrations of different light molecular weight organic acids

One gramme soil sample (Chromic Acrisol) portions were weighed into 50 ml bottles and mixed thoroughly with finely ground 0.9 g of manure, tithonia, lantana or grilicidia and incubated for 0, 14 and 28 days. After incubation the samples were refrigerated for 24 hrs. Samples were extracted with 100 ml of dionized water by shaking them for 30 minutes on an end-over-end shaker, and centrifuged at 6000 rpm (Bolan *et al.*, 1994). Extracts were filtered through 0.45 millipore filters and their contents of LMWOA were determined according to the method of Bolan *et al.* (1994) as briefly explained in section 3.4.2.1.

3.5.3 Effect of organic materials on MPR dissolution

This incubation study was carried out to investigate the effects of farmyard manure, gliricidia, lantana and tithonia on MPR dissolution. Two sets each having two hundred grams of the soil passed through the 2 mm sieve were mixed with organic materials and MPR at the rates of 2.27 g kg^{-1} (equivalent to 5 t ha^{-1}), and 0.30 g P kg^{-1} for organic materials and MPR, respectively. All organic materials were combined at an equal rate of 2.27 g kg^{-1} (equivalent to 5 t ha^{-1}) with MPR at 0.30 g P kg^{-1} without considering their P contents. The mixtures were placed in 30 ml plastic containers and the treated soil samples were moistened to 80% field capacity (Klute, 1986). The containers were covered with perforated aluminium foil to allow aeration. Samples were incubated in triplicate at 27°C for 112 days. Sub samples weighing about 50 g were withdrawn at 0, 1, 7, 14, 28, 56, and 112 days after initiation of incubation. Whenever the first set of soil was finished, sampling was done on the second set. At each sampling time, the sub samples that were withdrawn from the incubation containers were air-dried, crushed and analysed for soil pH, exchangeable Al and 0.1M NaOH-extractable P. The experiment was arranged in a completely randomized design (CRD) with three replications, and with the following treatments:

Treatment 1=Control (Soil alone); Treatment 2=Soil + MPR; Treatments 3=Soil + manure; treatment 4=Soil + tithonia; Treatment 5=Soil + lantana; Treatment 6=Soil + gliricidia; treatment 7=Soil + manure + MPR; Treatment 8=Soil + tithonia + MPR; Treament 9=Soil + lantana + MPR; Treatment 10=Soil + gliricidia + MPR.

Dissolution of MPR was determined by the 0.1 M NaOH method (Mackay *et al.*, 1986) besed on the observations reported by Mackay *et al.* (1986) and Wright *et al.*, (1992), apatite group minerals had limited solubility in 0.1 M NaOH. The difference in NaOH-extractable P between a treated PR and untreated PR gives a better estimate of phosphate rock dissolution than the Bray 1 extraction method because the latter tends to overestimate MPR dissolution (Wright *et al.*, 1992). The method includes pre-washing of the soil with NaCl to remove excess Ca in order to avoid precipitation of $Ca(OH)_2$ and re-adsorption of the dissolved P in the succeeding NaOH extraction. The 0.1M NaOH extractable P data at every sampling period were used to calculate the dissolution of MPR in soil (Mackay *et al.*, 1986). For the samples taken at 14 and 112 days of incubation, soil inorganic P (P_i) and organic P (P_o) fractions were determined by sequential extraction with $NaHCO_3$, NaOH and HCl by the method of Tiessen and Moir (1993). This was done to gain an insight into the effect of MPR fertilization on P dynamics.

3.5.4 Effect of organic materials on phosphorus adsorption

This incubation study was undertaken to investigate the effects of the above-mentioned organic materials on phosphorus adsorption by the Chromic Acrisol.

3.5.4.1 Incubation

Two hundred grams of soil in a 500 ml wide mouth plastic container were mixed with farmyard manure, gliricidia, lantana or tithonia each at rates of 2.27 g kg^{-1}or 5.54 g kg^{-1} (equivalent to 5 or 10 t ha^{-1}) on dry matter basis (DMB) and covered with a lid. The treatments were replicated three times and laid out in a completely randomised design. The amounts of organic materials to be mixed with the soil calculated based on soil bulk density of 1.1 g cm^{-3}. The soil organic material mixtures were each moistened to 80% field capacity (Klute, 1986) with distilled water and incubated in triplicates at 25-26°C for twelve weeks. The samples were aerated by opening the lids every two days. After two and twelve weeks, the soil samples were withdrawn from the incubating plastic containers and air-dried at room temperature for four days after which soil pH and exchangeable Al were determined. Dried soil-organic material mixtures described above were used to determine the phosphorous adsorption isotherms according to the method of Fox and Kamprath (1970).

3.5.4.2 Development of phosphorus adsorption isotherms

Three-gram of the incubated soil-organic material mixture from Section 3.5.4.1 were equilibrated with 30 ml of 0.01 M $CaCl_2$ solution containing one of the six concentrations of KH_2PO_4-P (0, 10, 20, 30, 40, 50 or 60 mg P L^{-1}), equivalent to (0, 100, 200, 300, 400, 500 or 600 mg P kg^{-1}). Three drops of toluene were added to each of the extraction bottles to arrest microbial activity. Samples were equilibrated in duplicate at a room temperature (26-27°C) for six days. During this incubation time, the samples were shaken twice daily, each time for one half hour, at 175 rpm. The samples were filtered through Whatman No. 42 filter papers. The filtrates were analysed for P after colour development according to the method of Murphy and Riley (1962). Sorbed phosphorus was taken as the difference between the P added and P that was in solution at equilibrium. Data for every replicate was fitted into the Langmuir or Freundlich adsorption equations using the SAS program procedure for non-linear regression (SAS Institute, 1995) to determine the P adsorption parameters.

The Langmuir adsorption equations used was of the form:

$x/m = kbC/1 + bC$

where:

x/m = sorbed P, mg kg^{-1} (weight of adsorbate per unit weight of adsorbent)

C = P in equilibrium solution, mg P L^{-1}

b = adsorption maximum (P-max), mg P kg^{-1}

k = constant related to adsorption affinity, L mg^{-1}

The P max (b) and (k) values were used to calculate the standard phosphorus requirement (SPR) at solution P concentration of 0.2 mg P L^{-1} as follows:

$SPR = P\ max * k*0.2 / (1 + P\text{-}max* 0.2)$.

The Freundlich equation was:

$x/m = bC^{1/n}$

where:

x/m = sorbed P, mg kg^{-1}(weight of adsorbate per unit weight of adsorbent)

C = P in equilibrium solution, mg P L^{-1}

b and n = constants related to adsorption affinity.

The experiment was in a CRD, with five treatments replicated three times, namely: Treatment 1=Control (soil alone); Treatment 2=Soil + manure; Treatment 3=Soil + tithonia; Treatment 4=Soil + lantana; Treatment 5=Soil + Gliricidia.

3.6 Pot experiments

Three pot experiments were carried out in order to: (1) establish the response of maize to P applied from both MPR and TSP on the Chromic Acrisol (2) determine the effects of organic materials, MPR and TSP on soil pH, exchangeable Ca, exchangeable Al and resin P, and on P and Ca uptake and maize dry matter yields (DMY) and (3) to determine the residual effects of organic materials, MPR and TSP on soil pH, Ca and Al and on P and Ca uptake and maize DMY. This information would enable the selection of the best performing organic material to be adopted in the subsequent field experiment.

3.6.1 Effect of MPR and TSP applied to a Chromic Acrisol on maize dry matter yields

The rationale for carrying out this pot experiment was to obtain the P rate from the steep portion of the response curve (Terman, 1974) that could be used in conjunction with organic materials in subsequent pot experiments. Inorganic fertilizers, including TSP, were initially ground and sieved through 100 mesh sieve. Four kilogram of air-dry surface soil (0-20 cm) sample portions were spread on a plastic sheet and thoroughly mixed by hand with TSP or MPR at rates of 0, 10, 20, 50, 75, 100, 200 or 300 mg P kg^{-1} soil. Fertilizer amounts were calculated based on soil weight at a sampling depth of 15 cm and a bulk density of 1.1 g cm^{-3}, and the amounts of both TSP and MPR used was calculated based on the P contents of 13 and 20.5% P for MPR and TSP, respectively.

Soil-fertilizer mixtures were placed into 5 kg plastic pots and moistened to 80% field capacity using distilled water. The field capacity (FC) of the experimental soil was first determined by filling three five-kg plastic pots with 4 kg of soil each, saturating the soil and leaving it to drain for 72 hrs. Then the average value representing 80% of the amount of water added to the pots to bring the soil to FC was the one applied to the soil-fertilizer mixtures. Thereafter, four maize plants (*Zea mays* (L.) var TMV-1 were sown in each pot. Subsequently, pots were watered to maintain the soils moist. Plants in each pot were thinned to two per pot four days after emergence. Pots were rotated weekly to minimize positional effects.

In addition to the fertilizer treatments described above, all pots received basal N, K, Zn and Cu fertilizer at 160, 50, 5 and 5 mg kg^{-1} soil as ammonium sulphate [$(NH_4)SO_4$], potassium sulphate (K_2SO_4), zinc sulphate ($ZnSO_4$) and copper sulphate ($CuSO_4$), respectively. This was done in order to avoid limitation of other nutrients, besides phosphorus, on maize DMY. Fertilizer N was applied in splits, one third of the amount at planting and the remaining two-thirds at 18 days after planting. The other fertilizer sources were mixed with the soil at planting time. The experiment was laid out in a CRD, replicated three times. The maize plants were harvested after six weeks. At harvest, the plants were cut with a knife at 2 cm above the soil surface, washed and dried at 70° C in an oven to constant weight.

3.6.2 Effect of different organic materials, MPR or TSP on soil characteristics, Ca and P uptake and maize dry matter yields

This pot trial was carried out to determine the best organic material which, when combined with the optimum P rate obtained from the experiment in section 3.6.1, would give the best crop performance. Inorganic fertilizers were prepared as in section 3.6.1. Organic materials were ground to pass a 1 mm sieve. Appropriate amounts of TSP and MPR were thoroughly mixed with 4 kg air-dried surface soil (0-20 cm) portions and 2.27 g kg^{-1} soil equivalent to 9.0 g of organic material pot^{-1} of the four organic materials were added. In the inorganic fertilizer treated soils, MPR or TSP, were added at 100 mg P kg^{-1} soil equivalent to 400 mg P pot^{-1}. In the treatments where TSP or MPR were combined with the organic materials, P application rates from TSP or MPR took into consideration the P contents of different organic materials. The total nutrient contents from organic materials applied in every treatment are shown in Table 1. At the application rate of 2.27 g kg^{-1} equivalent to 5 t ha^{-1} of organic materials, total macronutrient contents in the organic materials (N, P, K, Ca) varied from one treatment to the other depending on the type of organic material. Total N ranged from 40 mg N kg^{-1} in FMY to 91 mg N kg^{-1} in tithonia. Phosphorus ranged from 5 mg P kg^{-1} in lantana to 11 mg P kg^{-1} in tithonia. Potassium ranged from 43 mg K kg^{-1} in manure to 92 mg K kg^{-1} in tithonia. Calcium ranged from 20 mg Ca kg^{-1} in manure to 46 mg Ca kg^{-1} in tithonia. Since basal application of N and K was carried out in all treatments (section 3.6.1), differences in crop perfomance would mainly be attributed to P.

Table 1. Total contents of N, P, K and Ca of the organic materials applied to the soil for the pot experiment

Type of organic material	Nutrient	Rate (t ha^{-1})	Contents (%)	Amounts (mg kg^{-1})	Nutrient applied (kg ha^{-1})
Manure	N	5	1.76	40	88
Lantana	N	5	3.00	68	150
Gliricidia	N	5	3.70	84	185
Tithonia	N	5	4.00	91	200
Manure	P	5	0.43	10	22
Lantana	P	5	0.21	5	11
Gliricidia	P	5	0.22	5	11
Tithonia	P	5	0.46	11	23
Manure	K	5	1.87	43	93
Lantana	K	5	2.78	63	139
Gliricidia	K	5	2.61	59	131
Tithonia	K	5	4.06	92	20
Manure	Ca	5	0.89	20	45
Lantana	Ca	5	1.10	25	55
Gliricidia	Ca	5	1.16	26	58
Tithonia	Ca	5	2.03	46	105

The total P content from either TSP or MPR when combined with different organic materials was 400 mg P pot^{-1}. The experiment was laid out in a CRD and treatments were replicated three times.

Treatments were: Treatment 1=Control for P, Treatment 2=Manure, Treatment 3=Tithonia, Treament 4=Lantana, Treatment 5=gliricidia, Treament 6=TSP (100 mg P kg^{-1}), Treatment 7=MPR (100 mg P kg^{-1}), Treament 8=MPR + manure, Treatment 9=MPR + tithonia, Treatmernt 10=MPR + lantana, Treatment 11=MPR + gliricidia, Treatment 12=TSP + manure, Treatment 13=TSP + tithonia, Treatment 14=TSP + lantana, Treatment 15=TSP + gliricidia.

The mixing procedure of inorganic and organic fertilizers with soil (including basal fertilizers), filling of pots with soil-fertilizer mixtures, watering, planting and harvesting of the maize plants was done as described in section 3.6.1. The dried maize biomass was ground to pass a 1 mm sieve and used for P and Ca uptake determinations by multiplying %Ca or %P in the maize plants by the maize DMY. Soil sampling was done at harvest time to determine, pH, exchangeable Al, resin P and exchangeable Ca.

3.6.3 Residual effect of different organic materials, MPR or TSP on soil characteristics, Ca and P uptake and maize dry matter yields

This pot experiment was conducted to determine the residual effect of organic materials, MPR or TSP on soil pH, Ca and Al, and P, Ca uptake and maize DMY. After harvesting the pot experiment described in section 3.6.2, all pots were emptied and the soil was spread on plastic sheets according to treatments. Maize roots were carefully removed and the soil was left to dry for one week in the glasshouse. After one week the same basal fertilizers (but not P) as described in section 3.6.2 were added to the dried soil. The soil was re-potted and watering, planting and harvesting of the maize plants was done as described in section 3.6.2. Similar procedure to that in section 3.6.2 was followed to get residual P and Ca uptake. Soil sampling was done at harvest to determine, pH, Ca, Al and resin P.

3.7 Field experiment

In section 3.6.2, it was observed that manure gave the highest maize DMY followed by tithonia. Growth conditions under glasshouse environment differ greatly from those under field conditions. Therefore, it was important to evaluate the effect of MPR or TSP amended with different rates of organic materials on P availability, soil pH, Ca and Al, and P, Ca uptake and maize yields under field conditions. Although the FYM tested was the best in increasing P availability and maize DMY in pot experiments, tithonia was chosen for use in the field experiment because of the high heterogeneity that is normally associated with different FYM samples as would be encouterd in different farms. The quality of FYM varies with age, animal feeds, storage conditions, kraal management and location (Wickama and Mowo, 1999). All these variables would result in low reproducibility of the results obtained and hence problems in making recommendations as compared to tithonia whose quality is more or less constant.

3.7.1 Layout and treatments

The trial was initiated in February 2001 and was conducted for three years during the long rain periods. Twelve treatments, replicated three times, in a completely randomized block design, were employed. Treatments included tithonia at 0, 2.5, 5.0 and 7.5 t ha^{-1} DMB, MPR or TSP alone at 80 kg P ha^{-1}, and TSP or MPR at 40 kg P ha^{-1} in combination with tithonia at 2.5, 5.0 or 7.5 t ha^{-1}. These treatments were imposed during each of the first and second seasons (in 2001 and 2002) and the third season (in 2003) was used for observing residue effects.

Experimental treatments were randomly allocated to plots of gross area 4 x 7 m. The net plot measured 18.9 m^2, with 7 inner rows each having 13 plants at a spacing of 30 cm along the row. Two outer rows were used for destructive sampling for the determination of DMY and P and Ca uptake for the second season (2002). The five inner rows were harvested for maize grain yield determination.

Basal fertilizers of N and Zn were applied in all plots at 80 and 5 kg ha^{-1}, respectively. Since tithonia has a high content of K (4%) it was considered unnecessary to add inorganic K to all tithonia treated plot. Potassium was applied at a rate of 50 kg K ha^{-1} in plots which did not receive tithonia, except in season 3. The recommended application rates for N and P on Chromic Acrisol is 60 and 80 kg ha^{-1}, respectively. Potassium is normally considered non-limiting for this Chromic Acrisol and usually is not applied. However, in this study, K was applied to make sure that it was non-limiting, and to match the high K contents that were brought in with the tithonia treatments. This, therefore, implies that both N and K were non-limiting in all treatments. Variations in maize yields would be caused mainly by P because P was below the recommended rate (80 kg P ha^{-1}) in all treatments except in sole MPR or TSP. The fertilizer sources were SA $(NH_4)_2SO_4$, muriate of potash (KCl) and zinc sulphate($ZnSO_4.4H_2O$). Fertilizer sources for K and Zn were broadcasted and incorporated into the plots at planting time.

In plots that had not received tithonia, one third of the nitrogen fertilizer was applied at planting time and the remaining two thirds were top-dressed six weeks after planting. On plots that received tithonia, no fertilizer nitrogen was applied at planting. In these plots two thirds of the N fertilizer was applied six weeks after planting. This was done on the assumption that tithonia (4% N) would release 50% of its N (Palm *et al.*, 2001), which would be enough for early crop establishment and hence eliminate the need of applying nitrogen at planting time. The total amounts of N, P and K added via amendments, on dry matter basis, for different treatments, are shown in Table 2. Triple super phosphate (TSP) and MPR fertilizers were applied at planting time. Triple super phosphate was banded along the rows while MPR was broadcasted on plot surfaces and incorporated using hand hoes. Two application methods were used because previous studies in the same area had shown that the best results were obtained when MPR was broadcasted and TSP banded.

3.7.2 Planting

Two maize (*Zea mays* L.) seeds var TMV-1 were planted per hill at a spacing of 75 by 30 cm and later thinned to one plant per hill 10 days after planting. Gap filling was done 7 days after germination. Gross plant population was 117 plants per plot.

In the first season, maize plants experienced a drought four weeks after germination, which resulted in poor plant growth, although the plants eventually managed to survive until when it rained again. In the second growing season, there was drought at maize grain filling stage (60 days after planting), which reduced the maize grain yields. In the third season, there was severe drought, which caused total crop failure. Dry matter yield was recorded at tasselling stage.

Table 2. Description of treatments used and amounts of N, P and K added from the different treatments in the field experiment

Treatment	Inorganic amendment			Organic amendment			Total added		
	N[1]	P	K[2]	N	P	K	N	P	K
	--------------------	--------------------	--------------------	--------------------	--------(kg ha^{-1})--------	--------------------	--------------------	--------------------	
Control (-P)	80.0	0.0	50.0	0.0	0.0	0.0	80.0	0.0	50.0
Tithonia 2.5 t ha^{-1} (T2)	53.3	0.0	0.0	100.0	11.5	101.5	153.3	11.5	101.5
Tithonia 5 t ha^{-1} (T5)	53.3	0.0	0.0	200.0	23.0	203.0	253.3	23.3	203.0
Tithonia 7.5 t ha^{-1} (T7)	53.3	0.0	0.0	300.0	34.5	304.5	353.3	34.5	203.0
MPR (P 80)	80.0	80.0	50.0	0.0	0.0	0.0	80.0	80.0	50.0
TSP (P 80)	80.0	80.0	50.0	0.0	0.0	0.0	80.0	80.0	50.0
MPR (P 40) + T2	53.3	40.0	0.0	100.0	11.5	101.5	153.0	51.5	101.5
MPR (P 40) + T5	53.3	40.0	0.0	200.0	23.0	203.0	253.0	63.0	203.0
MPR (P 40) + T7	53.3	40.0	0.0	300.0	34.5	304.5	353.0	74.5	304.5
TSP (P 40) + T2	53.3	40.0	0.0	100.0	11.5	101.5	153.0	51.5	101.5
TSP (P 40) + T5	53.3	40.0	0.0	200.0	23.0	203.0	253.0	63.0	203.0
TSP (P 40) + T7	53.3	40.0	0.0	300.0	34.5	34.5	353.3	74.5	304.5

(P 80) = P applied from sole MPR or TSP was at 80 kg P ha^{-1}; (P 40) = P applied from either MPR or TSP at 40 kg P ha^{-1}; [1] = N was applied in form of SA; 2 = K was applied in form of muriate of potash; 3 = All nutrients are on DMB

3.7.3 Weed and pest control

Hand weeding was used to control weeds twice per growing season. Maize stalk borers (*Busceolla fusca*) were controlled using Thiodan (endosulfan 35% emulsifiable concentrate) sprayed at 8 weeks after planting once per growing season. At grain filling stage, in all seasons, there was heavy termite infestation on the maize plants that coincided with drought periods. To reduce this, soils in all plots were sprayed twice with Gammalin (20% emulsifiable concentrate). In the second year, this infestation resulted to almost 70% of all the maize plants falling to the ground. It was, therefore, necessary to raise all the fallen maize plants and support them by stalks. Rats were a problem at planting time in the first year but this problem was subsequently controlled by the application of a zinc phosphide based rodenticide (mixed with maize bran) around the experimental plot.

3.7.4 Soil sampling

During the first and second growing seasons, soil sampling was done at 45 after planting (near tasselling) and at 110 days after planting (at harvest time). Due to lack of rains in the third season, maize plants dried out before harvesting time and therefore soil sampling was done only at 45 days after planting (DAP). Sampling involved taking ten soil sub-samples (0-20 cm depth) at random, between maize plants in the net-plot area, of every treatment using a calibrated knife. The sub-samples were combined to form one composite sample for every treatment. Composite soil samples were air-dried, ground to pass a 2mm sieve and used for the determination of pH, Ca, Al and resin P. In second season, phosphorus fractions, P adsorption isotherms and adsorption characteristics, and LMWOA were determined on the samples taken at 45 DAP.

3.7.5 Plant sampling

Plant sampling was done in the second and third season and at 45 DAP and at ear leaf formation in the second season. To determine DMY and nutrient uptake, six plants per plot from the outer rows, outside the net plot, were randomly selected using random numbers and cut a few centimeters above the soil surface. The below ground plant stumps were carefully uprooted. Both the below- and above-ground maize plant parts were washed with distilled water, cut into small pieces and oven-dried at 70°C. After determination of DMY, they were ground to pass through 1 mm sieve and used for P and Ca determination. Nutrient uptake was obtained by multiplying %P or %Ca by DMY.

At ear formation stage, four maize leaves, opposite the first cob were randomly selected from the net plot area and cut with a knife. These leaves were washed with distilled water, dried at 70°C, ground to pass a 1 mm sieve and analysed for P and Ca contents. At harvest time during the first and second seasons, maize cobs were shelled; moisture content and grain weights were determined using an electronic moisture meter and spring balance, respectively. Due to lack of rains in the third season, plants died before ear formation and only dry matter yields were determined at 45 DAP.

3.8 Statistical and mathematical calculations

3.8.1 Statistical analysis

Analysis of variance was conducted using the general linear model procedure (GLM) of SAS (SAS Institute, 1995) to compare treatment effects at $P<0.05$, of the variables studied. Wherever significance is mentioned in the text it applies to 0.05 probability. Means were compared using the Duncan's New Multiple Range Test (DMRT) or, where appropriate, the single degree of freedom orthogonal contrasts were used. The P adsorption data was analyzed using the SAS statistical package according to the non-linear (NLIN) procedures for Langumuir and Freundlich (SAS Institute, 1995) to obtain the adsorption parameters. The means for the adsorption parameters were used to plot out the adsorption isotherms. Correlation analysis for the adsorption data with other variables was done by the SAS, PROC CORR procedure (SAS Institute, 1995).

3.8.2 Mathematical calculations

3.8.2.1 Relative agronomic effectiveness

The Relative Agronomic Effectivenes (RAE) of MPR compared to TSP was calculated as:

$RAE = (Y_{MPR} - Y_{control}) / (Y_{TSP} - Y_{control}) \times 100$

where :

Y_{MPR} = Maize grain yield from the MPR treatment at 80 kg P ha^{-1}

Y_{TSP}= Maize grain yield from the TSP treatment at 80 kg P ha^{-1}

$Y_{control}$ = Maize grain yield from the control treatment (-P, +N, +K)

3.8.2.2 Phosphorus recovery

Apparent phosphorus recovery (Pr) of applied fertilizers and organic material applied was calculated as:

Pr = (P uptake in treated soil – P uptake in control soil) / (P applied) x 100

The assumption underlying this calculation is that the quantity of P absorbed by plants from a fertilized plot in excess of the quantity absorbed from control treatment is derived entirely from the fertilizer. Since this is not an entirely true assumption the term apparent P recovery is used, rather than actual “P recovery.”

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Characterization of the materials used in the current study

4.1.1 Properties of the Magadu soil

Some physico-chemical characteristics of the surface (0–20 cm) soil layer and profile description of the Magadu soil are given in Table 1 and Appendix 1, respectively. The soil had a very strongly acid reaction, with low available P, low exchangeable Ca and a moderate degree of aluminium saturation. Further, the soil had low levels of total N, organic matter and low cation exchange capacity (Table 1), indicative of a low soil fertility status (Euroconsult, 1989; Landon, 1991). Based on the profile description and profile analytical data in Appendix 1, the soil was classified as Chromic Acrisol (WRB, 1998) taking into account the presence of the Bts horizon, reddish to yellowish colours and the CEC of the Bts horizon.

The very strong acid reaction of the soil, low status of exchangeable bases, and low cation exchange capacity could be attributed to extensive weathering of the soil, as evidenced by the presence of red to yellow colors in the profile, dominance of kaolinite type of clay and the low percent base saturation.

This soil was deficient in P for maize production, based on the critical level of Bray 1 P of 25 mg P kg^{-1} for most Haplustults in SUA farm as suggested by Singh *et al.* (1977). The low soil available P could be attributed to the low inherent P in the soil's parent material, continual P uptake or removal by plants without concurrent replenishment, transformation of the P into forms not available to plants, and the

low organic matter content. The transformation of the P added to soil through weathering, mineralization of organic amendments and P from inorganic fertilizers into forms not available to plants could have been enhanced by high activity of Al^{3+} and Fe^{3+} in the soil solution as evidenced by the presence of significant amounts of hydrous oxides of Al and Fe. The Al and Fe and their hydrous oxides have very high affinity for phosphate ions (Bohn *et al.*, 1979) and this happens under acidic soil reaction.

At such low soil pH the solubility of Fe and Al is high and the soil is dominated by hydrous oxides of Fe and Al (Table 3). Consequently, phosphorus is precipitated as Al and Fe phosphate and is also adsorbed on oxide surfaces, thereby making it unavailable to plants as described in section 2.3.2.1.

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Table 3. Some physicochemical properties of the topsoil (0-20 cm) of the experimental site at Magadu, Morogoro, Tanzania

Parameter (unit)	Magnitude	Rating	Reference
PH $_{(H2O)}$	4.8	very acidic	Landon (1991)
Organic C (g kg^{-1})	9.9	Low	Landon (1991)
Total N (g kg^{-1})	0.9	Low	Landon (1991)
Inorganic N (mg kg^{-1})	6.8	-	-
Extractable P (mg kg^{-1})			
Bray 1	6.4	Low	Singh *et al.* (1977)
Resin	4.1	Low	Landon (1991)
Olsen	3.9	Low	Singh *et al.* (1977)
Exch. Bases (cmol (+) kg^{-1})			
Ca	1.80	Low	Landon (1991)
Mg	1.34	Medium	Landon (1991)
K	0.53	Medium	Landon (1991)
Na	0.05	-	-
Base saturation (%)	46		-
CEC (cmol (+) kg^{-1})	12.5	Low	Landon (1991)
Exch. Acidity (cmol (+) kg^{-1})	2.1	-	-
Al	1.6	-	-
H	0.5	-	-
Micronutrients (mg kg^{-1})			
Zn	1.04	Low	Lindsay & Norvel (1978)
Fe	60.69	Very high	Lindsay & Norvel (1978)
Mn	71.63	Very high	Lindsay & Norvel (1978)
Cu	1.23	Adequate	Lindsay & Norvel (1978)
Oxides			
Free Fe_2O_3 ^{1} (%)	7.70	-	Szilas (2002)*
Al_2O_3^{1} (%)	0.12	-	Szilas (2002)*
Goethite^1	5.00	-	Szilas (2002)*
Particle size distribution (%)			
Sand	32	-	-
Silt	13	-	-
Clay	55	-	-
Textural class	Clay	-	-
Clay type	Kaolinite	-	-

* = Source: Szilas (2002)

4.1.2 Characteristics of the organic materials used in the current study

4.1.2.1 General chemical characteristics

Some chemical characteristics of the organic materials (farmyard manure, lantana, gliricidia and tithonia) used in the current study are given in Table 4.

Total nitrogen ranged from 1.66 to 4.0%, and was in the order tithonia >gliricidia>lantana>farmyard manure. Organic carbon ranged from 34.6 to 46.0%. Farmyard manure had the lowest amount of %C while gliricidia had the highest. The C:N ratio ranged from 10:1 in tithonia to 20:1 in farmyard manure while lantana and gliricidia had similar, intermediate values.

Total phosphorus ranged from 0.21% to 0.46%. Tithonia contained the highest amount of total P but this was somehow similar to that of farmyard manure. Gliricidia and lantana had 50% of the total P of tithonia. The ratio between soluble carbon to total phosphorus was narrowest in farmyard manure and widest in gliricidia and the order in this ratio, from the widest to the narrowest, was: gliricidia>lantana>tithonia>manure. Total K and Ca ranged from 1.87 to 4.06 and 0.89 to 2.03%, respectively. Both total K and Ca were highest in tithonia while lantana and gliricidia has similar values while farmyard manure having the lowest Ca levels.

Lignin content varied between 7.22 and 11.95%, tithonia having the lowest while the other organic materials had similar values. With the exception of farmyard manure, which had 0.05%, all organic materials had similar amounts of polyphenols, which were within a narrow range of 3.13% for gliricidia to 3.48% for lantana.

Table 4. Some chemical characteristics of the organic materials used in the present study

Material	pH (H$_2$O)	N	P	K	Ca	Mg	C	Csol	L	PP	C:N	L:P P	Csol:TP
						%							
FYM	8.50	1.66	0.43	1.87	0.89	0.59	34.61	1.21	11.51	0.05	21	230	3
Lantana	6.60	3.00	0.21	2.78	1.10	0.53	43.63	2.69	11.41	3.48	14	3.27	13
Gliricidia	5.70	3.70	0.22	2.61	1.16	0.56	47.09	3.37	11.95	3.13	13	3.81	15
Tithonia	6.90	4.00	0.46	4.06	2.03	0.64	41.42	2.65	7.22	3.17	10	2.27	6

Csol=soluble carbon, L=Lignin, PP = polyphenols, Csol:Tp = soluble carbon: total P. All values are means of two laboratory replications.

According to Palm *et al.* (1997), high quality organic materials have N>2.5%, P>0.24%, lignin<15% and polyphenol<4%. Based on these critical values, manure had low N but high P content. Lantana and gliricidia had P contents less than the critical P value while their N contents were above the critical value. The P and N contents of tithonia were all above the critical values. The threshold C:N and soluble carbon to total phosphorus ratios for fast decomposition and net P mineralization are 20:1 and 30:1, respectively (Palm *et al.*, 1997; Nziguheba *et al.*, 2000). Based on these critical values, all the organic materials used would undergo fast mineralization.

In addition to N and P, tithonia had the highest Ca, Mg and K contents. This implies that besides improving soil fertility through N and P addition, it has also the potential for ameliorating soil acidity. Decomposition of tithonia will release Ca and Mg, consequently causing an increase in pH. This will then reduce the activity of Fe^{3+} and Al^{3+}, which is a problem in this Chromic Acrisol.

The high nutrient content of tithonia compared to that of other green manures is due to its higher capacity in retrieving nutrients from the soil (Jama *et al.*, 2000). The mechanism which contribute to the high capacity to retrieve nutrients by tithonia may include mycorrhizal associations (Jama *et al.*, 2000). Values of macronutrient contents similar to those obtained in the present study have been reported by Gachengo *et al.* (1999), Phan Thi Cong, (2000), Nziguheba *et al.* (2000) and Baltazary (2002). Jama *et al.* (2000) reported that the primary macronutrient contents in tithonia could range from 3.1 to 4.0, 0.24 to 0.56, 2.7 to

4.8%, for N, P and K, respectively. The nutrient contents in tithonia may vary slightly depending on the plant age, plant part, soil fertility and agro ecological conditions. Palm *et al.* (2001) reported that nutrient contents in tithonia are higher in young plant parts before flowering. This would, then, be the best stage to use the plant material as green manure.

4.1.2.2 Light molecular weight organic acids

The concentrations and properties of the light molecular weight organic acids (LMWOA) contained in the experimental materials and their aluminium complexation constants are presented in Table 5 and Appendix 2, respectively. A variety of organic acids were identified in the organic materials whereas in the soil only small amounts of oxalic acid were detected. All types of the investigated LMWOA were detected in various concentrations in tithonia and lantana green manures. The conentrations of organic acids extracted from the tithonia green manure were relatively higher than those from the other green manures and FYM. Generally, the conentrations followed the trend: tithonia>lantana>gliricidia>FYM. Certain LMWOA like formic, malonic, citric and tartaric acids were not detected in farmyard manure samples, while succinic acid was not detected in gliricidia. Oxalic acid was the most dominant organic acid, followed by tartaric and formic acids in all GM materials, tithonia having the highest concentrations of these acids. The oxalate concentration obtained in the present Chromic Acrisol is within the range of values reported by Hue *et al.* (1986) and Bolan *et al.* (1994), who reported mineral soil solution oxalate concentrations ranging from 4 to 22 mmol kg^{-1}. Higher values of oxalic acid were reported by Fox and Comerford (1990), who observed concentration values ranging from 44 to 955 mmol kg^{-1} in a mineral soil on which pine tree seedlings grew.

Table 5. The types and concentrations of light molecular weight organic acids produced by the Chromic Acrisol and the organic materials at day 0 of incubation

Material	oxalic	malic	acetic	formic	succinic	malonic	citric	tartaric
		(mmol kg^{-1})						
Soil	10	npi	npi	npi	npi	npi	npi	npi
FYM	47	14	2	npi	2	npi	npi	npi
Lantana	468	110	11	36	10	17	13	177
Gliricidia	50	10	20	177	npi	52	52	36
Tithonia	1620	93	28	210	20	84	7	209

npi = no peak identified. All values are means from two laboratory replications.

The low concentrations of the organic acids in this Chromic Acrisol is attributed to the low organic matter content (Table 3; Appendix 1), and hence a low level of microbial activity. Concentrations of LMWOA tend to be higher in forest soils that usually have higher organic matter contents (Fox and Comerford, 1990).

The types and concentrations of these acids in litter and manure samples have been found to vary with the decomposition stage of the materials (Fox and Comerford, 1990). The low levels of organic acids in the present farmyard manure could be due to the relatively advanced decomposition stage of the farmyard manure compared to that of fresh organic materials. The present FYM was collected from an unsheltered location with high light intensity and temperatures. Under such conditions, most of the acids could have been lost due to leaching or through the dissociation that normally occurs in decomposing manures at high pH (Cooper and Cornforth, 1978).

4.1.3 Composition and characteristics of the MPR and TSP samples used in the current study

The MPR used in this study had very low Bray-1 P and moderate NAC P solubility. It had 6.9% calcium carbonate equivalent, high pH (8.5) and 36% Ca (Table 6). The present NAC P value indicates moderate to high reactivity of the MPR (Buresh *et al.*, 1997). High pH, high CaO and associated $CaCO_3$ are characteristics necessary for the amelioration of the acidic conditions and the low Ca status of the experimental soil (Table 1). However, these factors hinder PR dissolution due to decreased proton supply and reduced Ca sink (Mowo, 2000). The TSP sample that was used had higher total P_2O_5 content (44.24%), higher NAC (43.75, lower CaO (19%) and lower pH (2.1) than had MPR.

Table 6. The composition and some properties of the Minjingu phosphate rock and TSP samples used in this study

Parameter	Magnitude	
	MPR	TSP
pH $_{(H2O)}$	8.50	2.10
Total P_2O_5 (%)	29.70	44.24
CaO (%)	50.00	19.12
$CaCO_3$ (%)	6.90	nil
Bray 1-P (%)	0.01	20.12
NAC solubility (%)	3.60	43.75

NAC = neutral ammonium citrate solubility

4.2 Effects of organic materials on MPR dissolution

4.2.1 Effects of organic materials, MPR and combinations of organic materials and MPR on soil P fractions

4.2.1.1 Inorganic P fractions

The influence of organic materials, MPR or organic material combined with MPR on sequentially extracted P fractions at 14 and 112 days of incubation is shown in Tables 7 and 8. At day 14, sole application of organic materials significantly increased the $NaHCO_3$-Pi fraction compared to that in the control (Table 7). FMY had the greatest influence while lantana had the lowest. The increase in $NaHCO_3$-Pi above that in control was 60, 37, 29 and 19% for manure, tithonia, gliricida and lantana, respectively. Similar trends were observed at day 112, but slightly higher values than those at day14 were observed in all treatments.

Sole application of MPR produced significantly higher bicarbonate extractable inorganic P than did the control at both sampling dates. Net $NaHCO_3$-Pi production by MPR alone was 51 and 75 mg P kg^{-1} at days 14 and 112, respectively (Table 8). Combining MPR with different organic materials at day 14 produced significantly less $NaHCO_3$-Pi than sole application of MPR, with the exception of farmyard manure that had 9.8 mg P kg^{-1} higher than the MPR alone treatment (Table 8). At day 112 both farmyard manure and tithonia had a significant interaction on this P fraction. Combining lantana and gliricidia with MPR had no interactive effect at both sampling periods.

Table 7. Soil P fractions of Chromic Acrisol as affected by application of organic materials at 14 and 112 days of incubation

Treatment	P fractions (mg P kg^{-1}) at 14 and 112 days of incubation									
	Bic-Pi		Bic-Po		NaOH-Pi		NaOH-Po		HCl-Pi	
	14	112	14	112	14	112	14	112	14	112
Control	10.3 d	12.8 c	18.9 b	21.5 b	54.2 b	55.9 b	129.3 a	140 a	2.5 b	4.9 a
Manure (M)	16.5 a	19.4 a	21.8 a	23.2 ab	63.9 a	68.9 a	122.1 a	143.4 a	4.1 a	4.2 a
Lantana (L)	12.3 c	13.7 bc	22.9 a	22.8 ab	54.2 b	59.8 b	130.7 a	140.8 a	3.9 a	4.5 a
Gliricidia (G)	13.4 bc	13.7 bc	22.1 a	22.3 ab	54.7 b	61.1 b	126.5 a	145.8 a	4.9 a	4.2 a
Tithonia (T)	14.21 b	16.4 b	22.9 a	24.1 a	62.4 a	60.3 b	124.1 a	150.1 a	3.7 a	4.0 a
CV (%)	3.99	6.21	4.13	3.71	3.98	4.73	3.75	7.08	15.08	14.56

In this and subsequent tables, Bic-Pi=$NaHCO_3$ extractable inorganic P, Bic-Po=$NaHCO_3$ organic P, NaOH-Pi=NaOH extractable inorganic P, NaOH-Po=NaOH organic P, HCl-Pi=HCl extractable inorganic P. Means followed by the same letter in a column are not significantly different at $P<0.05$ according to DMRT.

The NaOH-Pi fraction at day 14 was significantly increased by addition of manure and tithonia. Increase in incubation period to 112 days produced a similar effect for manure as that of day 14 at 112 days manure produced 13 mg P kg^{-1} net extractable NaOH-Pi (NaOH-pi from treatment-NaOH-pi from control) while the effect of other organic materials was similar to that in the control (Table 7).The influence of applying MPR alone on NaOH-Pi at days 14 and 114 was similar to that observed for bicarbonate extractable P (Table 8). Combining MPR with different organic materials either depressed this fraction or was similar to MPR alone at both days 14 and 112. Increase in incubation period resulted in more NaOH-Pi (Table 8).

The HCl-Pi fraction at day 14 was significantly increased by addition of all organic materials. However, the differences between different organic materials were not statistically significant. At day 112 there were no treatment effects on this P fraction (Table 7).

Addition of MPR to soil resulted in significant incrases in HCl-Pi at both days 14 and 112 (Table 8). Net increase was 78% and 37% relative to control at day 14 and 112 respectively. Organic materials had no significant interaction on this pool at days 14 and 112.

Table 8. **Soil P fractions of Chromic Acrisol as affected by MPR alone and organic material in combination with MPR in incubation study**

Treatment	P fractions (mg P kg^{-1}) at 14 and 112 days of incubation									
	Bic-Pi		Bic-Po		NaOH-Pi		NaOH-Po		HCl-Pi	
	14	112	14	112	14	112	14	112	14	112
Control	10.3 d	12.8 c	18.9 c	21.5 b	54.2 c	55.9 c	129.3 a	140.0 a	2.5 c	4.9 c
MPR	61.3 b	87.9 b	20.7 bc	21.2 b	107.8 b	134.9 a	110.0 c	117.7 bc	79.3 ab	38.3 b
MPR + M	71.1 a	93.3 a	24.2 a	26.8 a	116.0 a	132.3 a	113.1 bc	113.3 c	77.9 ab	48.0 a
MPR + L	56.3 c	88.0 b	24.3 a	23.5 ab	101.5 b	126.3 b	131.8 a	131.3 ab	76.9 ab	39.0 b
MPR + G	55.9 c	91.6 ab	22.5 ab	24.3 ab	107.5 b	133.8 a	137.3 a	127.0 ab	74.32 b	39.0 b
MPR + T	55.1 c	93.3 a	23.8 ab	24.0 ab	103.4 b	136.2 a	127.4 ab	112.7 c	86.0 a	40.3 b
CV (%)	6.24	3.50	7.21	5.00	4.67	2.07	6.76	6.75	8.24	8.79

Means followed by the same letter in a column are not significantly different $P<0.05$ according to DMRT.

4.2.1.2 Organic P fractions

At day 14 of incubation, all organic materials produced significantly higher $NaHCO_3$-Po than that of the control treatment (Table 7). At day 112, $NaHCO_3$-Po from all organic treated soil was not statistically higher than that of the control with the exception of $NaHCO_3$-Po from tithonia alone.

MPR alone had no effect on $NaHCO_3$-Po at both day 14 and 112. However, when MPR was combined with organic materials more $NaHCO_3$-Po was produced from manure both at days 14 and 112, and from lantana at day 14, as compared to the MPR alone (Table 8). Organic materials did not have a significant effect on NaOH-Po both at days 14 and 112 (Table 7). Addition of MPR significantly depressed production of NaOH-Po compared to that in the control. At day 14, MPR combined with organic materials produced NaOH-Po quantities that were not significantly different from those under MPR alone. Generally, similar trends were observed at day 112.

The $NaHCO_3$ inorganic P ($NaHCO_3$-Pi) has been defined as the labile P pool that is highly related to P uptake by plants (Fixen and Grove, 1990). An increase in this fraction that was caused by tithonia and manure are due to contribution of P from these organic sources, which have high P contents (P>0.25%) (Table 4). These results show that these organic materials can cause significant increases in the P fraction that is clearly related to plant available P. The high $NaHCO_3$ inorganic P values produced from MPR compared to that of the control can be attributed to its moderate to high solubility in this Chromc Acrisol. A similar influence of organic material quality on the $NaHCO_3$ extractable P fraction has been reported by Iyamuremye *et al.* (1996b) for high quality manure and alfalfa, and by Nziguheba *et al.* (2000) for different agroforestry prunings.

The NaOH extractable inorganic P has been defined as the capital P that provides the main sink of excess P from fertilizers (Buresh *et al.*, 1997). It represents the P that is strongly adsorbed on hydrous oxides of Fe and Al through chemosorption, but is less related to plant P uptake than $NaHCO_3$-Pi (Tiessen and Moir, 1993). Phosphorus in the NaOH-Pi fraction was primarily from MPR and the organic materials at 5 t ha^{-1} contributed very little to this pool. Since most of the inorganic P was in this fraction (NaOH-extractable) it suggests that the P from MPR dissolution, and the little P from the organic residues as a result of their mineralization, had possibly undergone some transformation like chemo-sorption. The higher increase of this pool at 2 weeks of incubation, due to manure and tithonia than due to lantana and gliricidia was accompanied by lower P adsorption maximum in the former as compared to the latter treatments (Table 11), which means that some of the labile inorganic P was quenching some P fixation sites. Therefore, manure and tithonia appear to have an impact on the P fraction that is important in P adsorption reactions.

The decrease in organic P pools under the organic materials compared to that in the control may be attributed to rapid mineralization of organic P fractions. $NaHCO_3$-Po is readily mineralizable and less stable compared to NaOH-Po (Buresh *et al.*, 1997). This is because the major component of labile Po is a diester PO_4^- (Tiessen *et* *al.*, 1984), which prevents it from binding strongly to soil minerals and makes it susceptible to rapid mineralization on incubation. The lower values obtained for this fraction might indicate the conversion of this P pool into a more stable NaOH-Po. Due to increased microbial activity after application of available P, conversion of NaOH-Po to microbial P may take place, which eventually may be converted to inorganic P pools.

The major changes in HCl-Pi were caused by MPR because HCl-P is associated mainly with insoluble Ca-P present in MPR, and it depicts the extent of PR dissolution (Mutuo *et al.*, 1999). The acid soil used in this study (Table 3) favours the formation of Al and Fe-P complexes over Ca-P products. The HCl-P fraction is, therefore, associated mainly with undissolved PR rather than lower levels of native soil Ca-P. The levels of HCl-Pi were lower at day 112 compared to those at day 14, reflecting increased MPR dissolution with longer incubation period. This increase in MPR dissolution resulted in a concomitant increase in $NaHCO_3$-Pi and NaOH-Pi. The higher HCl-P in MPR plus tithonia treatment is due to the higher Ca content of tithonia compared to that in the other organic materials (Table 4).

4.2.1.3 Effect of organic materials on MPR dissolution as depicted by 0.1 M NaOH extractable P

The influence of the different organic materials and MPR on 0.1 M NaOH extractable P (NaOH–P) at different incubation periods is shown in Table 9. There were no significant differences between the organic material treatments and control at most incubation periods. However, soils treated with manure produced higher

NaOH-P than did control at days 7, 14 and 112. Generally, organic materials released similar amounts of NaOH-P at all sampling times, with the exception of that on day 14 when manure released significantly higher NaOH-P than the other organic materials, and on day 112 when the P resulting from manure or tithonia was higher than that from lantana or gliricidia.

Sole MPR produced higher NaOH-P than that of the control or organic materials, at all sampling dates (Table 9). The difference between P extracted from soil treated with MPR and that extracted from control indicates the extent of MPR dissolution.

Table 9. **Effect of organic materials and MPR on NaOH extractable P at different periods of incubation**

Treatment	Incubation period (days)						
	0	1	7	14	28	56	112
	---NaOH-P (mg P kg^{-1})---						
Control	108.0 b	101. 7b	100 d	104.3 c	99.0 b	100.0 b	100.0 cd
MPR	220.7 a	219.7 a	225.0 a	264 a	271.7 a	276.0 a	290.0 a
Manure	113.7 b	115.3 b	118.0 b	118.7 b	106.7 b	107.3 b	124.0 b
Lantana	111.7 b	114.7 b	114.0 b	96.3 cd	109.3 b	102.7 b	102.3 c
Gliricidia	104.7 b	111.7b	101.7c	91.3 c	101.3 b	103.0 b	92.0 c
Tithonia	107.0 b	112.7 b	100.7 c	110.0 c	102.7 b	103.7 b	120.0 b
CV (%)	8.04	11.78	3.63	3.71	4.71	3.26	5.45

Means followed by the same letter in a column are not significantly different $P<0.05$ according to DMRT.

There was fast dissolution of MPR when it was added to soil as shown by the net NaOH-P in Appendix 3. Dissolution of MPR was fast during the first 14 but stabilized from day 28 up to the end of incubation as shown by the low slope of the curves in Figure 2.

Combining MPR with different organic materials either had no effect on, or significantly depressed, MPR dissolution. There were differences in this depressing effect even at day 0 and the effect was more evident at day 28 and beyond, when MPR dissolution was much higher (Appendix 3). The order of the depressing effect by day 112, when the incubation was stopped, was tithonia>manure> gliricidia>lantana (Figure 2).

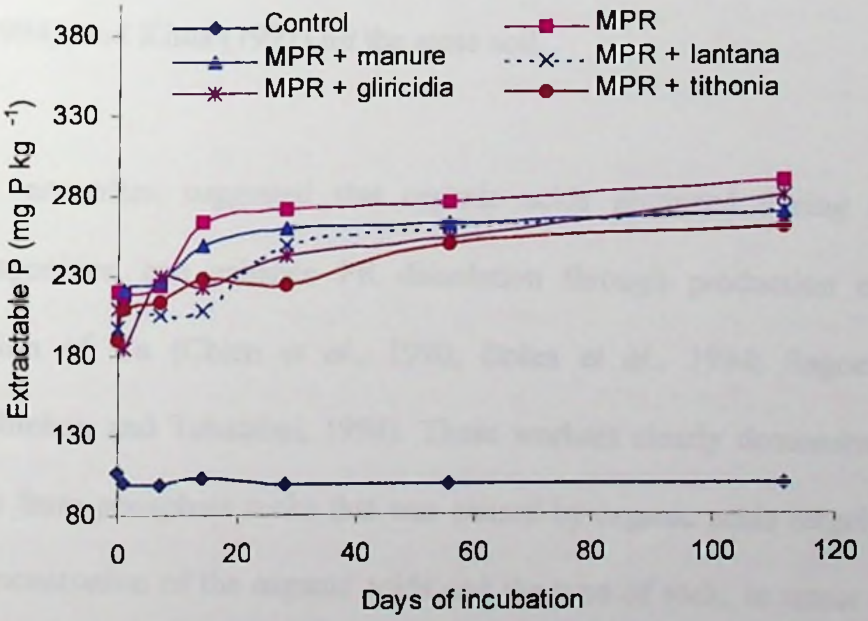


Figure 2. Effect of organic material treated MPR on P release from MPR

The lack of significant P release, by day 112 from sole application of lantana or gliricidia as compared to manure or tithonia can be attributed partially to their low P contents (Table 4). Given the acidic nature of this Chromic Acrisol (Table 3) whatever P was released by the organic materials might have been fixed by exchangeable Al and Fe and their hydrous oxides. Since manure and tithonia had lower exchangeable Al (Figure 7), higher pH (Figure 5) and lower P fixing capacity (Table 11), this resulted in more extractable P in these treatments at the end of the incubation.

The high dissolution of MPR observed in this study was activated by the low soil pH, P and Ca contents (Table 3). According to the law of mass action, PR dissolution is high when pH, exchangeable Ca and soil solution P are low (Rajan *et al.*, 1996). These results are in agreement with those reported by Mnkeni *et al.* (1991), Ikerra *et al.* (1994), and Kitua (1997) for the same soil.

It is very often suggested that organic acids produced during organic matter decomposition can enhance PR dissolution through production of protons and chelation of Ca (Chien *et al.*, 1990; Bolan *et al.*, 1994; Sagoe *et al.*, 1998; Kpomblekou and Tabatabai, 1994). These workers clearly demonstrated that the P release from phosphate rocks that was caused by organic acids largely depended on the concentration of the organic acids and the type of rock, in terms of presence of proton consuming substances. This was partly confirmed in section 4.3.2. Using analytical grade oxalic acid in the present study, it was observed that increase in oxalic acid concentration resulted in increase in P release from MPR (Figures 3 and

4). However, a certain concentration of oxalic acid (0.1M L^{-1}) had to be attained before appreciable decrease in pH and substantial release of P (10 mg P kg^{-1} MPR) could be realized from MPR. Due to the low concentration of organic acids produced by organic materials during normal decomposition under field conditions (Table 5) there might not be enough protons to neutralize the $CaCO_3$ in MPR particles to enhance MPR particles to effect a substantial level of MPR dissolution through proton supply mechanisms.

The organic materials, particularly tithonia, contained high contents of basic cations (Table 4), and these can consume some of the released protons, thereby reducing MPR dissolution through the proton supply mechanism. The implication from this study, therefore, is that high quantities of organic materials have to be applied in order to obtain a positive proton balance that can cause appreciable P release as a result of dissolution of MPR. Such a positive proton balance will depend on the amount of basic cations and pH of the organic materials. It is evident that tithonia and farmyard manure, with their high contents of basic cations, will result in a greater release of the basic cations, thereby raise soil pH, and consequently reduce MPR dissolution. Other experiments (section 4.3) showed that decomposition of organic materials, alone or in combination with MPR, resulted in an increase in soil pH (Figure 5, Appendix 4), a decrease in exchangeable Al (Figure 7), a reduction in P sorption capacity (a) and bonding energy (k) of the soil (Tables 11 and 12) and released both P and Ca during decomposition (Tables 4). These parameters negatively influenced PR dissolution because of low proton supply or pH increase, and low P and Ca sinks (Khasawaneh and Doll 1978; Rajan *et al.*, 1996; Robinson and syers, 1991; Robinson *et al*., 1992a,b), all of which are necessary pre-conditions for enhanced MPR dissolution.

The highest depressing effect of the organic materials was from tithonia. This was also contributed by the common ion effect, in which the Ca and P added through tithonia (Table 4) probably increased soil solution Ca and P and exchangeable Ca and P, thereby reversing and driving the solubility reaction of MPR (reaction xx) to the left. This contention is supported by the fact that the Ca and P contents of the organic materials are in the order of tithonia>gliricidia>lantana (Table 4), which agrees with the order for the reduction in MPR dissolution at least beyond day 28 of incubation. Manure had Ca values similar to those of lantana and gliricidia. Hence, the depressing effect of manure could be attributed to its initial high pH and P contents and not to Ca content.

These findings agree with those of Purnomo and Black (1994) who reported that Al saturation of 15% and high sorption capacity caused relatively high PR dissolution while low Al (3% saturation) caused relatively low PR dissolution. Similar observations have also been reported by Zaharah and Bah (1997), Savini (2000) and Tossah (2000). Zaharah and Bah (1997) reported that organic materials increased the solubility of unreactive PRs but depressed that of more reactive ones, and this was dependent on Ca contents of the organic materials used. Savini (2000) reported that co-application of tithonia at 4.54 g kg^{-1}soil (equivalent to 10 t ha^{-1}) and MPR at 66 mg P kg^{-1} resulted in a 25% increase in soil exchangeable Ca compared to unamended soil, thus depressing MPR dissolution as a result of increase in soil solution Ca. This was again attributed to the Ca common ion effect. Tossah (2000) also did not observe any increased dissolution of a Togo PR due to co-application of Togo PR and mucuna or tithonia, and this was attributed to the high P and Ca contents of the organic materials.

Contradicting results have been reported by Ikerra *et al.* (1994) and Kitua (1997) who reported enhancement of MPR dissolution by farmyard manure in the same soil as used in the present study. These workers attributed the positive interaction to the released organic acids, but identity and quantity of these acids were not determined at the times of their studies.

Organic acids produced by different organic materials upon decomposition and the influence of these organic materials (and presumably of the organic acids) on soil pH, Al, P adsorption and MPR dissolution were presently evaluated (section 4.3). The conclusion obtained from the present experiments is that organic materials did not enhance MPR dissolution *per se*. These organic materials rather increased soil pH and Ca, and depressed both exchangeable Al and P adsorption capacity. The amounts of organic acids produced are in very low concentrations to effect substantial dissolution and they were possibly neutralized by the basic cations as well as the $CaCO_3$ associated with MPR.

For the forward PR dissolution reaction to continue, removal of the dissolution products is essential. This is normally achieved, among other pathways, through plant uptake (Bolan and Hedley 1990; He *et al.*, 1996). Since there were no plants grown in this purely incubation experiment, removal of MPR dissolution products due to plant uptake or rhizosphere effects was lacking. Removal of MPR products creates a sink for Ca and P. Therefore, lack of this might have hindered MPR further dissolution.

Due to this probability, pot and field studies were carried out (sections 4.4 and 4.6) to examine the dissolution of MPR when combined with organic materials in the presence of maize plants, and to relate these to the trends observed in laboratory incubation studies which were performed under controlled environment.

4.3 Mechanisms underlying the increased dissolution of MPR upon use of organic materials

4.3.1 Effects of incubation of organic materials on concentrations of light molecular weight organic acids

The concentrations of organic acids released by farmyard manure, lantana, grilicidia and tithonia when they were incubated with the soil, for 28 days, are shown in Table 10. There was a decrease in concentration of LMWOA when the soil amended with different organic materials was incubated for 28 days compared to that obtained at day 0 of incubation (Table 5). After 28 days oxalic acid was detected in all treatments and it ranged from 11 to 1410 (mmol kg^{-1}). The concentration of this acid was highest in soil amended with tithonia and lowest in farmyard manure-treated soil, the order being tithonia>lantana>gliricidia= manure>control soil. Malic, acetic and formic acids were detected in soil amended with lantana, gliricidia and tithonia, while malonic and tartaric acids were produced in gliricidia and tithonia amended soils, with tithonia producing the highest quantity of tartaric acid. Succinic and citric acids were not detected in all treatments.

The decrease in LMWOA concentration that took place when the organic materials were mixed with the Chromic Acrisol and incubated for 28 days could be attributed to changes in temperature, pH, microbial activity that take place during incubation and dilution effect caused by soil organic matter. Microorganisms, in search of energy supply, feed on these carbon containing organic acids, thereby utilizing some of the carbon (Krzyszowska *et al.*, 1996). This decline in LMWOA concentration could also be due to complexation reactions that take place between LMWOA and Fe and Al, thereby causing a decreasing in LMWOA concentration. These results indicate the instability of these acids with change in environmental conditions. Higher concentrations of oxalic and tartaric acids in tithonia, even after 28 days of incubation, imply their high degree of stability and thus suitability of tithonia as green manure as compared to the other organic materials.

Table 10. Organic acid concentrations in soil solution after 28 days of incubation with different organic materials

Material	oxalic	malic	acetic	formic	succinic	malonic	citric	tartaric
	------------------------(mmol kg^{-1})------------------------------							
Soil	11	npi	npi	npi	npi	npi	npi	npi
FYM+S	20	npi	npi	npi	npi	npi	npi	npi
Lantana+S	190	10	34	36	npi	npi	npi	36
Gliricidia+S	20	70	48	47	npi	81	npi	47
Tithonia+S	1410	60	57	188	npi	10	npi	188

npi = no peak identified S = Soil, FMY = Farmyard manure. All values are means from two laboratory replications.

4.3.2 Effect of oxalic acid on MPR dissolution

It was observed from section 4.1.2.2 of this study that oxalic acid was generally the dominant acid among all organic materials. Its influence on MPR dissolution was tested using different concentrations of analytical grade oxalic acid. The increase in concentration of oxalic acid resulted in an exponential increase in extractable P from MPR (Figure 3). The amount of extractable P was almost zero at oxalic acid concentrations less than 20 mmol L^{-1}. This could be attributed to low H^+ proton supply that was present at low oxalic acid concentration. Low oxalic acid concentrations (<20 mmol L^{-1}) would release only small amounts of H^+ that are immediately neutralized by the $CaCO_3$ associated with MPR. Consequently, no net dissolution of MPR would take place and hence no P released from MPR. Kpomblekou and Tabatabai (1994) reported similar results indicating that among the ninenteen LMWOA tested the P release from Kodjari Pr (low reactive PR) and North Carolina PR (high reactive PR) increased with increase in organic acid concentration. The P released from these rocks was 10 times higher as the acid concentration was increased from one mmol L^{-1} to 10 mmol L^{-1}.

The increase in oxalic acid concentration resulted in large amounts of protons, as evidenced by the corresponding decrease in pH (Figure 4). However, the $CaCO_3$ of MPR did not neutralize all of these protons. Some of the remaining protons reacted with MPR, thus solubilizing the MPR and releasing P from MPR. During MPR dissolution Ca is also released from the MPR (reaction xx), and this reacts with oxalic acid to form insoluble Ca oxalate, consequently creating a Ca sink which enhances more MPR dissolution (Robinson and Syers, 1990; Robinson *et al.*, 1992a,b; Kpomblekou and Tabatabai; 1994; Rajan *et al.*, 1996; Sagoe *et al.*, 1998). Thus the acid enhanced MPR dissolution through proton consumption by MPR as well as through precipitation of Ca oxalate, thereby creating a Ca sink, which resulted in more dissolution of MPR.

Under natural soil environments, it is ordinarily unlikely to get as high concentrations of organic acids as those of oxalic acid presently tested, or cited, because under natural conditions LMWOA are produced at very low concentrations (Fox and Comerford, 1990; Jones, 1998) (Table 5). Moreover, LMWOA are also unstable and their concentrations can vary depending on pH, light, temperature and microbial activity (Krzyszowska *et al.*, 1996) and these environmental conditions are highly variable in the field. This argument is supported by the results shown in Table 10 whereby after 28 days of incubation the concentrations of organic acids decreased, and some organic acids could no longer be detected. The release of P from MPR under field environment will also depend on the chemical structure, the type and the position of the functional groups of the LMWOA released from organic matter decomposition. The higher the $\log K_{Al}$ of the LMWOA the higher will be the P released from the MPR (Kpomblekou and Tabatabai, 1994). However, over time, a cumulative effect on MPR dissolution by the organic acids, which have high $\log K_{Al}$, could probably be substantial.

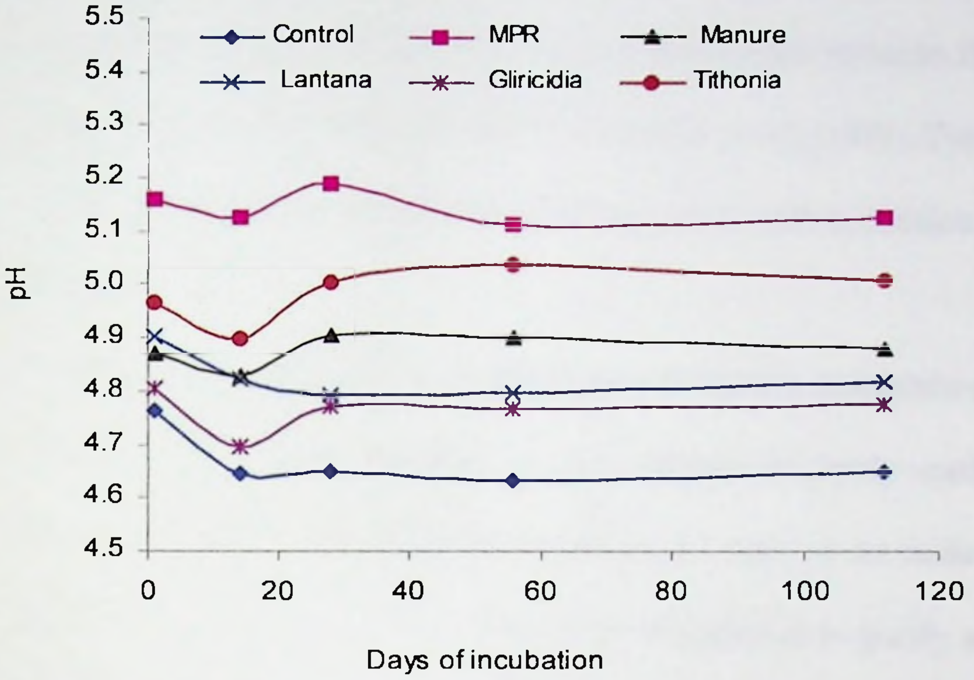


Figure 5. Effect of organic materials and MPR on the pH of the Chromic Acrisol

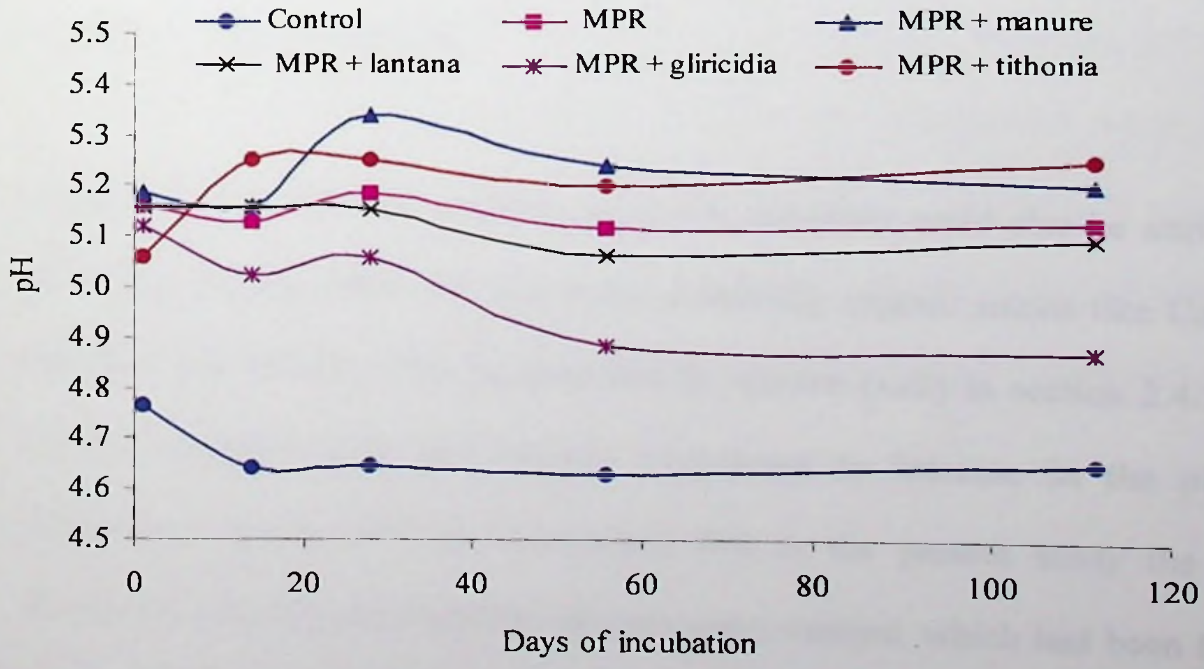


Figure 6. Effect of organic material treated MPR on pH of the Chromic Acrisol

The decrease in pH that occurred in all treatments between days 0 and 28 of incubation, was probably due to the nitrification process that usually takes place once a dry soil becomes moisteined (Bolan *et al.*, 1991; Tyson and Cabrera, 1993) (normaly referred to as nitrate flush) as explained in section 2.4.1.2 and illustrated in equation (xvii).

The increase in pH due to application of organic materials may be attributed to a liming effect which caused by the release of basic cations and OH^- during decomposition of the organic materials, as well as to reduction of Mn or Fe at anaerobic microsites (Hue, 1992). This suggestion is partly substantiated presently by the observation that between the green manures the greatest pH increase was caused by tithonia, which also had the highest levels of basic cations (Table 4) and oxalic acid (Table 5). Ligand exchange mechanisms that occur between organic acids and hydroxyl, Fe or Al in soils could also be a cause of increase in pH upon addition of organic manures.

Increase in soil pH upon addition of organic materials could also be attributed to microbial decomposition of basic cation containing organic anions like Ca oxalate (Messini and Favilli, 1990) as illustrated in reaction (xvii) in section 2.4.1.2. The $CaCO_3$ produced from this reaction contributes to increase in the pH. This observation agrees with the observation that in the present study the biggest increase in soil pH was caused by tithonia green manure, which had been found to produce the highest amounts of organic acids but particularly so with oxalic acid (Table 5).

Pocknee and Summer (1997) reported that soil pH changes upon incorporation of plant materials were positively correlated with the amount of basic cations present in the plant materials. Increase in pH due to application of organic materials has also been reported by Hue (1992), Hue *et al.* (1994), Noble *et al.* (1996), Wong *et al.* (1998), Tang *et al.* (1999), Whalen *et al.* (2000), Phan Thi Cong (2000) and Tyson and Cabrera (1993). The increase in pH due to sole application of MPR was due to the associated calcium carbonate and the alkaline reaction of MPR (Table 6).

4.3.4 Effect of organic materials on soil exchangeable Al

At 14 days of incubation all organic materials reduced exchangeable Al compared to that in the control, but the biggest decrease was caused by tithonia (Figure 7*)*. The decreases in exchangeable Al by tithonia, manure, gliricidia and lantana were 44, 41, 21 and 20%, respectively, compared to that in the to control. The MPR alone reduced exchangeable Al by 84% compared to that in the control. Combining MPR with the organic materials had a greater effect on reducing exchangeable Al than did any organic materials alone (Figure 7). The effect of organic materials on exchangeable Al at day 112 did not differ significantly from that observed at day 14 showing that microbial activity had probably reached maximum levels after 14 days of incubation.

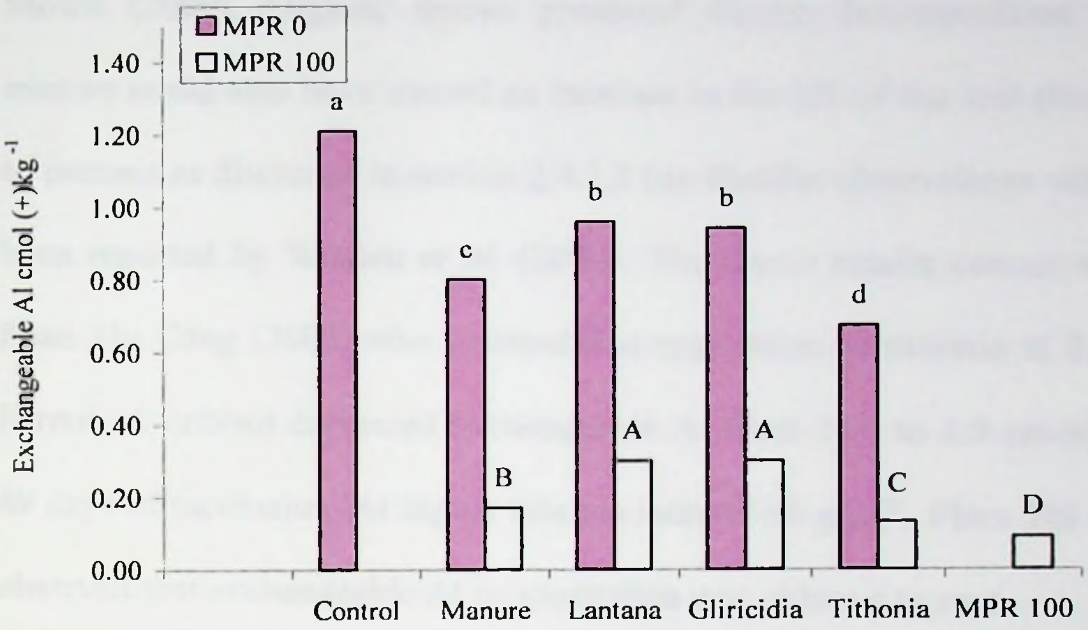


Figure 7. Effect of organic materials alone and organic materials combined with MPR on soil exchangeable Al of the Chromic Acrisol on day 14 of incubation

The observed decrease in exchangeable Al was a result of increase in soil pH, which reduced the activity of Al in the soil solution. The decrease in exchangeable Al could also be attributed to the binding of the Al by the LMWOA released during the decomposition of the organic materials (Table 5). This is partly supported by the observation that tithonia, which had the highest contents of both oxalic and tartaric acids, consequently resulted in the highest reductions in exchangeable Al. Oxalic and tartaric acids have been reported to form stable Al-organic complexes due to their high $\log K_{Al}$ or high complexation constants (Appendix 2) (Hue, 1991; Bolan *et al.*, 1994; Staunton and Leprince, 1996; Jones, 1998; Jones and Farrar, 1999). Although farmyard manure had low concentrations of LMWOA it was second to tithonia in reducing exchangeable Al, and this could be due to its initial high pH (pH=8.4) and OH^- ions produced upon its decomposition. Similar findings of high pH values in FYM have been reported by

10 t ha^{-1} while it was 5.9, 5.8, 5.7, 5.8 mg P L^{-1} for manure, tithonia, lantana and gliricidia, respectively, for 5 t ha^{-1}. The lowest P sorbed at 10 t ha^{-1} was produced by manure and the decreasing trend in amounts of P adsorbed was manure<tithonia< lantana<gliricidia<control. Increasing the incubation period to 12 weeks at 10 t ha^{-1} (Figure 10) produced similar effects as those at 2 weeks incubation (Figure 8). Reduction in P sorption resulted in a corresponding increase in solution P compared to that in the control and the trend was manure>tithonia>lantana >gliricidia>control.

Mowo (2000). Organic anions produced during decomposition of farmyard manure could also have caused an increase in the pH of the soil through removal of protons as discussed in section 2.4.1.2 (a). Similar observations with FYM have been reported by Whalen *et al.* (2000). The above results concur with those of Phan Thi Cong (2000) who reported that application of tithonia at 2.5 g kg^{-1} to a Ferralic Cambisol decreased exchangeable Al from 2.16 to 1.5 cmol(+) kg^{-1} after 49 days of incubation. At higher tithonia rates of 40 g kg^{-1}, Phan Thi Cong (2000) observed that exchangeable Al concentration was reduced to zero.

4.3.5 Effect of organic materials on P adsorption by the Chromic Acrisol

4.3.5.1 P adsorption isotherms

The P adsorption isotherms obtained for different rates of the organic materials at various incubation periods are presented in Figures 8, 9 and 10. The different organic materials incorporated into soil at the rate of 2.27 g kg^{-1} soil (equivalent to 5 t ha^{-1}) and incubated for 2 weeks generally resulted in decreases in P sorption by the treated soil compared to that in the control (Figure 8). The lowest P sorbed was under tithonia and the trend was tithonia<manure<lantana<gliricidia<control. Increase in application rate of organic materials from 5 to 10 t ha^{-1}, for the same incubation period, produced similar effects as those under 5 t ha^{-1} but 10 t ha^{-1} produced a better separation of treatment effects and had generally more P in solution (equilibrium P concentration) at the same level of P addition (Figure 9) compared to that of 5 t ha^{-1}. For example at the highest sorbed P (600 mg P kg^{-1}), which corresponds to a P addition of 60 mg P L^{-1}, mean solution P was 6.8, 6.6, 6.3, 5.5 mg P L^{-1} for manure, tithonia, lantana and gliricidia, respectively, for

10 t ha^{-1} while it was 5.9, 5.8, 5.7, 5.8 mg P L^{-1} for manure, tithonia, lantana and gliricidia, respectively, for 5 t ha^{-1}. The lowest P sorbed at 10 t ha^{-1} was produced by manure and the decreasing trend in amounts of P adsorbed was manure<tithonia< lantana<gliricidia<control. Increasing the incubation period to 12 weeks at 10 t ha^{-1} (Figure 10) produced similar effects as those at 2 weeks incubation (Figure 8). Reduction in P sorption resulted in a corresponding increase in solution P compared to that in the control and the trend was manure>tithonia>lantana >gliricidia>control.

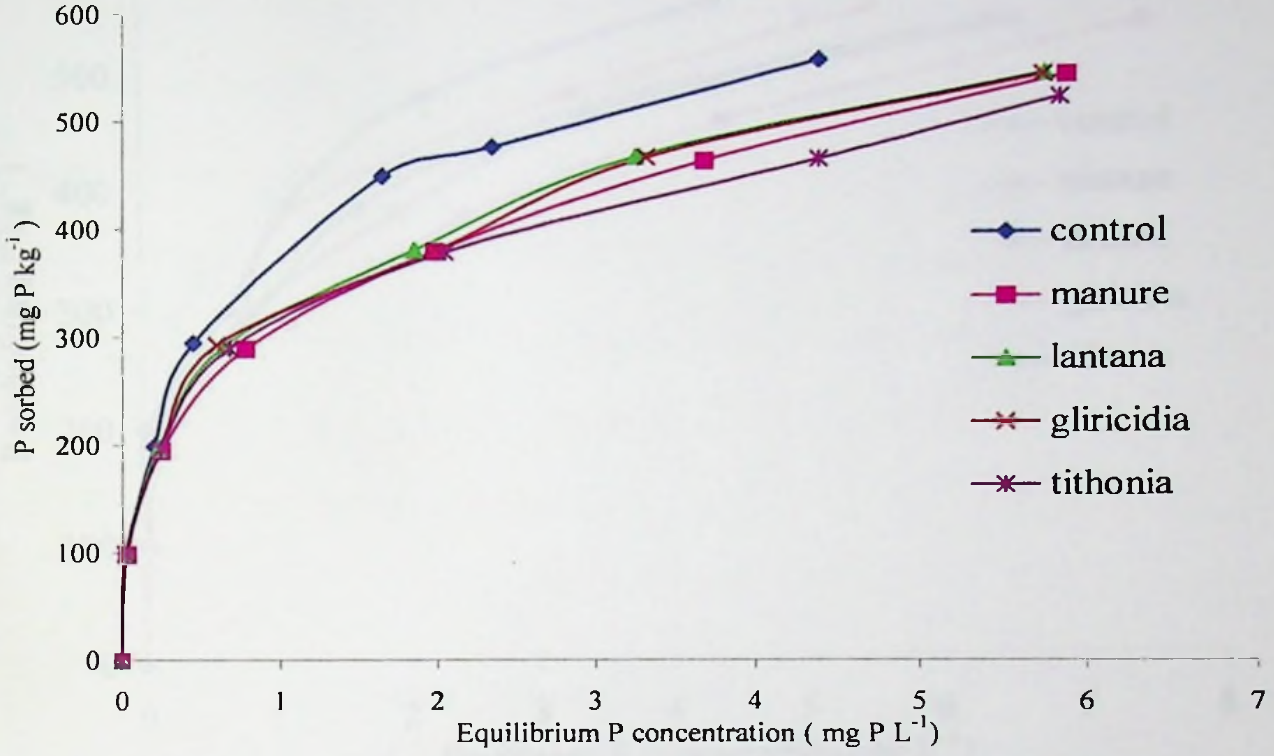


Figure 8. **Adsorption isotherms for the Chromic Acrisol incubated for 2 weeks with organic materials at 5 t ha^{-1}**

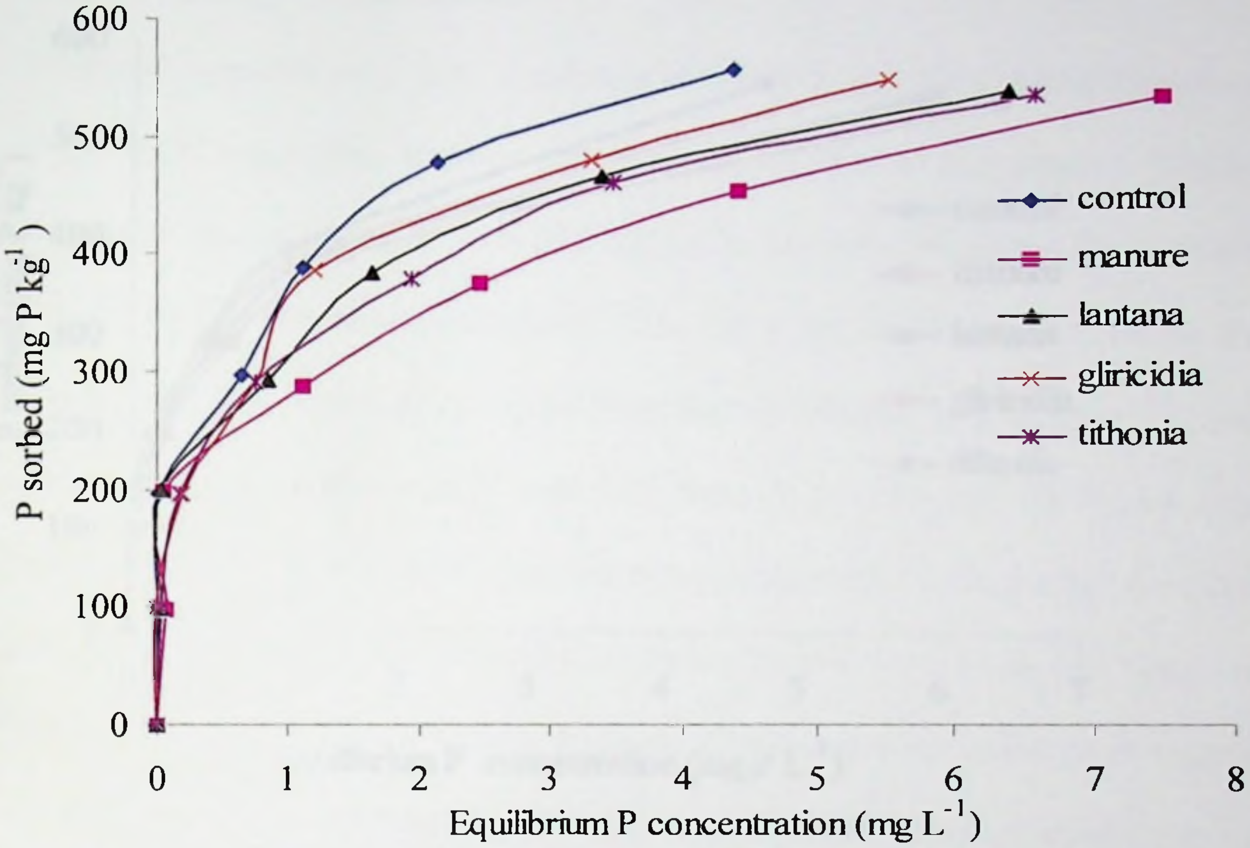


Figure 9. Adsorption isotherms for the Chromic Acrisol incubated for 2 weeks with organic materials at a rate of 10 t ha^{-1}

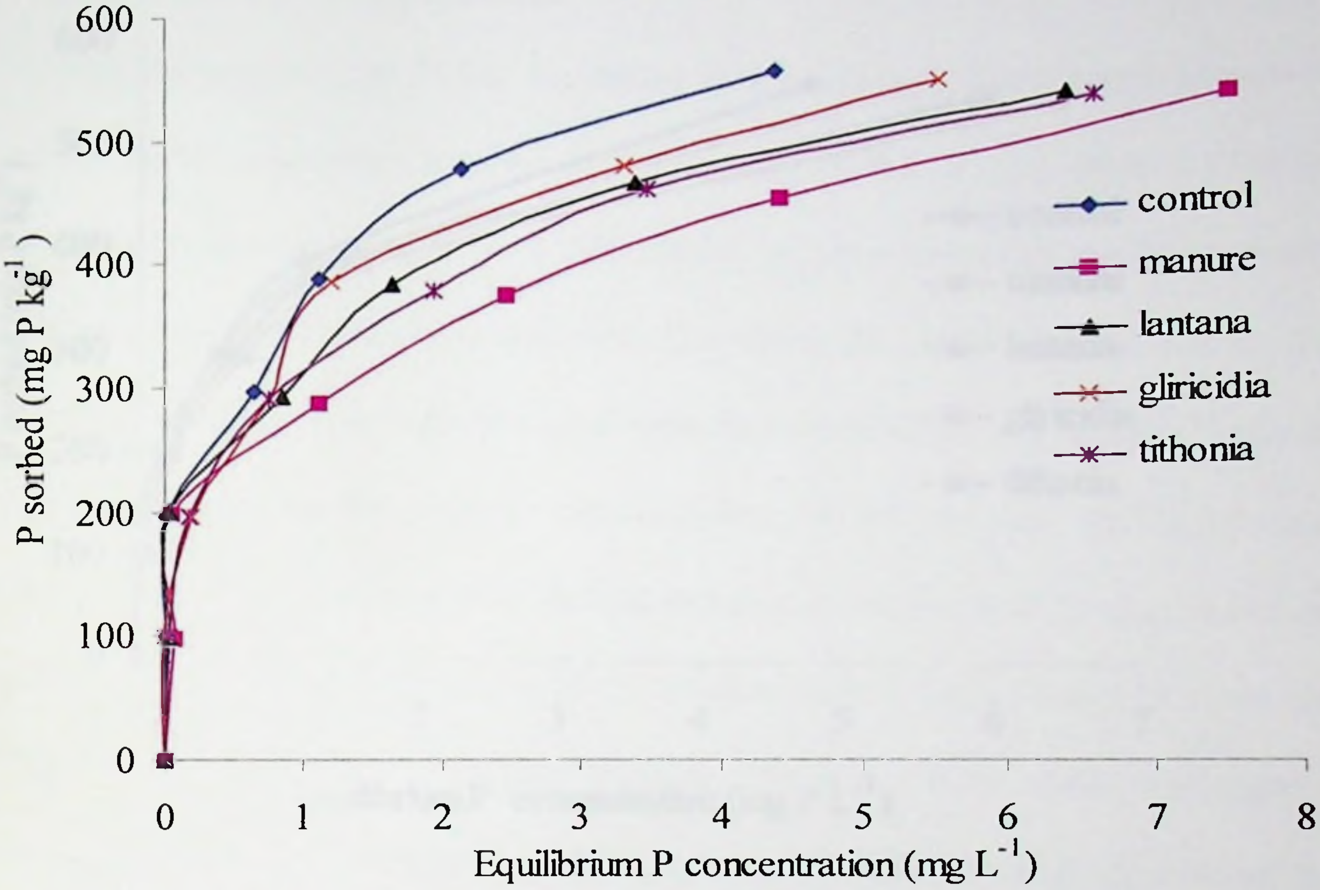


Figure 9. Adsorption isotherms for the Chromic Acrisol incubated for 2 weeks with organic materials at a rate of 10 t ha^{-1}

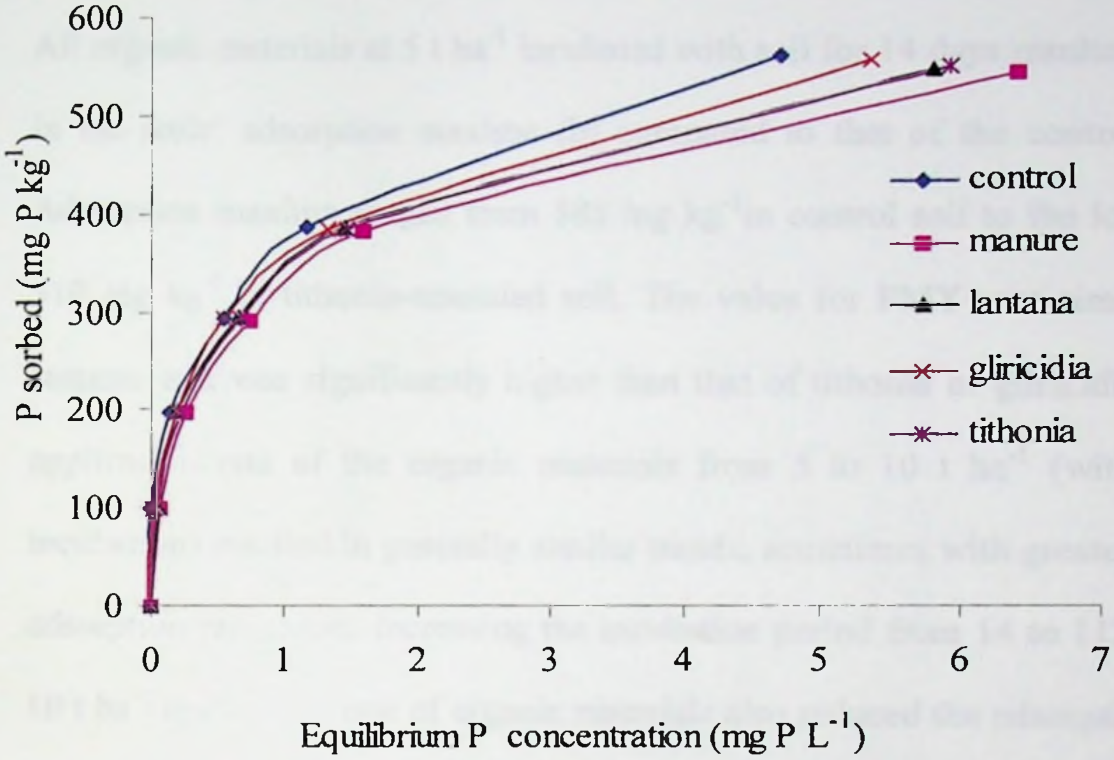


Figure 10. Adsorption isotherms for the Chromic Acrisol incubated for 12 weeks with organic materials at 10 t ha^{-1}

4.3.5.2 P adsorption parameters

All organic materials at 5 t ha^{-1} incubated with soil for 14 days resulted in decreases in the soils' adsorption maxima (b) compared to that of the control (Table 11). Adsorption maxima ranged from 585 mg kg^{-1}in control soil to the lowest value of 510 mg kg^{-1} in tithonia-amended soil. The value for FMY was similar to that of lantana, and was significantly higher than that of tithonia or gliricidia. Increase in application rate of the organic materials from 5 to 10 t ha^{-1} (with 14 days of incubation) resulted in generally similar trends, sometimes with greater decreases in adsorption maximum. Increasing the incubation period from 14 to 112 days for the 10 t ha^{-1} application rate of organic materials also reduced the adsorption maximum compared to that of the control, although this reduction was not significant in the case of manure and tithonia.

Table 11. Effect of organic materials on adsorption maxima (b), adsorption affinity (k) and SPR (q) at 5 and 10 t ha^{-1} incubated for 14 and 112 days as obtained from the Langmuir equation

Week / rate	Variable unit	Control	Manure	Lantana	Gliricidia	Tithonia	R^2	CV
2wks, 5t	b (mg P kg^{-1})	585 a	552 b	552 b	524 c	510 c	0.82	2.48
	k (L mg^{-1})	2.95 a	1.63 c	2.2 b	2.74 a	1.73 bc	0.53	22.94
	q (mg P kg^{-1}	217	136	169	185	131		
2wks, 10t	b (mg P kg^{-1})	606 a	451 d	540 c	562 b	523 c	0.96	2.25
	k (L mg^{-1})	2.2 a	1.80 c	2.00 b	1.93 b	2.22 b	0.81	9.20
	q (mg P kg^{-1})	185	119	154	157	161	-	-
12wks, 10t	b (mg P kg^{-1})	589 a	573 ab	563 b	580 b	577 ab	0.50	1.65
	k (L mg^{-1})	2.12 a	1.59 c	1.98 ab	2.03 ab	1.77 cb	0.55	8.10
	q (mg P kg^{-1}	175	138	160	167	151	-	-

SPR=(q), P needed to obtain a soil solution concentration of 0.2 mg P L^{-1}, calculated from Langmuir equation. Means followed by the same letter in a row are not significantly different $P<0.05$ according to DMRT.

The effect of the organic materials on bonding energies (k) (L mg^{-1}) at both 5 and 10 t ha^{-1} incubated for 14 days (Table 11) followed similar trends as those of adsorption maximum with the exception of gliricidia which produced a k value that was similar to that of the control at 5 t ha^{-1}. FMY had the lowest bonding energy, the increasing trend in k values was control>gliricidia>lantana>tithonia>manure. Increase in application rate did not seem to decrease the bonding energy further. Increasing the incubation period from 14 to 112 days significantly decreased the k values in the case of manure and tithonia, manure resulting in the lowest bonding energy.

The amount of P adsorbed (q) at a solution P concentration of 0.2 mg P L^{-1} (SPR) was less in organic material-treated soils as compared to that of the control. At the rate of 5 t ha^{-1} with 14 days incubation, the q values ranged from 217 in control soil to the lowest value of 131 in the tithonia-amended soil. The decreasing trend in q values was control>gliricidia>lantana>manure>tithonia. Increase in application rate from 5 to 10 t ha^{-1} produced similar effect but higher organic material rates in most cases reduced the amount of P that would have to be applied in order to attain SPR of 0.2 mg P L^{-1}. For example, in case of manure the amount dropped from 136 to 119 mg P kg^{-1} (Table 11). Increase in incubation period from 14 to 112 days had similar effects as that under 14 days of incubation. Based on the R^2 values of 0.96 and 0.81 for P adsorption maximum and affinity capacities, respectively, the best influence from organic materials on adsorption parameters were obtained from the 10 t ha^{-1} application rate at an incubation period of 14 days, and increasing the incubation period to 112 days did not reduce the adsorption parameters any further.

Generally similar trends for adsorption capacities and affinities were observed using the Freundlich equation (Table 12). All organic materials applied at 5 t ha^{-1} and incubated for 14 days decreased the sorption capacity (a) compared to that in the control, but there were no significant differences between different organic materials. Increase in application rate from 5 to 10 t ha^{-1} at the same incubation period similarly reduced the “a” value, with the exception of the “a” value in the gliricidia treatment. Increasing the incubation period from 14 to 112 days gave similar effects and trends as those at 14 days. Generally, extending incubation period to 112 days did not reduce the sorption capacity any further.

The decrease in adsorption capacity was not accompanied by a significant decrease in adsorption affinity, b, for the 5 t ha^{-1} at 14 days incubation treatment as compared to that in the control. When the application rate was increased from 5 to 10 t ha^{-1} there was a significant reduction of bonding energy values compared to that of the control. However, there were no significant differences between different organic materials. After increasing the incubation period from 14 to 112 days, the organic materials did not change the adsorption affinities as compared to that in the control. Based on the R^2 values obtained from the non-linear regression analysis for the Langmuir and Freundlich equations following the procedures of the SAS Institue, (1995) (Tables 11 and 12), the adsorption affinities of the best rate and incubation period (10 t ha^{-1}, 112 days incubation) were better estimated by the Freundlich equation.

Table 12. Effect of organic materials on adsorption capacity (a) and adsorption affinity (b) at 5 and 10 t ha^{-1} incubated for 14 and 112 days as obtained from Freundlich equation

Week/rate	Variable unit	Control	Manure	Lantana	Gliricidia	Tithonia	R^2	CV
2wks, 5t	a (mg P kg^{-1})	362 a	292 b	301 b	307 b	295 b	0.76	2.6
	b (L mg^{-1})	0.38 a	0.35 ab	0.35 ab	0.35 ab	0.34 ab	0.58	5.4
2wks, 10t	a (mg P kg^{-1})	334 a	288 d	314 b	328 a	303 c	0.94	1.52
	b (L mg^{-1})	0.36 a	0.31 b	0.30 b	0.30 b	0.32 b	0.88	2.87
12wks, 10t	a (mg P kg^{-1})	352 a	300 c	321 b	344 c	318 b	0.89	2.41
	b (L mg^{-1})	0.31 a	0.33 a	0.32 a	0.31 a	0.32 a	0.69	5.35

Means followed by the same letter in a row are not significantly different $P<0.05$ by DMRT.

The decrease in P adsorption capacity of soil when for GM samples were applied at 10 t ha^{-1} and incubated for 2 weeks, as evaluated by both the Langmuir and Freundlich equations, was closely correlated to the oxalic acid concentration of the GMs ($R^2 = 0.95$, $R^2 = 0.98$ respectively), (when data for farmyard whose organic acid concentratration was not related to P sorption capacity, was omitted from the regression equation). The higher the oxalic acid concentration the lower was the P adsorption capacity. This data showed that 98% of the variation in phosphorus adsorption capacity from green manures could be explained by the oxalic acid concentration (Figure 11).

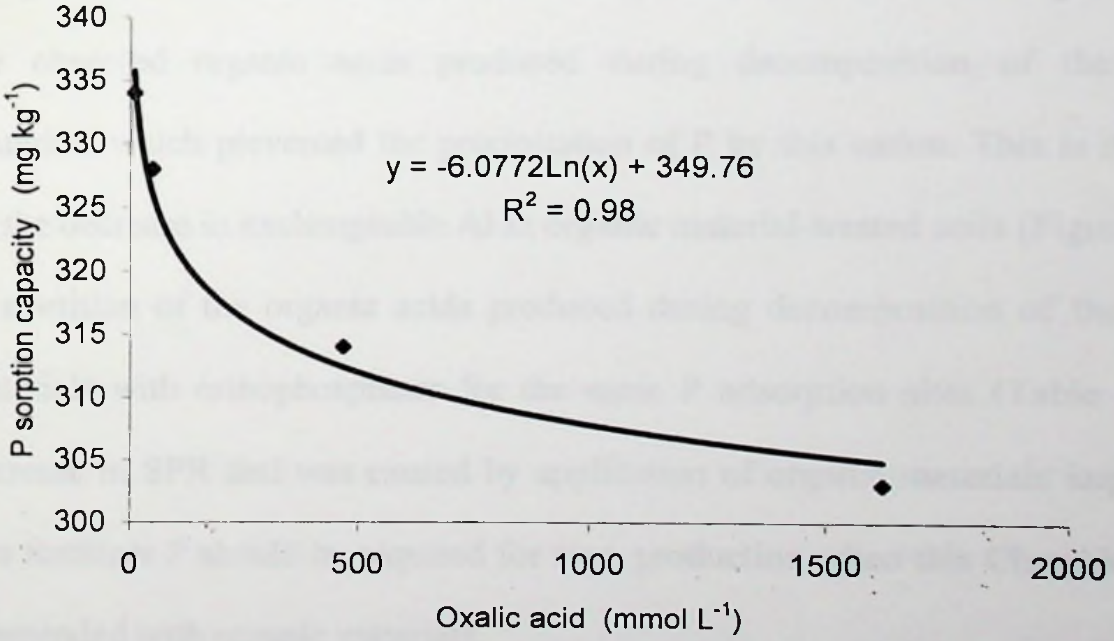


Figure 11. Relationship between P sorption capacities and oxalic acid concentration of Green Manure

The decreases in P sorption, adsorption maximum and affinity constants due to application of organic materials can be attributed to several factors, which include: (i) Quenching of P sorption sites by the P released during decomposition of the organic materials (Table 4). This is supported by the observation that the decrease in P sorption was greater in cases of manure and tithonia, which contained P levels greater than the critical value of 2.2 g P kg^{-1}. Singh and Jones (1976) reported that organic materials with P content greater than 2.2 g P kg^{-1} reduced P sorption while those with P content less than 2.2 g P kg^{-1} increased P sorption. This was partially confirmed in this study whereby the decrease in P sorption was in the order manure<tithonia<lantana<gliricidia <control, which agrees with the trend in the P content of the organic materials (Table 4). (ii) Increase in pH, which was observed in the soil samples amended with organic materials (Figure 5). The increase in soil pH reduced Al^{3+}activity and favours production of OH^- ions that compete with othophosphate ions for adsorption sites (iii)) complexation of exchangeable Al by the observed organic acids produced during decomposition of the organic materials which prevented the precipitation of P by this cation. This is supported by the decrease in exchangeable Al in organic material-treated soils (Figure 7). (iv) competition of the organic acids produced during decomposition of the organic materials with orthophosphates for the same P adsorption sites (Table 10). The decrease in SPR that was caused by application of organic materials implies that less fertilizer P should be required for crop production when this Chromic Acrisol is amended with organic materials.

The more pronounced influence of tithonia compared to the other green manures is attributed to its higher content of P and organic acids (Table 4). Tithonia contained a higher concentration of both oxalic and tartaric acids than the other organic materials. These acids have higher Al complexing constants (greater than 4) (Appendix 2), and this normally causes P desorption (Hue, 1991; Staunton and

Leprince, 1996; Jones, 1998). This argument is supported by the observation that 95% of the variation in phosphorus adsorption capacities due to GM could be explained by the oxalic acid concentration (Figure 11). Manure had low concentrations of these acids and its depressing effect on P sorption was possibly caused by these low concentrations, its tendency of influence in increasing pH (Figure 5) and its high P content (Table 4). The higher depressing effect on P sorption that was caused by increase in application rate from 5 to 10 t ha^{-1} would be due to greater production of LMWOAs, PO_4 and OH^- ions that occur at higher application rates (Iyamuremye *et al.*, 1996b). Incubating the organic materials for 112 days did not result in better effects than those from the 14 days of incubation period probably because over a long time some of the organic acids were transformed or neutralized as pH rose with time (Krzyszowska *et al.*, 1996) that take place upon longer-term incubation (Table 10).

The results obtained from the present study are in conformity with those of Singh and Jones (1976), Iyamuremye *et al.* (1996b) and Nziguheba *et al.* (2000). However, these workers did not give a comprehensive characterization of the organic materials used and, hence, no correlation of LMWOA with adsorption capacity was established.

The present results, however, contradict those by Ohno and Crannel (1996) who observed that green manures which produced LMWOAs had a greater depressing effect on P sorption than that of animal manures which produced high molecular weight organic acids (HMWOA). In this study farmyard manure had a higher depressing effect on P sorption than GMs. These differences might have been caused by the variation in manure composition, decomposition stage, and storage conditions.

4.4 Glasshouse pot experiments

4.4.1 Response of maize to MPR and TSP in terms of dry matter yields

The response of maize dry matter yields (DMY) to MPR and TSP are presented in Table 13 and Appendix 5. It was observed that TSP or MPR significantly increased the maize DMY as compared to that of the control (Table 13). The highest maize DMY was attained at between 200 and 300 mg P kg^{-1} soil.

Table 13. Response of maize DMY to P application as MPR or TSP on Chromic Acrisol

P rate (mg kg^{-1})	DMY (g pot^{-1})^{2}	
	TSP	MPR
0 (-N, -K)^{1}	4.9 i	4.9 i
0^{3} (+N, +K)	10.6 h	10.6 h
10	14.7 f	12.6 g
20	15.6 f	17.6 de
50	17.2 e	18.3 d
75	20.5 c	21.9 b
100	21.2 bc	21.9 b
200	24.0 a	23.3 a
300	24.3 a	23.7 a
CV (%)	3.08	

^{1} absolute control; ^{2} DMY= dry matter yield; ^{3}N and K were applied at 80 kg N ha^{-1} and 50 kg K ha^{-1}; Means followed by the same letter in a column are not significantly different; P<0.05 according to DMRT.

Maize dry matter yield response was generally more pronounced with MPR than with TSP at rates less than 75 mg P kg^{-1}, with the exception of very low rates less than 10 mg P kg^{-1}. There were no significant differences in response to P application between MPR and TSP at rates greater than 100 mg P kg^{-1}

(Appendix 5). Increase in DMY over the control due to P application confirms the observation that the present Chromic Acrisol is deficient in plant available P (Table 7). Besides having a significant response to P addition, there was also response to N + K application (Table 13, Plate 1) but this response was lower than that due to P. The implication derived from this observation is that P application from external sources in the form of inorganic or organic fertilizers is essential for attaining and maintaining high productivity from this Chromic Acrisol, but the P has to be combined with N and K. The more pronounced response to MPR as compared to TSP, especially at the low rates of application, could be an effect of $CaCO_3$ in the former (Table 6). Unlike at high MPR rates, at low MPR rates there was probably less $CaCO_3$ and other proton consuming compounds; hence relatively more protons were available in the soil solution for MPR dissolution than when high rates of MPR were used. According to the MPR dissolution reaction equation (xx) shown in section 2.5.1.1, low rates of MPR are likely to create both P and Ca sinks, hence to increase MPR dissolution. At low rates, therefore, the net solution P is higher in MPR treatments than in TSP, consequently resulting in higher response from the former than from the latter.

Similar findings, of MPR producing greater responses at lower rates than those of TSP, have been reported by Kanabo and Gilkes (1988), Rajan *et al.* (1991) and Mowo (2000). These workers attributed the greater response from low rates of MPR to less proton consumption by the low contents of $CaCO_3$ and other proton consuming compounds as a result of the low MPR rates. Recently, Kosia (2002)

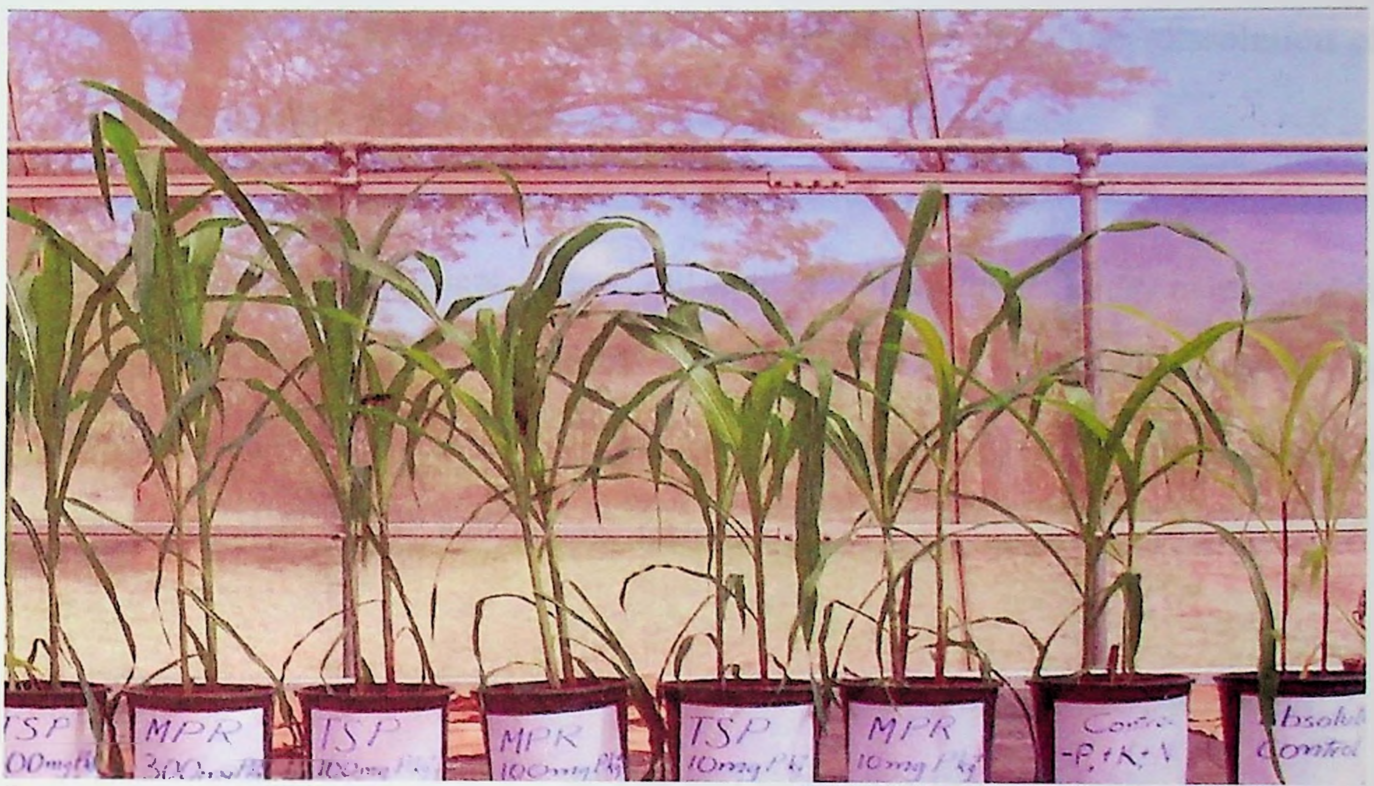


Plate 1. Response of maize to P, N and K applications in pot experiment

Plate 1. Response of maize to P, N and K applications in pot experiment

reported higher RAE from MPR at the rate of 60 mg P kg^{-1} than that at the rate of 180 mg P kg^{-1} of Sasanda soil, which was attributed to the higher dissolution of MPR that happens at lower application rates than at higher rates.

From the present experiment, highest and significant increments in dry matter yields occurred at rates less than or equal to 100 mg P kg^{-1} on the response curve (Appendix 5). This P rate was, therefore, adopted in later pot studies when combining MPR or TSP with organic materials.

4.4.2 Effect of MPR and TSP combined with different organic materials on soil properties, Ca and P uptake and maize dry matter yields

4.4.2.1 Effect on soil properties

The influence of organic materials and inorganic fertilizers on some soil properties is shown in Table 14. All organic materials significantly increased pH compared to that of the control, at 45 DAP. MPR caused a significant increase of 0.24 pH units compared to that of the control, but the effect of TSP was non significant. Combining MPR with each of the organic materials produced significantly higher pH than that of the control. Tithonia and lantana, when co-applied with TSP, increased significantly the soil pH as compared to that of the control.

Exchangeable Ca was significantly increased by organic materials when compared to that of the control (Table 14). Manure resulted in the largest increase in exchangeable Ca (2.03 cmol (+) kg^{-1}) compared to that of the control (1.41 cmol(+) kg^{-1}) while GMs had similar effects. Both TSP and MPR significantly increased exchangeable Ca but the influence of TSP on exchangeable Ca was lower than that of MPR. Net increases in exchangeable Ca were 65% and 103% for TSP and MPR, respectively.

The combination of each of the organic materials with MPR produced significantly higher exchangeable Ca than that of the control. Sole application of MPR resulted in higher exchangeable Ca than that of MPR + organic material treatments. There was no significant increase in exchangeable Ca in TSP + organic material treatments as compared to sole TSP.

Table 14. Effect of MPR and TSP combined with different organic materials on some of the Chromic Acrisol characteristics

Treatment	pH-water	Ca	Al	Resin P
		cmol (+) kg^{-1}		(mg kg^{-1})
Control	4.31 f	1.41 h	0.70 a	2.80 g
Manure (M)	4.54 abc	2.03 f	0.48 bcd	4.51 f
Tithonia (T)	4.52 abc	1.83 g	0.50 bcd	4.21 f
Lantana (L)	4.49 bcd	1.84 g	0.46 bcd	3.22 g
Gliricidia (G)	4.47 cd	1.91 g	0.51 bcd	3.26 g
MPR	4.56 ab	2.91 a	0.40 cd	20.15 bc
TSP	4.30 f	2.32 cd	0.55 b	24.87 a
MPR + M	4.46 cd	2.25 de	0.46 bcd	16.46 e
MPR + T	4.51 abc	2.61 b	0.54 b	20.13 bc
MPR+ L	4.56 ab	2.43 c	0.38 d	16.61 e
MPR + G	4.59 a	2.28 de	0.58 b	20.05 c
TSP + M	4.34 ef	2.16 ef	0.44 bcd	24.36 a
TSP + T	4.43 d	2.40 cd	0.45 bcd	20.13 d
TSP + L	4.42 d	2.39 cd	0.52 bc	21.19 b
TSP + G	4.30 f	2.44 c	0.79 a	20.95 bc
CV (%)	1.07	3.63	12.75	4.63

In this and subsequent tables, means followed by the same letter in the same column is not significantly different $P<0.05$ according to DMRT; All organic materials were applied at 2.27 g kg^{-1} and both MPR and TSP were applied at 100 mg P kg^{-1}.

The observed significant increases in soil pH and exchangeable Ca that were caused by organic materials resulted in concomitant decreases in exchangeable Al compared to that of the control. Both MPR and TSP significantly decreased exchangeable Al compared to that of the control. The decrease in exchangeable Al compared to control was in the order of 42% and 21% for MPR and TSP treatments, respectively. The MPR + organic materials treatments either had a similar or less exchangeable Al compared to that of the MPR. Generally, the same trend of exchangeable Al was followed for the TSP + organic material treatments.

Resin P ranged from 2.8 in control to the highest value of 4.51 mg P kg^{-1} in the manure treatment. Significant increases in resin P compared to that of the control were caused by manure and tithonia (Table 14). Application of MPR and TSP significantly increased resin P above that of the control by 619% and 788%, respectively. Combining organic materials with MPR produced significantly much higher resin P than that of the control, and the increase in resin P was equal to or less than that under sole MPR. A similar trend of resin P was observed when TSP was combined with organic materials.

The decrease in pH from 4.8 observed during soil characterization (Table 3) to 4.31 in control soil (Table 14) was probably caused by (i) acidification that could have been caused by the ammonium and zinc sulphate that were used as basal N and Zn sources. The sulphate anion from these fertilizers normally reacts with water to form sulphuric acid, thereby reducing the pH (ii) maize uptake of basic cations and (iii) production of protons from the nitrification process as shown in reaction (xvi) in section 2.4.1.2.

The increase in soil pH and exchangeable Ca, and the decrease in exchangeable Al, caused by organic materials is attributed to the following mechanisms:

(i) Displacement of hydroxyls (OH^-) from sesquoxides surfaces by organic anions which are produced when the organic materials decompose (Parfitt *et al.*, 1978); (ii) Different organic materials produce various types and concentrations of organic acids upon decomposition (Jones, 1998) and certain organic acids can cause increase in pH through decarboxylation of organic anions as shown for the case of Ca oxalate in reaction (xvii) in section 2.4.1 (Messini and Favilli, 1990). (iii) The organic acids produced during decomposition of organic materials complex Al and reduced Al^{3+} activity in soil solution (Hue *et al.*, 1986; Fox *et al.*, 1990; Jones, 1998; Xia and Pierzynski, 2003). This was evidenced by the decrease in exchangeable Al upon addition of organic materials shown as in Figure 7, section 4.3.4. (iv) Addition of basic cations from decomposition of organic materials. Since the organic materials contained Ca, Mg and K (Table 4), their decomposition released these basic cations into soil solution and this resulted in increases both in exchangeable Ca and in pH. This is partly confirmed by the earlier observations reported in Figures 5. Similar observations on increases in soil pH and exchangeable Ca, and decrease in exchangeable Al due to application of organic materials, have been reported by Bessho and Bell (1992), Hue *et al.* (1994), Noble *et al.* (1996), Wong *et al.* (1998), Tang *et al.* (1999), Whalen *et al.* (2000) and Phan Thi Cong (2000).

Manure and tithonia had the highest effect on increasing pH and exchangeable Ca because these organic materials had higher pH (manure) and higher basic cation Ca, Mg, K concentrations (tithonia) (Table 4) than those of lantana or gliricidia. These basic cations reflect the contents of weak organic acid functional groups that are capable of binding protons and Al (Tanga and Yu, 1999). Similar observations were reported by Besso and Bell (1992), Hue *et al.* (1994), Tanga and Yu (1999) who indicated that the magnitude of pH change upon application of organic materials depended largely on the concentration of organic anions, initial soil pH and the degree of residue decomposition. Since tithonia and manure were of higher quality, their degree of decomposition must have been higher than that of lantana or gliricidia.

The higher increase of soil pH and exchangeable Ca, and the decrease of Al caused by MPR compared to that under TSP, are due to the $CaCO_3$ associated with MPR and its relatively higher calcium oxide (CaO) concentration compared to that of TSP (Table 6). Release of Ca from the associated $CaCO_3$, and from MPR dissolution, resulted in increase in pH and exchangeable Ca according to the following reactions:

(1) $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$ (associated) $CaCO_3$ ---------(xxi)

(2) $Ca_5\,(PO4)_3\,F + 7H^+ \rightarrow 5Ca^{2+} + 3H_2PO^{4-} + HF$ (MPR dissolution) ---------(xxii)

The consumption of protons and release of Ca from these reactions resulted in increase in pH. Although TSP also contains $H_2PO_4^-$ and Ca^{2+}, and could increase soil pH and decrease exchangeable Al, it does not consume soil protons when it releases $H_2PO_4^-$ (Hu *et al.*, 1994; Okalebo *et al.*, 2003). Decrease in pH due to TSP $[Ca(H_2PO_4)_2]$ is also attributed to its initial low pH (Table 6) and production of phosphoric acid (H_3PO_4) during hydrolysis of TSP as follows:

$Ca(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4 + H_3PO_4 + H_2O$--------------------------------(xxiii)

The above reactions (xxi-xxiii) indicate that besides supplying P, MPR has an extra advantage over TSP of having a higher potential for Ca release than has TSP (Hu *et al.*, 1994,1997; Okalebo *et al.*, 2003). Since the soil under study was Ca deficient, application of organic materials or MPR can improve soil exchangeable Ca and reduce exchangeable Al, consequently increasing yields.

Although the organic materials had a significant effect on resin P, the highest value of 4.51 mg P kg^{-1}obtained from manure was still below the critical value of 6.5 mg kg^{-1} suggested by Landon (1991). According to Landon (1991), resin P values ranging between 3.0-6.5 mg P kg^{-1} are rated as being deficient and P application at this point is likely to produce one third to two thirds increases in maize yields. It, therefore, implies that the present 5 t ha^{-1} application rate of organic materials, which corresponds to 9.8, 4.8, 5 and 10.5 mg P kg^{-1} from manure, lantana, gliricidia or tithonia, respectively, does not supply enough soil P for supporting high maize yields.

Landon (1991) suggested that resin P values ranging between 13-22 mg P kg^{-1} are rated as being adequate for maize production. Based on this value, both MPR and TSP at the rate of 100 mg P kg^{-1} equivalent to 220 kg P ha^{-1} produced extractable P that was within this range of critical values, for maize production. MPR produced lower values than did TSP due to the lower initial dissolution of the former. The lack of significant positive interaction between different organic materials and MPR on resin P shows that organic materials, even in the presence of the crop, could not bring about MPR dissolution. This argument agrees with the results already presented in section 4.2.1.3 (Figure 2).

In conclusion, manure and tithonia used in this study have the potential of increasing soil pH and Ca, decreasing exchangeable Al, and consequently increasing resin P. While lantana and gliricidia had no significant effect on resin P. Combining MPR or TSP with organic materials did not result in significant increase in resin P compared to using sole MPR or TSP and in certain cases they decreased resin P. Although the TSP treatment could supply more resin P to the Chromic Acrisol in the pot experiment, MPR was superior to TSP in supplying Ca, increasing pH, and decreasing exchangeable Al. Decrease in exchangeable Ca when MPR was combined with organic materials in relation to when MPR was used alone could not be easily explained.

4.4.2.2 Effect on P and Ca concentration and uptake

The effect of organic materials, MPR and TSP, singly or combined, on the concentration and uptake of P and Ca by maize is presented in Table 15. Phosphorus concentrations in maize plant shoots ranged from 0.13% to 0.19%. All treatments, except MPR + tithonia, had more or less similar P concentrations. MPR amended with tithonia produced P concentrations similar to that of the control. The Ca concentrations in the maize plants followed trends somewhat similar to those of P where some treatments had significantly lower Ca concentration than that of the control, while others had Ca values similar to those of the control. Organic materials significantly increased P uptake compared to that under the control, except for that under gliricidia (Table 14). The greatest increase was caused by manure while the lowest was from gliricidia. Tithonia and lantana had intermediate and similar values. Phosphorus uptake was also significantly increased by MPR and TSP compared to

Table 15. Effect of MPR and TSP combined with different organic materials on the concentration and uptake of P and Ca by maize

Treatment	P concentration (%)	P uptake (g pot^{-1})	Ca concentration (%)	Ca uptake (g pot^{-1})
Control	0.17 ab	11.11 i	0.44 a	27.64 l
Manure (M)	0.16 bc	27.37 g	0.36 de	62.32 hi
Tithonia (T)	0.17 bc	22.03 h	0.37 de	48.39 jk
Lantana (L)	0.16 bcd	19.92 h	0.43 ab	56.42 ij
Gliricidia (G)	0.15 cde	14.37 i	0.43 ab	41.84 k
MPR	0.14 de	33.37 f	0.28 f	67.06 gh
TSP	0.15 bcd	40.83 cde	0.34 e	90.52 bc
MPR + M	0.14 de	37.23 def	0.30 f	78.42 ef
MPR + T	0.19 a	48.49 a	0.41 bc	104.19 a
MPR+ L	0.14 de	37.18 def	0.37 de	94.24 abc
MPR + G	0.14 de	36.55 ef	0.38 cd	97.76 ab
TSP + M	0.16 bcd	46.50 ab	0.30 f	89.33 abc
TSP + T	0.14 de	41.54 cd	0.29 f	85.62 cde
TSP + L	0.13 e	34.21 f	0.29 f	74.67 g
TSP + G	0.15 bcd	42.02 bc	0.30 f	80.36 def
CV (%)	7.79	5.58	5.34	8.21

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

That of the control, and the effect of each inorganic fertilizer was higher than that of each organic material applied singly. Phosphorus uptake under TSP treatments was higher than that under MPR, with per cent phosphorus recovery in maize shoots for MPR and TSP being 22% and 29%, respectively.

Combining MPR with tithonia significantly increased P uptake compared to that of the control or sole MPR, but combining MPR with the other organic materials did not result in significantly higher P uptake than sole application of MPR. There was a similar trend in P uptake when TSP was combined with organic materials as compared to that of the control. A significant interaction was observed when TSP was co-applied with manure.

Calcium uptake was significantly increased by singular applications of organic materials and by both MPR and TSP, compared to that of the control (Table 15). Like in P uptake, the effect of TSP on Ca uptake was higher than that of MPR. Combining MPR with each organic material produced significantly greater Ca uptake than that of sole MPR. The treatment of MPR + tithonia produced the greatest influence on Ca uptake, which was 55% higher than that of MPR alone. TSP + organic material treatments had no significant effect on Ca uptake as compared to TSP alone.

The higher P concentration in the control in comparison with those of some other treatments was due to the small dilution effect that resulted in from the lower maize DMY in this treatment. According to Jones and Eck (1973) the range of P sufficient for maize seedlings (35 to 45 DAP) is 0.25 to 0.4%. Basing on this critical value, P concentrations in all treatments were below sufficiency levels. This implies either that the P supplied from both organic and inorganic inputs could not supply enough P to reach the critical values or that something else limited P uptake by the maize plants. In the case of the organic materials alone, this could be due to the low (resin) P that came from the decomposition of the organic materials in these treatments (Table 14). However, resin P was above the critical value in the soil that was treated with either TSP or MPR at 100 mg P kg^{-1} soil, and hence some other factors must have hindered a higher level of P uptake. The most probable reason for the low P uptake is that, since the present Chromic Acrisol has only moderate P fixing capacity (Table 11 and Table 12), it probably fixed only a portion of the labile P before it was taken up by maize plants. This argument is supported by the earlier results (Table 8) whereby most of the inorganic P released from inorganic and organic amendments was in the NaOH-Pi fraction, a fraction that reflects the proportion of P that was chemosorbed by Al and Fe.

The high maize DMY in the organic and inorganic treatments as compared to that of the control caused a significant dilution effect that resulted in low plant Ca concentrations values in these treatments as compared to that of the control. According to Tandon (1993), Ca concentration in maize shoots (at 42 DAP) of<0.3%, 0.3 to 0.7% and >0.7% are considered as being low, sufficient and high, respectively. Since all the treatments had Ca concentrations within the sufficieny range, all treatments had sufficient levels of Ca in maize shoots (Table 15).

The influence of organic materials on P and Ca uptake could be attributed to their extra P and Ca contents as compared to that supplied by the control (Table 4). Organic materials also supplied other nutrients like nitrogen, potassium, magnesium, sulphur and micronutrients which contributed to increase in dry matter yields and hence enhancement of P and Ca uptake (Table 15). Manure and tithonia generally produced greater P and Ca uptake values than did other organic materials because of their higher Ca and P contents, and their supply of other nutrients like K and Mg that altogether resulted in higher maize DMY (Table 4). The higher Ca and P uptake in the TSP treatment as compared to MPR was due to the higher maize DMY in TSP than in the MPR treatment (Figure 12) and not due to the P concentration because TSP and MPR had almost similar P concentrations (Table 15).

4.4.2.3 Effects on maize dry matter yields

The influence of organic materials on maize DMY was significant (Figure 12, Appendix 6). Manure resulted in the highest maize DMY, followed by tithonia which was somehow similar to lantana (Figure 12). Both MPR and TSP increased maize DMY as compared to that of the control but the effect of MPR was less than that of TSP, with a RAE of 84%. When compared to sole organic materials, the increases caused by MPR were 35, 79, 84 and 141% higher than that of manure, tithonia, lantana and gliricidia, respectively. Corresponding increases in DMY for TSP as compared to organic materials were 54, 103, 109 and 174% for manure, tithonia, lantana and gliricidia, respectively. Minjingu phosphate rock + each organic material significantly produced higher maize DMY than sole MPR but there were no significant differences between the different organic materials (Figure 13). The treatments of TSP + tithonia or manure produced significantly higher maize DMY than sole TSP.

Maize DMY was highly correlated to the resin P (R^2=0.86, P<0.0001) determined at harvesting time. Both the concentration of Ca in the maize shoots and its uptake could account for 51% and 80%, respectively, of the variability in maize DMY.

Although 89% of maize DMY could be explained by P uptake, the concentration of P in maize shoots had little relationship with maize DMY (Table 16).

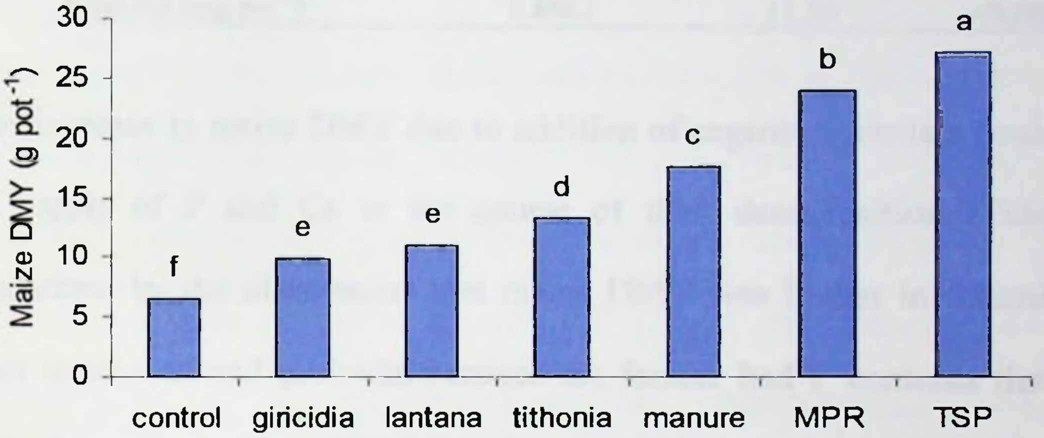


Figure 12. Effect of sole organic materials, TSP and MPR on maize dry matter yields from the Chromic Acrisol

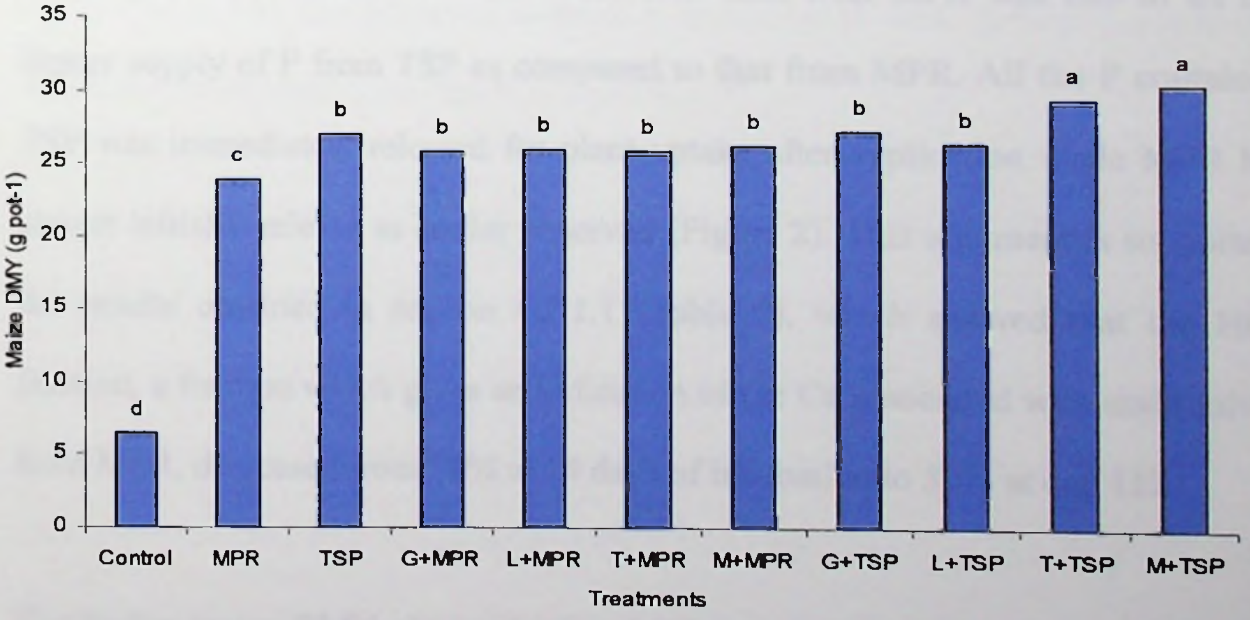


Figure 13. Influence of MPR and TSP when combined with organic materials on maize DMY from the Chromic Acrisol

Table 16. Relationship between maize dry DMY and other variables as observed in pot experiment

Variable	R^2	CV	Probability
Resin P (mg kg^{-1})	0.8550	13.30	<0.0001
Ca concentration (%)	0.5061	24.60	<0.0001
Ca uptake (mg pot^{-1})	0.8014	15.40	<0.0001
P concentration (%)	0.0886	33.40	0.0470
P uptake (mg pot^{-1})	0.8862	11.80	<0.0001

The increase in maize DMY due to addition of organic materials could be attributed to supply of P and Ca in the course of their decompsition (Table 4). This is confirmed by the observation that maize DMY was higher in tithonia and manure than in lantana and gliricidia because the former had P contents that were greater than the critical value (P=0.25%) for net P mineralization while the latter had P values which were below the critical value (Table 4).

The higher maize DMY obtained with TSP than with MPR was due to an initial higher supply of P from TSP as compared to that from MPR. All the P contained in TSP was immediately released for plant uptake after application while MPR had a slower initial P release as earlier observed (Figure 2). This argument is supported by the results obtained in section 4.2.1.1 (Table 7), which showed that the HCl-Pi fraction, a fraction which gives an indication of the Ca associated with undissolved P from MPR, decreased from 78% at 14 days of incubation to 37% at day 112.

The higher maize DMY obtained when MPR was combined with organic materials as compared to sole application of MPR cannot be attributed to enhancement of MPR dissolution caused by organic materials because combining MPR with organic materials either depressed resin P (an index of P availability) or gave similar results to sole application of MPR (Table 9). Further, earlier results shown in Figure 2 also indicated that combining MPR with organic materials produced less 0.1 N NaOH extractable P compared to that of sole MPR, indicating that organic materials were not enhancing MPR dissolution process.

Since resin P explained 85% of the maize DMY, the lack of significant interaction between MPR and organic materials for this variable means that the organic materials were not enhancing MPR dissolution. The positive interaction between MPR and organic materials on maize DMY was therefore, due to the following reasons: (i) supply of P and other macro and micronutrient from both inorganic and organic materials (Table 1); (ii) improvement of soil chemical characteristics like increased pH and Ca and a decrease of Al, all of which enhanced P availability, as shown in Table 14; (iii) liming effect by both MPR and organic materials and supply of Ca (Table 14). The observed increase in maize DMY was, therefore, partly due to addition of macronutrients like N, Ca and K.

Supply of essential macro and micronutrients results in a nutrient balance that enhances P absorption and uptake (Kretzschmar *et al.*, 1991; Hue *et al.*, 1994; Iyamuremye and Dick 1996; Gachengo *et al.*, 1999). Besides this, application of organic materials improves soil structure and moisture holding capacity which enhance microbial activity, consequently P turn over (Goyal *et al.*, 1999). It, further, improves soil aggregation and decreases soil bulk density, enhance P diffusion rates, decreases specific surface area, consequently increasing P availability (Linquist *et al.*, 1997b; Phan Thi Cong, 2000). Chemically, application of organic materials increases the surface charge and CEC of the soil (Moshi *et al.*, 1974; Phan Thi Cong, 2000), resulting in higher capacity of the Chromic Acrisol to hold and exchange cations that are essential for plant nutrition and hence increase in yields.

Resin P is the inorganic soil P fraction that is strongly related to plant available P (Fixen and Grove, 1990). The significant correlation between resin P and maize DMY for this Chromic Acrisol indicates that maize yields could be increased by raising the resin P level through addition of organic amendments, but this will depend on the rates applied. High correlation between P or Ca uptake and DMY implies that the greater the uptake of Ca or P the greater the likelihood of increasing maize yields. Since the present Chromic Acrisol is deficient in both Ca and P (Table 4) addition of organic materials high in Ca and P should result in increase in maize yields. Minjingu phosphate rock has a higher content of Ca than has TSP. Therefore; addition of the former is more likely to produce better maize yields than the latter, particularly in the residual effects phase.

In conclusion, manure proved to be the best organic material in improving soil properties (increasing pH, exchangeable Ca, resin P, and decreasing exchangeable Al) followed by tithonia. This observation tallies with a similar observation from the incubation study in section 4.2 where manure was the best, followed by tithonia, in increasing P availability through reduction of P adsorption, increase in pH and decrease of exchangeable Al. The application rate of 5 t ha^{-1} for all the organic materials used did not raise the soil resin P above the critical values of 6.5 mg P kg^{-1}. The increase in maize DMY could not, therefore, be attributed to P addition from the applied organic materials alone but rather to the influence of organic materials in rendering the non-labile P to become labile P, as evidenced by the decrease in P adsorption caused by these organic materials, as well as improvement in soil chemical and physical properties section (4.3.3, 4.3.4, 4.3.5) as was also reported by Nziguheba (2000); and Phan Thi Cong (2000).

Both MPR and TSP significantly increased soil pH, Ca, and resin P and reduced exchangeable Al, but the effect of MPR on pH, Ca and Al was greater than that of TSP. These inorganic fertilizers increased Ca and P uptake and maize DMY but the influence of TSP on these agronomic parameters was higher than that of MPR, possibly because the P in TSP is soluble. These results implied that the direct application of MPR could significantly improve the properties of this Chromic Acrisols and other similar soils. Similar results were obtained from laboratory study when using North Carolina phosphate rock on similar soils (Easterwood *et al.*, 1989; Hellums *et al.*, 1989; Wright *et al.*, 1991; Hu *et al.*, 1994; 1995; 1997).

Combined application of each organic material with MPR produced higher maize DMY than singular application of MPR, but this was not due to enhancement of MPR dissolution but rather due to increased P availability as a result of decreased P adsorption, addition of other macronutrients, and improvement of other chemical and physical characteristics by the organic materials.

Results from MPR, as presented in Table 7 and Figure 2, indicated that the HCl-Pi fraction as well as the 0.1 M NaOH extractable P increased with time. MPR has a slower initial release of P than TSP. The present Chromic Acrisol is dominated by

Al, Fe and their hydrous oxides, which tend to immediately convert labile P (resin P and $NaHCO_3$-Pi) from TSP to less labile forms (NaOH-Pi) through P fixation. This implies that the residual effect of MPR on this Chromic Acrisol could be higher than those from TSP because most of the P released rapidly from TSP would have been converted into less labile P fractions (NaOH-Pi) while P would be released from MPR more gradually.

Release of organic P pools from organic materials presumably would produce a greater residual P effect than that from inorganic P fertilizers, particularly TSP, because the P maintained in the organic form ($NaHCO_3$-Po and NaOH-Po) is better protected from P fixation than the P present in labile inorganic P fractions (Linquist *et al.*, 1997a). Prompted by these contentions on probable benefits of both organic materials and MPR in the residual phase, a third pot experiment (presented in section 4.5) was laid out using the same soil to examine the residual effects of both organic and inorganic P fertilizers.

4.5 Residual effects of MPR and TSP combined with different organic materials on soil properties, P and Ca uptake and maize DMY

4.5.1 Effect on soil properties

The residual effects of organic materials, MPR and TSP, when applied singly or in combination, are shown in Table 17. All treatments except MPR + tithonia, had no significant effect on pH compared to that of the control. However, there was a noticeable drop in pH in all treatments during the residual effects phase (Table 17) compared to that in the application phase (Table 14). Exchangeable Ca was significantly higher under organic material treatments as compared to that in the control. The trend in exchangeable Ca was manure>tithonia =lantana=gliricidia>control. Both MPR and TSP produced significant residual effects on exchangeable Ca as compared to that of the control. There was no positive effect of organic materials on Ca when they were combined with MPR or TSP.

Resin P from the control treatment was lower than in organic material treatments but significant differences were observed only for manure and tithonia. MPR and TSP produced significantly higher resin P than that of the control and the magnitude of the effect above the control level was 118% and 66% for MPR and TSP, respectively. Combining MPR with organic materials produced either similar or lower resin P levels than that from sole application of MPR, with the exception of manure + MPR. Combining TSP with organic materials produced higher residual effects on resin P than sole application of TSP, the trend being TSP + tithonia>TSP + manure=TSP + lantana>TSP + gliricidia.

The noticeable drop in pH in the residual effects phase (Table 14 and Table 17) was due to the acidification that could have been caused by ammonium and zinc sulphate basal fertilizers, uptake of basic cations by maize, and nitrification process during the fertilizer application phase, as mentioned in section 4.4.2.1, and illustrated in equation (xvi) in section 2.4.1.2. The significant effect of organic materials on exchangeable Ca and resin P during the residual effects phase implies that these organic materials were still undergoing decomposition.

Table 17. Residual effects of MPR and TSP combined with different organic materials on soil pH exchangeable Ca and RP of the Chromic Acrisol

Treatment	PH (H_2O)	Ca	RP
		cmol (+) kg^{-1}	mg kg^{-1}
Control	4.30 a	1.25 h	1.37 h
Manure (M)	4.22 abc	2.25 def	1.98 g
Tithonia (T)	4.22 abc	2.01 f	1.93 g
Lantana (L)	4.30 a	1.95 fg	1.64 h
Gliricidia (G)	4.23 abc	1.81 g	1.64 h
MPR	4.18 abc	2.58 abc	2.99 e
TSP	4.12 abc	2.27 cde	2.28 f
MPR + M	4.24 ab	2.60 ab	3.64 c
MPR + T	4.08 c	2.77 a	3.12 de
MPR+ L	4.17 abc	2.76 a	3.01 e
MPR + G	4.14 bc	2.36 bcd	2.36 f
TSP + M	4.10 bc	2.35 bcd	4.12 b
TSP + T	4.24 ab	2.38 bcd	6.15 a
TSP + L	4.13 bc	2.09 defg	4.07 b
TSP + G	4.29 a	2.19 def	3.67 c
CV (%)	1.90	7.52	5.2

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

Although the TSP treatment had higher resin P than that of MPR in the application phase (Table 14) the latter treatment had significantly higher resin P than TSP during residual phase (Table 17), indicating continued dissolution of the MPR as earlier shown in Table 7. The general lack of significant interaction between organic materials and MPR on resin P implies that organic materials were not directly enhancing MPR dissolution, even in the residual phase. The main reason for lack of significant interaction would be that organic materials were still producing Ca and P (Table 17) and probably were still contributing to reduce P fixation during residual phase. Since low Ca and P sinks hinder MPR dissolution (section 2.5.1.2 and 2.5.1.3; equation xx) there was no MPR dissolution enhancement in residual phase. There was a general drop in pH during the residual phase compared to the application phase. Such a condition would normally result in enhanced MPR dissolution in MPR + organic material treatments because it would provide protons (Rajan *et al.*, 1996). Lack of such MPR dissolution enhancement probably implies that the decrease in the Ca sink had a bigger influence on the MPR dissolution reaction than does proton supply.

4.5.2 Residual effect on Ca and P uptake

The residual effects caused by organic and inorganic amendments on maize shoot Ca and P uptake are shown in Table 18. Both manure and tithonia had significantly higher residual effects on Ca and P uptake by maize as compared to their uptake in the control. There were significant residual effects from both TSP and MPR on maize Ca and P uptake (Table 18) as compared to that in the control. The Ca and P uptake values from MPR were not significantly different from those of TSP. Combining MPR or TSP with each of the organic materials had no significant interaction on maize Ca and P uptake as compared to that under sole MPR or sole TSP.

Increase in Ca and P uptake due to tithonia and manure application were due to the continued decomposition of manure and tithonia, which resulted in increases in Ca and resin P, as well as in other macronutrients (N, K, Mg) and micronutrients (Baltazary, 2002). These nutrients then contributed to increased maize DMY as a result of increased Ca and P uptake.

4.5.3 Residual effect on dry matter yield

Maize DMY from both organic and inorganic treatments during the residual phase were lower than during the initial application phase (Figure 14). Manure and tithonia had significantly higher residual effects on maize DMY compared to yields of the control. The increase in maize DMY above that of the control was 217% and 159% for manure and tithonia, respectively. The residual effects of lantana and gliricidia on maize DMY were not significantly, higher than control yields.

Both MPR and TSP had a significant residual effect on maize DMY compared to that of the control. The residual effect of TSP was lower than that of MPR though these treatments had similar Ca and P uptake values. The RAE of MPR increased from 84% during fresh application to 90% during residual phase (Figure 14). When compared to sole organic materials, the residual effect on maize DMY from MPR was significantly higher than that from all organic materials.

Table 18. Residual effect of MPR and TSP combined with different organic materials on Ca and P uptake by maize

Treatment	Ca uptake	P uptake	DMY
	------------------------(g pot^{-1})--------------------------		
Control	4.02 e	0.28 d	3.68 f
Manure (M)	12.94 bcd	0.96 c	12.12 cde
Tithonia (T)	11.44 d	1.04 c	9.56 e
Lantana (L)	6.98 e	0.54 d	6.47 f
Gliricidia (G)	5.14 e	0.34 d	3.72 f
MPR	16.92 a	1.87 a	15.29 abc
TSP	13.56 abcd	1.70 ab	12.95 cd
MPR + M	15.94 ab	1.87 a	16.72 ab
MPR + T	15.72 ab	1.56 ab	13.93 bc
MPR+ L	16.28 ab	1.42 b	13.39 bcd
MPR + G	16.19 ab	1.65 ab	13.93 bc
TSP + M	16.71 a	1.76 a	14.57 abc
TSP + T	16.81 a	1.82 a	15.01 abc
TSP + L	14.93 abc	1.54 ab	17.75 a
TSP + G	11.75 cd	0.96 c	10.20 de
CV (%)	14.16	13.4	15.20

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

Tithonia and manure had similar residual effects on maize DMY as that of TSP (Figure 14). Generally organic materials did not cause a significant residual effect on maize DMY when combined with MPR (Figure 15).

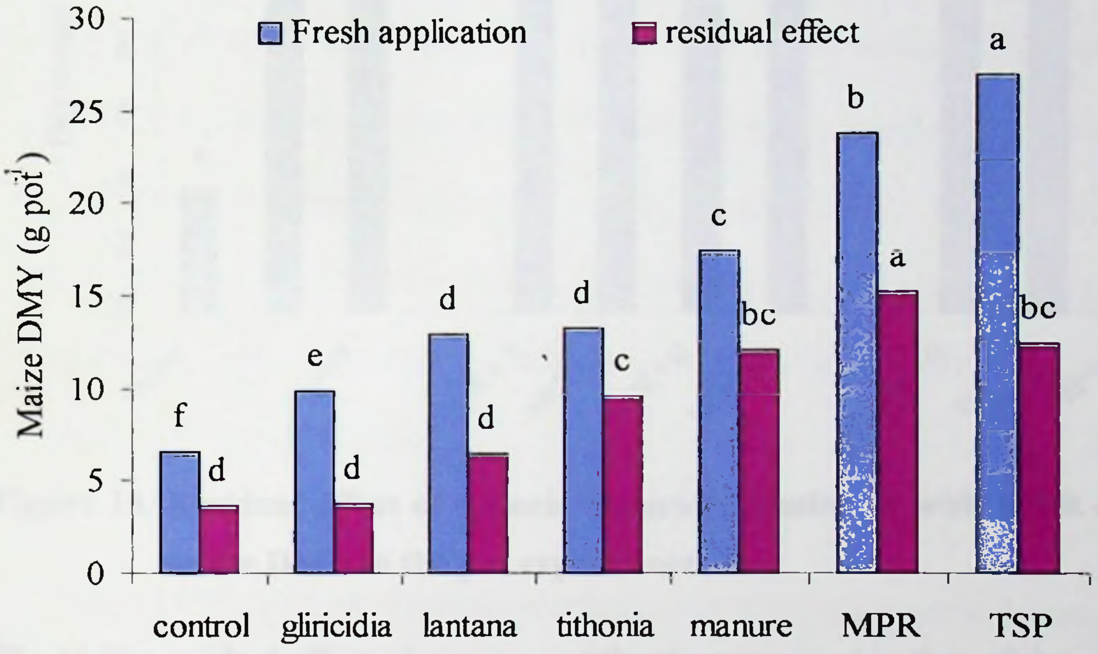


Figure 14. Residual effects caused by application of organic materials, MPR and TSP on maize dry matter yields

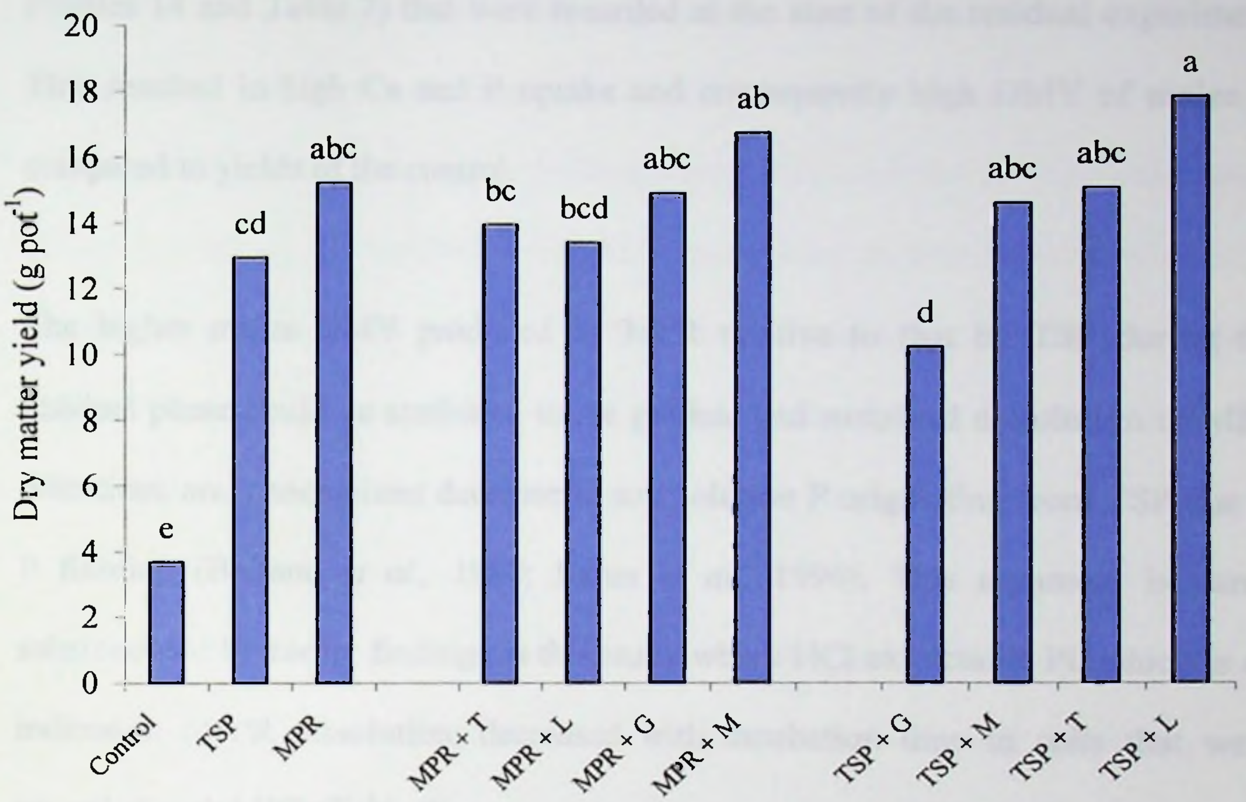


Figure 15. Residual effect of organic materials combined with MPR or TSP on maize DMY in the pot experiment

The higher residual effect of manure or tithonia, compared to that of the control, on Ca and P uptake is due to their high P and Ca contents (Table 4) and high soil exchangeable Ca and resin P (Table 17). The crop removal that took place in fresh application phase decreased the levels of these nutrients, but there was further mineralization during the residual phase, consequently producing higher maize DMY than that in the control. The higher residual effect on maize DMY caused by manure and tithonia was also due to release by the organic materials of other nutrients like N, K, Mg and micronutrients.

The significant increase in Ca and P uptake caused by MPR and TSP can be attributed to the high soil exchangeable Ca and resin P values

(Tables 14 and Table 7) that were recorded at the start of the residual experiment. This resulted in high Ca and P uptake and consequently high DMY of maize as compared to yields of the control.

The higher maize DMY produced by MPR relative to that by TSP during the residual phase could be attributed to the gradual and sustained dissolution of MPR with time, and concomitant decrease in soil solution P originating from TSP due to P fixation (Bolland *et al.*, 1988; Rajan *et al.*, 1996). This argument is partly substantiated by earlier findings in this study where HCl extractable Pi, which is an indication of PR dissolution, decreased with incubation time in soils that were amended with MPR (Table 8).

Unlike MPR, TSP has immediate release of P after application because it is water-soluble. Some of the phosphorus released from TSP may be immediately transformed by Al^{3+}, Fe^{3+} and Mn^{2+} into unavailable forms or fixed by sesquioxides and alumio-silicates (Bohn *et al.*, 1979), resulting in lower effectiveness from TSP during the residual phase. The phosphorus from MPR is slowly released, for a longer period, hence reducing the extent of its fixation by the above mentioned soil components.

This study has shown that high quality organic materials like farmyard manure and tithonia, applied at 5 t ha^{-1}, had a significant residual effect on maize DMY. This residual effect was similar to that produced by TSP but was less than that of MPR applied at 100 mg P kg^{-1} (equivalent to 220 kg P ha^{-1}). This study has also shown that MPR had a higher residual effect in terms of exchangeable Ca and resin P, consequently contributing to higher maize DMY than that from TSP at the same rate of 100 mg P kg^{-1}. The better perfomance of MPR may be due to its continued dissolution during the residual phase. This proposition of continued dissolution of MPR is supported by the fact that MPR treatments had lower resin P than that of TSP at the start of the experiment (Table 14) but the former treatment had more resin P than the latter at the end of the residual phase (Table 17).

Although Ca and P uptake were similar in both TSP and MPR treatments during residual phase, the latter fertilizer had significantly higher maize DMY than the former. This shows that it is not only the Ca and P released from MPR that caused better crop performance but also a contribution of other factors. Better crop performance was also probably due to the supply of other macronutrients like Mg which are contained in MPR but lacking in TSP. Other results that indicate better residual effect of MPR compared to TSP have been reported by Kimbi *et al.* (1996), Mowo (2000) and Hosea (2002).

The best organic material as indicated by crop performance during both application and residual phase was FYM, followed by tithonia. This better performance of FYM compared to tithonia could not be attributed to higher P content because tithonia had a similar P content as FYM. It also had lower N, Ca, Mg and K contents than had tithonia (Table 4). Its better performance was probably due to its higher effect on P availability through reduction of P sorption (Figure 9; Figure 10) rather than its P content. In addition to this, manure probably imparted a greater effect than tithonia on other soil properties like organic matter, moisture holding capacity and soil aggregation, all which improve nutrient availability and, consequently, increased maize DMY (Mowo, 2002).

The soil volume from which plant roots can extract nutrients as well as the roots' rhizosphere effects, are smaller under pot experiments than under the field conditions. The dissolution of MPR and decomposition of organic materials is likely to change under bigger soil volume, larger rhizosphere effects and uncontrolled moisture situations in the field. Similarly, there is little environmental variability in pot experiments. The dry matter yields obtained under non-limiting moisture conditions, which exist in pots, cannot be extrapolated to the grain yields that would have been obtained from field experiments. Thus, pot studies are only indicative and no conclusive recommendations can be drawn from them.

In the pot experiments only one application rate of organic materials was employed (5 t ha^{-1}). It was, however, noted that the amount of P released from organic materials at this application rate was not enough to attain the critical resin P values for increased maize yields. Therefore, a field trial was set up to test the effect of tithonia combined with MPR or TSP, at different rates of tithonia application, on soil characteristics and maize yields. Tithonia was selected, though it was manure that had the best performance, to avoid the high heterogeneity associated with different batches/collections of manure as compared to tithonia.

Table 19. Some soil chemical properties as influenced by tithonia combined with MPR or TSP in three seasons at 45 days after treatment application

Treatment	pH (water)			Ca (cmol (+) kg^{-1})			Al (cmol (+) kg^{-1})		
	Season1	Season2	Season3	Season1	Season2	Season3	Season1	Season2	Season3
Control (-P)	4.80f	4.57d	4.41f	1.73h	1.78h	1.43g	0.55b	0.36a	0.68a
Tithonia 2.5 t ha^{-1} (T2)	5.20cde	4.85b	4.51e	2.47def	2.45ef	1.65f	0.22de	0.25b	0.57bc
Tithonia 5 t ha^{-1} (T5)	5.40b	4.80bc	4.62c	2.53def	2.44ef	1.66ef	0.20e	0.22bc	0.53bcd
Tithonia 7.5 t ha^{-1} (T7)	5.30bc	5.30a	4.60cd	2.90c	2.57e	1.94cd	0.10fg	0.22bc	0.42de
MPR (P 80)	5.22cde	4.83bc	4.70b	4.45a	3.32b	2.12b	0.17ef	0.20bc	0.47cde
TSP (P 80)	4.70g	4.34e	4.35g	3.73b	2.24g	1.88d	0.73a	0.39a	0.62ab
MPR (P 40) + T2	5.14e	4.86b	4.57cd	2.44def	2.34fg	1.70ef	0.40c	0.22bc	0.50cde
MPR (P 40) + T5	5.14e	4.88b	4.55de	2.26fg	2.84d	2.09bc	0.28d	0.17c	0.42de
MPR (P 40) + T7	5.57a	4.87b	4.55de	2.67cde	3.12c	2.17b	0.08gh	0.20bc	0.42de
TSP (P 40) + T2	5.16de	4.68cd	4.85a	1.98gh	2.45ef	1.83de	0.18e	0.21bc	0.47cde
TSP (P 40) + T5	5.18de	4.82cb	4.45f	2.32efg	2.55e	2.05bc	0.10fg	0.18c	0.38ef
TSP (P 40) + T7	5.30bc	5.36a	4.82a	2.69cd	3.68a	2.42a	0.01h	0.02d	0.28g
CV (%)	1.33	2.04	0.80	8.12	3.35	4.83	19.03	16.06	13.13

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

In the present study, the main mechanisms that caused an increase in soil pH were: (i) addition of basic cations (section 4.1.2.1) (ii) production of organic acids (section 4.1.2.2) and (iii) presence of $CaCO_3$ (section 4.1.3). As ealier explained in section 4.1.2.1, tithonia has high contents of basic cations (Ca, Mg and K) (Table 4), which contributed to raise soil pH upon being hydrolysed to form hydroxides. Tithonia also had relatively higher concentrations of oxalic acid (Table 5), which in the due course of decomposition could have produced Ca through microbial degradation of oxalate Ca oxalate (CaC_2O_4), under aerobic conditions, resulting in an increase in pH through formation of calcium carbonate ($CaCO_3$) (Messini and Favilli, 1990), as illustrated by the following equation:

$$CaC_2O_4 + \frac{1}{2} O_2 \rightarrow Ca\,CO_3 + CO_2\uparrow \text{--}(xvii)$$

The decrease in soil pH caused by TSP was due to hydrolysis of monocalcium phosphate contained in the TSP, which releases phosphoric acid according to reaction (xxiii), consequently decreasing the soil pH. The increase in soil pH from MPR as compared to that of the control is attributed to OH^- ions produced during hydrolysis of CaO contained in the MPR. The MPR also contains associated $CaCO_3$, which, upon dissolution, released Ca into solution. The Ca was then hydrolysed, resulting in an increase in pH due to the OH^- produced as shown and explained in equations (xxi) and (xxii). Similar effects of increasing soil pH by tithonia and MPR, and decrease in soil pH by TSP, were also observed in soils in the pot experiment (section 4.4.2.1). The higher pH in tithonia combined with TSP than that in the control and TSP treatments was due to the effect of tithonia in that combination treatment. The increase in soil pH observed in the Chromic Acrisols in this study has practical implication because at higher soil pH, the solubility of Al is reduced (section 2.3.2). Since Al fixes P, reduced concentration of Al under higher pH will result in a decrease in P fixation.

Since the use of TSP alone resulted in a decrease in pH while combining it with tithonia increased the pH, co-application of organic inputs with TSP may have the potential to slow down acidification of the soil if TSP were to be used on such soil over a long period of time.

The decrease in pH that was observed in season 3 as compared to the initial pH of 4.8 was probably due to the rainfall fluctuations that occurred during the experimental period. Fluctuation in both amount and distribution of rainfall resulted in changes in processes like nitrification that influence the soil pH (Bolan *et al.*, 1991) as depicted in equation (xvii) in section 2.4.1.2. The drop was highest in season three because during this year there was no fresh application of both organic and inorganic fertilizers which could have produced basic cations and hydroxyl anions to buffer the protons produced from nitrification. The decrease in pH that was observed compared to the initial pH of 4.8 could also be due to ammonium sulphate that was used as N source in all seasons as earlier explained in sections 3.7.1 and 4.4.2.1. Similar results on increase in pH due to application of tithonia biomass has been recently reported by Phan Thi Cong (2000) in Vietnam and George *et al.* (2002) in western Kenya when both were using soils with Ferralitic properties.

4.6.1.2 Effect on exchangeable Ca

Tithonia significantly increased soil exchangeable Ca compared to that of the control (Table 19). Tithonia at 7.5 t ha^{-1} generally had significantly higher exchangeable Ca than the other tithonia rates, which had similar exchangeable Ca values.

Both MPR and TSP resulted in increase in exchangeable Ca as compared to that of control but the increase in exchangeable Ca was higher under MPR than under TSP treatments. Combined application of MPR and tithonia resulted in increase in exchangeable Ca compared to that of the control. Similar trends in exchangeable Ca were observed for TSP compared to that of control.

Combining MPR with tithonia at 5 or 7.5 t ha^{-1} resulted in higher exchangeable Ca than that of tithonia alone. Minjingu phosphate rock alone had more exchangeable Ca than that of MPR + tithonia except in the residual phase, in season 3. Combined application of TSP + tithonia resulted in increase in exchangeable Ca compared to that of the control. Values from TSP + tithonia treatments were generally higher than in TSP alone except in season 1 when TSP alone produced more exchangeable Ca than TSP + tithonia. During the residual phase TSP + tithonia at 7.5 t ha^{-1} had more exchangeable Ca than sole TSP.

The increase in exchangeable Ca following addition of tithonia is attributed to the high Ca content of tithonia as shown in Table 4, and this was also observed in the pot experiment in section 4.3.2.1. Treatments with MPR had higher Ca contents than those with TSP because MPR has a higher content of CaO and associated $CaCO_3$

(Table 6). These results from the field experiment agree with those from the pot experiment (section 4.4.2.1), where tithonia increased soil exchangeable Ca by 30%. Similar observations of increase in exchangeable Ca due to tithonia have been reported by Savini (2000), Phan Thi Cong (2000), George *et al.* (2002) and Baltazary (2002).

The increase in exchangeable Ca on a Chromic Acrisol that has low exchangeable Ca (Table 3) is partly the cause of the increase in pH reported in section 4.6.1.1. This increase in Ca is important because it improves the Ca supplying capacity of the Chromic Acrisol and consequently, improved nutrition and maize plant yields (section 4.6.2.1.). Since MPR + tithonia had higher residual effect on exchangeable Ca than had MPR alone or TSP + MPR it is advisable to combine tithonia with MPR on the Chromic Acrisol rather than resort to TSP alone or TSP + tithonia.

4.6.1.3 Effect on exchangeable Al

Tithonia significantly reduced exchangeable Al compared to that in the control (Table 19). Generally, there were only small differences in exchangeable Al between different application rates of tithonia.

Minjingu phosphate rock significantly reduced exchangeable Al compared to that of the control. Conversely, TSP either increased exchangeable Al above that of the control or was similar to that of the control. When MPR and TSP were each combined with tithonia, significant reductions of exchangeable Al compared to that of control were observed. Combining MPR or TSP with tithonia generally resulted in lower exchangeable Al than sole MPR or TSP. The differences in exchangeable Al between MPR + tithonia and TSP + tithonia were generally similar. The decrease in exchangeable Al for the tithonia and MPR treatments was a consequence of increase in pH in these treatments (section 4.6.1.1).

The decrease in exchangeable Al might also be due to complexation of Al by the organic acids produced during the decomposition of tithonia (Bolan *et al.*, 1994). Tithonia decomposition in the present study resulted in the release of different carboxylic acids (section 4.1.2.2; Table 5). The influence of organic materials in reducing the concentration of exchangeable Al has been shown to vary with the type of organic acid produced during decomposition (Hue *et al.*, 1986; Jones, 1998). The capacity of the organic acids to reduce exchangeable Al is in the order of tricarboxylic>dicarboxylic>monocarboxylic (Jones, 1998) as explained in section 2.4.1.2 (c). Oxalic and tartaric acids, which were produced in relatively large amounts by tithonia (Table 5), are among the dicarboxylic acids that have high organic acid-Al complexation constants (Appendix 2) (Bolan *et al.*, 1998; Jones, 1998). These acids might have reduced soil exchangeable Al during tithonia decomposition, by complexing the Al.

The more pronounced reduction of exchangeable Al caused by MPR as compared to TSP is due to its higher levels of $CaCO_3$ associated with the MPR, relatively higher CaO concentration compared to that of TSP and its higher initial pH (Table 6). As earlier explained in section 4.4.2.1, release of Ca from the MPR associated $CaCO_3$ caused MPR to increase soil pH as indicated in reactions (xxi) and (xxii) and, consequently, a decrease in solubility of Al. The increase in exchangeable Al due to TSP compared to that in the control is attributed to the hydrolysis of monocalcium phosphate in TSP and its initial low pH (Table 6). Hydrolysis of monocalcium phosphate produces phosphoric acid as shown in equation (xxiii) in section 4.4.2.1, consequently increasing the solubility of Al.

The fact that combining MPR with tithonia at 7.5 t ha^{-1} in most cases resulted in lower exchangeable Al than that caused by MPR alone is attributed to the higher pH (section 4.6.1.1) and higher Ca (section 4.6.1.2), which resulted in lower solubility of Al. It also implies that MPR application rates could be reduced to 50% by co-applying it with tithonia and still result in higher pH, higher Ca and lower exchangeable Al than that brought by the sole MPR alone applied at higher rate.

Since TSP resulted in similar or higher exchangeable Al than that of the control, and TSP + tithonia had lower exchangeable Al than sole TSP, TSP should therefore be co-applied with organic materials to avoid possible acidification after a long-term use in the soil under study (Chromic Acrisol). The decrease in exchangeable Al due to tithonia is in conformity to that of Phan Thi Cong (2000) on a Ferralic Cambisol in Vietnam and George *et al.* (2002) on a Chromic Acrisol in western Kenya.The decrease in exchangeable Al on this Chromic Acrisol will result in decrease in P adsorption because less Al will now react with P to form insoluble aluminium phosphate that makes P unavailable for plant uptake.

4.6.1.4 Effect on soil extractable P

(a) Non sequential extractable resin P

Generally, tithonia significantly increased resin P compared to that of the control in season 2 (Table 20). There were no significant differences in resin P between tithonia application rates of 2.5 and 5 t ha^{-1}. During the residual phase, season 3, resin P decreased drastically and ranged from 0.76 to 1.66 mg P kg^{-1}, and all the resin P values were similar to that of the control.

Both TSP and MPR resulted in significantly more resin P than that of the control or sole tithonia. The MPR and TSP treatments had significant residual effects on resin P compared to that of the control but the residual effect of MPR was 58% higher than that of TSP (Table 20). Combining MPR with tithonia at 5 or 7.5 t ha^{-1} in season 1 produced higher resin P than from MPR alone. There was no significantly interaction between tithonia and MPR in the residual phase. Combining TSP with tithonia produced lower resin P than TSP alone except for TSP + tithonia at 7.5 t ha^{-1} in seasons 2 and 3.

The influence of MPR + tithonia on resin P was significantly higher than that of TSP + tithonia in season 1. Resin P has been defined as the most labile P pool that is highly correlated to plant P uptake. The significant increase in resin P that was caused by tithonia was due to the high P content in tithonia and its effects on increasing soil pH, increasing exchangeable Ca and decreasing exchangeable Al (Table 19).

Table 20. Resin P as influenced by tithonia combined with MPR or TSP in three seasons at 45 days after treatment application

Treatment	Resin P (mg kg^{-1})		
	Season 1	Season 2	Season 3
Control (-P)	4.19g	2.37l	0.76d
Tithonia 2.5 t ha^{-1} (T2)	6.85fg	4.90h	1.47d
Tithonia 5 t ha^{-1} (T5)	6.59fg	5.13h	1.66d
Tithonia 7.5 t ha^{-1} (T7)	9.36f	8.00g	1.50d
MPR (P 80)	22.08d	48.70a	9.86a
TSP (P 80)	34.59b	37.83b	4.13c
MPR (P 40) + T2	22.95d	21.07e	5.28c
MPR (P 40) + T5	32.90b	20.50e	3.70c
MPR (P 40) + T7	43.36a	17.73f	5.10c
TSP (P 40) + T2	16.10e	28.90d	4.65c
TSP (P 40) + T5	24.45cd	36.00c	4.54c
TSP (P 40) + T7	26.56c	57.83a	7.31b
CV (%)	8.45	4.98	22.70

Means followed by the same letter in the same column are not significantly different $P<0.05$ by DMRT.

The increase in soil pH and Ca, and decrease in exchangeable Al, caused a decrease in the P adsorption capacity and increase in equilibrium P concentration as earlier shown in sections 4.3.5.1 and 4.3.5.2. Since the P added via the tithonia treatment, even at the highest tithonia rate, was still small compared to the recommended rate of 80 kg P ha^{-1}, it implies that the influence of tithonia on resin P was not due to P addition alone but rather to (i) its ability to render the less available P forms to labile P pools through reduction of P sorption (ii) supply of basic cations (Table 4) and (iii) modification of soil physical, chemical and biological properties as reported by Phan Thi Cong (2000), Nziguheba *et al.* (2000) and Baltazary (2002) which, in turn, improved P availability through microbial decomposition.

The pronounced decline in resin P during the residual phase in season 3 particularly at 7.5 t ha^{-1}. confirms its role as a P source for plants. This observation agrees with that in section 4.5.1 where there was a drastic decline in resin P in the residual phase of the pot experiment. The best application rate of tithonia was 7.5 t ha^{-1} because this rate gave resin P values which are above the critical level of 6.5 mg P kg^{-1} for high maize yields as reported by Landon (1991).

The substantially low extractable resin P values as estimated by resin P method, in all the inorganic and organic treatments in season 3, were probably due to the drought period (Plate 2), which might have hindered the mineralization processes. It could also be due to the rapid conversion of labile P to non-labile P forms through chemo-sorption processes. These P pools are not detected by the resin P extraction method. The Chromic Acrisol used in the field study had moderate P- fixing capacity (Table 11) (Fox and Kamprath, 1970), which implies that some of the labile P must have been rendered unavailable through chemo-sorption in season 3. The highest P pool in this Chromic Acrisol observed in incubation study (section 4.2.1.1) and field experiment (section 4.6.1.4b) was the NaOH-Pi (Table 7, Table 8, Figure 16), which supports the above argument that there was more chemo-sorption in season 3.

The better performance of TSP than of MPR at the same application rate as depicted by resin P in season 1 was due to the initial slow dissolution of MPR. Higher performance of MPR in season 2 and 3 compared to that of TSP indicates continued dissolution of the former and hence higher residual effects than TSP, as was earlier shown in section 4.2.1.1. The P added from TSP is more easily transformed into non-labile forms than that from MPR, gradually reducing its availability in subsequent years as compared to MPR.

Plate 2. Maize crop failure due to drought in season 3 (2003)

The higher soil pH, higher exchangeable Ca and lower exchangeable Al in the MPR compared to the TSP treatments (Table 19) allows conversion of some of the non-available P forms, into labile forms and it also protects labile P from rapid fixation. At higher pH values, the solubility of Al was reduced, and some of the fixed P in the form of aluminium phosphate was rendered available (Phan Thi Cong, 2000; Nziguheba *et al.*, 2000).

The lack of significant increase in resin P when MPR was combined with tithonia relative to sole application of MPR implies that tithonia was not directly enhancing MPR dissolution, as earlier shown in Figure 2, to the point of exceeding the resin P that was produced by sole MPR applied at 80 kg P ha^{-1}. The very low levels of resin P in all treatments in season 3 (residual phase), may be related to the drought that prevailed (Plate 2).

(b) Effects on sequentially extractable P pools

The influence of tithonia, MPR and TSP on sequentially extracted P fractions at 45 DAP in season 2 are presented in Table 21. Resin P values increased with increasing rates of tithonia additions but there were no significant differences between 2.5 and 5.0 t ha^{-1}. The influence of tithonia on NaHCO$_3$-Pi was similar to that on the resin P except that significant increases in NaHCO$_3$-Pi compared to that of the control were observed at 7.5 t ha^{-1} rate of tithonia. Although there was an increase in the moderately labile P pool (NaOH-Pi) with increase in tithonia application rates compared to that of the control, the increase at the lowest rate at (2.5 t ha^{-1}) was not significant. Tithonia significantly increased labile organic P

($NaHCO_3$-Po) compared to that of the control, but it had similar effects to that of the control in the case of labile organic Po (NaOH-Po).

Both MPR and TSP significantly increased inorganic P pools compared to that of the control, but had no effect on labile organic P pool ($NaHCO_3$-Po). MPR had relatively higher increasing influence on total labile Pi (RP + $NaHCO_3$-Pi) than that of TSP, but its influence on moderately labile P (NaOH-Pi) was lower than that of the TSP treatment (Figure16).

Table 21. Influence of tithonia, MPR and TSP on sequentially extracted soil P pools at 45 days after planting in season 2

Treatment	Resin P	Bic.-Pi	Total labile P (RP + Bic-P)	Bic-Po	NaOH-Pi	NaOH-Po	HCl-P
			(mg kg^{-1})				
Control (-P)	2.6 k	6.7 e	9.3 i	10.4 e	51 h	139 bc	1.6 gh
Tithonia 2.5 t ha^{-1} (T2)	5.1 j	8.4 e	13.5 h	12.3 cd	55 gh	143 abc	1.1 h
Tithonia 5 t ha^{-1} (T5)	5.7 j	7.9 e	13.6 h	12.5 cd	59 g	131 c	1.4 h
Tithonia 7.5 t ha^{-1} (T7)	8.0 i	12.6 d	20.6 g	11.7d	69 f	136 bc	2.0 fg
MPR (P 80)	48.7 b	33.6 b	82.2 b	9.9 e	100 b	145 abc	11.1 a
TSP (P 80)	37.8 c	41.3 a	79.1 c	10.6 e	118 a	160 a	5.4 b
MPR (P 40) + T2	21.1 h	20.5 c	41.5 f	13.3 bc	93 c	133 bc	3.3 d
MPR (P 40) + T5	23.2 g	18.5 c	41.7 f	13.9 b	81 e	145 abc	2.9 de
MPR (P 40) + T7	31.6 e	14.1 d	45.7 e	15.4 a	87 d	150 ab	2.4 ef
TSP (P 40) + T2	28.9 f	32.9 b	61.8 d	15.3 a	95 c	148 abc	3.1 d
TSP (P 40) + T5	36.0 d	41.5 a	77.5 c	15.2 a	85 de	140 bc	4.5 c
TSP (P 40) +T 7	58.4 a	34.8 b	93.22 a	15.4 a	84 de	149 ab	4.5 c
CV (%)	3.53	6.07	3.37	4.56	3.74	6.37	7.85

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

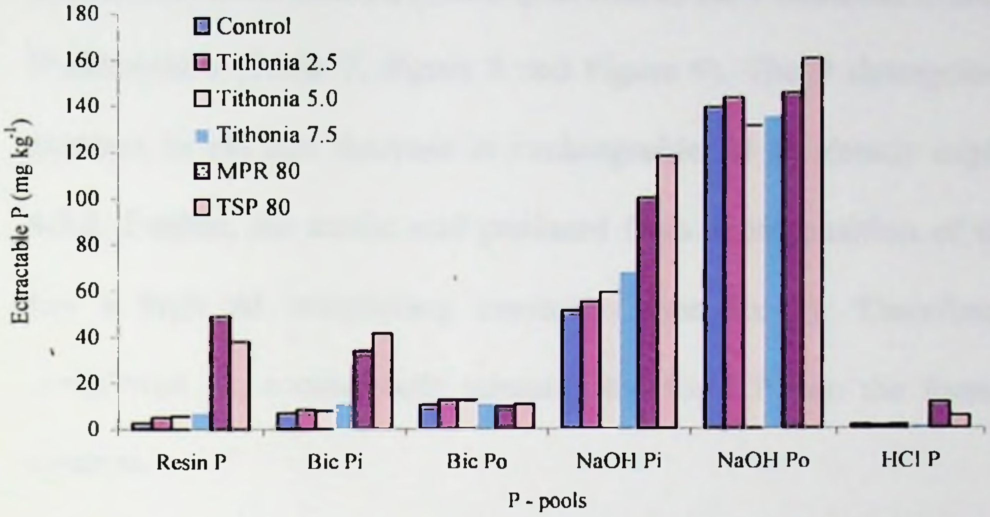
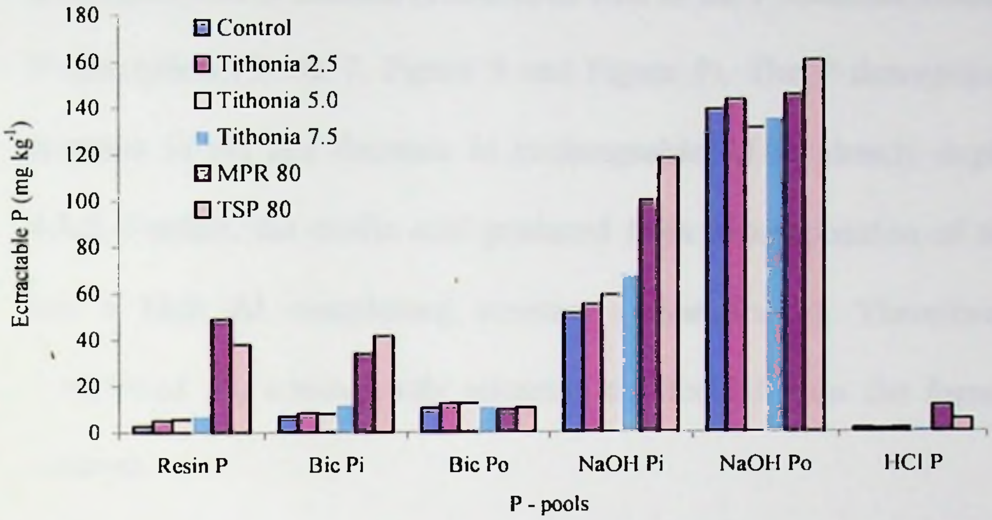


Figure 16. Influence of tithonia, MPR and TSP on various P pools in second season of field experiment

Combining tithonia with MPR or TSP resulted in higher total labilePi (RP-P + $NaHCO_3$-Pi) and moderately labile P (NaOH-Pi) than that of sole tithonia but the values were less than from sole MPR and TSP except for the TSP + tithonia at 7.5 t ha^{-1}. Although application of inorganic P fertilizers at 80 kg P ha^{-1} had no effect on labile organic P ($NaHCO_3$-Po) when these fertilizers were combined with tithonia they resulted in significant increase of this P pool compared to that of sole MPR or TSP. Lower rates of tithonia had no significant effect on HCl-P but both MPR and TSP significantly increased HCl-Pi with the effect of MPR on this P pool being 105% higher than that of TSP. Combining MPR or TSP with tithonia resulted in higher HCl-Pi than that in the control but these were significantly lower than those for sole MPR or sole TSP.



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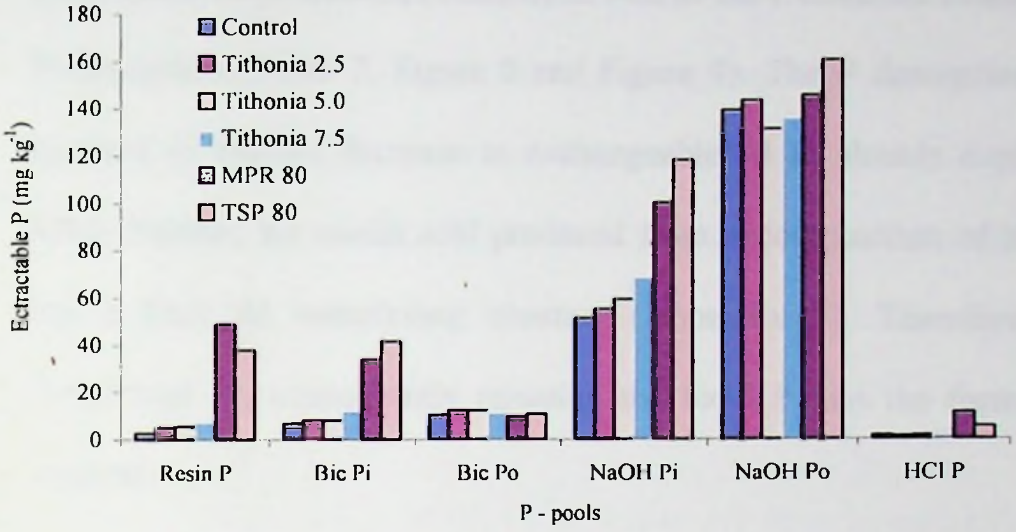

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The increase in labile P due to tithonia was due to P contribution from decomposition of tithonia (Table 6) as well as the P rendered available as a result of P desorption (Table 7, Figure 8 and Figure 9). The P desorption was caused by increase in pH and decrease in exchangeable Al as already explained in section 4.3.5. Further, the oxalic acid produced from decomposition of tithonia (Table 7) has a high Al complexing constant (Appendix 2). Therefore, it must have complexed Al, consequently releasing the fixed P into the form of resin P into solution.

The increase in NaOH-Pi that was caused by tithonia implies that some of the inorganic P released from tithonia decomposition was being fixed by Fe and Al, and adsorbed on hydrous oxides of Fe and Al, because the NaOH-Pi pool is related to the P chemisorbed by Fe and Al. The lack of significant increase of HCl-Pi from the tithonia treatment is due to the fact that HCl-P estimates active soil Pi from undissolved PR that potentially can supply plant available P (Buresh *et al.*, 1997) and not from organic inputs. These findings are in agreement with those of Iyamuremye *et al.* (1996b) and Nziguheba *et al.* (2000).

The increase in bicarbonate organic P that was caused by tithonia and tithonia + MPR or TSP treatments is very important for this Chromic Acrisol and in similar soils because P maintained in the organic form may be better protected from fixation than P present in the inorganic pools (Linquist *et al.*, 1997a; Mengel, 1997). This implies that at the same rates of P addition from tithonia, MPR or TSP higher residual effects could result from tithonia addition than from MPR or TSP. In

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The increase in NaOH-Pi that was caused by tithonia implies that some of the inorganic P released from tithonia decomposition was being fixed by Fe and Al, and adsorbed on hydrous oxides of Fe and Al, because the NaOH-Pi pool is related to the P chemisorbed by Fe and Al. The lack of significant increase of HCl-Pi from the tithonia treatment is due to the fact that HCl-P estimates active soil Pi from undissolved PR that potentially can supply plant available P (Buresh *et al.*, 1997) and not from organic inputs. These findings are in agreement with those of Iyamuremye *et al.* (1996b) and Nziguheba *et al.* (2000).

The increase in bicarbonate organic P that was caused by tithonia and tithonia + MPR or TSP treatments is very important for this Chromic Acrisol and in similar soils because P maintained in the organic form may be better protected from fixation than P present in the inorganic pools (Linquist *et al.*, 1997a; Mengel, 1997). This implies that at the same rates of P addition from tithonia, MPR or TSP higher residual effects could result from tithonia addition than from MPR or TSP. In unfertilised highly weathered soils there is low organic matter content to complex Al. Hence, most of the P is sorbed by hydrous oxides of Fe and Al or reacts with Fe^{3+} and Al^{3+} to form iron and aluminium precipitates as explained in section 2.3.2.1. Mineralization of organic P pools in soils has been identified as one of the main source of plant available P (Tiessen *et al.*, 1984; Beck and Sachenz, 1994; Guo and Yost, 1998; Yaobing *et al.* 1999; Guo *et al.*, 2000; Oberson *et al.*, 2001; Buehler *et al.*, 2002).

Since sole application of MPR or TSP had no effect on bicarbonate organic P pool, it shows that it would be more advantageous to co-apply tithonia, or other suitable organic materials, even at the lowest rate (2.5 t ha^{-1}), with MPR or TSP at 40 kg P ha^{-1} to the Chromic Acrisols, than to adopt sole TSP or MPR at 80 kg P ha^{-1}.

The increase both in readily available P ($NaHCO_3$-Pi) and moderately labile P (NaOH-Pi) pools caused by MPR and TSP implies that these fertilizers greatly contributed to both plant available and capital P. The relatively higher influence of MPR on total labile Pi (RP + $NaHCO_3$-Pi) and its lower increase on moderately labile P (NaOH-Pi) compared to that of TSP (Figure 16) means that most of the inorganic P released from TSP was being fixed by soil components as compared to that from MPR. This argument is supported by the observation (section 4.6.1.6) that at the same application rate, MPR led to less sorbed P than did TSP (Figure 16).

These results also show that MPR had a higher contribution than TSP to plant available P as reflected by a higher level of total labile P (RP and Bic-Pi. This condition was partly caused by continued dissolution of MPR (Table 7) and the high pH, high exchangeable Ca, low exchangeable Al, and lower P sorption capacity under MPR compared to those under TSP (Table 19 and 22).

The moderately labile P (NaOH-Pi) was the largest fraction because when inorganic soluble P fertilizers are applied to soil they undergo dissolution and the released P subsequently becomes transformed to different P fractions. But the principal sink for applied P is the moderately labile NaOH-Pi pool (Linquist *et al.*, 1997b; Oberson *et al.*, 2001). Since this P fraction is not readily available to plants, strategies that aim at reducing P sorption are very important for P management. This implies that sole application of TSP to this Chromic Acrisol would not solve the problem of P availability because TSP caused a decrease in pH and increase in exchangeable Al (Table 19). Application of organic amendments and or MPR seems to be one of the strategies of increasing P availability of such soils.

The highest HCl-P was produced by MPR because this P pool reflects the amount of P that is still in undissolved form, as Ca mono-phosphate. It, therefore, reflects the possibility of higher residual effects from MPR in subsequent years compared to that of the TSP. This was evidenced in season 3 (Table 19) when addition of both MPR and TSP had been stopped. The dissolution of the remaining calcium mono-phosphate from MPR produced more P and more Ca, resulting in a higher increase

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4.6.1.5 Effect on oxalic acid production

In the present study, organic and inorganic P treatments significantly increased oxalic acid concentration compared to that of the control (Figure 17). The concentration of oxalic acid ranged from 0.14 to 0.93 mmol L^{-1}. The oxalic acid concentration increased with increase in tithonia rates. The concentrations of oxalic acid in the MPR or TSP treatments were always lower than those from tithonia. Oxalic acid concentrations from MPR were, however, higher than that from TSP treatments. Light molecular weight organic acids, like oxalic acid, are usually produced in soils from the decomposition of organic residues, root exaudates and microbial metabolites (Fox and Comerford, 1990; Bolan *et al.*, 1994). The higher

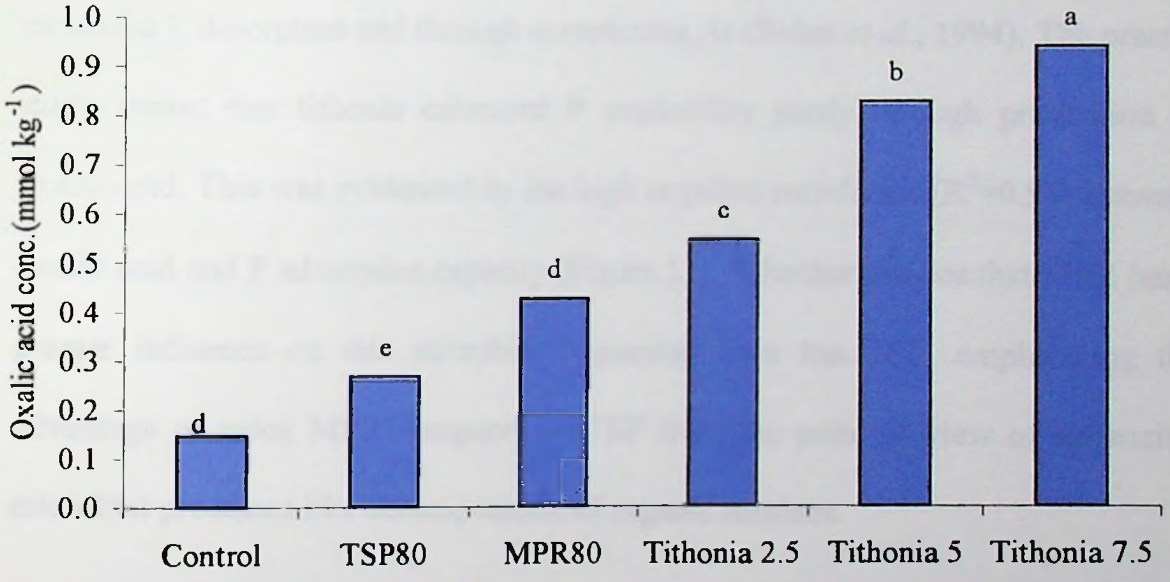

Figure 17. Effect of tithonia and inorganic P fertilizers on oxalic acid concentrations during second season at 45 DAP in the Chromic Acrisol

concentration of oxalic acid in tithonia treatments reflects the higher organic matter contents under tithonia as compared to that of control and the inorganic treatments. Sole MPR treatments had higher pH, higher exchangeable Ca, resin P and lower exchangeable Al (Table 19, Table 20, Table 21) than those of sole TSP. Such soil conditions probably resulted in higher microbial activity under MPR than under TSP treatments hence more oxalic acid production under the former than in the latter fertilizer.

Production of oxalic acid in mineral soils has been shown to influence P desorption (Fox *et al*., 1990). Oxalic acid influences P availability in soils mainly through increased P desorption and through complexing Al (Bolan *et al*., 1994). The present study shows that tithonia enhanced P availability partly through production of oxalic acid. This was evidenced by the high negative correlation (R^2=0.98) between oxalic acid and P adsorption capacity (Figure 11). It further implies that MPR has a greater influence on this microbial bi-product than has TSP, emphasizing the advantage of using MPR compared to TSP from the point of view of enhancing microbial processes like decomposition of organic residues.

4.6.1.6 Effect of tithonia on soil P adsorption isotherms and parameters

Sole tithonia significantly reduced the P sorption capacity of the soil in the field experiment as shown by the P adsorption isotherm (Figure 18) and the Langmuir and Freundlich adsorption parameters (Tables 22 and 23). Tithonia treatments resulted in less P sorption compared to that of the control. This effect on P sorption was more

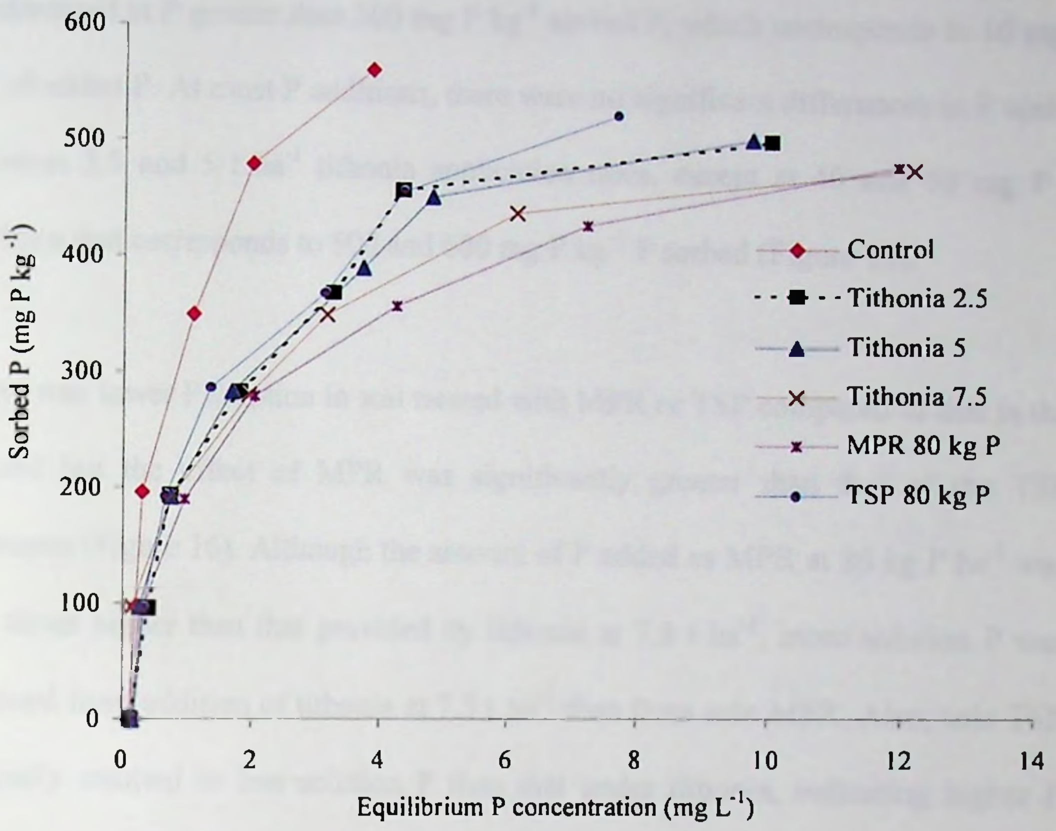

Figure 18. Effect of tithonia at different rates on P sorption isotherms of the Chromic Acrisol in field experiment

pronounced at P greater than 200 mg P kg^{-1} sorbed P, which corresponds to 10 mg P L^{-1} of added P. At most P additions, there were no significant differences in P sorbed between 2.5 and 5 t ha^{-1} tithonia application rates, except at 40 and 50 mg P l^{-1} addition that corresponds to 500 and 600 mg P kg^{-1} P sorbed (Figure 18).

There was lower P sorption in soil treated with MPR or TSP compared to that in the control but the effect of MPR was significantly greater than that of the TSP treatment (Figure 16). Although the amount of P added as MPR at 80 kg P ha^{-1} was two times higher than that provided by tithonia at 7.5 t ha^{-1}, more solution P was obtained from addition of tithonia at 7.5 t ha^{-1} than from sole MPR. Also, sole TSP generally resulted in less solution P than that under tithonia, indicating higher P adsorption under TSP. Co-application of MPR with tithonia at 7.5 t ha^{-1} resulted in less P adsorption than that of the control, but higher than that under MPR alone. TSP + tithonia at 7.5 t ha^{-1} resulted in higher solution P than all other treatments (Figure 19).

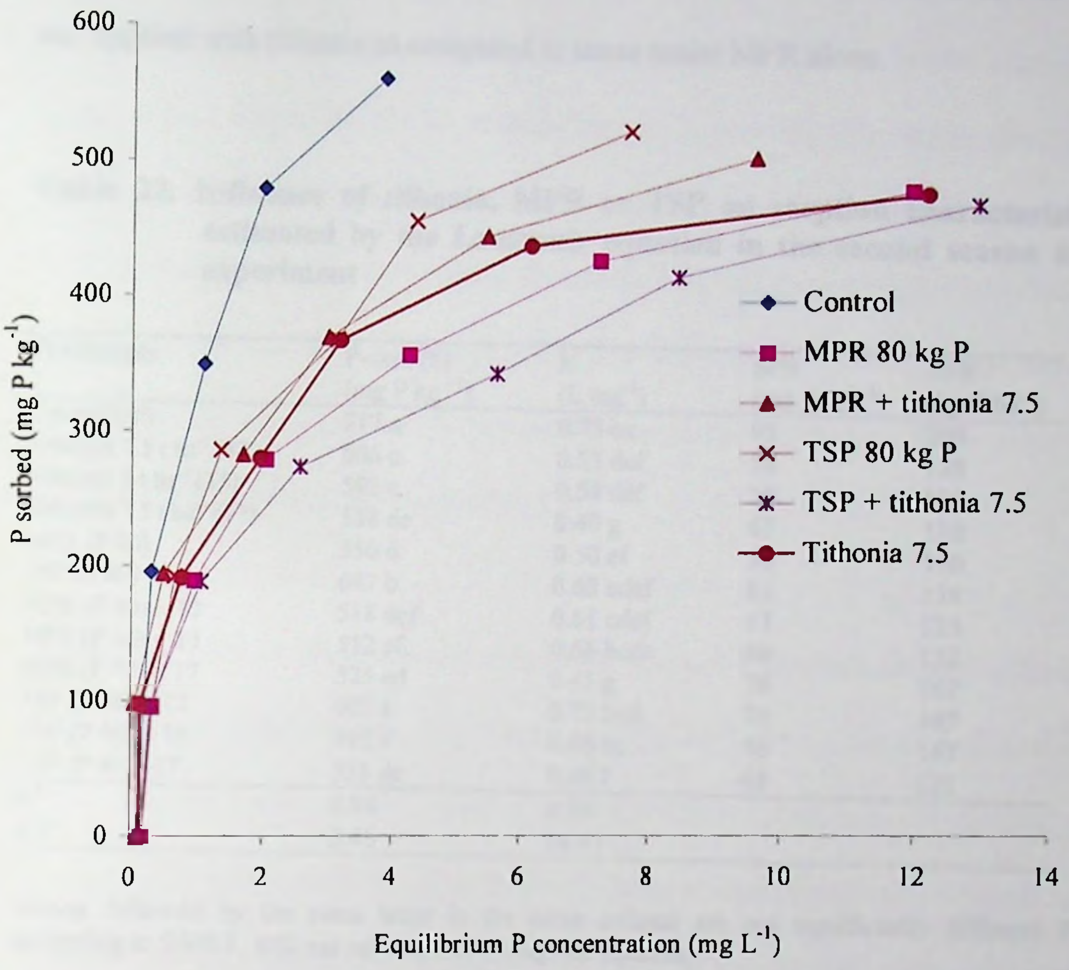

Figure 19. Effect of MPR and TSP combined with tithonia at 7 t ha^{-1} on P sorption isotherms of the Chromic Acrisol in field experiment

Reduction in P sorption by tithonia was accompanied by corresponding decreases in Langmuir adsorption maximum (b) and adsorption affinity (k) compared to those of the control (Table 22). These parameters showed no significant differences between tithonia at 2.5 and 5 t ha^{-1}.

Although sole MPR and TSP decreased "b" and "k" values, the influence of MPR on "b" values was greater than that of TSP. Co-application of MPR with 7.5 t ha^{-1}

tithonia resulted in significantly less "b" values than those of the control or MPR alone. Similar trends in adsorption affinity (k) values were obtained when MPR was co- applied with tithonia as compared to those under MPR alone.

Table 22. Influence of tithonia, MPR or TSP on sorption characteristics as estimated by the Langmuir equation in the second season of field experiment

Treatments	P-max (b) (mg P kg $^{-1}$)	k (L mg^{-1})	SPR (mg P kg $^{-1}$)	SPR (kg P ha^{-1})
Control (-P)	717 a	0.75 bc	93	205
Tithonia 2.5 t ha^{-1} (T2)	606 c	0.53 def	58	128
Tithonia 5 t ha^{-1} (T5)	592 c	0.54 def	58	128
Tithonia 7.5 t ha^{-1} (T7)	538 de	0.40 g	63	138
MPR (P 80)	550 d	0.50 ef	50	110
TSP (P 80)	641 b	0.63 cdef	63	138
MPR (P 40) + T2	518 def	0.61 cdef	57	125
MPR (P 40) + T5	512 ef	0.66 bcde	60	132
MPR (P 40) + T7	525 ed	0.41 g	76	167
TSP (P 40) + T2	602 c	0.72 bcd	76	167
TSP (P 40) + T5	592 c	0.66 bc	76	167
TSP (P 40) +T7	525 de	0.46 f	44	121
R^2	0.94	0.76		
CV	3.46	14.47		

Means followed by the same letter in the same column are not significantly different P<0.05 according to DMRT; SPR was calculated from Langmuir equation.

Combined application of TSP with tithonia similary decreased the "b" and "k" values compared to those under the control or TSP alone. All treatments resulted in a lower level of the "P adsorbed in equilibrium with solution P of 0.2 mg P L^{-1} (SPR value) " compared to that of the control, as calculated by the Langmuir equation. The lowest SPR value was in TSP + tithonia at 7 t ha^{-1}, corresponding to P addition of 121 kg P ha^{-1}. When the two inorganic P sources were compaed, less P is required from MPR than from TSP to supply 0.2 mg P L^{-1} in soil solution.

The sorption parameters as estimated by the Freundlich equation, which is based on different assumptions from those of the Langmuir equation, produced similar trends but this equation estimated P sorption capacity and affinity better than did the Langmuir as shown by the R^2 values (Tables 22 and 23). The differences may be attributed to the fact that the assumptions underlying the Freundlich equation are more realistic than those of Langmuir equation as ealier explained in section 2.3.3. The better estimations of the P adsotption capacities observed from using the Freundlich as compared to the Langmuir equations have also been reported by Warren *et al.* (1992) and Gikonyo (1997).

Combining MPR + tithonia resulted in lower sorption capacities (a) and affinity (b) than those of under control. There was positive MPR and tithonia interaction on sorption affinity but not on sorption capacity when MPR was co-applied with tithonia. The effect of TSP, when applied alone or combined with tithonia, on P sorption capacity and affinity compared to those of the control followed a similar trend as that of MPR. Like in the Langmuir equation, estimates of these values were generally lower under MPR than under TSP.

Table 23. Influence of tithonia, MPR or TSP on P sorption characteristics as estimated by Freundlich equation in the field experiment

Treatments	a	b
	(mg P kg $^{-1}$)	(L mg^{-1})
Control (-P)	273 a	0.54 a
Tithonia 2.5 t ha^{-1} (T2)	205 de	0.43 c
Tithonia 5 t ha^{-1} (T5)	204 de	0.44 c
Tithonia 7.5 t ha^{-1} (T7)	199 f	0.38 d
MPR (P 80)	177 f	0.43 c
TSP (P 80)	207 de	0.48 b
MPR (P 40) + T2	213 c	0.33 e
MPR (P 40) + T5	226 b	0.38 d
MPR (P 40) + T7	224 b	0.30 f
TSP (P 40) + T2	226 b	0.44 c
TSP (P 40) + T5	200 de	0.43 c
TSP (P 40) + T7	161 g	0.36 d
R^2	0.98	0.97
CV (%)	1.94	3.56

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

The decrease in P sorption capacity due to organic matter like tithonia was also observed and discussed in section 4.3.5 in the incubation experiment and can be explained by one or a combination of the following mechanisms: (1) competition by the released organic acids for P sorption sites. Dicarboxylic LMWOA like oxalic acid (Table 5) have been shown to compete for P sorption sites (Jones, 1998), thereby releasing P. Since tithonia produced this acid when it was incubated with soil (Table 10), it may have competed for P sorption sites. (2) saturation of P sorption sites. Tithonia had a high P content (P=0.46%), which was above the critical value of 0.24% for enhancement of P desorption (Singh and Jones, 1976) (Table 4). Therefore, the P released from tithonia decomposition occupied some of the P sorption sites. This proposition is confirmed by the observation that the decrease in sorption capacity caused by tithonia was accompanied by an increase in NaOH-Pi (Table 21), the P fraction that reflects chemi-soption of P by Al. This implies that some of the released P occupied the P sorption sites of the soil (3) Solubilization of the Al-phosphates by organic acids through formation of Al- organic acid complexes, thereby releasing P into solution. Further evidence of this mechanism is the high negative correlation between the decrease in P sorption capacity with increase in oxalic acid concentration of GMs (R^2=0.99) (Figure 11). (4) Reduction of Al activity in soil solution due to the liming effect of tithonia. Aluminium normally causes P fixation in acidic soils, through formation of aluminium phosphate, which makes P unavailable to plants (Gerke and Hermann, 1992; Warren, 1992; Phan Thi Cong 2000; Xia and Pierzynski, 2003). Therefore, the increase in pH and decrease in exchangeable Al due to tithonia or MPR that was observed in this study (Table 19) must have caused a decrease in P sorption as a resukt of P complexation by Al. Similar observations have been reported by Fox and Comerford (1990) who reported increased P release from the Bh and Bs horizons of Spodosols due to the presence of oxalic acid.

Since lower application rates of tithonia had relatively little influence on the concentration of oxalic acid and P sorption capacity, higher rates may result in greater reduction of P sorption as result of greater production of oxalic acid (Figure 17). These findings are in conformity with those of Iyamuremye *et al.* (1996a) who reported decrease in P sorption capacities with increase in application rates of manure and alfalfa, although the influence was not directly correlated to the amounts of organic acids produced by the organic materials but rather to their liming effects.

The differences in R^2 values for adsorption capacity and affinity, as determined by Freundlich and Langmuir equations, may be attributed to the differences in the assumptions underlying the two equations as pointed out by Syers *et al.* (1973) and Warren (1992). The Langmuir equation has a major advantage of making it possible to calculate an adsorption maximum and a relative binding energy term for P sorption. However, it has poorer estimation of the binding affinities when compared to the Freundlich equation, as discussed in section 2.3.3.1 and as revealed in this study. The lower CVs and higher R^2 values obtained from the Freundlich than those under the Langmuir equation (Tables 22 and 23) could be attributed to the difference in the assumptions underlying these the two equations.

The higher reduction of P sorption by MPR compared to TSP was due to its higher liming effect as compared to the liming effect of TSP, as explained in section 4.4.2.1. A higher liming effect reduced the activity of Fe and Al to a greater extent, thereby causing more P desorption.

Although addition of MPR or TSP at 80 kg P ha^{-1} contributed more total P than MPR or TSP at 40 kg P ha^{-1} combined with tithonia (Table 2), which means more P was there for saturating the soils' P fixation sites, there were higher P sorption capacities and bonding affinities under sole inorganic treatments than under the inorganic + organic treatments. This shows that reduction in P sorption was not only due to addition of P but it was also due to other factors, particularly the influence of organic acids produced following tithonia decomposition which increased P desorption as already explained. It further emphasizes the fact that reduction of P fixation through application of high rates of inorganic fertilizers is neither the best option in terms of the chemical mechanisms nor in terms of its economics. Generally, combining tithonia with MPR or TSP at 40 kg P ha^{-1} always produced better results than sole MPR or TSP at 80 kg P ha^{-1}, and may have better economics too.

When considered in terms of amounts of P fertilizers that have to be applied per hactare to obtain 95% of the maximum yield (SPR) as defined by Fox and Kamprath (1970), it was observed in the second season that less fertilizer was required to produce similar maize yields when MPR was used as P source than when TSP. This shows that in subsequent years less MPR fertilizer would be used to obtain 0.2 mg P L^{-1} in soil solution, a P concentration that is necessary for obtaining 95% of maximum yield for most crops (Fox and Kamprath, 1970).

4.6.2 Effect of tithonia, MPR and TSP on agronomic characteristics

4.6.2.1 Maize yields and agronomic effectiveness of different treatments

(a) Maize yields

The effects of P source and tithonia application rates on maize grain yields are shown in Table 24. There was a significant effect of P source and tithonia rates on maize grain yields. The interaction between P source and tithonia rates was in most cases not significant (Appendix 7). The influence of tithonia when applied singly or when combined with inorganic P fertilizers and single degree of freedom orthogonal contrasts of treatments for maize grain yields are as shown in Table 24 and Appendix 8, respectively.

Table 24. Effect of tithonia when applied alone or combined with MPR or TSP on maize yields

Treatments	MGY t ha^{-1}		DMY t ha^{-}
	Season 1	Season 2	Season 3
Control (-P)	1.34 f	0.87 e	0.44 f
Tithonia 2.5 t ha^{-1} (T2)	2.10 bcde	1.50 d	0.62 e
Tithonia 5 t ha^{-1} (T5)	2.33 abc	1.69 cd	0.65 de
Tithonia 7.5 t ha^{-1} (T7)	2.29 abcd	2.06 bcd	0.98 b
MPR (P 80)	1.87 e	2.21 abc	1.2 a
TSP (P 80)	2.50 a	1.81 cd	0.65 de
MPR (P 40) + T2	2.36 ab	2.30 abc	0.76 cde
MPR (P 40) + T5	2.34 abc	2.31 abc	0.91 bc
MPR (P 40) + T7	2.36 ab	2.74 a	1.18 a
TSP (P 40) + T2	2.07 cde	2.50 ab	0.72 de
TSP (P 40) + T5	2.29 abcd	2.72 a	0.83 bcd
TSP (P 40) + T7	2.48 a	2.84 a	1.16 a
CV (%)	7.62	15.69	11.93

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT; MGY=Maize grain yield; DMY = Maize dry matter yield

Maize grain yields were significantly increased by tithonia application relative to yields of the control (Table 24). Although maize plant vigour (Plate 3) and grain yields increased with increase in tithonia application (Table 24), there were no significant differences between different tithonia rates in terms of maize grain yields.

Plate 3. Plant vigour as shown by maize plants at different tithonia application rates

The yield response to tithonia was higher in season 1 than in season 2 (Figure 20) and the relationship between tithonia application rates and maize grain yields was significantly linear ($P=0.011$; $R^2=0.97$) in season 2. The maize yield response to tithonia in season 1 was at rates lower than or equal to 5 t ha^{-1}, and yields started to decrease beyond this rate. In season 2, maize yield continued to increase at all tithonia rates up to 7.5 t ha^{-1}. An average of season 1 and season 2 resulted in a response curve that started to show decrease in maize grain yield when you reach 7.0 t ha^{-1} of tithonia. The tithonia rate which gives the agronomic optimum corresponds to the point where the slope of the response equations shown in Figure 20 is zero. Basing on this, the calculated agronomic optimum for seasons 1, and 2, and for the average of season 1 and 2, were 5.7, 11 and 7.0 t ha^{-1} tithonia application rates, respectively.

During the residual phase maize plants were affected by drought (Figure 1), resulting in zero grain yields (Plate 2), but the maize DMY obtained at 45 DAP followed the same trend as that observed during treatment application phases.

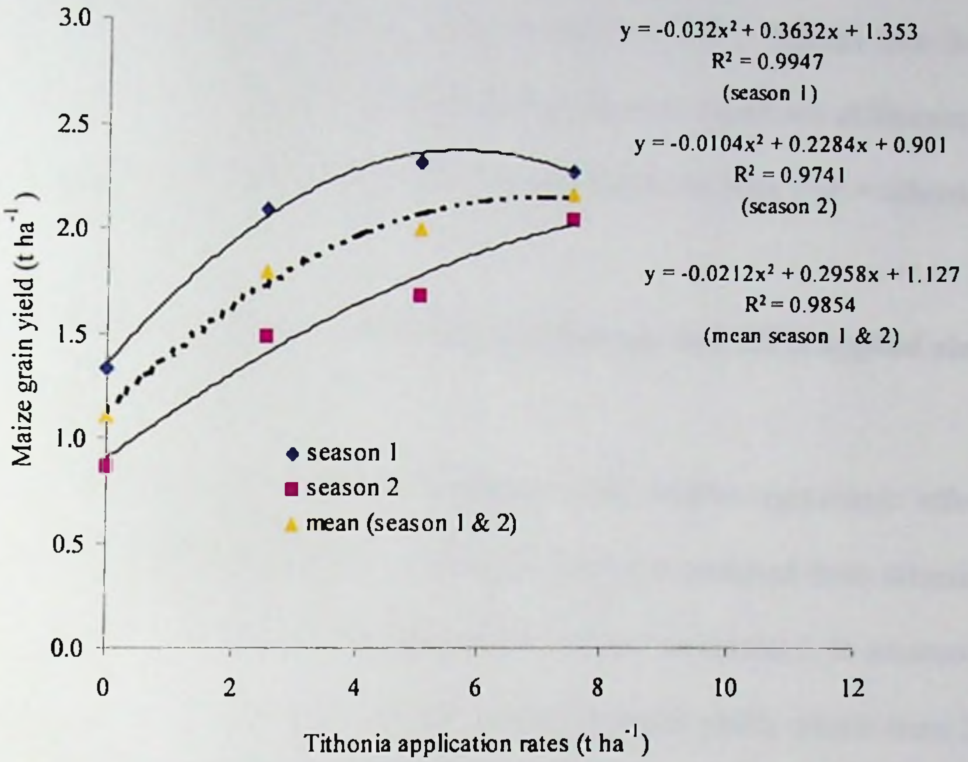

Figure 20. Relationship between maize grain yields and rates of tithonia applied in the field experiment

Both MPR and TSP at 80 kg P ha^{-1} increased maize grain yields significantly as compared to that of the control. The effect of TSP was significantly higher than that of MPR in season 1 but there was no significant difference between MPR and TSP in season 2. The residual effect of MPR on maize DMY was higher than that of TSP in season 3 (Table 24). Combining tithonia with either MPR or TSP resulted in higher yield than that of the control. Single degree of freedom orthogonal contrasts showed significant differences between MPR + tithonia and sole tithonia in season 2 (Appendix 8).

Combining MPR with tithonia at 5 or 7.5 t ha^{-1}produced significantly higher maize grain yields than sole application of MPR in season 1. During the residual phase in season 3, MPR + tithonia at 2.5 or 5 t ha^{-1} produced less maize DMY than sole MPR. Significantly higher maize grain yields in TSP + tithonia than in sole TSP were obtained in season 2. Generally there were no significant differences between maize yields obtained from MPR + tithonia and those from TSP + tithonia.

(b) Relative agronomic effectiveness of tithonia and MPR applied singly or in combination

The effect of the different treatments on the relative agronomic effectiveness (RAE) is shown in Table 25. The lowest RAE was obtained from tithonia at 2.5 t ha^{-1} and the highest was from tithonia at 7.5 t ha^{-1} in season 1. In seasons 2 and 3, application of tithonia at 7.5 t ha^{-1} produced maize yields which were 27% and 157% above the reference TSP fertilizer, respectively.

The RAE of MPR increased from 46 in season 1 to 142% in season 2. During the residual phase, in season 3, MPR produced 262% more maize DMY than did the reference fertilizer (TSP). Generally combining tithonia with MPR had higher RAE than sole tithonia in all seasons. The RAE for MPR + tithonia increased with increase in tithonia application rates. Higher RAE values were obtained for MPR + tithonia treatments than for sole MPR except in residual phase (season 3).

Triple super phosphate + tithonia had higher RAE than the reference fertilizer (TSP) except in season 1 (Table 25). Generally the RAE of TSP + tithonia was higher than that of MPR + tithonia, except in residual phase (season 3).

Table 25. Relative agronomic effectiveness of tithonia and MPR and of the combination of tithonia with MPR or TSP

Treatment	P added per season (kg P ha^{-1})	RAE* (%)		
		Season 1	Season 2	Season 3
Tithonia 2.5 t ha^{-1} (T2)	11.5	66	67	86
Tithonia 5 t ha^{-1} (T5)	23.3	83	87	100
Tithonia 7.5 t ha^{-1} (T7)	34.5	82	127	257
MPR	80	46	142	362
MPR + T2	51.5	58	152	152
MPR + T5	63.3	86	153	224
MPR + T7	74.5	88	199	352
TSP + T2	51.5	63	173	133
TSP + T5	63.3	82	197	186
TSP + 7	74.7	98	209	343
TSP	80	100	100	100

*RAE (%) = yield (treatment) – Yield (control)/yield TSP (80 kg ha^{-1}) – Yield (control)

The increase in maize grain yields that was caused by tithonia was attributed to P and Ca addition from tithonia decomposition (Table 4) because the Chromic Acrisol was deficient in both P and Ca (Table 3). This suggestion is supported by the increase in both shoot and root P and Ca uptake (Table 27) and the observation that 41%, 57% and 58% of the variance in maize grain yields was being explained by Ca uptake in shoots, P uptake in shoots and P uptake in roots, respectively (Appendix 9) that was determined at 45 DAP of maize.

Maize yield increases were also partly due to improvement in soil chemical characteristics (pH, Al, Ca, oxalic acids) (Table 19; Figure 17). Both Al and oxalic acid play opposing roles in P fixation, as earlier explained in sections 4.6.1.3 and 4.6.1.5. Aluminium reacts with orthophosphate and forms aluminium phosphate, which is unavailable for plant P uptake. On the other hand, oxalic acid reacts with aluminium and forms aluminium oxalate, rendering the phosphate ions free. Hence, through reduction of exchangeable Al and production of oxalic acid, there was decrease in P adsorption as shown in Figures 18 and 19 and an increase in P availability as reflected by increase in total labile P (Table 21).

It is also possible that other soil physical characteristics (moisture holding capacity, bulk density and soil aggregation) might have improved resulting into increase in nutrients supply from the soil and consequently increase in maize yields (Tiessen *et al.*, 1992; Nziguheba *et al.*; 2001; Phan Thi Cong, 2000).

Since tithonia contained other nutrients like N, K, Ca, Mg, (Table 4), and S and micro nutrients (Gachengo *et al.*, 1999; George *et al.*, 2002; Baltazary, 2002), increase in maize yields may also be attributed to inputs of these elements into the system. However, the high residual effect of tithonia was due to its organic P pools ($NaHCO_3$-Po pools), which were mineralized with time. This assertion is consistent with the significant correlation (R^2=0.4339) between maize grain yields and $NaHCO_3$-Po pools (Table 26).

The lower response to tithonia application in season 2 compared to season 1 was due to the moisture stress that occurred from the tasselling up to the grain filling stages in season 2. Rainfall was low and its distribution was erratic during the experimental period (Figure 1), which caused zero grain yield in season 3 (Plate 2). In season 1 there was drought four weeks after planting and erratic rains continued up to maturity period. In season 2, the onset of drought was at 45 DAP, during tasselling, up to the grain filling stage. In season 3, there were prolonged dry spells four weeks after planting which continued up to tasselling stage in April (Figure 1), and this caused a total crop failure (Plate 2). The occurrence of drought at tasseling and grain filling stages greatly affected grain formation and nutrient uptake, consequently a lower response of maize grain yields in season 2 compared to season 1.

The different rates of tithonia contributed different amounts of P and other nutrients (Table 2) and significantly changed soil chemical properties including P availability (Tables 19 and 21). Although this resulted in differences in plant vigour (Plate 3), there were no differences in maize grain yields from tithonia rates. Lack of significant differences in maize grain yields from different tithonia rates was due to low and poor distribution of rainfall (Figure 1). Lack of enough moisture at tasselling and grain filling stages must have hindered P mineralization from tithonia and hence the different tithonia rates could not express their real potential.

The calculations for the agronomic optimum from Figure 20 showed that in low and poorly distributed rainfall years (like in season 2), tithonia at 11.5 t ha^{-1} might have to be applied to obtain the agronomic optimum while in higher rainfall seasons (like in season 1), 50% less tithonia would be sufficient to attain the agronomic optimum. The average of the bad year and the good year in terms of rainfall amounts and distribution indicates that under the present climatic conditions the agronomic optimum would be obtained at 7.5 t ha^{-1} tithonia.

According to Fox and Kamprath (1970), soils with SPR ranging from 100 to 400 are considered as moderately P fixing soils. The soil that was used in this study, is therefore, a moderately P fixing soil (Tables 11 and 22). Therefore, the P released from TSP was fixed following its release and this was the reason why the effect of MPR was similar to that of TSP in season 2, and better than that of TSP in season 3. Similar findings have been reported and explained in section 4.5.3 (Figure 14). The better performance of MPR in seasons 1 and 2 can also be attributed to increased dissolution of MPR with increase in contact time as earlier shown in section 4.2.1.3 (Figure 2 and Table 7).

The higher maize yields from MPR treatments in seasons 2 and 3 were also due to higher P availability from MPR plots. These plots had higher pH, higher exchangeable Ca, higher oxalic acid contents and lower exchangeable Al. These resulted in lower P sorption capacities and affinities than those under TSP (Tables 22 and 23) and higher total labile P in MPR than in TSP treatment (Table 21), consequently resulting in better growth and higher maize grain yields. This is supported by the significant positive correlations between exchangeable Ca, pH, as well as the negative correlation between exchangeable Al, and maize grain yields in season 2 (Appendix 9).

The higher levels of oxalic acid that were extracted under MPR treatments than under TSP (Figure 17) indicate that even the microbiological activities, which lead to better soil aggregation and greater organic P mineralization, were higher under MPR than under TSP treatments. The increase in maize grain yields from MPR treatments compared to TSP in season 2 could also be partly due to the better plant Ca nutrition as reflected by the higher soil exchangeable Ca (Table 19) and shoot and root Ca uptake (Table 27) under the MPR treatments.

Although TSP supplied more labile P in season 1 (Table 19), MPR was better than TSP in modifying soil properties that are related to P availability (pH, Ca, Al and oxalic acid) both in the application and residual phases. This was due to its higher pH, higher CaO, higher associated $CaCO_3$, and slower dissolution (Table 6). Although dissolution of both MPR and TSP releases Ca, this process consumes protons in case of MPR dissolution but does not do so under TSP. Consequently, higher changes in pH, Ca and Al resulting from MPR than from TSP, leading to higher P availability in subsequent seasons in the MPR than in TSP treatments.

Similar findings of better initial response of maize grain yields from TSP, which diminished in season 2, from this Chromic Acrisol and other similar soils have been reported by Kimbi *et al.* (1996), Mowo (2000) and Szilas (2002). These workers observed superior performance of TSP compared to MPR in the first season followed by diminishing perfomance in subsequent seasons, and attributed this trend to continual dissolution of MPR with increase in contact time.

Although there was a significant positive interaction between MPR and tithonia on P uptake, this was not reflected in maize grain yields, particularly in season 1. Lack of significant positive interaction between MPR and tithonia on maize grain yields could be due to low and poorly distributed rainfall. The higher maize grain yields in TSP or

MPR + tithonia compared to sole MPR or TSP even though the latter had more total P than the former (Table 2), implies that the increase in maize yields was not due to addition of P alone. As earlier explained, it was probably also due to provision of other nutrients like N, K, Ca, Mg and micronutrients. This was partly shown by the positive response to addition of N + K that was reported in section 4.4.1 (Table 13; Plate 1). The implications derived from this observation are that this Chromic Acrisol needs an amendment that can supply P and other limiting nutrients in order to obtain optimum maize yields.

The observation that combining TSP with tithonia produced similar or higher maize grain yields than those of sole TSP indicates that there is merit in combining tithonia with TSP instead of applying sole TSP. This argument is suppoted by the fact that tithonia + TSP had higher RAE of 173%, 197% and 209% when tithonia was applied at 2.5, 5.0 and 7.5 t ha^{-1}, respectively. However, it is not clear how long this effect could be sustained from one such tithonia application and it calls for additional studies. Similar trends were observed with MPR.

Although TSP + tithonia resulted in a little bit higher yield than MPR + tithonia and had higher RAE in the application phase, the latter treatment had much higher RAE than the former in the residual phase. It is also more expensive to get 40 kg P by resorting to TSP than to MPR. Also, in view of the higher increase in pH, Ca, labile P, oxalic acid and the decrease in exchangeable Al accruing from MPR treatments compared to TSP, with higher RAE in subsequent seasons, it seems that MPR at 40 kg P ha^{-1} combined with tithonia would be more beneficial than TSP + tithonia (at the same P rate) on this Chromic Acrisol.

In cases where neither TSP nor MPR is available, or affordable, application of tithonia alone at either 2.5 or 5 t ha^{-1} can improve maize grain yields significantly above that of the control, and this should definitely be recommended to farmers. Tithonia applied at 7.5 t ha^{-1} produced the best results when used alone or when combined with MPR or TSP in terms of its RAE (Table 25). This was due to greater quantities of nutrients supplied (Table 2), better influence on soil properties (Table 19), and less P sorbed (Figures 18 and 19), leading to more labile P (Table 21), and higher nutrient uptake (Table 27) from the tithonia treatment.

The above findings on the possibility of increasing maize grain yields using sole tithonia or combining it with TSP are in conformity with those of Gachengo *et al.* (1999), Jama *et al.* (2000) and Nziguheba *et al.* (2000; 2002). Since TSP is more expensive than MPR, combining tithonia with MPR rather than with TSP is more attractive on this Chromic Acrisol and possibly other similar soils that are not far from the Minjingu phosphate factory. Szilas (2002) reported that MPR was not more beneficial than TSP if used in areas that were more than 1000 km from the mine because of the huge transport costs involved in transporting it over long distances.

The relationships between sequentially extracted P fractions and maize grain yields are presented in Table 26. Maize grain yields were more correlated with resin P than with any other inorganic P fraction, and this P pool could explain 42% of the variation in maize grain yields. Sodium hydroxide extractable inorganic P (NaOH-Pi) which indicates less labile and chemo-sorbed P, explained 22% of the variance in maize grain yields. Sodium hydroxide bicarbonate organic P ($NaHCO_3$-Po) explained 43% of all the variation in maize yields. Sodium hydroxide organic P (NaOH-Po) had no influence ($P=0.25$) on maize grain yields. Hydrochloric acid extractable P (HCl-Pi) was not correlated ($R^2=0.07$; $P=0.123$) with maize grain yields.

Table 26. Relationship between maize grain yields and different P pools in season 2

P pool	R^2	Probability	Equation
Resin P	0.4200	<0.0001	Y = 1.53 + 0.023 RP
Bic-Pi	0.2687	0.0012	Y = 1.55 + 0.025 Bic-Pi
Total labile P (TLP)	0.3866	<0.0001	Y = 1.48 + 0.013 TLP
Bic-Po	0.4339	<0.0001	Y = -0.49 + 0.202 Bic-Po
NaOH-Pi	0.2210	0.0038	Y = 0.88 + 0.015 NaOH-Pi
NaOH-Po	0.0038	0.2571	Y = 0.59 + 0.010 NaOH-Po
HCl-Pi	0.0690	0.1230	Y = 1.90 + 0.063 HCl-Pi

Forty five percent of the variance in maize grain yields could be explained by increase in soil pH ($R^2=0.45$) while the influence of exchangeable Ca on maize grain yields accounted for 39%. Aluminium correlated negatively ($R^2=-0.45$) with the yields. Ear leaf Ca and P concentration had no relationship with maize grain yields (Appendix 9) while both shoot and root P, and shoot Ca uptake had significant positive influence on maize grain yields.

4.6.2.2 Effect on Ca and P uptake

The uptake of Ca and P is presented in Table 27. Tithonia had a significant linear effect on P uptake both in shoot and root P, compared to its uptake in control. However, there were significant treatment differences only in season 2 when tithonia at 7.5 t ha^{-1} produced significantly higher P and Ca uptake than the other rates of tithonia. There were significant effects from tithonia at 5 and 7.5 t ha^{-1} compared o the control, on Ca and P uptake in the residual period.

Both inorganic P sources (MPR and TSP) increased shoot and root P and Ca uptake compared to that in the control. The influence of MPR on shoot P uptake was lower than that of TSP but MPR resulted in higher root Ca uptake than that from TSP. In the residual phase, shoot Ca and P uptake from MPR were significantly higher than from the control or TSP treatments.

Generally, combining MPR with tithonia increased shoot and root Ca and P uptake compared to that from the control. Almost similar trends were observed in shoot P and Ca uptake in the residual phase. There were significant linear interaction effects (MPR-P x tithonia rates) on shoot and root Ca and P uptake. P uptake in both shoots and roots from MPR + tithonia treatments was significantly higher than in sole tithonia treatments in the fresh and residual phases.

Combining TSP with tithonia generally resulted in increase in Ca and P uptake by maize shoots and roots compared to that under the control or sole tithonia. During the residual phase, TSP + 7.5 t $ha^{-1}$of tithonia had significant interactions on Ca and P uptake.

Table 27. Influence of tithonia applied alone or co-applied with MPR or TSP on shoot and root Ca and P uptake in the field experiment

Treatment	Shoot P and Ca uptake (kg ha^{-1})		Roots P and Ca uptake (kg ha^{-1})		Shoots P and Ca uptake (kg ha $^{-1)}$	
	P Season 2	Ca Season 2	P Season 2	Ca Season 2	P Season 3	Ca Season 3
Control (-P)	1.25 h	1.77 g	0.04 g	0.09 e	0.54 g	0.72 g
Tithonia 2.5 t ha^{-1} (T2)	2.63 fg	2.36 ef	0.07 f	0.14 cd	0.78 fg	1.02 fg
Tithonia 5 t ha^{-1} (T5)	2.45 g	2.62 de	0.08 f	0.13 d	0.91 ef	1.34 def
Tithonia 7.5 t ha^{-1} (T7)	2.70 fg	2.63 de	0.16 d	0.20 b	1.38 bcd	1.41 def
MPR (P 80)	3.02 ef	3.38 bc	0.15 d	0.24 a	1.63 b	2.65 a
TSP (P 80)	4.14 bc	2.53 ef	0.14 de	0.14 cd	1.17 cde	1.28 ef
MPR (P 40) + T2	3.91 cd	1.92 fg	0.14 de	0.15 c	1.22 cd	1.25 ef
MPR (P 40) + T5	4.39 bc	3.26 bcd	0.15 de	0.16 c	1.43 bc	1.69 cd
MPR (P 40) + T7	4.62 b	4.41 a	0.19 c	0.15 c	2.13 a	2.05 bc
TSP (P 40) + T2	3.50 de	2.84 cde	0.13 e	0.08 e	1.09 de	1.44 de
TSP (P 40) + T5	4.45 b	3.85 ab	0.22 b	0.13 d	1.11 de	1.33 def
TSP (P 40) + T7	5.76 a	4.35 a	0.25 a	0.24 a	2.00 a	2.19 b
CV (%)	7.97	13.35	7.02	7.52	12.21	13.88

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

Both shoot and root P uptake were very highly ($P<0.0001$) correlated with soil resin P ($R^2=0.57$ and $R^2=0.63$, respectively) than with any other inorganic P pool. Although Bic - Po is moderately labile, and acts as a reserve for P release in soils with low organic matter content, it explained 34% and 44% of the shoot and root P uptake, respectively. The NaOH-Po had no influence on shoot or root P uptake (Appendix 10).

The increase in Ca and P uptake was partly attributed to the high P and Ca released from the decomposition of tithonia (Table 4). The increase in P uptake was also due to decrease in soil acidity and associated exchangeable Al (Table 19), because root development and nutrient uptake by roots is normally hindered by high exchangeable Al (Tisdale *et al.*, 1993). Increased P availability that resulted from the decrease in P adsorption upon application of tithonia (Table 22) must also have contributed to increased P uptake.

Observed increases in P and Ca uptakes were also due to addition of other nutrients contained in tithonia (Gachengo *et al.*, 1999; Baltazary, 2002) (Table 4) as earlier disccused in section 4.4.2.2. However, the highest correlation between P uptake and resin P ($R^2=0.57$) implies that P was the factor that contributed most to increased P uptake.

Addition of tithonia to soil increased the total amount of nutrients held in microbial biomass, the amount of mineralizable N and C, and the sizes of the labile and organic fractions (Nziguheba *et al.*, 2001). It also resulted in improvements in other soil chemical parameters (Linquist *et al.*, 1997b; Phan Thi Cong, 2000) as earlier explained in section 4.4.2.3.

The above argument on the merits of tithonia are confirmed by the observation that tithonia both at 5 and 7.5 t ha^{-1} caused increases both in Ca and P uptake during the residual period similar to that of sole TSP. This implies that organic materials may have higher residual influence on soil properties than TSP. It further points out that the residual effects are not due only to P addition because TSP had much higher P content than tithonia (Table 2) and yet resulted into similar residual increases of both Ca and P uptake similar to those under tithonia.

The higher residual effects of MPR on Ca and P uptake than the effects of tithonia suggest that there was a continued and gradual dissolution of MPR, which provided both P and Ca, consequently increasing and maintaining higher levels of soil pH and Ca nutrition of the maize plants. The greater influence of MPR on shoot Ca and P uptake compared to those under TSP in the residual phase implies that MPR had better residual effects on both Ca and P than had TSP.

4.6.2.3 Effects on Ca and P concentration in maize ear leaves

The concentrations of Ca and P in maize ear leaves are shown in Table 28. Tithonia significantly increased the concentrations of Ca and P compared to those in the control. However, there were no significant differences between the tithonia application rates. The plant Ca and P concentrations ranged from 0.22 to 0.29% and 0.14 to 0.21% for Ca and P, respectively. Minjingu phosphate rock and TSP significantly increased the Ca and P concentrations compared to those in the control. The effect of MPR on Ca was higher than that of TSP while similar values were observed between MPR and TSP in the case of P. The concentrations of Ca and P in the MPR+tithonia treatments were similar to those in sole application of tithonia or MPR. Similar trends were observed in the TSP+tithonia treatments.

Table 28. Concentration of Calcium and P in maize ear leaves as influenced by the tithonia, MPR or TSP application in field experiment

Treatment	Ca (%)	P (%)
Control (-P)	0.22 d	0.14 d
Tithonia 2.5 t ha^{-1} (T2)	0.27 abc	0.19 abc
Tithonia 5 t ha^{-1} (T5)	0.28 abc	0.20 ab
Tithonia 7.5 t ha^{-1} (T7)	0.28 abc	0.21 a
MPR (P 80)	0.29 a	0.19 abc
TSP (P 80)	0.25 bc	0.18 bc
MPR (P 40) + T2	0.28 abc	0.16 cd
MPR (P 40) + T5	0.29 ab	0.18 bc
MPR (P 40) + T7	0.28 abc	0.18 bc
TSP (P 40) + T2	0.25 cd	0.18 bc
TSP (P 40) + T5	0.28 ab	0.17 bc
TSP (P 40) + T7	0.28 ab	0.18 bc
CV (%)	6.77	9.18

Means followed by the same letter in the same column are not significantly different $P<0.05$ according to DMRT.

The lowest Ca and P concentrations in the control soil were due to the inherently low P and Ca status in this soil as shown in Table 3. The increase in maize ear leaf Ca and P concentrations caused by all the treatments implies that there was increased uptake of the Ca and P supplied via these treatments. According to Okalebo *et al.* (1993) the critical P concentration in maize ear leaf is 0.25% P. Since this value in most cases was not reached presently, it implies that there were some factors which hindered uptake of P. The most probable reason is the moisture stress that prevailed beginning mid April, at tasselling and silking stages, in all seasons (Figure 1). Lack of enough moisture must have hindered uptake of both Ca and P.

Another possible reason is that since this soil has moderate P fixing capacity (Table 22) some of the P released from decomposition of tithonia, or from MPR or TSP dissolution, was rendered unavailable for plant uptake through P fixation. This argument is supported by the observation that among all the P fractions determined, the NaOH-Pi pool, the pool which reflects chemo-sorption of P, was the largest P pool at 45 DAP (Figure 16), coinciding with the the tasselling period (Figure 1). The variety of maize that was used in this study (TMV-1) starts to tassel at 42 to 45 DAP, and since this period was associated with unreliable rainfall and drought in the study area, maximum uptake of P at this critical time could not be achieved. Growing a short duration maize variety that would tassel earlier could probably result in high P concentrations in ear leaves because such a variety would have tasselled before the onset of drought, and be able to capture the released P.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and conclusions

This chapter highlights the general conclusions in relations to the objectives as stated in chapter one. It, further, outlines the implications inferred from the conclusions and finally proposes future research needs that will extend the comprehension of the processes, reactions and factors that influence P availability with respect to maize growth perfomance and yields, on the present Chromic Acrisol.

From the laboratory analysis farmyard manure, tithonia, lantana and gliricidia, had N, P, lignin, polyphenol, C:N and soluble carbon:total P ratios, which ranged from 1.66 to 4.00%, 0.21 to 0.46%, 7.22 to 11.95%, 0.05 to 3.48%, 10 to 21 and 3 to 15, respectively. Based on the critical values of N>2.5%, P>0.24%, lignin<15% and polyphenol<4%, C:N <20 and soluble carbon:total P<30, these organic materials can generally be classified as of medium to high quality organic materials. The manure and tithonia had high P content (%P=0.45) but lantana and gliricidia had lower P contents (P=0.21 and 0.22%, respectively) compared to the critical value (P=0.24%). In addition to these quality parameters all the organic materials studied had a wide range of LMWOA concentrations, with tithonia having the highest concentrations and manure the lowest. The most abundant LMWOA was oxalic acid. The oxalic acid concentrations in GMs were highly negatively correlated with the P adsorption capacities of the Chromic Acrisol. The higher the oxalic acid concentration the lower the P adsorption capacity of the Chromic Acrisol. This implies that the level of oxalic acid in GMs could be used as a criterion for selecting GMs intended to be used for increasing soil P availability, in addition to the conventional quality characteristics (N, P, C/N, polyphenol and lignin).

Contrary to many findings that decomposition of organic materials enhanced PR dissolution through production of protons and chelation of Ca by organic acids, the present results from incubation and pot studies indicated that the organic materials used in this study depressed MPR dissolution. The depressing effect was closely related to pH, and P, Ca, Mg and K contents of the organic materials. The higher the pH and P, Ca, Mg and K of the organic material, the lower was the P release from MPR when MPR was co-applied with the organic materiasl. Manure and tithonia treatments, which had high pH (section 4.3.3), basic cations and P contents, reduced MPR dissolution. However, lantana and gliricidia, which had lower pH, basic cations and P contents, demonstrated the least depressing effect on MPR dissolution.

Studies with analytical grade oxalic acid (section 4.3.2) confirmed the previous findings and showed that the release of P from MPR increased with addition of oxalic acid, and the extent of P release from MPR depended on the oxalic acid concentration. However, the critical acid concentration of 0.02 ML^{-1} had to be reached before any P could be released from MPR. The LMWOA produced from the tested organic materials were in very low concentrations, implying that these LMWOA could not neutralize all the released basic cations and $CaCO_3$ associated with the MPR. Application of large quantities of organic materials, which might produce greater quantities of LMWOA, could concurrently release greater amounts of basic cations and induce a Ca common ion effect, hence reduce the dissoluton of MPR. Therefore, selection of organic materials that are aimed at enhancement of P dissolution from MPR should be based on pH, basic cations and P contents. The higher the pH, basic cations (paricularily Ca) and P the lower the effect of such organic materials on MPR dissolution, hence the lower the release of P for plant uptake.

The capacity of different organic materials used in this study to modify soil characteristics that influence P availability (i.e pH, Ca and Al) appeared to be governed by their chemical composition. The results from incubation, pot and field studies indicated that all the organic materials increased soil pH, exchangeable Ca, and resin P and decreased exchangeable Al. The influence of organic materials on these soil parameters depended on their contents of the basic cation (Ca, Mg and K), P, oxalic acid concentrations, and their application rates. From incubation and pot studies, the influence of the organic materials at 2.27 g kg^{-1} soil (5 t ha^{-1}), on these soil parameters followed the trend manure>tithonia>lantana>gliricidia. Although all tithonia application rates improved these soil parameters in the field experiment the best application rate of tithonia was 7.5 t ha^{-1}. It is, therefore, concluded that manure and tithonia could be used to improve soil properties related to P availability in this Chromic Acrisol, based on their high levels of pH, P content and oxalic acid concentration.

The influence of inorganic P fertilizers on soil characteristics depended on the P source. Results from pot and field experiments showed that TSP decreased or had no effect on soil pH and in some cases increased exchangeable Al. It also increased exchangeable Ca and oxalic acid but to a lower extent than did MPR. Combining MPR or TSP with tithonia increased soil pH, exchangeable Ca and decreased exchangeable Al compared to that under sole application of TSP, MPR or tithonia. This was due to addition of basic cations and LMWOAs from tithonia. MPR resulted in higher residual effects in terms of high levels of exchangeable Ca and low levels of exchangeable Al than did TSP, and this was attributed to its slow dissolution rate in soils, its higher $CaCO_3$ contents and its greater ability to consume protons as compared to TSP. Although TSP had more resin P than had MPR when added to the Chromic Acrisol in the first year of application, MPR was superior to TSP in improving the Chromic Acrisol properties related to acidity and nutrient deficiencies like Ca in field experiment in all seasons. Certainly, the influence of MPR + tithonia green manure on soil pH, Ca, Al, oxalic acid and different P pools under field conditions would largely depend on the amount and distribution of rainfall because dissolution of MPR and decomposition of tithonia are influenced by soil moisture status.

Based on the results from incubation studies (section 4.3.5) on the influence of organic materials and inorganic P fertilizers on P availability it was obseved that all organic materials, applied at 2.27 $g\ kg^{-1}$ soil (equivalent to 5 $t\ ha^{-1}$), increased soil solution P. This increase was due to the fact that organic materials reduced the P adsorption capacity of the Chromic Acrisol as depicted by reduction of P adsorption maximum (b), P bonding affinities (k) and the standard phosphorus requirement (SPR) at a solution P concentration of 0.2 mg P L^{-1}. The trend of the depressing effect on P adsorption was manure>tithonia>lantana>gliricidia, and this was related to differences of the GMs in P and oxalic acid contents. The higher the P content the higher was the depressing effect on P adsorption. The mechanisms involved in reducing P adsorption were: (i) addition of P from decomposition of organic materials, (ii) competition of LMWOA, in particular oxalic acid, for adsorption sites, (iii) complexation of Al by LMWOA leading to P release and (iv) increase in pH which caused a reduction of exchangeable Al^{3+} in soil solution, with resultant P desorption. In the field experiment (section 4.6.1.6), P adsorption decreased with increase in tithonia addition rates. Phosphorus fixation by this Chromic Acrisol can be reduced, resulting in increased P in soil solution, through application of tithonia even at the lowest rate of 2.5 t ha^{-1}. However, the best results were obtained at 7.5 t ha^{-1} tithonia.

In the field experiment, MPR and TSP (80 kg P ha^{-1}) increased P availability through a decrease in P adsorption as well as addition of labile P due to dissolution. However, the influence of MPR was higher than that of TSP because of the high pH, high oxalic acid and lower exchangeable Al in MPR treatments. When compared to sole tithonia, the effect of MPR on P adsorption was superior to tithonia except at 7.5 t ha^{-1}. The results, further, showed that combining MPR or TSP (40 kg P ha^{-1}) with tithonia at 7.5 t ha^{-1} had greater depressing effect on P adsorption maximum and bonding affinities than sole MPR or TSP. Thus, phosphorus availability of Chromic Acrisol can be increased by application of

MPR or TSP at 40 kg P ha^{-1}, co-applied with tithonia. Since MPR had a higher depressing effect on P adsorption than had TSP, it is advisable wherever feasible to use MPR combined with an organic material like tithonia at 7.5 t ha^{-1} or even at much lower rates in cases where tithonia availability is constrained.

The results from the incubation study (section 4.2.1) indicated that the amounts and distribution of different soil P pools upon amendment with GMs depended on the amount of P in a given organic material. Manure and tithonia, which had higher P contents, resulted in higher concentrations of labile P fractions compared to those under lantana and gliricidia, which had much lower P contents. This indicates that the former could improve plant available P and lead to increased maize yields.

MPR had the higher concentration of HCl-Pi than that of TSP and this probably gives an indication of correspondingly higher residual effects of MPR when applied to this Chromic Acrisol and other similar soils. Most of the inorganic P was in the NaOH-Pi pool, indicating that P applied to this Chromic Acrisol entered into this P sink (capital P) that is not readily available to plants. This implies that proper management of P in this Chromic Acrisol should target at reducing the P adsorption capacity of this soil in order to increase the plant available pools (labile P).

The results from field study (section 4.6.1.4b) showed that tithonia increased total labile inorganic and organic P fractions in the Chromic Acrisol. Further, MPR and

TSP increased the total labile P but the effect of MPR was higher than that of TSP. It was further revealed that TSP contributed more to the NaOH-Pi than did MPR, indicating that MPR had a higher depressing influence on the soil's P adsorption capacity than had TSP. Inorganic P fertilizers had no significant influence on labile organic P, probably indicating low residual effects from organic P mineralization. Combining MPR or TSP with tithonia resulted in more labile P than the sole application of inorganic or organic P, due to the depressing effect of tithonia on the soil's P adsorption capacity. Therefore, combined application of MPR and tithonia would increase the inorganic and organic labile P pools, with the possibility of longer residual effects, on the Chromic Acrisol.

Results from pot and field experiments (sections 4.4.2.2) showed that all organic materials increased both Ca and P uptake by the maize plants and the extent of the uptake was influenced by the Ca and P content of the given organic material as well as content of other nutrients like N, K and Mg. Consequently farmyard manure and tithonia, which had higher P and basic cations (Ca, Mg, K) resulted in higher Ca and P uptake values than did lantana or gliricidia. Results from the field experiment (section 4.6.2.2) showed that only 52% of maize shoot P uptake could be explained by total labile P, implying that other factors also were influencing the uptake of P by maize plants. This observation also indicated that P uptake could be improved by raising labile P through adoption of strategies which reduce P adsorption and increase P in soil solution, provided that other essential macronutrients as well as soil moisture are not limiting. The influence of total labile P on maize grain yields was only 42%, implying that besides P there were other factors also like moisture availability and macro nutrients, that limited maize yields on the Chromic Acrisol of the present study area.

Although both MPR and TSP increased P uptake and maize yields, the influence of MPR on P uptake was higher than that of TSP in 2 out of 3 seasons. The RAE of MPR increased with cropping seasons, increasing from 46 to 362%. Combining MPR with tithonia produced significantly higher maize grain yields than sole MPR in season 1 when rainfall amount and distribution were better than in the other two seasons. Higher RAE values were obtained for MPR + tithonia treatments than for from sole MPR or sole tithonia in 2 out of the 3 seasons. Although TSP + tithonia had maize yield similar to thse of MPR + tithonia, it is advisable to use the latter combination than the former, on this Chromic Acrisol, because MPR was superior to TSP for supplying Ca, increasing pH, and reducing P adsorption. In addition to this, TSP might be more expensive than MPR in locations that are near the Minjingu phosphate mine.

5.2. Recommendations

Based on the data generated in this study, the following recommendations can be made.

(a) Observations from this study showed the organic materials to increase P availability and that the influence of organic materials on P availability depended on their nutrient contents. It is, therefore, recommended that more studies be undertaken to characterize other organic materials to ascertain their qualities. In cases where high quality organic materials are found on-farm, this will allow their effective use for improving P availability to crop plants.

(b) Tithonia was identified as the best green manure among the tested green manures in enhancing P availability in this Chromic Acrisol. However, no data is available in Tanzania on where tithonia can be easily obtained and how much of it is present in existing niches. Therefore, there is a need to conduct a comprehensive survey that will document the localities where abundant quantities of tithonia are found.

(c) Yield response to tithonia depended on climatic conditions. Based on the present study, application of tithonia at 7.5 t ha^{-1} gave the agronomic maize yield optimum under the prevailing climatic conditions. There is, therefore, a need to prolong such studies to confirm the tested rates, including testing much higher rates. There is also a need to broaden these studies to other areas with different climatic conditions to determine applicability of these results in diverse enviroments.

(d) This study evaluated the usefulness of tithonia basing on soil and agronomic aspects but did not include the economic analysis. It is, therefore, recommended that in studies recommended in (c) above, economic analysis of the use of tithonia be included.

(e) Unlike in other East African countries, there is a lack of knowledge on the potential of tithonia to improve soil fertility, in particular P, in Tanzania. It is, therefore, recommended that in addition to further research, creation of awareness be undertaken through extension services to farmers who at present treat tithonia as a weed and simply remove it from their farms.

(f) More research on characterization of a wider range of GMs for different LMWOA and their influence on the LMWOA contents of different soils, as proxy of potential for enhancing MPR dissolution and induction of P desorption be undertaken so as to broaden the choice for organic materials that would lead to availability of P and to high crop yields. This characterization should include identification of other local shrubs that have high nutrient contents but are at present not well documented, for example *Venonia subligera* and *Albizia schimperiana.* Research on their influence on P availability when used alone or combined with MPR should be undertaken.

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7.0 APPENDICES

Appendix 1. Soil profile description of the Magadu site

Location:	Magadu rock phosphate experimental site, 150 m north of the Morogoro– Mzinga road, Mvomero district, Morogoro region, Tanzania
Elevation:	568 m.a.s.l (GPS estimate
Coordinates:	37°38′E and 6°51′S
Elevation:	568 m.a.s.l (GPS estimate)
Soil Climate:	Ustic moisture regime and Isohyperthemic temperature regime
Parent material:	Alluvial, from metamorphic rocks of Uluguru mountains
Landform:	Peneplain, AEZ=E1
Topography:	Gently undulating, Slope 2 - 3%, straight
Land use:	Cultivation of maize, cowpeas and sorghum
Surface characteristics:	Erosion: no signs of erosion, Deposition: none, Surface stoniness: none
Natural drainage class:	Moderately well drained
Natural vegetation:	Cleared land planted with trees mostly *Acacia spps.*
Date of description:	May, 24 – 2000 by Ikerra S. T. and Kimaro, D.N.
Soil:	Very deep, well drained, red clays with thin yellowish red clay topsoil. Few crotovinas and black ants were observed at Ap, AB and Bt1 horizons
Ap 0 – 10 cm	Reddish brown (5 YR 4/4, dry), dark brown (7.5 YR 3/4, moist); clay; slightly hard dry, friable moist, sticky and slightly plastic wet; weak to moderate fine and medium sub angular blocky; many very fine pores; many very fine roots; clear smooth boundary
Bts1 10 – 35 cm	Red (2.5 YR 5/8, dry); yellowish red (5 YR 4/6, moist); clay; slightly hard dry, friable moist, sticky and slightly plastic wet; moderate fine and medium sub angular blocky; many very fine pores; few diffuse clay cutans; common fine soft irregular clay and sesquioxides nodules; common very fine roots; gradual smooth boundary
Bts2 35 – 70 cm	Red (2.5 YR 5/8, dry); yellowish red (5 YR 4/6, moist); clay; soft dry, very friable moist, sticky and slightly plastic wet; moderate fine and medium sub angular blocky; many very fine pores; few diffuse clay cutans; many fine soft irregular clay and sesquioxides nodules; few very fine roots; diffuse smooth boundary
Bts3 70 – 120+ cm	Yellowish red (5 YR 5/8, dry); red (2.5 YR 4/6, moist); clay; soft dry, very friable moist, sticky and slightly plastic wet; weak very fine subangular blocky; many very fine pores; few diffuse clay cutans; common fine soft irregular clay and sesquioxides nodules; very few; very fine roots
Soil Cassification:	Soil Taxonomy: Isohyperthemic very fine kaolinitic, kanhaplic Haplustults (Soil Survey Staff, 1975); WRB: Chromic Acrisol (WRB, 1998)

Appendix 1, continued

Analytical data for soil profile

Horizon	Ap	Bts1	Bts2	Bts3
Depth (cm)	0 - 10	10 - 35	35 - 70	70 - 120+
Clay (%)	52	63	62	60
Silt (%)	8	7	6	7
Sand (%)	40	30	32	33
Textural class	Clay	Clay	Clay	Clay
Bulk density (g cc^{-1})	1.3	1.1	1.1	1.2
AWC	10	11	14	14
pH $_{H2O}$	4.9	4. 8	4.8	4.5
pH $_{KCl}$	3.9	3.7	3.8	3.7
Organic ((%)	1.2	0.9	0.5	0.3
Total N (%)	0.10	0.09	0.09	0.07
C/N	12	10	10	10
P Bray-1 (mg kg^{-1})	4.1	0.45	0.22	0.11
CEC (cmol$_c$kg^{-1})	12	16	16	12
Exch. Ca (cmol$_c$kg^{-1})	2.8	1.8	0.6	0.3
Exch.Mg (cmol$_c$ kg^{-1})	1.9	1.4	1.8	1.6
Exch. K (cmol$_c$ kg^{-1})	0.5	0.2	0.1	0.2
Exch.Na (cmol$_c$ kg^{-1})	0.1	0.1	0.1	0.1
Exch. H (cmol$_c$ kg^{-1})	0.2	0.2	0.2	0.1
Exch.Al (cmol$_c$ kg^{-1})	1.4	3.2	3.8	3.9
BS %	56	43	41	51

AWC = Available water content

Appendix 2. Fomulae and aluminium–organic acid complexation constants of the detected LMWOA in the GM

Organic acid	Formula	Complexation constant, logK$_{Al}$
Acetic acid	CH_3COOH	1.57
Citric acid	$(COOH)CH_2C(OH)(COOH)CH_2COOH.H_2O$	7.98
Formic acid	HCO_2H	1.36
Malic acid	$(CHOHCH_2)(CO_2H)_2$	5.34
Malonic acid	$CH_2(CO_2H)_2$	5.24
Oxalic acid	HO_2CCO_2H	6.1
Succinic cid	$(CH_2CO_2H)_2$	2.09
Tartaric acid	HO_2 CC H(OH)CH(OH)CO_2H	5.62

Source: Fox *et al.* (1990)

Appendix 3. Effect of organic materials on MPR dissolution as measured by net NaOH-P

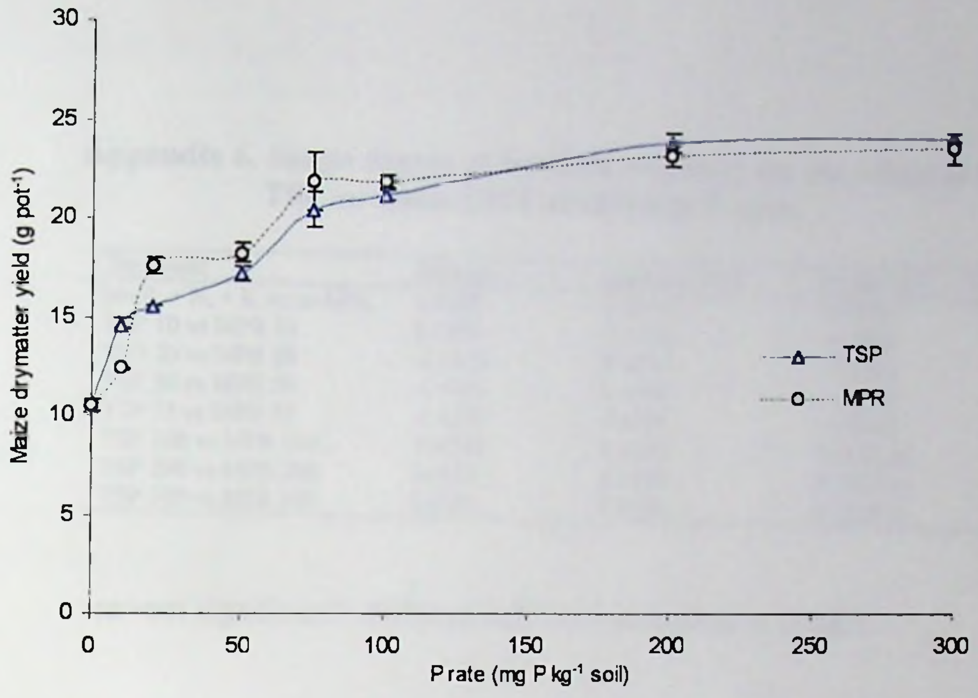
Treatment	Sampling period (days)						
	0	1	7	14	28	56	112
	NaOH-P (mg P kg^{-1})						
MPR	102 a	114 a	121 b	149 a	182 a	170 a	205 a
MPR + manure	78 b	105 a	109 c	134 b	124 c	147 b	157 c
MPR+ lantana	93 ab	61 c	96 d	127 b	159 b	178 a	189 ab
MPR + gliricidia	105 a	87 b	141 a	110.3 c	151 b	153 b	184 b
MPR + tithonia	94 a	82 b	105 cd	136.7 d	106 c	152 b	156 c
CV (%)	8.17	7.81	5.24	6.76	4.38	3.22	8.86

Means followed by the same letter in a column are not significantly different $P<0.05$ acording to DMRT.

Appendix 4. Effect of organic materials combined with MPR on soil pH

Treatment	Sampling period (days)				
	1	14	28	56	112
	Soil pH				
Control	4.77 f	4.65 f	4.65 h	4.63 f	4.65 g
MPR	5.16 a	5.14 b	5.19 c	5.12 bc	5.13 b
Manure	4.87 de	4.83 e	4.90 f	4.9 d	4.88 d
Lantana	4.91 cd	4.83 e	4.79 g	4.8 ed	4.82 ef
Gliricidia	4.81 ef	4.70 f	4.77 g	4.77 e	4.78 f
Tithonia	4.97 c	4.9 d	5.01 e	5.04 c	5.01 c
MPR + Manure	5.19 a	5.17 b	5.34 a	5.24 a	5.2 a
MPR + Lantana	5.05 b	5.16 b	5.15 c	5.06 c	5.02 c
MPR+ Gliricidia	5.12 ab	5.03 c	6.06 d	4.89 d	4.87 de
MPR + Tithonia	5.20 a	5.25 a	5.25 b	5.20 ab	5.25 a
CV (%)	0.87	0.53	0.41	1.33	0.74

Means followed by the same letter are not significantly different $P>0.05$ according to DMRT.



Appendix 5. Relationship between P rates from MPR or TSP on maize DMY on the Chromic Acrisol in the pot experiment. Error bars are stadard deviations from the means of three replicates.

Appendix 6. Single degree of freedom contrasts for the effect of MPR and TSP on maize DMY at different P rates

Treatment	Estimate	Standard error	Probability
No P, + N, + K vs no NPK	5.6986	0.4590	<0.0001
TSP 10 vs MPR 10	2.2930	0.4590	<0.0001
TSP 20 vs MPR 20	-2.0150	0.4590	<0.0001
TSP 50 vs MPR 50	-1.0436	0.4590	<0.0001
TSP 75 vs MPR 75	-1.4223	0.4590	<0.0303
TSP 100 vs MPR 100	-0.6583	0.4590	0.1619 ns
TSP 200 vs MPR 200	0.6913	0.4590	0.1425 ns
TSP 300 vs MPR 300	0.5553	0.4590	0.2358 ns

ns=not significantly different at $P<0.05$ according to DMRT.

Appendix 7. Anova Table for maize grain yields in season 2 partitioned into linear and quadratic effects for tithonia alone and tithonia combined with inorganic fertilizer treatments

Source of variation probability	df	ss	ms	vr	F
P source	2	4.274	2.137	19.13	<0.001
Rate	2	0.966	0.483	4.23	0.029
Linear	1	0.902	0.902	8.07	0.011
Quaratic	1	0.064	0.064	0.57	0.459
P sourse * rate	4	0.106	0.027	0.24	0.911
P source linear	2	0.033	0.017	0.15	0.861
P source quadratic	2	0.072	0.036	0.32	0.729
Residual	18	2.011	0.111		
Total	26	7.356			

Appendix 8. Single degree of freedom orthogonal contrasts for the different treatment combinations for the maize grain yields in application phase

Parameter	Estimate	Probability	Estimate	Probability
	Season 1		Season 2	
TSP vs Control	1.147	<0.0001	1.142	<0.0001
MPR vs Control	1.147	0.0007	1.340	0.0020
MPR vs TSP	-0.617	0.0001	0.943	0.1600
MPRtith 2.5 vs tith 2.5	0.260	0.0670	0.800	0.0077
MPRtith 5.0 vs tith 5.0	0.010	0.9415	0.616	0.0340
MPRtith 7.5 vs tith 7.5	-0.277	0.0522	0.683	0.0201
TSPtith 2.5 vs tith 2.5	0.183	0.1876	1.000	0.0040
TSPtith 5.0 vs tith 5.0	-0.260	0.0668	1.030	0.0010
TSPtith .5 vs tith 7.5	0.1900	0.1727	0.783	0.0089

Appendix 9. Relationships between maize grain yields in season 2 and other parameters

Parameter	R^2	Estimate	CV	Probability
PH	0.4549	1.2971	26.139	0.0001***
Exch. Al	0.4549	-4.5060	22.239	0.0001***
Resin P	0.3249	0.0204	24.794	0.0003***
Exch. Ca	0.3937	0.7841	23.4531	0.0001***
Ca conc. ear leaf	0.0241	4.6893	29.756	0.3651 ns
Ca uptake shoots	0.4179	0.4524	22.981	0.0001***
Ca uptake roots	0.1181	4.3610	28.280	0.0401 *
P conc. ear leaf	0.0241	4.6893	29.756	0.3651ns
P uptake shoots	0.5684	0.3943	28.280	0.0401*
P uptake roots	0.5846	8.092	19.414	0.0001***

Appendix 10. Relationships between shoot and root P uptake in season 2 and different P pools

P pool	Shoot P uptake (kg ha^{-1})		Root P uptake (kg ha^{-1})	
	R^2	Probability	R^2	Probability
Resin P	0.5708	<0.0001	0.6350	<0.0001
Bic-Pi	0.3640	<0.0001	0.4310	<0.0001
Total labile P	0.5230	<0.0001	0.5930	<0.0001
Bic-Po	0.4380	<0.0001	0.3360	0.0002
NaOH-Pi	0.3290	<0.0001	0.3040	0.0005
NaOH-Po	0.1110	0.0466	0.0680	0.1233
HCl-Pi	0.0540	0.1708	0.0143	0.0228