A COMPARISON OF RATE OF DISSOLUTION OF DIFFERENT SOURCES OF PHOSPHATE ROCK AND THEIR AGRONOMIC EFFECTIVENESS IN THREE BENCHMARK SOILS OF GHANA

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Master of Philosophy

in the

Department of Soil Science

University of Ghana

by

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August, 1999.

DEDICATION

Dedicated to all my uncles and aunties.

DECLARATION

I hereby declare that this thesis has been written by me and that it is the record of my own research work. It has neither in whole nor in part been presented for another degree elsewhere. Work of other researchers have been duly cited by references to the authors and all assistance received also acknowledged.

SAMUEL KWESI ASOMANING
Candidate's Name

The above declaration is affirmed ....
Senior Supervisor

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Finally, MAY THE NAME OF THE LORD BE PRAISED. TO HIM BE THE GLORY.

CERTIFICATION

This thesis **A comparison of rate of dissolution of different sources of phosphate rock and their agronomic effectiveness in three benchmark soils of Ghana** by Samuel Kwesi Asomaning meets the regulations governing the award of the degree of Master of philosophy (Soil Science) of the University of Ghana is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

Soils of the semi-deciduous forest zone of Ghana are known to be moderately acid and very low in plant available phosphorus (P). These soils need to be fertilised to improve their potential for crop production. However high cost of commercial, water soluble fertilizers makes them beyond the reach of local farmers. Instead of expensive superphosphates, the use of less expensive phosphate rocks such as Togo rock phosphate (TRP), Gafsa rock phosphate (GRP) and 50% partially acidulated rock phosphate (PAPR-50) are possible alternative P sources for these soils. A major limitation of phosphate rock (PR), however, is its inability to satisfy early requirement of available P due to its slow rate of dissolution. The objectives of this research were to compare the rate of dissolution of TRP, GRP, PAPR-50 and TSP and their agronomic effectiveness in three benchmark soils of Ghana ; Bekwai, Nzima and Kokofu.

The dissolution of the P sources in the three soil series, was investigated in an incubation study Two-hundred grammes of each soil were incubated with TRP, GRP, PAPR-50 and TSP at a rate of 60 mg P kg^{-1} soil. A control treatment with no addition of P source was also included. Incubation of the P sources in the various soils was done at 60% field capacity and at a temperature range of 20-25°C. The extent and rate of dissolution of the fertilizers, were determined by Anion Exchange resin Membrane (AEM) extraction in chloride form , 0.1M NaOH and 1M HCl extractions at 21 days interval for 105 days. In a greenhouse study, each P source was added at the rate of 60 mg P kg^{-1} soil, incubated for 7 days and sown to maize (Zea mays. var.Toxpino) for 28 days. The same variety of maize was sown in the field, in the three soils and the various P sources were applied at the rate of 60 kg P ha^{-1} to evaluate the stubble and grain yield

yield and also to determine the relative agronomic efficiency of the P sources with respect to the grain yield.

The results of the incubation study showed that, the amount of P extracted by the AEM, (AEM-P) following the addition of GRP, PAPR or TSP decreased with time whereas TRP addition did not change with incubation time in all the three soils. There was a decrease in NaOH-Pi after a short period of incubation in both Bekwai and Nzima, the two well drained upper slope soils from the 3rd week to the 12th week followed by a slight increase in the rate of extraction as incubation progressed. In the lowland soil, Kokofu, there was a gradual increase from the 3rd week to the end of incubation period. In the case of HCl-extractable P, the HCl-Pi decreased between the 3rd and the 6th week, followed by a fairly uniform extraction with incubation period in all the three soils. The greenhouse results showed that in all the soils the following trend was observed in terms of dry matter yield: TSP = PAPR-50 > GRP > TRP. The relative agronomic efficiency (RAE) of the P sources compared with TSP also followed the trend: PAPR-50 > GRP > TRP. The field results indicated that, the application of the P fertilizers gave significantly high maize growth in the soils as a result of increased P uptake by the crop. Stubble yield, grain yield and the RAE followed the trend similar to what was obtained from the greenhouse.

The main conclusion from the study was that TRP may have little or no potential for direct application because of its insolubility in these soils. However the PAPR-50 was found to be soluble enough to sustain maize growth and development and it may be prefered to TSP considering the high cost of the latter. It was inferred that the residues of

PR and TSP in the Kokofu soil, long after first application can be more effective sources of P for plant growth than in the well drained upper slope, Bekwai and Nzima soils.

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CHAPTER ONE

1.0 INTRODUCTION

Phosphorus (P) deficiency is one of the most important soil fertility constraints in the tropics (Sanchez, 1976). This is common with some West African forest soils which are heavily leached and contain low amounts of total and available P. Acquaye and Oteng (1972), Owusu-Bennoah and Acquaye (1989) have shown that total P in 48 top soils from different ecological zones of Ghana ranged between 60 and 173 mg P kg^{-1} while the average available P value (Bray 1) was below 9 mg P kg^{-1} . Similarly, majority of soils studied in Nigeria had available P values ranging from traces to 12 mg P kg^{-1} (Uzu *et al*., 1975). Under low input agriculture as prevails in Ghana, native P supply to crops limits production and farmers who want to increase productivity must apply P fertilizers to the soils. Water soluble commercial P fertilizers are rather expensive and unaffordable by most local farmers (IFDC, 1997). The need to increase crop production with less expensive indigenous phosphate rock (PRs) must be considered as a possible option by researchers and farmers.

Africa has vast deposits of phosphate rocks (McClellan and Notholt, 1996) and large areas are occupied by acid soils. Some African countries with large PR deposits include Morocco, Senegal, Tunisia, Mali and Togo. For effective use of these deposits there is the need to evaluate their agronomic effectiveness to increase crop yield in these acid soils. Direct application of PR to increase productivity has been practised with varying degree of success over the years (Khasawneh and Doll, 1978; Hammond, *et al*., 1986; Sale and Mokwunye, 1993). For example, Togo PR was found to be agronomically ineffective in supplying P to sustain crop yield in a near neutral Savannah concretionary soil in northern Ghana (Owusu-Bennoah and Acquaye, 1996) while Gafsa rock phosphate (GRP) has been found to be reactive (Leon et al, 1986). Some greenhouse and field trials have, however, shown that PRs are more effective in acid soils than in neutral or alkaline soils (Sale and Mokwunye, 1993; Hanafi and Syers, 1994; Zapata, 1995).

Less reactive PRs which are unsuitable for direct application can be partially acidulated to convert a fraction of the phosphate rock to water-soluble form. Partially acidulated phosphate rock (PAPR) is a treated PR with less than the stiochiometric amounts of either phosphoric or sulphuric acids that are used to manufacture a water-soluble triple or single superphosphate(TSP or SSP).

In addition to factors such as chemical composition (Lehr and McClellan, 1972) and particle size (Joos and Black, 1950), the initial rate of dissolution of PR in soil is influenced by the concentration of Ca and P in the soil solution (Mackey et al., 1986). Although dissolution is a prerequisite for plant uptake of P from soil to which PR has been added, an increase in the extent of dissolution may not necessarily result in an increase in the amount of plant-available P. The P present in a slowly-soluble PR material is expected to become available to plants during the first and subsequent growing seasons, depending on the interactions between several factors such as properties of the PR material and the soil characteristics. This is because the form in which P is applied affects its reactions with the soil and its availabilty to plants and in the long-term, sorption reactions probably control the P available to plant(Syers and Mackey 1986).

Acid soils abound in some agro-ecological zones of Ghana where rainfall is very high, ranging between 1200 to 1650 mm per annum. These soils are low in P, consequently, crop yields are also low. Because local farmers are unable to afford the purchase of expensive imported water soluble P fertilizers There is the need to test the potential to use indigenous PRs in these soils to increase agricultural productivity in the country. Few studies have investigated the reactions affecting the initial dissolution and amounts of plant-available P in soils to which rock phosphate (RP) materials have been added (Owusu-Bennoah and Acquaye, 1996). A better understanding of the reactions of PR materials in soils would be useful in assessing in which soils PR materials could be used to best advantage.

The objectives of the study were;

1. to compare the rate of dissolution of Togo rock phosphate (TRP), 50% partially acidulated Togo rock phosphate (PAPR-50), Gafsa rock phosphate (GRP) and Triple superphosphate (TSP) when added to three benchmark soils of different landscape positions and
2. to determine the agronomic efficiency of these P sources in field trials.

CHAPTER TWO

2.0 LITERATURE REVIEW

21 Introduction

This chapter reviews studies that have been carried out with phosphate rocks. Attention will be focused on the relative agronomic effectiveness of phosphate rock (PR) and partially acidulated phosphate rock (PAPR). The chapter has been sectioned into five. Section A deals with phosphorus (P) status in Ghanaian soils and factors influencing it. Section B considers PR, its mineralogy, chemistry and deposits in West Africa and Africa as a whole. Section C reviews the effectiveness of PRs in tropical environment and the major factors which influence the initial effectiveness of PR when appplied to the soil. Section D considers the agronomic effectiveness of PAPR and its advantages. Section E deals with the residual effectiveness of PR and PAPR.

SECTION A

2.2 Phosphorus Status in Ghanaian Surface Soils

Generally, the nutrient that limits crop production most on Ghanaian soils is phosphorus (P), (Nye 1952; de Endredy and Montgomery, 1954). Available value, (Bray I) was below 9 mg P kg^{-1} soil in 48 top soils from different ecological zones in Ghana (Acquaye and Oteng, 1972). The low P in Ghanaian soils is attributed to the low content of mineral apatite [$Ca_3(PO_4)_2$] in the parent rocks and also the great age and intense weathering which the rocks had been subjected to (Nye and Bertheux, 1957).

However, differences in P content also exist among the soils of the three main ecological zones, namely, Savannah, Forest / Savannah intergrade and the Forest.

Deficiency of phosphate occurs widely in the savannah soils. In some soils of the savannah zone of western Africa, deficiency is so acute that plant growth ceases as soon as the phosphorus stored in the seed is exhausted (Mokwunye et al., 1986).

Total P contents of 67 top soils from high-grass savannah of Ghana averaged 134 mg P kg^{-1} (Nye and Bertheux, 1957), which are far lower than the mean values reported for some Australian (350 mg P kg^{-1}) and American (560 mg P kg^{-1}) soils by Jones and Wild, (1975). Nyamekye (1987) reported 3.5 mg P kg^{-1} (Bray 1) phosphorus for Tingoli soil series of the Nyankpala Agricultural station and Kanabo et al., (1978) reported a value of less than 10 mg P kg^{-1} in some soils of northern Ghana. The low P levels in these highly weathered soils have been attributed to low P content of the parent materials which are principally sandstone or shale (Adu, 1957) The soils are high in sesquioxides Acquaye and Oteng (1972) reported mean total inorganic P values of 81, 93 and 124 mg P kg^{-1} of 26, 8 and 14 top soils (0 - 22 cm layer) from the savannah, Forest / Savannah intergrade and forest ecological zones respectively. Total P of the 0 - 22 cm layer of profiles of 9 typical savannah soils ranged from 50 to 173 mg p kg^{-1} soils, whereas organic P values ranged from 36 to 100 mg P kg^{-1} soils (Owusu-Bennoah and Acquaye, 1989). In the forest / savannah intergrade the total P values of three typical soil series ranged from 208 to 280 mg P kg^{-1} soil whereas organic P values ranged from 91 to 221 mg P kg^{-1} soil.

Owusu-Bennoah and Acquaye (1989) also reported that the total P values of top soils of four typical forest soils ranged from 270 to 530 mg P kg^{-1} soil whereas organic P values ranged from 54 to 243 mg P kg^{-1} soil. Thus the total organic P and total inorganic

P contents of the soils of the three ecological zones follow the trend forest > Forest / Savannah intergrade > savannah.

2.2.1 Factors affecting P availability

Acquaye and Oteng (1972) have carried out studies on the influence of parent material, pH, clay content, organic matter and vegetative cover on the total, organic and inorganic P status of top-soils of 48 soil series developed over the principal parent materials in different ecological zones of Ghana.

2.2.1.1 Effect of parent materials

The apparent effect of parent materials on the P status of these soils was found to be a reflection of the natural contents of the parent rocks. Soils derived from the basic and near-neutral materials such as limestone and hornblende gneiss, Birrimain rocks and phyllite and alluvium (including shales and mudstones) were found to have higher total P status with mean contents of 240, 235 and 210 mg P kg^{-1} soil respectively. On the other hand soils derived from granite and acidic gneisses and sandstone and tertiary sands (i.e. acidic parent material and rocks) have low P contents with mean contents of 158 and 104 mg P kg^{-1} soil respectively. Junner and James (1947) found the average total P contents of 15 granitic and 10 basic rocks of Ghana to be 700 and 750 mg P kg^{-1} respectively. World averages, of 870 mg P kg^{-1} for granitic and 1230 mg P kg^{-1} for intermediate and basic rocks have been quoted by Goldschmist (1954).

2.2.1.2 Influence of pH and vegetation

The influence of pH and vegetation on the P status of the soils are a reflection of the influence of climate. In high rainfall areas the soils are acidic with low base saturation owing to extensive leaching. The mean organic and total inorganic P contents of 97 and 20.7 mg P kg^{-1} respectively of soils of pH > 5.0 were found higher than in soils of pH < 5.0 with 8.5 and 16 mg P kg^{-1} , respectively. This is due to the fact that soils with pH < 5.0 are likely to support less vegetative growth and therefore lower build up of organic P. Similarly, the higher percent organic P of forest soils, as compared with savannah soils, derives from the higher organic matter from the associated forest cover. The total, organic and inorganic P contents of soils of the three main vegetation zones were in the order; forest > forest / savannah intergrade > savannah. Nye and Bertheux (1957) also found that soils developed over similar parent materials showed higher total P in the forest belts than in the savannah zones. Nye and Greenland (1960) showed that a greater amount of vegetative matter is returned to soils under close forest as compared with open savannah.

2.2.1.3 Effect of organic carbon

In general, soils with organic C > 0.8% contained more than twice as much P as soils with organic C < 0.8%. (Acquaye and Oteng, 1972). Acquaye (1963) indicated that greater part of the total P of Ghanaian soils is usually in the organic form which becomes an important source of P supply to plants only after mineralization. Several workers (Eid et al, 1951; Friend and Birch, 1960; Acquaye, 1963; Omotoso, 1971) have stressed the importance of organic P in plant nutrition. It is presumed that organic P compounds associated with the organic matter mineralize to supplement the supply of inorganic P to growing plants.

2.2.1.4 Effect of clay content

It has been reported that the total, organic and inorganic P contents of soils increase with increasing clay content in both temperate (Williams and Saunders, 1956) and tropical soils (Acquaye and Oteng, 1972). Acquaye and Oteng (1972) showed that soils ranging in texture between sand and loamy sand had a mean total P of 101 mg P kg^{-1} whereas the heavier textured soils ranging from loam, sandy clay and clay had a mean of 216 mg P kg^{-1} soil. This was attributed to the retention and stabilization of organic phosphates by the clay (Black and Coring, 1953). It seems that the greater part of the total P is largely in combination with clay fraction which in tropical soils is mainly hydrous oxides of iron, and aluminium

SECTION B

2.3 Phosphate Rock

Phosphate rock consists of apatite, which is chemically calcium phosphate [$Ca_3(PO_4)_2$]. Phosphate rocks are important because they contain sources of calcium and phosphorus. Apatite geologically, can be igneous, sedimentary or metamorphic origin. Fluorapatite [$Ca_{10}(PO_4)_6F_2$] constitutes the principal mineral in both igneous and metamorphic PR whereas carbonate apatite [$Ca_{10}(PO_4)_6CO_3$] is the most common constituent of sedimentary PR (Mokwunye, 1995). However carbonate-fluorapatite (Francolite) [$Ca_{10}(PO_4)_{5.3}(CO_3)F_2$] may also occur (Tisdale et al,.1985). In some cases

OH^- also substitutes for part of F^{-1} to form hydroxyfluorapatite in the form of $Ca_{10}(PO_4)_6\ F_2\text{-}x(OH)x$.

2.3.1 Mineralogy and Chemistry of Phosphate Rock Sources

Work done by Lehr and McClellan (1972) on the mineralogical composition of seven sources of PR indicated that primary accessory minerals in PR included quartz, calcite, dolomite carbonates, illite clay, hydrous iron oxide and other heavy metals.

Francolites are the commonest apatites in commercial PR's. They exhibit an isomorphic substitution of $CO_3^=$ and F^- for PO_4^{3-} (McClellan and Lehr, 1969) and show a systematic decrease in P content as the moles of $CO_3^=$ and F^- increase. One important consequence of the $CO_3^=$ substitution for PO_4^{3-} in fracolite is a decrease in the a-axis unit-cell dimension of francolite It is therefore possible to estimate the degree of CO_3 substitution for PO_4 in the francolite by calculating the length of a dimension based on X-ray diffraction measurements (Chien, 1995). Previous work has shown that the degree of isomorphic substitution in the apatite structure is the key factor in determining the chemical reactivity of PR containing carbonate apatite (Lehr and McClellan, 1972). Thermodynamically, carbonate substitution for phosphate should increase the reactivity of the PR (Chien and Black, 1976; Chien, 1977). A plot of neutral ammonium citrate soluble -P versus the mole ratio of CO_3 to PO_4 of the apatites in 49 different PRs demonstrated that, the solubility of those PRs increased as the carbonate substitution for phosphate in the apatite structure increased(Lehr and McClellan, 1972). These results agree with the earlier report by Caro and Hill (1956) that the solubility increased as the "bound CO_2" in the apatitic minerals increased. The unit cell a-dimension, in turn, is indicative of the degree of carbonate substitution for phosphate, decreasing as the mole ratio CO_3:PO_4 increases. However, Na and Mg may also substitute for part of the calcium. Total P_2O_5 contents of metamorphic and igneous PRs are higher than that of sedimentary PR. This relationship, has been used to show that the composition of (sedimentary) apatites can be expressed by the following generalized formula (Khasawneh and Doll, 1978);

$Ca_{10-a-b}\,Na_a\,Mg_b\,(PO_4)_6 - x(CO_3)\,x\,F_2 + 0.4x$, in which

a - dimension = $9.374 - [0.204x / (6 - x)]$;

a(Na) = $1.327(x) / (6 - x)$;

b(Mg) = $0.515x / (6 - x)$

x = mole fraction of CO_3 in the apatite.

Chien and Van Kauwenberg (1992) attributed the effect of CO_3 substitution for PO_4 on the chemical reactivity of apatite to the following:

1. Substitution of CO_3 for PO_4 causes a decrease in unit - cell a-axis that results in a decrease in crystalline size of apatite. Because the apparent chemical reactivity of apatite increases with a decreased crystalline size, solubility of apatite increases with an increase in CO_3^{2-} substitution for PO_4^{-3} in apatite structure.
2. The PO_4^{-3} ion is a tetrahedral structure, whereas the CO_3^{-2} ion is a planar structure. Substitution of planar CO_3^{-2} for tetrahedra PO_4^{-3} thus causes structure instability that results in an increase in reactivity.

Thermodynamic considerations indicate that highly substituted francolites are less stable than fluorapatite (Chien, 1977). Using the following reactions: $Gr^{\square}$, KCal

$$PO_4^{-3} \quad + \quad 2H^+ \rightleftharpoons H_2PO_4^{-1} \qquad - \quad 26.2 \qquad [1]$$

$$CO_3^{-2} \quad + \quad 2H^+ \rightleftharpoons H_2O + CO_2 \qquad - \quad 29.6 \qquad [2]$$

Chien and Van Kauwenberg (1992) argued that thermodynamically, neutralization of CO_3^{2-} with H^+ ions is more reactive than that of PO_4^{-3} , because CO_3^{-2} has lower free energy of reaction ($Gr^{\square}$). In other words, the chemical reactivity of apatites increases with an increase in CO_3^{-2} substitution for PO_4^{-3}.

2.3.2 Indigenous Phosphate Deposits in some parts of the world

Phosphate rock deposits occur in several parts of the world (Table 2.1) especially in Asia, Africa and Latin America (Menon *et al.*, 1991).

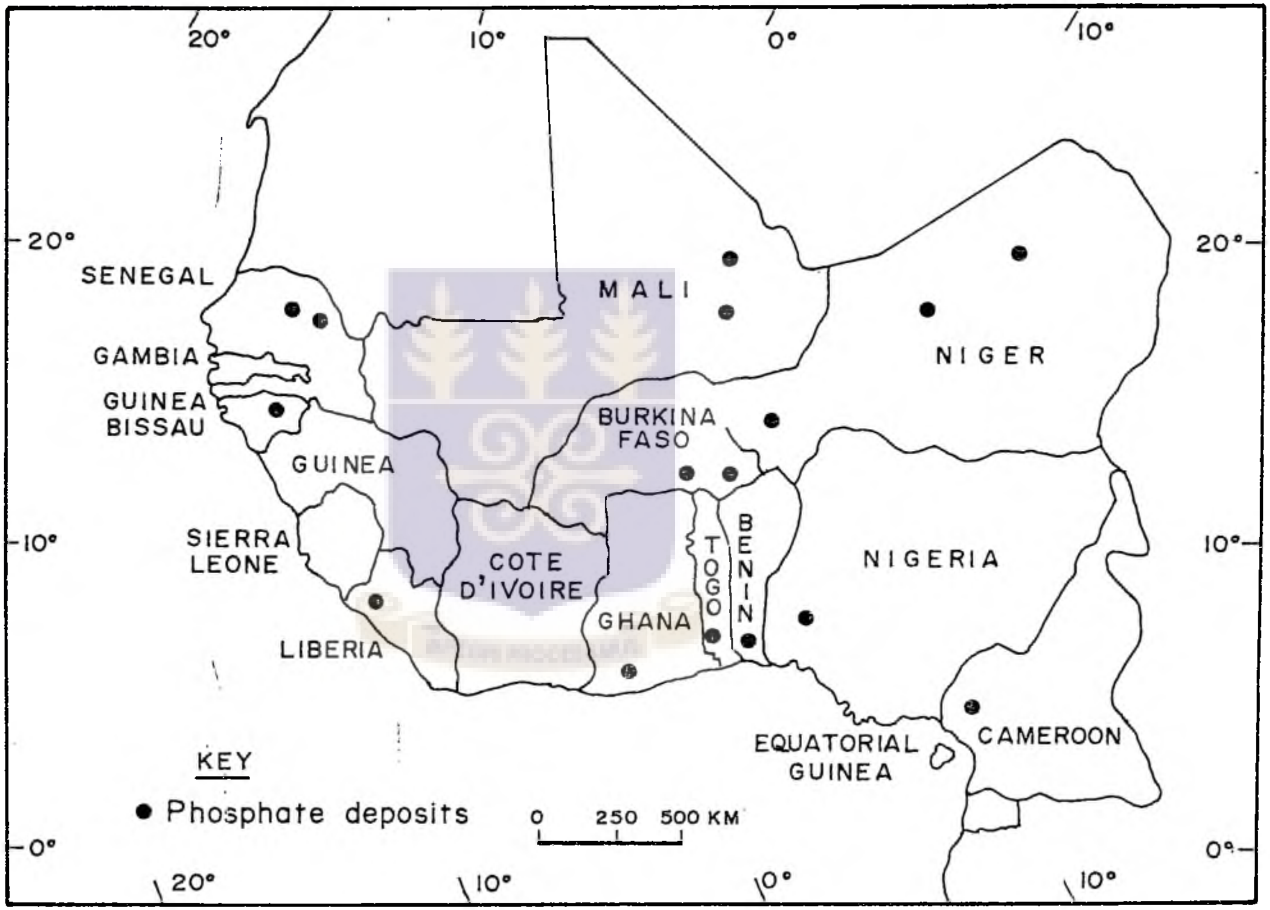
Table 2:1 Names of some phosphate rocks and countries where they occur

Country	**Phosphate Rock** (PR)
Bolivia	Capinota
Brazil	Tapira, Araxa, Patos de Mina
Burundi	Matongo
Canada	Martison
Chile	Bahia Inglesa
China	Kaiyang
Christmas Island	Christmas Island A - grade
Colombia	Pesca, Huila, Media Luna, Sardinata
India	Mussories
Israel	Arad
Jordan	El-Hassa
Mexico	Baja California
Peru	Bayovar PR, Sechura
South Africa	Phalaborwa
Tunisia	Gafsa
Uganda	Sukulu Hills
USA	North Carolina, Tennessee, Central Florida
Zambia	Chilembure
Zimbabwe	Dorowa

Source: Chien and Menon (1993b).

In West Africa, phosphate rock (PR) deposits can be generally divided into two groups: . Older sedimentary phosphates of the Proterozoic age (> 600 million years old) located to the western border of the Taoudeni Basin and the Mauritanides, and in the Volta Basin and Dahomeyides chain. Younger sedimentary phosphates of the cretaceous - Tertiary age (approximately 18 to 40 million years old) of the coastal Basins, Villemedia Basin and the Tilemsi Valley (North of Detroit de Gao) (Johnson, 1995).

Fig. 2.1 PHOSPHATE DEPOSITS IN WEST AFRICA



SOURCE: International Fertilizer Development Centre — Africa

Many of the phosphate rocks from these sedimentary deposits have granular textures. Phosphate rocks (PRs) from the younger deposits generally have clayey gangue and tend to be friable. Phosphate rocks (PR) from the older deposits are well cemented usually with silica (quartz) and sometimes with carbonate (calcite, dolomite) cements.

In the West African sub-region, PR is widely distributed and deposits occur in 12 countries (Fig 2.1) However, those deposits which are developed and mined are Taiba and Thies PRs in Senegal, Hahotoe and Kpogame PRs in Togo (Table 2.2). Those deposits in development phase are: Kodjari PR in Burkina Faso, Tilemsi: in Mali and Tahoua in Niger (Table 234). Some deposits under development are shown in table 2.4

Table 2:2 Developed phosphate deposits in West Africa

Country, Location	% P_2O_5	Production of concentrate ('000 mt, 1989)
Senegal		
Taiba	35 - 38	2.20
Thies		3.12
Togo		
Hahotoe & Kpogame	35 - 38	3.30.

Sources: Johnson (1995).

Table 2:3 Phosphate deposits of West Africa under development

Country, Location	% P_2O_5	Production of concentrate ('000 mt,/ year)
Burkina Faso		
Kodjari	25 - 27	2
Mali		
Tilemsi	29.5	15
Niger		
Tahoua	32	1

Sources: Johnson (1995).

Table 2:4 Some undeveloped phosphate deposit in West Africa

Country	Area	% P_2O_5
Benin	Pobe	27 - 30
	Kpome	29
	Toffo	23
	Lokossa	*
	Mékrou	20 - 26
Burkina Faso	Aloub Djouana	15 - 32
	Arly	26 - 32
Cameroon	Vallée du fleuve	*
	Bonge	12 - 18
	Zone Côtiere	8 - 32
Ghana	Keta Basin	25
	Sekondi System	15
Niger	Region du Nord	23
	Tapoa	23
Nigeria	Sokoto State	34
	Ifo Junction at Oshoun	22 - 32
Sénégal	Matam	29
	Pire Goureye	23
Togo	Bassar	24 - 39

Sources: Johnson (1995).

* denoted data not available

The constraints to the development of the phosphate deposits in West Africa may be summed up as follows:

- most of the deposits are limited in quantity and the quality is low

- many deposits have limited accessibility or are remote from the farming areas when they are needed
- financing and infrastructure are lacking

SECTION C

2.4 Effectiveness of Phosphate Rocks in Tropical Environment

The tropics occupy that area of the world located between 23.5° North and South of the Equator. Around 40% of the land surface of the tropics consists of highly weathered acid soils classified mainly as Oxisols and Ultisols (Sanchez and Salinas, 1981). In the continent of Africa, more than 50% of the surface is occupied by acidified Alfisols and Entisols. The excessive weathering in these soils has reduced the total P levels in the soils. Also the high content of iron and aluminium oxides and exchangeable aluminium result in high P sorption capacities, leading to low P concentrations of plant available P in the soil solution (Sanchez, 1976). In the more humid parts of tropical Africa, the Alfisols have been formed from granite and sandstone but prolonged pedogenesis has obscured the influence of these parent materials on these soils. Excessive leaching and cultivation have accelerated the depletion of bases. The textures of both the Alfisols and Entisols range from sandy to sandy loam creating an ideal environment for greater than expected effectiveness of PRs even for annual crops (Mokwunye *et al*., 1986).

The extent to which PRs have direct role to play as P inputs in management systems for production on acid tropical soils depends on their agronomic effectiveness relative to other available P fertilizers and the relative costs of alternative products.

Because added fertilizer P reacts with soils and continues to be available over time, the effectiveness of PRs will be considered in terms of both their initial effects and their residual effectiveness over time.

2.4.1 Studies on agronomic effectiveness of PRs in Latin America

The agronomic effectiveness of directly applied Latin American PRs has been observed to be highly variable. This is because of the differences in the chemical solubility of the PRs and the great diversity in soil and cropping systems. In Oxisols from the Colombian Llanos, a number of experiments have been conducted to comapare P sources. Results of experiments conducted by some researchers during the period 1969 - 1971 in which Turmegue PR (Pesca - type PR) was compared with TSP, both at 200 kg P_2O_5 ha^{-1}, and with a mixture of PR and TSP. Corn was the indicator crop, and the soils were extremely acidic (pH 4.5 - 4.6, Al Saturation 65 72%). The studies revealed that the Colombian PR was relatively ineffective during the first year at one site but was equally as effective as TSP during the next two years. Also reviewed were experiments conducted during 1974-1975 with the same PR and with peanut as the indicator crop. In this case, the PR was only about one-half as effective as TSP during the first cropping period but, as before, gave results similar to those with the more soluble sources during the second year of cropping.

On a similar Oxisol, Hammond and Leon (1984) reported on a study with the use of Huila PR (Colombia) and with rain-fed rice as the indicator crop. It was observed that there was no significant difference in effectiveness between Huila PR (medium reactivity) and TSP under the conditions tested, irrespective of the level of supplemental fertilizers supplied or the variety of rice utilized.

The results described above were all obtained on Oxisols from the Colombian Llanos and are highly encouraging with regard to the possibility of substituting national PRs for the more expensive fertilizers in that region if the value of the residual P is taken into consideration. However, on other Latin American Oxisols results have not been as encouraging. In the Cerrado of Brazil, for example, a number of researches have reported that local Brazilian PRs exhibit low agronomic effectiveness (Van Raij and Van Diest, 1980; Smyth and Sanchez, 1982). In a review, Geodert (1983) cites an example in which the Patos, Araxa and Cattalo PRs were only 43, 36 and 20% respectively as effective as TSP, when measured over six annual crops. These differences are explained by a number of factors. First, the reactivities of the Brazilian PRs are substantially lower than those of the sources tested in the Colombian Llanos. Second, the yield levels in the Brazilian Cerrado may have been higher and third, the soils of the Cerrado exhibit higher P retention capacity.

Results more similar to those observed on the Colombian Oxisols have been obtained on Ultisols of the Amazon basin. In Peru, experiments with Bayovar PR have been conducted in experiment stations both in Yurimaguas and Pucallpa. In Yurimaguas a rotation of corn, soyabean and rice was utilized to compare the effectiveness of the highly reactive Bayovar PR with soluble TSP, (Bandy and Leon, 1983). From these studies, it was concluded that the PR was equally as effective as TSP and offered a good substitute for imported fertilizer.

Although Oxisols and Ultisols dominate the lowland tropics, the highlands are characterized by Andepts and associated Inceptisols. In experiments conducted with field beans on an Andept from Colombia (Chien and Hammond, 1978b), positive initial response to PR was observed only with highly reactive sources. Gafsa PR (Tunisia), for example, was 87% as effective as TSP. during the first cropping period: Huila PR (Colombia), however, was reduced to 66% as effective as TSP., and Pesca PR (Colombia) was only 7% as effective as TSP. When cropping was continued without additional applications of P to observe the difference in residual P availability between sources, the highly reactive PRs (Gafsa and North Carolina) were found to be equal to or better than TSP in providing residually available P in each of the three subsequent crops. The medium-reactivity PRs (Central Florida and Huila) tended to increase in effectiveness until they became equal to residual TSP in the third crop. The PR with the lowest reactivity in the trial (Pesca) increased sharply in effectiveness through the first three crops as compared with TSP, increasing from only 7% in the first crop to 27 and 82% as effective as TSP, in the second and third crops respectively.

In experiments conducted on high P-fixing Andepts in Tulcan and Canar, Ecuador, it was observed that response to freshly applied P by both potatoes and forage grass increased as the amount of water-soluble P in the fertilizer increased (INIPA / IFDC, unpublished, 1981). In the case of Potatoes, yields resulting from the use of Central Florida PR acidulated with 40% of the H_2SO_4 required for SSP was similar to those obtained with TSP, but it was not known whether part of the response may be due to the S supplied by the PAPR. The unacidulated PR was almost completely ineffective in those trials, even when residual effect was measured by a subsequent planting of forage grass. It was concluded that PAPR was the most appropriate alternative under these conditions. Extensive farm - level testing of PAPR was subsequently initiated by IFDC in 1982 using 40% Pesca PAPR and 50% Huila PAPR in varied cropping systems and agroclimatic zones of Colombia. Multiple-site trials were established where test crops included both potatoes and intercropped maize and beans grown on Andepts of the high-altitude region in Naririo, Cassava and beans grown on Oxic Inceptisols of the mid-altitude region Cauca, and rice on Oxisols in the low-altitude region in Meta (IFDC, 1984). It was concluded that there was no statistically significant difference between the effectiveness of TSP and that of the PAPR irrespetive of the crop / soil combination. This was not the case with unacidulated PR, which was found to be significantly lower in effectiveness than the fertilizers containing soluble P in the majority of the cases.

2.4.2 Use of PRs in West Africa

In Francophone West Africa, use of PR for annual maintenance fertilization after initial basal dressings of PR from Senegal was investigated in experiments at Saria and Farako Ba in Burkina Faso Yields of sorghum, cotton and groundnut were improved with PR addition. However, TSP. was superior to PR in the first year of application. At Saria, this advantage disappeared during the second year. In Nigeria, Juo and Kang (1978) evaluated the initial response of North Carolina PR in greenhouse trials using an Alfisol and an Ultisol. Under similar pH conditions, both phosphate rocks performed better in the Alfisol than in the Ultisol. It was concluded that to obtain 80% of maximum yield, the rates of P required were 80, 100 and 200 mg kg^{-1} soils for TSP, North Carolina PR and Morocco PR, respectively, in one of the Alfisols. Considerably higher quantities of PR were needed for the Ultisol. In another experiment in the Nigerian Savannah environment, Mokwunye (1979) reported that Togo PR was 63% as effective as SSP in the first year of application. Continued applications of PR for two additional years raised the P fertility level and by the third year, the mean yield of the phosphate rock plots was 96% of that of the SSP treatments which were also reapplied.

Truong *et al.* (1978), summarized the results of several experiments that compared some of the West Africa phosphate rocks [Togo PR ; Kodjari, (Burkina Faso); Tahoua (Niger,); and Tilemsi (Mali)]. The conclusion was that only Tahoua and Tilemsi were suitable for direct application. These results were confirmed by experiments conducted at three sites in Mali by Thibout *et al.*, (1980), in which Tilemsi PR and Taiba PR from Senegal were compared. The conclusion was that Tilemsi PR was reactive enough to be used for direct application. Tilemsi PR was also evaluated in trials at Sapu in the Gambia, using maize and groundnut. Although 1984 was a very dry year, finely ground Tilemsi PR was 74 and 92% as efficient as SSP for maize and groundnut respectively.

In Ghana, Owusu-Bennoah and Acquaye (1996) evaluated the initial and residual response of Togo PR and 50% partially acidulated Togo phosphate rock (PAPR-50) in greenhouse trials in a concretionary soil (Alfisol) with maize as an indicator crop. Their results showed that the relative agronomic effectiveness (as compared with SSP) of PAPR - 50 was 58% while that of Togo PR was only 23% in increasing growth of the crop. The residual effect of either PAPR-50 or PR on dry matter yield and uptake was found to be negligible compared with SSP, suggesting that the apatitic P was poorly effective relative to SSP in the soils used. The results of the study are consistent with the earlier work with maize on Alfisols in Togo (Bruce and Marquette, 1977; IFDC, 1985); they also confirmed the finding that finely ground untreated Togo phosphate rock gave lower yields than superphosphate and the phosphate rock acidulated to 50%, the latter two being equal in effectiveness (Mokwunye and Pinto-Toyi, 1991).

2.5 Factors Affecting PR Dissolution in Soil

The extent to which the P uptake rate required for plant growth is maintained by the dissolution rate of the PR determines how effective that PR is (Sale and Mokwunye, 1993). Interactions of several factors such as PR properties, soil characteristics, crop species and plant effects, effect of climate and management practices determine the dissolution of PR materials in soils (Khasawneh and Doll, 1978; Bolan *et al.*, 1990). This review will focus on each of these factors.

2.5.1 Influence of phosphate rock properties

In relation to its agronomic effectiveness, the most important property of PR is its solubility and hence chemical reactivity as measured conventionally using 1N neutral ammonium citrate, 2% citric acid or 2% formic acid (Chien and Hammond, 1978; Chien, 1993). The solubility or chemical reactivity of a PR however depends on the chemical and mineralogical composition, free carbonate (calcite dolomite) effect, effect of apatite crystallinity and cementing of apatite with silica and effect of monocalcium phosphate and gypsum in the mixture of the PR (Chien, 1993). In general, the solubility increases as carbonate substitution for phosphate in the apatite structure increases. Therefore the level of isomorphic substitution of carbonate for phosphate within the lattice of the apatite in the rock controls the amount of phosphorus (P) that is released when PR is applied to soils (Smith and Lehr, 1966).

The presence of free carbonates in a significant amount can however suppress the apatite solubility. This is due to the fact that free carbonates are more soluble than apatite resulting in the calcium common-ion effect which reduces the solubility of apatite. In a study with seven PRs (Chien and Hammond, 1978), the reactivities of the PRs were measured by chemical extractions and also calculated by x-ray diffraction (absolute citrate solubility). The P solubility in neutral ammonium citrate remained relatively constant between the first and second extractions for each of the PRs except Huila, PR. The citrate-soluble P of this PR increased from 0.4% to 1.5% in the second extraction. The Huila PR contains approximately 10% $CaCO_3$ that increased from 1.4% in the first extraction to 4.4% in the second extraction.

The intermix of apatite and silica significantly reduce the chemical solubility of PR (Chien, 1993). For example, Pesca PR would be more soluble than Tennessee PR, on the basis of its absolute citrate solubility (x-ray diffraction method). However, the measured chemical solubilities of Pesca PR were less than those of Tennessee PR. The scanning electron microscope revealed that the apatite in Pesca PR is intermixed (cemented) with silicious minerals in such a way that it rendered the apatite less accessible to attack by the chemical solution or by the soil solution.

According to Chien (1977), thermodynamically, the solubility of hydroxyfluorapatite in the form of $Ca_{10} (PO_4)_6 F_2 - x (OH)x$ would be expected to be greater than that of carbonate fluorapatite in the form of $Ca_{10-a-b} Na_a Mg_b (PO_4)_6 - x (CO_3)x F_2 + 0.4x$, regardless of the degree of carbonate substitution for phosphate. For example, the apatite formula of an igneous Tapira PR in Brazil was approximated as $Ca_{10} (PO_4)_6 (OH)_{1.05} F_{1.01}$, and the apatite formula of a sedimentary Lumphum PR in Thailand was approximated as $Ca_{10} (PO_4)_{5.98} (CO_3)_{0.12} (OH)_{1.43} F_{0.57}$ (Chien and Van Kauwenbergh, 1992). Both apatites have substantial amounts of OH substitution for F. However, the citrate solubility of Tapira PR was only 1.9%, whereas that of Lumphum PR was 7.2%. The igneous PRs, characterised by having coarse, well-crystalline, non-porous apatite crystal structure are expected to have low reactivity despite the fact that they have substantial OH substitution for F. A sedimentary PR, characterized by having a high OH substitution for F in the apatite structure, would be relatively high in reactivity even with no significant CO_3 substitution for PO_4 in the apatite structure.

One physical property of a PR which affects it solubility is the particle size (Chien and Friesen, 1992). Barrow (1990) contended that, the PR dissolution process is a reaction that occurs at the surface of the PR particles, hence reducing the particle size by grinding increases the surface area of PR exposed to the soils and consequently increases the rate of P release from the PR. He however, cautioned that fine grinding is not a substitute for reactivity. Reducing PR particles to a size less than 100 mesh (150 um) by grinding is generally not warranted as finer particles do not increase effectiveness greatly (Khasawneh and Doll, 1978; Rogers *et al.*, 1953).

The solubility of PR has been reported (Engelsted et al., 1974; Chien and Van Kauwenberg, 1992), to correlate well with crop response, however, Chien et al., (1990b) noted that it was difficult to compare crop responses to PRs and water soluble P fertilizers because of the interactions between fertilizer and soil. It is therefore difficult to predict the relative agronomic effectiveness (RAE) of P fertilizers based on their solubility alone.

2.5.2 Influence of Soil Properties

The dissolution of Peru (Bayovar) PR, one of the most reactive carbonate apatite located in the tropics, can be described (Hammond *et al.*, 1986a) by the equation:

$$Ca_{9.03}\ Na_{0.74}\ Mg_{0.13}\ (PO_4)_{4.88}\ (CO_3)_{1.12}\ F_{1.73}\ (OH)_{0.72} \rightleftharpoons {}_{9.03}Ca^{2+} + {}_{0.74}Na^{+} + {}_{0.13}Mg^{2+} + {}_{4.88}PO_4^{3-} + {}_{1.12}\ CO_3^{2-} + {}_{1.73}F^{-} + {}_{0.72}OH^{-} \qquad [3]$$

Chien and Menon (1993a) identified soil pH, exchangeable Ca, organic matter content, soil P-fixing capacity, soil texture as the soil properties that have the greatest influence on the solubility and the agronomic effectiveness of PR for direct application.

2.5.2.1 Soil pH

The driving force for the dissolution of this carbonate apatite is the neutralization reaction between soil H-ions and the PO_4-ions, CO_3-ions, F-ions and OH-ions resulting from dissolution, which are neutralized to H_2PO_4-ions, H_2CO_3, HF and H_2O respectively (Chien, 1993). Thermodynamic considerations indicate that these reactions occur spontaneously as the apatite dissolves (Chien, 1977). Many field and laboratory observations confirm that low soil pH (Bolan, 1989), with a high buffer capacity (Kanabo and Gilkes, 1987) and also a high rate of soil acid generation (Apthorp *et al.*, 1987) all contribute to enhance PR dissolution. Ellis *et al.* (1955), Peaslee *et al.* (1962), Barnes and Kamprath (1975) have investigated the effect of soil pH on the dissolution of phosphate rock (PR) in soils by indirectly inferring from plant yield or P uptake from soils which had received PR treatments. In these experiments increased dissolution was assumed to be proportional to increased yield and P uptake. Vijay Kumor *et al.*, (1993) reported that the relative effectiveness of non-granulated North Carolina PR was four times higher in a more acidic soil (pH 4.2) than for a high pH (6.2) soil. Experiments with a single soil adjusted to various pH levels show that phosphate rock dissolution increased linearly with decreasing pH (Kanabo and Gilkes, 1987). In a study to show the influence of soil pH on the effectiveness of various PRs with respect to triple super phosphate (TSP.), Engelstad *et al.* (1974) reported that soil pH had little effect on rice response to TSP.; however, the effectiveness of the PRs greatly depended on soil pH. At pH 4.6, flooded rice responded to PRs, the degree of response depending on the PR's reactivity. At pH 8.0, all PRs were ineffective and did not differ from the check in grain yield produced. Since plant yield and P uptake from soil depend not only on the extent of PR dissolution but also on the crop used and P-soil interactions, estimates of the effect of pH on PR dissolution are inconsistent (Kanabo and Gilkes, 1987). Ellis et al., (1955) found that lower pH values between the range of 4.9 - 7.4 favoured PR dissolution and growth of oats. Phosphorus uptake from applied PR was reduced at extremes of this pH range.

2.5.2.2 Exchangeable Ca

The law of mass action (Barnes and Kamprath, 1975) would indicate from equation [3] that PR dissolution would be favoured by soil conditions that maintain low concentrations of Ca and P in the soil solution. Soils with high exchangeable Ca content would therefore slow down the dissolution of PR. Many tropical acid soils have relatively low exchangeable Ca hence provide favourable conditions for PR application (Chien and Menon, 1993a). Cation exchange capacity (CEC), which is closely related to soil texture and soil Ca is another soil property which influences PR dissolution. Khasawneh and Doll (1978), Kanabo and Gilkes (1988) suggested that sandy soils with low CEC do not provide a sink for Ca-ions released from PR hence, slow down the dissolution of the PR, and this may result in a reduction in agronomic effectiveness. In a study to evaluate the effect of leaching on the dissolution of PR materials, Hanafi and Syers (1993) reported that the highest and the lowest dissolution occurred in the sandy clay loam and clay soils, respectively. They concluded that the greater permeability of the sandy clay loam than the clayey soil resulted in continuous removal (leaching) of the product of PR dissolution, Ca^{2+} and H_2PO_4, from the site of reaction. This maintained sinks for Ca^{2+} and H_2PO_4 and thereby promoted dissolution.

2.5.2.3 Effect of soil organic matter

Soil organic matter is known to enhance the dissolution of PR (Drake, 1964). Some types of soil organic matter, upon hydrolysis, may supply some organic functional groups or anions such as citrate and oxalate that can effectively chelate Ca^{2+} ions and thus lower the Ca^{2+} activity in soil solution. This in turn provides a driving force for further dissolution of PR. The mechanism also may explain, at least in part, the beneficial effect of farmyard manures on increasing P availability from PR (Guzman et al., 1980; Villarroel and Augstburger, 1984).

2.5.2.4 Phosphorus sorption capacity

Phosphorus sorption capacity does affect PR dissolution. In an incubation study with acid soils from the Cerrado of Brazil, Smyth and Sanchez (1982) showed that the decomposition of PR increased with an increased P retention capacity of the soils. A similar conclusion was also reached by Syers and Mackay (1986) in a study involving Bayovar PR and acid soils in New Zealand. Chu *et al.* (1962) reported that the increased decomposition of PR may be due to the more effective removal of $H_2PO_4^-$ ions from solution by Fe minerals in the high - Fe soil. Although PR dissolution increases as soil P retention capacity increases, it does not necessarily result in an increase in the amount of plant available P in the soil. Smyth and Sanchez (1982) and Syers and Mackay (1986) found that Olsen extractable P, resin and Bray 1 in soils treated with PRs decreased as soil P retention capacity increased. Syers and Mackay (1986), subsequently found that plant yield obtained with PR, as well as with single superphosphate (SSP), decreased with increasing soil P retention capacity. Hammond and León (1983) indicated that finely ground PRs applied to Latin American Oxisols and Ultisols were relatively more effective with respect to TSP. than the same PR sources applied to Adepts which exhibited significantly higher P retention capacities than did the Oxisols and Ultisols. Harris *et al.* (1984) also tended to support the finding that high P retention capacity could have a strong negative influence on the effectiveness of PR. In experiments conducted with corn on an Andept and on Ultisols, both with pH near 5.0, PR was found to be similar in effectiveness to TSP on the Ultisols but inferior on the Andept. It was concluded that low P-retention capacity contributed to the positive performance of PR on the Ultisol. Despite the fact that high P retention by the soil may promote a more rapid dissolution of the PR, concentration of P in the soil solution will be limited to a low level controlled by the solubility product of the solid-phase apatite in the PR (Khasawneh and Doll, 1978). This P, of course, is just as susceptible to retention by the soil as is P derived from TSP. If development of the plant root system is depressed by the initial low concentrations of P from the PR, it follows that the probability for interception of immobile P concentrations in the soil by the roots will be reduced and the proportion of P left to react with the soil will increase.

2.5.3 Effect of crop species

The utilization of P fertilizer with different degrees of solubility has been found to vary with crop species. In general, the Relative Agronomic Efficiency (RAE) of PRs with respect to water-soluble P sources (such as SSP and TSP.) would be higher for long-term or perennial crops (e.g. oil palms, tea, rubber pastures, fruits) than for shorter-term or annual food crops (e.g. Rice, maize, millet) (Chien *et al*., 1990b). Khasawneh and Sample (1979) suggested that the concentration of soil solution P required by cowpea for maximum growth potential may be only two-thirds the concentration required by maize. Thus the RAE of PRs would be higher for crops with lower P demands, such as legumes than for cereal crops.

Several workers have attributed the differences in the ability of various crop species to utilize PR to the mechanism of acidulation in the plant's rhizoshphere environment (Van Ray and Van Diest, 1979; Bekele *et al*. 1993). Imbalances in the uptake of cations and anions by plant roots, balanced by excretion of a proton or a bicarbonate anion, are the main causes for plant related pH changes in the rhizosphere, which influence P dissolution from sparingly soluble sources (Kirk and Nye, 1986). Van Ray and Van Diest (1979) using six plant species (wheat, paspalum grass, maize, molasses grass, soybean and buckwheat), found that a PR was as effective as TSP for buckwheat, which produces much lower soil pH than did other plant species through inbalance of cation and anion absorption by the roots.

Plant with greater root densities in the surface layers of the soil in which the PR is located would be expected to acquire dissolved P from the PR at a faster rate, because there would be a greater likelihood of a root encountering localised ‘high concentration pockets’ of soluble P adjacent to the PR. This proposition is supported by evidence in greenhouse pot trials where the effectiveness of the reactive Bayovar PR was greater with the high-root-density ryegrass than with wheat or maize which have lower root densities (Chien *et al*., 1990). It is also likely that plants which are better able to acquire dissolved P from PR because of the greater volume of soil into which the mycorrhizal root system can extend, compared to non-mycorrhizal roots. Positive benefits have been reported from the addition of mycorrhizal innoculum to sterilized tropical soil in which moderately reactive PR had been mixed (Waidyanatha *et al*., 1979).

2.5.4 Effect of management practices

The effectiveness of PR can be influenced by the practices used in management of crop and soil. Maximization of surface area contact between the PR and soil is required to promote adequate dissolution of the PR, so is maximization of contact between the root surface and the PR, to promote adequate uptake of the P by the plant. Hammond et al. (1990) observed that the performance of PR, is enhanced in flooded systems even though increased pH resulting from flooding of rice fields is expected to depress the dissolution of PR. Kirk *et al*., (1991) attributed this observation to the acidification of the rhizosphere by the roots of the rice and the chelation of Ca and P in the soil by the dissolved organic matter in the flooded soil solution, and that there would be a lag phase following flooding, before the soil pH increases during which time significant amounts of PR, applied pre-flooding, might have dissolved.

The method of PR placement in the soil also influences the rate of P release from the PR. Savant and Chien (1990) showed that the effectiveness of North Carolina PR was greatly influenced by placement method. When broadcast and incorporated, it was found to be as good as TSP in increasing rice grain yield, but it was less effective than TSP when deep placed. Barrow, (1990) attributed this to banding which reduces the rate of dissolution as a result of overlapping diffusion zones around the closely spaced PR particles and the build up in the products of dissolution on the surface of the PR particles limits further dissolution. The influence of method of application has also been shown to vary depending on the crop to which the PR is applied. In a greenhouse experiment, Peng and Hammond (1979) reported that surface application of both TSP and Bayovar PR (Peru) significantly reduced dry matter production of corn whereas only a slight influence was noted when guinea grass was used as the indicator crop.

Another management practice that will increase the rate of P uptake from PRs is to apply the PR to the soil well in advance of the time of planting the crop (Ellis *et al.* 1955). This enables more dissolved P from the PR to accumulate in the soil so that there is a greater P supply at the time the crop sown. However, Chien *et al.* (1990) suggested that this practice may not be suitable for acid tropical soils with high P-fixing capacity. They showed that the effectiveness of North Carolina PR was the same whether the PR was applied at the time of planting or six weeks before planting in soil with low P-fixing capacity. With a high-fixing capacity soil, the effectiveness of PR was reduced when applied six weeks before planting.

The use of lime on acid soils is another practice that will lower PR dissolution rate. Liming will both reduce the supply of H-ions and increase the supply of Ca-ions in the soil solution (Hammond *et al.*, 1986). Chien and Friesen (1992) cautioned that lime rates should be carefully chosen to alleviate the Al toxicity problem and, at the same time, to avoid adverse effects on PR dissolution in acid soils. One solution to the negative interaction between lime and PR dissolution is to apply the PR in advance of the lime. This would allow significant amounts of PR to dissolve before the pH and the calcium status of the soil is raised by lime application (Sanchez and Salinas, 1981).

2.5.6 Effect of climate

Rainfall is important for PR dissolution because PRs will not dissolve in dry soils (Sale, 1990). Incubation studies confirm that PR dissolution declines as the soil moisture content is decreased (Gregg *et al.*, 1978). Work done in Senegal (Bambey, 1957) showed that the fertilizer uptake efficiency of PR increased with increasing rainfall. In a series of trials over a range of mean annual rainfall between 500 and 1300 mm, the yield increases of groundnuts over control showed a highly significant linear correlation with the mean annual rainfall for the first two (2) years following basal fertilization. High annual rainfall in the humid tropics combined with the stable aggregates of tropical Oxisols (Sanchez, 1976) would result in a substantial water movement throughout the soil. The high leaching indices would promote PR dissolution by facilitating the removal of the products of dissolution away from the surface of the PR particles.

Temperature has been found to have no significant effect on PR dissolution in soil (Chien *et al.*, 1980). The implication is that the availability of P released from PRs in the tropical soils may be less affected by temperature than the P released from water-soluble fertilizers (Hammond *et al.*, 1986). This would tend to improve the effectiveness of PRs in warm environments, relative to soluble P forms. Such an outcome would depend on the extent to which P sorption reactions were operating in the soils as temperature does not have a marked effect on the rate of P sorption by soil (Barrow, 1983).

SECTION D

2.6 Partially Acidulated Phosphate Rock (PAPR)

Direct application of PR does not always give satisfactory results due to low PR reactivity or combination of the PR with inappropriate soil or crop (Chien and Menon, 1993b). For PRs with low reactivity which may not be suitable for direct application, partial acidulation can be employed to produce highly effective P fertilizers (PAPR). Partial acidulation involves treating the PR with less than the stoichiometric amounts of sulphuric acid or phosphoric acid required to fully convert insoluble phosphate minerals to water soluble monocalcium phosphate monohydrate (MCP) in SSP and TSP respectively. Single superphosphate (SSP) is manufactured by reacting H_2SO_4 with PR:

$$\underset{\text{(RP)}}{Ca_{10}(PO_4)_6F_2} + 7H_2SO_4 + 3H_2O \longrightarrow \underset{\text{(MCP)}}{3Ca(H_2PO_4)_2H_2O} + 7CaSO_4 + 2HF \quad [4]$$

For partial acidulation:

$Ca_{10}(PO_4)_6F_2 + 7YH_2SO_4 + 3YH_2O \longrightarrow 3YCa(H_2PO_4)_2 \cdot H_2O + 7CaSO_4 + 2HF + 7YCaSO_4 + 2YHF + (1\text{-}Y)\,Ca_{10}(PO_4)_6F_2$ (IFDC, 1986). [5]

Triple or concentrated superphosphate (TSP) is manufactured by reacting H_3PO_4 with RP:

$Ca_{10}(PO_4)_6F + 12H_3PO_4 + 9H_2O \longrightarrow 9Ca(H_2PO_4)_2\,H_2O + CaF_2$ [6]

For partial acidulation:

$Ca_{10}(PO_4)_6F_2 + 12YH_3PO_4 + 9YH_2O \longrightarrow 9YCa(H_2PO_4)_2\,H_2O + YCaF_2 + (1\text{-}Y)\,Ca_{10}(PO_4)_6F_2$ [7]

In the equations [2.4] and [2.5] the Y term represents the degree of acidulation; i.e Y = 1.0 for 100% acidulation and Y = 0.5 for 50% PAPR. The equation, however does not reflect the role of the non fluorapatite components of the PR, which may significantly alter the reaction chemistry. In H_2SO_4 - based PAPR, therefore, the final product is essentially a mixture of moncalcium phosphate monohydrate (MCP), unreacted PR and $CaSO_4$, whereas in H_3PO_4-based PAPR, CaF_2 is formed instead of $CaSO_4$. The "% PAPR" nomenclature used in this review refers to the proportion of acid used to prepare the PAPR relative to the quantity of acid which would have been required to produce superphosphate from that particular PR. Thus, 50% H_2SO_4 acidulation refers to the use of 50% of the H_2SO_4 required to produce SSP, and 50% H_3PO_4 acidulation refers to 50% of the phosphoric acid required for TSP.

Work done by Bationo *et al.* (1986) in Nigeria, Togo and Sierra Leone showed an increase in the agronomic effectiveness of Togo PR following partial acidulation. At

50% acidulation, the agronomic efficiencies were 72%, 82% and 103% that of SSP in Nigeria, Togo and Sierra Leone, respectively. Menon *et al.* (1991) reported that Huila PAPR was 88% as effective as TSP in increasing P uptake by beans when direct application of Huila PR achieved 79% that of TSP. They also observed that finely ground Capinota PR was 51% as effective as TSP but partial acidulation increased its efficiency to 78% that of TSP. Some important factors which affect the agronomic effectiveness of PAPR include the reactivity of the PR, the acidulant and the quantity of acidulant used, the impurities in the rock as well as soil properties and soil reactions.

Laboratory studies indicate that when PAPR is applied to soils, the P apparently released from the PR component is proportional to the reactivity of the original PR as measured by formic acid extractable P (Hagin *et al.*, 1990). Under field conditions, however, this pattern could be modified because of the soil-plant-fertilizer interactions. McLean and Logan (1970) found that in 45 of the 53 fields trials conducted, PAPR prepared from an unreactive Florida rock was as effective as superphosphate. The degree of acidulation was about 20% with phosphoric acid so that 43% or more of the total P was in water-soluble form. Marwaha *et al.* (1983) also reported that 10% phosphoric PAPR prepared from an unreactive Mussoorie rock (India) was as effective as SSP for wheat, peas and potatoes but not for berseem. On the contrary, findings from IFDC indicate that PAPRs from unreactive or medium reactive rock could be less effective than superphosphate except in soils of very low pH (pH < 5) (Hammond *et al.*, 1980; Chien and Hammond, 1989; Hammond *et al.*, 1989; Bationo et al., 1990; Menon and Chien, 1990). Greenhouse studies conducted in Australia indicated that PAPRs prepared from unreactive Nauru, Christmas Island "A" grade and Duchess PRs were less effective than SSP. The degree of acidulation was up to 50% on H_2SO_4 to SSP (Water-soluble P about 42% of Total P). From the above findings there seems to be no single conclusion on the effectiveness of the PAPRs prepared from unreactive rocks.

Partially acidulated phosphate rock (PAPR) products prepared with orthophosphoric acid (H_3PO_4) always contain more total and water-soluble P_2O_5 than do those prepared with sulphuric acid (H_2SO_4) (Hammond *et al.*, 1980; Hammond *et al.*, 1989). Partial acidulation of PR with H_2SO_4 always results in a decrease of total P_2O_5 and an increase of water-soluble P_2O_5 as the degree of acidulation increases (Shultz, 1986). The relative effectiveness of different acids in terms of production of water-soluble P, may be rated as $H_3PO_4 > H_2SO_4 > HNO_3 > HCl$ (Dincu, 1961; Pand and Misra, 1970; Shinde *et al.*, 1978; Marwaha, *et al.*, 1981; Marwaha, 1983; Al faris *et al.*, 1991). The high production of water-soluble P with H_3PO_4 is not unexpected considering that the acid itself contains soluble P. With sulphuric PAPRs an inhibitory coating of gypsum on PR particles may develop which adversely affects the quality of the products and reduces their agronomic effectiveness (Leon and Fenster, 1979; Al faris *et al.*, 1991). Leon and Fenster (1979) in a field experiment conducted on a Carimagua Oxisol, tested the agronomic response of peanuts and rice to Florida and North Carolina PRs partially acidulated with sulphric acid. Despite the fact that the North Carolina PR was a highly reactive rock, the PAPR was found to be ineffective even for a P responsive crop like peanut. Chatterjee *et al.* (1983) compared a series of PAPRs prepared by reacting H_2SO_4 with Purulia PR of India and a Sri Lankan PR, with single superphosphate on a Sindri red soil of near neutral pH and having high phosphate fixing capacity. They concluded that 20% acidulated Purulia rock and 46% acidulated Sri

Lankan rock were as effective as superphosphate. But increasing the degree of acidulation beyond specified levels was observed to reduce the agronomic effectiveness of the products. The above findings were explained on the basis of work done at the IFDC, that partial acidulation with H_2SO_4 and subsequent drying of the granules produced a material which is almost completely covered by a thin layer of insoluble anhydrous or hemi-hydrate $CaSO_4$ that either prevented the release of phosphorus or the physical contact of PR with the soil. Meagre information is available with respect to relative agronomic effectiveness of products acidulated with different acidulants at similar levels of acidulation. This is because of two basic problems: PAPR has still to be accepted as a universal commercial product. Secondly, the intrinsic problem of successful acidulation and drying non-phosphoric PAPRs do not permit fair comparisons at acidulation levels above 30%. For example, nitric acid acidulated product with 30% or more acidulation does not dry up completely (Marwaha, 1983; Basak *et al.*, 1991). The relationship between effective acidulation levels with H_2SO_4 and H_3PO_4 was investigated by Hammond *et al.* (1980) who found 50% H_2SO_4 effective acidulation level to be approximately the same as that with 20% H_3PO_4. Numerous field trials conducted by IFDC have demonstrated that PAPR at 40% - 50% acidulation with H_2SO_4 or at 20% with H_3PO_4 approaches the effectiveness of SSP or TSP for some crops in certain tropical soils (Chien and Menon, 1993b).

Hammond *et al.* (1989) and Bationo *et al.* (1990) found that the agronomic effectiveness of PAPRs prepared from PRs of moderate to low reactivity from sulphuric acid, significantly decreased when they contained increasing iron and aluminium oxide. They observed that PAPR prepared from Kodjari PR in Burkina Faso (containing 7.1%

$Fe_2O_3 + Al_2O_3$), at 50% acidulation with H_2SO_4 was only 49% as effective as TSP in increasing dry-matter yield of maize. On the other hand, PAPR made from Hahotoe PR in Togo (containing 1.9% $Fe_2O_3 + Al_2O_3$ at 50%) was 84% as effective as TSP. They noted that if the $Fe_2O_3 + Al_2O_3$ content of the PR is > 7%, the water soluble P content of the PR becomes reduced appreciably and also the effect of $Fe_2O_3 + Al_2O_3$ is more pronounced at 50% acidulation than at 30% acidulation. In general, those PAPRs made from PRs containing low $Fe_2O_3 + Al_2O_3$ content are more effective than those with high $Fe_2O_3 + Al_2O_3$ content. This was attributed to the reaction of the acid with iron and aluminium oxides during partial acidulation resulting in less conversion of apatite P to the water-soluble P formed. In addition, some of the water-soluble P formed during acidulation is converted to citrate-soluble and even to citrate-insoluble P upon reacting with iron and aluminium and thus become less available to plants.

Several workers (McLean and Wheeler, 1964; McLean *et al.*, 1965; McLean and Balam, 1967; McLean and Logan, 1970) have reported that PAPR can be as effective as or sometimes better than superphosphates on acid soils possessing high P-fixing capacity. On the other hand, granulated PAPR was observed (Terman *et al.*, 1964; Terman and Allen, 1967; Hammond *et al.*, 1980) to be inferior to TSP in greenhouse studies on soils with relatively low P-fixing capacity. Mokwunye and Chien (1980) also found that soil solution P concentrations obtained with PAPR, relative to TSP, increased with increasing P-fixing capacity of three tropical soils. In a study conducted by Chien and Hammond (1989), the calculated RAE values for PAPR with respect to SSP obtained on three soils with low, medium and high P-fixing capacity were 84%, 101% and 124%, respectively.

SECTION E

2.7 Residual effectiveness of P-fertilizers

Only a small fraction of the phosphate fertilizers applied to soil is taken up by crop in the year of application. Stangel (1985) stated that, at most, 15% of a water soluble P fertilizer is taken up by the crop in the year of application. Part of what is left, goes to increase the labile pool of P in the soil. Part is also converted, in slow reactions, to less soluble phosphorus forms (Mokwunye, 1995) which continue to supply P to crops for several years (residual effect). The agronomic effectiveness of PRs relative to that of water-soluble fertilizer has been observed to improve appreciably with time. This is attributed to the continuing dissolution of the PR compared to the declining availability of P from the residues and reaction products of the water-soluble P sources over time.

The magnitude and duration of the residual effect of a P fertilization depend on the rate of initial application, crop removal, soil characteristics (i.e soil reactions) and also the type of phosphorus source that is used for fertilization. Holdford (1982) suggested that after dissolution of a P fertilizer in the soil solution, the P ion reacts with the soil constituents and can undergo the following types of reactions:

i. Adsorption by reactive iron and aluminium oxides and hydroxides. Some of the adsobed P become occluded in the structures of the soil minerals.

ii. Precipitation and transformation into increasingly stable forms.

iii. Adsorption by organic compounds.

These reactions vary greatly among soils and depend on soil factors like organic matter content, kind of cations present, texture and pH.

The dissolution characteristics of P sources contribute to the differences in their residual effectiveness. All phosphate fertilisers from which the phosphate ion migrates into the soil solution will undergo reaction with the soil constituents. The availability of phosphate to the plants is governed by the conversion rate of such transformation reactions. Because of the relatively slow dissolution rate of phosphate rock the phosphate concentrations in the soil solution after a phosphate rock application remains fairly low. Dilute solutions of P are not expected to participate in precipitation reactions (Mokwunye and Hammond, 1992). On the other hand, water soluble P sources dissolve immediately in the soil solution and the released phosphate ions are quickly transformed by reactions with soil constituents into less soluble forms

The initial application rate, the crop removal and losses of P by other pathways determine the amount of P that is left in the soil. However, the actual availability of the residual phosphate is influenced by the soil reactions and the characteristics of the different P sources (Visker *et al.*, 1995). Tisdale *et al.* (1985) showed with a low-P-fixing capacity soil that, irrespective of the rate of P, there was a residual effectiveness up to the seventh crop year, and the response to initial and residual P increased with increasing rates. Using data obtained from a trial conducted over 12 years, Roesch and Pichot (1985) reported that the duration of the residual effect of Tahoua phosphate rock depended on the application rate and ranged between 5 and 9 years. The improvement in the residual effect of PRs compared to water soluble P sources does not mean that they will necessarily out-yield, or even give equal yield in comparison with the water soluble source (Khasawneh and Doll 1978). Owusu-Bennoah and Acquaye (1996) found that the residual effect of either Togo PR or partially acidulated (50%) Togo rock phosphate (PAPR-50) on dry matter yield and total P uptake to be negligible compared with SSP. and concluded that apatitic P was poorly effective relative to SSP in the concretionary soils.

2.8 Summary of Literature Review

From the literature review, it is obvious that rock phosphate is a resource available to quite a number of developing countries, which can be utilized to increase crop yield. It must however be kept in mind that, while each deposit does differ in mineralogy, P content and chemical reactivity, all natural deposits indigenous to tropical regions share certain properties with those well-known rocks used for production of commercial P fertilizers. That is the P is contained in a form which is not readily plant available when applied to the soil but which will convert to plant-available forms at varying period of time.

Direct application of PR does not always give satisfactory results due to low reactivity or combinations of the PR with inappropriate soil and or crop. These problems are overcome by acidulation to convert the P in the PR to a form that is readily plant available. Acid soils deficient in available P and exchangeable Ca and having high P-fixing capacity as found in the semi-decidous rainforest zones of Ghana, would be expected to favour dissolution of PR.

Direct application of PR is suitable for perennial crops and crops with lower P demands than for annual crops and crops with high P demands.

The success of partial acidulation depends on the amount of impurities present in the form of $Fe_2O_3 + Al_2O_3$ which should not exceed 7%.

As regards to management practices, broadcasting and incorporating PR into the soil should be preferred to banding or deep-placement and liming of acid soils should be avoided whenever possible. For soils with low P-fixing capacity, applying PR at least four weeks before planting is advantageous, on the other hand, for a high P-fixing capacity soil it would be advisable to apply at planting.

Because of the slow dissolution rate of applied PR in the soil, it remains in the soil for a long time and continues to contribute slowly to soil solution P. Hence its agronomic effectiveness relative to water soluble P improves significantly with time.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Introduction

In this chapter the basic analytical techniques used, the incubation study, the greenhouse work and the field experiment will be described.

3.2 Soils

The soils used for this study namely Bekwai, Nzima and Kokofu series were sampled from the Agricultural Research Station (ARS) at Kade (6° 43' N: 1° 36' W) in the Eastern region of Ghana (Figure 3.1). Bekwai, and Nzima, which are up-slope soils are classified as Paleudult whereas Kokofu, which is a lowland soil is classified as Paleudalf (USDA, 1975). According to the FAO - UNESCO legend(1974), Bekwai and Nzema series are classified as Ferric Acrisol and contain various amounts of ironstone concretions whereas Kokofu is classified as Eutric Nitosol. All the soils are developed over lower Birrimian phyllite.

3.2.1 Site Characteristics

The experimental site is located in the semi-deciduous forest zone (fig 3.1). The major rainfall occurs from May to July and a minor season between September and November (Table 3.1). The mean annual precipitation is 1300 to 1650 mm. Fig 3.2 shows the monthly total rainfall for the year 1998 at ARS, Kade, the site of the field experiment. The cultivated areas are occupied by forest re-growth with *Chromolaena odorata, Mimosa pudica* and *Centrosema pubescense* as prevailing plant species.

Table 3.1. Average monthly rainfall at study site (ARS) for the period 1978 to 1998 (21- year average).

		Major rainy season							Major dry season			
	April	May	June	July	Aug	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.
Rainfall(cm)	147	176	198	128	103	142	188	110	32	14	63	125

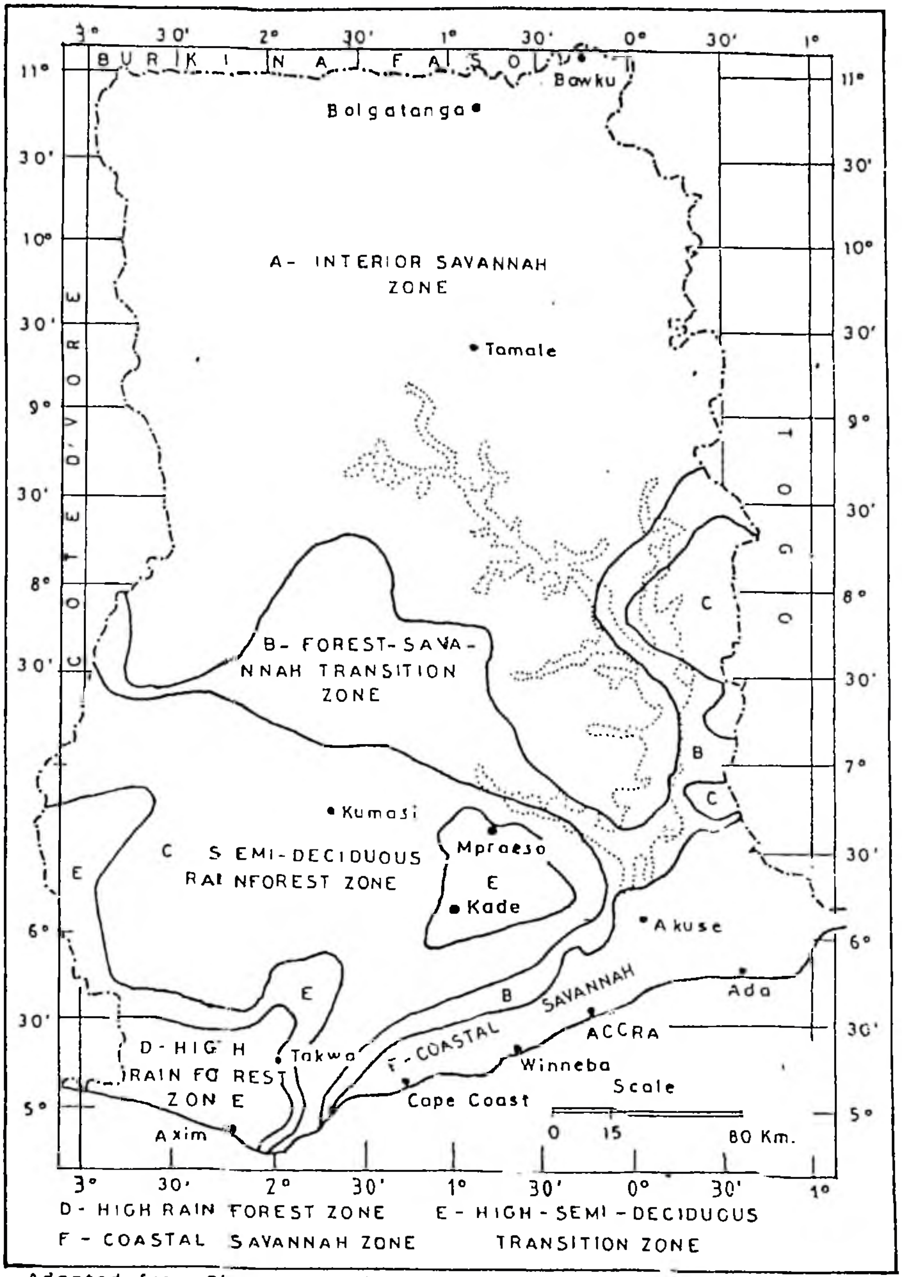
3.2.2 Sampling

Surface soils (0-20 cm) of Bekwai, Nzima and Kokofu series were sampled from their respective profiles. The bulk soil samples were brought to the laboratory, air-dried, crushed, sieved through a 2 mm sieve to remove twigs, plant roots and ironstone concretions; stored for physico-chemical analyses, the incubation and the greenhouse studies.

3.3 Laboratory analyses of soil samples

3.3.1 Particle size analysis

Particle size analysis was carried out by the method of Bouyoucos (1962). To 40 g sample of 2 mm air dried soil of each soil series was added 100 ml of 5% calgon (sodium hexametaphosphate) solution. It was shaken on a mechanical shaker for 30 min. The suspension was transferred into a graduated sedimentation cylinder. Water was added to make it to the



Adapted from Obeng et al. (1990).

Fig. 3·1 Ecological zones of Ghana and sampling area .

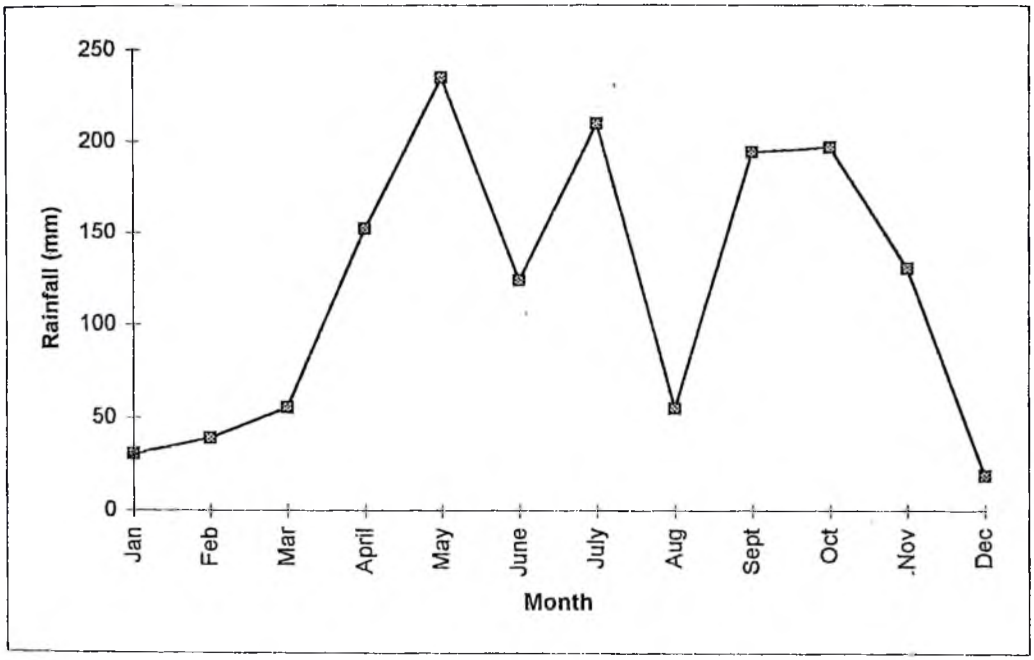


Fig 3.2 Monthly total rainfall at ARS for the year 1998 (courtesy of ARS)

litre mark. A plunger was lowered into the cylinder and the suspension stirred vigorously by moving the plunger up and down, about 5 times. Timing was started immediately with a stop watch after stirring and the first hydrometer reading taken, 5 min from the time of mixing of the suspension. The second hydrometer reading was taken 5 h later. The first and second hydrometer reading represent silt and clay respectively .The sand fraction was obtained after decanting the suspension from the sedimentation cylinder into a 0.2mm sieve. The 0.2mm fraction (sand) was washed with tap water on the sieve and then oven dried at 105^{oc} for 3 days and the dried weight recorded. The textural class of the soils was determined using the USDA textural triangle.

3.3.2 Soil pH

The pH of each soil sample was measured electrometrically, using a Pracitronic M.V 88 pH glass electrometer in both distilled water and in 0.01M $CaCl_2$ solution at a ratio of 1:2 soil: water / and 1:2 soil: 0.01M$CaCl_2$ solution. Ten grammes each of the soil sample was weighed into a 50 ml beaker. Twenty millilitres of distilled water was added and the soil-liquid suspension was stirred several times for 30 min. The suspension was allowed to stand for 30 minutes to allow most of the suspended clay to settle out. The pH electrometer was then standardised using buffer solutions of pH 7.0 and 4.0. The electrode was inserted into the suspension to measure the pH of the sample. The above procedure was repeated for the measurement of pH in the 0.01M $CaCl_2$ solution.

3.3.3 Organic Carbon

Organic carbon was determined using the wet combustion method of Walkley and Black (1934). Ten ml of 1N potassium dichromate ($K_2Cr_20_7$) solution and 20 ml of concentrated sulphuric acid (H_2SO_4) were added to 0.5 g sample of 2 mm sieved soil in a 250 ml Erlemeyer- flask. The flask was swirled to ensure full contact of the soil with the solution after which it was allowed to stand for 30 min. Two hundred ml of distilled water and 10 ml of orthophosphoric acid were also added. The unreduced K_2 Cr_2 0_7 remaining in solution after the oxidation of the oxidizable organic material in the soil sample was titrated with 0.2 N ammonium ferrous sulphate solution after adding 2 ml of barium diphenylamine sulphate indicator. The percent organic carbon was calculated as:

$$\% \text{ C} = 0.3\,\frac{(10.0\text{-XN})}{\text{W}} \times 1.33 \qquad [\,3.1\,]$$

Where:

X = ml of Fe $(NH_4)_2$ $(SO_4)_2$ required for the titration.

N = normality of Fe $(NH_4)_2$ $(SO_4)_2$

W = weight of soil sample.

3.3.4 Total nitrogen

A 0.5 g soil sample was weighed into a 250 ml Kjeldahl flask and a tablet of digestion accelerator, selenium catalyst was added and was followed by 5 ml conc. H_2SO_4. The mixture was digested until the digest became clear. The flask was then cooled and its content transferred into a 100 ml volumetric flask with distilled water and made to volume quatitatively.

An aliquot of 5 ml of the digest was taken into a Markhan distillation apparatus. Five ml of 40% NaOH solution was added to the aliquot and the mixture distilled. The distillate was collected in 5 ml of 2% boric acid. Three drops of mixed indicator containing methyl red and methylene blue were added to the distillate in a 50 ml Erlemeyer flask and then titrated against 0.01N hydrochloric acid (HCl) solution (Bremmer, 1965). The % nitrogen was calculated as:

$$\% \text{ N} = \frac{\text{Normality of HCL x Titre volume x 0.014 xvolume of extractant x 100}}{\text{weight of soil sample x volume of aliquot}}$$

Where:

0.014 = Milliequivalent of Nitrogen

3.3.5 Total phosphorus

Total P was determined by digesting 2 g soil sample that has been passed through a 0.5 mm sieve with 25 ml 1.5: 1 60% perchloric / nitric acid mixture for 40 min. Digesting was done for 20 min. The digest was filtered through a No. 42 Whatman filter paper into a 100 ml volumetric flask and made to volume. Phosphorus in the filtrate was determined using the molybdate ascorbic acid method of Watanabe and Olsen (1965) as follows:

3.3.5.1 Measurement of Phosphorus

Three millilitres aliquots of the filtrate were taken (in duplicate) into 50 ml volumetric flasks containing distilled water.The pH was adjusted using P-nitrophenol indicator and a few drops of concentrated ammonium hydroxide (NH_4OH) until the solution turned yellow. The solution was diluted to about 30 ml with distilled water after which 8 ml of ammonium molybdenum-ascorbic acid solution (reagent B) was added and made to volume, with distilled water. The solution was mixed thoroughly by shaking and allowed to stand for 15 minutes for the colour to stabilize

Reagent A was prepared as follows:

1. 140 ml of conc. H_2SO_4 in 1000 ml of distilled water (5N H_2SO_4)

2. Ammonium hepta molybdate $(NH_4)_6 Mo_7 O_{24}.4H_2O)$.12g in 200 ml of distilled water

3. Potasium antimony tartrate ($KSbOC_4H_4O_6.1/2H_2O$). 0.29g in 100 ml of distilled water

Solutions 1, 2 and 3 are mixed together and made up to 2000ml in a volumetric flask.

The reagent B was prepared by dissolving 1.056g of L-ascorbic acid in 200ml of reagent A in a volumetric flask. This should be freshly prepared.

. A blank was prepared with the digestion mixture and 8 ml of reagent B. The intensity of the blue colour was measured using the Philips PU 8620 spectrophotometer at a wavelength of 712 nm.

3.3.6 Available phosphorus

Available phosphorus was determined using the method of Bray and Kurtz (1943). Five grammes of soil sample were weighed into a 100 ml centrifuge tube and 35 ml of Bray 1 solution (0.03M NH_4 F in 0.025M HCl) was added. The suspension was shaken for 1 min on a reciprocating shaker and filtered. Phosphorus in the filtrate was measured as under 3.3.5.1

3.3.7 Exchangeable bases

Ten grammes of soil sample were weighed into 100 ml centrifuge tube and 20 ml of 1N neutral ammonium acetate (NH_4OAC, pH 7.0) solution added. The suspension was shaken for 1 h, centrifuged at 1000 rpm for 10 min and filtered. through No 31

Whatman paper The ammonium saturated soil was washed three times with 95% ethanol by shaking for 15 min. using the mechanical shaker and centrifuged at 1000 rpm for 10 min. The exchangeable bases, Ca^{2+} and Mg^{2+} were determined from the extract using atomic absorption spectrophotometer, AAS 3 CALZEISS JENA. Potassium and Na^+ were determined using a flame photometer.

3.3.8 Exchangeable acidity (Exchangeable Al^{3+} + H^+)

Twenty- five ml of 1N potassium chloride (KCl) solution was added to 10 g of soil sample, mixed by swirling and allowed to stand for 30 min and filtered through a No 42 Whatman filter paper. The soil was successively leached with 5 batches of 25 ml of 1N KCl to a total volume of about 150 ml. Four drops of phenolphthalein were added to the leachate and titrated with 0.1N NaOH to the first permanent pink endpoint. Correction for a blank of NaOH titre on 150 ml KCl solution was made and the KCl-extractable acidity calculated as:

$$\text{Meq KCl acidity} = \frac{(\text{ml NaOH sample} - \text{ml NaOH blank}) \times N \times 100}{\text{g sample}} \qquad [3.2]$$

Where, N is normality of NaOH.

The effective cation exchange capacity (ECEC) was obtained by summation of the exchangeable bases and the exchangeable acidity (Coleman *et al.*,1959).

3.4 Incubation study

Two replicates of 200 g air-dried sieved (< 2 mm) samples of Bekwai, Nzima and Kokofu series were weighed into 250ml plastic beakers. Togo rock phosphate (TRP), GRP, PAPR-50 and TSP were added to each of the soils at a rate of 60 mg P kg^{-1}. In adding the P sources, the soil in each beaker was transferred into a large plastic basin and the measured amount of P was added. The soil and the P source were thoroughly mixed and returned to the beaker according to treaments. A control treatment without P was included. Distilled water was added to each soil to bring it to 60% field capacity. The set up was incubated at room temperature for 105 days. To assess the reaction of the different P sources with the soil, sub-samples of the incubated soils were taken every 21days (i.e. 21, 42, 63, 84 and 105 days) and analysed for resin-P, Ca-P and Fe/Al-P as described below:

3.4.1 Resin extractable-P from incubated soil

Resin-P was extracted using anion exchange resin membrane (AEM). The AEM (9 x 62.5 mm) was charged by washing for three days with several batches of 0.5 M HCl and finally rinsed with distilled water. The membranes were kept moist until ready to use. One resin strip membrane was put in a 100 ml plastic bottle and 0.5 g of the incubated soil sample was weighed into it and then 30 ml of distilled water added. The plastic bottle was shaken end to end for 16 h on a mechanical shaker overnight at room temperature. The resin membranes were removed from the soil suspension using forceps and then washed with distilled water to remove adhering soil particles. The soil suspension was then discarded and the bottles thoroughly washed. The resin strip membranes were placed in the clean bottles and 20 ml of 0.5 M HCl was added. This was shaken for another 16 h overnight to desorb the soil phosphate adsorbed on to the membrane. An aliquot, 5ml of the extract was taken and the phosphate was analysed colourimetrically by the method of Murphy and Riley (1962).

3.4.2 0.1 M NaOH extractable-P from the incubated soil

The amount of P dissolved from the fertilizers, which had been chemisorbed by Fe, and Al was also monitored using 0.1 M NaOH. An amount of 0.5 g of the incubated soil sample was weighed into another batch of 100 ml plastic bottles and 30 ml of 0.1 M NaOH was added to each, and shaken for 16 h overnight. The soil suspension was centrifuged at 1000 rpm for 10 min, and filtered. An aliquot of 5 ml was pipetted into a centrifuge tube and 1.6 ml of 1.8N H_2SO_4 was added and kept in the fridge for 30 min to precipitate the organic matter. This was centrifuged at 1000 rpm for another 10 min. The clear supernatant was then decanted into 50 ml volumetric flasks and NaOH-P analysed as under 3.4.1

3.4.3 1 M HCl extractable-P from the incubated soil

To assess the amount of P sources that remained undissolved at a particular time, 0.5 g of the incubated soil sample was weighed into another batch of 100 ml plastic bottles and 30 ml of 1 M HCl was added to each. The bottles were shaken for 16 hours overnight. The soil suspension was filtered and an aliquot 5ml of the filtrate was taken for P determination.

3.5 Greenhouse Experiment

The experimental design for the greenhouse was a randomized complete block design (RCBD) involving the three soil series (Bekwai, Nzima and Kokofu), four P sources, at a rate of 60 mg P Kg^{-1} soil and control. The experiment was replicated four times, giving a total of (5 treatments x 3 Soils x 4 Reps) 60 experimental units. Equal amount (1.5 kg) of each soil was weighed into plastic pots and the P fertilizers (TRP, GRP, PAPR and TSP) were added at the rate of 60 mg P kg^{-1} soil. In adding the P sources, the soil in each pot was transferred into a large plastic basin and the weighed amount of the P source was added, thoroughly mixed and returned to the respective pots. Nine maize seeds were sown in each pot and distilled water added to bring the soils to 60% field capacity. Pots were arranged on greenhouse benches in randomized complete block design (RCBD) with the pots randomised within each block. The blocks were rotated weekly to minimize uneven environmental effects within the greenhouse. The plants were thinned to two per pot three days after germination. To ensure adequacy of nutrients other than P, the soils were fertilized as follows 60 mg N kg^{-1} soil as $(NH_4)_2 SO_4$, 40 mg K kg^{-1} as KCl; 20 mg Ca kg^{-1} soil as $Ca(NO_3)_4$. $4H_2O$ and 20 mg Mg kg^{-1} soil, as $Mg(SO_4)$ $7H_2O$. The plants were allowed to grow for 28 days. Plants were cut at the soil surface, and immediately weighed for the fresh weight. The plants were dried in an oven at 90^{o} C to a constant weight. The dried plant materials were ground to pass through a 1 mm sieve and later stored in small plastic bags for subsequent P analyses.

3.5.1 Digestion of Plant material

Approximately 1.0 g of the plant material was weighed into 500 ml conical flask and digested with 5 ml concentration H_2SO_4 and H_2O_2 (30% reagent grade) (Thomas *et al.*, 1967). The digest was transferred quantitatively with distilled water into a 100 ml volumetric flask. The solution was allowed to stand for some hours to permit silica to settle out, after which aliquots of the solution were taken for the determination of P concentration in the plant material using the ammonium molybdate ascorbic acid method (Watanabe and Olsen, 1965) as described under 3.3.5.1

3.6 Solubility of P sources

The solubility of the fertilizer materials used was determined in neutral ammonium citrate and 2% citric acid. One gramme of each fertilizer material was weighed into 150 ml plastic extraction bottles and 100 ml of each of the extractants added. The suspension was shaken for 1 h and filtered through a No 6 Whatman filter paper. The filtrates obtained for triple superphosphate (TSP) and partially acidulated phosphate rock (PAPR) were diluted to 500 ml and 2 ml of the diluted solution was used to determine the P concentration. For the filtrates obtained from Togo rock phosphate (TRP) and Gafsa rock phosphate (GRP) 5 ml aliquot was used to determine the P concentration using the ammonium molydate ascorbic acid method as described under 3.3.5.

3.7 Field Experiment

About 600 m^2 (ie 30 m x 20 m) of land was cleared on the Bekwai, Nzima and Kokofu Series. Stumps were removed and all debris were gathered and collected from the plots without burning. Each plot was divided into four equal subplots (or blocks) measuring 13.75 m x 8.75 m with a distance of 1 m between each of them. Each block was further divided into five equal sub-subplots, each measuring 2.7 m x 8.75 m. These were further, divided into three equal rows. The five treatments; TRP, GRP, PAPR, TSP and the control were applied to the sub-subplots in a randomized complete block design (RCBD) as shown in fig. 3.3

3.7.1 Planting and P application

Maize was sown as a test crop in each row on each sub-subplot at a recommended spacing of 90 cm between rows and 30 cm within rows and at a rate of three seeds per stand and thinned to one seedling per stand 7 d after germination.

Togo rock phosphate(TRP), GRP and PAPR were applied in bands along the rows and worked into the soils two weeks before planting. This is to allow some dissolution to take place prior to sowing and to concentrate P from the dissolved PRs for the effective uptake by plants. TSP was applied two weeks after germination. Each P source was applied at the rate of 60 kg P ha^{-1}. To ensure adequacy of nutrients, other than P, 80 kg N ha^{-1} as sulphate of ammonia [$(NH_4)_2SO_4$] and 50 kg K ha^{-1} as muriate of potash (KCl) were also applied in bands along the rows four weeks after germination and worked into the soil.

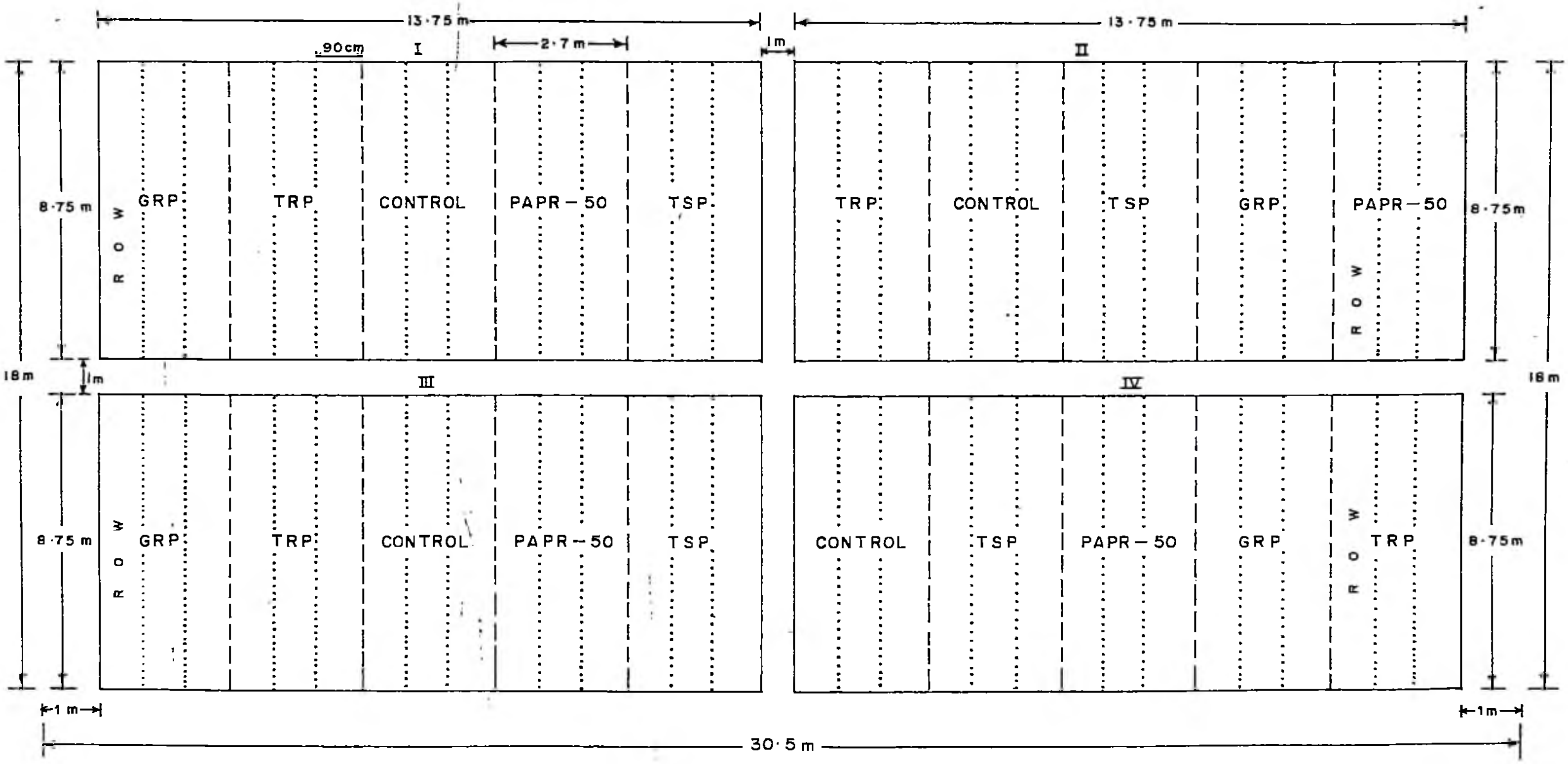


Fig. 3·3 FIELD PLAN : Randomized complete block design (RCBD)

3.7.2 Weed control

The predominant weeds on Bekwai series were *Chromolaena odorata* and on Nzema and Kokofu were *Centrosema pubscense* and *Mimosa pudica*. A Knapsack Sprayer was used to spray Altrazine herbicide to control the weeds. Spraying was done when the maize plants were three weeks old.

3.7.3 Harvesting, plant sampling and drying

Harvesting was done at maturity, when the cobs were 80 % ripe. On each soil, 10 healthy stands were harvested from the middle row on each sub-subplot. The cobs and the husks were separated from the stubbles. The stubbles were tied and weighed on the field. The cobs and sub samples of the stubbles were brought to the laboratory. The cobs were dehusked and the maize grains were shelled. Both the empty cobs and the husk were weighed separately. Sub-samples of the leaf, the stem of the stubbles, and the husk were cut into pieces and weighed separately into paper envelopes. They were oven-dried at 90^{oC} to a constant weight. Their percent moisture contents were calculated and used to adjust their initial weights recorded on the field to obtain their dry weights. The grains were sun dried over a period of time, till constant weight was attained.

3.7.4 Plant analysis

Samples of the oven dried leaf, stem, husk and the grains were milled to pass through a 1 mm sieve. The milled samples were stored for determination of P concentration as described in 3.5.1

The P uptake was obtained by multiplying the dry matter weight by the corresponding phosphate concentration.

3.7.5 Statistical Analys

An analysis of variance (ANOVA) using randomized complete block design (RCBD) was performed to determine differences among treatments and possible interactions. The least significant difference (LSD) was used to separate the means.

CHAPTER FOUR

4.0 RESULTS

4.1 General Soil characteristics.

Some selected physical and chemical properties of the soils are shown in Table 4.1. The results of the particle size analysis, indicated that Bekwai had the highest sand content of 51.2% while Kokofu had the least (39.8%). The clay content was high in all the soils ranging from 34.6% in Bekwai to 36% in Kokofu.

The soils were moderately acid with pH values varying between 5.4 and 4.9 in water. None of the soil samples exhibited pH in water less than that in $CaCl_2$ solution; consequently, soils from the three sites had a negative Δ pH.define as [pH = (pH $CaCl_2$) - (pH H_20), and suggesting that the surfaces of the soil colloids are negatively charged. Levels of organic carbon in the soils ranged from 11.2 to 20.2 g kg^{-1} (mean 15.1 g kg^{-1}). Total N also varied between 1.5 and 2.2 g kg^{-1} and decreased with decreasing organic carbon of the soils. The results showed that the amount of total P in the soils ranged from 314 to 339 mg kg^{-1} with an average of 328 mg kg^{-1}. The available P was generally low, ranging from 2.50 to 3.48 mg kg^{-1} . None of these soils had a recent history of phosphorus fertilization, so the available P parameters represent a background level for agricultural soils in the area.

The mean exchangeable Ca of 5.6 $cmol_c$ kg^{-1} was higher than for Mg and constituted more than 50% of the ECEC. Exchangeable Na values which ranged from 0.31 to 0.52 $cmol_c$ kg^{-1} , were consistently higher than the exchangeable K in Bekwai and Kokofu but in Nzima the contents of these two bases were about the same. The exchangeable acidity (Al + H) ranged between 0.27 and 0.5 $cmol_c$ kg^{-1}. A significant negative correlation existed between

Table 4.1: Some selected physical and Chemical Properties of the Soils

Soil Properties	Bekwa upslope	Nzima upslope	Kokofu lowland
Sand (%)	51.2	44.2	39.8
Silt (%)	14.2	21.0	24.2
Clay (%)	34.6	34.8	36.0
Texture	SCL*	CL**	CL**
pH (1:2, soil : water)	5.4	5.2	4.9
pH (1:2, soil : $CaCl_2$)	4.9	4.9	4.2
Organic Carbon (g kg^{-1}))	20.2	13.8	11.2
Total N (g kg^{-1})	2.2	1.8	1.5
Total P (mg kg^{-1})	339	330	314
Available P (Bray 1 mg kg^{-1})	3.48	2.50	3.16
Exchangeable bases ($cmol_c$ kg^{-1})			
Ca	5.65	5.46	5.57
Mg	1.54	1.47	1.52
K	0.08	0.34	0.18
Na	0.52	0.31	0.49
Exchangeable acidity ($cmol_c$ kg^{-1})	0.30	0.27	0.50
ECEC	8.09	7.85	8.26
Ca : Mg	3.7	3.7	3.7

*SCL = Sandy clay loam; **CL = Clay loam.

ECEC = Effective cation exchange capacity

Table 4.2: Total Phosphorus (P) and extractable P contents of the various P sources.

Phosphorus Sources	Total P (%)	P extracted by 2% Citric acid	P extracted by Neutral ammonium citrate
		%w/w	
Togo rock phosphate (TRP)	16.5	4.3	0.9
Gafsa rock phosphate(GRP)	13.2	6.3	2.2
Partially acidulated Togo rock phosphate(PAPR)	12.0	10.0	10.2
Triple superphosphate(TSP)	20.0	18.4	18.1

pH of the soils determined in water and their exchangeable acidity ($r = -0.814^*$). This means that as exchangeable acidity increases, there is a corresponding decrease in pH (H_20). The ECEC values were fairly similar in all the three soils ranged from 3.85 to 8.26 $Cmol_c Kg^{-1}$ (mean 8.07 $Cmol_c Kg^{-1}$).

4.2 Characteristics of the P sources.

The total P contents of the P sources ranged from12% in PAPR-50 to 21% in TSP. (Table 4.2). The high total P content of TSP is attributed to the acidulant (orthophosphoric acid) used in its manufacturing. The most important property of PR in relation to its agronomic effectiveness is its solubility, which is normally measured by 1N neutral ammonium citrate, 2% citric acid or 2% formic acid (Chien and Hammond, 1978).The 2% citric acid extractable P of the P sources ranged from 4.3% in TRP to 18% in TSP while the 1N neutral ammonium citrate P also ranged between 0.13% and 18.1%. Togo RP had the least percent P in both extracting solutions confirming its low solubility, while TSP had the highest. From Table 4.2, the the ease of solubility of the P sources followed the trend TSP > PAPR-50 > GRP > TRP.

4.3 Incubation Study

4.3.1 Resin extractable-P

The resin extractable P obtained from the three soils during the incubation period is given in Fig 4.1. In general, the pattern of P extraction from the various P sources can be categorised into three depending on the ease of P release from the various P sources. Category 1 which is of highest solubility is made up of TSP and PAPR; category 11 which is of medium solubillity is GRP and category 111 which is least soluble is made up of Togo RP. The pattern was consistent among all the soils. The results (Fig 4.1) showed that the amount of P dissolved from all the P sources in the three soil series decrease with incubation time, that is, from the 3rd to the 12th week. The decrease was more obvious in Bekwai and Nzima than in Kokofu. At the 12th week, very low amount of P was extracted in all the soils and after this period, there was a slight increase in the amounts of P extracted from all the P sources. In general Fig 4.1 showed that the decline in Resin-P with incubation period followed the trend, Bekwai > Nzima > Kokofu.

Irrespective of soil series, there was no significant difference between the amounts of P extracted from TSP and PAPR. The amount of P extracted from GRP however was between TSP and PAPR on one hand and TRP on the other. As observed in Fig 4.1, there were little differences between the amounts of P extracted from Togo rock phosphate and the control. This observation was consistent in all the soils.

It is important to note that in Kokofu, a lowland soil, differences among the three categories of P dissolution in the soils were slight with increasing incubation period, compared to the two upland soils, Bekwai and Nzima. In general the results do show that at each extraction, the amounts of resin-P extracted were in the order; TSP = PAPR-50 > GRP > TRP = control.

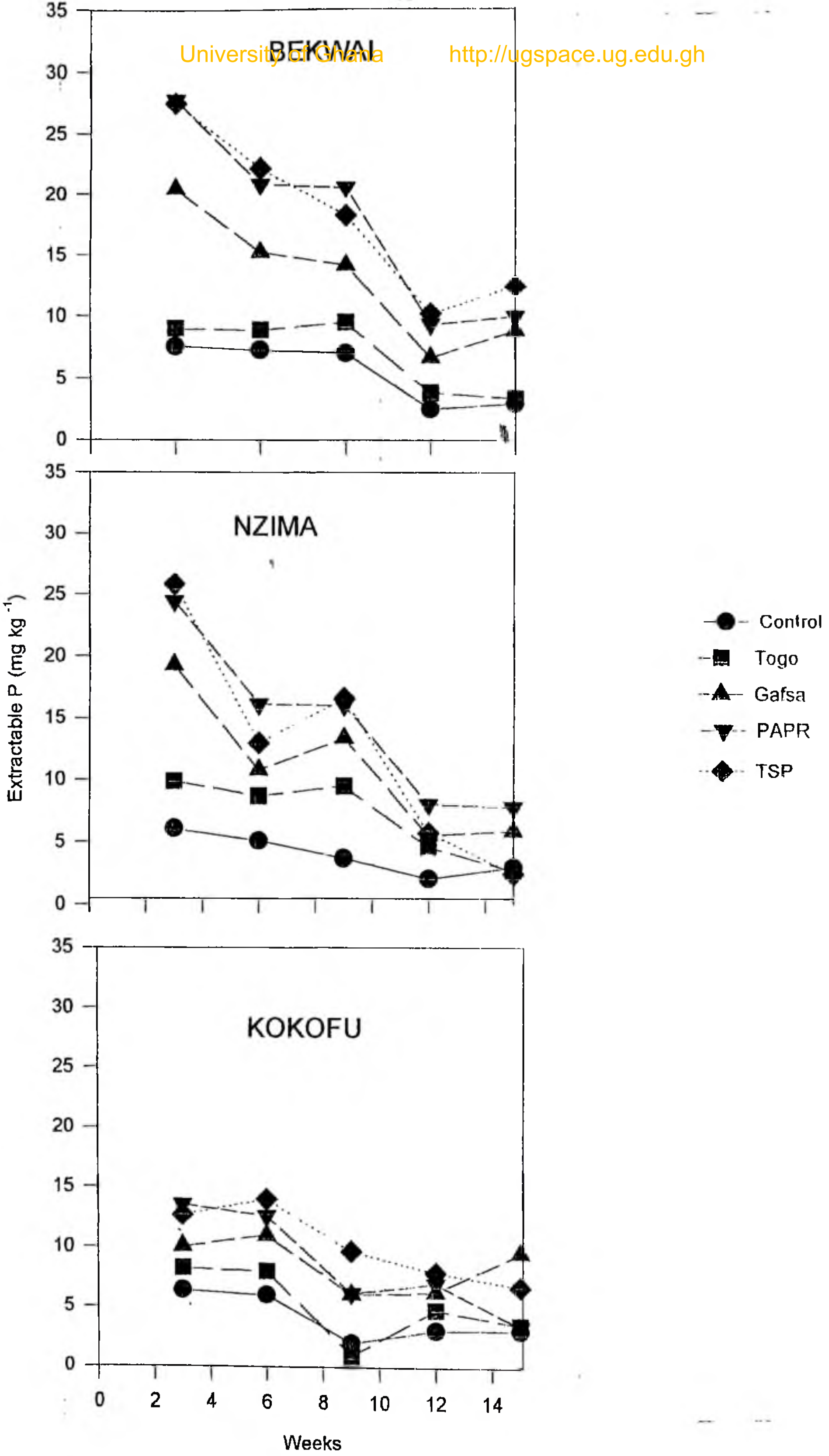


Fig 4.1 Resin extractable P mg kg^{-1} of the various P sources

4.3.2 0.1M NaOH extractable-P

Figure 4.2 shows the NaOH extractable-P obtained from the three soils during the incubation. The rate of extraction was different among the three soils. In Bekwai and Nzima soil series, the two upland soils, there was a general decline in NaOH-P with time up to the 9th week. This was followed by an increase in the amount extracted. The NaOH-P from TSP treated Nzima soil decreased up to the 6th week and then consistently increased with extraction period. With the exception of TSP in Nzima there were no marked differences in the rate of extraction among TSP, PAPR and GRP in the two soils. The rate of NaOH-P extraction from the Togo PR with time was generally much better than in the control.

In the case of Kokofu, which is a lowland soil, there was a gradual increase in the P extracted from all the P sources with incubation. The amounts of NaOH extractable P from TSP, PAPR-50 and GRP were not significantly different from each other, although at each extraction period, the amount of P extracted from TSP was consistently higher than the other P sources. The NaOH-P, extracted from Togo RP was fairy similar to that of the control.

4.3.3 1M HCl extractable-P

The 1M HCl extractable-P from the three soils during the incubation is shown in Fig. 4.3. The results showed a similar trend among all the soils. The level of HCl-P extracted dropped after 6 weeks of incubation, remained constant up to the 15th week in Nzima and Kokofu except in Bekwai in which there was a slight increase. At each

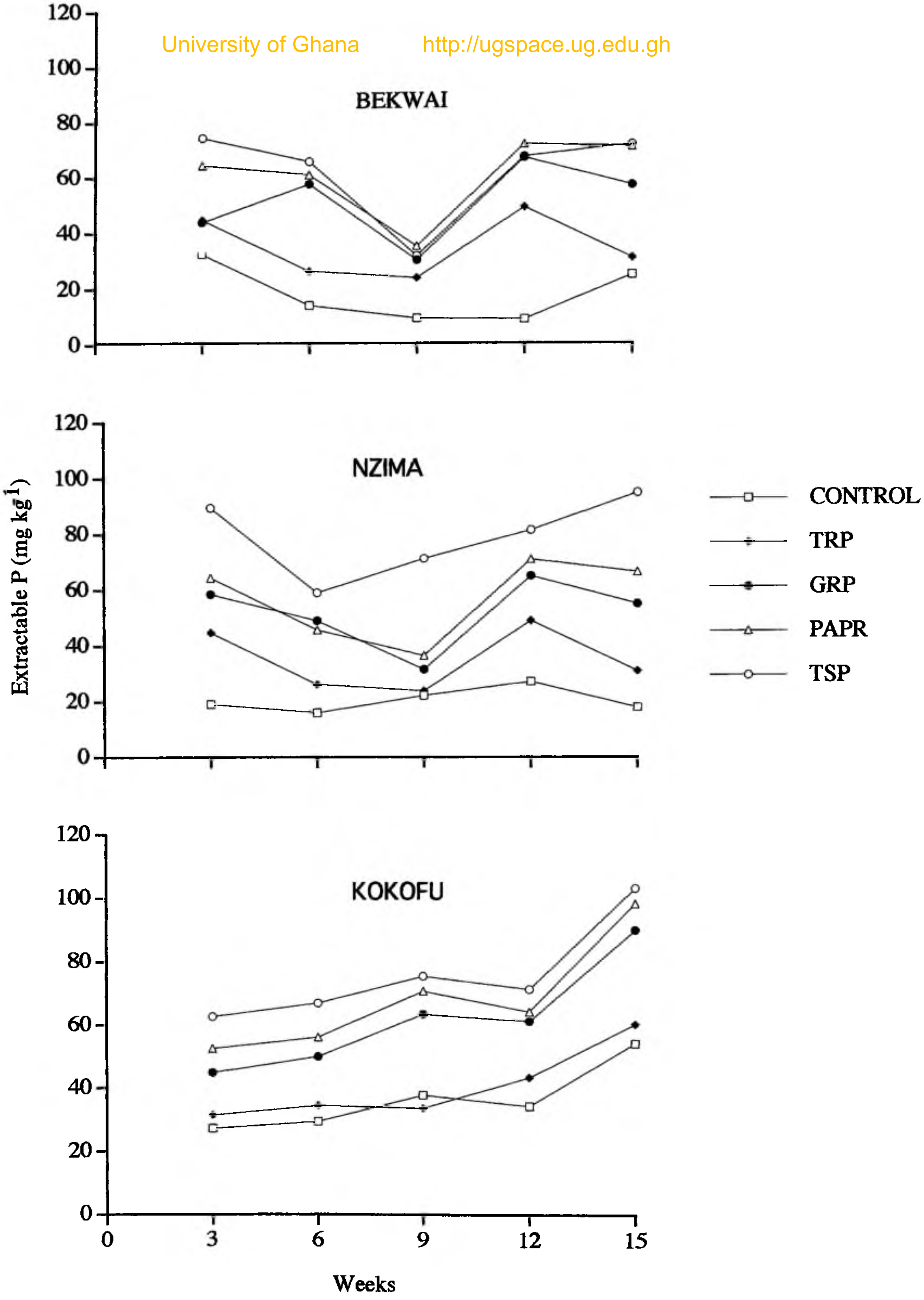


Figure 4.2. 0.1 M NaOH extractable P mg kg^{-1} of the various P sources

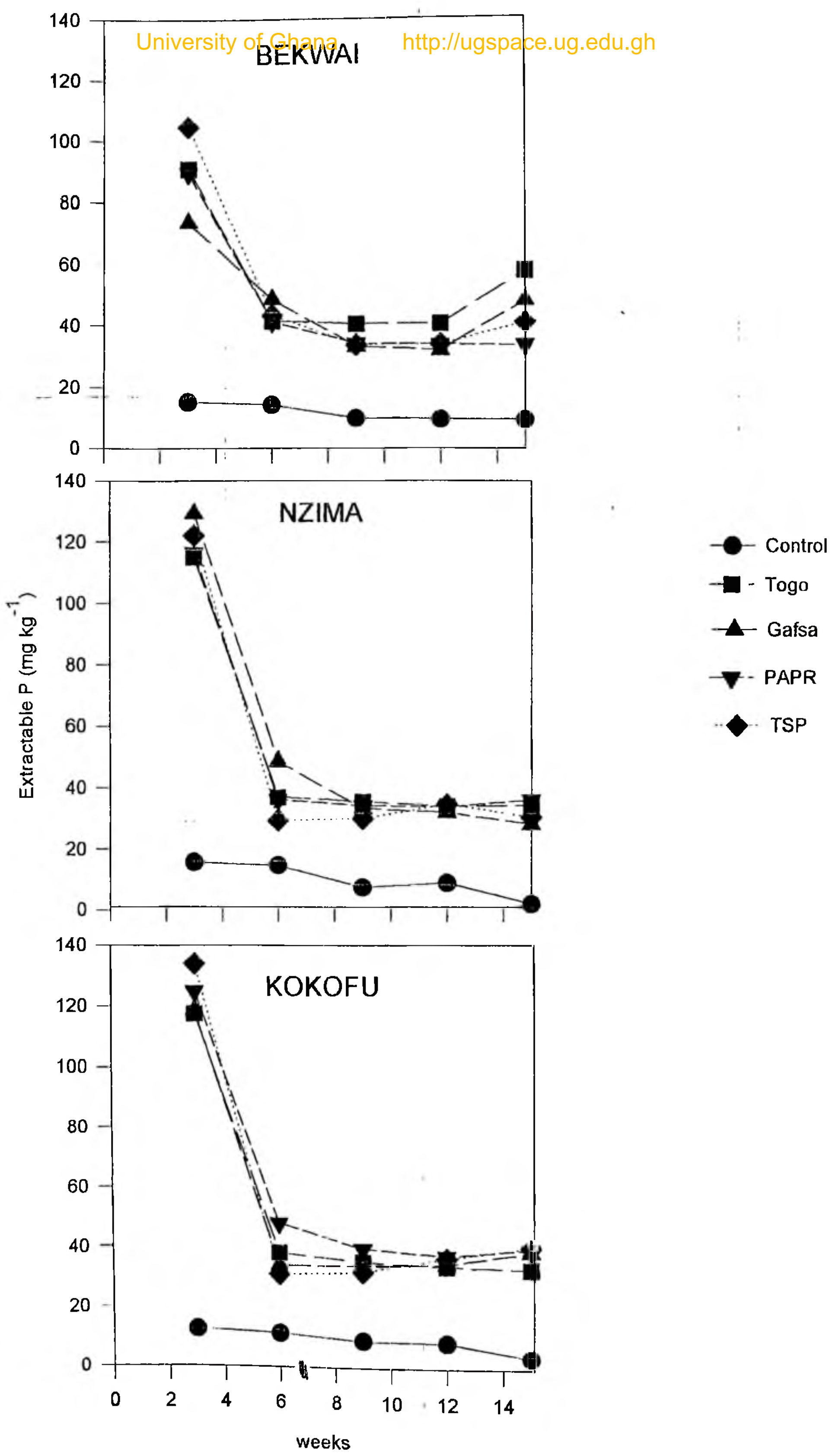


Fig 4.3 1M HCl extractable P mg kg^{-1} of the various P sources

incubation period the amount of HCl-P extracted from TRP was similar to those from the other P sources. In general there were no marked differences among the P sources with respect to the HCl extractable P.

4.4 Greenhouse Experiment

4.4.1 Effect of P Sources on Dry Matter Yield (DMY)

The effect of P sources on fresh and dry matter weights of maize in the three soils is given in Table 4.3. The results showed that there was a positive response to the application of P fertilizers, especially TSP, PAPR-50 and GRP by the maize crop (Table 4.3). The variations in yield due to P sources were statisticallly significant ($P < 0.05$). There was also positive interaction between P source and soil type with respect to DMY (Appendix 1a). This shows the effect P fertilizers differed from soil to soil with respect to DMY.

In all the three soil series, there was significant difference in yield between TSP and GRP or TRP but the yields for TSP and PAPR-50 were statistically similar. There was also significant difference ($P < 0.05$) between GRP and TRP. As shown in Table 4.3 there was no significant diffference between TRP and the control. Similar to the results of the incubation study, the DMY of the maize crop may be grouped into three categories; TSP and PAPR-50 (category I) giving the highest yield, followed by GRP (categoryII) and TRP (categoryIII) giving the least DMY of shoot. These results are consistent with the amount of water soluble P content and reactivity of the P carriers. Togo rock phosphate did not dissolve well enough to significantly increase DMY of maize over the control.

Table 4.3: Effect of P source on the yield, total P uptake of shoot and relative agronomic efficiency of the P sources in Bekwai, Nzima and Kokofu soils for the Greenhouse study.

P Source	Fresh shoot weight	Dry shoot Weight	P Conc.	Total P-Uptake of shoot	RAE (%)	
	g plant^{-1}	g plant^{-1}	%	mg P plant^{-1}	DMY	P-UP
			BEKWAI			
Control	31.26 c	3.59 c	0.25 b	8.82 c	-	-
Togo RP	33.22 c	3.82 c	0.26 b	9.78 c	8	7
GAFSA RP	40.30 b	4.86 b	0.28 b	13.39 b	47	31
PAPR-50	44.10 a	5.86 a	0.37 a	21.37 a	83	85
TSP	45.90 a	6.32 a	0.38 a	23.58 a	100	100
LSD (0.05)	2.47	0.71	0.05	2 .85		
cv (%) =	4.12	9.51	9.26	12.0		
			NZIMA			
Control	22.70 c	2.15 c	0.21 e	4.65 c	-	-
Togo RP	25.10 c	2.41 c	0.23 d	5.59 c	8.0	7
GAFSA RP	31.63 b	3.58 b	0.25 c	8.93 b	43.0	32
PAPR-50	37.93 a	5.40 a	0.32 b	17.26 a	98.0	93
TSP	42.11 a	5.46 a	0.35 a	18.19 a	100.0	100
LSD (p 0.05)	4.26	1.46	0.002	1.46		
cv (%)	8.68	9.26	7.34	15.1		
			KOKOFU			
Control	22.70 c	2.35 c	0.19 c	4.51 c	-	-
Togo RP	25.58 c	2.38 c	0.22 c	5.27 c	2.0	7
GAFSA RP	29.33 b	3.59 b	0.28 b	9.98 b	61.0	50
PAPR-50	35.58 a	4.27 a	0.35 a	14.67 a	94.0	93
TSP	37.85 a	4.38 a	0.35 a	15.42 a	100.0	100
LSD (p 0.05)	4.67	0.42	0.05	1.51		
cv (%)	9.60	8.12	10.75	9.81		

$$* \text{RAE} = \frac{(\text{Yield of P source}) - (\text{Yield of control})}{(\text{Yield of TSP}) - (\text{Yield of control})} \times 100$$

(DMY) = Dry shoot weight; P-UP = Total P-Uptake of shoot

Figures in the same column followed by the same letter are not significantly different.

Table 4.4: Mean separation of soil for dry matter yield (DMY) of shoots and P-uptake (in ranked order)

Soil	DMY (shoot) (g plant^{-1})	P - Uptake (mg plant^{-1})
Bekwai	4.89 a	15.38 a
Kokofu	3.80 b	10.93 b
Nzima	3.40 b	9.97 b
LSD ($P < 0.05$)	0.55	0.98
cv (%)	9.63	12.75

Figures in the same column followed by the same letter are not significantly different.

4.4.2 Effect of P Sources on Total P-Uptake

The P concentration and the total P uptake of maize grown in the soils in a greenhouse are also given in Table 4.3. The results showed that the P concentration and the total P uptake of maize in the soils increased significantly following the application of the P fertilizers ($P < 0.05$). The variations in P uptake due to P sources were significant ($P < 0.05$)

In terms of P-uptake, there was no significant difference between TSP and PAPR-50. Total P uptake from GRP however was statistically lower than those from TSP and PAPR-50. P-uptake from TRP and the control were found to be similar in all the soils. Table 4.3 also showed that there were significant differences among GRP, TRP and the control. Gafsa RP produced significantly higher total P uptake higher than those of TRP and the control as observed in the soils. In general the variations in P-uptake followed closely those of the dry matter yield.

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4.4.3 Relative Agronomic Efficiency (RAE) of the P Sources with respect to DMY and P-uptake

The calculated values of relative agronomic efficiency (RAE) in terms of dry matter yield and P uptake for the various P sources in the three soils are given in Table 4.3. The RAE of these sources ranged from 2 to 98% as effective as TSP in terms of dry matter production and from 7 to 93% as effective as TSP in terms of P uptake of the crop. In all the three soils the RAE of the P sources in increasing both DMY and P uptake, followed the trend TSP > PAPR-50 > GRP > TRP. The effectiveness of Togo rock phosphate (TRP) was consistently poor in all the moderately acid soils. The RAE of TRP was only 8%, 9% and 2% as effective as TSP in Bekwai, Nzima and Kokofu respectively in terms of DMY and 7%, as effective as TSP in Bekwai, Nzima and Kokofu soils respectively in terms of P uptake. The relative agronomic effectiveness of PAPR-50 was higher in Nzima and Kokofu than in Bekwai and that of GRP was generally higher in Kokofu than in the two upland soils (Table 4.3).

4.5 Field Experiment

4.5.1 Effect of P sources on the Yield of stubble

The results obtained from the field trials as produced in Table 4.5 which shows that there was significant difference between the P sources with respect to stubble yield in all the soils. Although there were increases in stubble yield due to the application of the P sources, stubble yield obtained from TSP and PAPR fertilizers were not significantly

Table 4.5 Effect of P source on stubble yield, grain yield, P uptake of maize and relative agronomic efficiency of grain yield on Bekwai, Nzima and Kokofu soils.

Soil	Phosphate Source	Stubble yield kg ha^{-1}	Grain yield kg ha^{-1}	P uptake kg ha^{-1}	*RAE (%)
Bekwai	Control	4306 c	3825 c	10.86 c	-
	Togo RP	4351 c	4500 c	15.10 bc	16
	Gafsa RP	5962 b	6275 b	19.46 b	56
	PAPR-50	7352 a	7991 a	27.31 a	96
	TSP	7848 a	8162 a	32.93 a	100
	LSD ($P < 0.05$)	961.5	1559	5.64	
	cv (%)	10.46	16.45	17.32	
Nzima	Control	4299 c	4508 c	11.62 c	-
	Togo RP	4361 c	4768 c	13.26 c	7
	Gafsa RP	5957 b	6268 b	21.18 b	49
	PAPR-50	7166 a	8058 a	25.58 a	99
	TSP	7155 a	8102 a	28.41 a	100
	LSD ($P < 0.05$)	950.7	861.8	3.08	
	cv (%)	3.19	10.08	10.00	
Kokofu	Control	4415 d	4340 c	12.08 e	
	Togo RP	4419 d	4604 c	14.45 d	9
	Gafsa RP	5949 c	5498 b	18.87 c	40
	PAPR-50	7270 b	7067 a	27.37 b	94
	TSP	7899 a	7242 a	29.71 a	100
	LSD ($P < 0.05$)	170	1233	3.83	
	cv (%)	3.19.	14.13	11.53	

$$\text{*RAE} = \frac{\text{(Grain Yield of P Source) - (Grain yield of control)}}{\text{(Grain Yield of TSP) - (Grain Yield of Control)}}$$

Table 4.6: Mean separation of soil for stubble and grain yield from the field experiment

Soil	Stubble kg ha^{-1}	Soil	Grain kg ha^{-1}
Kokofu	5990 a	Bekwai	6342 a
Bekwai	5964 a	Nzima	6151 a
Nzima	5819 a	Kokofu	5750 a
LSD ($P < 0.05$)	303.5		1043
CV (%)	8.03		12.02

Figures in the same column followed by the same letter are not significantly different

different in both Bekwai and Nzima, while in Kokofu these were significantly different from each other. The yield of stubble from the TSP treated plots was the highest in all the soils. In Bekwai and Nzima increases in stubble yield followed the trend: TSP = PAPR-50 > GRP > TRP = control, whereas in Kokofu the trend observed was : TSP > PAPR-50 > GRP > TRP = control. Similar results were obtained from the greenhouse.

The results of the field trials also showed that the interaction between the P sources and soil types was not significant (Appendix 2c) contrary to what was observed in the greenhouse.

4.5.2 Effect of P Sources on Grain yield

The grain yields given by the P sources from the field are produced in Table 4.5 There were significant differences among the P sources with respect to grain yield in all the soils. Grain yields obtained from TSP and PAPR-50 were similar, and significantly higher than those of GRP, TRP and the control.

Application of TRP resulted in small increases in grain yield in all the soils. The yield trend observed was similar in all the three soils; TSP = PAPR > GRP > TRP = control.

4.5.3 Effect of P Sources on Total P Uptake

Effect of P sources on total P uptake of maize grown in the three soils in the field is also given in Table 4.5. In Bekwai and Nzima there was no significant difference between TSP and PAPR-50. Total P-uptake from GRP was however significantly higher than for TRP while that of TRP was not significantly different from the control.

P-uptake from Bekwai and Nzima followed the trend: TSP = PAPR-50 > GRP > TRP = control

In Kokofu soil series, total P-uptake from TSP, PAPR-50, GRP and TRP were statistically different from each other, and followed the trend: TSP > PAPR-50 > GRP > TRP > control.

4.5.4 Relative Agronomic Efficiency of the P Sources with respect to Grain yield

The calcuated values of relative agronomic efficiency (RAE) for grain yield obtained for the various P sources in the different soils are shown in Table 4.5. The RAE ranged from 7% to 94% as effective as TSP in terms of grain yield. In all the soils, the RAE of the P sources in increasing grain yield follow the trend, TSP > PAPR-50 > GRP > TRP. The effectiveness of TRP was consistently poor in all the soils, similar to what was obtained for the DMY from the greenhose experiment.The RAE of TRP was only 16%, 7% and 9% as effective as TSP in terms of grain yield in Bekwai, Nzima and Kokofu. In Kokofu, the RAE values of GRP and PAPR-50 were consistently lower than those of Bekwai and Nzima. This was however contrary to what was obtained in the greenhouse studies.

CHAPTER FIVE

5.O DISCUSSION

5.1 Soil characteristics

Bekwai and Nzima are classified as Paleudult whilst Kokofu series is Paleudalf (USDA,1975). The texture of the soils varied according to their positions on the toposequence. Surface soil (0-20 cm) of Bekwai is sandy clay loam whereas Nzima and Kokofu are clay loam. The high amount of clay in the soils can be explained by the fact that soils are developed over phyllite parent material. Kokofu had the highest silt and clay content possibly due to its position on the lower slope and therefore there is deposition of fine soil material eroded from upslope leaving coarse sandy particles upslope. The soils were moderately acid. The low pH of the soils may be attributed to leaching of basic cations by the high rainfall (1300-1650 mm per annum) which is characteristic feature of the moist semi-deciduous forest zone.The high organic carbon and total nitrogen contents of the soils are also characteristics of semi-deciduous forest zone.

The total P content in the soils showed a decrease down the slope (Table 4.1). The level of total P in the soils was comparable to those reported for similar soils of the same ecological zone (Owusu-Bennoah and Acquaye, 1989). Inorganic plant-available P (Bray 1) values are low for all the soils suggesting that the soils are strongly deficiency of P. Thomas and Peaslee (1973) reported that most soils containing extractable P of less than 15 mg P kg-^{1} as determined by Bray 1 method were low in available P. Nye and Bertheux, (1957) attributed the low P in Ghanaian soils to the low content of mineral apatite in the parent rocks and also the great age and intense weathering to which the rocks had been subjected. The low available P content of the soils despite a high total P seems to suggest that considerable proportion of the P may be in the organic form. This suggestion agrees with Acquaye and Oteng (1972) that forest soils contain substantial levels of organic P. Acquaye (1963) found out that 46-70% of the total phosphorus in different soils in Ghana was in the organic form.

The effective cation exchange capacity (ECEC) was generally low and did not vary markedly among the three soils. The low ECEC may have been caused among other factors by the excessive leaching of the basic cations from the soil profiles. The exchange complex was dominated by Ca and Mg with Ca contributing about 50% of the ECEC. The mean Ca : Mg ratio of 3.7 of these soils was far below the critical value of 5.0 set out by Horvath and Todd (1968) which showed that Ca was generally more deficient than Mg in these soils. However the Ca : Mg ratio obtained for the soils studied was higher than the 1.3, 1.7, and 2.0 reported by Ainoo-Ansah, (Unpublished, M.phil.1996) for Abenia, Boi and Ankasa soils, respectively, of humid forest zone. This indicates that Bekwai, Nzima and Kokofu soils of the semi-deciduous zone are perhaps less leached than those in the humid forest zone. Chien and Menon (1993a) identified some soil properties such as pH, low exchangeable Ca and low available P as having the greatest influence on the solubility of PRs.

$$Ca_{10}(PO_4)6F_2 + 2H^+ \rightleftharpoons 10Ca^{2+} + 6H_2PO_4^- + 2F^- \qquad [5.1]$$

From equation 5.1, the low amounts of Ca^{2+}, $H_2PO_4^-$ and the low pH of the three soils seem to suggest that dissolution in these soils will be adequate for plant growth.

5.2. Incubation study

5.2.1 Resin extractable P

The resin-P has been shown to be a useful index for estimating plant available P in a soil to which PR materials have been added (Amer et al., 1955). The differences found for the resin extractable P derived from the P sources highlight the marked differences in reactions of these P fertilizers on contact with the soils. The decrease in resin-extractable P in Bekwai and Nzima as compared with Kokofu from the 3rd to the 12th week seems to suggest the positional differences of the soils on the toposequence and the level of sand content. The well drained upper soils, Bekwai and Nzima may be dominated by high levels of aluminium, iron, manganese and hydrous oxides of these elements such as gibbsite ($Al_2O_3 .3H_2O$) and goethite ($Fe_2O_3 .3H_2O$) . The $H_2PO_4^-$ released from the fertilizers as a result of dissolution, may have reacted with these minerals to form insoluble hydroxyphosphates through P sorption process leading to the decline in the phosphate capable of being extracted by the resin from the soils. Similar results have been reported by Syers and Mackey (1986).

In the Kokofu, an alfisol the decrease in Resin-P was more gradual with time. This trend was similar to what was obtained by Mackenzie (1971), when monocalcium phosphate was added to Ultisol, and incubated at room temperature and extracted at different time intervals.

As shown in Fig 4.1 at the 12th week most of the phosphate released may have been adsorbed by the soil constituents, thus leaving only small amounts of the phosphate in soil solution to be extracted from the different P sources. In the three soils, resin extractable P from Kokofu was the lowest for all the P sources. This may be attributed to the nature of the clay fraction in the Kokofu soil compared with either Bekwai or Nzima. Soil constituents responsible for P adsorption have been shown to be associated more with the nature of clay minerals. (Owusu-Bennoah and Acquaye, 1989). The amounts of resin-P extracted from TSP, PAPR-50 and GRP were higher than TRP which followed the solubility characteristics of the P sources (Table4.2)

The slight increase in resin-P from the 12th to 15th week even in the control sample especially in the upper slope soils (Fig.4.1) may be difficult to explain but the possibilty of mineralization of the native organic P after a prolonged period of incubation time cannot be ruled out.

5.2.2 0. 1 M NaOH extractable-P

According to Chang and Jackson (1957) apatite is essentially insoluble in NaOH and because this reagent is an effective extractant of sorbed inorganic P (Williams et al., 1971), any increase in NaOH-extractable P in a soil to which a PR is added provides a good estimate of the amount of P dissolved and retained by the soil solution (Hanafi and Syers, 1994). The results obtained showed that there was a decrease in the NaOH-P extracted from all the P sources, from Bekwai and Nzima soils, from the 3rd to the 9th week (Fig 4.2). This is, because, these soils are located on the well drained upper slope positions on the catena and are in highly oxidized environments. The decrease can be attributed to the possible transformation of most of the Fe-P and Al-P into a less soluble Fe (111) phosphate and the Al-P into a more stable form, so that the 0.1M NaOH was not able to extract these occluded compounds. The increase in NaOH-P from the 9th to 12th week may be due to more freshly formed Fe-P and Al-P as a result of mineralization,which would release more inorganic P into the soil solution. The amounts of NaOH-P extracted from TSP in the three soils were always higher than from the other P sources which can be explained as due to the high solubility of the TSP. In the Kokofu soil, gradual increase in the NaOH-P extracted may possibly be due to its position on the lower slope and the ability of the soil to retain more moisture. This condition may have enhanced forms of Fe and Al in the soils. It is possible that the residual effects of these P sources may be highest in the Kokofu soil. (1994).

5.2.3 1 M HCl extractable-P

The HCl-P indicates the amount of Ca-P extracted from the P fertilized soils (William et al., 1971). From Fig.4.3, the high amount of Ca-P extracted from the P sources indicated that the materials were all rich in Calcium phosphate. The rapid decline in the Ca-P extracted after the 3rd week may be attributed the dissolution of the P sources in all the soils. The slight increase in the P extracted from the 12th to the 15th week, in Bekwai soils may again be attributed to probable mineralization of organic P to inorganic P which tended to combine with the native Ca in the soil to form Calcium phosphate.

5.3 Effect of P sources on growth and grain yield.

Field experiment results were generally consistent with those obtained in the pot experiment. As shown in Tables 4.3 and 4.5 the DMY of shoot and grain yield increased significantly ($p < 0.05$) following the application of the P fertilizers except for TRP. The increased growth was caused by the improved uptake of P from the soils by the test crop. There was no interaction between the P sources and the soil pH with respect to P uptake

Thus the differences in P concentration and P uptake by the shoot biomas and grain yield of crop obtained from both the greenhouse and the field experiments, were due to the differences in the solubility of the P sources in neutral ammonium citrate. This is contrary to some published results (Kanabo and Gilkes, 1988). As shown in Table 4.2, TSP had the highest neutral ammonium citrate soluble P (18.1%) whereas Togo phosphate rock (TRP) was almost negligible. This, therefore, explains why TSP gave the highest mean DMY of shoot as well as grain yield in all the soils, while TRP produced the lowest. These results, are consistent with the results obtained from the resin-extractable P of the P sources in the incubation studies (Fig. 4.1). As shown in Table 4.5, there were no significant yield differences due to the application of TSP and PAPR-50 in all the soils. Elsewhere in in Ghana similar results have been reported (Owusu-Bennoah and Acquaye, 1996), Similar results have also been obtained by Bationo et al.in Nigeria,Togo and Sierra Leone (1986),and by Hammond et al. (1986b) and Chien and Hammond (1988). Mokwunye and Pinto-Toye (1991) also reported that finely ground untreated TRP gave lower yield than superphosphate and PAPR-50, the later two being equal in effectiveness. Chien and Menon (1993b), attributed such observation to the "starter effect" of the water soluble component of the PAPR. They hypothezised that PAPR is essentially a mixture of monocalcium phosphate (MCP), which is water soluble P, and unreacted PR, which is insoluble in water. Therefore, the water soluble P component encourages early plant root development, which enables the plant to use the unacidulated PR component more effectively than could a plant treated with PR alone. Yields obtained from GRP were found to be signficant in all the three soils, higher than that obtained from TRP even though the former produced lesser yield than either TSP or PAPR-50. This is due to the higher reactivity of GRP in terms of its agronomic potential as compared with TRP as indicated by its neutral citrate soluble P. Leon et al. (1986) have suggested that GRP is more available to plants than many PR sources. In general the results from the incubation, greenhouse and the field studies have clearly indicated that the fertilizer pontential of TRP is low in these three soils of the catena. This is in consonance with the results obtained from the incubation studies. Similar results have been reported by Uyovbisere and Lombin (1991) from a field work done on an Alfisol in a similar ecological zone in Nigeria. In all the soils DMY of shoot and grain obtained from both TRP and the control were similar showing least of interaction between the TRP fertilizer and the soil.

5.4 The relative agronomic efficiency (RAE) of the P sources.

The calculated values of RAE for dry matter yield, P uptake and grain yield showed that TRP performed poorly in all the soils. because to its low reactivity resulting in its inability to supply adequate P in the soil solution for plant uptake.

The high RAE values of PAPR-50 in all the three soils may be explained by the fact that about 50% of PAPR-50 is soluble and contributed significantly large amouts of plant available P for the development of the stubble and grain yield. The results for the PAPR-50 from the greenhouse and the field experiments are in agreement with the results of other workers who have reported that PAPR is less effective than TSP (Terman and Allen., 1967., Hammond et al., 1980) even though the contrary has also been reported elsewhere (Lutz, 1971).

The RAE of GRP in terms of DMY was higher in Bekwai than in Nzima series(Table 4.4). This may be due to the sandy clay loam texture of the surface layer of Bekwai as compared with clay loam of Nzima soil. The greater permeability of sandy clay loam results in continuous removal of the product of RP dissolution from the site of reaction (Hanafi and Syers , 1993). This maintained sinks for Ca^{2+} and H_2PO_4 and thereby promoted dissolution.

The low RAE values generally obtained from Kokofu in the field could be attributed to its high clay content which tends to adsorb most of the phosphate released from the PRs. This is supported by the low resin-P values extracted from the Kokofu soil in the incubation work than those extracted from Bekwai and Nzima (Fig.4.1). These results tend to show the reduction in reactivity of the applied P fertilizers with time in the Kokofu soil.

CHAPTER SIX

6.0 SUMMARY AND CONCLUSION

Phosphorus (P) and nitrogen (N) are the most limiting nutrients for crop production in tropical soils, including soils of the semi-decidous forest zones in Ghana. Therefore , there is the need to add phosphatic fertilizers to these soils for economic and sustained crop production.

Phosphate rock, which is relatively abundant in sub-Saharan Africa and the partially acidulated forms can be used as an fertilizers in the highly phosphorus deficient acid soils, to represent an alternative to imported soluble P fertilizer like triple superphosphate for crop production in the acid soils of the humid and semi-humid tropics. The objectives of this research were to compare the rate of dissolution of TRP. GRP, PAPR-50 and TSP and their agronomic effectiveness in three benchmark soils of Ghana.

Togo Rock Phosphate GRP, PAPR-50 and TSP were incubated in each of the three benchmark soils; Bekwai , Nzima and Kokofu series for 105 days to assess the reaction of the various P sources using resin membrane , 0.1M NaOH and 1M HCl extractions. Resin-P which is a useful index for estimating plant available P assesed for TSPand PAPR-50,to be of similar availability and higher than GRP at all extraction times. In general, the pattern of P extractions from the various P sources was categorised into three, depending on the ease of P released from the P fertilizers: categories I, II and III, indicated that TSP and PAPR-50 had the highest solubility, GRP was of medium solubility and TRP had the lowest solubility, respectively. Three weeks after incubation, the resin-P extraction followed the trend TSP = PAPR-50 > GRP >TRP = Control. The

Fe-P and the Al-P contents used for measuring the dissolution of the PR materials in soil decreased in both Bekwai and Nzima, soils with time from the 3rd week to the 9th week and then increased till the 12th week. At the 15th week, there was gradual decline in the P extracted from the TRP and GRP. In Kokofu, which is a lowland soil there was gradual increase from the 3rd week to the 12th week. The 1M HCl-P decreased from the 3rd week and attained an equilibrium afterwards in all the three soils indicated that dissolution of the P sources had occured.

In the greenhouse studies, in all the soils the following trend was observed with respect to DMY anmd P uptake of shoot; TSP = PAPR-50 > GRP >TRP = Control .This trend was similar to what was obtained for the resin extractable P in the incubation studies at the 3rd week, the RAE also followed the trend :TSP > PAPR-50 > GRP > TRP. The mean separation of soil for DMY and P uptake for the 4 weeks of growth of the maize indicated this trend Bekwai > Nzima = Kokofu. Thus Bekwai produced the highest DMY among the three soils.

Following good and consistent results obtained in both the incubation and greenhouse studies, the same variety of maize was sown in the field on the same soils and the same fertilizers were applied to evaluate stubble yield, grain yield and also to determine RAE with respect to the grain yield. Results indicated that, except for TRP the application of the P fertilizers gave significantly higher growth in the soils as a result of increased P uptake by the crop. The stubble yield, grain yield and the RAE followed the trend similar to what was obtained from the greenhouse. There were no significant differences between TSP and PAPR-50 and then between TRP and the control. However the yields by GRP, were significantly lower than TSP and PAPR-50, but higher than TRP and the control.

There was no significant difference among the soils with respect to grain and stubble yield, thus indicating that the soils are similar in terms of physico chemical properties. Due to the consistent pattern obtained from the Bekwai and Nzima soils, the two upland soils in the incubation studies, it is strongly recommended that, other criteria should be examined to assess the need for putting these two soil series together.

The conclusion from the studies was that, Togo Rock Phosphate is not an effective P source for direct application to these soils for maize cultivation However partial acidulation of this PR should be a better alternative. The mean separation of soil with respect to grain yield indicated, all the three soils, produced about the same amount of grain.

For future resarch work, it is strongly recommended that, the following should be considered.

1. The P sources should be applied to the soils at different rates and incubation studies should be extended over a longer period of time. Subsamples of the incubated soil be analysed at every two weeks intervals for plant available P

2. The following soil parameters such as pH, Ca^{2+} and Al^{3+} of the incubated soils should be analysed within the same time interval, that is, forthnightly to assess the changes of these parameters as a result of the dissolution of the P sources.

3. Residual effectiveness of the P sources in these soils on plant growth in the field should be carried out.
4. Economic analyses of the P sources should be examined.

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APPENDICES

Appendix 1a. Analysis of variance (ANOVA) for dry matter yield of shoot of maize, potted plants.

Source	Degress of Freedom	Sum of Squares	Mean Square	F Value	Probability
Replication	3	0.798	0.266	1.7672	0.1681
Soils	2	24.063	12.032	79.9178 *	0.0000
P sources	4	75.414	18.853	125.2308 *	0.0000
Soils x P sources	8	3.656	0.457	3.0354 *	0.0087
Error	42	6.323	0.151		
Total	59	110.254			
cv (%)	9.63				

* denotes significance at 5%; NS denotes not significance

Appendix 1b: Analysis of variance (ANOVA) for P uptake of potted plants

Source	Degress of Freedom	Sum of Squares	Mean Square	F Value	Probability
Replication	3	7.436	2.498	1.0432	0.3834
Soils	2	333.843	166.922	70.2524 *	0.0000
P sources	4	1765.228	441.307	185.7333 *	0.0000
Soils x P sources	8	36.768	4.596	1.9343 NS	0.0799
Error	42	99.793	2.376		
Total	59	2089.810			
cv (%)	12.75				

* denotes significance at 5%; NS denotes not significance

Appendix 2a: Analysis of variance (ANOVA) of field experiment for P uptake of maize

Source	Degress of Freedom	Sum of Squares	Mean Square	F Value	Probability
Replication	3	45.092	15.031	1.2310	0.0986
Soils	2	12.618	6.309	0.9365 NS	
P sources	4	3072.117	768.029	113.9996 *	0.0000
Soils x P sources	8	60.430	7.554	1.1212 NS	0.3691
Error	42	514.230	9.886		
Total	59	3473.217			

cv (%) 12.63

* denotes significance at 5%; NS denotes not significance

Appendix 2b: Analysis of variance (ANOVA) of field experiment for for grain yield of maize

Source	Degress of Freedom	Sum of Squares	Mean Square	F Value	Probability
Replication	3	1366546.717	455515.572	0.8533	
Soils	2	3651949.9	1825974.95	3.4204NS	0.0421
P sources	4	135617594.1	33904398.5	63.51*	0.0000
Soils x P sources	8	3692200.1	461525.012	0.8645 NS	
Error	42	22421408.03	533843.048		
Total	59	166749698.8			

cv (%) 12.02

* denotes significance at 5%; NS denotes not significance

Appendix 2c: Analysis of variance (ANOVA) of field experiment for for stubble yield of maize

Source	Degress of Freedom	Sum of Squares	Mean Square	F Value	Probability
Replication	3	1834909.765	611636.588	2.7052	0.0574
Soils	2	342171.207	171085.604	0.757 NS	
P sources	4	117971315.6	29492828.9	130.442 *	0.0000
Soils x P sources	8	544346.576	68043.322	0.3009 NS	
Error	42	9496145.99	226098.714		
Total	59	130188889.2			

cv (%) 8.03

* denotes significance at 5%; NS denotes not significance