

**THE EFFECTS OF COMBINATION OF MINJINGU PHOSPHATE ROCK AND
SINGLE SUPERPHOSPHATE FERTILISER ON DISSOLUTION OF MINJINGU
PHOSPHATE ROCK IN SOILS**

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DECLARATION AND RECOMMENDATION

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I declare that this is my original work and has not been presented for a Masters degree or any other award before in any University or institution elsewhere.

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DEDICATION

This work is dedicated to my late brother Charles Ng'eno, my wife Caroline and the children.

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ABSTRACT

The effect of combinations of superphosphate and Minjingu phosphate rock (a sparingly water-soluble fertiliser) in the percentage ratios of superphosphate to Minjingu phosphate rock of 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20 and 90:10 was studied in a laboratory incubation experiment. Three acid soils from Rift Valley Province having contrasting chemical properties were used.

The treatments consisted of three P sources (superphosphate, Minjingu phosphate rock and mixtures of superphosphate and Minjingu phosphate rock), and three rates of applications (0, 200 and 800 mg P kg⁻¹ dry soil). The fertilisers were separately mixed with each soil at the three rates of application and were brought to field moisture capacity with distilled water. The samples were incubated for 30, 60 and 90 days under laboratory conditions. Soil pH and extractable P were measured for all the periods of reaction, while extractable Ca, Fe and Mn were measured only at the 90 days of incubation period.

Results showed that the solubility of Minjingu phosphate rock in the mixtures was enhanced in all the soils. The solubility increased with increasing proportion of superphosphate component in the mixtures. This was attributed to phosphoric acid produced from the hydrolysis reaction in soil of monocalcium phosphate in superphosphate. The results also indicated that the phosphoric acid not only dissolved the phosphate rock in the mixtures but also the Fe and Mn minerals in the soils. Results further showed that application of the fertilisers decreased the extractable Fe and Mn in all the soils. Negative correlation coefficients though only significant for one soil, were obtained between extractable P and Fe, and P and Mn concentrations and these indicated that the dissolved Fe and Mn minerals may precipitate P in solution and thereby reduce P availability.

Key words: Superphosphate, Minjingu phosphate rock, mixtures of superphosphate and Minjingu PR, solubility, acid soils, incubation experiment, Kenya.

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LIST OF ABBREVIATIONS

Cmolkg ⁻¹	- centimole per kilogram
ppm	- parts per million
FAO	- Food and Agriculture Organization
UNESCO	- United Nations on Educational, Scientific and Cultural Organization

Statistical Terms

LSD = Least significant differences

r = Correlation coefficient

P = Probability

ns = Not significant

*, ** and *** indicates significance at 10 % ($P \leq 0.1$), 5 % ($P \leq 0.05$) and 1 % ($P \leq 0.01$) respectively

CHAPTER ONE

INTRODUCTION

1.1 Background

Phosphorus (P) deficiency is a major biophysical constraint affecting quality crop production in many highly weathered acid soils of Eastern Africa (Smaling *et al.*, 1993; Buresh *et al.*, 1997; Jama *et al.*, 1997). Addition of P fertilisers is therefore frequently required for quality crop production. Usually, conventional inorganic P fertilisers are added to correct the deficiency, but the high costs of these fertilisers limit their use by resource-poor farmers engaging in small-scale subsistence agriculture.

Direct application of finely ground phosphate rock (PR) fertilisers is considered as a cheaper alternative to the more expensive high solubility P fertilisers in managing P deficiency (Khasawneh and Doll, 1978; Hammond *et al.*, 1986; Zapata and Roy, 2004). Despite intensive studies over the years, however, the use of PRs as an alternative source of P is limited by their low solubility in soils (Khasawneh and Doll, 1978; Rajan *et al.*, 1996). Dissolution of PRs is affected by a host of complex interactive factors, including PR factors, soil factors, plant factors, management factors, climate factors and environmental factors.

In general, the dissolution reaction is favoured under conditions of low pH, and low concentrations of Ca^{2+} , P and F^- ions (Khasawneh and Doll, 1978). These conditions, however, restrict the use of PRs to certain soils and technologies need to be developed so that they can be used in a variety of soils and crops, and farmers can benefit from this cheaper source of P. Physical mixtures of superphosphate and PR may be a cheaper technology of lowering the cost of using the more expensive superphosphate fertiliser while at the same time improving the solubility of PR fertiliser.

Indeed, studies have shown that physical mixtures of PR and water-soluble P fertilisers such as superphosphate can enhance the solubility of raw PR fertiliser (Hagin and Katz, 1985; Chien *et al.*, 1987; Thibaud *et al.*, 1993). Chien *et al.* (1987) reported that a mixture of North Carolina PR and triple superphosphate was just as effective as triple superphosphate when mixed at P ratios of at least 1:1 with respect to triple superphosphate. Thibaud *et al.* (1993) found that combinations of superphosphate and a South African PR gave better maize yields than when the PR was added alone, but all the mixtures were less effective than superphosphate. Kundu and Basak (1999) investigated the availability of P from Purulia PR-superphosphate mixtures and reported that the effectiveness of the mixtures

increased with increasing proportion of superphosphate in the mixture. Chien *et al.* (1999) reported that a mixture of a Syrian PR and triple superphosphate was as effective as triple superphosphate on a limed soil where phosphate rocks performed poorly.

In all the above studies, it has been suggested that the strongly acidic triple point solution of pH 1.5 resulting from the hydrolysis reaction of monocalcium phosphate component in superphosphate (Lindsay and Stephenson, 1959) reacts with the PR material rather than with the soil thereby enhancing PR solubility and availability in soil (Chien *et al.*, 1987; Kundu and Basak, 1999). In addition, the presence of readily-available P from superphosphate is also believed to stimulate early plant root development thereby enhancing effective utilization of P from PR fertiliser (Chien *et al.*, 1987; Rajan and Watkinson, 1992).

While the explanation that the acidic triple point solution arising from the hydrolysis of monocalcium phosphate in superphosphate reacts with the PR material rather than with the soil seems logical, it is also likely that the solution may dissolve aluminium, iron and manganese minerals in the soil which may subsequently react with dissolved P and thus reduce P concentrations in soil solution. Furthermore, precipitation reactions of aluminium, iron and manganese by P released from dissolving PR and P retention in soil colloids occurring through ligand OH^- exchange reactions may increase pH values of the soil (Ikerra *et al.*, 1994). These reactions may reduce the ability of phosphoric acid released from the hydrolysis reaction of monocalcium phosphate to dissolve PR material.

1.2 Statement of the problem

Small holder farmers in the densely populated highlands of Kenya are faced with the problem of P deficiency and declining soil fertility. Increased population has led to replacement of traditional shifting cultivation with shorter duration fallow systems and sedentary agriculture. Conventional P fertilisers such as superphosphates are often used to correct the deficiency and improve the declining soil fertility problem. However, these fertilisers are expensive to resource-poor farmers practicing small-scale subsistence agriculture. Insufficient use of P fertilisers by the resource-poor farmers practicing small-scale subsistence agriculture further contributes to the problem.

1.3 Objectives

The main aim of this study was to investigate the effect of combinations of Minjingu PR and superphosphate fertilisers on the dissolution of Minjingu PR in three highland acid soils.

The specific objectives of the study were to:

- i. Determine initial chemical properties (e.g. pH, exchangeable bases, organic carbon, extractable Fe and Mn) of the soils used which may influence dissolution chemistry of single superphosphate and Minjingu PR mixtures in soils,
- ii. Investigate the effect of combinations of single superphosphate and Minjingu PR on dissolution of Minjingu PR fertiliser,
- iii. Investigate the effect of combinations of Minjingu PR and single superphosphate fertilisers on extractable P,
- iv. Investigate the effect of combinations of Minjingu PR and single superphosphate fertilisers on pH, extractable Fe and Mn concentrations, and
- v. Establish the relationship between pH and extractable Fe and Mn, and between extractable P and extractable Fe and Mn

1.4 Justification

Phosphorus (P) deficiency is a major biophysical constraint affecting quality crop production in many highly weathered acid soils of Eastern Africa (Smaling *et al.*, 1993; Buresh *et al.*, 1997; Jama *et al.*, 1997). Usually, conventional inorganic P fertilisers are added to correct the deficiency, but the high costs of these fertilisers limit their use by resource-poor farmers engaging in small-scale subsistence agriculture. Consequently, there is an indisputable need to correct the soil P deficiency by using economically cheaper sources of P such as combination of fully acidulated P fertilisers and phosphate rocks.

CHAPTER TWO

LITERATURE REVIEW

2.1. Introduction

Phosphate rocks (PRs) are the principal sources of manufacturing conventional P fertilisers. Their use as alternative fertilisers for crop production has been widely studied over the years and the literature is riddled with conflicting reports on their effectiveness. The effectiveness of PR fertilisers has been reported to be better or poorer than that of conventional P fertilisers. This may be partly explained by several interactive factors, which include PR factors, soil factors, plant factors, management factors, climate factors and environmental factors, which complicate their solubility in soils. An attempt is made in this chapter on the influence of these factors on PR dissolution and availability. Literature on the effect of water-soluble P fertilisers on dissolution of PRs in soils will also be reviewed.

2.2. Chemistry and mineralogy of phosphate rocks

Phosphate rock materials exist as sedimentary, igneous or metamorphic deposits and differ in chemical, mineralogical and textural characteristics. Of these deposits, sedimentary ores are economically the most important deposits and contribute approximately 75% of the world P resources (Van Kauwenbergh, 1995).

The principal minerals in PR materials are the calcium- phosphates (fluoroapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$). Fluoroapatites are also the main constituents of sedimentary rocks. Pure fluoroapatite rarely exists in nature due to various degrees of substitution in their crystal lattices. They are found in association with a variety of accessory minerals such as silicates, gypsum, carbonates and oxides (Chien, 1977). Isomorphous substitution of PO_4^{3-} and F^- in the apatite structure alter the crystal, chemical and optical properties of PR material and this consequently influence their reactivity in soil. Substitution of PO_4^{3-} with CO_3^{2-} makes the crystal lattice less stable so that P is released more readily in soil (Chien, 1977). The generalised formulae of substituted carbonate fluoroapatite can be written as:



where a and b are functions of x, the extent of carbonate substitution (Khasawneh and Doll, 1978).

2.3. Dissolution reactions and factors affecting the process

Dissolution of PR materials in soil is an important process, which releases P in PR materials into the soil before it is taken up by plants. The dissolution reaction may be represented as follows (Hammond *et al.*, 1986):



The rate and extent of dissolution are influenced by PR properties, soil properties, plant factors, management practices, climate and environmental factors (Khasawneh and Doll, 1978; Rajan *et al.*, 1996). In general, conditions that alter the above equilibrium reaction towards the right enhance the release of P from PR materials, and hence their usefulness as direct application fertilisers. These factors are reviewed below.

2.3.1. Phosphate rock properties

The solubility of a PR fertiliser in soil depends on the source of the PR material. The differences in the extent and rate of dissolution of PR materials are largely attributed to variations in chemical, crystallogical and mineralogical properties (Khasawneh and Doll, 1978). The apatite lattice composition, and the quantity and nature of accessory minerals uniquely influence the chemical composition of a particular PR material and hence its solubility.

The degree of isomorphous substitution of PO_4^{3-} in the fluoroapatite crystal lattice by CO_3^{2-} is the key factor determining the chemical reactivity of carbonate apatites (Khasawneh and Doll, 1978). It has generally been observed that increasing substitution of the planar CO_3^{2-} for tetrahedral PO_4^{3-} increases the solubility of sedimentary apatites in chemical extractants and soil, and hence the agronomic value of the PR materials (Chien, 1977). This fact has been exploited commercially for the production of soluble-P fertilisers and in their use as direct application fertilisers (Hammond *et al.*, 1986; Sanyal and De Datta, 1991). The increased solubility is attributed to the decreased unit cell a-dimension and crystal instability by the incorporation of planar CO_3^{2-} for tetrahedral PO_4^{3-} (Khasawneh and Doll, 1978).

McClellan and Van Kauwenbergh (1992) characterised various PR sources and determined their unit cell a-dimensions by X-ray crystallography. They found that the greater the CO_3^{2-} for PO_4^{3-} substitution, the smaller the unit cell a-dimension, and the greater the solubility of PR material (Table 2.1). Further studies by McClellan and Van Kauwenbergh (1992) showed strong negative correlation between solubility of PRs in chemical extractants e.g. neutral ammonium citrate and unit cell a-dimension of PR material (Figures 2.1 a-c).

Table 2.1: Relationship between unit cell a-dimension and the calculated empirical formulae of carbonate fluoroapatites in some sedimentary PRs (McClellan and Van Kauwenbergh, 1992)

PR source	Length of a-axis (Å)	Empirical formula
North Carolina, USA	9.322	$\text{Ca}_{9.53}\text{Na}_{0.34}\text{Mg}_{0.13}(\text{PO}_4)_{4.77}(\text{CO}_3)_{1.23}\text{F}_{2.49}$
Gafsa, Tunisia	9.325	$\text{Ca}_{9.54}\text{Na}_{0.32}\text{Mg}_{0.12}(\text{PO}_4)_{4.84}(\text{CO}_3)_{1.16}\text{F}_{2.46}$
Bahia Inglesa, Chile	9.328	$\text{Ca}_{9.59}\text{Na}_{0.30}\text{Mg}_{0.12}(\text{PO}_4)_{4.90}(\text{CO}_3)_{1.10}\text{F}_{2.44}$
Huila, Colombia	9.340	$\text{Ca}_{9.69}\text{Na}_{0.18}\text{Mg}_{0.07}(\text{PO}_4)_{5.14}(\text{CO}_3)_{0.86}\text{F}_{2.34}$
Central Florida, USA	9.345	$\text{Ca}_{9.74}\text{Na}_{0.19}\text{Mg}_{0.07}(\text{PO}_4)_{5.26}(\text{CO}_3)_{0.74}\text{F}_{2.30}$
Tennessee, USA	9.357	$\text{Ca}_{9.85}\text{Na}_{0.11}\text{Mg}_{0.04}(\text{PO}_4)_{5.54}(\text{CO}_3)_{0.46}\text{F}_{2.18}$
Patos de Minas, Brazil	9.370	$\text{Ca}_{9.95}\text{Na}_{0.03}\text{Mg}_{0.01}(\text{PO}_4)_{5.88}(\text{CO}_3)_{0.12}\text{F}_{2.05}$

Chien *et al* (1987) investigated the residual effect of six carbonate apatite PRs of varying citrate solubility and found a positive correlation between PR dissolution and the citrate-soluble P of PR materials. Rajan (1987) reported that, in one year after surface application to permanent pastures, 27 % Florida PR of low carbonate substitution dissolved compared with 42 % for a North Carolina PR of high carbonate substitution.

The quantity and nature of accessory minerals also influence the reactivity of PR materials in soil. Calcium carbonates, the most abundant accessory mineral in PR materials depress the solubility of the apatites because they are preferentially dissolved thus partially consuming protons that would otherwise be used for dissolving PR materials. Dissolution of

calcium carbonates also increases Ca concentration, and pH of soil and thereby reducing PR solubility (Anderson *et al.*, 1985; Robinson *et al.*, 1992).

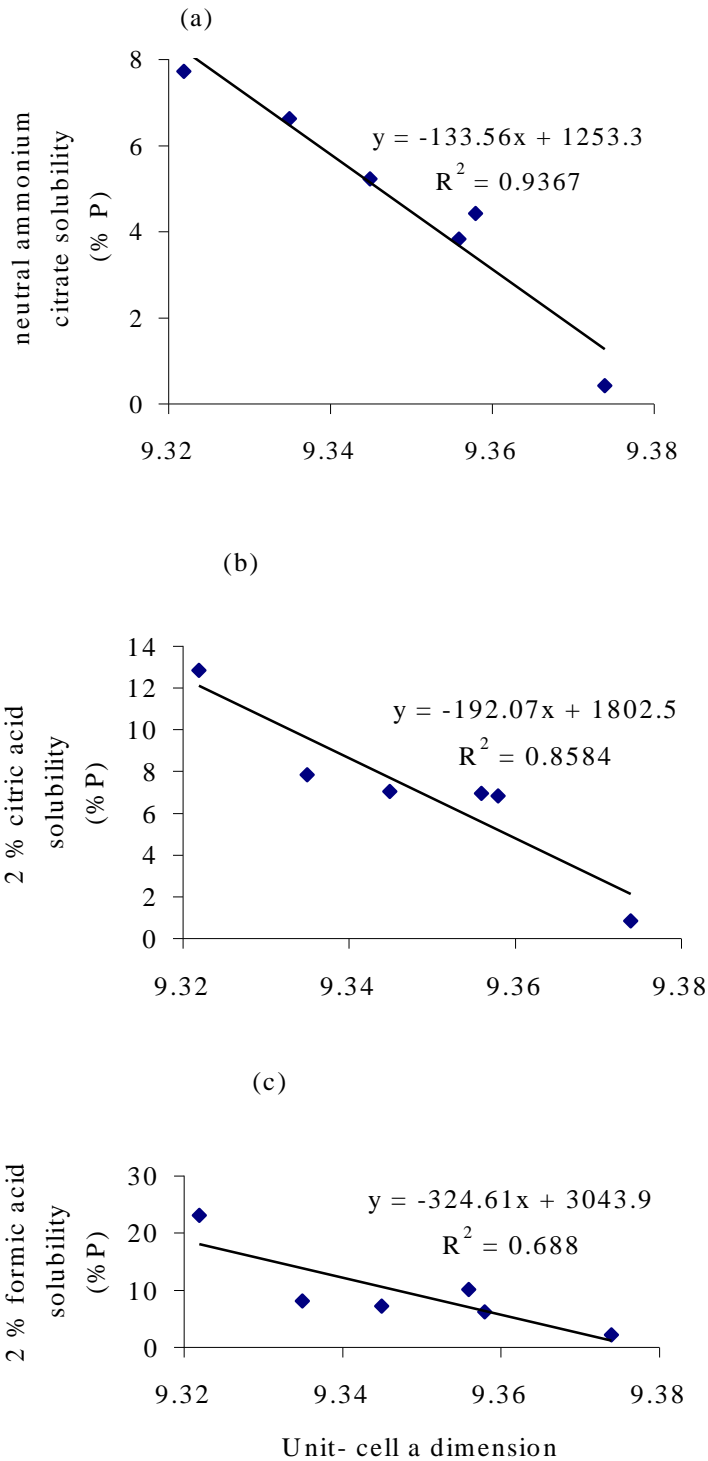


Figure 2.1: Relationship between unit-cell a-dimension of apatite and solubility of PR in neutral ammonium citrate, 2 % citric acid and 2 % formic acid (McClellan and Van Kauwenbergh, 1992)

Particle size of PR materials is also an important factor affecting PR solubility in soil. It has been shown that the solubility of PR materials increases as the particle size decreases (Kanabo and Gilkes, 1988b; Bolan *et al.*, 1990). The finer the particle size, the greater the degree of contact between PR material and soil, and the greater the rate of dissolution (Bolan *et al.*, 1990; Chien and Menon, 1995). Kanabo and Gilkes (1988b) investigated dissolution of finely ground North Carolina PR ranging from 0.15-0.25 mm to < 0.04 mm and found dissolution to increase with decreasing particle size. Watkinson (1994b) investigated dissolution rate of finely ground Sechura PR and found that 30 % of the PR material dissolved in the first year of application. Rajan *et al.* (1992) reported a greater response of ryegrass to ground PR than unground PR. Sinclair *et al.* (1993) evaluated unground and ground Sechura and North Carolina PRs, and triple superphosphate on ryegrass/clover pastures. Unground PRs were initially inferior to triple superphosphate but became comparable six years after application. In contrast, ground PRs were generally as effective as triple superphosphate from the year of application. Amdany (2005) in a study on the effect of particle size on dissolution of Gafsa and Minjingu PRs found that dissolution, yield and P uptake increased with decreasing particle sizes of the PR materials.

Grinding PRs below 150 μm (100 mesh) has however, been reported to be of no beneficial agronomic value (Hammond *et al.*, 1986). The dusty nature of fine particles, and the material loss during transportation and application however, has disadvantaged their use in most soils. It is generally recommended that grinding should be done to ensure that at least 80% of the materials pass through a 100-mesh sieve. Clumped PR particles tend to reduce the rate of dissolution due to saturation of the soil around the particles (Rajan *et al.*, 1996). Thus, attempts have been made to granulate PR materials, but this also decreases dissolution and increases the cost of production (Khasawneh and Doll, 1978). Microgranulation of PR materials is considered as an effective method of improving the handling characteristics of the PR fertilisers (Khasawneh and Doll, 1978).

2.3.2. Dissolution reactions and soil properties

Soil pH is thought to be the most important property affecting the dissolution of PRs in soils. Dissolution of PRs increases as the soil pH decreases (Figure 2.2) because the excess H^+ ions in acidic soils shift the dissolution reaction (Equation 2) to the right according to the Le Chatelier's principle. Dissolution of PR fertilisers (and hence their agronomic effectiveness) has been reported to be higher in acidic soils than in neutral or alkaline soils

(Rajan *et al.*, 1991; Hanafi *et al.*, 1992). Bolan and Hedley (1990) investigated dissolution of three PRs of varying reactivities using a volcanic ash soil in a laboratory incubation experiment. They found that dissolution correlated well with decreasing soil pH. Rajan *et al.* (1991) studied the dissolution of Sechura PR under field conditions and reported similar results. Usually, strongly acidic soils have high P-sorption capacities, which in turn enhance PR dissolution by removing dissolved P. Highly acidic soils are also rich in Al concentrations, and hence may pose a problem of Al toxicity to plants resulting in reduced growth (Haynes, 1984). Chepkwony (1991), using a highly acidic New Zealand soil and two reactive PRs, found a low response to the two PR materials and attributed this to soil acidity factors other than P deficiency. Kanabo and Gilkes (1987c), also in a glasshouse experiment, showed that dissolution of a PR fertiliser is highly favoured at low pH, but there was virtually no plant response to PR application.

Figure 2.2: Influence of pH on dissolution of Gafsa PR in water with time; unbuffered pH (\square), pH buffered at 5.2 (∇) and pH buffered at 4.5 (O): (a) P dissolved and (b) Ca dissolved (Adapted from Robinson and Syers, 1990).

The concentration of Ca ions in soil solution also determines the rate and extent of PR dissolution. This is because dissolution releases Ca ions into the soil. Thus, low Ca concentration in soil solution enhances dissolution. Mackay and Syers (1986) reported a four-fold decrease in the extent of dissolution of PRs as soil Ca concentration is increased. The affinity of soil for Ca (i.e. cation exchange capacity, CEC) enhances PR dissolution because it provides sinks for Ca ions that are dissociated from the apatites (Khasawneh and Doll, 1978; Rajan *et al.*, 1996). Indeed, the percentage Ca saturation of the cation exchange complex and the size of cation exchange sites have been reported to affect dissolution (Mackay *et al.*, 1986). Soils with low Ca saturation percentage have high affinity for dissolved Ca and promote PR dissolution. The same authors studied the relationship between Ca saturation percentage of cation exchange sites and PR dissolution. The results indicated that Ca saturation percentage had a large effect on the extent of dissolution of PR materials than either pH or P sorption capacity. De Datta *et al.* (1992) also stated that dissolution of PRs depends more on exchangeable Ca than P retention and pH. Robinson and Syers (1990) also concluded in a laboratory study that soil Ca sink plays a greater role in PR dissolution than either pH or P sink (Table 2.2). Dissolution of the PR material stopped after 60 days despite an adequate supply of protons. They attributed this to the saturation of the Ca exchange sites in soil. Dissolution of the PR material increased when a cation exchange resin (Ca sink) was added.

As for the case of soil Ca status, the concentration of P in soil plays a significant role in the dissolution of apatite PR minerals. Soils with low P concentrations favour PR dissolution (Khasawneh and Doll, 1978; Hammond *et al.*, 1986). In general, moderately fertile soils with high P concentrations in soil solution can benefit little from the additions of PRs. In contrast, PRs may be beneficial in soils that are severely to moderately deficient in P. Soils with low P concentrations characteristically have high P sorption capacities, which facilitate removal of dissolved P from soil solution. Dissolution of PRs increases as the P sorption capacity of soils increases (Chien *et al.*, 1980; Smyth and Sanchez, 1982). An increase in dissolution however, may not necessarily lead to an increase in availability of PR to plants since dissolved P may be subsequently adsorbed and thus made unavailable to plants. Kanabo and Gilkes (1987a) varied the adsorption capacity of an Australian soil by adding goethite, a strongly adsorbing material. Dissolution of the PR material increased significantly with increasing goethite content, but the amount of plant-available P decreased significantly. Glasshouse studies indicated reduction in both yield and P content of the test plants by 19 and 34 % respectively. Similar results have been reported by Harris,

(1994). De Datta *et al.* (1992) noted that high P retention only aids in initial dissolution reactions of a PR material but has a negative effect on availability of dissolved P to plants. Kowenje (1997) in a study of six acid soils from Rift Valley Province established a highly significant negative correlation ($r = -0.95$) between dissolution of a Tanzanian PR fertiliser and NaHCO_3 -extractable P (plant-available P). He concluded that maximum benefits of using the PR material would be expected in acid soils having intermediate P fixation capacities. It has also been recognized that P buffering capacity of soils has small effect on the rate of PR dissolution (Anderson and Sale, 1993).

Table 2.2: Individual and combined influence of pH, P sink and Ca sink on P dissolution from Gafsa PR at 44 days (Reproduced from Robinson and Syers, 1990).

pH	P sink size (mg P)	Ca sink size (mg Ca)	P dissolution (% P)
6.1	0	0	0
5.2	0	0	0
4.5	0	0	0
6.2	12	0	3.2
6.2	50	0	3.2
4.5	12	0	8.7
4.5	50	0	9.8
6.2	0	48	30.0
4.5	0	48	60.0
4.5	12	48	85.0
4.5	50	48	95.0

Soil organic matter is also known to influence PR dissolution. Dissolution of PR materials generally increases with an increase in soil organic matter (Chien *et al.*, 1990; Le Mare, 1991). Chien *et al.* (1990) using two soils having essentially the same pH, exchangeable Ca and P sorption capacities but varying organic matter contents in a pot trial observed greater dissolution of the Sechura PR in the soil containing higher organic matter content and attributed the observation to high cation exchange capacity and buffer capacity of

the soil. Ikerra *et al.* (1994) showed that incorporation of farmyard manure and compost with Minjingu PR enhanced the dissolution of the PR material. Organic acids produced as a result of microbial and chemical transformation of organic debris, solubilize PRs directly by providing protons and/or indirectly by removing dissolved Ca through chelation reaction. Kpombrekou and Tabatabai (1994) reported that organic acids dissolved North Florida and Kodjari PRs through chelation mechanism of the metals associated with P in the PRs.

Soil moisture is believed to affect PR dissolution in soils. Dissolution of PR materials is generally thought to be higher in moist soils than in dry soils (Bolan *et al.*, 1990). Diffusion of dissolved Ca and P ions away from the apatite surfaces is a limiting process in the dissolution of PR materials (Kirk and Nye, 1986). Thus, an increase in soil moisture level facilitates the diffusion of these dissolved ions away from the PR surfaces thereby resulting in enhanced PR dissolution (Kanabo and Gilkes, 1988a).

Weil *et al.* (1994) in an incubation study reported that dissolution of North Carolina PR increased with increasing moisture content of upto 80% field capacity in a medium P retentive soil, and it also increased dissolution in a higher P retentive soil upto field moisture capacity. Short dry periods do not, however, affect PR dissolution (Kanabo and Gilkes, 1988a) but longer dry periods substantially limit the process. Chepkwony (1991) reported that alternate drying of about nine weeks and re-wetting cycles of a New Zealand soil had no effect on dissolution of two PR materials. Greater yield and P uptake were observed in soils subjected to drying and wetting cycles than in soils kept continuously moist. The enhanced P availability in dried and re-wetted soils was attributed to net mineralization of soil organic P rather than increased PR dissolution.

2.3.3. Dissolution reactions and plant properties

Different crops have different abilities to utilize P from PR. The density of roots in the soil influences greatly the amount of P taken up by a plant from PR. PR dissolution is greater for crops with well-developed and extensive root systems due to their effective utilization of P and Ca from PRs. Chien *et al.* (1990) compared the abilities of five crops to utilize Sechura PR and found that upland rice (*Oryza sativa*) and ryegrass (*Lolium multiflorum*) utilized the PR material better than the other crops due to their well-developed root system. Inoculation of plant roots with mycorrhizae facilitates extension of the root system thus, enhancing effective utilization of P from PR materials (Tinker, 1980). Perennial crops utilize PRs more

effectively than annual crops due to their long growth periods (Chien *et al.*, 1990; Pushparajah *et al.*, 1990; Sale and Mokwunye, 1993).

Changes in rhizosphere pH may also occur as a result of differences in proportion of cation and anion uptake by a crop. Increased uptake of cations relative to anions by a plant induces the plant release of H⁺ ions, which eventually lower the rhizosphere pH (Hoffland *et al.*, 1989; Haynes, 1992). For example, leguminous plants promote PR dissolution more than non-legumes because they absorb more cations than anions (Le Mare, 1991). Rajan *et al.* (1995) conducted a field experiment to determine the abilities of finger millet (*Eleusine coracana*), maize (*Zea mays*) and blackgram (*Phaseolus mungo*) to utilize Mussoorie PR. Finger millet (*Eleusine coracana*) utilized the PR greater than maize (*Zea mays*) and blackgram (*Phaseolus mungo*) and this was attributed to greater uptake of Ca by finger millet (*Eleusine coracana*).

Rhizosphere pH may also be lowered by secretion of organic acids by plant roots (Marschner, 1995). Such acids may complex the Ca of PR (Hoffland *et al.*, 1989) thus promoting PR dissolution. Hoffland (1992) investigated the effect of organic acid exudates released by rape (*Brassica napus*) on P uptake from Mali PR and reported increased uptake of P from PR. This was attributed to reduced rhizosphere pH and complexation of Ca with organic acids.

2.3.4. Dissolution reactions and management practices

Methods of application of fertilisers in soils such as broadcasting, incorporation and banding can influence dissolution of PR materials. Broadcasting and incorporation enhance PR dissolution better than banding (Chien and Menon, 1995; Rajan *et al.*, 1996). Broadcasting and incorporation permit increased area of contact between the PR particles and soil while banding enhances dissolution zones of PR materials to overlap thereby hindering continuous dissolution. On the other hand, broadcasting without incorporation may decrease the availability of P from PR by restricting only the dissolved P to a shallow depth of soil where the plant roots are not able to explore (Rajan *et al.*, 1991). Purnomo and Black (1994) found that dissolution of North Carolina PR decreased in the order: Incorporation, broadcasting and banding.

Increasing the rate of application of PR fertiliser leads to an increase in the amount of plant available P (Kanabo and Gilkes, 1988d; Rajan *et al.*, 1991). However, PR dissolution diminishes from the point at which the ionic product of PRs equals the solubility product.

This is attributed to the fact that at this point PR particles get closer such that the zones of dissolved Ca and P overlap (Rajan *et al.*, 1991). This probably explains the decrease in PR dissolution with increasing rate of application reported by Kanabo and Gilkes (1988d), Bolland and Barrow (1988), and Rajan *et al.* (1991).

Timing the application of PRs in soils is also an important management factor for their effective utilization. In general, PR fertilisers have low solubility in soil and therefore require a period of time for their significant dissolution (Sinclair *et al.*, 1993). Because of this, it is recommended that finely ground PR should be applied at least one month before planting crops in order to allow time for the dissolution to occur (Khasawneh and Doll, 1978; Hammond *et al.*, 1986). This practice however, may not be beneficial for highly weathered acid soils with high P-sorption capacities (Chien *et al.*, 1990; Purnomo and Black, 1994). This is because dissolved P may react with active soil components such as hydrous oxides of Fe and Al to form nonavailable P forms. Kowenje (1997) reported a decrease in P extractability with period of reaction in four soils of Rift Valley Province having high P-sorption capacities. A decrease in P availability was reported to be more for water-soluble P fertiliser than for the PR because PRs continue to dissolve with increasing time (Figure 2.3).

Both organic and inorganic amendments are added to soils to improve PR dissolution. These materials include lime, organic residues and acidifying fertilisers such as sulphuric acid or those that contain ammonium ions, which lower soil pH when nitrified.

Liming strongly acidic soils through application of liming materials such as calcium carbonate is often recommended to reduce P fixation problem and other factors arising from soil acidity such as Al toxicity. While liming reduces the Al toxicity and fixation of soluble phosphates, it can on the other hand, depress dissolution of PR since soil pH and Ca concentration increase upon liming. Thus, liming should be carefully undertaken to alleviate problems associated with soil acidity while avoiding adverse effects on PR dissolution. A practical approach often recommended to overcome the two counteracting effects is to apply PR at relatively low rates to soils several months before liming (Chien and Menon, 1995).

Application of organic residues to soils is an important management practice often done to improve the soil nutrient status and nutrient cycling (Haines and Uren, 1990), in addition to detoxification and immobilisation of toxic cations (e.g. Al, Fe and Mn) (Bell and Besho, 1993; Woomer *et al.*, 1994). Organic materials are typically low in plant nutrients including P and therefore are more suited as supplements with inorganic P sources (Palm *et al.*, 1997). Composting PRs with organic materials enhances their solubility (Singh and

Amberger, 1991; Ikerra *et al.*, 1994; Van den Bergh, 1996) depending on the kind of organic waste materials and the rate of decomposition (Bangar *et al.*, 1985; Mahimairaja *et al.*, 1995).

Figure 2.3: Mean Olsen P values of superphosphate (SSP) and Minjingu PR (MPR) treatments after 15, 30 and 60 days of reaction time (Kowenje, 1997)

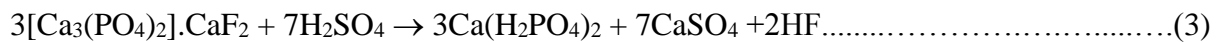
2.4 Dissolution reactions of completely acidulated and other modified phosphate rock fertilisers in soils

In order to improve the solubility of PRs, the apatite structure of the PR materials is broken down into water-soluble forms using various methods. Some of the methods are discussed below.

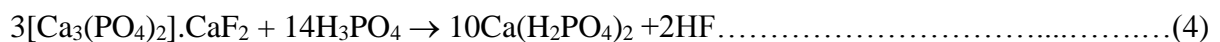
2.4.1 Completely acidulated phosphate rocks

Soluble P fertilisers exist in two categories. These are acid-and heat-treated fertilisers. Acid-treated fertilisers are obtained by treating reactive PRs with mineral acids, while heat-treated fertilisers are manufactured by heating PRs to varying temperatures with or without additives. The most important fertilisers are the acid-treated fertilisers to which fully acidulated (100%) P fertilisers (e.g. superphosphates) and the partially acidulated PRs (PAPR) belong.

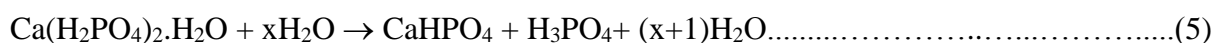
Single and triple superphosphates are manufactured by treating reactive PR with sulphuric and phosphoric acids respectively, in equal stoichiometric quantities. The treatment converts the insoluble tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) in the PR material into the water-soluble monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) form. The reaction for the production of single superphosphate is as follows:



Reactions for triple superphosphate proceed according to the equation shown below.



Essentially the reactions of soluble P fertilisers in soil involve a reactive P component in superphosphates i.e. monocalcium phosphate and soil (Sample *et al.*, 1980). Initially, water is absorbed by osmotic process from the soil into the fertiliser granules. This leads to the formation of a highly concentrated acidic solution of P around the granule microsite (Sample *et al.*, 1980) as shown below:



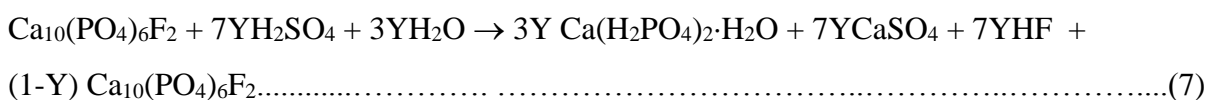
Dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) dissolves gradually with time to form a less soluble compound, dicalcium phosphate anhydrate (CaHPO_4) (Stephen and Condon, 1986). The dicalcium phosphate anhydrate in the fertiliser granule dissolves incongruently with time leading to the formation of highly insoluble P compound, hydroxyapatite and phosphoric acid according to the reaction:



This acidic solution may diffuse from the granule site and can dissolve Fe, Mn and Al compounds in the soil environment. This leads to the precipitation or fixation of the dissolved P as less soluble Fe, Mn and Al phosphates in acidic soils. In calcareous soils, dicalcium phosphate (CaHPO_4) is the dominant initial reaction product and in the presence of large amounts of calcium carbonate, octacalcium phosphate also forms.

2.4.2 Partial acidulation

Partial acidulation is one of the PR modification techniques employed for increasing the solubility of PR. Partially acidulated phosphate rocks (PAPRs) are fertilisers which have been acidulated using smaller quantities of either sulphuric or phosphoric acids than the amounts required for complete acidulation as in the production of single superphosphate or triple superphosphate. The products are usually monocalcium phosphate, the unreacted PR and small amounts of dicalcium phosphate (Rajan *et al.*, 1996). The chemical reaction for the production of PAPR from a PR material and sulphuric acid can be represented by the following equation (Hammond *et al.*, 1986).



Where Y = degree of acidulation.

Partially acidulated PRs undergo similar reactions in soil as those of fully acidulated fertilisers producing phosphoric acid and dicalcium phosphate. Partial acidulation has been reported to enhance dissolution of unreacted PR component in PAPR material (Sanyal and De Datta, 1991). Rajan and Watkinson (1992) demonstrated that the rate of PR dissolution increased with an increasing level of partial acidulation. The agronomic effectiveness of PAPR has also been reported to be similar or better than that of fully acidulated P fertilisers in acidic or even in calcareous soils (Rajan *et al.*, 1994; Xiong *et al.*, 1995). Chien and Menon (1995) found that PAPR was more effective on sandy soils with low P sorption capacity in West Africa. The presence of calcium sulphate coatings on the PR particles, however, may depress and delay disintegration of PAPR granules (Hammond *et al.*, 1980).

Also high levels of Fe and Al oxides in PRs may decrease the availability of P from PAPR due to the reaction of water-soluble P with these oxides to form insoluble phosphates. Thus, the removal of Fe and Al oxides before acidulation may improve the quality of the PR ore, but this usually increases the cost.

2.4.3 PR Blending techniques

An alternative practice to enhance the agronomic effectiveness of low reactive PRs is to blend with water-soluble phosphates, such as superphosphates. This technique has proved to be agronomically effective in sub-Saharan Africa (Govere *et al.*, 1995; Chien *et al.*, 1996; MnKeni *et al.*, 2000). Blending process involves either compacting or pelletizing the PR with a water-soluble P fertiliser in various ratios. Low energy and capital investments are required for compaction and pelletizing techniques compared to partial or full acidulation. It has also been suggested that compaction with soluble P is more agronomically effective than partial acidulation on both soils high in Al and Fe oxide contents (Chien and Menon, 1995; Menon *et al.*, 1991, 1995), and soils high in P-sorption capacities (Chien and Hammond, 1988). MnKeni *et al.* (2000) found that a low reactive Panda PR compacted with triple superphosphate, increased wheat (*Triticum aestivum*), maize (*Zea mays*) and soyabean (*Glycine max*) yields and P uptake significantly compared to the uncompact PR. Butegwa *et al.* (1996), however, reported that partial acidulation and compaction of unreactive Sukulu Hills PR from Uganda with triple superphosphate did not improve agronomic effectiveness of Sukulu Hills PR on limed soils of high P sorption capacities. Liming probably reduced available P by forming insoluble Ca-P compounds as well as the dissolution of PR. In contrast, Govere *et al.* (1995) observed improved solubility of unreactive Dorowa PR when compacted with triple superphosphate.

2.4.4 Physical mixtures of PR and water- soluble phosphates

Whereas the manufacturing costs of PAPRs are lower than those of fully acidulated fertilisers, their market prices are comparable. Physical mixing of PR with water-soluble P is considered to be a cheaper technology of lowering the cost of the more expensive processed P fertilisers while at the same time improving the agronomic effectiveness of the PR material. As in the case of PAPR and compacted PR-soluble P products, physical combination of PR

with water-soluble P can result in chemical interaction that can enhance the dissolution of PR and thus improve its agronomic value (Mokwunye and Chien, 1980).

It is generally believed that the hydrolysis of monocalcium phosphate in the water-soluble P fertilisers creates an acidic triple point solution of phosphoric acid, which would subsequently dissolve the PR material thereby releasing additional P into soil solution (Chien and Menon, 1995; Xiong *et al.*, 1996). It is also believed that the presence of P in water-soluble form will facilitate early plant root development thereby enabling effective utilization of P from PR (Chien *et al.*, 1987). Furthermore, the acidic hydrolysis product of soluble P in soil may probably be neutralized by the dissolving PR resulting in the precipitation of aluminium hydroxide and iron hydroxide and hence minimizing the reaction of P with Al and Fe minerals in the soil to form insoluble Al- Fe phosphates (Buresh *et al.*, 1997).

Thus, in recent years attempts have been made to enhance the solubility of unreactive PRs by physically mixing with water-soluble P fertilisers (Chien *et al.*, 1987, 1996, 1999; Thibaud *et al.*, 1993; Xiong *et al.*, 1996; Rajan *et al.*, 1995; Kundu and Basak, 1999; MnKeni *et al.*, 2000). Chien *et al.* (1996) studied the effect of mixtures of Central Florida PR and triple superphosphate in an acidic soil with maize (*Zea mays*) and cowpea (*Vigna sinensis*) as test crops. They reported that mixing Central Florida PR and triple superphosphate at a total P ratio of 50:50 significantly increased dry-matter yield and P uptake. Chien *et al.* (1987) reported that a mixture of North Carolina PR and triple superphosphate was just as effective as triple superphosphate when mixed at P ratios of at least 1:1. They suggested that the increased P availability in the superphosphate-PR mixture either arose from enhanced PR solubility by the acidic triple point solution or good root development by readily available P from superphosphate. Kundu and Basak (1999) investigated the availability of P from Purulia PR-superphosphate mixtures and reported that the agronomic effectiveness of PR-single superphosphate mixtures increased with increasing proportion of superphosphate. Thibaud *et al.* (1993) reported similar findings on investigating the effect of a wide range of combinations of superphosphate and Langebaan PR. They also found that all combinations were less effective than superphosphate but performed better than PR alone. They, however, found little evidence to suggest that dissolution of Langebaan PR was enhanced owing to the acidic triple point solution.

Other studies on the agronomic performance of the mixtures of phosphate rocks and water-soluble P fertilisers on alkaline or calcareous soils have been reported. Rajan *et al.* (1995) evaluated agronomic effectiveness of Mussoorie PR from India and a mixture of the PR and single superphosphate at a ratio of 2:1. They found increased performance of

Mussoorie PR and single superphosphate mixture against the PR alone. Chien *et al.* (1999) reported also that a mixture of a Syrian PR and triple superphosphate was as effective as triple superphosphate for rape (*Brassica napus*) on a limed soil. They attributed this observation to a synergic interactive effect between the water-soluble P of triple superphosphate and the insoluble P fraction from PR and improved root development that led to better utilization of P from the PR material. They however, found little evidence to suggest that P availability was enhanced on the PR material. Mnkeni *et al.* (2000) evaluated rape response to Panda Hills PR from Tanzania and its mixture with triple superphosphate at a ratio of 50:50 on a limed soil in United States. They reported greater performance of the PR-triple superphosphate mixtures compared to PR alone.

While the theory advanced above, that the triple point solution arising from hydrolysis of monocalcium phosphate in superphosphate is responsible for improved solubility of PR in the mixtures, it is also possible that the solution may dissolve Al, Fe and Mn soil minerals which may subsequently reduce the availability of P in solution through precipitation reactions.

2.5 Fixation reactions and factors affecting the process

Dissolved P from P fertilisers may be rendered unavailable for plant uptake through fixation reactions with the soil and its components. The processes involved are adsorption, precipitation and microbial immobilisation.

2.5.1 Adsorption reactions

Adsorption is the major mechanism regulating the concentration of soil solution P in highly weathered acid soils (Sanchez, 1976). The process involves net accumulation of P on active sites of the soil components.

The adsorption process is influenced by several factors including the nature and amounts of soil components, pH, type and valency of constituent ions and saturation of sorption sites. The soil components involved are hydrous oxides of Al and Fe, aluminosilicate clays and organic matter (Sanchez, 1976). The active adsorption sites in hydrous oxide surfaces are mainly hydroxyl (OH⁻) and water (H₂O) groups, exposed hydroxyl groups at the edges of clay minerals, and carboxyl and phenolic groups in organic matter.

Hydrous oxides of Al and Fe, the dominant components in highly weathered acid soils (Sanchez, 1976), adsorb greater amounts of P than clay minerals. 1:1 clay minerals such as Kaolinite adsorb greater amounts of P than 2:1 type minerals such as illites probably because of hydrous oxides, which are associated with 1:1 lattice clays. Amorphous aluminosilicates are much more effective in adsorbing P than crystalline clays due to their large and exposed surface areas (Ryden and Pratt, 1980). Organic matter in soils can indirectly influence P adsorption through the formation of complexes with Al and Fe associated with organic matter. Positive correlation between soil organic matter and P adsorption has been reported (Owusu-Bennoah, and Acquaye, 1980; Le Mare and Leon, 1989). Reduction of P adsorption by high organic matter has also been reported (Sanyal and De Datta, 1991) and is thought to be caused by anionic competition between the negatively charged organic anions and P for adsorption sites.

Soil pH is an important factor known to influence P adsorption by soil and its components. Changes in pH tend to affect the surface charges of variably charged soils and hence the P adsorption by soil and its components. An increase in pH increases hydroxyl and active groups on oxide surfaces which become deprotonated to leading a net surface negative charge (Figure 2.4). This causes a reduction in P adsorption due to an increase in electrostatic attraction between the negatively charged P ions and the negatively charged adsorption surface. Conversely a decrease in pH leads to protonation of hydroxyl and water groups of the soil components leading to a net positive charge. This consequently increases P adsorption.

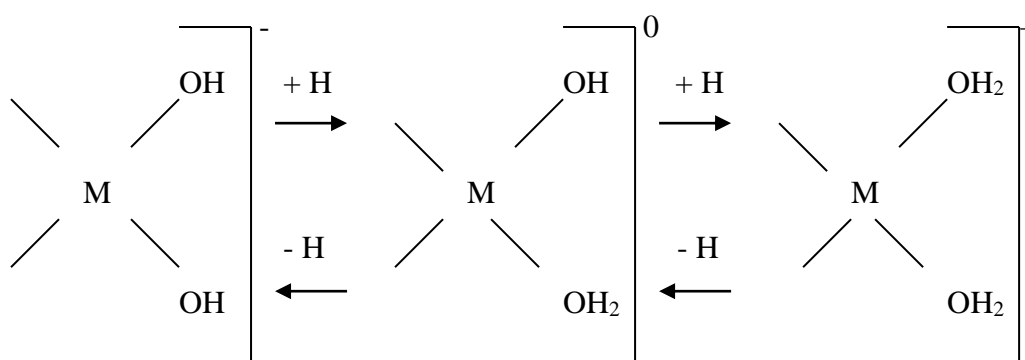


Figure 2.4: A simple model of pH-dependent surface charges on amphoteric metal oxide (Adapted from Bowden *et al.*, 1980).

Exchangeable cations may also influence P adsorption. The presence of Al on the exchange sites of clay minerals tends to increase P adsorption as the pH increases (Haynes, 1982). P adsorption takes place on the newly formed hydroxy-Al complexes, which may be found to occur independently or coat the surfaces of clay minerals.

The cations and anions in soil solution also influence the adsorption of P. Cations tend to increase P adsorption, the effect being greater for divalent cations than monovalent cations (Bowden *et al.*, 1980). In contrast, anions tend to reduce P adsorption by competing with P for adsorption sites. Inorganic anions adsorb onto oxide surfaces in the order: $\text{PO}_4^{3-} > \text{AsO}_4^{2-} > \text{SiO}_4^{2-} > \text{SiO}_3^{2-} > \text{MoO}_4^{2-} > \text{SO}_4^{2-} > \text{SeO}_4^{2-} > \text{Cl}^- \sim \text{NO}_3^-$ (Ryden *et al.*, 1987).

Available P adsorption sites also influence the amount of P adsorbed by the soils and its components. Soils that have had previous heavy applications of P fertilisers tend to adsorb less P due to saturated adsorption sites (Smyth and Sanchez, 1982).

Thus the effect of adsorption reactions on dissolved P depends on the net interacting factors governing the adsorption process.

2.5.2. Precipitation reactions

Dissolved P may also react with Al, Fe and Ca in the soil to form insoluble P compounds through precipitation reactions. The stability and type of precipitated P compounds in the soil is influenced by the pH as predicted from solubility isotherms of the various P compounds (Figure 2.5). Al- and Fe- P compounds are the dominant minerals in acid soils, whereas in alkaline soils Ca-P minerals tend to form. The isotherms also indicate that as the pH is increased, the Al- and Fe-P compounds become unstable and dissolve, and conversely, Ca-P compounds become unstable at low pH.

The surface characteristics of the precipitated P compounds change with time (Sanyal and De Datta, 1991). Their crystal sizes increase leading to a decrease in surface area and reduced P availability held by precipitated P compounds (Brady, 1984). Indeed, Al-P, Fe-P and Ca-P compounds precipitated in soil usually have extremely low solubilities (Sanyal and De Datta, 1991).

Thus, fixation of dissolved P through precipitation reactions may represent in the long run a substantial loss of available P for plant uptake.

Figure 2.5: Solubility of calcium phosphates compared with strengite and variscite when Ca ($10^{-2.5}$ M) is fixed by calcite and CO₂ at 0.0003 atm. (Lindsay, 1979)

2.5.3 Immobilization reactions by soil microorganisms

Soil microorganisms play an important role in the mineralization and immobilisation of organic and inorganic P in soils (Stevenson, 1986). The rapid decomposition of organic

matter under favourable soil conditions (moisture, pH and temperature) stimulates microbial activities causing a temporary tying up of inorganic P in the organic tissues (Brady, 1984). Immobilisation of inorganic P to organic P by microorganisms can occur rapidly upon addition of P fertilisers to the soil. This leads to a buildup of organic P in the soils. McLaughlin *et al.* (1981) found out that microbial biomass assimilate a significant proportion of added P fertiliser equal to plant uptake. Conversely, long-term cultivation of soils and under favourable soil conditions, mineralization of organic P occurs leading to a decline in microbial P and total organic P in the soils (Stevenson, 1986).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Soils

Three virgin highland acid soils (Njoro clay loam, Kericho sandy clay and Molo silty clay) having contrasting chemical properties were used in this study. The samples were collected at selected sites as shown in Figure 3.1. Samples from each site were collected randomly at the depth of 0-30 cm. After removing large particles and vegetation, the samples from each site were thoroughly mixed, bulked and labeled. In the laboratory, the soils were air-dried and screened to pass through less than 2 mm sieve. The chemical properties of the three soils were then determined as described in section 3.3.1.

The Kericho sandy clay, classified as humic Nitisol (Ekirapa and Shitakha, 1996), is found in the humid south-western highlands of Mau forest. The soil is developed from intermediate igneous-andesites and phonolites, an extension of volcanic eruptions from Mau escarpment. Top soils are dark-reddish brown in colour. The soils are deep, permeably well-drained and moderate to high in fertility. The area receives mean annual rainfall of about 1,800-2000 mm and means temperatures of 15-18 °C. The soil samples were collected in a virgin area about 3 km southwest of Kericho town within 00°20'06''S and 35°15'01''E, at an altitude of 2000-2100 m above sea level (asl).

The Njoro clay loam occurs at the eastern edge of Mau ranges and it is developed from volcanic eruptions. The soil is classified as Mollic Andosol (FAO/UNESCO, 1990). Top soils are reddish brown to dark in colour. The area receives mean annual rainfall of approximately 980-1012 mm and temperatures of 15-18° C. The soil samples were collected at Egerton University, Njoro within 00°21'58'' S and 35°55'42''E, at an altitude of 2250-2300 m asl

The Molo silty clay was sampled from National Pyrethrum Research Centre of KARI, Molo. The region occurs towards the eastern edge of Mau forest at 00° 12' S and 35 ° 41' E, at an altitude of 2500 m asl. The soils are acidic, well-drained, deep, dark-reddish brown with a Mollic A horizon. The soil is also classified as humic Nitisol (FAO/UNESCO, 1990). The mean annual rainfall is 1171 mm and is distributed in two seasons in a year i.e. April to

August (long rains) and September/ October to December (short rains). The mean maximum and minimum air temperatures are 20.6 and 6.9 ° C, respectively.

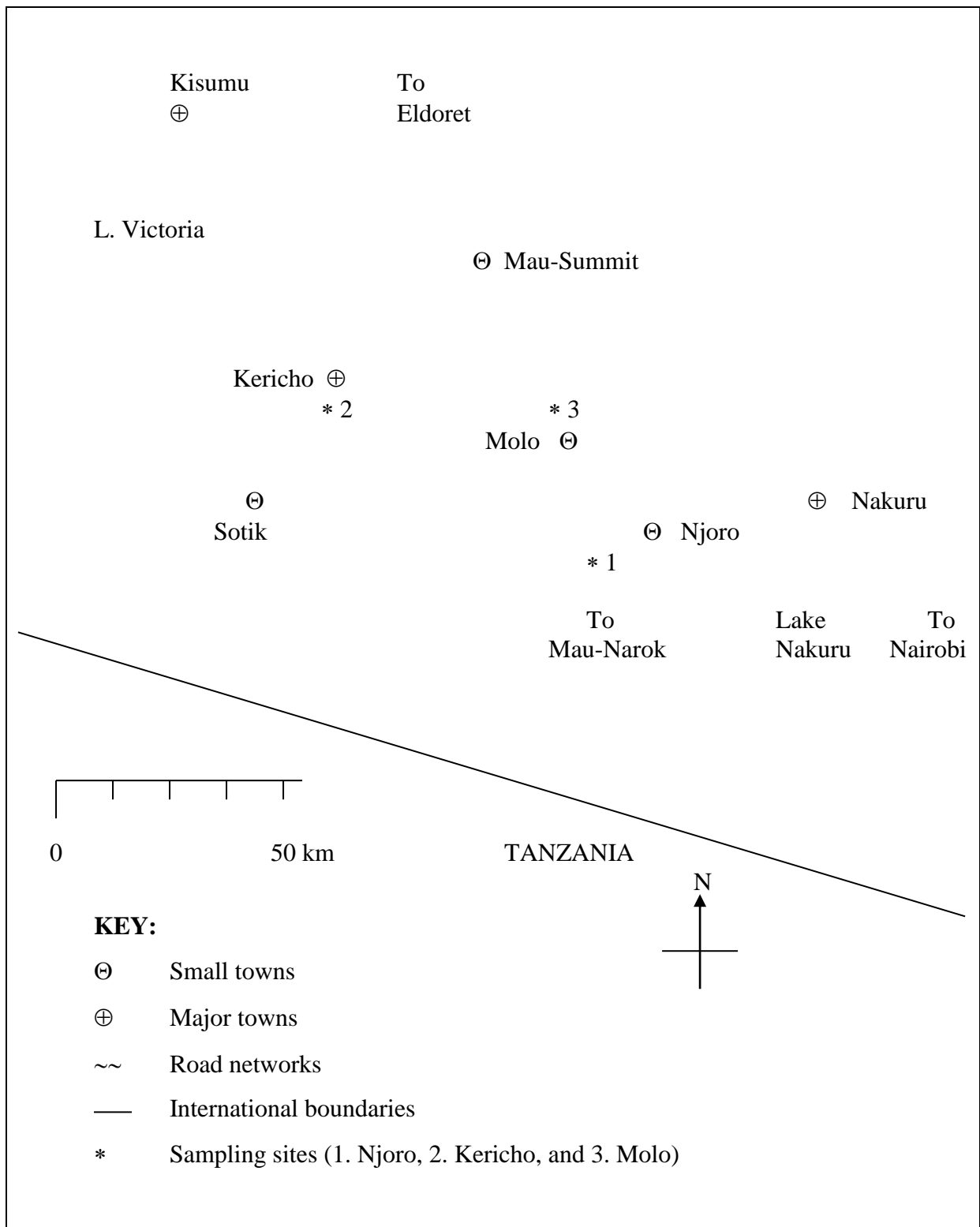


Figure 3.1: Soil sampling sites

3.1.2 Phosphate fertilisers

One reactive PR material (Minjingu phosphate rock) from Tanzania and a commercially available soluble P fertiliser (single superphosphate) were used. The two fertilisers were ground to pass through a 100 mesh (≤ 2 mm) sieve in order to improve its surface area and to mix well with the soils. The PR and single superphosphate fertilisers were mixed in various ratios on the basis of their total P contents. Mixtures of fertilisers were made by combining appropriate amounts of the two fertilisers in the percentage ratios of superphosphate to Minjingu PR fertilisers of 0:0, 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 and 0:100. Total P and Ca in the fertiliser materials were determined as described in section 3.3.2. The total P values in the superphosphate and Minjingu PR fertilisers were 82 and 122 g P kg⁻¹ while the total Ca values were 234 and 341 g Ca kg⁻¹ respectively.

3.2 Laboratory incubation experiment

A laboratory incubation experiment was conducted as follows:

Air-dried samples (400 g, < 2 mm) of each soil were treated with the P sources at the two rates: 200 (P-1) and 800 (P-2) mg P kg⁻¹ soil. A control treatment of 0 (P-0) mg P kg⁻¹ soil was also included. The two P fertilisers were mixed and applied at the same rates to the soils as a mixture of single superphosphate and Minjingu PR in the ratios of single superphosphate to Minjingu PR fertilisers of 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 and 0:100. A total of twenty three (23) treatments were used.

Each of the sample mixtures was replicated twice and placed into clean polythene bags. Appropriate amounts of distilled water were added to the samples to bring the moisture content to about 70 % of field capacity. The soil samples and the added fertilisers were then mixed thoroughly and incubated under laboratory conditions for 90 days. The moisture content was maintained gravimetrically at about 70 % of field moisture capacity and adjustments were made by adding distilled water as required. Subsamples of the moist soils were taken at intervals of 30, 60 and 90 days, air-dried, ground and sieved through less than 2-mm sieve. Soil pH and NaHCO₃-extractable P were determined after 30, 60 and 90 days of reaction time, while extractable Ca, Fe and Mn were determined at the end of the reaction time (i.e. after 90 days). For quality control and reliability of data, the treatments of soil samples were made and analysis done in duplicates. Reagent blanks were included and

treated the same way as the soil samples. The reagents used, for extraction processes and preparation of standards were of Analar Reagent grades.

3.3 Laboratory analyses

3.3.1 Soil properties

Soil pH was determined in suspension of water at a soil to solution ratio of 1:2.5 (w/v). The soil solutions were stoppered well and shaken using a reciprocal shaker for 30 minutes (Okalebo *et al.*, 1993) and the pH was determined using a fully calibrated pH meter fitted with glass-calomel reference electrode.

Soil organic carbon content (%) was determined according to Walkley and Black dichromate oxidation method (Black, 1965). The amount of organic matter (%) was obtained by multiplying organic carbon value by a factor of 1.724, which is based on assumed C content of 58 % for the organic matter.

Extractable Ca was determined by shaking 2 g air-dried soil samples with 20 ml of 1.0 M BaCl₂-triethanolamine (BaCl₂ –TEA) at pH 8.1 on an end-over-end shaker for one hour (Kanabo and Gilkes, 1988a). The extracts were filtered through Whatman No. 2 filter paper. To 1 ml of the filtrate in a 50-ml volumetric flask, 1 ml of 1 % Lanthanum chloride was added and made to the mark with distilled water. The concentrations of Ca in the extracts were determined using Atomic Absorption Spectrophotometer (AAS), model S11. Calibration standards in the range of 0 - 5 ppm Ca, made from 1000 ppm Ca stock solution were used.

The amounts of dissolved P in the soil samples were determined by extracting air-dried samples with 0.5 M NaHCO₃ (pH 8.5) at a soil (g) to solution (ml) ratio of 1:20 (Okalebo *et al.*, 1993). The extracts were filtered through Whatman No. 2 filter paper. 5 ml of 0.8 M boric acid, 10 ml of ascorbic acid as a reducing agent were added to 10 ml of the soil filtrates in a 50-ml volumetric flask and made to the mark with distilled water. After one hour of colour development, the concentrations of P in the filtrates were determined colorimetrically by Molybdenum blue method as modified by John (1970) using Novaspec II UV-Visible spectrophotometer at the wavelength of 880 nm. Calibration standards in the range of 0-12.5 ppm P, made from 250 ppm P stock solution were used.

Cation exchange capacity (CEC) of initial soils was determined by leaching appropriate amounts of air-dried soil samples (≤ 2 mm) with 1M neutral ammonium acetate

(pH 7.0) at a soil (g)/solution (ml) ratio of 1:50. The extracts were further leached with 1M potassium chloride. The concentrations of the NH_4^+ ions in the leachate removed from the exchange sites were then determined by steam distillation and CEC calculated from the values obtained.

The exchangeable bases (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) were determined from the leachates in the original extracts of CEC. The concentrations of K and Na in the leachates were measured using flame emission spectrophotometer, model 410 while those of Ca and Mg by atomic absorption spectrophotometer (AAS), model S11.

Extractable Fe and Mn were determined by shaking 2 g of air-dried soil samples with 50 ml 0.2 M ammonium acetate (pH 4.8) on a reciprocal shaker for 30 minutes (Olson and Carlson, 1950). The extracts were filtered through Whatman No. 44 filter paper. The concentrations of Fe and Mn in the extracts were determined using AAS, model S11 at the wavelengths of 248.3 nm and 279.5 nm respectively. Calibration standards in the ranges of 0-10 ppm Fe and 0-5 ppm Mn were used.

3.3.2 Properties of phosphate fertilisers

Total P in the P fertiliser materials was determined by digesting 2.5g of the fertiliser samples with 5 ml of conc. HNO_3 and 20 ml conc. HCl. The concentrations of P in the extracts were determined colorimetrically as earlier described. Total Ca of the P fertilisers was determined in the same extracts of total P using AAS as in the methods outlined earlier.

3.4 Data analysis

Analysis of variance (ANOVA) for the soil parameters measured was carried out using IRRISTAT version 4.0 Computer Program. Significance tests of the various treatments were carried out using calculated least significant differences (LSD) method at $P < 0.05$. Simple linear regression analysis was also carried out.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Initial chemical properties of the soils

Results for some initial chemical properties of the soils used are given in Table 4.1 below. The analyses were necessary in order to study the various chemical properties, which may influence the dissolution of Minjingu PR in the mixtures of superphosphate and Minjingu PR in soils.

Table 4.1: Initial soil chemical properties of the soils

Chemical property	Soil		
	Njoro	Molo	Kericho
pH (1: 2.5 in water)	5.6	5.4	4.6
Organic carbon (%)	2.2	3.0	3.8
Olsen P (mg kg ⁻¹)	6.0	4.8	4.5
Extractable Ca (mg kg ⁻¹)	1967	1607	1198
Fe (mg kg ⁻¹)	30.2	101.4	76.7
Mn (mg kg ⁻¹)	7.0	9.8	7.2
CEC (cmol (+) kg ⁻¹)	24.7	16.5	13.8
Exchangeable bases (cmol (+) kg ⁻¹)			
Ca	16.2	7.9	4.8
Mg	3.1	1.9	1.0
K	1.7	1.3	0.8
Na	1.0	0.7	0.5
Total exchangeable bases (cmol (+) kg ⁻¹)	22.0	11.8	7.1
Fe _(ox) (%) *	0.5	0.9	1.5
Al _(ox) (%) *	1.3	1.5	2.0
P adsorption capacity (mg P/kg)	836	1632	2487

* Adapted from Fertiliser Use Recommendation Project (FURP, 1987)

All soils were generally acidic with the pH values in water ranging from 4.6 to 5.6. The pH for the Kericho sandy clay indicated that the soil was strongly acidic while the Molo silty clay and the Njoro clay loam were moderately acidic. These values are due to relative amounts of H^+ and Al^{3+} ions on the surface charges of the soils and their associations with soil exchangeable colloids. Leaching and weathering processes in high rainfall areas result in loss of base cations, and lowering of pH (Sanchez, 1976).

The organic carbon content of the soils ranged from 2.2 to 3.8. The values were quite high for the Kericho sandy clay (3.8 %) and the Molo silty clay (3.0 %) and moderate for the Njoro clay loam (2.2 %). This may be due to plant residues arising from intensive agricultural activities and the favourable climatic conditions of these regions. Soils with high clay contents such as the Kericho sandy clay (75 %) and the Molo silty clay (42 %) (Macharia, 1992) form stabilised organo-mineral complexes with the soil humus, and thus may account for the observed organic carbon contents.

The extractable P values for all the soils were low ranging from 4.5 to 6.0 mg P kg^{-1} . The values were lower than the critical threshold value of 10 mg P kg^{-1} for most Tropical soils. The Kericho sandy clay had the lowest Olsen P value while the Njoro clay loam had the highest value. These values are consistent with the pH, Fe, Al and P adsorption capacity values of the soils (Table 4.1).

The cation exchange capacity (CEC) values for the soils ranged from 13.8 to 24.7 cmol (+) kg^{-1} . They were moderate for the Njoro clay loam (24.7 cmol (+) kg^{-1}) and the Molo silty clay (16.5 cmol (+) kg^{-1}) but low for the Kericho sandy clay (13.8 cmol (+) kg^{-1}) soil. The values are within the medium CEC measurements of ± 15 cmol (+) kg^{-1} common in Tropical soils. The exchangeable bases (Ca, Mg, K and Na) for the Njoro, Molo and Kericho soils were 22.0, 11.8 and 7.1 cmol (+) kg^{-1} respectively. This trend reflects the order observed for the CEC and pH values. Generally in all the three soils, the values for the exchangeable bases decreased in the order of Ca, Mg, K and Na.

The extractable acidic cations (Fe and Mn) were generally low for all the soils, with Mn values being relatively lower than Fe values. The lowest levels were observed in the Njoro clay loam followed by the Molo silty clay and then the Kericho sandy clay. This trend is consistent with the order observed for pH values.

4.2. Effects of P sources, application rates and superphosphate to Minjingu PR ratios on soil pH and extractable Ca concentrations

The pH values of the soils after 30, 60 and 90 days of fertiliser reactions with the soils are shown in Tables 4.2, 4.3 and 4.4 and illustrated in Figures 4.1 (a)-(c).

Addition of Minjingu PR increased the pH values of all the soils over the control treatments for all the periods of reaction (Figures 4.1 a-c). The increases were similar in all the soils. In all the soils also, greater increases were observed at the high rate of application (800 mg P kg⁻¹ soil) than at the lower rate (200 mg P kg⁻¹ soil).

Increases in pH during PR dissolution have often been attributed to the consumption of H⁺ ions by substituted carbonate in the crystal lattice of a PR material and free carbonates associated with the PR material (Khasawneh and Doll, 1978). Other possible reasons which have been advanced for increased pH values in PR-treated soils over the controls are precipitation of Al and Fe by P released from dissolving PR material and P retention in soil colloids occurring through ligand OH⁻ exchange reactions (Ikerra *et al.*, 1994; Chien and Menon, 1995). Thus, the observed increases in pH of the PR-treated soils over the controls are indicative of PR dissolution in soils.

The finding that the pH increases in all the soils were greater at the higher rate of application than at the lower rate is expected since a greater amount of carbonates would be neutralized by soil acidity per unit weight of PR applied at the higher rate of application.

In contrast, application of either superphosphate or mixtures of superphosphate and Minjingu PR decreased the pH values of all the soils throughout the reaction periods (Figures 4.1 (a)-(c)). The decreases were, however, greater for superphosphate fertiliser than for the mixtures of superphosphate and Minjingu PR. As in the case of Minjingu PR fertiliser, the pH decreases were also greater at the higher rate of application than at the lower rate.

The observed decreases in pH by either superphosphate alone or in combinations with Minjingu PR are attributable to the strongly acidic triple point solution (pH 1.5), which arises from the hydrolysis reaction of monocalcium phosphate present in superphosphate (Lindsay and Stephenson, 1959). The finding that the pH decreases were much lower in the treatments of superphosphate and Minjingu PR than in treatments of superphosphate alone can be attributed to a certain portion of phosphoric from the hydrolysis reaction of monocalcium phosphate being used to solubilize Minjingu PR.

Table 4.2: Effects of P sources, P application rates and ratio of superphosphate to Minjingu PR on pH of Njoro clay loam

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Reaction time (days)		
			30	60	90
Control	0	0:0	5.70	5.46	5.64
SSP	200	100:0	5.15	5.18	5.40
		800	100:0	5.05	5.08
		Mean	5.10	5.13	5.12
MPR	200	0:100	5.70	5.59	5.91
		800	0:100	5.85	5.78
		Mean	5.78	5.69	6.02
SSP+MPR	200	90:10	5.20	5.15	5.41
		80:20	5.30	5.19	5.43
		70:30	5.35	5.20	5.48
		60:40	5.35	5.27	5.48
		50:50	5.35	5.24	5.55
		40:60	5.35	5.38	5.52
		30:70	5.30	5.42	5.54
		20:80	5.35	5.40	5.62
		10:90	5.40	5.38	5.72
		Mean	5.33	5.29	5.53
	800	90:10	4.75	4.97	5.17
		80:20	5.05	5.03	5.23
		70:30	5.25	5.06	5.26
		60:40	5.10	5.09	5.19
		50:50	5.25	5.14	5.26
		40:60	5.00	5.19	5.26
		30:70	5.20	5.30	5.33
20:80		5.25	5.35	5.51	
	Mean	5.17	5.18	5.32	
LSD (P ≤ 0.05)			0.06	0.07	0.17

Table 4.3: Effects of P sources, P application rates and ratio of superphosphate to Minjingu PR on pH of Kericho sandy clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Reaction time (days)				
			30	60	90		
Control	0	0:0	4.39	4.39	4.40		
SSP	200	100:0	4.26	4.30	4.39		
		800	100:0	4.24	4.25	4.38	
		Mean	4.25	4.28	4.39		
MPR	200	0:100	4.73	4.44	4.48		
		800	0:100	4.75	4.48	4.93	
		Mean	4.74	4.46	4.71		
SSP+MPR	200	90:10	4.33	4.20	4.38		
		80:20	4.35	4.19	4.41		
		70:30	4.31	4.25	4.40		
		60:40	4.35	4.21	4.44		
		50:50	4.31	4.31	4.46		
		40:60	4.37	4.26	4.48		
		30:70	4.35	4.22	4.55		
		20:80	4.27	4.32	4.57		
		10:90	4.35	4.28	4.60		
			Mean	4.33	4.25	4.48	
		800	800	90:10	4.39	4.37	4.39
				80:20	4.40	4.38	4.48
				70:30	4.35	4.33	4.51
				60:40	4.46	4.34	4.52
				50:50	4.45	4.35	4.54
40:60	4.52			4.32	4.54		
30:70	4.46			4.37	4.58		
20:80	4.67			4.41	4.64		
10:90	4.54			4.47	4.67		
	Mean	4.47	4.37	4.54			
LSD (P ≤ 0.05)			ns	0.07	0.16		

Table 4.4: Effects of P sources, P application rates and ratio of superphosphate to Minjingu PR on pH of Molo silty clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Reaction time (days)			
			30	60	90	
Control	0	0:0	5.17	4.97	4.96	
SSP	200	100:0	5.08	4.76	4.73	
	800	100:0	5.06	4.30	4.66	
		Mean	5.07	4.53	4.70	
MPR	200	0:100	5.30	5.17	5.07	
	800	0:100	5.53	5.42	5.29	
		Mean	5.42	5.30	5.18	
SSP+MPR	200	90:10	5.09	4.77	4.76	
		80:20	5.06	4.81	4.76	
		70:30	5.13	4.89	4.77	
		60:40	5.14	4.92	4.81	
		50:50	5.14	4.96	4.83	
		40:60	5.16	4.97	4.89	
		30:70	5.22	5.05	4.92	
		20:80	5.30	5.03	5.03	
		10:90	5.31	5.15	5.11	
			Mean	5.17	4.95	4.88
		800	90:10	5.04	4.69	4.69
			80:20	5.08	4.81	4.78
			70:30	5.13	4.76	4.79
			60:40	5.12	4.77	4.83
50:50	5.19		4.80	4.89		
40:60	5.25		4.91	4.93		
30:70	5.22		5.05	4.99		
20:80	5.34		5.03	5.09		
10:90	5.42		5.13	5.14		
	Mean		5.20	4.88	4.90	
LSD (P ≤ 0.05)			0.12	0.14	0.08	

Table 4.5: Changes in pH values (Δ pH) for Njoro clay loam, Kericho sandy clay and Molo silty clay

Treatment	Rate (mg P g ⁻¹)	Ratio (SSP: MPR)	Soil			
			Njoro	Kericho	Molo	
SSP	200	100:0	-0.36	-0.07	-0.17	
	800	100:0	-0.46	-0.1	-0.20	
		Mean	-0.41	-0.09	-0.18	
MPR	200	0:100	0.13	0.16	0.15	
	800	0:100	0.32	0.41	0.38	
		Mean	0.23	0.29	0.27	
SSP+MPR	200	90:10	-0.12	-0.16	-0.18	
		80:20	-0.06	-0.15	-0.17	
		70:30	-0.02	-0.14	-0.08	
		60:40	-0.03	-0.13	-0.05	
		50:50	0.01	-0.1	-0.03	
		40:60	0.06	-0.09	0	
		30:70	0.06	-0.08	0.05	
		20:80	-0.01	-0.07	0.11	
		10:90	0.06	-0.05	0.17	
			Mean	-0.01	-0.11	-0.01
		800	90:10	-0.50	-0.42	-0.41
			80:20	-0.36	-0.38	-0.32
			70:30	-0.27	-0.39	-0.32
			60:40	-0.33	-0.36	-0.30
			50:50	-0.24	-0.35	-0.22
40:60	-0.31		-0.34	-0.18		
30:70	-0.19		-0.33	-0.12		
20:80	-0.09		-0.23	-0.06		
10:90	0.16		-0.22	0.03		
	Mean		-0.24	-0.34	-0.22	

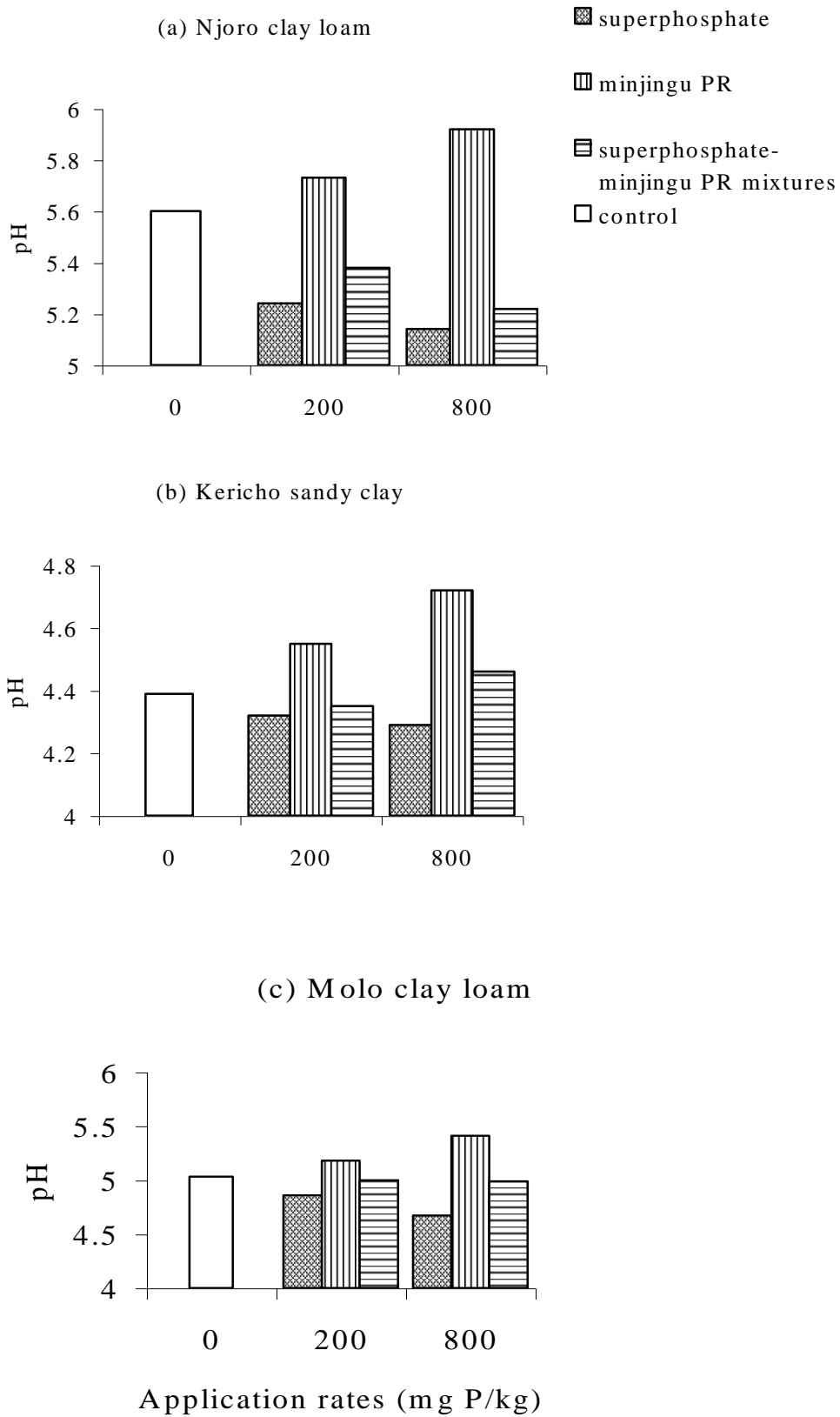


Figure 4.1. The effect of P sources and application rates on soil pH: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo clay loam

It can also be seen that the pH values of all the soils significantly decreased with increasing proportion of superphosphate component in the mixtures (Figures 4.2 (a)-(c)). Highly significant negative correlation coefficients were obtained between the pH and percentage of superphosphate component in the mixtures for the Njoro clay loam ($r = -0.9268$), Kericho sandy clay ($r = -0.9789$) and Molo silty clay ($r = -0.9878$) soils. The drops in pH increased with increasing percentage of superphosphate in the mixtures and this indicated that a greater portion of phosphoric acid was being generated. The observed decreases in pH values with increasing percentage of superphosphate component in the mixtures have similarly been reported by Thibaud *et al.* (1993) in two South African soils. The greater drop in pH observed in all the soils for superphosphate treatments alone or mixtures of superphosphate and Minjingu PR at the higher rate of application than at the lower rate is due to greater portion of phosphoric acid generated per unit weight of the superphosphate applied at the higher rate.

Table 4.6 shows results for the effect of P sources, application rates and superphosphate to Minjingu PR ratio on extractable Ca in the soils.

Addition of the P fertilisers increased the extractable Ca levels in all the soils over their respective controls (Figures 4.3 (a)-(c)). As in the case of extractable P data (Tables 4.8-4.10) dissolution of a P fertiliser in soils releases Ca ions. The increases were greatest for Minjingu PR followed by mixtures of Minjingu PR and superphosphate, and lowest for superphosphate alone. This observation is due to the higher Ca content in Minjingu PR fertiliser (34.1 %) compared to single superphosphate (23.4 %). Similar results were reported by MnKeni *et al.* (2000).

The finding that the Kericho sandy clay gave the largest increases in extractable Ca concentrations (and pH) while the Njoro clay loam gave the lowest values upon application of Minjingu PR fertiliser (Tables 4.5 and 4.7) may be attributed to the differences in the chemical properties of the soils (Table 4.1). Similar observation and conclusion were made by Kowenje (1997) in a study on dissolution of Minjingu PR in some six acid soils of Rift Valley Province. Dissolution of PR materials has been reported to be influenced by soil chemical properties (Chien *et al.*, 1980; Hammond *et al.*, 1986; Kowenje, 1997).

Extractable Ca levels of the P sources increased with increasing rate of application in all the three soils (Figures 4.3 (a)-(c)) in agreement with the results of other workers (Robinson and Syers, 1991; Kowenje, 1997). As expected, greater amounts of Ca (and P) are released into the soils per unit weight of P fertiliser at the higher rate of application.

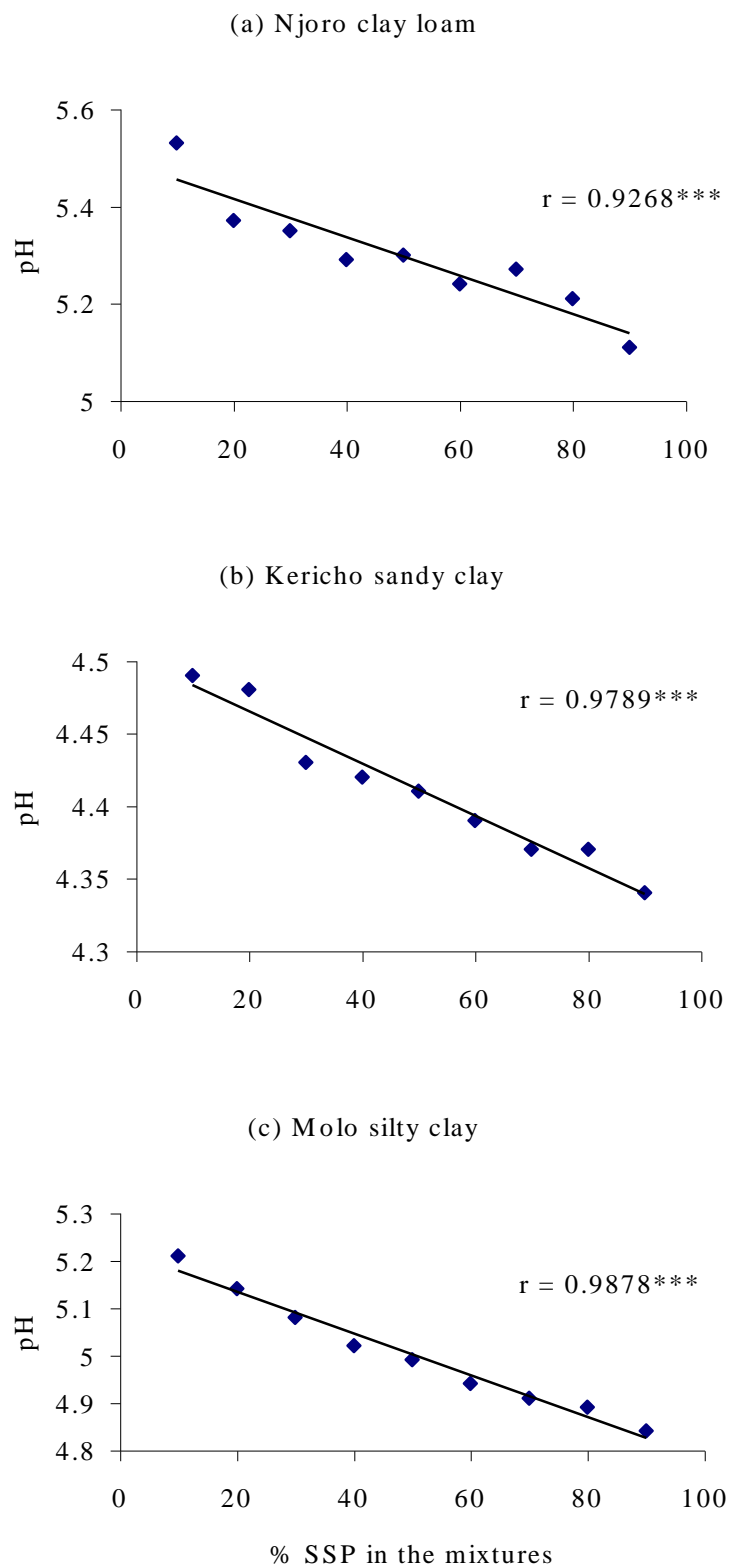


Figure 4.2. Relationship between pH and percentage (%) superphosphate (SSP) component in the mixtures of superphosphate and Minjingu PR fertilisers: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

Table 4.6: Effects of P sources, P application rates and superphosphate to Minjingu PR ratio on BaCl₂-TEA extractable Ca values (mg Ca kg⁻¹) in Njoro clay loam, Kericho sandy clay and Molo silty clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Soil		
			Njoro	Kericho	Molo
Control	0	0:0	1804	1273	1702
SSP	200	100:0	1897	1542	1743
		800	100:0	1981	1689
		Mean	1939	1616	1774
MPR	200	0:100	2200	1879	1868
		800	0:100	2728	2090
		Mean	2464	1985	2146
SSP+MPR	200	90:10	2133	1644	1910
		80:20	2083	1705	1882
		70:30	1914	1580	1895
		60:40	2067	1578	1819
		50:50	2044	1633	1748
		40:60	1948	1604	1796
		30:70	1862	1632	1801
		20:80	1824	1653	1743
		10:90	1864	1592	1725
			Mean	1982	1625
	800	90:10	2440	2259	2326
		80:20	2273	2313	2306
		70:30	2310	2119	2233
		60:40	2277	2192	2207
		50:50	2256	2081	2180
		40:60	2114	1917	2115
		30:70	1968	1842	1946
		20:80	1901	1834	1817
		10:90	1878	1868	1841
	Mean	2157	2047	2108	
LSD (P ≤ 0.05)			208	190	166

Table 4.7: Changes in extractable Ca values (Δ Ca) after 90 days of fertiliser reaction with Njoro clay loam, Kericho sandy clay and Molo silty clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Soil			
			Njoro	Kericho	Molo	
SSP	200	100:0	93	269	41	
	800	100:0	177	416	102	
		Mean	135	343	72	
MPR	200	0:100	396	606	166	
	800	0:100	324	817	722	
		Mean	360	712	444	
SSP+MPR	200	90:10	329	371	208	
		80:20	279	432	180	
		70:30	110	307	193	
		60:40	263	305	117	
		50:50	240	360	46	
		40:60	144	331	94	
		30:70	58	359	99	
		20:80	20	380	41	
		10:90	60	319	23	
			Mean	167	352	111
		800	90:10	636	986	624
			80:20	469	1040	604
			70:30	506	846	531
			60:40	473	919	505
			50:50	452	808	478
40:60	310		644	413		
30:70	164		569	244		
20:80	97		561	115		
10:90	74		595	139		
	Mean		353	774	406	

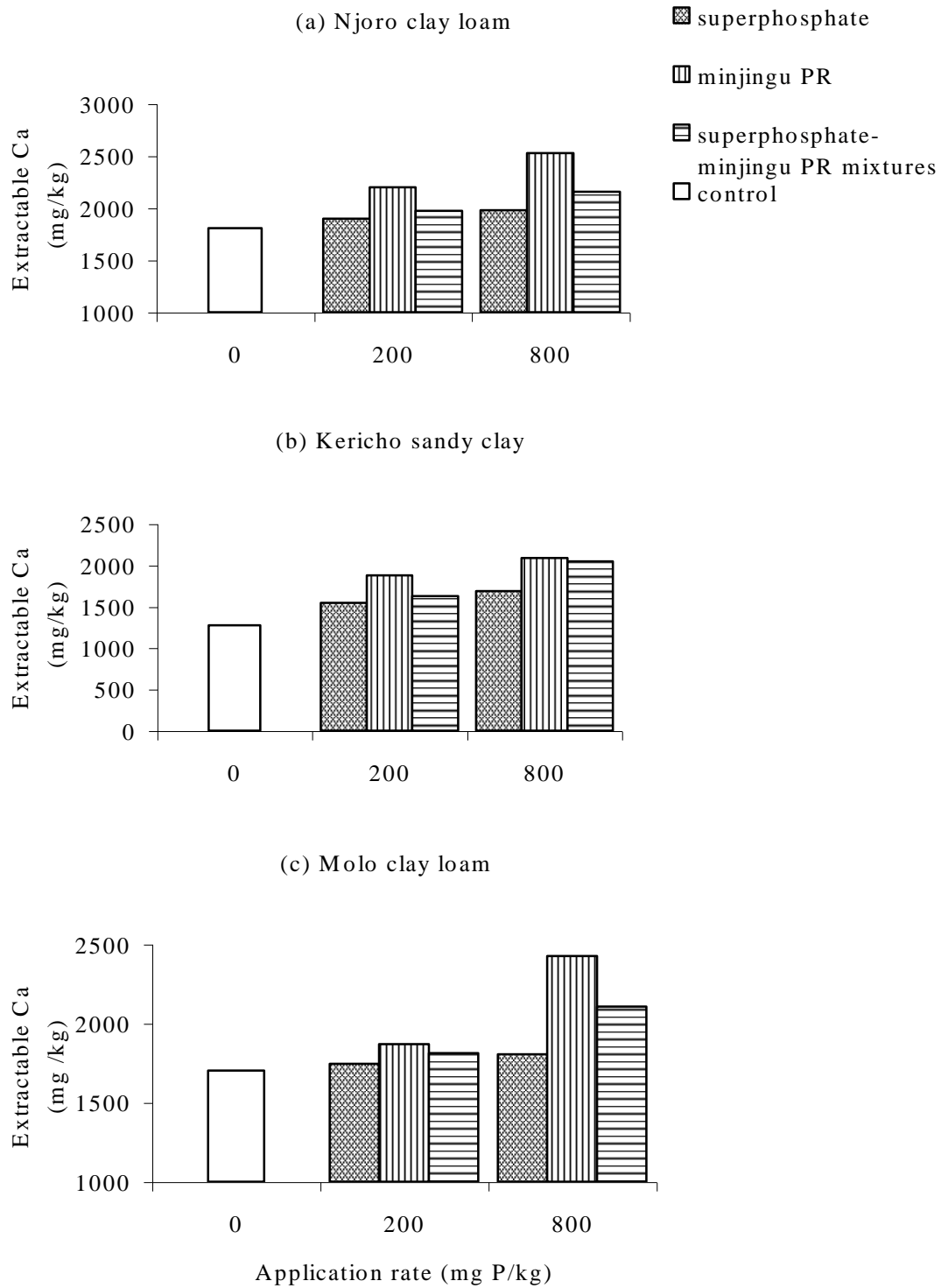


Figure 4.3: The effects of P sources and application rates on extractable Ca: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

The cation exchange sites which act as sinks for dissolved Ca are expected to be saturated at the higher rate of application and prevent further dissolution of PR material. However, results obtained from this study suggest that such a stage had not been reached even at the application rate of 800 mg P kg⁻¹ dry soil.

The extractable Ca levels also significantly increased with increasing proportion of superphosphate component in the mixtures (Figures 4.4 (a)-(c)). Highly significant differences in extractable Ca concentrations among the various mixtures were noticeable. The increases in extractable Ca values with percentage of superphosphate component in the mixtures may be attributed to the influence of superphosphate on the dissolution of the PR in the mixtures. The relationship between pH and extractable Ca (Figure 4.5) supports this observation. It can be suggested that the greater acidity arising from the higher percentage of superphosphate may have dissolved the PR material in the mixture. It appears that at low percentage superphosphate, the acidity produced was not enough to dissolve the PR.

Highly significant positive correlation coefficients ($P \leq 0.001$) were obtained between extractable Ca and the amount of extractable P for the mixtures in all the soils (Figures 4.6 (a)-(c)). This is expected since dissolution of P fertilisers releases both Ca and P ions (see Chapter 2, Equation 2). The amount of Ca extracted increased exponentially with increasing P concentration. Similar results have been reported by other workers (Hammond *et al.*, 1986; Robinson and Syers, 1990).

Table 4.8: Mean changes in pH (Δ pH) and Ca (Δ Ca) after 90 days of fertiliser reactions with Njoro clay loam, Kericho sandy clay and Molo silty clay

% SSP	Δ pH			Δ Ca		
	Njoro	Kericho	Molo	Njoro	Kericho	Molo
10	-0.23	0.27	0.18	67	457	81
20	-0.37	0.25	0.11	59	471	78
30	-0.45	0.20	0.05	111	464	172
40	-0.5	0.19	-0.01	227	488	254
50	-0.49	0.18	-0.06	346	584	262
60	-0.55	0.16	-0.10	368	612	311
70	-0.52	0.14	-0.12	308	577	362
80	-0.58	0.14	-0.15	374	736	392
90	-0.68	0.11	-0.19	483	679	416

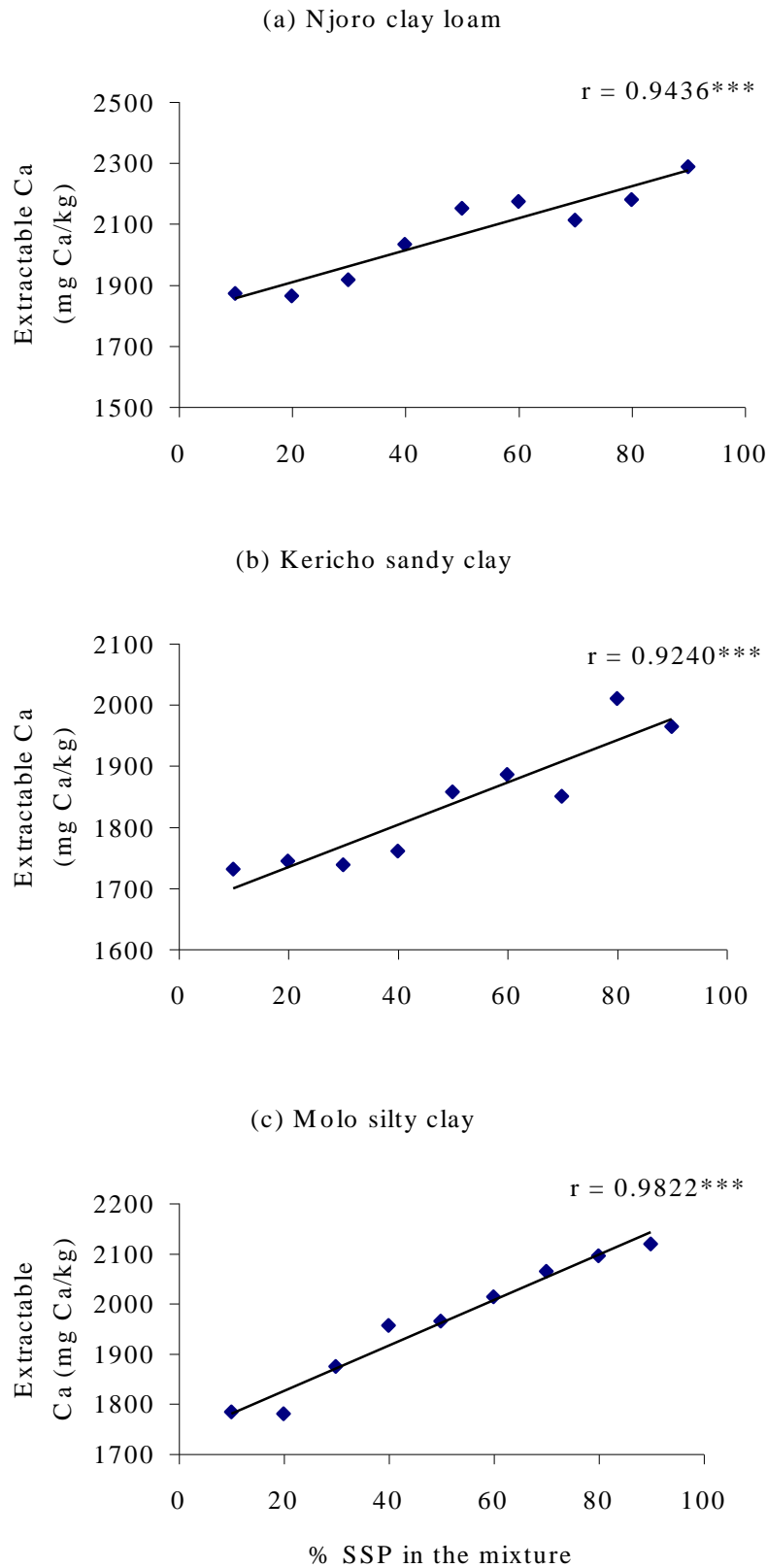


Figure 4.4: Relationship between extractable Ca and percentage (%) superphosphate (SSP) in the mixtures of superphosphate and Minjingu PR fertilisers: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

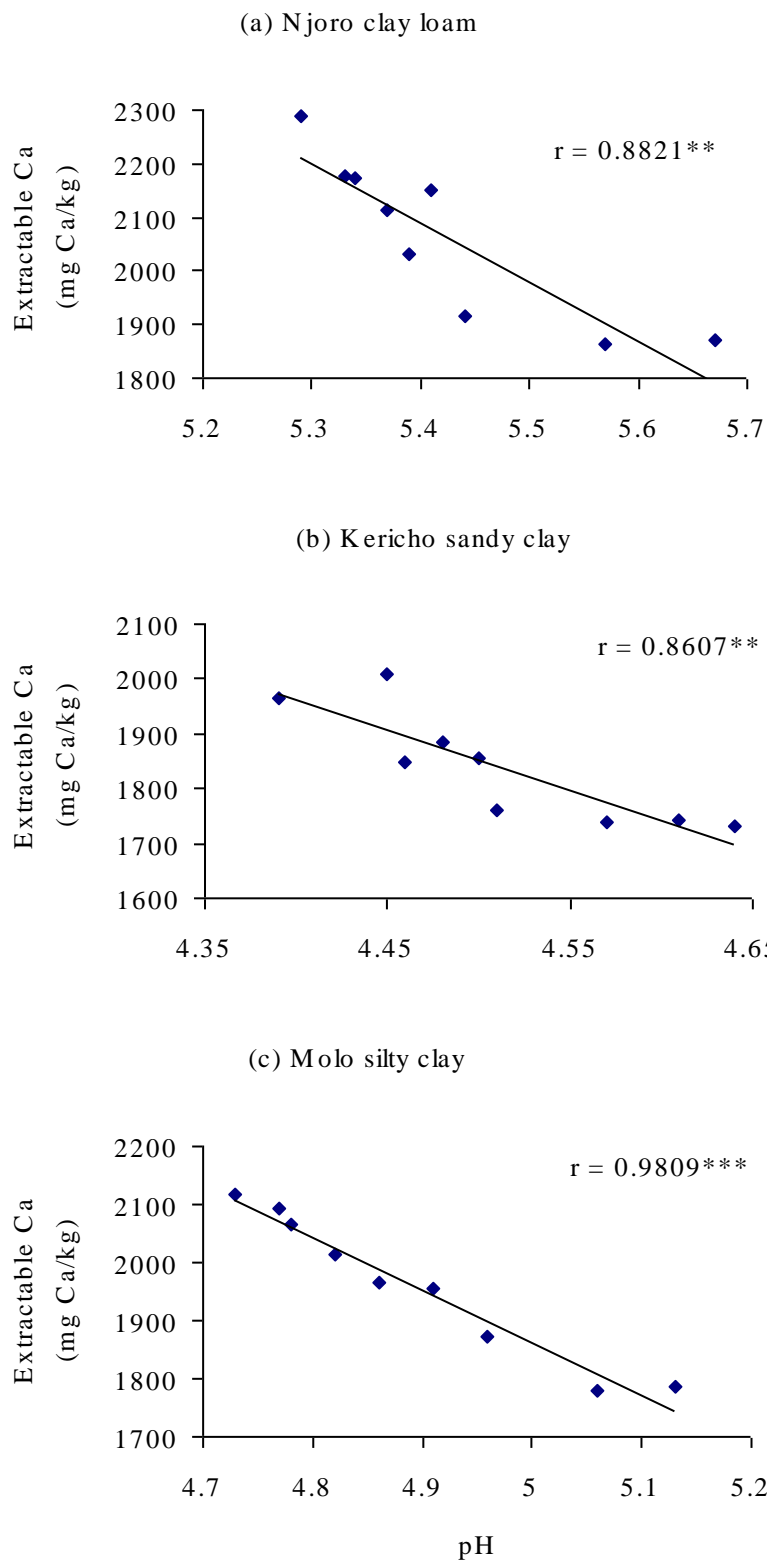


Figure 4.5: Relationship between pH and extractable Ca of mixtures of superphosphate and Minjingu PR: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

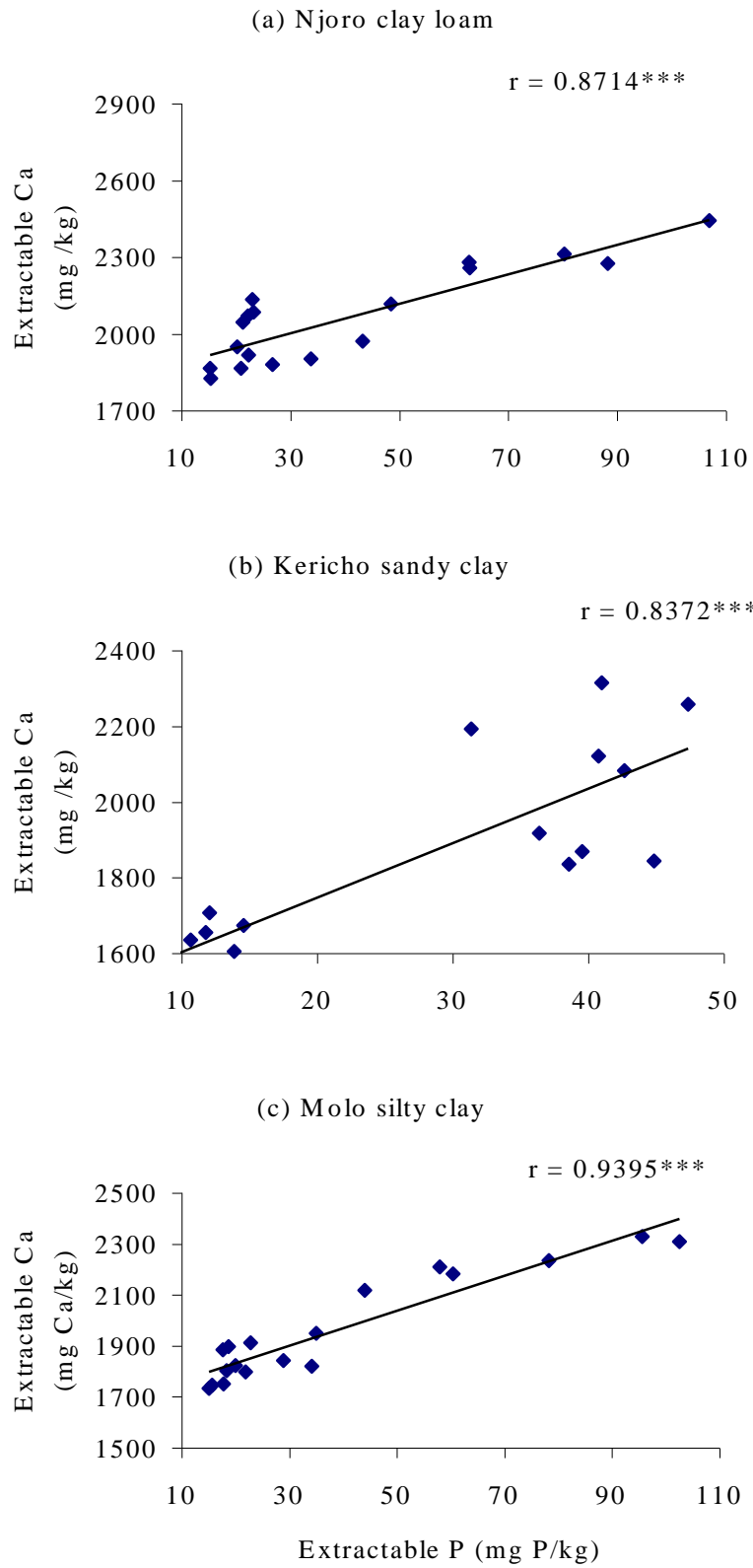


Figure 4.6. Relationship between extractable Ca and P extractability: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

4.3 Effects of P sources, rates of application and superphosphate to Minjingu PR ratio on NaHCO₃- extractable P

The effect of P sources, rates of application and ratios of superphosphate to Minjingu PR on extractable P is shown in Tables 4.9, 4.10 and 4.11, and illustrated in Figures 4.7 (a)-(c).

As mentioned in Chapter 2, dissolution of P fertilisers in soils is a necessary prerequisite before P becomes plant-available.

Soil tests for plant-available P frequently use extracting solutions, which dissolve and remove specific forms of soil P from solid phase. Sodium-bicarbonate extractant preferentially extracts Al-P and Fe-P reaction products that are formed after P fertiliser dissolves in soil, and little of the unreacted PR material (Khasawneh and Doll, 1978; Sanyal and De Datta, 1991). It is reasonable therefore to suggest that the measured increases in NaHCO₃-extractable P concentrations in the added P treatments (P-1 and P-2) over the control (P-0) (Tables 4.9, 4.10 and 4.11) in all the soils and for all the periods of reaction originate from plant-available P pool.

Superphosphate at both rates of application gave the highest amounts of extractable P followed by mixtures of the two fertilisers while Minjingu PR gave the lowest amounts (Tables 4.9, 4.10 and 4.11). The observed differences between the P sources (i.e. superphosphate and Minjingu PR) in the amounts of extractable P at both rates of application are attributable to the differences in the dissolution patterns of the two P fertilisers. Superphosphate is a readily water-soluble fertiliser and hence gives rise to higher amounts of extractable P concentrations. In contrast, Minjingu PR fertiliser dissolves slowly over time in soils resulting in lower amounts of extractable P concentrations (Hammond *et al.*, 1986; Sanyal and De Datta, 1991).

The extractable P for all the fertilisers increased significantly with the rate of application for all the soils (Figure 4.7 (a)-(c)). This observation is attributable to greater amounts of P released per unit weight of the fertilisers applied at the higher rate. It can also be seen that for all the sources the extractable P differed among the soils. At both rates of P application, the Njoro clay loam (a slightly acidic soil) gave the largest amount of extractable P followed by the Molo silty clay (a moderately acidic), and the Kericho sandy clay (a strongly acidic soil) produced the lowest values. This observation is in agreement with the P adsorption capacities of the soils (Table 4.1). Soils having relatively high P adsorption capacities such as the Kericho sandy clay and the Molo silty clay tend to maintain lower

Table 4.9: Effects of P sources, P application rates and superphosphate to Minjingu PR ratios on extractable P values (mg P kg⁻¹) in Njoro clay loam

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Reaction time (days)		
			30	60	90
Control	0	0:0	6.1	7.2	7.2
SSP	200	100:0	26.4	24.8	22.4
	800	100:0	104.4	101.3	91.1
		Mean	65.4	63.1	56.8
MPR	200	0:100	11.6	15.9	24.7
	800	0:100	16.4	27.1	30.7
		Mean	14.0	21.5	27.7
SSP+MPR	200	90:10	18.2	20.2	23.1
		80:20	13.2	19.4	23.3
		70:30	14.9	17.4	22.4
		60:40	12.8	20.1	22.3
		50:50	13.6	18.2	21.4
		40:60	12.8	15.0	20.3
		30:70	11.5	13.8	21.0
		20:80	9.7	13.3	15.4
		10:90	9.90	10.8	15.3
			Mean	11.9	16.5
	800	90:10	100.9	105.0	107.0
		80:20	93.6	93.7	88.3
		70:30	67.3	90.7	80.4
		60:40	73.1	63.0	62.9
	50:50	48.4	62.3	63.0	
	40:60	46.5	45.3	48.5	
	30:70	29.3	47.4	43.3	
	20:80	20.2	34.9	33.9	
	10:90	21.8	31.6	26.8	
	Mean	55.7	63.8	61.6	
LSD (P ≤ 0.05)			16.9	15.0	10.4

Table 4.10: Effects of P sources, P application rates and superphosphate to Minjingu PR ratios on extractable P values (mg P kg⁻¹) in Kericho sandy clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Reaction time (days)			
			30	60	90	
Control	0	0:0	4.80	4.80	6.40	
SSP	200	100:0	14.6	12.0	9.80	
	800	100:0	56.9	52.3	41.2	
		Mean	35.8	32.2	25.5	
MPR	200	0:100	8.60	12.7	14.4	
	800	0:100	20.4	27.3	34.6	
		Mean	14.5	20.0	24.5	
SSP+MPR	200	90:10	21.5	17.9	14.6	
		80:20	18.7	15.5	12.1	
		70:30	14.7	14.2	14.0	
		60:40	17.4	11.3	14.0	
		50:50	10.4	13.6	10.7	
		40:60	9.20	10.1	13.9	
		30:70	8.20	12.8	9.80	
		20:80	7.60	10.2	11.8	
		10:90	6.80	10.8	11.8	
			Mean	12.7	12.9	12.5
		800	90:10	42.9	55.3	47.4
			80:20	35.1	41.0	41.0
			70:30	28.1	37.0	40.8
			60:40	28.4	33.7	31.4
50:50	26.2		42.3	42.7		
40:60	16.4		35.9	36.4		
30:70	19.2		35.5	44.9		
20:80	18.0		34.6	38.6		
10:90	22.1		31.7	39.6		
	Mean		26.3	38.6	40.3	
LSD (P ≤ 0.05)			6.90	9.50	14.8	

Table 4.11: Effects of P sources, P application rates and superphosphate to Minjingu PR ratios on extractable Olsen P values (mg P kg⁻¹) in Molo silty clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Reaction time (days)			
			30	60	90	
Control	0	0:0	5.0	7.1	7.2	
SSP	200	100:0	22.2	17.6	16.2	
	800	100:0	97.6	95.6	92.0	
		Mean	59.9	56.6	54.1	
MPR	200	0:100	12.2	15.2	30.4	
	800	0:100	16.5	23.4	53.8	
		Mean	14.4	19.3	42.1	
SSP+MPR	200	90:10	32.5	18.8	22.9	
		80:20	12.4	19.1	17.7	
		70:30	15.2	19.0	18.8	
		60:40	14.7	13.7	20.1	
		50:50	18.2	14.9	17.9	
		40:60	17.4	12.1	21.9	
		30:70	17.0	14.8	18.4	
		20:80	15.9	12.7	15.8	
		10:90	14.1	15.4	15.2	
			Mean	17.5	15.6	18.7
		800	90:10	80.1	85.9	95.7
			80:20	73.3	62.3	102.6
			70:30	66.8	60.4	78.3
			60:40	61.0	45.9	58.1
50:50	45.2		49.5	60.5		
40:60	43.8		44.8	44.1		
30:70	27.3		34.1	35.1		
20:80	23.9		32.3	34.3		
	Mean	48.8	50.0	59.7		
LSD (P ≤ 0.05)			14.9	38.0	38.3	

Table 4.12: Changes in extractable P values (ΔP) after 90 days of fertiliser reaction with Njoro clay loam, Kericho sandy clay and Molo silty clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Soil			
			Njoro	Kericho	Molo	
SSP	200	100:0	17.7	6.8	12.3	
	800	100:0	92.1	44.8	88.7	
		Mean	54.9	25.9	50.5	
MPR	200	0:100	10.6	6.6	12.8	
	800	0:100	17.9	17.8	24.8	
		Mean	14.3	12.2	18.9	
SSP+MPR	200	90:10	13.7	12.7	18.3	
		80:20	11.8	10.2	10.0	
		70:30	11.4	9.0	11.3	
		60:40	11.6	8.9	9.8	
		50:50	10.9	6.3	10.6	
		40:60	9.3	5.8	10.7	
		30:70	8.6	5.0	10.3	
		20:80	6.0	4.6	8.4	
		10:90	5.2	4.5	8.5	
			Mean	9.5	7.4	10.9
		800	90:10	97.7	43.2	80.8
			80:20	85.0	33.8	73.0
			70:30	72.7	30.0	62.1
			60:40	59.5	26.1	48.6
			50:50	51.1	31.8	42.4
40:60	39.8		24.3	37.8		
30:70	33.2		27.9	25.7		
20:80	22.9		25.2	23.6		
10:90	19.9		25.8	20.7		
	Mean		53.6	29.8	46.4	

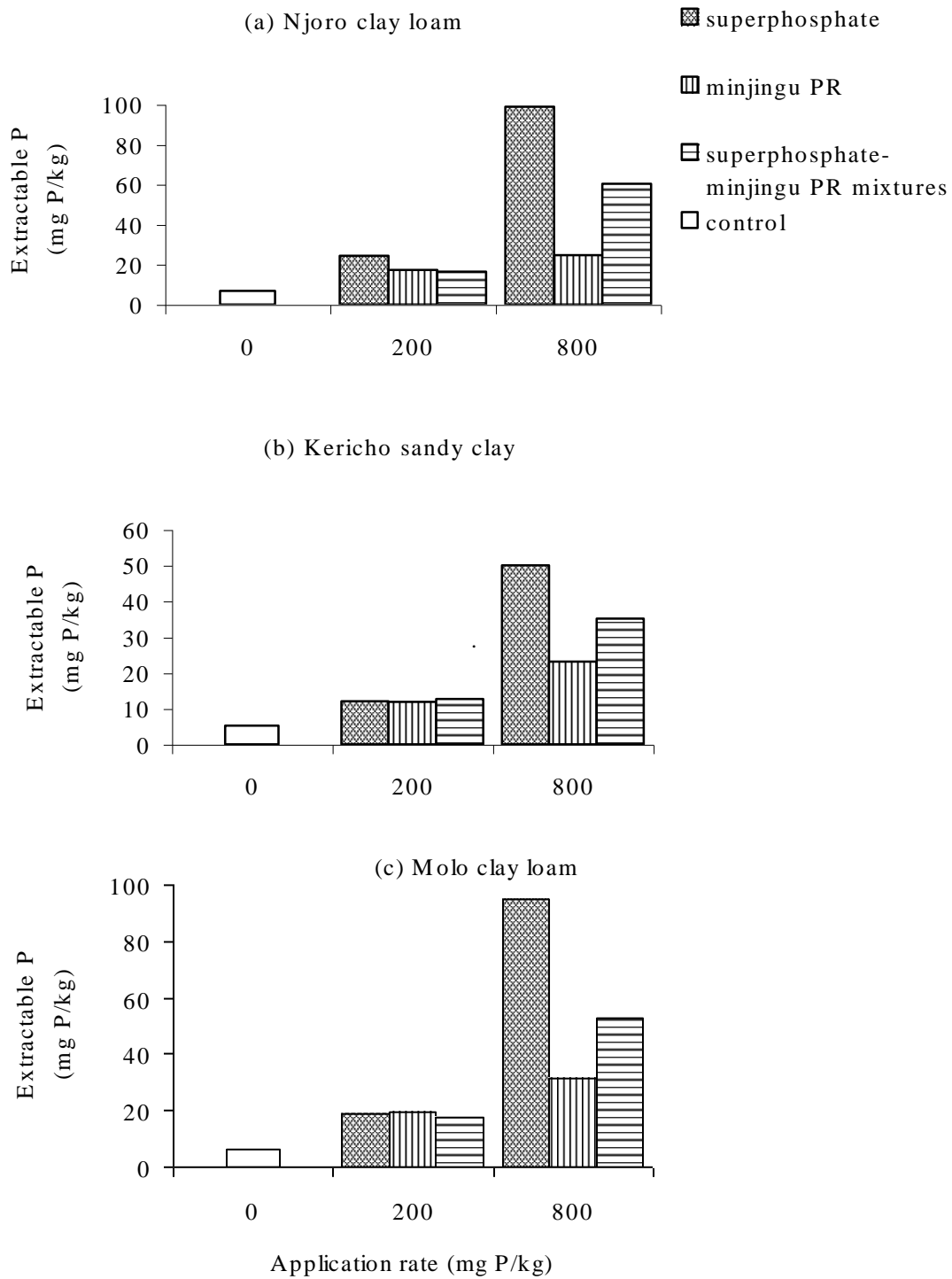


Figure 4.7: Effects of P sources and application rates on extractable P: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

levels of extractable P concentrations compared to the soils with relatively low P adsorption capacities (Sanchez, 1976). This finding suggests that, although soils having high P adsorption capacities may favour increased dissolution of a PR material, the dissolved P may not be readily available for plants. Similar conclusions have been drawn by other workers (Le Mare, 1991; Sanyal and De Datta, 1991).

Superphosphate and Minjingu PR fertilisers displayed different pattern of reactions with the soils with increasing time (Tables 4.9, 4.10 and 4.11). The Olsen P values for the superphosphate treatments declined with increasing period of fertiliser reaction in all the soils. In contrast, the Olsen P values for Minjingu PR treatments increased with increasing period of fertiliser reaction in all the soils. There were no significant noticeable trends in extractable P concentrations in the mixtures with increasing time. The difference shown by the effect of reaction time on the amounts of extractable P concentrations can, again, be attributable to differing solubilities of the P sources in the soils and subsequent fixation reactions of dissolved P by soil and soil components. For the readily water-soluble superphosphate, virtually all the P would be released immediately once the fertiliser is in contact with the soil (Sanyal and De Datta, 1991). Consequently dissolved P would be exposed to fixation reactions for a longer period of time. This would result in a larger decrease in the amount of extractable P concentrations as observed in this study.

For the water-insoluble Minjingu PR fertiliser, both dissolution reactions of the PR material and fixation reactions of dissolved P occur concurrently. The observed increase in extractable P with increasing time in all the soils suggests that the reaction of the PR fertiliser with the soils was continuing. Similar findings have been reported by other workers (Robinson and Syers, 1991; Hannafi *et al.*, 1992; Kowenje, 1997).

It is also evident that in all the soils, P extractability increased with increasing proportion of superphosphate component in the mixtures of superphosphate and Minjingu PR (Figure 4.8 (a)-(c)). Significant positive correlation coefficients between the amount of P extracted and percentage of superphosphate component in the mixtures were clearly evident in all the soils. Highly significant negative correlation coefficients between extractable P and pH were observed for all the soils (Figure 4.9 (a)-(c)). The amount of P extracted increased exponentially with decreasing soil pH. The values varied with the rate of application and among the soils. The values were highly significant for the Kericho sandy clay ($r = -0.9943$) followed by the Molo silty clay ($r = -0.9572$) and the Njoro clay loam ($r = -0.8701$).

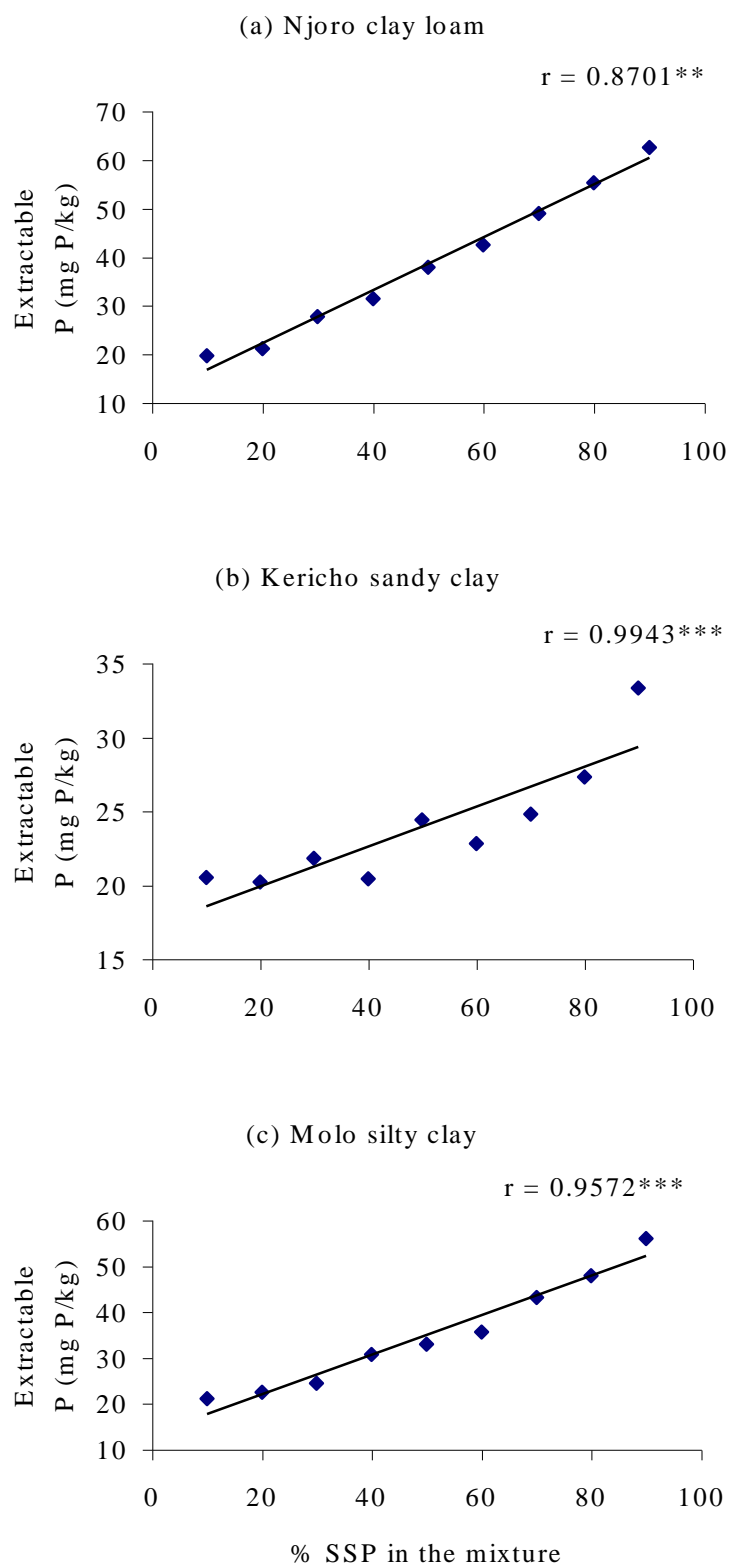


Figure 4.8: Relationship between P extractability and percentage (%) superphosphate (SSP) of total P in the mixtures of superphosphate and Minjingu PR fertilisers: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

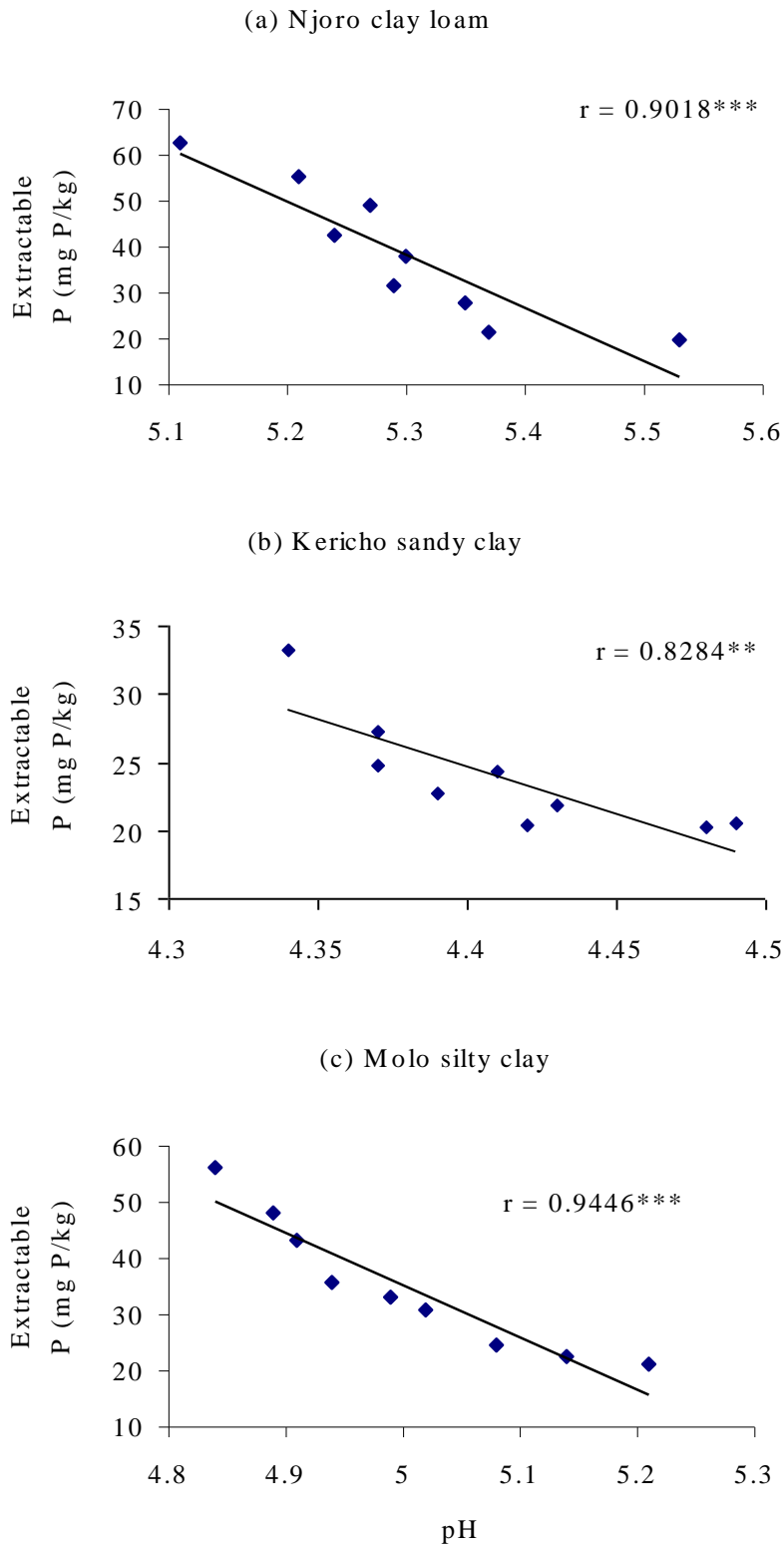


Figure 4.9: Relationship between pH and P extractability: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

This finding indicates that the increases in extractable P values with decreasing pH were due to acidity arising from the hydrolysis of monocalcium phosphate in superphosphate was responsible in the dissolution of PR in the mixtures. Furthermore, the significant negative correlation coefficients between pH and extractable P (Figure 4.9 (a)-(c)) further support this conclusion.

Table 4.13: Mean changes in extractable P (Δ P) after 90 days of fertiliser reaction with Njoro clay loam, Kericho sandy clay and Molo silty

% SSP	Δ P		
	Njoro	Kericho	Molo
10	12.6	15.2	14.6
20	14.5	14.9	16.0
30	20.9	16.5	18.0
40	24.5	15.1	24.3
50	31.0	19.1	26.5
60	35.6	17.5	29.2
70	42.1	19.5	36.7
80	48.4	22.0	41.5
90	55.7	28.0	49.6

4.4. Effects of P sources, P application rates and superphosphate to Minjingu PR ratio on ammonium acetate extractable Fe and Mn concentrations in Njoro, Kericho and Molo soils

Results for the effect of P sources, rates of application and superphosphate to Minjingu PR ratio on extractable Mn and Fe concentrations in the three soils are shown in Tables 4.14 and 4.15 respectively.

In general, the amounts of ammonium acetate (pH 4.8) extractable Mn and Fe were very low in the soils. In all the soils, application of P fertilisers at both rates decreased both

Table 4.14: Effects of P sources, P application rates and superphosphate to Minjingu PR ratio on acetate extractable Mn values (mg Mn kg⁻¹) in Njoro clay loam, Kericho sandy clay and Molo silty clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Soil		
			Njoro	Kericho	Molo
Control	0	0:0	8.4	10.9	8.9
SSP	200	100:0	7.8	8.9	8.7
		800	100:0	6.6	8.7
		Mean	7.2	8.8	8.1
MPR	200	0:100	7.0	7.8	7.2
		800	0:100	5.5	6.8
		Mean	6.3	7.3	6.7
SSP+MPR	200	90:10	8.4	8.7	9.6
		80:20	7.7	8.7	8.6
		70:30	8.3	8.6	6.9
		60:40	6.9	8.6	9.5
		50:50	7.9	8.6	6.9
		40:60	7.5	8.5	6.9
		30:70	7.7	8.4	7.0
		20:80	7.6	8.4	7.3
		10:90	7.1	8.1	7.1
		Mean	7.6	8.5	7.8
	800	90:10	7.9	8.7	6.9
		80:20	6.6	7.9	7.2
		70:30	6.2	7.8	6.6
		60:40	6.3	7.8	6.9
		50:50	7.2	7.7	6.6
		40:60	6.2	7.6	7.0
		30:70	6.5	7.5	5.8
		20:80	5.3	7.1	5.5
		10:90	5.5	7.3	5.8
		Mean	6.5	7.6	6.5
LSD (P ≤ 0.05)			0.8	1.3	0.9

Table 4.15: Effects of P sources, P application rates and superphosphate to Minjingu PR ratio on acetate extractable Fe values (mg Fe kg⁻¹) in Njoro clay loam, Kericho sandy clay and Molo silty clay

Treatment	Rate (mg P kg ⁻¹)	Ratio (SSP: MPR)	Soil		
			Njoro	Kericho	Molo
Control	0	0:0	44.2	113	85.2
SSP	200	100:0	40.5	98.1	82.7
		800	29.4	87.7	70.2
		Mean	35.0	92.9	76.5
MPR	200	0:100	29.1	86.5	48.6
		800	23.7	70.2	40.6
		Mean	26.4	78.4	44.6
SSP+MPR	200	90:10	41.5	80.5	72.2
		80:20	39.1	95.2	69.4
		70:30	38.4	97.7	71.5
		60:40	37.9	91.7	68.9
		50:50	33.7	93.9	63.9
		40:60	30.8	83.1	62.3
		30:70	35.7	84.0	50.5
		20:80	31.4	80.5	50.3
		10:90	35.6	78.8	50.9
			Mean	32.5	88.6
	800	90:10	35.2	87.7	62.3
		80:20	28.1	75.5	49.0
		70:30	29.0	77.4	53.0
		60:40	26.2	73.2	47.7
		50:50	25.6	75.4	44.0
		40:60	23.5	70.2	47.7
		30:70	33.3	66.5	42.5
		20:80	31.4	66.3	42.1
		10:90	26.5	65.0	37.3
	Mean	28.7	74.0	47.3	
LSD (P ≤ 0.05)			5.9	17.7	6.5

the levels of extractable Mn and Fe values over the control treatments (Tables 4.14 and 4.15). The decreases were, however, greatest for Minjingu PR followed by mixtures of single superphosphate and Minjingu PR, and lowest for single superphosphate. The observed decreases in extractable Mn and Fe concentrations in all the soils following P application (Figures 4.10 and 4.11) may be attributed to precipitation of Mn and Fe by P released from dissolving P fertilisers (Ikerra *et al.*, 1994). Indeed, the negative correlation coefficients between extractable P and extractable Mn and Fe (Figures 4.12 and 4.13) observed in the soils are indicative of precipitation of Mn and Fe phosphates.

The finding that Minjingu PR-treatments gave the largest decreases compared to either Minjingu PR or combinations of superphosphate and Minjingu PR (Figures 4.10 and 4.11) can be explained in terms of the dissolution reactions of the two fertilisers in soil. Minjingu PR fertiliser undergoes slow and continuing dissolution reactions, which increase pH (and extractable P concentrations). An increase in pH may not favour the release of Mn and Fe from the soil minerals.

In contrast, superphosphate virtually releases all the P into the soil and decreases the pH (Tables 4.2-4.4) upon application. This change in pH may have led to larger amounts of Fe and Mn soil minerals being released into soil solution.

The larger decreases of extractable Mn and Fe concentrations at the higher rate of application than at the lower rate (Figures 4.10 and 4.11) may be attributed to greater precipitation of Mn and Fe phosphates (Sloan *et al.*, 1995) at higher rate of application.

The largest drops in extractable Mn and Fe concentrations were observed in the Kericho sandy clay, followed by the Molo silty clay and the lowest drop was observed in the Njoro clay loam (Tables 4.14 and 4.15). This observation is similar to that of extractable P data (Tables 4.9 - 4.11) and it is possible that greater precipitation of Mn and Fe phosphates may have occurred due to the presence of high concentrations of Mn and Fe in the Kericho sandy clay (Table 4.1). Indeed, the significant negative correlation coefficient between extractable P and extractable Mn and Fe (Figures 4.12 and 4.13) observed in the Kericho sandy clay is indicative of precipitation of Mn and Fe phosphates.

The correlation coefficients obtained between extractable Mn and percentage of superphosphate in the mixtures (Figure 4.14) and extractable Fe and percentage of superphosphate in the mixtures (Figure 4.15), extractable Mn and pH (Figure 4.16), extractable Fe and pH (Figure 4.17) clearly show that the phosphoric acid arising from the hydrolysis reaction of monocalcium phosphate component was not only dissolving the PR in

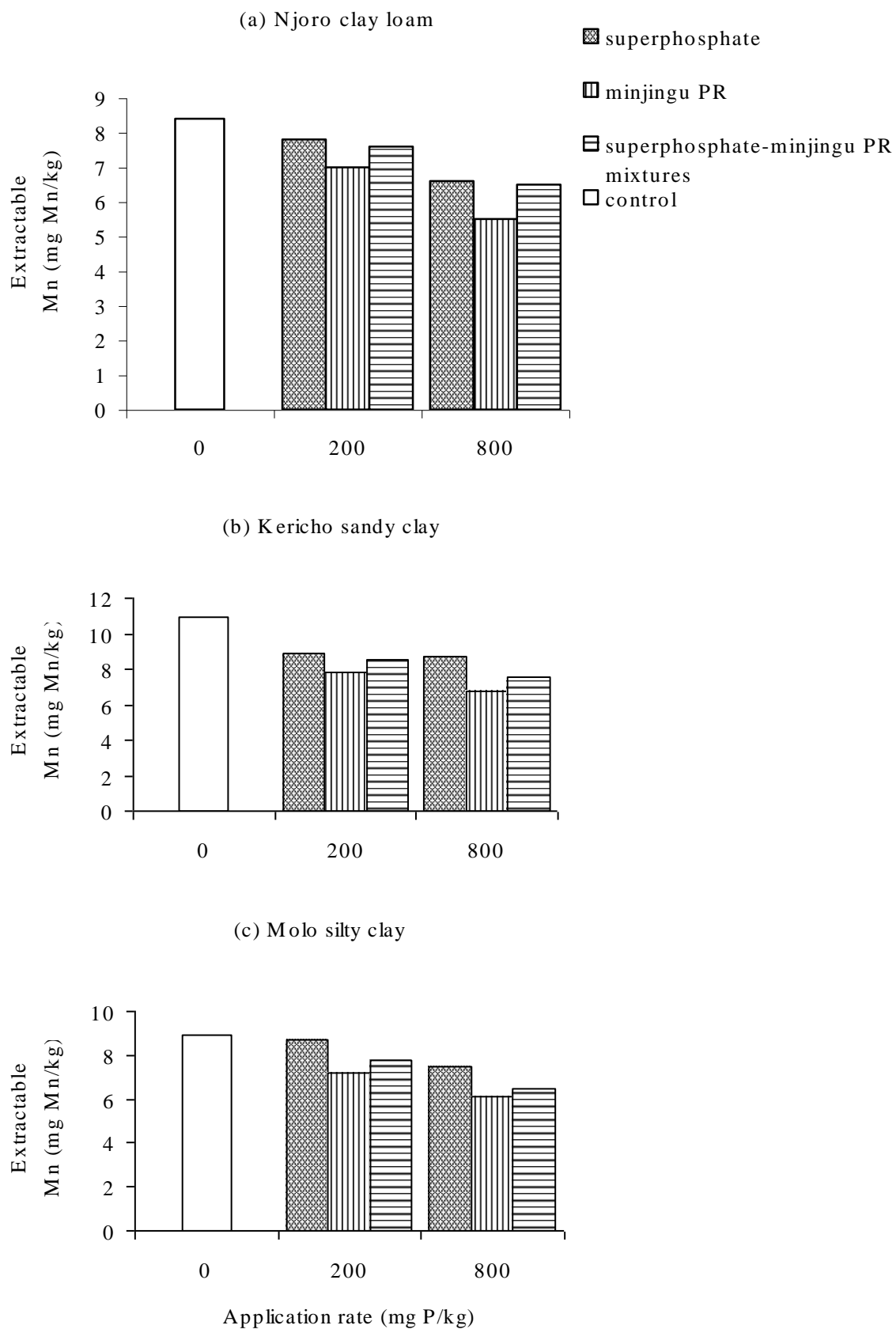


Figure 4.10: The effects of P sources and application rates on extractable Mn: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

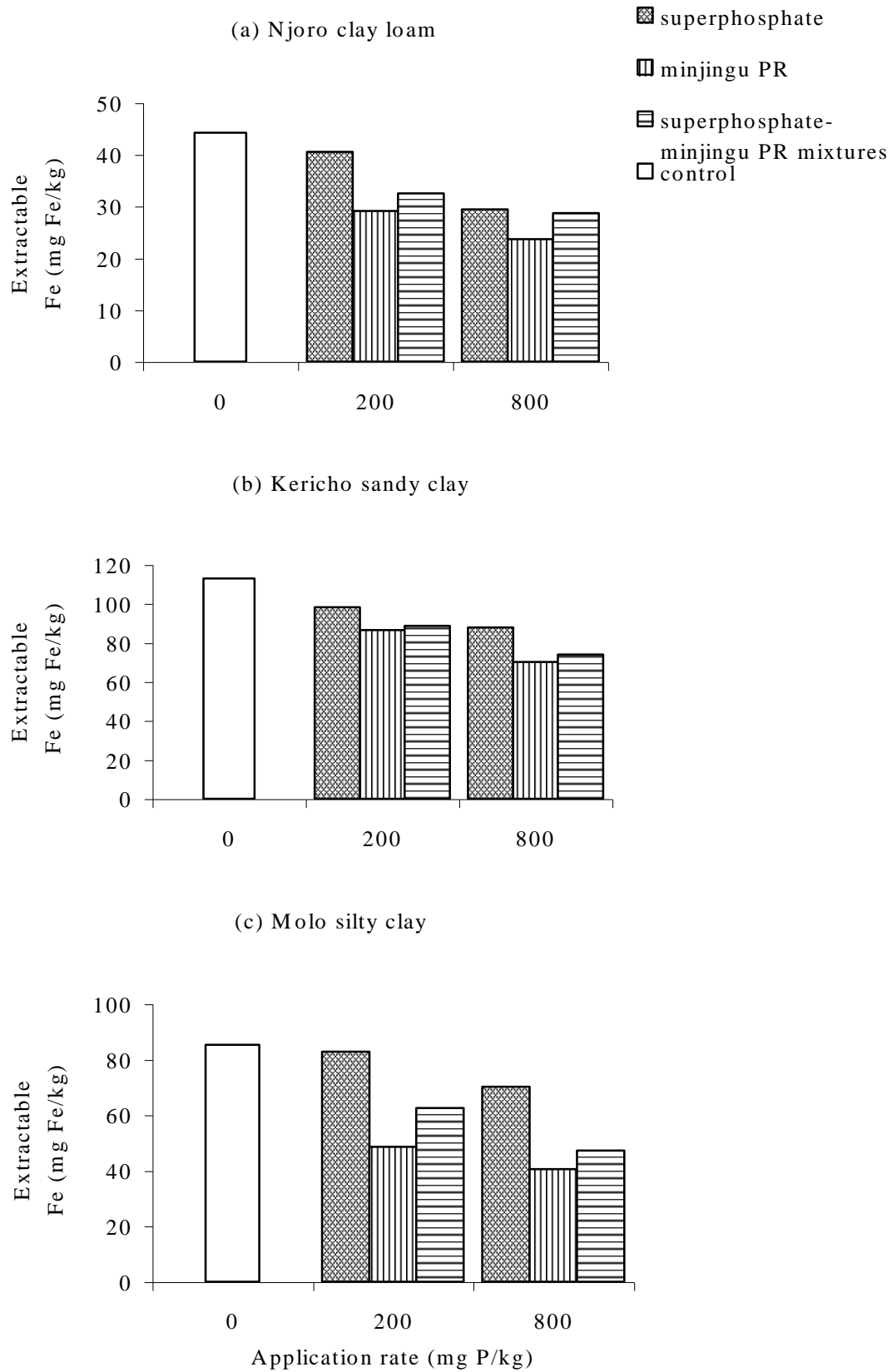


Figure 4.11. The effects of P sources and rates of application on extractable Fe: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

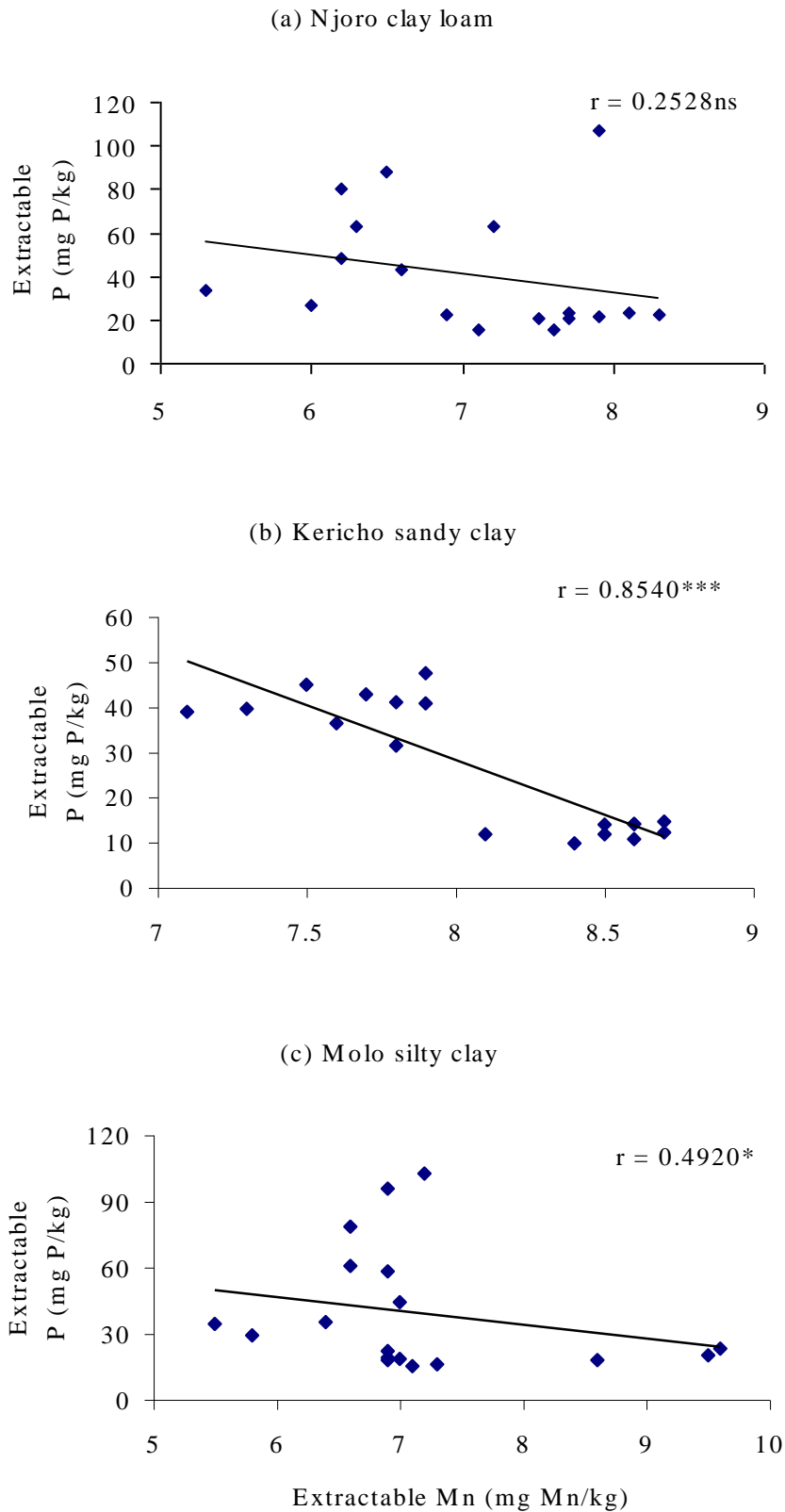


Figure 4.12. Relationship between extractable Mn and P extractability: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

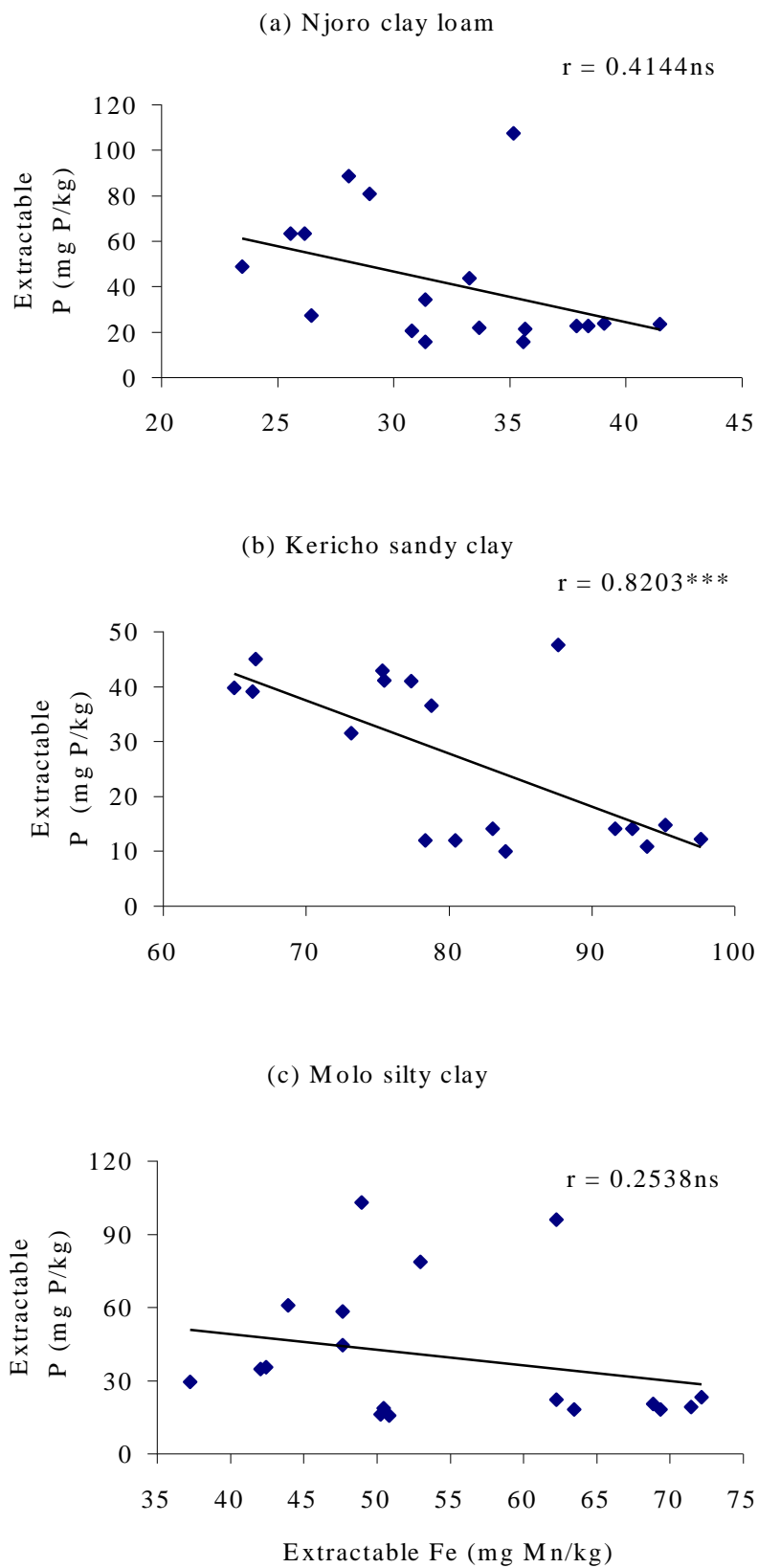


Figure 4.13. Relationship between extractable Fe and P extractability: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

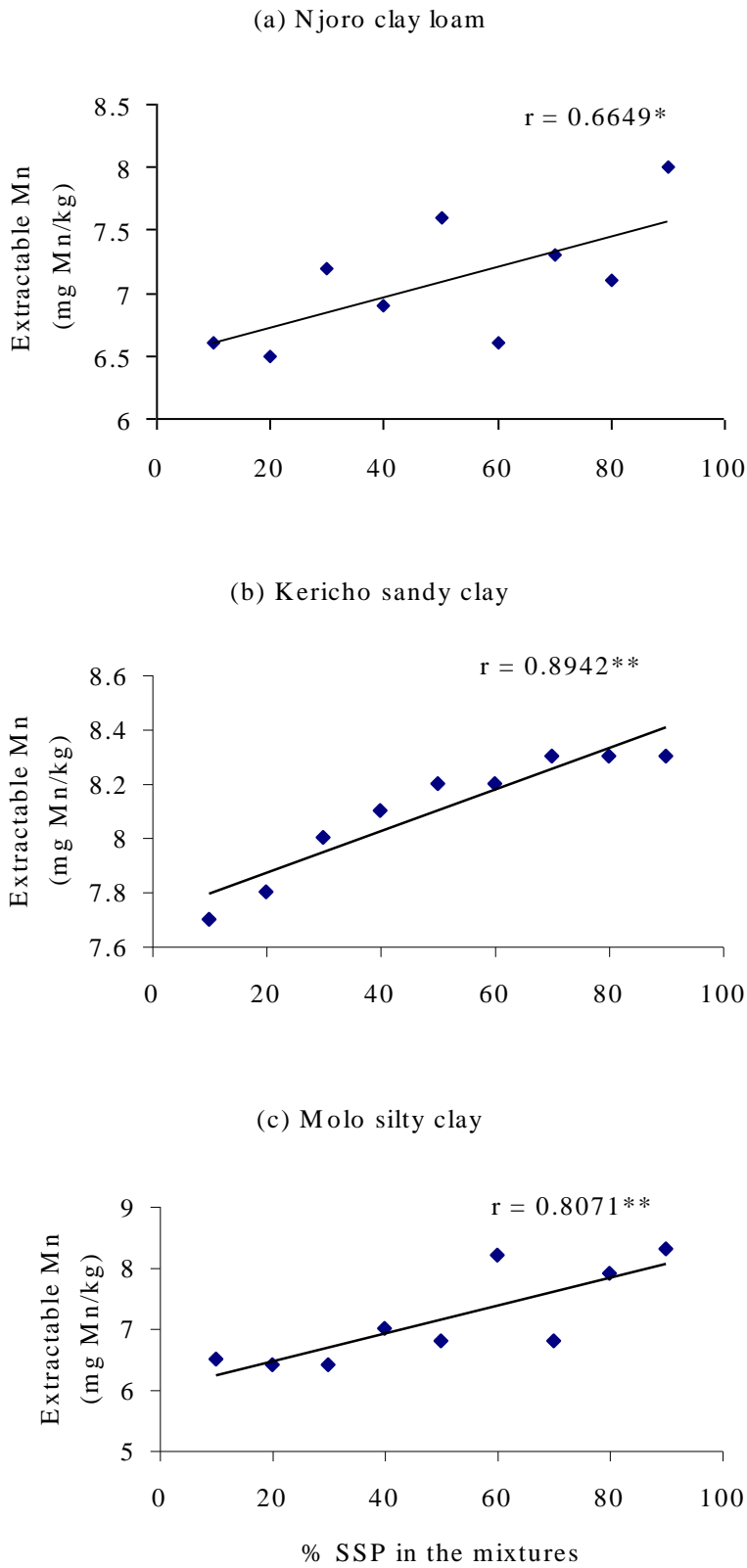


Figure 4.14: Relationship between extractable Mn and percentage superphosphate (SSP) in the mixtures of superphosphate and Minjingu PR fertilisers: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

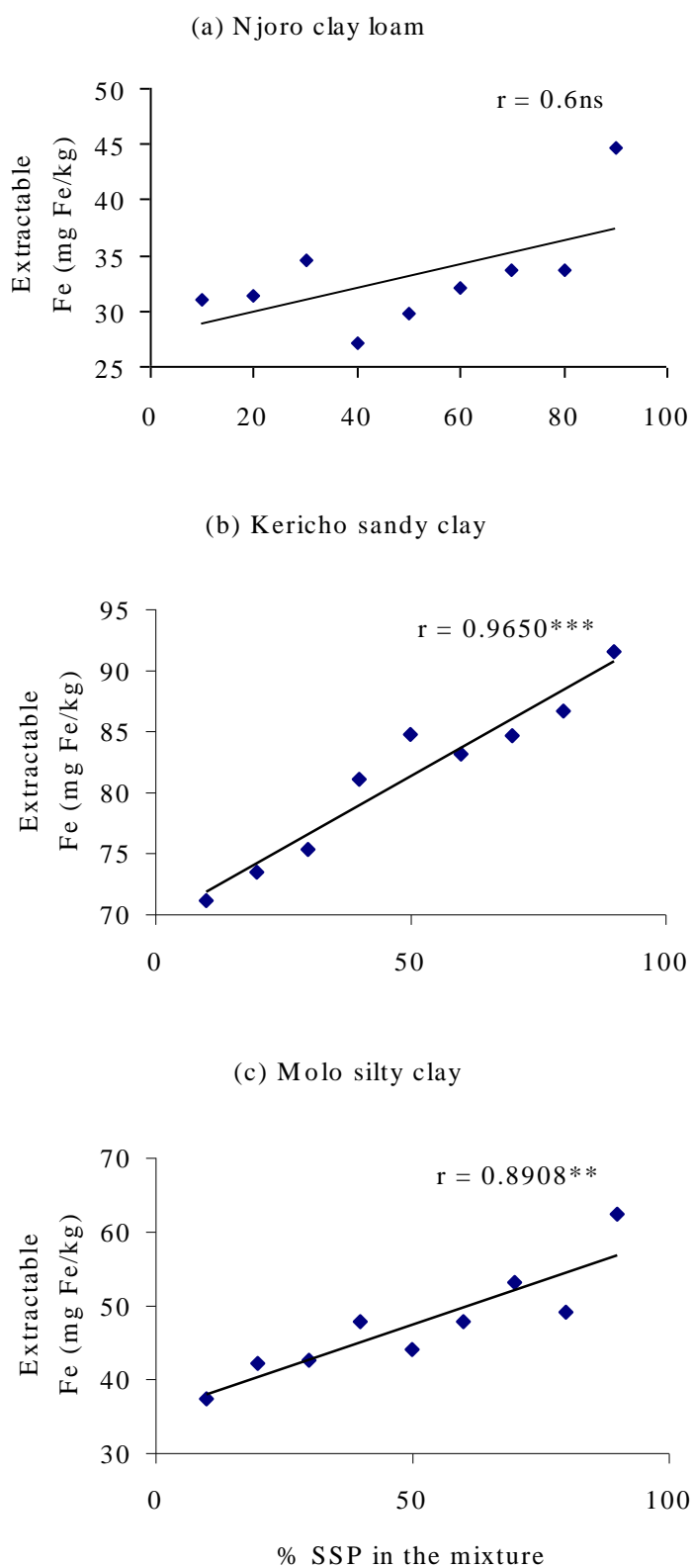


Figure 4.15. Relationship between extractable Fe and percentage superphosphate (SSP) in mixtures of superphosphate and Minjingu PR fertilisers: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

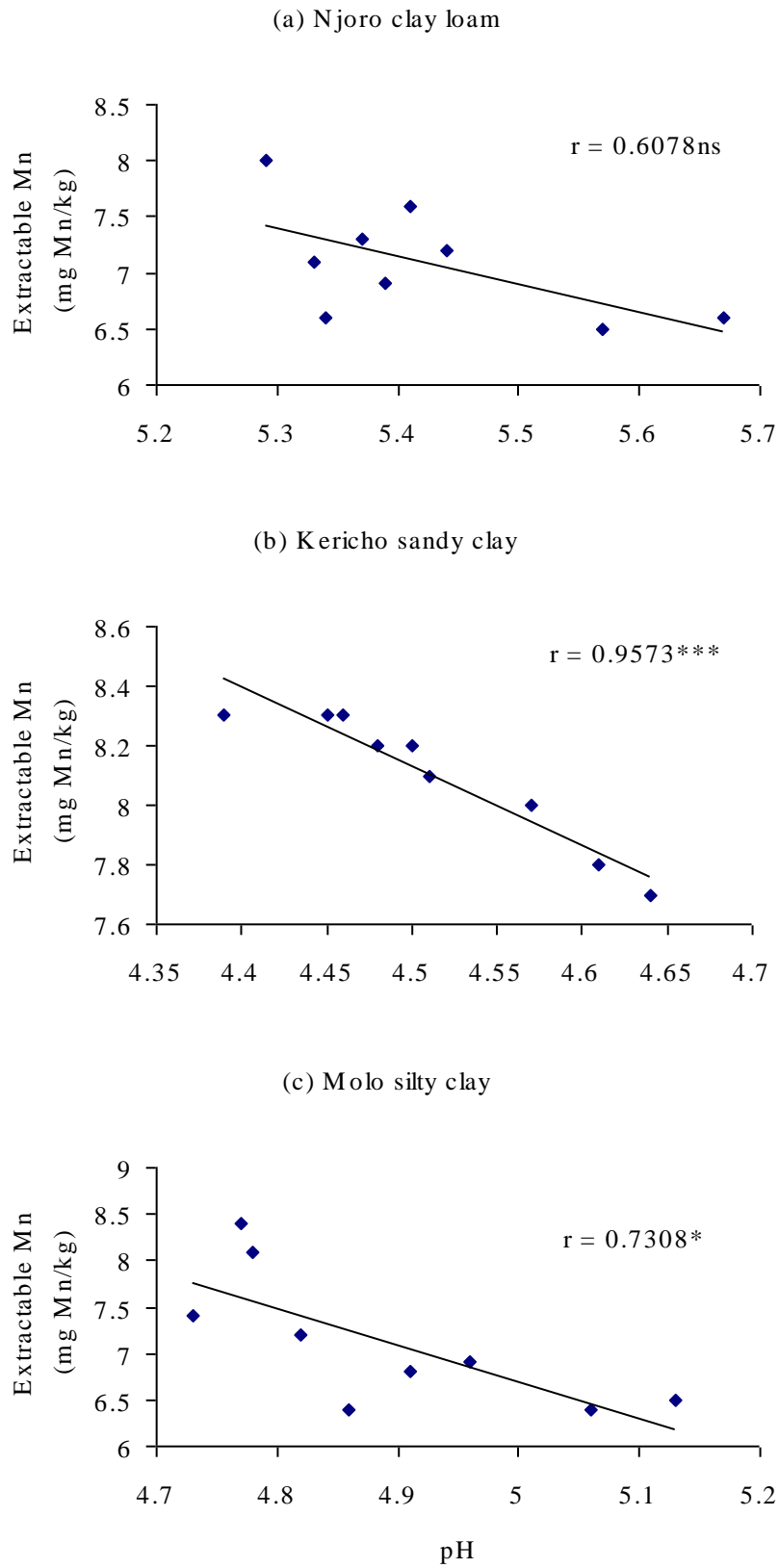


Figure 4.16: Relationship between pH and extractable Mn: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

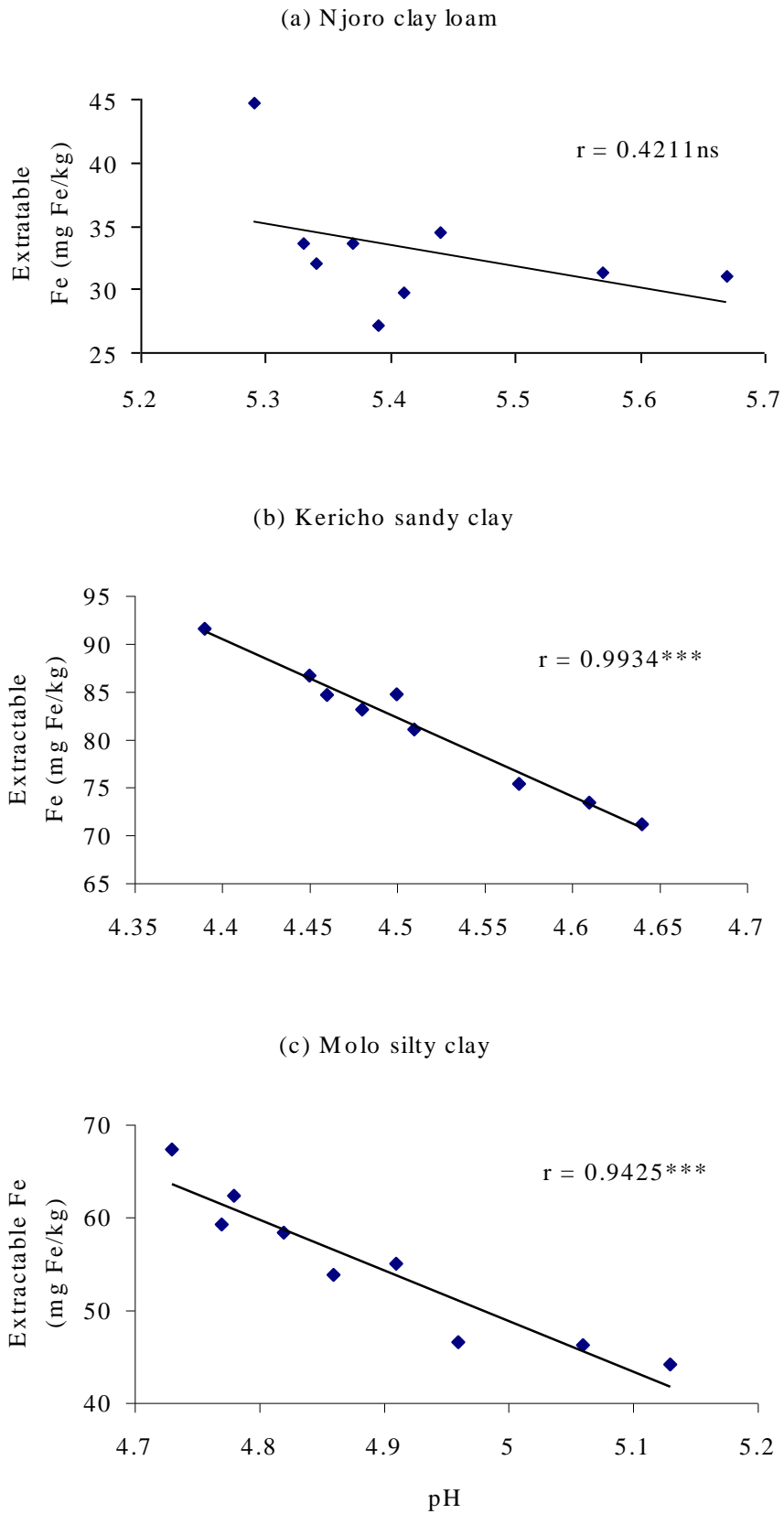


Figure 4.17: Relationship between pH and extractable Fe: (a) Njoro clay loam, (b) Kericho sandy clay and (c) Molo silty clay

the mixtures but also the Mn and Fe minerals in soil. Indeed, the extractable Mn and Fe levels tended to increase with increasing percentage of superphosphate component in the mixture and decreasing pH in all the soils. The low correlation coefficients between percentage of superphosphate and extractable Mn and Fe in the PR-superphosphate fertiliser mixtures in Njoro clay loam is probably due to the low levels of Mn and Fe in this soil.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The increases in pH, and extractable Ca and P concentrations observed in all the soils following application of Minjingu PR indicated that dissolution of the PR fertiliser had occurred. The extent of dissolution was greatest in the Kericho sandy clay followed by the Molo silty clay, and the lowest dissolution was observed in the Njoro clay loam. This was attributed to the differences in the chemical properties of the soils.

The extent of dissolution of Minjingu PR also increased with the rate of application due to the greater amounts of fertiliser input per unit weight of soil at the higher rate of application than at the lower rate. Dissolution of the fertiliser also increased with the period of fertiliser reaction with the soils, and this was attributed to the slow and continuing dissolution reaction of PRs in soils over time.

Results also showed that dissolution of Minjingu PR in the mixtures of superphosphate and the PR was significantly enhanced in all the soils. Soil pH values significantly decreased, and extractable Ca and P concentrations of all the soils significantly increased with increasing proportion of superphosphate in the mixtures. This finding indicated that the acidic environment generated by the hydrolysis reaction of monocalcium phosphate component in superphosphate was responsible for increased solubility of Minjingu PR in the mixtures. Dissolution also increased with the rate of application.

The extractable Mn and Fe concentrations also increased, and soil pH values concomitantly decreased with increasing proportion of superphosphate in the mixtures in all the soils. This further showed that the hydrolysis reaction of monocalcium phosphate not only dissolved the PR material but also dissolved the Mn and Fe minerals in the soils.

The extractable P results for all the added P treatments for all the soils indicated that superphosphate was a better fertiliser at both rates of application than either Minjingu PR alone or mixtures of superphosphate and Minjingu PR. However, combinations of Minjingu PR and superphosphate improved the fertiliser quality (P release) of Minjingu PR in the mixtures over that of PR alone. The extractable P values for the mixtures in all the soils increased with increasing proportion of superphosphate in the mixtures and this may be attributed to increased solubility of Minjingu PR fertiliser by the hydrolysis of monocalcium phosphate in superphosphate. However, it was not clear from this study whether the increased

extractable P values with increasing proportion of superphosphate in the mixtures were due to increased amounts of superphosphate or increased solubility of Minjingu PR. Further studies using P ³² isotope as a tracer and/or dilution of phosphoric acid with water need to be carried out in order to monitor P release and extent of dissolution of Minjingu PR in the mixtures of superphosphate and Minjingu PR by phosphoric acid.

The extractable P results also differed among the soils. The values were lowest for the Kericho sandy clay followed by the Molo silty clay and the highest values were observed in the Njoro clay loam. This was attributed to the differences in P adsorption capacities of the soils. Soils with high P adsorption capacities such as the Kericho sandy clay and the Molo silty clay are known to maintain low P values compared with soils of low P adsorption capacities (e.g. the Njoro clay loam).

Negative correlation coefficients, though not always significant, were obtained between extractable P, and Mn and Fe concentrations in all the soils. This was more evident in the Kericho sandy clay than in Molo silty clay and Njoro clay loam soils. This finding suggested that the dissolved Mn and Fe minerals by the phosphoric acid may precipitate P in soil solution as insoluble Mn and Fe phosphates thereby reducing P availability in soil.

5.2 Recommendations

- i. Further studies using P ³² isotope as a tracer and/or dilution of phosphoric acid with water need to be carried out in order to monitor P release and extent of dissolution of Minjingu PR in the mixtures of superphosphate and Minjingu PR by phosphoric acid.
- ii. Further studies need to be undertaken to compare the effectiveness of superphosphate-Minjingu PR mixtures, Minjingu PR and superphosphate under field situations.

CHAPTER SIX

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