

DISSOLUTION AND EXTRACTABILITY OF MINJINGU
PHOSPHATE ROCK FERTILIZER IN SOME ACID SOILS OF RIFT
VALLEY PROVINCE AS RELATED TO SOIL
CHEMICAL PROPERTIES.

BY

KOWENJE C.B.O.

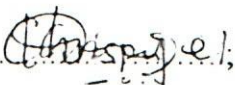
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This thesis is my original work and has not been presented for a degree award in any other University.

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This thesis has been submitted with my approval as the University supervisor.

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DEDICATION

To
My wife, Carren,
Our children, Edna and Robert,
and
to
My parents
Sabastian and the late Benta (1949-1981).

Polo ong'e yuora

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Dissolution and extractability of Minjingu phosphate rock fertilizer in some acid soils of Rift Valley province as related to soil chemical properties

by

Kowenje C.B.O.

ABSTRACT

Phosphorus (P) is a critical nutrient needed to improve soil fertility for sustainable crop production in large areas of developing countries. The use of phosphate rocks (PRs) as directly applied fertilizers in tropical acid soils is considered as a potentially cheaper alternative to the more expensive conventional water-soluble P fertilizers. However, the major factor limiting the use of the PR materials is their low solubility in soils. The dissolution of PRs in soils is affected by several factors including soil chemical properties.

The dissolution and extractability of Minjingu PR (MPR) fertilizer from Tanzania in relation to some selected soil chemical properties were investigated in a laboratory incubation experiment. Six acid soils from Rift Valley Province of Kenya were used. Four soils (two Nitisols and two Ferralsols) were moderately acidic (pH 5.1-5.5) and had P adsorption capacities ranging from 1220-2487 mgP/Kg soil, while the other two soils (an Andosol and a Phaeozem) were slightly acidic (pH 6.3-6.8) and had P adsorption capacities of 836-904 mgP/Kg soil.

The treatments consisted of two P sources (MPR fertilizer, and a water-soluble P fertilizer, Single Superphosphate (SSP)) and three rates of P addition (0 mgP/Kg soil, 200 mgP/Kg soil, and 500 mgP/Kg soil). The SSP fertilizer was included to compare the effectiveness of MPR as a fertilizer in maintaining plant-available P. The fertilizers were mixed separately with each soil at the different rates of P addition, and the soil treatments were brought to field capacity with distilled water. The amounts of MPR fertilizer that had dissolved were determined by measuring increases in 1 M BaCl₂-triethanolamine (TEA) extractable Ca (Δ Ca) in

soils amended with MPR fertilizer compared to the control (Zero-P) treatments at various periods of reaction up to 60 days. Plant-available P was determined in both the PR-treated and SSP-treated soils by measuring increases in 0.5 M NaHCO_3 - extractable P (Olsen P) over the control treatment after 15,30 and 60 days of reaction time. Simple linear correlation was performed to investigate the relationships between the selected soil chemical properties and the extent of PR dissolution.

The extent of MPR dissolution increased with the rates of application, incubation time and varied among the soils. In the moderately acid soils, 2.8 % of the total added P had dissolved after 4 days, and this increased to a mean value of 29.3 % of the total added P after 60 days. In the slightly acid soils, 2.3 % of the total added P had dissolved after 4 days, and after 60 days, 11.7 % of the total added P had dissolved. The increase in the dissolution of the PR material with time indicated that the dissolution reaction was continuing. The increase in the dissolution with the rate of fertilizer application was attributed to the greater amount of fertilizer input per unit weight of soil at the higher rate of application. The differences between the soils in the amount of MPR dissolved were attributed to their differences in the chemical properties.

Of the initial soil chemical properties selected, exchangeable Ca, (exch. Ca) Olsen P, % C, and P-sorption capacity were significantly related to the extent of PR dissolution time, with the most predictive property being P-sorption capacity. Soil pH and CEC were not significantly correlated to the extent of PR dissolution. No single soil chemical property significantly related to the PR dissolution at the early stages of incubation. Also no single soil chemical property tested was significant in predicting the initial rate of MPR dissolution.

The Olsen P values increased over the control treatment following P addition with the SSP-treated soils showing higher values than the MPR-treated soils. This was attributed to the differences in the solubilities of the P sources. The Olsen P values for the SSP treatments consistently decreased with time due to fixation reactions by soil components. On the other hand, the Olsen P values for the MPR treatments initially increased with time due to dissolution reactions, and then declined

subsequently because dissolution reactions had slowed down, and fixation reaction had become the dominant reaction.

The Olsen P values for both the P sources differed among the soils. The moderately acidic soils indicated relatively lower values compared to the values of the slightly acidic soils. This was attributed to the differences in the P-sorption capacities of the soils. Highly significant negative correlation was obtained in the PR treatments between the % P dissolved and the corresponding Olsen P values. This finding suggested that high PR dissolution does not necessarily produce proportional increases in Plant-available P in acid soils having high P fixation capacities.

Key words: Minjingu, Phosphate rock, dissolution, extractability, chemical properties, incubation, correlation, Kenya, acid soils.

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CHAPTER 1

INTRODUCTION

Phosphorus (P) is an important element limiting crop production in many highly weathered acid soils of temperate and tropical countries (Sanchez and Uehara, 1980). This is because added P fertilizer is strongly fixed by soil components in non-available forms for plant use. Consequently, P fertilizers are frequently added so as to correct P deficiency problems and hence achieve quality crop yields.

Traditionally, P deficiency has been corrected by addition of highly soluble P fertilizers (e.g. single superphosphate, SSP). However, the high cost of these conventional water-soluble P fertilizers constrains their use by resource-poor farmers who are largely engaged in non-intensive subsistence agriculture. Direct application of finely ground phosphate rock (PR) may be an economically attractive alternative to the more expensive water-soluble P fertilizers in acid soils (Sanchez, 1976; Khasawneh and Doll, 1978; Hammond *et al.*, 1986).

Despite intensive studies over the years, the use of PR as a low cost alternative P fertilizer has not attracted much attention in many developing countries (e.g. Kenya). One major problem limiting the use of PR fertilizers in agricultural systems is their low solubility in soils (Khasawneh and Doll, 1978). However, under conditions which favour their dissolution, PRs can be as effective as conventional water-soluble P fertilizers (Khasawneh and Doll, 1978; Hammond *et al.*, 1986). Indeed, experimental reports indicate that PRs are most effective when used on acid soils having typically low pH, low exch.Ca, and low P concentrations (Khasawneh and Doll, 1978, Butegwa *et al.*, 1996).

Kenya highland acid soils have low pH and are P deficient (FURP,1987). In addition, these soils are situated in high agricultural potential areas such as Rift valley, Central and Western provinces. In view of the frequent food shortages in this country, there is an urgent need to improve the fertility of the Kenya highland acid soils using the cheapest available P fertilizers (e.g PRs.).

Previous studies on the effectiveness of PRs as alternative P fertilizers in Kenya have been based on crop yield assessments (KARI,1994). However, crop response experiments may not adequately evaluate PRs as alternative fertilizers since increases in crop yields may not necessarily arise from increased dissolution of a PR material in soil (Hammond *et al.*, 1986; Chepkwony, 1991; Chien and Menon, 1995). In order to evaluate exhaustively the potential of a PR material as an alternative source of supplying P to P-deficient soils, dissolution studies need also to be carried out.

Several factors including soil chemical properties influence the dissolution of PR fertilizers in soils (Le Mare, 1991; Chien and Menon, 1995). Information on the dissolution of PR materials on Kenya highland acid soils as affected by soil properties is, however, not available. Such information is essential in view of the growing interest in the utilization of PRs as alternative P source in a number of other developing countries.

The main aim of this study was to establish the relationship between some pertinent soil chemical properties and the rate and extent of dissolution of a reactive PR fertilizer from Tanzania (Minjingu, MPR) in some selected acid soils of Rift Valley Province. The findings of the study may provide important information in identifying soils where PR can best be used as alternative P sources.

The specific objectives of this study were to:

- (a) Investigate the effects of rates of application and period of reaction on the extent of dissolution of MPR fertilizer in acid soils.
- (b) Investigate the effects of P-sources, rates of application and period of reaction on extractable P concentrations.
- (c) Investigate the relationship between the rate and extent of MPR dissolution and some soil chemical properties.
- (d) Investigate the relationship between the extent of MPR dissolution and extractable P concentrations.
- (e) Compare relative abilities of acid soils to react with MPR fertilizers.

CHAPTER 2

LITERATURE REVIEW.

2.1 Introduction

Phosphate rock fertilizers are the principal source of conventional P fertilizers. Their use as an alternative source of P for crop production has been extensively studied and the literature is riddled with conflicting results. PR fertilizers have been found to perform better or poorer than the conventional P fertilizers. These conflicting reports may be caused by a variety of factors such as differences in PR properties (e.g. particle size), soil properties (e.g. soil pH), plant species, and environmental factors (e.g. rainfall). The influence of these factors on PR dissolution and availability is reviewed in this chapter.

2.2 Chemical characteristics of phosphate rocks.

Flouroapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) is the main dominant mineral component in many PR materials. Flouroapatites occur mainly in sedimentary rocks in association with a variety of other minerals such as silicates, carbonates, oxides etc. (Khasawneh and Doll, 1978). The chemical components of flouroapatites vary widely due to isomorphous substitution in the apatite crystal lattice. Table 2.1 shows the chemical composition of some apatite PRs

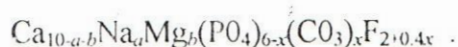
Table 2.1 Location, type, and chemical composition of some phosphate rock materials.

Source	type	Ca	P	F	C	Na	Mg	K	Al	Fe	Si
		%									
N. Carolina	s	34.7	13	3.5	1.5	0.7	0.3	0.1	0.2	0.5	0.7
N. Florida	s	34.7	14	3.7	1.1	0.5	0.2	0.2	0.4	0.5	1.3
I. Kotra	m	38.7	18	3.6	0.2	0.8	0.1	0.1	0.2	0.3	0.6
Missourri	I	36.1	15	3.4	0.8	0.2	0.4	0.1	0.2	1.8	1.3
Gafsa *	s	35.2	13	3.1	1.4	0.7	0.3				
P.Niger*	s	35.0	15	2.9	0.3	0.1	1.1				

Key: s - sedimentary, I - Igneous, m - Metamorphic.

source. Khasawneh and Doll (1978), * Sanyal and De Datta (1991) and Sauchelli (1965).

The generalised formula of substituted Carbonate Fluoroapatite can be written as;



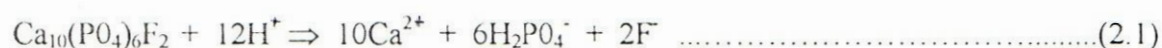
where a and b are functions of x , the extent of carbonate substitution (Khasawneh and Doll, 1978; Sanyal and De Datta, 1991).

As a result of this varying chemical composition of the apatites, PR materials undergo a wide range of differing chemical behaviour in soils which determine their effectiveness as direct application fertilizer (Hammond *et al*, 1986; Chien and Menon, 1995).

2.3 Measurement of PR dissolution in soil.

The rate and extent of PR dissolution in soil are two important factors that determine its suitability as an alternative P fertilizer for direct application.

Unlike water-soluble fertilizers which dissolve rapidly upon contact with the soil, the dissolution of a PR material takes place slowly and usually continues for a long time. The congruent dissolution reaction of PR with soil is shown in equation 2.1 using fluorapatite (Khasawneh and Doll, 1978);



It can be noted that the dissolution process involves consumption of protons (H^+), and the release of Ca^{2+} , H_2PO_4^- , and F^- ions from the apatite surface. The H^+ ions are furnished principally by the hydrolysis reactions of Al^{3+} in soil (equation 2.2) (Tisdale *et al.*, 1985).



It can also be noted that the driving force controlling the rate and extent of PR dissolution in soils involves the supply of H^+ ions and the removal of Ca^{2+} , H_2PO_4^- , and F^- ions from the site of dissolution.

Measurement of the extent of dissolution of PR in soil is beset with difficulties. The dissolution is frequently measured indirectly using chemical extraction solutions. These

solutions dissolve and remove specific forms of soil P from the solid phase through solubilization, complexation, or hydrolysis reactions. Several extraction methods have been used that measure increases in the concentrations of Ca or P (Khasawneh and Doll, 1978; Hammond *et al.*, 1986)

The Inorganic P-fractionation procedure of Chang and Jackson estimates dissolved P from PR material by measuring the increases in Fe-P and Al-P fractions in a soil treated with PR over non-PR treatment. Increases in Ca-P are considered to be associated with unreacted PR. Extraction with a reagent containing dilute hydrochloric acid and ammonium fluoride (Bray-1 extractant) measures mainly increases in Al-P compounds. Mehlich 1 extraction method (0.05 N HCl + 0.025 N H₂SO₄), mainly removes Al-P fraction but also some Ca-P fractions. The Olsen P method involves extraction of soil P with an alkaline extractant (0.5 M NaHCO₃). This method hydrolyses Al-P and Fe-P that have formed, but reacts very little with unreacted PR.

Measurement of changes in soil extractable Ca also attempts to measure a reaction product of PR dissolution. Extraction of Ca with BaCl₂-triethanolamine (2.0 M BaCl₂-TEA) at pH 8.1 is then considered to give a suitable estimate of dissolved PR under laboratory conditions where net immobilization / mineralization transformation of P is minimal. However the method tends to underestimate PR dissolution under field conditions since dissolved Ca and P would be lost through leaching and plant uptake. Dissolved Ca may also be extracted with NH₄OAc solution (pH 7.0).

Other methods have been developed that do not use extracting solutions. These are the anion exchange resin (Sibbesen, 1978) and the Pf paper (Menon *et al.*, 1989) method. Extraction with anion exchange resins simulates conditions similar to those occurring in soil solution from which plant roots absorb P. This method does not suffer from the problems

associated with other extraction methods. The amount of P extracted depends on the chemical form of the resin. Also the method is too slow for routine soil analysis. Saggar *et al.* (1990) modified the traditional resin bag method to a simpler method which uses cation and anion exchange resin strips instead of bags. The modified method does not involve the elution step. The Pi paper method uses an iron hydroxide-impregnated paper strip as a sink for P during extraction. Both methods are considered to be suitable for accurately measuring the plant-available P irrespective of the P sources and can therefore be used for the measurements of plant-available P in the PR treated soils (Menon *et al.*, 1989; Butegwa *et al.*, 1996).

A new technique which uses dialysis membrane tubes (Freese *et al.*, 1995) has recently been developed. The tubes are filled with hydrous ferric oxide (ferrihydrite) acting as an 'infinite' P sink. This system is more mechanically stable than Pi method.

Two assumptions are made when using the above extraction methods. First, the extractants should not promote any dissolution of PR material during extraction. Secondly, the extractants should extract most of the P and Ca released during the dissolution. Nonetheless most of these methods have limitations (Khasawneh and Doll, 1978; Hammond *et al.*, 1986; Butegwa *et al.*, 1996). In an evaluation study of some of these methods, Bolan and Hedley (1989) showed that most extractions tend to remove undissolved PR during the extraction procedure. Both 0.5 M NaOH and 0.5 M BaCl₂-TEA were found to be better extractants of PR dissolution products than were 0.5 M NaHCO₃ and 1 M NH₄OAc particularly when the soil P formation is negligible.

2.4 Factors affecting PR dissolution in soil.

As stated in chapter 1, the major factor limiting the use of PRs as alternative P fertilizers is their low solubility in soil. The factors regulating the dissolution of PR materials in soils are discussed below.

2.4.1 Phosphate rock properties

2.4.1.1 Chemical reactivity.

As mentioned in section 2.2, PR materials vary widely in their mineralogical and chemical compositions. Consequently, their dissolution behaviours in soils vary.

Dissolution of a PR material is greatly affected by the degree of CO_3^{2-} substitution for PO_4^{3-} in the apatite structure (Figure 2.1). The solubility (reactivity) of a PR material increases as the degree of CO_3^{2-} substitution in the apatite structure increases (Chien and Menon, 1995). Substitution of CO_3^{2-} for PO_4^{3-} profoundly influences the crystal structure, and physical and chemical stabilities of the apatites (Khasawneh and Doll, 1978). This is because the crystal sizes of the particles decrease as the degree of CO_3^{2-} substitution increases and this tends to increase solubility (Khasawneh and Doll, 1978). Several workers (Anderson *et al.*, 1985; Leon *et al.*, 1986; Chepkwony, 1991; Watkinson, 1994; Chien and Menon, 1995) have observed that PRs with higher CO_3^{2-} substitution tend to perform better than PRs with lower CO_3^{2-} substitution. This is illustrated in the figure 2.1 below.

Conventionally, the probable extent of PR dissolution and its suitability as a P fertilizer are predicted on the basis of solubility tests in chemical extractants (Khasawneh and Doll, 1978).

1978). There are three commonly used chemical extractants for measuring the solubility of PRs. These are neutral ammonium citrate, 2% citric acid, and 2% formic acid.

The 2% citric acid and 2% formic acids are beset with problems. The presence of impurities (e.g. CaCO_3 , Fe and Al oxides) affect PR solubility in these extractants and hence the classification of reactive and unreactive PRs becomes uncertain. For example, calcite (CaCO_3), dolomite ($\text{MgCO}_3, \text{CaCO}_3$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) depress the dissolution of apatites in neutral ammonium citrate due to the partial consumption of protons by accessory minerals. Because of these problems, some workers have suggested that the first extract should be discarded and the second should be used (Khasawneh and Doll, 1978, Hammond *et al.*, 1986).

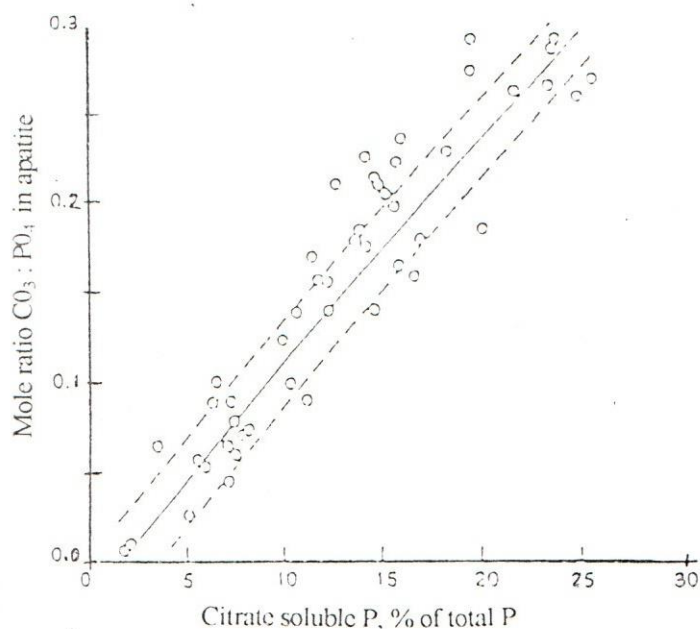


Figure 2.1; Relationship between citrate solubility of apatite and its composition as indicated by mole ratio of $\text{CO}_3:\text{P}_{04}$. (Reproduced from Chien and Menon, 1995).

Mackay *et al.* (1984), in a greenhouse study, compared the relative abilities of seven methods to predict the agronomic effectiveness of five PRs. Of the conventional single-extraction procedures evaluated, 2 % formic acid appeared to be the most useful. The others i.e. 2 % citric acid, neutral ammonium citrate, alkaline ammonium citrate at first extractions, were

poor indicators of P availability. Nevertheless, the solubility tests are arbitrary and cannot be reliably used to predict residual agronomic effectiveness of PR materials. They are only useful in ranking PRs in order of their solubility in the laboratory. The behaviour of PR materials in the real situation must, however, be studied in soil (Le mare, 1991; Chien and Menon, 1995).

2.4.1.2 Particle Size

Grinding PRs favour their dissolution in soils by increasing the surface area of contact between the soil solution and the PRs (Bolan *et al.*, 1990). Kanabo and Gilkes (1988b) reported that grinding of PR to 250 μ m increased the rate of PR dissolution. Grinding below 250 μ m did not produce any significant increase in the rate and extent of dissolution. The particle size effect may also interact with the rate of application. The influence of fine grinding may diminish as the rate of application increases and as the distribution of particles in soil is increased (Khasawneh and Doll., 1978).

Experiments conducted using finely ground PRs suggest that no additional benefit can be derived by grinding PRs below 150 μ m (Sanyal and Datta., 1991; Hammond *et al.*, 1986). Grinding PRs to very fine particles makes them dusty and very difficult to apply. Thus attempts have been made to granulate PRs, but this also decreases the dissolution and increases the cost of production (Khasawneh and Doll., 1978; Van der Berge, 1996).

2.4.2. Soil properties

2.4.2.1 Soil pH

Several workers have shown that PRs dissolve more effectively in acidic soils than in alkaline soils (Hanafi *et al.*, 1992; Sanyal *et al.*, 1991; Le mare, 1991). PR dissolution increases as the soil pH decreases (Figure 2.2). This is because excess H^+ ions in acidic soils shift the dissolution reaction shown in equation (2.1) to the right in accordance with Le Chatelier's principle.

The agronomic effectiveness of phosphate rocks would therefore be expected to be greater in acid soils than in alkaline soils. This generalisation is, however, not always applicable since plant response to increased P availability may be limited by factors due to soil acidity (e.g. Al and Mn-toxicities). Al toxicity is known to be a major factor limiting plant growth in many highly weathered acid soils (Haynes, 1984).

Chepkwony (1991), in a glasshouse experiment, studied the response of wheat to the application of two reactive PR fertilizers using one New Zealand acid soil. The plant response was small. He attributed this to factors arising from soil acidity other than P deficiency. Kanabo and Gilkes (1987b), also in a glasshouse experiment showed that dissolution of a PR fertilizer is highly favoured at low pH, but there was virtually no plant response to PR fertilizer application.

2.4.2.2 P and Ca Status.

Dissolution of PR material is higher in soils with low Ca and P concentrations than in soils with high Ca and P concentrations (Khasawneh and Doll, 1978). Soils having low Ca and

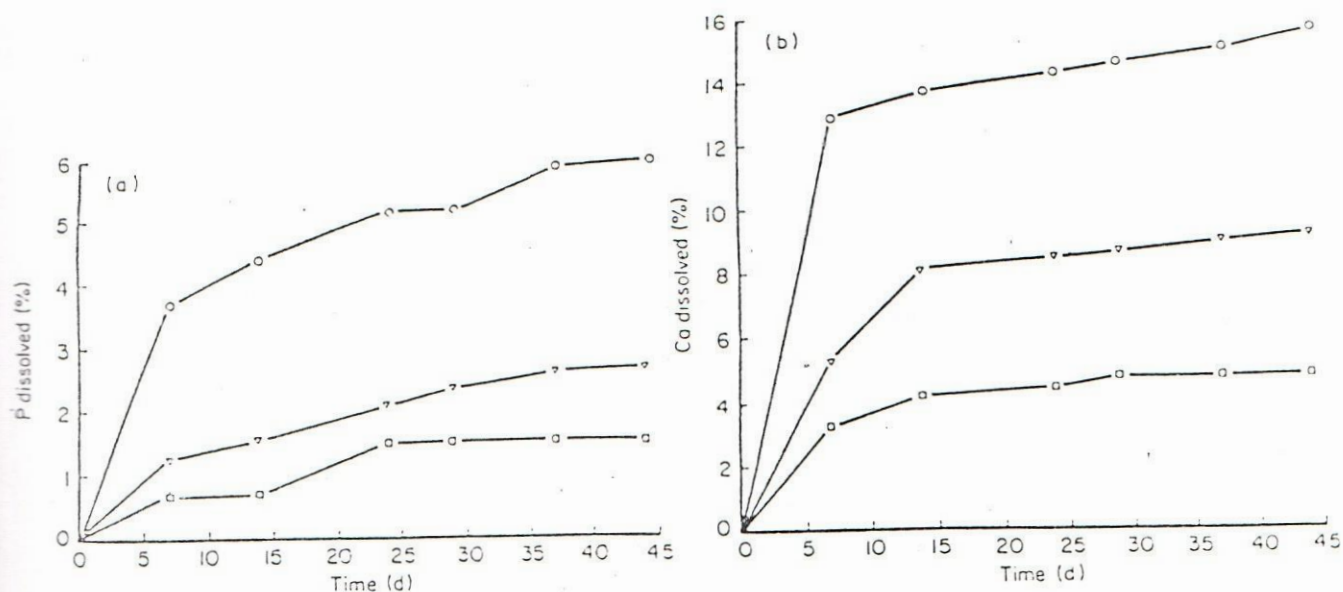


Figure 2.2. Influence of pH on dissolution of Gafsa PR in water with time; unbuffered pH (●), pH buffered at 5.2 (▼), pH buffered at 4.5 (○); (a) P dissolved and (b) Ca dissolved. (adapted from Robinson and Syers, 1990).

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	1.5
5.2	0	0	2.7
4.5	0	0	6.0
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

Dissolution of PR material is higher in soils with low Ca and P concentrations than in soils with high Ca and P concentrations (Khasawneh and Doll, 1978). Soils having low Ca and P concentrations are characteristically the highly weathered infertile soils of humid tropics with high P adsorption capacities and low cation exchange capacities (CEC.) (Mahimariraja *et al*, 1995; Chien and Menon, 1995).

The dissolution of PR materials has been found to increase as the P adsorption capacity (P retention) of soil increases (Chien *et al.*, 1980, Hedges and Gilkes., 1986, Mackay *et al.*, 1986). This is due to the removal of dissolved P from soil solution by soil and soil materials through adsorption processes. Samid-Sparif (1992) reported that P retention is more correlated to PR dissolution than pH and soil exchangeable Ca. Increased dissolution may not, however, lead to increased availability of P to plants since dissolved P may be subsequently adsorbed and made unavailable for plant use.

Morel and Fardeau (1990) found that the amount of P absorbed by plant was high in soils with low plant-available P, and low for soils with high plant-available P, indicating that an input of P fertilizers can induce a decrease in the utilisation of available soil P. Kanabo and Gilkes (1987b) varied the adsorption capacity of an Australian soil by adding goethite, a strongly P-adsorbing material. Dissolution of a PR material increased significantly with increasing goethite content in soil, but the amount of plant-available P decreased significantly. Glasshouse studies indicated reduction in both yield and P content of the test plant by 19 and 34 % respectively.

Harris *et al* (1984), and watkinson (1994) also reported that high P retention has negative influence on PR availability. De Datta *et al.* (1992) observed that high P retention only aids in the initial dissolution reaction of a PR material but has a negative effect on availability of

dissolved P to plants. These findings suggest that PR materials may be effective in soils of moderate to high P status.

Mackay and Syers (1986) reported a four-fold decrease in the extent of dissolution of PR as soil Ca concentration is increased. Mackay *et al.* (1986) studied the relationship between Ca saturation percentage of cation exchange sites and PR dissolution. Results indicated that the Ca saturation percentage had a larger effect on the extent of dissolution of PR materials than either pH or P sorption capacity. De Datta *et al.* (1992) also stated that the percentage dissolution of PRs depends more on exch.Ca than P retention and pH. Robinson and Syers (1990) 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).

2.4.2.3 Soil organic matter status.

Soil organic matter is the most active component of soil. It consists of living organisms, and their undecomposed, partially decomposed and completely decomposed remains. Humus is that dark-coloured fraction of soil organic matter containing decaying and partially resynthesized plant and animal residues. It has been observed (Hammond *et al.*, 1986; Chien and Menon, 1995) that high organic matter in soils increase the dissolution of PRs. Chien and menon (1995) reported differences in the effectiveness of a PR material on two soils having approximately the same pH, exch.Ca , and P sorption capacity. The performance was found to be greater in the soil with higher organic matter content (4.2 % C) than in soil with lower organic matter (1.8 % C). Soil organic matter acts as a sink for Ca by chelating the dissolved Ca thereby enhancing PR dissolution (Hammond *et al.*, 1986; Chien and Menon, 1995). This mechanism also may explain

partly the beneficial effect of added compost and farmyard manures on P released from PR materials (Figure 2.3). In addition, organic acids produced during decomposting of manure supply protons and hence enhance dissolution of PR materials. Increases in PR dissolution have been reported (Ikerra *et al.*, 1994; Mahimairaja *et al.*, 1995) in mixtures of PR and organic manures.

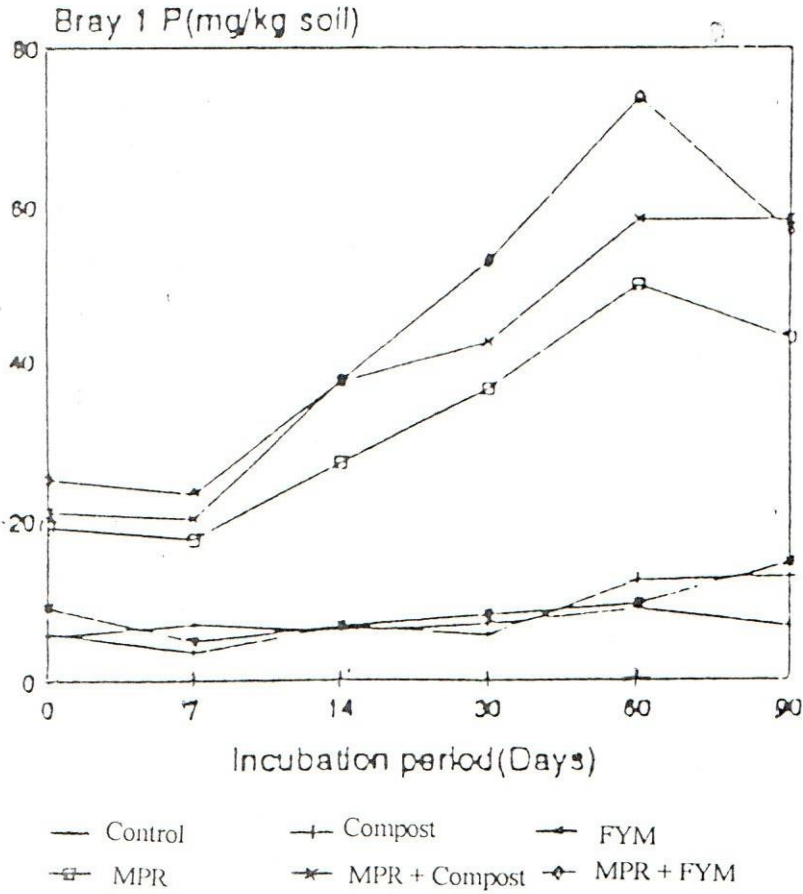


Figure 2.3. Changes in Bray 1 P with incubation time with Minjingu PR alone and in combination with compost (Co) or Farmyard Manure (FYM) (Adapted from Ikerra *et al.*, 1994)

2.4.2.4 Soil moisture

Soil moisture is thought to influence PR dissolution. The availability of PR is generally believed to be greater in moist soils than in dry soils. Moist soils are thought to facilitate diffusion of dissolved Ca and P ions away from PR surfaces thereby resulting in enhanced PR dissolution (Kanabo and Gilkes, 1988a). Kanabo and Gilkes (1988a) found that dissolution of PR material increased as the soil water content increased. Differential plant responses to PR applications in field experiments conducted in Australia and New Zealand have been attributed to soil moisture differences (Bolland *et al.*, 1988., Bolan *et al.*, 1990; Gilkes and Bolland, 1990). The effectiveness of PR materials have been found to be greater in areas which are wet for much of the growing season than in those that are dry for much of the growing season.

Chepkwony (1991) subjected one New Zealand acid soil to various drying and wetting cycles before carrying out a glasshouse experiment. Air-drying (for up to 9 weeks) and rewetting cycles did not affect dissolution of two PR materials. This finding conflicts with the widely held view that drying of soil would reduce dissolution of PR materials. This is because drying is thought to inhibit diffusion of dissolved P away from the fertilizer. Glasshouse results by Chepkwony (1991) indicated greater yield and P uptake in soil treatments subjected to air-drying and rewetting cycles than in soil treatments kept continuously moist. He attributed the increased PR availability in air-dried and rewetted treatments to net mineralization of soil organic P (i.e. Birch effect) rather than increased PR dissolution.

2.4.3 Crop properties.

Plant species differ considerably in their responses to PR fertilizers (Khasawneh and Doll, 1978; Chien and Menon, 1995). In general, reactive PRs have been reported to be more effective for legumes than they are for non-legumes (Bolland *et al.*, 1986; Flach *et al.*, 1987). Differential responses among plants to PR may be caused by a variety of factors including differences in Ca and P requirements and life span (Table 2.3). Plants with high P and Ca requirements would be expected to provide better sinks for P and Ca, and hence promote PR dissolution.

In addition, plants such as legumes that can acidify their rhizosphere as a result of excess absorption of cations over anions would also promote PR dissolution (Bekele *et al.*, 1983).

Table 2.3. Responses of three crop species to variations in P sources and in type of N fertilizer used in pot experiments (Adapted from Flach *et al.*, 1987).

Nature of P fertilizer used	Crop species	Type of N fertilizer	Dry matter yield, (g pot ⁻¹)	Yield of nutrients, (mg pot ⁻¹)			Final soil pH (H ₂ O)
				P	Ca	N	
Control (no P applied)	Maize	NH ₄	22.7	34	135	642	5.3
	Maize	NO ₃	15.4	20	106	438	6.0
	Pearl millet	NH ₄	40.9	27	281	914	5.2
	Pearl millet	NO ₃	33.0	20	348	1126	6.4
	Finger millet	NH ₄	68.1	57	618	946	5.1
	Finger millet	NO ₃	57.0	48	671	1151	6.4
Zimapan rock phosphate	Maize	NH ₄	30.7	43	153	778	5.3
	Maize	NO ₃	25.1	36	163	679	6.0
	Pearl millet	NH ₄	61.6	61	389	1110	5.0
	Pearl millet	NO ₃	48.8	51	430	1212	6.2
	Finger millet	NH ₄	97.4	85	892	1141	5.0
	Finger millet	NO ₃	68.1	61	712	1285	6.2
Khouribga rock phosphate	Maize	NH ₄	77.3	106	313	980	5.2
	Maize	NO ₃	26.4	38	155	675	6.3
	Pearl millet	NH ₄	72.2	137	371	980	5.3
	Pearl millet	NO ₃	59.3	51	362	1140	6.4
	Finger millet	NH ₄	113.1	179	726	1092	5.3
	Finger millet	NO ₃	89.7	86	926	1159	6.3
Triple superphosphate	Maize	NH ₄	106.3	135	410	1046	5.1
	Maize	NO ₃	107.2	103	407	1071	6.1
	Pearl millet	NH ₄	78.1	242	419	987	5.2
	Pearl millet	NO ₃	85.5	220	475	1125	6.2
	Finger millet	NH ₄	114.3	256	852	1024	5.1
	Finger millet	NO ₃	119.9	256	954	1235	6.0

2.4.4 Management practices.

The performance of PR fertilizers is influenced by management practices. The most important factors are methods of placement, time of application, and the liming of acid soils.

2.4.4.1 Methods of placement.

Studies indicate that optimum response to PR application is generally obtained when the PR is broadcasted and incorporated in the soil (Hammond *et al.*, 1986; Chien and Menon, 1995). Chien and Menon (1995) reported that the effectiveness of North Carolina PR relative to Triple Superphosphate (TSP) was greatly influenced by the method of placement (Figure 2.4). The PR, when broadcasted and incorporated, was found to be as good as TSP in increasing the rice yield, whereas it was less effective than TSP when deep placed. Banding of PR has also been found to be less effective than incorporating the PR material in increasing the rice yield (Hammond *et al.*, 1986; Chien and Menon, 1995).

Broadcasting and incorporation of PR into the soil maximises the surface contact of PR particles with the soil and minimises the interaction between PR particles (Chien and Menon, 1995).

2.4.4.2 Liming effects.

Liming of soils is a common agricultural practice to raise soil pH and decrease Al and Mn toxicities for optimal plant growth. However, the high pH values and the increased exch.Ca

concentrations resulting from liming are detrimental to PR dissolution (Chien and Menon, 1995). PR fertilizers should, therefore, be added to the soil several months before liming an acid soil in order to promote dissolution (Chien and Menon, 1995).

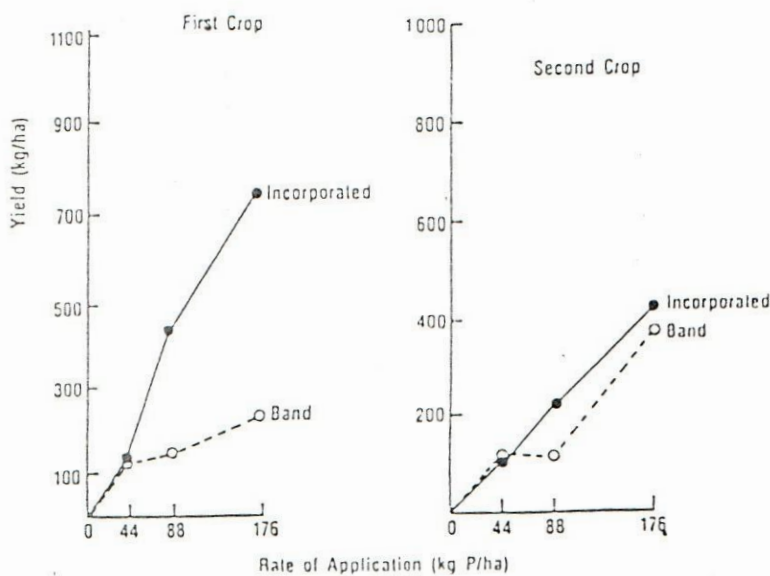


Figure 2.4; Response of beans to Huila PR in Popayan, Colombia, as influenced by method of application (adapted from Hammond *et al.*, 1986).

2.4.4.3. Application time.

As noted previously, PR fertilizers dissolve slowly in soil over a period of time. Hanafi *et al* (1992) studied the dissolution of Christmas Island (CIPR) and Gafsa (GPR) PR materials and found that the dissolution of the PR materials increased with time (Figure 2.5). Dissolution was virtually complete within 50 days. Chepkwony (1991) also reported similar results for North Carolina PR fertilizer. Jordan PR, a non-reactive PR material, was ~~not~~ affected by period of contact with soil. Chepkwony (1991) further noted that P availability declined with time of PR

reaction with soil but this decline had no significant effect on plant yield and P uptake. Such declines have been attributed to continued slow reaction of P with soil (Barrow, 1980).

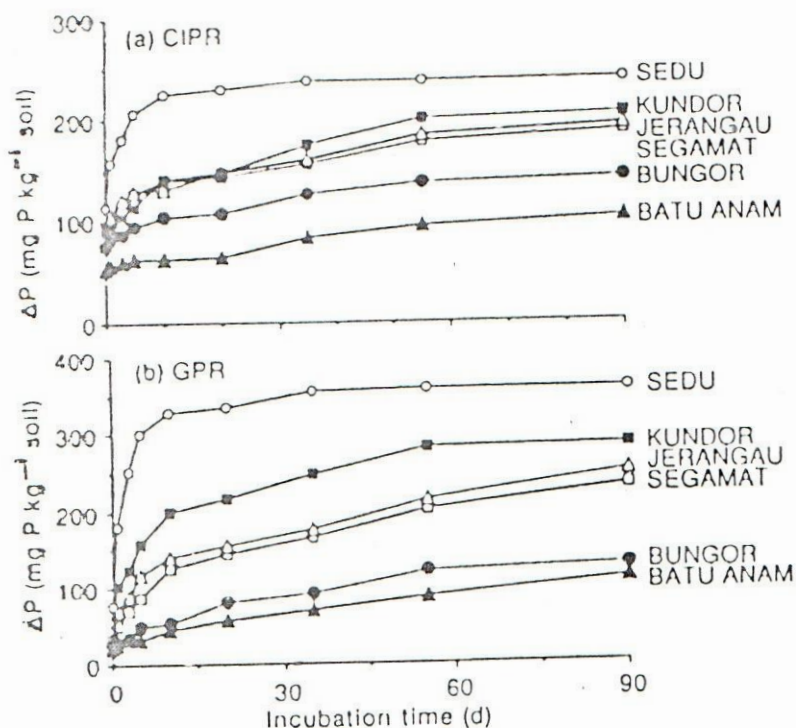


Figure 2.5; Changes in P(ΔP) in soils incubated with (a) Christmas Island PR (CIPR) and (b) Gafsa PR (GPR) in a close incubation experiment (adapted from Hanafi *et al.*, 1992).

The decrease in P availability has been found to be more for water-soluble fertilizers than for PR because PR materials continue to dissolve with increasing time (Chien *et al.*, 1980, Chepkwony, 1991). Cobala - Rosand and Wild (1982) studied the effect of reaction time (up to 270 days) for a number of PRs using Brazilian acid soils. In one soil, plant response decreased with reaction time while in two other soils the response was not affected by reaction time of PR with soil. They attributed these results to differences in the extents of the slow reactions of the fertilizers with these soil. Thus PR fertilizers should be applied as near as possible to the time of sowing.

2.4.4.4 Effects of inorganic additives.

Numerous studies have been conducted in which the effects of various additives applied with PR have been evaluated. These materials are mainly neutral or acid forming fertilizer substances.

The use of acidifying fertilizers, especially those that contain or yield NH_4^+ ions which lower soil pH when nitrified, improve conditions for PR to dissociate and hence enhance the release of P from PR (Khasawneh and Doll, 1978; Le Mare, 1991). Khasawneh and Doll (1978) and Le mare (1991) reported that the effectiveness of a mixture of PR and urea-nitrate, is slightly greater than using PR alone. This effect was demonstrated by Cobala-Rosand and Wild (1982). They grew grass in P deficient soil to compare the effect of NO_3^- and NH_4^+ in the absence and presence of one of the most inert PR from Patos in Brazil. The greater acidity due to NH_4^+ dissolved more P leading to greater P uptake than P uptake from PR / NO_3^- mixture.

Sulphuric acid (H_2SO_4) releasing compounds have also been effectively mixed with less reactive PR to enhance the fertilizers' effectiveness. The released H_2SO_4 acidulates PR and this leads to increased fertilizer effectiveness. These H_2SO_4 releasing compounds may be in the form of PR 'fortified' with elemental S or pyrite (10 % S) (Khasawneh and Doll, 1978; chien and Menon, 1995; Mahimairaja *et al.*, 1995). Studies also show that partial acidulation or compaction with Triple superphosphate (PR + TSP) or with SSP (PR + SSP) solutions, can produce highly efficient P fertilizers (Bolan *et al.*, 1990; Le Mare, 1991; Butegwa *et al.*, 1996).

2.5 Fixation reactions of dissolved P by soil and soil components.

The P released from PR dissolution may be rendered unavailable for plant uptake by physico-chemical and biological fixation processes. These processes are precipitation, adsorption and microbial immobilisation. Leaching is not usually a major contributor of P losses (Sanchez, 1976).

2.5.1 Precipitation reactions.

Insoluble complex P compounds of Al, Fe, and Ca may be formed in soils at high solution P concentrations (>1.0 M) through precipitation reactions. The initial compounds are metastable and poorly crystallised, but with time they tend to change to more stable less soluble compounds (Sanyal and De Datta, 1991). Their behaviours and relative stabilities may be predicted from solubility isotherms constructed from solubility product constants of the various P compounds (Figure 2.6).

As Figure 2.6 indicates, variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) are the probable P minerals in the acid soils, whereas in alkaline soils several Ca-P minerals (e.g. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$; CaHPO_4 etc.) tend to form. The isotherms also suggest that, changes in pH would greatly affect the stability (and hence availability) of the precipitated P compounds. As the pH increases, variscite and strengite dissolve and release P into the soil solution. Conversely, Ca-P minerals become unstable as the pH is lowered

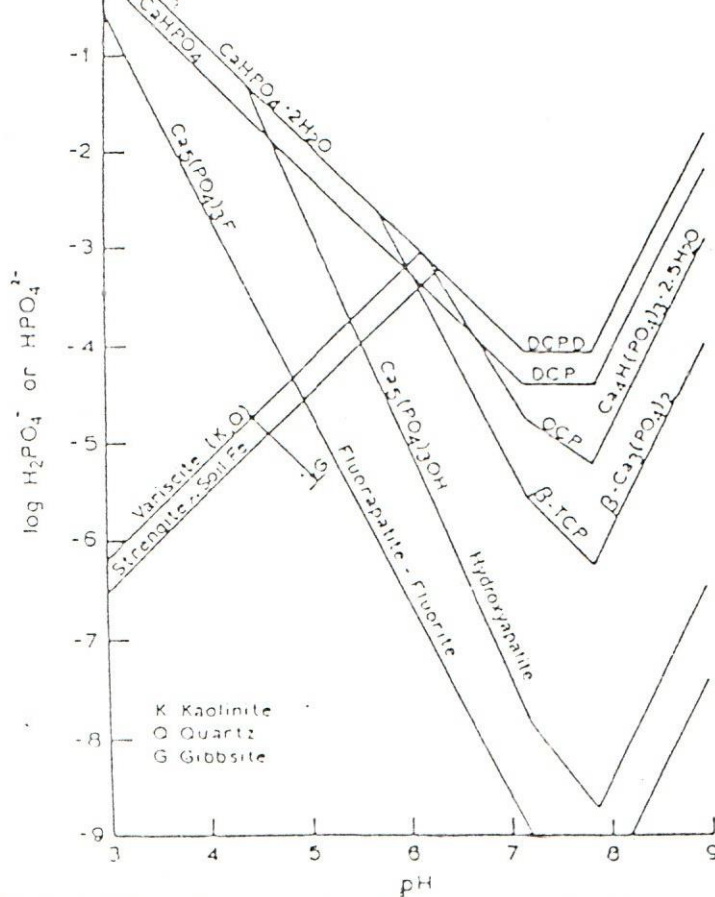


Figure 2.6. Solubility of calcium phosphates compared with strengite and variscite when Ca ($10^{-2.5}$ M) is fixed by calcite and $\text{CO}_2(\text{g})$ at 0.0003 atm. (After Lindsay, 1979).

The surface characteristics of the precipitated P compounds alter with time. Their crystal sizes increase leading to a decrease in their surface area, and also a decrease in P availability held by the precipitated P compounds (Brady, 1984). It is thus very unlikely that variscite and fluoroapatite, the ultimate reaction products of added P in acid soils and alkaline soils respectively, can control the P concentration in soil solution. Indeed, studies show that the dissolution rate of crystalline Al, Fe, and Ca-P compounds in soils are extremely slow (Sanyal and De Datta, 1991).

It may be observed, therefore, that fixation of dissolved P from PR through precipitation reactions may represent, at least in the long term, a substantial loss of available P for plant uptake.

2.5.2 Adsorption reactions.

Adsorption is the major mechanism regulating the concentration of soil solution P in highly weathered P deficient soils (Sanchez, 1976). The process involves net accumulation of P on active surface sites of the soil components. The interactions occurring between P and the active sites are electrostatic and chemical in nature (Bowden *et al.*, 1980).

The adsorption of P by soil is affected by several factors including the nature and amounts of soil components, pH, other ions, and saturation of sorption sites. Typical soil components in acid soils include hydrous oxides of Fe and Al, aluminosilicate clays and organic matter (Sanchez, 1976). The active adsorption sites in hydrous oxide surfaces are 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 Fe and Al, the dominant components in highly weathered acid soils (Sanchez, 1976) adsorb greater amounts of P than clay minerals. Kaolinitic clays (1:1) adsorb greater amounts of P than 2:1 clays (e.g. illites) probably because of Fe and Al oxides which are associated with Kaolinitic clays. Amorphous aluminosilicate clays are much more effective at adsorbing P than crystalline compounds because of their exposed surface area. Organic matter in soils can indirectly influence P adsorption through the formation of complexes with Al and Fe associated with organic matter (Sanyal and De Datta, 1991). Positive correlation between soil organic matter contents and P adsorption has been observed by various workers (Le Mare and Leon, 1989; Owusu-Bennoah and Acquaye, 1980). 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 compounds and P for adsorption sites.

The effect of pH on P adsorption by soil and soil components is full of conflicting literature. The adsorption capacity of soils has been reported to increase, decrease, or remain unaffected as the pH is raised (Haynes, 1982).

Changes induced by pH on the surface charges of variably-charged (pH-dependent) soils lead to changes in P adsorption by the components. As the pH is increased i.e. OH^- ions added, the active groups on oxide surfaces become deprotonated leading to a net surface negative charge (Figure 2.7).

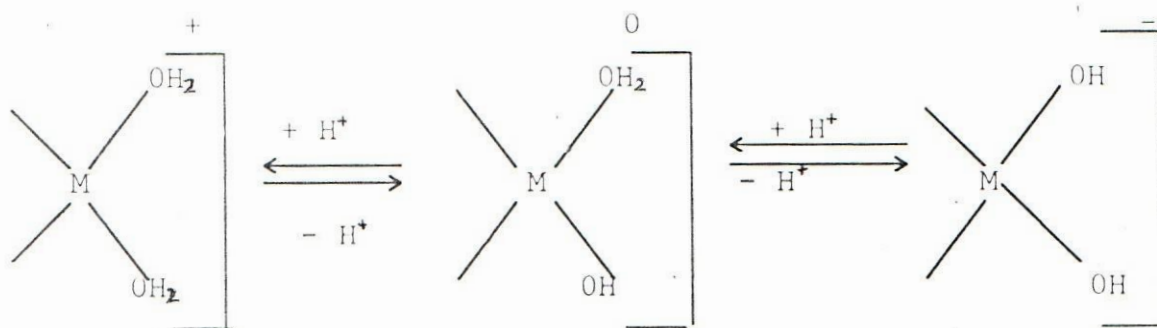


Figure 2.7. A simple model of pH-dependent surface charges on an amphoteric metal oxide (adapted from Bowden *et al.*, 1980)

These changes result in a reduction in P adsorption due to an increase in electrostatic repulsion between P ions and the negatively charged adsorbing surface. Conversely, a decrease in pH i.e. increase in H^+ ions cause protonation of OH^- and H_2O groups of the soil components leading to a net surface positive charge. Consequently, P adsorption increases. Kaolinitic clays and organic matter also behave similarly.

Exchangeable cations may also influence the amount of P that may be adsorbed. When Al is present on the exchange sites of clay minerals, P adsorption is frequently increased as the

pH increases (Haynes, 1982). This is due to the hydrolysis of Al to hydroxy-Al complexes having large surface areas (Haynes, 1982). The hydroxy-Al complexes may form independently or coat the surfaces of clay minerals.

Both the cations and the anions in the soil also influence the adsorption of P. Cations tend to enhance P adsorption, the effect being greater for divalent cations than for monovalent cations. Thus cations commonly present in soils i.e. Mg, Na, K, and Ca have been found to increase P adsorption in the order $\text{Na} < \text{K} < \text{Mg} < \text{Ca}$ (Sanyal and De Datta, 1990). Anions may compete with P for adsorption sites leading to a reduction in P adsorption. Inorganic anions adsorb onto oxide surface in the order $\text{PO}_4^{3-} > \text{AsO}_4^{2-} > \text{SiO}_3^{3-} > \text{SiO}_4^{2-} > \text{MoO}_4^{2-} > \text{SO}_4^{2-} > \text{SeO}_4^{2-} > \text{Cl}^- , \text{NO}_3^-$ (Ryden *et al.*, 1987).

The cationic and anionic effects occur through their actions on electrostatic potentials of the adsorbing surfaces. When the surface is positively charged such as at low pH, anions tend to accumulate on the positively charged adsorbing surface. This tends to make the potential in the plane of adsorption less positive and consequently P adsorption decreases. At high pH, the surface becomes more negatively charged leading to accumulation of cations on the negatively charged surfaces. Hence the potential is made less negative leading to an increase in P adsorption (Bowden *et al.*, 1980).

The amount of P adsorbed by the soils also depends on the number of available sites for P adsorption. Soils that have had heavy applications of P fertilizers tend to adsorb less P since previous applications saturate adsorption sites (Smyth and Sanchez, 1980).

Thus the effect of adsorption reactions on availability of dissolved P from PR materials depends on the net effect of the interacting factors governing adsorption processes.

2.5.3. Immobilisation by soil micro-organisms.

Soil microbial biomass constitutes about 2 to 3 % of the total organic carbon in soil (Stevenson, 1986). Despite its small size, soil microbial biomass plays an important role in the mineralization and immobilisation reactions of organic and inorganic P in soils (Stevenson, 1986).

The rapid decomposition of soil organic matter when soil conditions (e.g. moisture, pH, and temperature) favourably stimulate microbial activities may cause a temporary tying up of inorganic P in the organic tissues (Brady, 1984). McLaughlin *et al.*, (1981) demonstrated that microbial biomass assimilated a significant proportion of added P fertilizer equal to plant uptake. Immobilisation of inorganic P to organic forms by micro organisms can occur rapidly within hours of addition of P fertilizer (McLaughlin *et al.*, 1981).

Thus in P deficient soils, addition of P fertilizers has been found to result in a build-up of organic P due to microbial immobilisation (Brady, 1984). Conversely, long term cultivation of grassland soils has been reported to result in a decline of biomass P and a corresponding decline in total organic P (Stevenson, 1986) possibly due to enhanced mineralization of organic P.

CHAPTER 3

MATERIALS AND METHODS

The materials, experimental procedures, and analytical methods used in this study are described below.

3.1 Materials

3.1.1 Phosphate (P) Sources.

One PR material (Minjingu phosphate rock, MPR) from Tanzania and a water-soluble P fertiliser (Single superphosphate, SSP) were used. These P sources were ground to pass through a 100 μm sieve. The Ca, P, CaCO_3 contents and solubility indices of the fertiliser materials were determined according to the methods described in section 3.3.1

3.1.2 Soil.

Six soils from Rift valley province of Kenya (Figure. 3.1) were used. The soils were the Lanet sand / clay loam, Egerton clay loam, Sotik clay loam, Timboroa clay, Kericho sandy clay, and Kapta: at stony clay soils. Ten kg of soil samples were collected from 0-25 cm depth at each site. The samples were air-dried in an oven at 20°C , ground to pass through a 2 mm sieve and kept in polythene bags until use.

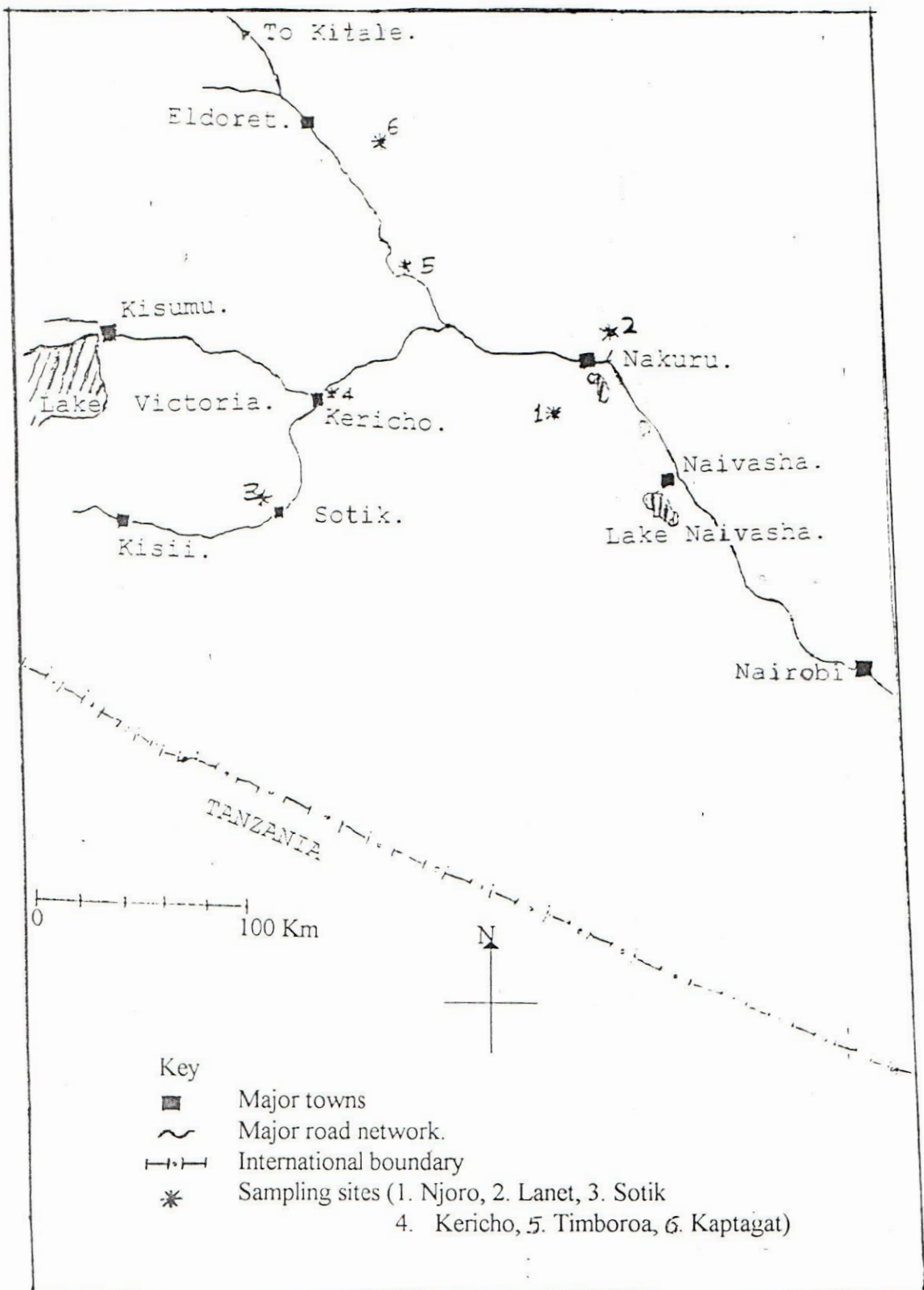


Figure 3.1. Soil sampling sites.

The Lanet sandy clay loam occurs in the expansive lacustrine plains of Nakuru district. The soil is developed from volcanic ash and is moderately calcareous (Kenya Soil Survey, 1974). The soil has moderate to high fertility. Top soils are dark greyish brown in colour. The soil samples were collected from Full Gospel Church compound (36°09'38"E and 00°16'59"S), Lanet, located along Nakuru Dondori road.

The Njoro clay loam occurs at the eastern edge of the Mau escarpment. The soil is developed from recent volcanic eruptions (Kenya Soil Survey, 1974). The soil is well drained, and has moderate to high fertility. Top soils are reddish brown to dark in colour. Soil samples were collected from Egerton university Taton farm (35°55'42"E and 00°21'58"S).

The Sotik clay loam is found in the sub-humid lower highland region west of Mau escarpment in Kericho district. The soil is developed from intermediate igneous rock-andesites and is moderately fertile (Kenya Soil Survey, 1974). Soil samples were collected at a site (35°00'15"E and 00°02'51"S), 6 Km North West of Sotik township.

The Kericho sandy clay occurs in the humid lower highland region west of Mau ranges. The soil is developed from intermediate igneous rock-andesites (Kenya Soil Survey, 1974), the soil is well-drained, and is moderate to high in fertility. The top soils are deep, dark reddish brown in colour. The samples were collected near Brooke Bond Company Field Station offices, 35°01'10"E and 00°01'36"S.

The Timboroa clay is found in the sub-humid climate of the upper highlands of Uasin Gishu district. This soil is developed on basic igneous rocks (basalts). The Timboroa clay is well drained. Top soils are extremely deep and dark reddish brown in colour. Soil samples were

collected at a location, 35°02'07"E and 00°00'21"N, ca. 3 Km North East of Timboroa Television booster station along Nakuru Eldoret road.

The Kaptagat stony clay occurs in the Uasin Gishu plateau of Uasin Gishu district. The fertility status of the soil is variable but is mainly low. The soil is developed from intermediate igneous rocks (phonolites etc.) and is well drained with light to heavy texture. Top soils are dark reddish in colour. The Kaptagat soil was taken at a location 35°01'37"E and 00°00'24"N, 23 Km east of Eldoret town along the Eldoret-Kaptagat road.

More description of the soils are given in the Table 3.1.

Table 3.1. Soil descriptions and sampling sites.

Soil	FAO/UNESCO(1988) Classification	Altitude(m) above sea level	Mean annual	
			Rainfall(mm)	Temp(°C)
Njoro	Mollic	2250-2300	980-1012	15-18
	Andosol			
Lanet	Phaeozem	1600-1800	950-1100	18-21
Sotik	Nito-rhodic	1820-1900	1200-1300	15-18
	Ferralsol			
Timboroa	Euric	2300-2700	1050-1171	13-15
	Nitisol			
Kaptagat	Rhodic	2400-2500	1090-1211	15-17
	Ferralsol			
Kericho	Ando-humic	2000-2100	1800-2000	15-18
	Nitisol			

Source of altitude, rainfall, and temperature. Farm Management Handbook of Kenya,(1982)

3.2 Experimental procedures.

Seven hundred (700) grams of air-dried soil sample (< 2 mm) for each soil were used for laboratory incubation experiment. Five treatments consisting of two types P fertilisers (MPR and SSP) and three rates of P application, P-0 (0 mg P Kg^{-1} soil), P-1 (200 mg P Kg^{-1} soil), and P-2 (500 mg P Kg^{-1} soil) for each soil in factorial combinations in duplicate were used in this experiment.

The amount of P added, P-1 and P-2, were determined from P-adsorption isotherms (section 3.3.2.). Each soil was subjected to the above treatments. The resultant treated soils were brought to a constant moisture content of 70 % of field capacity and incubated under laboratory conditions (temp. 18.6 ± 2.7 °C) for up to 60 days.

Sub-samples were taken from each treatment after 4 days (d), 7d, 15d, 30d, and 60d and the amount of fertiliser dissolved was subsequently determined using BaCl_2 -TEA extractable Ca method. Changes in soil pH (H_2O) and NaHCO_3 -extractable P (Olsen P) were similarly determined after 15 d, 30 d and 60 d of incubation while exch. Ca was determined at the end of incubation period (60 d).

3.3 Analytical methods.

Full details of the methods given below are described in Stewart (1989), unless otherwise stated. Determinations were made in duplicate.

3.3.1 Some of the chemical properties of the P sources.

Some of the chemical properties of the P sources (Table 3.2) were determined as follows.

Table 3.2: Some chemical properties of the P sources.

P-source	Total (%)			P - extracted by;		
	P	Ca	CaCO ₃	water	2% citric acid (% of total P)	2% formic acid
MPR	16.0	34.1	6.89	0.5	13.2	6.5
SSP	19.1	23.4	2.02	9.8	13.0	24.4

Total P in fertiliser materials was determined by digesting 2.5 g of fertiliser samples with 5 ml of concentrated HNO₃ and 20 ml of concentrated HCl (NZFMRA, 1983). The concentration of P in the extracts was determined using UV-spectrophotometer after colour development using ascorbic acid procedure.

The solubility of MPR material in chemical extractants was determined in water, 2% formic acid (w/v), and 2% citric acid (w/v) in a sample to extractant ratio of 1:100 (NZFMRA, 1983). The mixture was shaken for 30 minutes in an end-over-end shaker at ca. 70 r.p.m. before filtering using whatman no. 2 filter paper. The P concentrations were determined as described above.

Determination of total CaCO₃ content in the P sources was done by boiling for 30 minutes a mixture of fertilizer material and 2 M HCl in a 1:10 sample to solution ratio (w/v). The amount of CaCO₃ in the P sources was determined by back - titrating excess acid with

standard 2 M NaOH using phenolphthalein as the indicator and the percentage of CaCO_3 in the P source was calculated from the results.

Total Ca in the fertilizer materials was determined in the extracts of total P using Z-6100 zeeman polarised atomic absorption spectrophotometer (AAS).

3.3.2 Some of the initial soil chemical properties.

Some of the key soil chemical properties which were thought to influence PR dissolution were determined using air-dried samples (< 2 mm) and the methods described below.

Soil pH was determined in water and in 0.01 M CaCl_2 at soil/solution ratio of 1:2.5 and 1:2 (w/v) respectively. The mixture was agitated for about 10 minutes and left to stand overnight. The pH was then determined by pH meter fitted with glass-calomel reference electrode.

Soil organic carbon was determined according to the walkley and Black dichromate oxidation method. The amount of organic matter in each soil was obtained by multiplying soil organic carbon value by 1.724 (Black, 1965).

Cation exchange capacity (C.E.C) was determined by leaching air-dried soil samples (<2 mm) with 1 M NH_4OAc (pH 7) at a soil to solution ratio of 1:50. The concentrations of Ca and Mg in the leachate were determined by AAS. After washing with 95% ethyl alcohol, the column was further leached with 1 M NaCl solution. The concentrations of NH_4^+ ions removed

from the exchange sites were determined by steam distillation and the CEC was calculated from this value.

Exch.Ca was determined by shaking 5g of air-dried soil (<2 mm) samples in 100 ml of 1 M NH_4OAc solution (pH 7.0) for 30 min using an end-over-end shaker at ca. 70 r.m.p. After filtration, exch.Ca concentrations were determined as described above.

P adsorption capacity was determined by mixing 3.0 g of air-dried soil (<2 mm) with 30 ml of 0.01 CaCl_2 containing known quantities of P in shaking bottles. A drop of 0.1 % HgCl_2 was added to each mixture and the bottles were shaken for two 30 minutes periods, daily for six days. On the seventh day, the solutions were centrifuged at 5000 r.p.m and then filtered. P concentrations were determined as previously described. The amount of P adsorbed was calculated from the difference between the P added and the P remaining in the supernatant solution.

Olsen P was determined by extracting 2.0 g of air-dried soil (<2 mm) with 40 ml of 0.5 M NaHCO_3 at pH 8.5 (Okalebo *et al*, 1993). The solution was shaken for about 30 minutes in an end-over-end shaker. The extracts were centrifuged and then filtered through whatman no. 42 filter paper. 10 ml aliquots of filtrate were acidified with 5 ml of 0.8 M boric acid before colour development. The concentration of P (Olsen P) in the extracts was determined as described above.

Bray-1 P was determined by shaking 2 g of air-dried soil sample (<2 mm) with 20 ml of Bray-1 extractant (0.03 M NH_4F + 0.025 N HCl) for 1 minute. The P concentration in the extracts was determined as described previously.

3.3.3 PR dissolution measurement.

The amount of Ca released during the incubation period was extracted from air-dried sub-sampled PR-treated soil samples with 1.0 M BaCl₂-TEA (pH 8.1) at a soil to solution ratio of 1:10. The mixture was shaken for 1 hour (Kanabo and Gilkes, 1988a) on an end-over-end shaker. After centrifuging at 3,000 r.p.m. for 5 minutes, the samples were filtered and the concentration of Ca was determined by AAS as described above. By assuming that PR dissolves congruently, percent (%) dissolution was estimated using increases in extractable BaCl₂-TEA (pH 8.1) Ca concentrations in the PR treated soils over that in the control treatments as:

$$\text{PR dissolution(\%)} = \frac{\text{Ca}_{\text{fertilizer}} (\text{mg Ca kg}^{-1}) - \text{Ca}_{\text{control}} (\text{mg Ca kg}^{-1})}{\text{Total Ca in added PR (mg Ca kg}^{-1})}$$

3.4 Statistical analysis of data.

The Agstats version 2, Wye College (1987) analytical programme was used for the analysis of variance. The statistical significance of a treatment effect was tested using a calculated Least Significant Difference (LSD) values at $p < 0.05$. Simple linear regression analysis was also carried out.

CHAPTER 4

RESULTS

4.1 Some initial chemical properties of the soils

Table 4.1 below shows some initial chemical properties of the soils used.

Table 4.1 Some initial soil chemical properties.

Chemical property	Soil					
	Njoro	Lanet	Sotik	Timboroa	Kericho	Kaptagat
Soil pH(H ₂ O)	6.4	6.8	5.3	5.1	5.5	5.1
Soil pH (CaCl ₂)	5.7	5.1	4.8	4.4	4.7	4.5
Organic C(%)	2.5	2.6	2.3	3.0	3.5	3.2
CEC (me/100g)	27.3	28.0	17.4	16.6	21.2	15.6
Exch.Ca(me/100g)	13.4	7.2	7.8	5.4	3.4	2.0
Fe _{ox} (%)*	0.5	0.6	1.3	1.7	1.5	2.2
Al _{ox} (%)*	1.3	0.9	1.7	1.2	2.0	1.9
Olsen P (μg/g ⁻¹)	30.5	14.7	6.1	6.7	5.2	10.8
Bray-1 P (μg/g ⁻¹)	7.2	4.6	3.6	1.9	3.1	4.2

* Source: Fertilizer Use Recommendation Project (FURP, 1987).

The soil pH values in water ranged from 5.1 to 6.8. The values of four soils i.e Kaptagat, Kericho, Timboroa, and Sotik were below 5.5, while the values of the other two soils were

above 6.4. The pH values in 0.01 M CaCl_2 were lower than the pH values in water for all the soils.

The exch.Ca values were high for the Njoro soil, medium for the Lanet, the Sotik, and the Timboroa soil and low for the Kericho and Kaptagat soils. This trend generally reflected the order observed for C.E.C values (Table 4.1). The soils generally contained moderate organic C contents ranging from 2.3 % for the Sotik soil to 3.5 % for the Kericho soil.

The P adsorption capacities of the soils were higher for the moderately acidic soils (Kericho, Kaptagat, Timboroa and Sotik) than for the slightly acidic soils (Njoro and Lanet), a trend also reflected by the order of Fe_{OX} and Al_{OX} values (Table 4.1) reported by FURP (1987). Olsen P values were medium for the Njoro and the Lanet soils and low for the other soils, a trend also reflected by the P adsorption capacities. The Bray 1 values were medium for the Njoro soil, and low for all the other soils.

Table 4.2 shows the amounts of P adsorbed and equilibrium P concentrations at various concentrations of added P. P adsorption isotherms were obtained by plotting P remaining in the solution against the amount of P adsorbed by the soil (Figure 4.1a-c).

The results in Table 4.1 and Figure 4.1a-c indicated that the soils studied varied widely in their abilities to adsorb P (0 - 120 ppm). Four soils (Kericho, Kaptagat, Timboroa, and Sotik) distinctly showed relatively high P adsorption capacities while the other two soils (Njoro and Lanet) indicated low capacities to adsorb P.

Several equations including the Langmuir equation have been used to describe P adsorption by soils and soil components (Bowden *et al*, 1980). The Langmuir equation was originally developed to describe the adsorption of gases at solid surfaces. It is based on the

theoretical consideration of energy of adsorption and adsorption capacity. Due to its simplicity, the Langmuir equation has found wide application as an empirical equation.

Table 4.2 The amounts of P adsorbed, x , ($\mu\text{gP/g soil}$) and equilibrium P concentrations c , ($\mu\text{gP/ml}$) at different concentrations of added P.

Soil	Amount of added P (μgPml^{-1})									
	10		20		40		80		120	
	x	c	x	c	x	c	x	c	x	c
Njoro	9.5	0.5	18.2	1.8	32.4	7.6	56.0	24.0	75.0	45.0
Lanet	9.7	0.4	18.6	1.4	33.0	7.0	58.0	22.0	82.2	37.8
Sotik	9.8	0.2	19.6	0.4	39.3	0.7	75.0	5.0	107.0	13.0
Timboroa	9.6	0.4	19.5	0.5	39.5	0.5	77.0	3.0	109.0	11.0
Kaptagat	9.8	0.2	19.7	0.3	39.3	0.7	78.2	0.8	114.0	6.0
Kericho	9.9	0.1	19.8	0.2	39.7	0.3	79.5	0.5	119.0	1.0

The langmuir equation is usually given as:

$$x = \frac{kbc}{1 + kc} \dots\dots\dots(4.1)$$

where x is the amount of P adsorbed per unit weight of soil ($\mu\text{gP/g soil}$) at an equilibrium P solution concentration of ($\mu\text{gP/ml}$), and b and k are constants representing maximum amounts of P that can be adsorbed (P adsorption capacity in $\mu\text{gP/g soil}$) and binding energy ($\text{ml} / \mu\text{g}$) energy respectively (Bowden *et al.*, 1980).

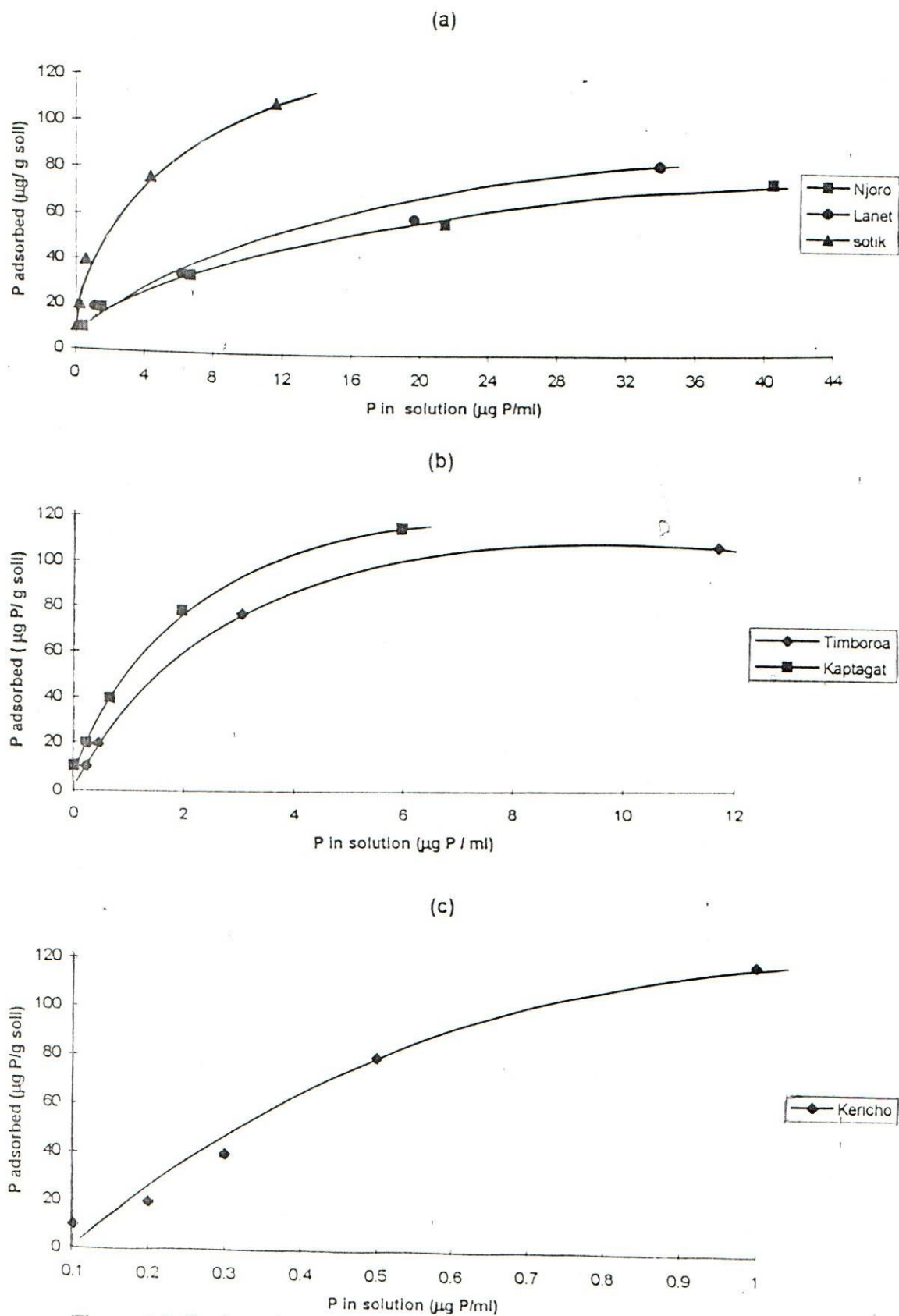


Figure 4.1. P adsorption isotherms for the soils (a) Sotik, Lanet and Njoro soils (b) Timboroa and Kaptagat soils, and (c) Kericho soil.

The equation can also be written in linear form as:

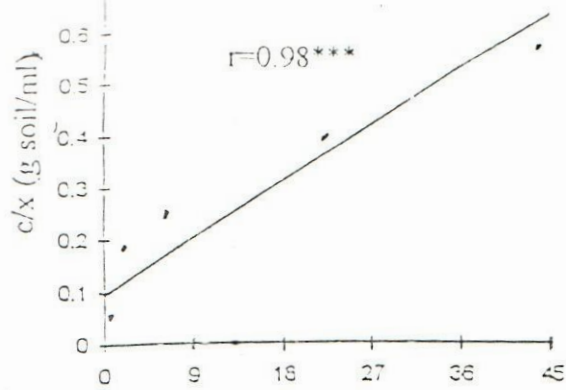
$$\frac{c}{x} = \frac{c}{b} + \frac{1}{kb} \dots\dots\dots(4.2)$$

The adsorption data were fitted in the linear form of the equation (Figure 4.2a-f) to obtain the b and the k constants (Table 4.3)

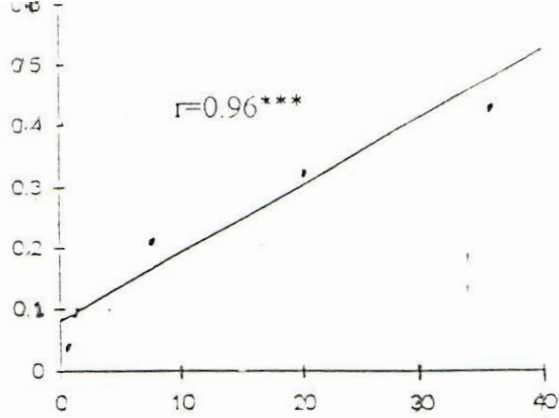
Table 4.3 The correlation coefficients (r) between the amount of adsorbed and equilibrium P concentration and the calculated Langmuir b and k values.

Soil type	Correlation coefficient (r)	P adsorption maximum, b ($\mu\text{gP/g soil}$)	Binding energy, k ($\text{ml}/\mu\text{gP}, \times 10^{-1}$)
Njoro	0.98***	836	1.2
Lanet	0.97***	904	1.4
Timboroa	0.96***	1220	3.1
Sotik	0.99***	1421	4.6
Kaptagat	0.98***	1538	5.1
Kericho	0.99***	2487	11.1

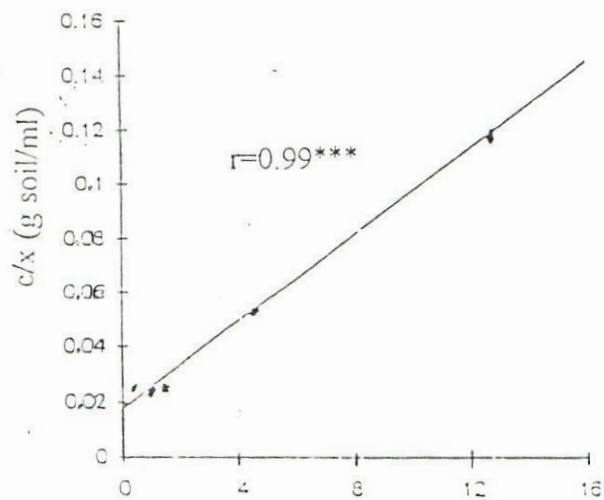
*** significance at ($p < 0.01$).



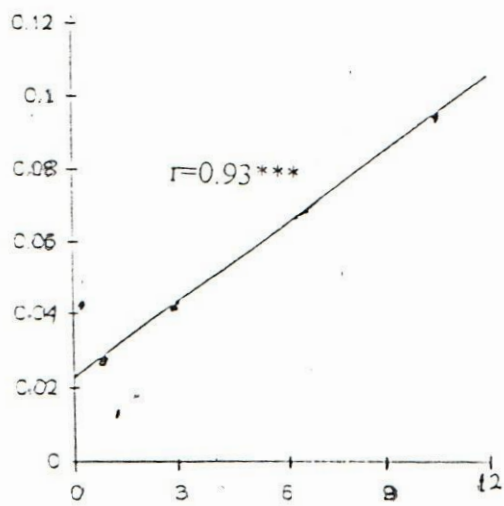
(c)



(d)



(e)



(f)

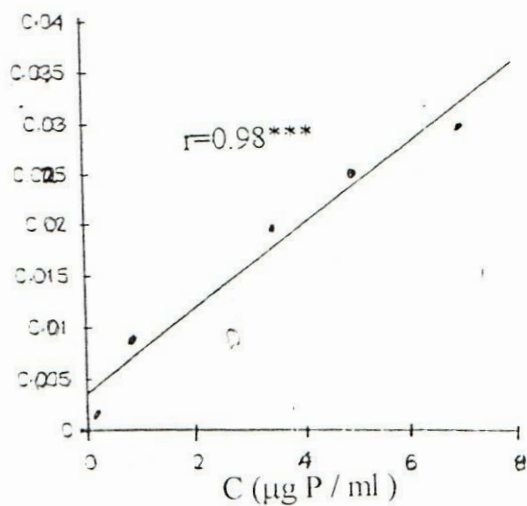
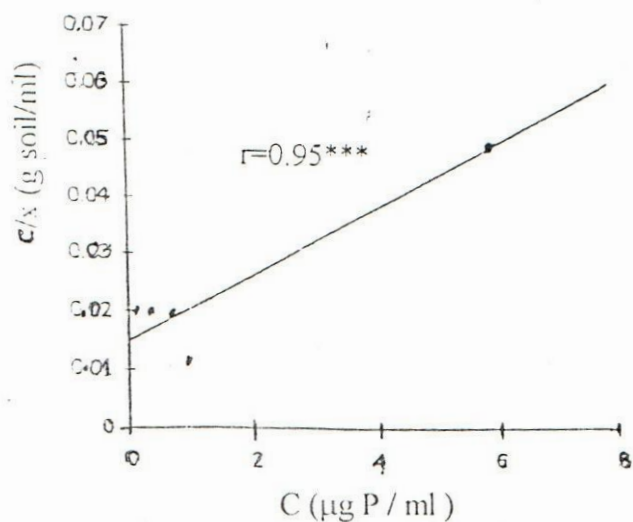


Figure 4.2(a-f). Langmuir plots for (a) Njoro, (b) Lanet, (c) Sotik, (d) Timbora, (e) Kaptagat, and (f) Kericho soils

***significance at $p < 0.01$, and $p < 0.05$, ns = not significant

Although the Langmuir b and k parameters should be treated as empirical constants, they reflect real features of adsorption isotherms, and can therefore be loosely identified with P adsorption capacity and the strength of P adsorption respectively.

The b and k values differed widely between the soils. These values decreased in the order Kericho > Kaptagat > Sotik > Timboroa > Lanet > Njoro (Table 4.3).

The relationships between P sorption parameter, b , and Olsen P, CEC, and Al_{OX} and Fe_{OX} values are illustrated in the figure 4.3 below.

Positive correlation coefficients (r) between P adsorption capacity constant, b , and Al_{OX} Fe_{OX} and % C were obtained. The values for Fe_{OX} were much higher than those of Al_{OX} . In contrast, negative correlation coefficients between b and Olsen P, pH and CEC values were obtained (Figure 4.3).

4.2 Effects of P sources, rates of application and periods of reaction on soil pH, exch.Ca and $BaCl_2$ -TEA extractable Ca.

The soil pH values in water of SSP and MPR treatments at various periods of reaction of the P fertilizers with the soils are shown in Table 4.4.

Addition of MPR fertilizer slightly increased the pH values of the soils. The increases were more marked for the Kericho, the Kaptagat, the Timboroa, and the Sotik soils than they were for the Njoro and the Lanet soils (Table 4.4). On the other hand, SSP addition tended to decrease the soil pH values. The pH values changed little with time in the presence or absence of added fertilizer.

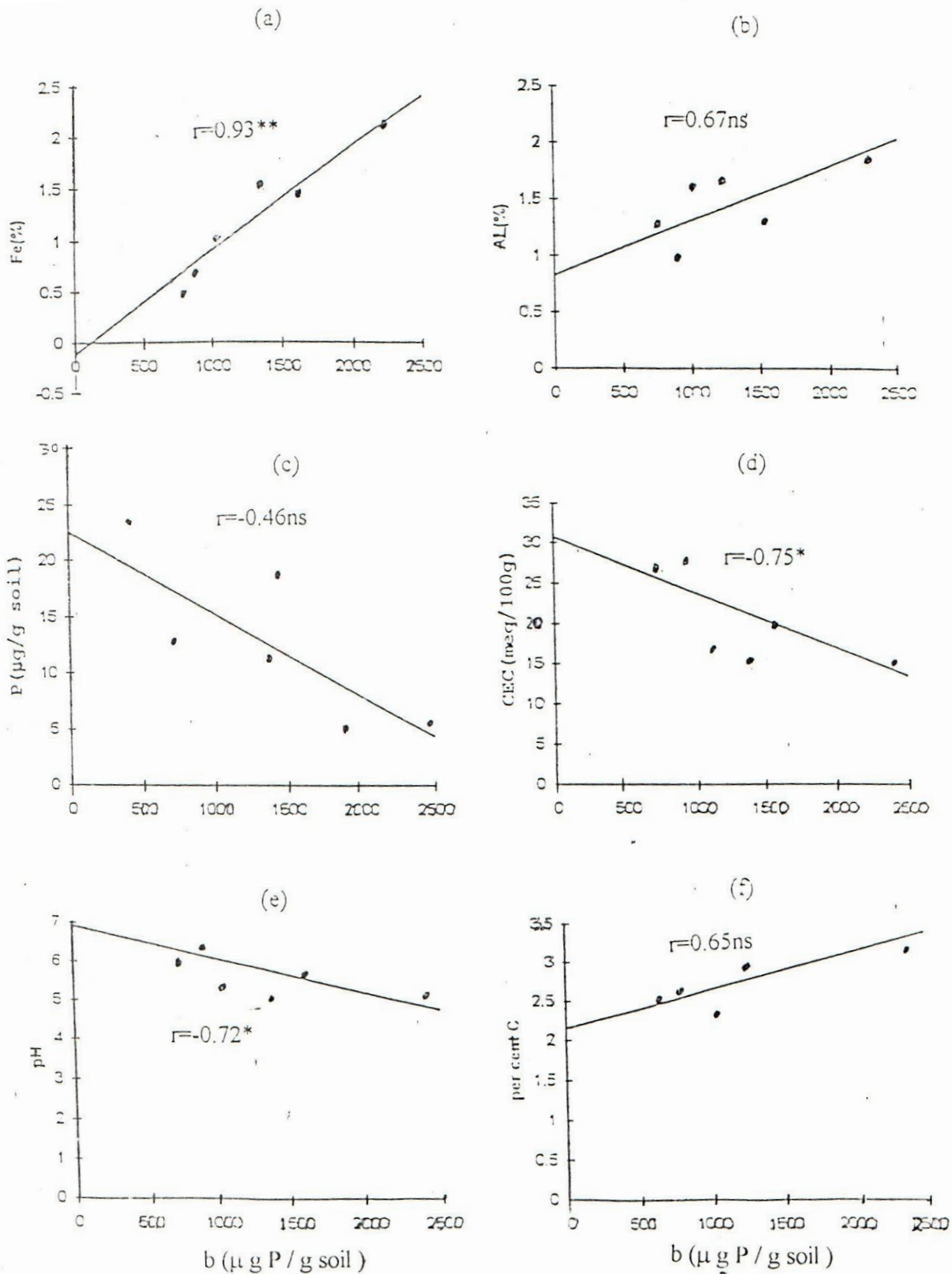


Figure 4.3; Correlation coefficient(r) between P sorption parameter, b , and (a) Fe_{ox} , (b) Al_{ox} , (c) Olsen P (d), C.E.C, (e) $\text{pH}(\text{H}_2\text{O})$, and (f) % C of the soils

Table 4.4. Soil pH values of SSP and MPR treatments at various periods of reaction with soils.

Soil	Time (weeks)	P source		
		None	SSP	MPR
Njoro	2	6.38	6.36	6.43
	4	6.40	6.35	6.46
	8	6.40	6.35	6.51
	mean	6.40	6.35	6.47
Lanet	2	6.79	6.73	6.85
	4	6.81	6.76	6.83
	8	6.86	6.80	6.96
	mean	6.82	6.76	6.88
Sotik	2	5.36	5.35	5.45
	4	5.30	5.28	5.38
	8	5.34	5.32	5.48
	mean	5.33	5.32	5.41
Timboroa	2	5.27	5.23	5.47
	4	5.20	5.16	5.39
	8	5.28	5.23	5.56
	mean	5.25	5.21	5.47
Kaptagat	2	5.20	5.21	5.46
	4	5.28	5.22	5.39
	8	5.20	5.18	5.28
	mean	5.23	5.20	5.38
Kericho	2	5.30	5.30	5.48
	4	5.32	5.28	5.53
	8	5.31	5.29	5.55
	mean	5.31	5.29	5.52
LSD(p<0.05)		0.025		

(N.B The LSD values are for Soil X Rate X Time interactions)

Results for the effects of P sources and rates of application on exch.Ca values are shown in the table below.

Table 4.5 Exch.Ca values (meq/100g) of soils after addition of two rates of SSP and MPR fertilizers.

Soil	None	MPR		SSP	
	P-0	P-1	P-2	P-1	P-2
Njoro	14.6	15.0	15.9	15.6	16.2
Lanet	9.3	9.6	10.1	9.7	9.9
Sotik	9.2	9.8	10.7	9.7	9.9
Timboroa	3.3	3.8	4.9	3.8	4.2
Kaptagat	5.6	5.9	7.3	5.8	6.3
Kericho	4.4	4.7	5.4	4.5	5.4
LSD (p<0.05)			0.3		

(N.B The LSD values are for Soil X P source X Rate interactions)

The exch.Ca values of all the soils were elevated over the control treatment (P-0) values following addition of P fertilizers. It is also apparent that exch.Ca concentrations in all soils increased with the rate of P fertilizer application. The increases were greater for MPR treatments than for SSP treatments at each rate of application.

Table 4.6 shows BaCl₂-TEA extractable Ca values of MPR treatments at various periods of reaction with the soils. Similarly, the results for the changes in BaCl₂-TEA extractable Ca (Δ Ca) at the various periods of reaction with the soils are shown in Table 4.7.

The corresponding % P dissolved values of the PR fertilizer are illustrated in Figure 4.4.

Table 4.6 BaCl₂-TEA extractable Ca (ppm) of MPR treatments at various periods of reaction with the soils.

Soil	P rate	Time (days)				
		4	7	15	30	60
Njoro	P-0	459.7	455.9	468.8	479.8	458.3
	P-1	463.3	478.4	484.8	496.6	475.2
	P-2	471.6	506.3	521.4	536.9	522.2
	mean	464.9	480.2	491.7	504.3	485.4
Lanet	P-0	409.2	413.4	418.8	401.3	402.3
	P-1	422.7	435.9	436.0	456.3	470.2
	P-2	452.5	584.8	610.4	615.8	624.8
	mean	420.5	477.7	496.9	491.2	489.7
Sotik	P-0	436.9	415.5	372.1	389.8	465.6
	P-1	447.8	471.3	436.7	461.1	538.3
	P-2	524.8	634.2	653.0	564.4	735.1
	mean	469.7	476.0	480.9	501.5	579.8
Timboroa	P-0	225.6	214.9	177.6	183.9	171.2
	P-1	227.1	248.4	240.1	252.5	248.4
	P-2	257.1	266.2	359.6	386.5	382.8
	mean	236.6	243.2	261.8	274.4	267.4
Kaptagat	P-0	82.8	90.2	103.2	87.3	81.6
	P-1	87.8	156.2	197.8	186.1	188.8
	P-2	104.8	258.2	343.1	401.5	451.9
	mean	91.2	167.9	114.8	224.4	240.3
Kericho	P-0	400.2	402.1	388.1	378.2	415.2
	P-1	405.2	438.1	544.8	559.7	613.2
	P-2	438.3	562.5	838.6	881.2	937.4
	mean	414.5	467.7	590.5	606.1	655.2
LSD (p<0.05)				79.4		

(N.B LSD values are for Time X Soil X Rate interactions)

Table 4.7. Changes in BaCl₂-TEA extractable Ca (ppm) values of MPR treatments at various periods of reaction.

Soil	P rate	Time (Days)				
		4	7	15	30	60
Njoro	P-1	3.6	12.5	15.9	16.7	17.2
	P-2	11.9	50.4	52.5	56.8	64.3
	mean	7.8	31.5	34.2	36.7	40.7
Lanet	P-1	12.9	21.8	42.5	55.3	68.2
	P-2	42.9	171.5	191.9	214.4	222.9
	mean	32.9	96.7	117.2	134.9	150.1
Sotik	P-1	11.6	55.8	64.4	72.1	73.4
	P-2	88.9	246.6	262.6	263.1	270.1
	mean	50.3	151.2	163.5	167.9	171.8
Timboroa	P-1	2.2	34.3	63.7	67.8	77.2
	P-2	32.2	52.6	182.2	203.7	211.2
	mean	17.2	43.4	123.1	135.6	144.2
Kaptagat	P-1	4.7	66.1	94.4	98.7	106.4
	P-2	21.4	209.0	240.0	314.1	370.9
	mean	13.1	137.8	117.8	206.4	238.1
Kericho	P-1	4.8	36.9	156.2	181.0	198.6
	P-2	37.5	160.8	450.2	502.8	522.1
	mean	21.4	98.9	253.2	341.9	360.4
LSD (p<0.05)		0.64				

(N.B LSD values are for Soil X Rate X Time interactions)

Table 4.8 Percent P dissolved of MPR fertilizer at various periods of reaction with the soils

Soil	P rate	Time (days)				
		4	7	15	30	60
Njoro	P-1	0.8	3.4	3.7	3.9	4.0
	P-2	1.1	4.7	4.9	5.3	6.0
	mean	1.0	4.1	4.3	4.6	5.0
Lanet	P-1	3.0	5.1	9.9	12.9	15.9
	P-2	4.0	16.0	17.9	20.1	20.8
	mean	3.5	10.5	13.9	16.5	18.4
Sotik	P-1	2.7	13.0	15.0	16.8	17.1
	P-2	8.3	23.0	24.5	24.6	25.2
	mean	5.5	18.0	19.8	20.7	21.2
Timboroa	P-1	0.5	4.9	14.9	15.8	18.0
	P-2	3.0	8.0	17.0	19.2	19.7
	mean	1.8	6.5	15.9	17.5	18.8
Kaptagat	P-1	1.1	15.4	22.0	23.1	24.8
	P-2	2.0	19.5	22.4	29.3	34.6
	mean	1.6	17.5	22.2	26.2	29.7
Kericho	P-1	1.1	8.6	36.4	42.2	46.3
	P-2	3.5	15.0	42.0	46.9	48.7
	mean	2.3	11.8	39.2	44.6	47.5
LSD (<0.05)				35.2		

(N.B LSD values are for Soil X Time X Rate interactions)

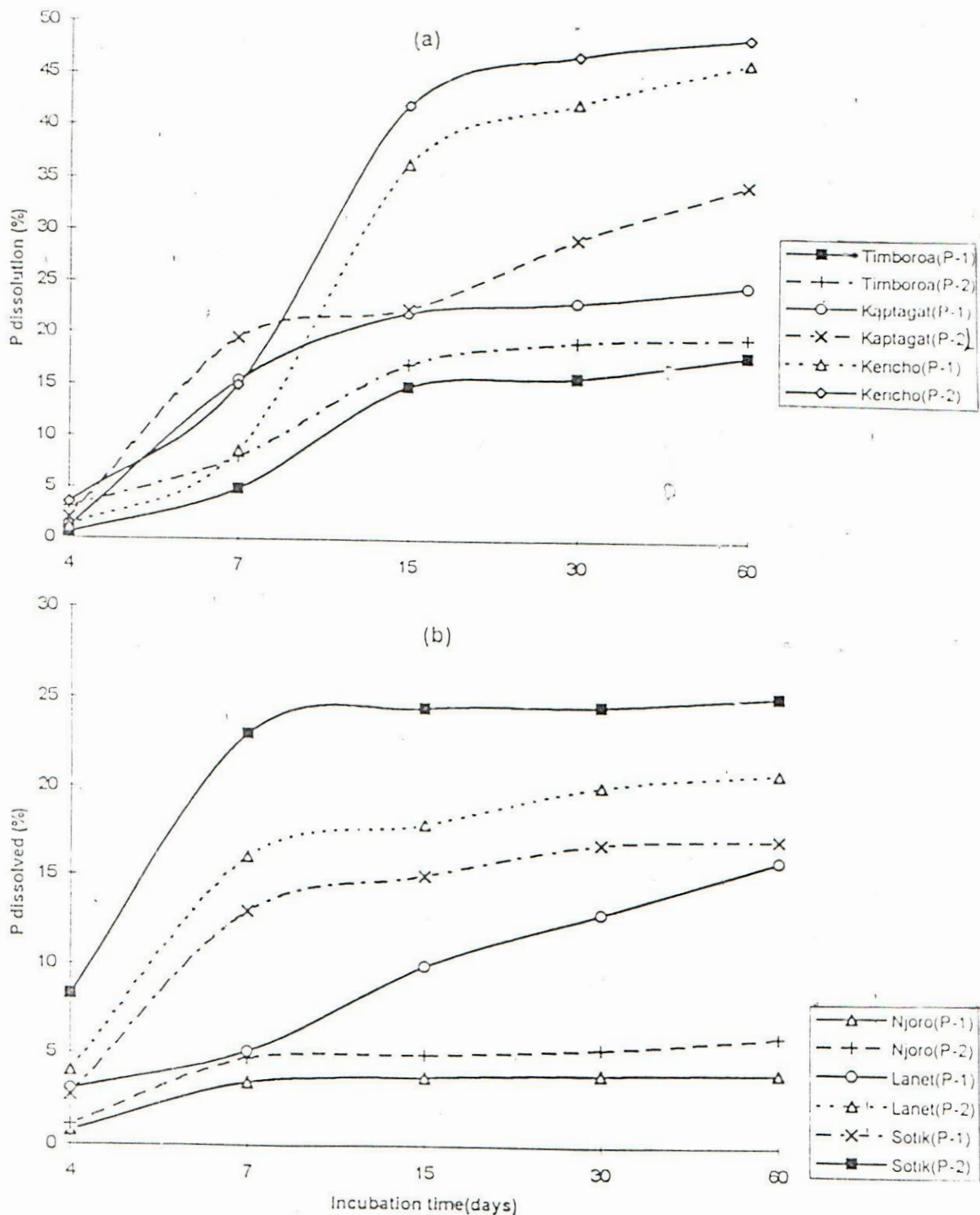


Figure 4.4 Percent P dissolved of MPR treatments as affected by rates of application (P-1 and P-2) and periods of reaction of the fertilizer with soil (a) Kericho, Kaptagat, and Timbora, (b) Njoro, Lanet, and Sotik..

It is evident that for all the soils, the concentrations of BaCl_2 -TEA extractable Ca were clearly greater in the MPR treatments than in the control (Zero-P) treatments. The concentrations also increased with the rates of application, periods of reaction, and varied between the soils. For all the soils, the dissolution rates were more rapid initially, but this tended to decrease with time.

The results further indicated that in the moderately acidic soils between 0.5 % to 8.3 % of total added P had dissolved after the MPR fertilizer had been in contact with the soils for 4d (Table 4.8). However, after 60 d of reaction of the fertilizer with the soils, the amount dissolved increased to between 17.1 % to 48.7 % of the total added P. For the slightly acidic soils (Njoro and Lanet), between 0.8 % to 4.0 % of the total added P had dissolved after 4d of PR reaction with the soils (Table 4.8). After 60 days of PR reaction with the soils, the amount dissolved increased to between 4.0 % to 20.8 % of the total added P.

Addition of P fertilizers significantly increased the extractable P concentrations over the control (P-0) treatments for all the soils (Table 4.9). The increases were greater for the SSP treatments than for the MPR treatments. It can also be observed that for both fertilizers, the extractable P concentrations increased with the rate of application in all the soils. Also for both fertilizer materials, the amount of added P extracted differed among the soils. The highest amount was noted in the Njoro soil and the lowest amount was observed for the Kericho soil.

The variation of mean Olsen P values of SSP and MPR treatments with reaction time are illustrated in Figure 4.5. Clearly, the two fertilizers displayed different patterns of reactions for the first 15d of the fertilizer reactions with the soils. The Olsen P values for the SSP treatments declined significantly with time. In contrast, the Olsen P values for the MPR

4.3 Effect of P sources, rates of application and periods of reaction on Olsen P concentrations.

Table 4.9 Olsen P values of SSP, and MPR treatments at various periods of reaction with the soils.

Soil	Time (days)	None	SSP		MPR	
		P-0	P-1	P-2	P-1	P-2
Njoro	15	32.8	53.8	96.3	35.6	51.3
	30	35.2	52.0	94.9	43.2	66.3
	60	33.3	48.3	86.8	39.0	47.2
	mean	33.8	51.4	90.6	39.3	54.9
Lanet	15	16.8	49.4	87.8	23.8	31.9
	30	15.6	46.1	68.6	30.5	48.5
	60	14.2	40.1	62.2	21.5	37.7
	mean	15.5	45.2	72.9	25.3	39.4
Sotik	15	6.9	26.1	50.4	16.8	30.9
	30	7.6	20.7	39.6	19.3	40.1
	60	5.8	17.6	25.0	18.0	30.6
	mean	6.8	21.5	38.3	18.0	33.9
Timboroa	15	9.8	18.4	32.4	13.2	39.1
	30	5.0	16.7	28.9	15.6	47.4
	60	8.9	12.5	29.3	14.1	35.1
	mean	7.9	15.9	30.2	14.3	40.5
Kaptagat	13	9.8	35.3	54.1	23.7	61.2
	30	7.5	30.1	38.3	28.3	59.6
	60	7.7	26.2	36.1	29.0	39.7
	mean	8.3	30.5	42.8	27.0	53.5
Kericho	15	5.3	15.3	35.9	9.2	16.2
	30	6.3	14.0	33.2	11.6	21.0
	60	7.1	12.9	11.9	11.1	17.4
	mean	6.2	14.1	27.0	10.6	18.2
LSD ($p < 0.05$)				21.4		

(N.B LSD values are for Soil X Rate X P source X Time interactions)

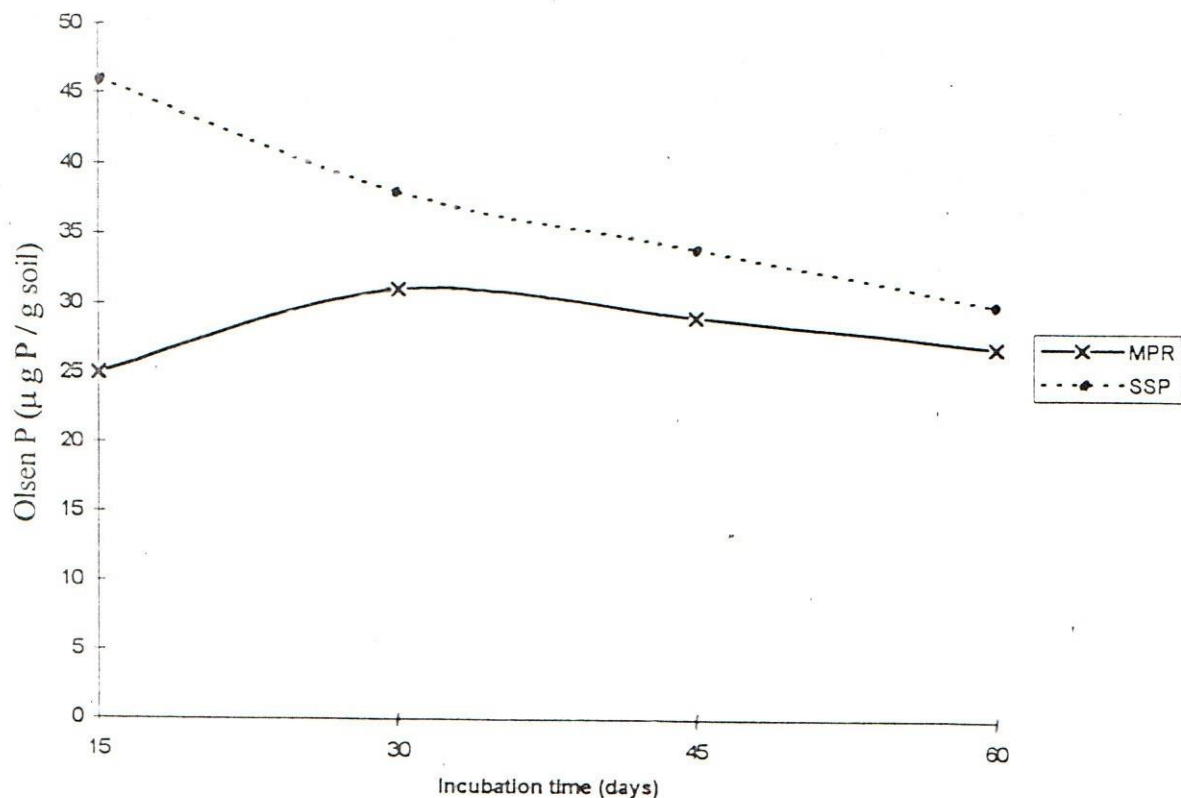


Figure 4.5 Mean Olsen P values of SSP and MPR treatments after 15, 30, and 60 days of incubation.

treatments reached their peak at 30 d, and declined thereafter (Figure. 4.5). The amount of native P (Zero added P treatment) changed little with time.

4.4 Relationship between percent P dissolved of MPR and some initial soil chemical properties.

The correlation coefficients (r) between the determined initial soil chemical properties (Table 4.1) with the corresponding values of % P dissolved for MPR treatments at various periods of reaction are shown in Table 4.10 below.

It can be noted that pH (H_2O), pH ($CaCl_2$), Exch.Ca, CEC, and Olsen P were all negatively correlated to % P dissolved of MPR fertilizer. Exch.Ca and Olsen P showed significant relationship with % P dissolved after 15d of MPR fertilizer reaction with the soils. In

contrast, % C, Fe_{ox}, Al_{ox}, b, and k were all positively correlated to % P dissolved. Similarly, significant relationship were observed for % C, Al_{ox}, b, and k after 15d of MPR fertilizer reaction with the soils (Table 4.10).

Table 4.10 Simple correlation coefficients (r) between some soil chemical properties and %P dissolved of MPR treatments.

Soil Chemical property.	Time (days)				
	4	7	15	30	60
pH(H ₂ O)	0.15	-0.22	-0.49	-0.48	-0.50
pH(CaCl ₂)	-0.14	-0.41	-0.61	-0.60	-0.61
%C	-0.51	0.07	0.74*	0.78*	0.80*
Exch.Ca	-0.01	-0.21	-0.76*	-0.77*	-0.81**
CEC	-0.12	-0.58	-0.43	-0.39	-0.41
Olsen P	-0.47	-0.60	-0.75*	-0.73*	-0.72*
Fe _{ox}	-0.21	0.56	0.48	0.56	0.58
Al _{ox}	0.01	0.35	0.74*	0.73*	0.72*
b	-0.10	0.33	0.96***	0.96***	0.95***
K	-0.10	0.50	0.90**	0.90**	0.90**

Significance levels $p < 0.01$ (***), $p < 0.05$ (**), and $p < 0.1$ (*).

4.5 Relationship between initial rate of PR dissolution and some initial soil chemical properties.

As mentioned in chapter Two, the effectiveness of a PR material as a fertilizer depends on the extent and rate of its dissolution in soils.

A number of equations have been developed and used to study the kinetics of PR dissolution in soils (Khasawneh and Doll, 1978; Chien *et al.*, 1980; Sanyal and De Datta, 1991).

An attempt was made in this study to estimate the rate constants of MPR dissolution in soils using a modified Elovich equation (Sanyal and De Datta, 1991). The modified equation can be written as:

$$q = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \dots \dots \dots (4.3)$$

where q is %PR dissolved in time t of reaction with soil and α and β are dissolution constants.

These constants have been shown to be unique for a particular soil (Sanyal and De Datta, 1991).

If it is assumed that as $q \rightarrow 0$, $\partial q / \partial t \rightarrow \alpha$. Then α may be taken to represent the initial rate of PR fertilizer reaction with the soils and can be obtained from a linear graph of q versus $\ln t$.

These values are shown in Table 4.11, while Table 4.12 shows the relationship between α and some initial single soil chemical properties.

Table 4.11 Initial rates (α) of MPR dissolution in soils as calculated from Elovich equation.

Soil	Njoro	Lanet	Sotik	Timboroa	Kericho	Kaptagat
Reaction rate α (gP/day)	1.9	3.8	11.1	2.8	5.6	4.9

Table 4.12: Simple correlation coefficient(*r*) values between the rates of MPR dissolution and various soil chemical properties.

Soil chem. property	pH(H ₂ O)	%C	CEC	Exch.Ca	Fe _{ex}	Al _{ox}	Olsen.P	b
<i>r</i>	-0.40	0.25	-0.43	-0.20	0.23	0.50	-0.57	0.20

Table 4.11 shows that the initial rate of reaction of MPR followed the order of Njoro < Timboroa < Lanet < Kaptagat < Kericho < Sotik.

The correlation coefficients between initial soil chemical properties and the initial rates of MPR dissolution showed similar trends to those of % P dissolved with soil chemical properties noted in Table 4.10. No single soil chemical property was found to be significant in predicting the initial rate of MPR dissolution (Table 4.12).

4.6 Relationship between % P dissolved of MPR, Olsen P values and P sorption capacity.

The relationship between % P dissolved of MPR, Olsen P and P adsorption capacities of the soils is illustrated in figure 4.6. Negative and highly significant correlation coefficient ($r = -0.95$) was obtained between % P dissolved of MPR material and the extractable P concentrations (Olsen P). It is also evident that the extent of dissolution increases, while that of P extractability decreases, as the P sorption capacity of the soils increases.

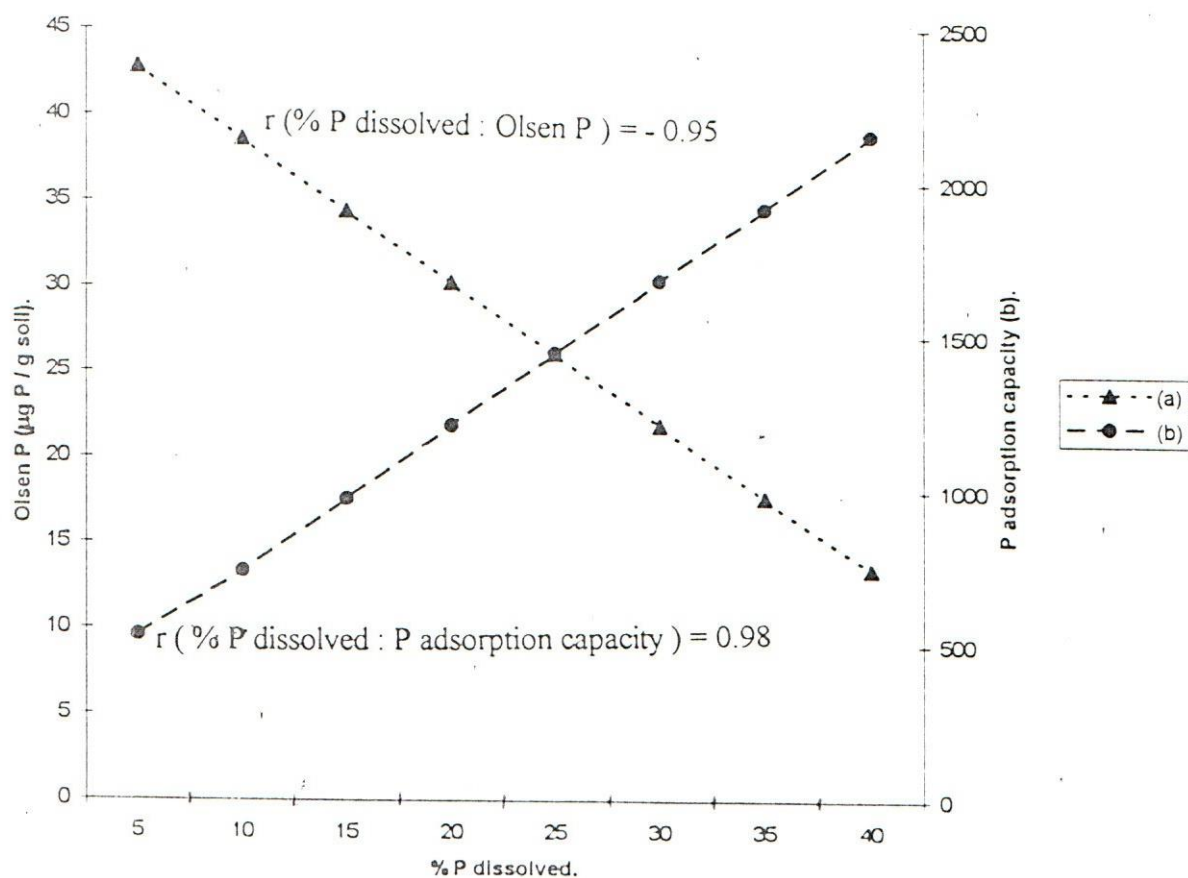


Figure 4,6 The relationship between (a) % P dissolved of MPR and Olsen P values, (b) % P dissolved of MPR and P sorption capacity.

CHAPTER 5

DISCUSSION

5.1 Initial soil properties.

The soils studied can generally be divided into four groups: andosol (Njoro), ferralsols (Sotik and Kaptagat), nitisols (Kericho and Timboroa), and phaeozems (Lanet) (FAO/UNESCO, 1988).

The measured soil pH values in water and CaCl_2 solutions are typical for tropical soils (Sanchez, 1976). The lower pH values in CaCl_2 than in H_2O suggest that the soils studied possessed variably charged components (Uehara and Gillman, 1981).

The moderately acidic soils such as the Kericho, Sotik, Timboroa, and the Kaptagat showed higher Fe_{OX} and Al_{OX} values than the slightly acid soils (Njoro and Lanet). This is probably due to the weathering and leaching of soil minerals in high rainfall areas which lead to the enrichment of soils with hydrated oxides of Fe and Al (Sanchez, 1976). Such processes tend to lower pH, and CEC values (Table 4.1). Similar observations have been made by other workers (Uehara and Gillman, 1981).

The organic C contents for all the soils were in the medium range. This may be due to plant residues arising from the intensive agricultural activities and the favourable climatic conditions of the studied regions (Table 4.1). In soils where organic matter plays significant role in cation exchange reactions, close correlation between % C contents and CEC would be expected (Sanchez, 1976). In this study, however, the lower correlation coefficients between %

C and CEC of the soils ($r=-0.35$) suggested that organic matter may not be a significant component of cation exchange reactions of the soils studied.

The CEC values are in agreement with the results of other workers (Okalebo *et al.*, 1991;). The moderate to high levels of Exch.Ca values suggest that minimal leaching losses of Exch.Ca in the soils studied occurred. This may be due to the medium organic C contents of the soils. Exch.Ca may complex with organic matter thereby preventing excessive leaching losses. In general the exch.Ca values paralleled the CEC values. Thus soils with low CEC values generally indicated low Exch.Ca values (Table 4.1).

Results from the P adsorption isotherms (Table 4.2 and Figure 4.1a-c) indicated that the soils studied had P adsorption capacities in the order Kericho > Kaptagat > Timboroa > Sotik > Lanet > Njoro. This trend was generally reflected, as expected, by the trend of Fe_{OX} and Al_{OX} values (Table 4.1). Positive correlation between P adsorption capacity (b) with Fe_{OX} and Al_{OX} as observed in this study (Figure 4.3a-f), is well established (Sanchez, 1976; Sanyal and De Datta, 1991; Lyamuremye *et al.*, 1996). As expected, the native Olsen P values were low for the moderately acidic soils and high for the slightly acidic soils in line with the order of the P adsorption capacities of the soils (Table 4.1., Figure 4.1a-c).

5.2 Effect of rate of application and period of reaction on dissolution of Minjingu PR.

When PRs dissolve in soils, Ca and P ions are released (See equation 2.1, Chapter Two). Thus increases in concentrations of Ca and P in PR-treated soils over the control are indicators of PR dissolution. In this study, the extractable Ca (Tables 4.5 and 4.6) and P (Table

4.9) concentrations increased in all the PR-treated soils over the control treatments. This suggests that the dissolution of MPR fertilizer must have occurred in all the soils studied.

Changes in pH may also occur during dissolution due to the consumption of H^+ ions by substituted CO_3^{2-} in the crystal lattice of a PR material, and free carbonates which are associated with a PR material (Khasawneh and Doll, 1978; Chien and Menon, 1995). Precipitation of Al by P released from dissolving PR, and P retention in soil colloids occurring through ligand OH^- exchange have also been advanced as possible causes of pH increases during PR dissolution (Ikerra *et al.*, 1994; Chien and Menon, 1995). Thus the slight increases of the soil pH values (Table 4.4) in the MPR treated soils over the control treatments are also indicative of dissolution of the PR material. The higher pH changes (0.11-0.22) observed in the moderately acidic soils (Kericho, Kaptagat, Sotik, and Timboroa) compared to the pH changes (0.006-0.007) in the weakly acidic soils (Njoro and Lanet) suggest that MPR dissolved better in the moderately acidic soils than in the weakly acidic soils. These observations are consistent with the observations reported by other workers (Utomo, 1995; Chien and Menon, 1995; Chepkwony, 1991).

Although the pH values tended to decrease following SSP addition, they were virtually similar statistically to the pH values in the control treatments (Table 4.4). It would be expected that addition of SSP fertilizer to soils would lower the pH values due to the resultant acidic solution arising when the SSP fertilizer dissolves in soils (Tisdale *et al.*, 1985). It is possible that the studied soils buffered the pH changes by releasing OH^- ions thereby counteracting the lowering of pH.

In all the soils, the amounts of MPR dissolved were greater at the higher rate of P application (P-2) than at the lower rate (P-1) (Table 4.7) in agreement with the results of other

workers (Hammond *et al.*, 1986). As expected, greater amounts of Ca (and P) would be released into the soils per unit weight of PR material at the higher rate of P application. Robinson and Syers (1991) found out that the Ca sink (i.e CEC of soils) is an important factor controlling PR dissolution. It would be expected that, higher rates of application would result in the saturation of cation exchange sites with the Ca ions thereby preventing further dissolution. Results obtained in this study suggest that such a stage had not been reached even at the application rate of 500 $\mu\text{gP/g}$ dry soil used in the study.

The increases in the amounts of MPR dissolved with time suggest that the reaction of the PR fertilizer with the soils was continuing. This continuing nature of the reactions tended to decrease with time as the equilibrium conditions were approached (Figure.4.4), when the Ca and the P sinks were becoming saturated with these ions. Similar findings have been reported by several workers working on other PR dissolution studies in incubated soils (Robinson and Syers, 1990; Chepkwony, 1991; Hanafi *et al.*, 1992; Samid-Sjarif, 1992).

The differences between the soils studied in the amounts of MPR dissolved (Tables 4.7, 4.8) were expected. This was attributed to the differences in the chemical properties of the soils such as pH, Ca and P status, CEC and P sorption capacity (Table 4.1). These soil chemical properties are known to influence PR dissolution (Le Mare, 1991; Chien and Menon, 1995) thereby resulting in different extents of PR dissolution in soils.

The relationship between the extents of MPR dissolution and some of the selected chemical properties of the soils studied are discussed in section 5.4.

The initial rapid dissolution stage and the subsequent slow dissolution in the dissolution kinetics of MPR fertilizer (Figure 4.4) are the characteristic features of PR dissolution in incubated soils (Hanafi *et al.*, 1992; Robinson and Syers, 1991). It should be noted from

equation 2.1 (Chapter Two) that for continuous dissolution of a PR material in soil, there must be a constant supply of H^+ ions, and limitless Ca and P sinks. This phenomenon can only occur under field conditions where the Ca and P ions are removed from dissolving PR environment through plant uptake or leaching processes. For incubated experiments, however, the sources of H^+ ions and sinks for Ca and P may be limiting. Hence PR dissolution frequently approaches an equilibrium state after an initial rapid stage. The initial rapid dissolution stage of the PR material can be attributed to the dissolution of $CaCO_3$ mineral which is present as an accessory mineral in the MPR fertilizer (Table 3.1), dissolution of a more soluble fraction of a PR material, or the favourable soil factors e.g. pH, Ca and P sinks (Hanafi *et al.*, 1992; Robinson and Syers, 1991). The slow dissolution rate occurring much later can be attributed to the dissolution of a less soluble PR fraction, or inhibition of further dissolution caused by increased pH, or saturation of Ca and P sinks (Sanyal and De Datta, 1991; Robinson and Syers, 1991).

5.3 Effects of P source, rate of application, and period of reaction on P extractability.

Dissolution of P fertilizer 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. $NaHCO_3$ extractant preferentially extract Al-P and Fe-P reaction products that are formed after P fertilizer 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 $NaHCO_3$ -extractable P concentrations in the

added P treatments (P-1 and P-2) over the control (P-0) (Table 4.9) originate from the plant-available P pool.

The differences between the P sources in the amounts of extractable P at both rates of the added fertilizer are attributable to the differences in the dissolution behaviours between water-soluble P and PR fertilizers. SSP is a readily water-soluble fertilizer and hence gives rise to higher amounts of extractable P concentrations. In contrast, MPR fertilizer dissolves slowly over time in soils resulting in lower amounts of extractable P concentrations (Table 4.9) (Hammond *et al*, 1986; Sanyal and De Datta, 1991).

The higher amounts of extractable P concentrations observed for the higher rates of P addition (P-2) compared to the lower rates (P-1) for the MPR treatments (and also for the SSP treatments) are in agreement with the corresponding dissolution data observed for the MPR material.

For both P sources, the amounts of extractable P concentrations differed among the soils. The generally lower amounts of extractable P concentrations in the moderately acidic soils (Kericho, Kaptagat, Timboroa, and Sotik) compared to the extractable P concentrations in the slightly acidic soils (Njoro and Lanet) (Table 4.9) are in line with their order of P adsorption capacities (Table 4.2, Figure 4.1a-c). Soils having relatively high P adsorption capacities such as the Kericho, Timboroa, Sotik and Kaptagat soils tend to maintain lower levels of extractable P concentrations compared to the soils with relatively low P adsorption capacities (Sanchez, 1976; Smyth and Sanchez, 1982; Sanyal and De Datta, 1991). This finding suggests that, although soils having high P adsorption capacities may favour increased dissolution of a PR materials, the dissolved P may not be readily available for plants. Similar conclusions have been drawn by

other workers (Harris *et al*, 1984; Watkinson, 1990). The relationship between PR dissolution, P adsorption capacities and P extractability is discussed in section 5.5.

The difference shown by the effect of reaction time on the amounts of extractable P concentrations of the P sources (Figure 4.5) can, again, be attributed to the differing solubilities of the P sources in the soils and the subsequent fixation reactions of dissolved P by soil components.

For the readily water-soluble SSP fertilizer, virtually all the P would be released immediately once the fertilizer is in contact with the soil (Sanyal and De Datta, 1991). Consequently dissolved P would be exposed for 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 (Figure, 4.5).

For the water-insoluble MPR fertilizer, both dissolution reactions of the PR material and fixation reactions of dissolved P occur concurrently. The observed initial rise in the amounts of extractable P concentrations (Figure 4.5) suggest that dissolution of the PR material dominated fixation reactions of dissolved P. As time progressed, the dissolution of the PR material approached equilibrium condition and thus the fixation reactions became the dominant reaction. Dissolved P therefore began to decline (Figure 4.5).

The above finding suggests that prolonged reaction of a PR material with soil before sowing a crop may result in a decline of dissolved P leading to decreased availability. This may be particularly the case in soils having high P adsorption capacities such as the Kericho, Sotik, Timboroa, and the Kaptagat soils (Figure 4.1a-c, Table 4.3)

5.4 Relationship between PR dissolution and some initial soil chemical properties.

The observed negative correlation coefficients between the rates and extents of MPR dissolution with soil pH, Exch.Ca, and Olsen P values (Table 4.10, 4.12) are in agreement with the chemical principles of PR dissolution in soils (see equation 2.1. Chapter Two). These findings suggest that dissolution of PR materials would be greater in acid soils with relatively low pH, exch.Ca, and Olsen P values than in acid soils with relatively high pH, exch.Ca and Olsen P values. A similar suggestion has been made by other workers cited by Khasawneh and Doll (1978), Bolan *et al.* (1990), and Chien and Menon (1995).

The lack of a significant correlation coefficient between % P dissolved with soil pH (Table 4.10) indicated that soil pH might have not been an important soil property influencing the dissolution of MPR material in the soils studied. This finding concurs with that of Mackay *et al.* (1986) who, in studying a range of contrasting temperate New Zealand acid soils, found that soil pH had a small influence on PR dissolution. Similar results have also been reported by De-Datta *et al.* (1990) in a study of PR dissolution in tropical Asian acid soils.

Several workers cited by Khasawneh and Doll (1978) have, however, regarded soil acidity as an important variable influencing the dissolution of PR materials in soils. These workers have, however, inferred the increases in PR dissolution from increases in crop yields and P uptake studies. However, incorrect conclusion may be drawn from such studies due to the indirect influence of plant species on PR availability (Hammond *et al.*, 1986; Chien and Menon, 1995) and the effect of pH on other P-soil interactions (Haynes, 1982; Chepkwony, 1991).

The high significant correlation coefficients between % P dissolved of MPR fertilizer with exch.Ca and Olsen P values (Table 4.10) indicated the relative importance of the Ca and P status of soils in influencing the dissolution of PR material. Mackay *et al.* (1986) also reported that exch.Ca had a significant effect on dissolution of PR materials in New Zealand acid soils. De Datta *et al.* (1990) found that dissolution of PRs depended strongly on exch.Ca content of the soils.

For continuous dissolution of a PR material in soil, however, continuous supply of H^+ ions and removal of dissolved Ca and P ions from dissolving PR environment are essential. In the absence of plant uptake and leaching, dissolved P and Ca ions would be removed through a number of fixation processes including cation and anion adsorption reactions (Khasawneh and Doll, 1978). The sink for P is predominantly the P sorption complex which is largely determined by the amount of Fe and Al hydrous oxides (Sanchez, 1976). The soil sink for Ca is provided by its CEC enabling the Ca which is dissociated from the apatite surface to become part of the soil exchange complex (Khasawneh and Doll, 1978).

Thus the observed positive and highly significant correlation coefficients between % P dissolved of MPR with P sorption parameter, b , values (Table 4.10) are expected. This finding is in agreement with a number of other studies which have shown that PR dissolution increases with increasing P sorption capacity of the soils (Mackay *et al.*, 1986; Symth and Sanchez, 1982; Kanabo and Gilkes, 1987; Samid-Sjarif, 1992). The positive correlation coefficients between % P dissolved of MPR with Fe_{OX} and Al_{OX} are not surprising since P sorption capacity parameter, b , is itself correlated with Fe_{OX} and Al_{OX} (Figure 4.3a-b). Hydrous Fe and Al oxides are known to play an important role in P fixation in acid soils. Sanchez (1976) attributed the greater

dissolution of PRs in soils containing large amounts of Fe, to the more effective removal of dissolved P by Fe minerals in high Fe soils.

The lack of significant correlation coefficient between % P dissolved and CEC (Table 4.10) suggests that the Ca sink (CEC) was not effective in reducing the build-up of Ca concentration around the dissolving PR material. This result can be explained by the fact that most of the soils studied generally had low CEC. Such soils provide poorer sinks for dissolved Ca than soils with relatively high CEC (Khasawneh and Doll, 1978).

The significant positive correlation coefficients observed between % P dissolved and % C indicated that organic matter was an important soil characteristic influencing PR dissolution. This finding is consistent with the results of Ikerra *et al.* (1994) who reported that application of compost and farmyard manure enhanced the dissolution of MPR fertilizer in a Tanzanian Ultisol. Organic matter may act as a sink for dissolved Ca through its Chelating effect and hence enhance PR dissolution (Hammond *et al.*, 1986).

The lack of significant correlation coefficients between % P dissolved with any single soil chemical property at the early part of the incubation experiment (4d) is consistent with the low extent of MPR dissolution at that time (Table 4.8). The finding that P sorption capacity gave the highest correlation coefficient ($r = 0.96$) with % P dissolved of MPR compared to the other soil chemical properties tested in this study indicated the importance of P sorption capacity in the prediction of PR dissolution in acid soils.

5.5 Relationship between percent dissolution, P extractability and P sorption capacity.

As mentioned above, the dissolution of a P source is normally a necessary pre-requisite for the added P to be plant available (Sanyal and De Datta, 1991).

If the extractable P in the soils is assumed to be principally derived from the P fertilizer, then the P concentrations in the soil solution (in the absence of plant uptake and leaching losses) is controlled by dissolution and fixation reactions. The dissolution reactions tend to increase the P concentration in soil, while fixation process tends to decrease P concentration in soil. Both processes occur concurrently. Thus in incubated experiments, the measured extractable P concentrations in soil solution are the net effect of the two counteracting processes.

The highly significant negative correlation coefficient ($r = -0.95$) between % P dissolved of MPR and the extractable P concentrations (Figure 4.6) indicated that the increased PR dissolution does not necessarily produce proportional increases in extractable P concentrations, particularly in acid soils having higher P fixation. For example, the high P-fixing soils e.g. the Kericho soil which favoured high PR dissolution, yielded the lowest extractable P concentration. On the other hand, the low P-fixing soils e.g. Njoro which favoured low PR dissolution, yielded highest extractable P concentrations (Tables 4.3, 4.8, 4.9, Figure 4.6).

It is apparent that high P fixing soils may stimulate the initial dissolution of a PR material but have a negative effect on the subsequent availability of the dissolved P. Similar results and conclusion have been reported by other workers (Harris *et al.*, 1987; Kanabo and Gilkes, 1986; Butegewa *et al.*, 1996).

CHAPTER 6

SUMMARY AND CONCLUSIONS

The dissolution reaction of a PR material in an acid soil (equation 2, Chapter Two) suggests, in general, that PR dissolution is greater in more acidic soils (low pH, low exch.Ca and P) than in less acid soils (high pH, high exch.Ca and P).

The results obtained in this study showed, indeed, that the extent of MPR dissolution was greater in the moderately acidic soils (Kericho, Sotik, Kaptagat, and Timboroa) than in the slightly acidic soils (Njoro and Lanet). This finding was attributed to the differences in the chemical properties of the soils.

The extent of MPR dissolution increased with the rate of P application. This result was attributed to the greater fertilizer input per unit weight of soil at the higher rate of application comparable to the lower rate of application.

Also the results showed that the extent of MPR dissolution increased with the period of the fertilizer reaction with the soils. This finding was attributed to the slow and continuing dissolution reaction typical of PR materials in soils.

Of the initial soil Chemical properties selected, Olsen P, % C, and P adsorption capacity were significantly related to the extent of MPR dissolution; the most predictive property being P adsorption capacity of the soil. Soil pH was not significantly related to the extent of MPR dissolution. This finding further indicated that exch.Ca, organic matter content (% C), P concentrations and P adsorption capacity were the key chemical properties influencing the dissolution of MPR fertilizer in the six soils studied. However,

further research needs to be done using a wider number of acid soils having contrasting chemical properties to verify this finding.

No single soil chemical property significantly related to the extent of MPR dissolution at the early stages of incubation, probably because low amount of fertilizer had dissolved. As in the above conclusion, further work needs to be done on a wider number of acid soils to verify this finding.

The extractable P concentrations were higher in the SSP-treatments than in the MPR-treatments. This was attributed to the differences in solubilities of the P sources. Also the extractable P concentrations differed among the soils. The moderately acidic soils (Kericho, Sotik, Timboroa, and Kaptagat) yielded lower extractable P than the values in the slightly acidic soils. This was attributed to the differences in the P adsorption capacities of the soils. This finding suggested that the effectiveness of the MPR fertilizer may be comparable in the two groups of the soils. This is a possible area for future research.

The extractable P concentrations increased with the rate of application for both fertilizers. This was attributed to the greater amount of P added per unit weight of soil at the higher rate of application compared to that of the lower rate of application.

The extractable P concentrations for SSP-treatments consistently decreased with time due to fixation reactions by the soil components. The decrease were more marked in the moderately acidic soils (high P-adsorbing) than in the slightly acidic soils (low P-adsorbing). On the other hand, the extractable P concentrations for the MPR-treatments initially increased with time due to the slow continuing dissolution reaction and then declined subsequently. It was suggested that the dissolution reactions slowed down with time as fixation reaction became the dominant reaction. This finding suggests that the

effectiveness of MPR material as fertilizer may decrease with time particularly in high P-adsorbing soils such as Kericho, Kaptagat, Sotik, and Timboroa.

Highly significant negative correlation was obtained in the MPR-treatments between the extent of dissolution and extractable P concentrations. This finding showed that, although the high P adsorbing soils (Kericho, Timboroa, Sotik, and Kaptagat) promoted the dissolution of MPR fertilizer, the dissolved P was subsequently fixed by the soil. It is concluded that an increase in PR dissolution does not necessarily result in high plant-available P values in high P-adsorbing soils. The major factor limiting the effectiveness of a PR fertilizer in such soils is fixation reactions. An evaluation study in real field situation of the effectiveness of MPR material as a fertilizer in high P-adsorbing tropical soils needs to be carried out in future.

REFERENCES

- Anderson, D.I.; Kussow, W.R. and Lorey, R.B. 1985. Phosphate rock dissolution in soil. Indication in plant growth studies. *Soil science society of American Journal* **49**:918-925.
- Bangar, K.C.; Yandar, K.S. and Mishra, M.M. 1985. Transformation of rock phosphate during composting and the effect of humic acid. *Plant and Soil* **85**:259-266.
- Barrow, N.J. 1980. Evaluation and utilization of residual phosphorus in soils. In ;F,E khasawneh, E,C Samples and E.J Kamrath(editors). The role of phosphorus in Agriculture. *America Society of Agronomy*, Madson, Wisconsin.
- Bekele, C.T.; Cino, B.J.; Ehlert, P.A.; Van Der Maas, A.A. and Van Diest, A. 1983. An evaluation of plant-borne factors promoting the solubilization of alkaline rock phosphates; *Plant and Soil* **75**:361-378.
- Black, C.A. 1965. *Methods of Soil Analysis*, part 2. Chemical and microbiological properties. American society of agronomy. Inc. publishing, Madison. U.S.A.
- Bolan, N.S. and Hedley, M.J. 1989. Dissolution of phosphate rocks in soils: Evaluation of extraction methods for the measurements of phosphate rock dissolution. *Fertilizer Research* **19**:65-75.
- Bolan, R.E.; White, and Hedley, M.J; 1990. A review of the use of phosphate rocks as fertilizers for direct application in Australia and New Zealand. *Australian journal of Experimental Agriculture* **30**:297-313.
- Bollan, M.A. and Gilkes, R.J. 1989. Reactive rock phosphate fertilizers and soil testing for phosphorus: The effect of particle size of the rock phosphate. *Fertilizer Research* **21**:75- 93.
- Bolland, M.D.; Gilkes, R.J. and D'Antuono, M.F. 1988. The effectiveness of rock phosphate fertilizers in Australian Agriculture: *Australian Journal Experimental Agriculture* **28**:653-68.
- Bowden, J.W.; Nagarajah, S.; Barrow, N.; Posner, A.M. and Quirk, J.PJ 1980. Describing the adsorption of phosphate, citrate, and selenite on a variable-charge mineral surface. *Australian Journal of Soil Research* **18**:49-60.
- Brady, N.C. 1984. *Nature and Properties of Soils*; 9th Edition. MacMillan Publishing Company, New York.
- Butegewa, C.N.; Mullins, G.L. and Chien, S.H. 1996. Agronomic evaluation of fertilizer products derived from Sukulu Hill phosphate rock. *Fertilizer Research* **44**:113-122.

- Chepkwony, C.K, 1991: *Availability of phosphate fertilisers in unlimed and limed acid soils as affected by wetting and Air-drying*, Ph.D Thesis (unpublished) Lincoln University, New Zealand.
- Chien, S.H; 1992: Reactions of Phosphate rocks with acid soils of humid tropics. Proceedings of the workshop on phosphate sources for acid soils in humid tropics of Asia, Kuala Lumpur *Malaysian Society of Soil Science*. Kuala Lumpur, Malaysia. pp 18-29.
- Chien, S.H.; Leon, L.A. and Tejera, H.R. 1980. Dissolution of North Carolina phosphate rock in acid Colombian soils as related to soil properties. *Soil Science Society of America Journal* **44**: 1267-1271.
- Chien, S. and Menon, R. 1995. Factors affecting agronomic effectiveness of rock phosphate for direct application. *Fertilizer research* **41**: 227-234.
- Chu, C.; Moschler, W. and Thomas, G. 1962. Rock phosphate transformations in soils. *Soil Science Society of America Journal* **26**: 476-478.
- Cobala-Rosand, P. and Wild, A. 1982a. Direct use of low grade phosphate rock from Brazil as fertilizer. I. Effect of reaction time in soil. *Plant and Soil* **65**: 351-362.
- Cobala-Rosand, P. and Wild, A. 1982b. Direct use of low grade phosphate rock from Brazil as fertilizer. II. Effect of mycorrhizal inoculation and nitrogen source. *Plant and Soil* **65**: 363-373.
- De-Datta, S.K.; Sanyal, S. and Chan, P. 1992. Dissolution and agronomic efficiency of phosphate rock and partially acidulated phosphate rocks fertilizers in some acid lowland rice soils in tropical Asia. Proceedings of the workshop on phosphate sources for acid soils in humid tropics of Asia, *Malaysia Society of Soils science*. Kuala Lumpur, Malaysia pp 145-162.
- Farm Management Handbook of Kenya, 1982(II). *Natural Conditions and Farm Management Information*. Nairobi, Kenya.
- Fertilizer Use Recommendation Project (FURP). 1987. *Fertilizer Use Recommendations*. Kenya Agricultural Research Institute.
- Food and Agriculture Organisation/UNESCO. 1988. *Soil Map of The World*. Legend, Rome.
- Flach, E.N.; Quak, W. and Van Diest, A. 1987. A comparison of rock phosphate mobilising capacities of various crops species. *Tropical Agriculture* **64**: 347-351.
- Fresse, D.; Lookman, R. and Van Reimsdijk, K.H. 1995. New methods for assessment of long-term phosphate desorption from soils. *Soil Science Society of America Journal* **59**: 1295-1300.

- Gilkes, R.J. and Bolland M.D.A. 1992. The Australian experience with rock phosphates; limitations and explanation. Proceedings of the workshop on phosphate sources for acid soils in the humid tropics of Asia. *Malaysia Society of soil Science*. Kuala Lumpur Malaysia 1, pp 177-205.
- Hammond, L.L.; Chien, S.H. and Mokwunye A.U. 1986: Agronomic value of unacidulated and partially acidulated phosphate Rocks indigenous to the tropics. *Advances in agronomy* **40**: 89-140.
- Hanafi, M.M.; Syers, J.K. and Bolan, U.S. 1992: Leaching effect on the dissolution of two phosphate rocks in acid soils. *Soil Science Society of America Journal* **56**: 1325-1330.
- Harris D. C. 1987. *Quantitative Chemical Analysis*. 2nd Edition Freeman and Co. New York.
- Haynes, R.J. 1982. Effects of liming on phosphate availability in acid soils. *Plant and Soil* **68**: 289-308.
- Hayne, R.J. 1984. Lime and phosphate in the soil-plant system. *Advances in Agronomy* **37**: 249-315.
- Hesse P.R. 1972. *Chemical Analysis*. Chemical Publishing Co. Inc. New York. U.S.A.
- Hudges, J.C. and Gilkes, R.J. 1986. The effect of rock phosphate properties on the extent of fertilizer dissolution in soils. *Australian Journal of Soil Research* **24**: 209-217.
- Ikerra, T.D.; Mkeni, P.S. and Singh, B.R. 1994. Effects of added compost and farmyard manure on phosphorus release from Minjingu phosphate rock and its uptake by maize. *Norwegian Journal of Agricultural Sciences* **8**: 14-23.
- Kanabo, I.R. and Gilkes, R.J. 1987a. The role of soil pH in the dissolution of phosphate rock fertilizers. *Fertilizer Research* **12**: 165-173.
- Kanabo, I.R. and Gilkes, R.J. 1987b. A comparison between plants response and chemical measurements of the dissolution of the reactive phosphate rock in soils of different pH and phosphate retention. *Australian Journal of Soil Research* **25**: 451-460.
- Kanabo, I.R. and Gilkes, R.J. 1988a. Effects of moisture regime and incubation period on dissolution of North carolina phosphate rock in soils. *Australian Journal of Soil Research* **26**: 153-163.
- Kenya Agricultural Research Institute (KARI), 1994. *Annual Report*. Nairobi, Kenya.
- Kenya Soil Survey, 1974. *Ministry of Agriculture (D14)*. Nairobi, Kenya.

- Khasawneh, F.E. and Doll E.C. 1978: The use of phosphate rock for direct application to soils. *Advances in Agronomy* 30:159-205.
- Kovar, J.L. and Barber, S.A. 1988. Phosphorus supply characteristics of 33 soils as influenced by seven rates of application. *Soil Science Society of America* 52: 416-421.
- Le mare, P.H. 1991. Rock phosphates in agriculture. *Experimental agriculture* 27:413-422.
- Le mare, P.H. and Leon, L.A. 1989. The effect of lime on adsorption and desorption of phosphate in five Colombian soils. *Journal of Soil Science* 40:59-69.
- Leon, L.A.; Fenster, W.A. and Hammond, L.L. 1986. Agronomical potential of eleven phosphate rocks from Brazil, Colombia, Peru and Venezuela. *Science Society of America Journal* 50:798-802.
- Lindsay, W.L. 1979. *Chemical Equilibria in Soils*. Wiley and Sons. New York
- Lyamuremye, F.; Dick, R.P. and Baham, J. 1996. Organic ammendments and phosphorus dynamics: Phosphorus chemistry and sorption. *Soil Science* 161:231-235.
- Mackay, A.D.; Syers, J.K. Gregg, P.H. and Tillman, R.W. 1984. A comparison of 3 soil testing procedures for estimating the plant availability of phosphorus in soils receiving either superphosphate or phosphate rock. *New Zealand Journal of Agricultural Research* 27:231-245.
- Mackay, D.A and Syers, J.K. 1986: Effect of phosphate, calcium and pH on the dissolution of a phosphate rock in soil. *Fertilizer Research* 10:175-84.
- Mackay, A.D.; Syers, J.K.; Tillman, R.W, and Gregg, P.H. 1986. simple model to describe the dissolution of phosphate rock in soils. *Soil Science Society of America Journal* 50:291-296.
- Marwaha, B.C.; Kanwar, B.S. and Tripathi, B.R. 1981. Direct and residual effectiveness of Mosoorie rock phosphate in wheat- maize rotation. *Indian Journal of Agricultural Sciences*. 51:870-874.
- Mahimairaja, S.; Bolan, S.N. and Hedley, M.J. 1995. Dissolution of phosphate rock during composting of poultry manure. *Fertilizer research* 40:93-104.
- Mclaughlin, J.R.; Ryden, J.C. and Syers. R.J. 1981. Sorption of phosphates by iron and aluminium containing compounds. *Journal of Soil Science* 32:365-377.
- Menon, R.G.; Chien, S.H. and Hammond, L.L. 1989. Comparison of Bray-1 and Pt tests for evaluating plant-available phosphorus from soils treated with different partially acidulated phosphate rocks. *Plant and Soil* 114: 211-216.

- Menon, R.G.; Chien and S.H. Gadall, A.N. 1991: Phosphate rocks compacted superphosphate verses partially acidulated rocks for beans and rice. *Soil Science Society of America Journal* **55**:1480-1484.
- Mokwunye, A.U; Chien, S.H, and Rhodes, E. 1986. Phosphate reactions with tropical Africa soils. In: A.U Mokwunye and Vlek (editors). *Management of nitrogen and phosphorus in sub-saharan Africa*. Kluwer Academic publishers. Lancaster, pp.253-281.
- Morel, C. and Fardeau, J.C. 1990. Uptake of phosphates from soils and fertilizers as affected by soil phosphorus availability and solubility of phosphorus. *Plant and Soil* **121**:217-224.
- New Zealand Fertilizer Manufacturers' Research Association (NZFMRA). 1983. *Analytical methods for fertilizer materials*. New Zealand Fertilizer Manufacturers' Research Association. Auckland.
- Okalebo, Gathua, and Woomer, 1993. *Laboratory Methods of Soil and Plant Analysis; A working manual*. Nairobi, Kenya.
- Owusu-Bennaoh, E and Acquaye, D.K. 1989. Phosphate sorption characteristics of selected Ghanaian soils. *Soil Science* **148**:114-123.
- Parfitt, R. L. 1977. Phosphate adsorption on an oxisol. *Soil Science Society of America Journal* **41**:1064-1067.
- Robinson J.S. and Syers J.K., 1990. A critical evaluation of the factors influencing the dissolution of Gafsa phosphate rock. *Journal of Soil Science* **45**:597-605.
- Ryden, J.C.; Syers, J.K and Tillman, R.W. 1987. Inorganic anion sorption and interaction of phosphates by hydrous ferric oxide gel. *Journal of Soil Science* **38**:211-217.
- Saggar, S.; Hedley, M.J. and White, R.E 1990. A simplified resin membrane technique for extracting phosphorus from soils. *Fertilizer Research* **24**:173-180.
- Samid-Sjarif, 1992. Phosphate rock dissolution in Indonesia andosols. Proceedings of the workshop on phosphates sources for acid soils in humid Tropics of Asia. Kuala Lumpur. *Malaysian Society of Soil Sciences* Kuala Lumpur. Malaysia. pp 43-58.
- Sanchez, P.A. 1976. *Properties and Management of Soils in the Tropics*. John Wiley and Sons. New York.
- Sanchez, P.A. and Gichuru, M.P. 1988. Phosphate rock fertilisation in tilled and non-tilled low-input systems in the humid tropics. *Plant and Soil* **24**:213-217.

- Sanchez and Uehara. 1980. Management consideration for acid soils with high phosphorous fixation capacity. In F.E. Khasawneh *et al.* (Editors). The Role of phosphorus in Agriculture. *American Society of Agronomy*. Madison, Wisconsin pp. 471-514.
- Sanyal, S.K. and De Datta S.K. 1990. Chemistry of phosphorus transformation in Soil. *Advances in Soil Science* 16:1-79.
- Sarkar, D. and Sarkar, M.C. 1992. Efficiency of Mussoorie rock phosphate for rice in acidic soils of Assam. *Journal of Indian Society of Soil Sciences*.30:48-52.
- Sauchelli, W. 1965. *Phosphates in Agriculture*. Reinhold Publishing Co. New York. USA.
- Sibbesen, E. 1978. An investigation of the anion-exchange resin method for soil phosphorus extraction. *Plant and Soil* 50:305-321.
- Shama, S.N. and Prasad, R. 1996. Mussoorie rock phosphate P-pyrite mixture as phosphate fertilizer. *Fertilizer Research* 45:187-191.
- Silva, E.M.R., Almeida, D.D.L., Franco, A.A., and Dobereiner, J. 1985. Effect of green manuring on the availability of phosphate in an acid soil. *Revista-Brasileira-de-Ciencia-do-Solo* (Brazil) 9:85-88.
- Sposito, G. 1989. *The Chemistry of Soils*. Oxford University press. New York.
- Sri-Adiningsih, J. and Sri-Rochayat. 1992. Use of phosphate fertilizer in arable food crop production in Indonesia. Proceedings of the workshop on phosphate sources in acid soils in humid Tropical soils of Asia, Kuala Lumpur. *Malaysian Society of Soil Science* Kuala Lumpur, Malaysia. pp 117-133.
- Stevenson, F.J. 1986. Cycles of Soil, Carbon, Nitrogen Phosphorus, Sulphur, and Micronutrients. Wiley, New York.
- Stewart, E.A. 1989. *Chemical Analysis of Ecological Materials*. 2nd Ed. Blackwell Scientific Publications. Oxford.
- Symth, T.J. and Sanchez, D.A. 1982. Phosphate dissolution and availability in Cerrado soils as affected by phosphorus sorption capacity. *Soil Science Society of America Journal* 46:339-345.
- Tisdale, S.L.; Nelson, W.L.; and Beston, J.D. 1985. *Soil Fertility and Fertilizers*, 4th Edition. MacMillan Publishing Co. New York.
- Uehara, G. and Gillman, G. 1981. *The Mineralogy, Chemistry, and Physics of Tropical Soils With Variable Charge Clays*. Westview Press. Boulder, Colorado.

- Utomo M. 1995. Effects of rock phosphates and apparent phosphorus recovery in acid soils of Sumatra. *Plant and Soil* **171**:199-202.
- Van der Berghe, C.H. 1996. The effects of Matongo rock phosphate and Urea as compared to diammonium phosphate in the composting process and the yield of potatoes in the Mugamba region of Burundi. *Fertilizer Research* **45**:51-59.
- Watkinson, J.H. 1994. A test for phosphate rock reactivity in which solubility and size are combined in a dissolution rate function. *Fertilizer Research* **39**:205-215.